COMPARATIVE CATION SOLVATION
IN VARIOUS MEDIA

by

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ERRATA

page 5 line 7

The term 'measured' in reference to single ion thermodynamic parameters denotes those values determined experimentally on the basis of an extrathermodynamic assumption.

page 34 line 27

Equation E3.4 should read $\ln \frac{\overset{R}{S}^{y}}{\overset{R}{R}^{y}} = \ln \frac{\overset{R}{S}^{y}{}_{o}}{\overset{R}{R}^{y}{}_{o}} + \ln \frac{\overset{S}{S}^{y}}{\overset{R}{R}^{y}}$

page 35 line 1

'Meduim' should read 'medium'.

page 36 line 12

'Have' should read 'has'.

page 71 line 3

'PIC^{+}' should read 'PIC^{-}'.

page 76 line 1

'Assumtion' should read 'assumption'.

page 142 line 17

'Studies' should read 'studied'.

The work described in this thesis is, except where otherwise noted, exclusively the author's own and was performed in the Research School of Chemistry at The Australian National University during the tenure of an Australian National University Postgraduate Scholarship (1972-1975). Neither this thesis in its entirety, nor any part thereof, has been submitted in support of an application for any other degree.

Dwain Alan Owensby

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To those who have made this work possible.

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ABSTRACT

The unambiguous determination of solvation parameters for single ions remains one of the classical unsolved problems of contemporary solution chemistry. Although the problem cannot be solved by means of rigorous thermodynamics, significant progress has been achieved by using 'extrathermodynamic' assumptions to estimate the single ion contributions to the free energies, enthalpies, and entropies of solvation of complete electrolytes. Such single ion values are essential for the understanding of solvation behaviour in any solvent. Until recently, most 'explanations' of solvation behaviour had relied on interpretation of data collected for aqueous systems. Subsequently, there has been an extension of interest beyond this historical preoccupation with water to a number of less complicated nonaqueous systems.

At the outset, this thesis presents a compendium of various extrathermodynamic assumptions currently being used for determining the single ion contributions to the parameters characterising the relative solvation behaviour of complete electrolytes in various media. One of these, the so-called tetraphenylarsonium tetraphenylboride assumption, is critically analysed, for it was used in the determination of most data presented in this work. The main body of this study, however, centres around the relative solvation behaviour of representative Group I and Group IIA and IIB metal cations in water and in various nonaqueous solvents. For the first time, a comprehensive set of free energy data for potassium cation solvation in several dipolar aprotic and protic solvents is presented. Furthermore, the simple, essentially electrostatic nature of potassium cation solvation allows its behaviour to serve as a model for that of various other monovalent and divalent cations. The model is illustrated (through single ion free energies of transfer) for the comparative solvation of the alkali metal, silver, and thallous cations in *N*,*N*-dimethylformamide and in *N*,*N*-dimethylthioformamide. Results are consistent with the Hard and Soft Acids and Bases principle. Comprehensive data are also presented for the relative free energies and enthalpies of solvation of representative divalent metal cations in several dipolar aprotic and protic solvents. From these data, single ion entropies of transfer between solvents are derived, and are interpreted in terms of changes in the induced solvent structure around the cation. (In addition, values are presented, from the literature, for a collection of parameters relevant to the inherent liquid structure of the various solvents considered.) Interpretation of single ion entropy data is simplified by considering ion transfers to real solvents from hypothetical 'ideal' solvents, having the same structures, molecular weights, and densities as the corresponding real solvents, but having no ion-solvent or ion-ion interactions. Entropy changes attending these transfers must be attributable to ion-induced solvent structural changes. Comparison of the single ion entropies of transfer from ideal to corresponding real solvents, with the solvent entropies of freezing, allows minimum estimates of ion solvation numbers to be made. Results indicate that in both dipolar aprotic and protic solvents, divalent cations orient solvent molecules beyond an ion-centred first solvation shell.

ACKNOWLEDGEMENTS

The author is especially indebted to his supervisor, Professor A.J. Parker, for his guidance, encouragement, and enthusiasm during the (occasionally haphazard) course of this work. Thanks also are due to Drs. M.R.J. Dack and B.G. Cox for providing preprints of some of their work shortly to be published, and to Drs. G.R. Hedwig and J.W. Diggle for their considerable resourcefulness and extraordinarily helpful discussions. A special debt of gratitude is owed to the Research School of Chemistry librarians, Ms. J. Weatherley and Ms. J. Smith, for their cheerful and unflagging assistance in obtaining (often obscure) reference materials. Professor A.N. Hambly and the School of General Studies, The Australian National University, deserve thanks for making available their LKB Precision Calorimeter System. In addition, it is a pleasure to express appreciation to members of the technical staff for willingly providing their specialised skills: to Mr. D. Bogsányi for general laboratory services, to Mr. B. Machan for assistance with the calorimeter, and to Mr. W. Tys for constructing the glass potentiometric cells. Finally, financial support through the award of an Australian National University Postgraduate Scholarship is gratefully acknowledged.

CHAPTER 1

INTRODUCTION

The present study may be summarised as an attempt to elucidate comparative aspects of cation solvation in various media. This chapter outlines the contents of the subsequent chapters, the scheme of presentation, and the chronological development of the work included.

Recent years have witnessed a marked increase of interest in the properties of nonaqueous solutions as evidenced by a phenomenal proliferation of the chemical literature dealing with this subject. Much of the impetus for endeavour in this field has been provided by the search for high energy density battery systems,[1] by observation of remarkable changes in the chemical behaviour of electrolytes in solution upon transferring them from aqueous to nonaqueous media,[2] and by the discovery of some spectacularly large organic bimolecular reaction rates in certain nonaqueous solvents when compared with water.[3,4] Significant contributions to the understanding of chemistry in nonaqueous solvents, particularly in the dipolar aprotics, have been made by workers in almost every area of chemical research, and recently a number of important texts on the subject has appeared.[5-13]

This thesis centres around one particular aspect of nonaqueous chemistry, namely that of comparative cation solvation in a variety of protic and dipolar aprotic solvents. (In this context the term 'cation solvation' is intended to be generic, encompassing all ion-solvent interactions experienced by the cation at infinite dilution in the solvent being considered.[14]) By definition, water cannot be classed as a nonaqueous solvent; nevertheless, it has been included for consideration in this work both because of its unique properties as a solvent and because the wealth of reliable data that exist for aqueous electrolyte solutions renders water an obvious reference point for comparisons with nonaqueous solvents. The nonaqueous solvents studied include the protic solvents formamide, methanol, ethanol, and *2,2,2*-trifluoroethanol along with the dipolar aprotic solvents nitromethane, acetonitrile, tetramethylenesulphone (sulpholane), *N*-methyl-*2*-pyrrolidone, hexamethylphosphorotriamide, propylene carbonate (propanediol-*1,2*-carbonate), dimethylsulphoxide, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and *N,N*-dimethylthioformamide. Taken collectively, these solvents span a wide range of bulk dielectric constants, represent a variety of molecular structures, and include a number of different coordinating atoms or functional groups which participate in cation solvation. Selected properties of these solvents and their relation to cation solvation are considered in chapter 2.

Elucidating comparative aspects of cation solvation is practically possible only if means are available for determining the individual ion contributions to the overall thermodynamic functions which characterise the solvation or solution of complete electrolytes. Obviously the magnitude of the electric field about an ion precludes macroscopic transfers of single ions between solvents, so that with conventional experimental techniques, measurements are possible only on electrically neutral combinations of ions.[15,16] Nevertheless, it is of great theoretical and practical importance to be able to divide thermodynamic quantities (*e.g.* the free energy, enthalpy, and entropy changes accompanying the transfer of a species between solvents) for complete electrolytes into individual ion contributions. (*N.B.* Popovych[17] has noted valid criticisms to the use of the term 'transfer' when comparing the solvation of single ionic species in different solvents; as an alternative, he advocates use of the term 'medium effect'. Nevertheless, the term 'transfer' has been used without objection for comparison of solvation of complete electrolytes in various solvents, and this terminology is extended to single ionic species throughout this work. However, the energy required for an ionic species to cross an interface between solvents[17-19] is not implied as constituting part of the energy associated with the hypothetical transfer.) A number of rather ingenious 'extrathermodynamic' methods has been posited to achieve this end. Several of these so-called extrathermodynamic assumptions are discussed in chapter 3 along with a critical appraisal of the tetraphenylarsonium tetraphenylboride assumption (abbreviated TATB assumption) which was used for the collection and interpretation of most data in the present study.

The already alluded to importance of ascribing thermodynamic quantities to single ions in various media has been eloquently discussed in several excellent reviews.[4,14,17,20,21] Specific objectives[17] include the exciting possibility of correlating acidities (and basicities) in various media,[22] the establishment of a solvent-independent scale of standard electrode potentials,[2] and the determination of liquid junction potentials between dissimilar solvents,[23,24] but the general aim is for a more fundamental understanding of the process of ion solvation.

Up to the present, progress in this direction has been hampered largely by the lack of agreement as to which extrathermodynamic assumption (or assumptions) should be used, and consequently, there has been little agreement on the individual values of thermodynamic quantities for single ions. However, recently reported studies of monovalent silver cation solvation indicate relatively good agreement for values of the free energies of transfer between solvents as obtained by several different assumptions.[25] This observation served as a starting point for the work reported in this thesis.

With the experimental methods employed discussed in chapter 4, the main body of this thesis begins in chapter 5 with a comparative study of the solvation of monovalent potassium cation by various solvents. Free energies of transfer of potassium cation between solvents were evaluated on the basis of both the tetraphenylarsonium tetraphenylboride (TATB) assumption and the negligible liquid junction potential (NLJP) assumption (*cf.* chapter 3) with discrepancies between the methods being taken as an indication of the magnitude of the liquid junction potentials involved in the experimental cells. An attempt was made to account for the observed free energies of transfer in terms of Pearson's Hard and Soft Acids and Bases principle (the HSAB principle).[26] Success led to a proposal for using the potassium cation as the reference for a model to be used in predicting free energies of transfer of other monovalent cations between solvents. Observed anomalous free energies of transfer were interpreted as being indicative of the influence of specific solvation effects. An investigation of transfer of other alkali metal cations from *N*,*N*-dimethylformamide to its thio analogue *N*,*N*-dimethylthioformamide was used to illustrate the method, data interpretation once again being made on the basis of the HSAB principle as reported in chapter 6. Concurrent work involved combination of measured single ion free energies and enthalpies of transfer to infer single ion entropies of transfer. Data were extended to divalent barium, zinc, and cadmium cations, and results were interpreted in terms of physical models of cation solvation as reported in chapter 7. The final chapter of this thesis recounts the major conclusions from the individual sections and makes a subjective judgement regarding the proposed direction of future efforts.

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CHAPTER 2

SOLVENTS

A study of comparative cation solvation (the transfer of a species from the gaseous phase to the solution phase) in various organic dipolar aprotic and protic solvents must consider the effects of ion-ion, ion-solvent, and solvent-solvent interactions. Of course, both changing the ionic species and changing the solvent itself will alter these interactions. In this chapter the nature of the solvent is considered with especial emphasis on the inherent 'structure' of the solvent (the solvent-solvent interactions). The structural changes in the solvent imposed by the introduction of a cationic species (the ion-solvent interactions) are considered in subsequent chapters in terms of single ion entropies of solvation, whilst experimental conditions were chosen to minimise the ion-ion interactions.

2.1 Choice of Solvents

Several considerations influenced the choice of solvents to be used throughout the course of this work. Of the solvent properties known to affect the solvation free energy of cations, the solvent bulk dielectric constant is perhaps the most important and has certainly received the most attention. Thus, the solvents were chosen to span a wide range of values for this variable. As will be seen in chapter 3, the elementary Born[1] theory of ion solvation considers the ion-solvent interaction to be purely electrostatic in nature, and its strength to be simply related to the reciprocal macroscopic dielectric constant of the solvent. However, the inadequacy of this approach can be anticipated because cation solvation must ultimately be interpreted on a molecular level in terms of ion-molecule interactions rather than merely in terms of bulk solvent electrical properties. Nevertheless, the Born theory is successful in attributing the major part of cation solvation free energies to electrostatic interactions.

To a better approximation, however, the solvent dipole moment can be thought of as the molecular counterpart of solvent bulk dielectric constant, and ion-solvent interactions can be described by ion-dipole or ion-multipole coulombic attractions.[2] (Smyth[3] has discussed the relationship between dipole moment and dielectric constant as expressed by the Debye[4] equation.) The solvents chosen also cover rather a large range of dipole moments. This simple molecular electrostatic approach, too, has not met with universal success primarily because of the neglect of such factors as covalent contributions to ion-solvent interactions and because of the neglect of solvent structural and stereochemical effects. Although these contributions to the interaction energy must be essentially electrical in nature, their complete formulation in mathematical terms has not yet been achieved.

To obviate these difficulties associated with the interpretation and prediction of the nature and strength of ion-solvent interactions, many workers have preferred to categorise solvents on an empirical basis in terms of their basicities,[5] donicities,[6] hardness or softness,[7-11] relative degrees of electrostatic *versus* covalent interactions with ionic solutes,[12] coordinating abilities,[13] or ionising tendencies[14]. All of these schemes depend to some extent upon the properties of the coordinating or interacting atom or functional group of the solvent molecule participating in cation solvation. The set of solvents employed in this study were chosen to include possibilities of solvent interaction with cations through oxygen, nitrogen, or sulphur atoms, with the strength of interaction being modified by a variety of chemical moities present as the remaining part of the various solvent molecules. Unfortunately, but perhaps inevitably, these empirical correlation schemes have not led to unanimity among workers regarding quantitative or, often, even qualitative estimates of the respective 'solvating powers' of various solvents towards cations.

Evidently, any truly successful description of cation solvation in various media must take cognizance not only of ion-solvent interactions but also of ion-ion and solvent-solvent interactions. Ion-ion interactions can be minimised in solvents of moderate or high dielectric constant both through proper choice of electrolytes and through use of low electrolyte concentrations in solution. For a particular solvent however, solvent-solvent interactions can neither be minimised nor be neglected, for such interactions constitute one of the defining characteristics of the liquid state.[15,16] Apart from the effect of ubiquitous dispersion forces, the extent, strength, and nature of pure solvent intermolecular interactions are influenced by solvent multipole moments (*i.e.* by the electronic distribution throughout a solvent molecule), by steric factors governing the molecular and intermolecular geometric configuration, and especially by the presence or absence of functional groups capable of acting as hydrogen bond donors or acceptors. Such interactions collectively help to determine the inherent 'structure' characteristic of a particular solvent. These factors were a third consideration in the choice of solvents for this work.

A final consideration in the choice of solvents was the availability of reasonably reliable results from the literature for use in comparisons with results obtained in this work. Once confidence was established in the experimental methods, the methods were used for extending data to hitherto little-studied solvent systems.

2.2 Solvent Physical Properties

The solvents chosen for this work are listed in table T2.1 along with selected physical properties. Only representative properties deemed relevant to the establishment of solvent purity, to the description of cation-solvent interactions, or to the characterisation of the structure of the pure solvent have been included. More comprehensive comparative tabulations of the physical properties of these solvents have been compiled by a number of workers including Riddick and Bunger,[17] Covington and Dickinson,[18] Janz,[19] Mann,[20] Parker,[21] and Drago[13].

Of the properties listed in table T2.1, only the last five require special comment. The donor number *DN*, as defined by Gutmann, *et al.*, is the negative of the enthalpy of formation of the one-to-one complex of a solvent with antimony pentachloride at high dilution in *1,2*-dichloroethane.[22] The strength of this Lewis base-Lewis acid covalent interaction can be considered to reflect the general 'solvating ability' of a solvent towards cations in the absence of complications such as steric effects and interactions which are either highly specific or strongly electrostatic in nature.[6] The next listing, the Kirkwood correlation parameter[23,24]

TABLE T2.1

SELECTED SOLVENT PROPERTIES[a]

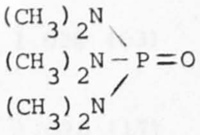
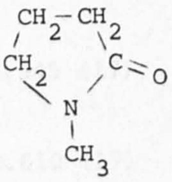
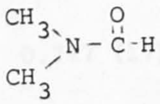
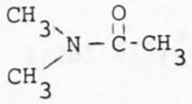
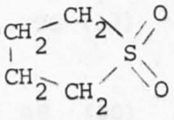
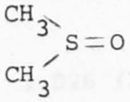
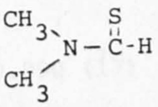
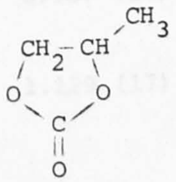
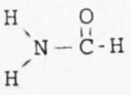
SOLVENT	ABBREVIATION	MOLECULAR REPRESENTATION
Ethanol	E	CH_3CH_2OH
2,2,2-Trifluoroethanol	TFE	CF_3CH_2OH
Hexamethylphosphorotriamide	HMPT	
N-Methyl-*2*-pyrrolidone	NMP	
Methanol	M	CH_3OH
Nitromethane	NM	CH_3NO_2
N,N-Dimethylformamide	DMF	
Acetonitrile	AN	$CH_3C\equiv N$
N,N-Dimethylacetamide	DMA	
Tetramethylenesulphone (Sulpholane)	TMS	
Dimethylsulphoxide	DMSO	
N,N-Dimethylthioformamide	SDMF	
Propylene Carbonate	PC	
Water	W	H_2O
Formamide	F	

TABLE T2.1
(Continued)

ABBREVIATION	BOILING POINT[b]	FREEZING POINT[b]	DENSITY ρ[c]	VISCOSITY η[d]
E	351.6 *78.4* (53)	159.1 *-114.1* (17)	0.785 (53)	1.084 (53)
TFE	346.90 *73.75* (53)		1.383 (53)	1.78 (53)
HMPT	506 *233* (17)	280.4 *+7.2* (17)	1.020 (63)	1.084 (63)
NMP	475 *202* (17)	248.8 *-24.4* (17)	1.028 (17)	1.666 (17)
M	337.85 *64.70* (17)	175.47 *-97.68* (17)	0.787 (17)	0.545 (17)
NM	374.35 *101.20* (17)	244.60 *-28.55* (17)	1.131 (17)	0.610 (17)
DMF	426.2 *153.0* (17)	212.8 *-60.4* (17)	0.944 (17)	0.802 (17)
AN	354.8 *81.6* (17)	229.31 *-43.84* (17)	0.777 (17)	0.325 (17)[j]
DMA	439.3 *166.1* (17)	253 *-20* (17)	0.937 (17)	0.92 (81)
TMS	560.5 *287.3* (17)	301.60 *+28.45* (17)	1.261 (17)[j]	10.286 (17)[j]
DMSO	462.2 *189.0* (17)	291.69 *+18.54* (17)	1.096 (17)	1.996 (17)
SDMF		264.7 *-8.5* (80)	1.024 (80)[k]	1.98 (80)
PC	514.9 *241.7* (20)	224.0 *-49.2* (20)	1.026 (20)[l]	2.530 (18)
W	373.15 *100*	273.15 *0*	0.997 (17)	0.890 (17)
F	483.7 *210.5* (17)	275.70 *+2.55* (17)	1.129 (17)	3.302 (17)

TABLE T2.1
(Continued)

ABBREVIATION	DIELECTRIC CONSTANT D[e]	DIPOLE MOMENT μ[f]	ENTHALPY OF FUSION[g]	DONOR NUMBER *DN*[h]
E	24.33 (53)	5.50 *1.65* (53)[m]	5.02 *1.20* (17)	17.9 (82)
TFE	26.67 (53)	6.77 *2.03* (53)[m]		
HMPT	28.3 (64)	17.47 *5.24* (64)[n,t]	16.95 *4.05* (17)	38.8 (6)
NMP	32.0 (17)	13.63 *4.09* (17)[j,p]		27.3 (6)
M	32.70 (17)	9.57 *2.87* (17)[n]	3.205 *0.766* (17)	19.1 (83)
NM	36.67 (20)	11.87 *3.56* (17)[l,q]	9.703 *2.319* (17)	2.7 (6)
DMF	36.7 (17)	12.87 *3.86* (17)[p]	7.88 *1.88* (87)	26.6 (6)
AN	37.5 (17)[l]	11.23 *3.37* (20)[p]	8.167 *1.952* (17)	14.1 (6)
DMA	37.78 (17)	12.40 *3.72* (17)[p]	10.418 *2.490* (17)	27.8 (6)
TMS	43.3 (17)[j]	16.03 *4.81* (17)[p]	1.427 *0.341* (17)	14.8 (6)
DMSO	46.68 (17)	13.0 *3.9* (17)[p]	13.93 *3.33* (17)	29.8 (6)
SDMF	47.5 (80)	14.57 *4.37* (80)[r]		37.3 (84)
PC	64.4 (20)	16.60 *4.98* (18,68)[p]		15.1 (6)
W	78.39 (17)	6.13 *1.84* (21)[s]	6.008 *1.436* (17)	18.0 (6)
F	109.5 (21)	10.83 *3.25* (21)[s]	6.694 *1.600* (17)	

TABLE T2.1
(Continued)

ABBREVIATION	KIRKWOOD CORRELATION FACTOR g^{e}	MOLAR COHESIVE ENERGY $m.c.e.^{i}$	MOLAR INTERNAL PRESSURE $m.i.p.^{i}$	TROUTON CONSTANT Tr^{h}
E	3.0 (53)	39.3 *9.4* (29)	17.2 *4.1* (29)	26.8 (53)
TFE	3.0 (53)			28.0 (53)
HMPT	1.1 (64)	102.9 *24.6* (29)	70.3 *16.8* (29)	26.7 (17)
NMP				
M	2.94 (25)^{l}	35.6 *8.5* (29)	12.1 *2.9* (29)	25.0 (17)
NM		36.0 *8.6* (29)		22.0 (17)
DMF	1.0 (85)	45.2 *10.8* (29)	36.8 *8.8* (29)	21.5 (17)
AN	0.82 (86)	30.5 *7.3* (29)	21.3 *5.1* (29)	20.1 (17)
DMA	1.1 (85)			23.6 (17)
TMS				26.2 (17)
DMSO	0.9 (26)	50.2 *12.0* (29)	36.8 *8.8* (29)	22.3 (17)^{t}
SDMF				
PC	1.18 (65)^{t}	75.7 *18.1* (29)	53.6 *12.8* (29)	22.9 (17)
W	2.68 (33)	41.4 *9.9* (29)	2.9 *0.7* (29)	26.0 (21)
F	1.5 (85)	62.8 *15.0* (29)	21.8 *5.2* (29)	37.3 (21)

TABLE T2.1
(Continued)

a. Definitions and implications of the various solvent properties are discussed in the text. References from which values of the various properties were taken are given in parentheses after the value. Unless noted otherwise, *Système International d'Unités* proposed standard units are used throughout.

b. Degrees Kelvin at 1.01×10^5 Pa (atmospheric pressure). The italicised values are in degrees Celcius.

c. g cm^{-3} at 298 K unless noted otherwise.

d. mN s m^{-2} at 298 K unless noted otherwise.

e. 298 K unless noted otherwise.

f. C m in the stated solvent at 298 K unless noted otherwise. The italicised values are in debye units.

g. kJ mol^{-1} at the freezing point. The italicised values are in kcal mol^{-1}.

h. The original units from the literature are used. Thus, *DN* is expressed in kcal mol^{-1} whilst *Tr* is expressed in cal K^{-1} mol^{-1}.

i. kJ mol^{-1} at 298 K. The italicised values are in kcal mol^{-1}.

j. Determined at 303 K.

k. Determined at 300 K.

l. Determined at 293 K.

m. At high dilution in cyclohexane.

n. Pure liquid.

p. At high dilution in benzene.

q. At high dilution in hexane.

r. At high dilution in carbon tetrachloride.

s. Vapour.

t. *Cf.* discussion in text.

(the so-called *g*-factor), is related to the extent of solvent intermolecular association or 'structure'. Specifically, it measures the mutual hindering of rotation resulting from the interaction of one solvent molecule with other molecules in its immediate neighbourhood, the interaction being between specifically oriented molecular dipoles.[25,26] There follows in table T2.1 values for the 'molar cohesive energy', *m.c.e.*, of the various solvents. This quantity is obtained from the product of the molar volume (the ratio of solvent molecular weight to density) and the cohesive energy density[27,28] of the solvent. Defined to measure the energy required for the vaporisation of one millilitre of solvent at a particular temperature, the cohesive energy density can be interpreted as an indication of the total solvent structure or intermolecular association per millilitre (for these purposes, $\text{ml} \equiv \text{dm}^3 \times 10^{-3}$). The multiplication of this quantity by the solvent molar volume merely constitutes a normalisation procedure to facilitate comparisons between different solvents. The solvent 'molar internal pressure', *m.i.p.*, defined as the product of molar volume and internal pressure (the internal pressure, P_i, being the first order partial derivative with respect to volume of the total internal energy per millilitre of a solvent under isothermal conditions[28]), is listed next in table T2.1. It has been taken as a quantitative estimation of intermolecular association through both dispersion forces and nonspecific dipole-dipole interactions, collectively called 'nonchemical' interactions. The significance of the molar cohesive energy and the molar internal pressure in structural terms is based upon their difference being interpreted as a measure of all solvent *specific* intermolecular associations, *i.e.* hydrogen bonding and specific dipole-dipole (and higher multipole) coulombic effects, collectively termed 'chemical' interactions.[28,29] The final listing in table T2.1 is the Trouton constant, *Tr*, the ratio of the enthalpy of vaporisation at the boiling point to the absolute temperature of boiling.[30] Positive deviations of this parameter from the ideal value of 21 for an ideal 'unassociated' liquid can also reflect the presence of some degree of structure in a real solvent.[21]

2.3 Solvent Structure

2.3.1 General Considerations. As mentioned before, cation solvation must necessarily involve ion-ion interactions, ion-solvent interactions, and solvent-solvent interactions. The former two types of interactions will be dealt with in subsequent chapters; the latter type, often referred to as solvent 'structure', is considered here.

Solvent structure is extraordinarily difficult to define rigorously, but it must superficially embody both the spatial configuration of solvent molecules (taken individually as well as relative to one another) and the energetics of intermolecular interactions. Ultimately, the fluxional or dynamic nature of the interactions must also be taken into account. Of the factors in table T2.1 relating to solvent structure, most are empirical and do little more than to indicate the presence or absence of structure without attempting to describe the nature of the interaction. However, the difference between the molar cohesive energy of a solvent and its molar internal pressure has been related both to the extent of hydrogen bonding[31] and to the extent of 'chemical' interaction (*i.e.* specific dipole-dipole interactions together with hydrogen bonding)[29,32] between solvent molecules. The Kirkwood correlation parameter or g-factor[23] perhaps holds more promise of elucidating aspects of solvent structure, for its value can either be measured experimentally or be determined from *a priori* calculations based upon an assumed model of intermolecular association for a particular solvent system.[25] The g-factor values reflect the orientation of neighbouring molecular dipoles, with $g < 1$ for net antiparallel dipole alignment and $g > 1$ for net parallel arrangement.[26,33] Deviation of g from unity is thus a measure of the extent of specific dipolar interaction in the solvent. Values of g near unity indicate lack of *specific* dipole-dipole interactions between neighbouring molecules and hence, the absence of well-defined associated molecular complexes; strong nonspecific dipolar interactions can, however, persist in such systems.[26] The experimental determination of the g-factor from the Kirkwood-Fröhlich[23,34] modification of the Onsager[35] equation relies on the measurement of the low (static) and high (infinite) frequency dielectric constant of a solvent system. This latter quantity cannot be measured unambiguously, so it is often assigned either a somewhat arbitrary value of $1.1n^2$ where n is the solvent refractive index[36] or some other value estimated from the dielectric relaxation behaviour of the solvent.[37] Agreement between a g-factor thus determined and one calculated from a statistical mechanical treatment of an assumed model solvent structure cannot prove the validity of the model, but certainly it can demonstrate that the model is consistent with experimental observations. However, the approximations involved in both the experimental and theoretical determinations of the g-factor render the usefulness of this parameter somewhat equivocal in qualitatively assessing the extent of solvent structure. At present, a realistic picture of solvent intermolecular association evidently can only be obtained by combining empirical data, such as that mentioned above, with data from spectroscopic measurements which examine the nature of solvent-solvent interactions on a molecular level.

2.3.2 Individual Solvents. In this section the various solvents studied in this work are considered individually on the basis of their respective structures as reported in the literature. The literature cited is by no means exhaustive, but rather, it is intended to be illustrative of the concensus (or lack thereof) among workers regarding the nature of various solvent-solvent association phenomena. For convenience, and following numerous similar categorisations in the literature, the solvents are divided into the dipolar protic solvents which are capable of associating through hydrogen bonding and the dipolar aprotic solvents which do not self-associate to any appreciable extent through hydrogen bonding mechanisms. Structural implications (*i.e.* the attendant entropy changes) of introducing ionic solutes into the various solvents are considered in subsequent chapters.

2.3.2.1 Dipolar protic solvents. Hydrogen bonding interactions are generally considered to be the major contributors to specific structure in protic solvents. The subject has been treated thoroughly by Pimentel and McClellan[38] and more recently by Kollman and Allen[39].

2.3.2.1.1 Water. A recent series of monographs on water reviews completely the current status of opinion regarding the interpretation of experimental data pertinent to the structure of water.[40] Liquid water is considered to enjoy a unique three-dimensional structure based upon tetrahedrally arranged hydrogen bonded water molecules. Regions structured in this manner are in dynamic equilibrium with monomeric water molecules.[41] This view represents the model of 'icebergs' or 'flickering clusters' proposed by Frank, *et al.*[42,43] All of the structural parameters listed in table T2.1 support the qualitative statement that water is a highly associated liquid.

2.3.2.1.2 Formamide. Pimentel and McClellan[38] quote the existence of puckered hydrogen bonded 'sheets' of molecules in crystalline formamide with layers of these sheets interacting through van der Waals forces.[44] Criss, *et al.*, speculate on the persistence of fragments of such hydrogen bonded structures in the liquid state.[45] The X-ray study of De Sando and Brown confirms this hypothesis with experimental evidence for highly associated liquid formamide involving hydrogen bonded cyclic dimers and higher order intermolecular associations.[46] Kollman and Allen cite theoretical calculations which also predict a high degree of association through hydrogen bonding.[39] In addition, all of the empirical structural parameters in table T2.1 indicate that formamide is an extraordinarily highly associated liquid, indeed, more highly associated than any of the other solvents studied with the possible exceptions of water and the alcohols.

2.3.2.1.3 Methanol. A large amount of data supports the view that methanol, too, is a highly associated hydrogen bonded liquid. Fletcher[47] has presented infrared data giving evidence for dimers and tetramers in the vapour phase, the conclusions being somewhat at variance with the implications of the data of Tucker, *et al.*,[48] who posited the existence of vapour phase trimers and octamers. Suggestion that similar associations persist in the liquid state has been propounded by Sandorfy, *et al.*,[49] based on their infrared study of the temperature dependence of hydrogen bonding in methanol. Evidence supports the existence of monomers, oligomers (two, three, or four molecule associations) and polymers (associations involving more than four molecules of solvent), probably in both linear and cyclic forms, in the liquid at ambient laboratory temperature.[50] This evidence is consistent with the implications of most of the empirical structural factors for methanol listed in table T2.1, although the value of the Trouton constant is probably low for a highly associated liquid.

2.3.2.1.4 Ethanol. The structural behaviour of ethanol is expected to parallel that of methanol except that ethanol might be expected to exhibit a rather less extensive hydrogen bonded structure as a simple result of the greater steric bulk of its ethyl group.[45] Indeed, the nuclear magnetic resonance study of Rao, *et al.*,[51] and the infrared study of Liddell, *et al.*,[52] indicate the presence of extensive association in the liquid through hydrogen bonding. The structural parameters of table T2.1 cannot serve as a basis for indicating whether ethanol is more or less associated than methanol, but the evidence that they both are associated is unequivocal.

2.3.2.1.5 *2,2,2*-Trifluoroethanol. Most of the literature reports on the structure of *2,2,2*-trifluoroethanol compare its behaviour with that of ethanol. Kirkwood *g*-factors (*cf.* table T2.1) indicate a similar degree of specific dipolar association for the two solvents. From the Trouton constant (*cf.* table T2.1) it appears that the fluoro-substituted alcohol is the more highly associated liquid whereas the nuclear magnetic resonance data[51] support the opposite view. Certainly the electron withdrawing effect of the CF_3 group renders the hydroxyl proton highly acidic and readily available for participation in hydrogen bonding, but the basicity of the oxygen atom is correspondingly reduced. Complications arise from the possibility of intramolecular hydrogen bonding between the acidic hydroxyl proton and the fluorines of the CF_3 group.[53,54] In any case, there is concensus that liquid *2,2,2*-trifluoroethanol appears to be highly associated.

2.3.2.2 Dipolar aprotic solvents. Intermolecular association in the dipolar aprotic solvents is considered to be fundamentally different from that occurring in dipolar protic solvents because of the greater difficulty of forming intermolecular hydrogen bonds. Interactions between dipolar aprotic solvent molecules are generally believed to result primarily from dispersion forces and from dipole-dipole attractions with hydrogen bonding being a relatively minor consideration. Consequently, one might anticipate that the dipole moments of the respective solvents should parallel their relative degrees of internal structure.

2.3.2.2.1 Nitromethane. The relatively high dipole moment of nitromethane (*cf.* table T2.1) might be expected to be conducive to intermolecular association in the liquid state. Indeed, de Maine, *et al.*, have found spectroscopic evidence for the dimerisation of nitromethane in dilute solutions of methanol and several nonpolar organic solvents.[55] Farmer and Kim, however, found no evidence for such dimerisation based upon their cryoscopic measurements in similar systems.[56] The paucity of data for various structural parameters (*cf.* table T2.1) precludes one's making a definitive statement regarding the structure of nitromethane, but the Trouton constant supports the view of little or no specific association.

2.3.2.2.2 Acetonitrile. Coetzee and Sharpe infer from various literature sources that acetonitrile is expected to exhibit little association through hydrogen bonding, but that dipole-dipole interactions are evidently significant.[57] Indeed, Lambert, *et al.*, found evidence for vapour phase dimeric association and assumed an antiparallel arrangement of dipoles.[58] This postulated configuration was criticised by Murray and Schneider on the basis of expected repulsion between the π-electrons of the nitrile groups of neighbouring molecules.[59] The negative deviation from unity of the Kirkwood g-factor listed in table T2.1 supports the proposed antiparallel arrangement (probably skewed) of adjacent dipoles in liquid acetonitrile. However, the low Trouton constant is indicative of a small degree of intermolecular association. Apparently both steric effects and dipole-dipole interactions are involved in determining the structure of liquid acetonitrile.

2.3.2.2.3 Tetramethylenesulphone (Sulpholane). Evidence for the self-association of tetramethylenesulphone is somewhat contradictory.[57] On one hand, the low enthalpy of fusion suggests a similarity in the structures of the liquid and the initial solid phase (a solid to solid phase transition occurs some 11 degrees below the temperature characterising the liquid to solid phase transition[60]), and this conclusion is supported by the increase of dielectric constant upon freezing the liquid.[61] On the other hand, the insensitivity of both dipole moment and dielectric constant to temperature change indicates the contrary.[61] The Trouton constant (*cf.* table T2.1) lends support to the assumption of significant specific structure in the liquid state.

2.3.2.2.4 *N*-Methyl-2-pyrrolidone. The extent and nature of self-association in *N*-methyl-2-pyrrolidone is not currently known. The dearth of data relating to its structure is evident both from an examination of the incomplete listings in table T2.1 and from the lack of mention of structural considerations in the recent review of Bréant.[62] One can only speculate that the observed high dipole moment should favour some degree of dipole-dipole interaction.

2.3.2.2.5 Hexamethylphosphorotriamide. Measurements of the variation of both dielectric constant and density with temperature have enabled Kessler, *et al.*, to determine 'structural characteristic factors' which reflect self-association in liquid hexamethylphosphorotriamide.[63] Gal, *et al.*, have studied both the variation of dielectric constant with frequency, thus enabling the determination of the Kirkwood *g*-factor, and the variation of viscosity with temperature.[64] As inferred from the *g*-factor value listed in table T2.1, hexamethylphosphorotriamide is apparently associated through short range specific interactions of dipoles arranged in a parallel configuration. Without revealing the nature of the interactions, the Trouton constant for hexamethylphosphorotriamide also indicates a relatively high degree of intermolecular association. The uncertainty in the reported values of the dipole moment is noted.[63,64]

2.3.2.2.6 Propylene carbonate. The intermolecular structure of liquid propylene carbonate has been the subject of some controversy in the literature. Dack has found evidence consistent with a significant degree of internal structure for this solvent.[32] The evidence relies on the difference between the molar cohesive energy and the molar internal pressure of the solvent being related to the extent of hydrogen bonding and specific dipole-dipole interaction. Furthermore, Dack has noted an approximately linear empirical correlation between this difference and the solvent dipole moment; thus, the high dipole moment of propylene carbonate could be interpreted as support for the view of specific inherent structure in the liquid. The intermediate value of the Trouton constant, however, cannot be considered as unequivocal support for this view. Nor can the question be decided on the basis of the Kirkwood correlation factor values. Both Cogley[65] and Simeral and Amey[66] report a value for this parameter of 1.18 at 298 K using $1.1n^2$ as the estimate of the high frequency dielectric constant. Using the data of Payne, *et al.*, and the same estimation of the high frequency dielectric constant in the Kirkwood-Fröhlich equation, a value of g near unity is obtained.[67] More recently Cavell estimated the value of the g-factor to lie between 0.8 and 0.9 in the temperature range 275-323 K, and he concluded that 'specific short range forces capable of generating a degree of local structure are not a significant feature of liquid propylene carbonate in the temperature range studied'.[68] In summary, the degree of specific structure present in liquid propylene carbonate is uncertain.

2.3.2.2.7 Dimethylsulphoxide. Throughout the dipolar aprotic solvent literature dimethylsulphoxide is often referred to as being highly structured (or ordered or associated) in the liquid state.[69] Both dielectric studies[26] and neutron inelastic scattering data[70] support the view of the existence of strong, nonspecific dipole-dipole interactions in the liquid. Cryoscopic[69,71] and nuclear magnetic resonance[57] data also indicate extensive intermolecular association. Infrared spectral data have been interpreted as indicating dimerisation, cyclisation, and possible polymerisation of dimethylsulphoxide into chains in carbon tetrachloride and in benzene solution.[72] This interpretation has been criticised by Amey on the basis of the Kirkwood correlation factor value.[26] The extraordinarily high value of the Trouton constant for dimethylsulphoxide (29.6 cal K^{-1} mol^{-1}) which has been reported[21,57] is apparently in error. The early work of Douglas[73] and its recent corroboration[17,74] indicate a much lower value (22.3 cal K^{-1} mol^{-1}) which appears to be more realistic when compared with other dipolar aprotic solvents. The reviews by Butler[75] and by Szmant[76] give additional data relevant to the self-association of dimethylsulphoxide. There can be little doubt that this solvent is highly associated in the liquid state at ambient laboratory temperature, in spite of the uncertainty attending the precise nature and geometry of the association.

2.3.2.2.8 *N,N*-Dimethylacetamide. Several authors have commented upon the inability of *N,N*-dimethylacetamide to form strong hydrogen bonds.[39,77,78] Nevertheless, infrared and Raman spectral evidence indicates the presence of dimers in the neat liquid at ambient temperature.[79] The intermediate value of the Trouton constant, together with both the relatively high dipole moment and the Kirkwood correlation factor, is consistent with some degree of solvent structure.

2.3.2.2.9 *N,N*-Dimethylformamide. The absence of strong hydrogen bonding in *N,N*-dimethylformamide is also well substantiated in the literature.[39,77,78] On the basis of the structural parameters listed in table T2.1, the extent of self-association in *N,N*-dimethylformamide is expected to parallel approximately that of *N,N*-dimethylacetamide.

2.3.2.2.10 *N,N*-Dimethylthioformamide. At present, the only basis for estimating the degree of intermolecular association in *N,N*-dimethylthioformamide are analogies to *N,N*-dimethylformamide structure and recognition of the relatively high dipole moment.[80] Consideration of these factors makes some form of dipole-dipole interaction seem likely.

2.3.2.3 Summary. It is apparent from the evidence presented that all of the solvents used in this study exhibit some degree of self-association behaviour beyond that which can be expected to arise from simple dispersion forces. Hydrogen bonding, where possible, and dipole-dipole interactions, either specific or nonspecific, can account qualitatively for most of the observed interaction behaviour of these polar liquids. In most cases insufficient data exist for the unambiguous determination of structural models for the interaction phenomena. However, the available data collectively suggest the following approximate order of decreasing extent of solvent intermolecular structure (abbreviations are as in table T2.1):

W, F > M, E, TFE, DMSO > HMPT, TMS > PC, NMP, DMA, DMF, SDMF, AN, NM.

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CHAPTER 3

EXTRATHERMODYNAMIC ASSUMPTIONS

A suitable means for estimating the contributions of single ions to the solvation energy of a complete electrolyte is prerequisite for the study of comparative cation solvation. The significance of the so-called 'solvent transfer activity coefficient' or 'medium effect' is discussed, and several proposed methods for estimating its numerical value are noted. One of these, the tetraphenylarsonium tetraphenylboride assumption (abbreviated TATB assumption) which was used in interpreting most of the experimental data collected in this work, is examined in some detail.

3.1 Introduction

A knowledge of the partial molar free energy of a species in solution is of fundamental importance to the understanding of single ion solvation in various media, for this quantity reflects the influence of the solvent on the dissolved species, and *vice versa*. For meaningful comparison of data collected in different solvents it is essential to compare standard partial molar free energies of the species in the various solvents being studied. Standard partial molar free energies are determined at rather arbitrarily chosen standard conditions (for experimental convenience, generally chosen to correspond to those of the laboratory) of temperature, pressure, and activity of the species being investigated.

The activity a of a species is related to its molar concentration c by equation E3.1 where y is termed the molar scale activity coefficient of the species. Activities, too, are expressed relative to an

$$a = cy \tag{E3.1}$$

arbitrarily chosen standard state, often an idealised hypothetical state. For a species in solution, the standard state is usually defined such that $y \rightarrow 1$ as $c \rightarrow 0$, *i.e.* the activity coefficient approaches unity in the limit of infinite dilution of the dissolved species in the solvent under consideration. However, if standard partial molar free energies are to be determined and compared for a single species in different solvents, then the activities of this species in the various solvents must be normalised or be referred to a single standard state in a single solvent. Furthermore, if comparisons are to be made between equimolar solutions in various media (as was done, experimentally, in this work), it is convenient merely to consider the activity coefficients referred to the same single standard state because in this case the molar concentration factor c in equation E3.1 can be eliminated. This was the approach followed by Owen[1] who expressed the activity coefficient of a species i at a finite concentration in solvent S referred to the standard state of infinite dilution in a different reference solvent R (left hand side of equation E3.2) in terms both of the activity coefficient of i at infinite dilution in S referred to the standard state of infinite dilution in R (first term on the right hand side of equation E3.2) and of the activity coefficient of i at the original finite concentration in solvent S referred to the standard state of infinite dilution of i in solvent S (second term on the right hand side of equation E3.2). Left hand subscripts indicate the medium in which

$$\ln {}^{R}_{S}y = \ln {}^{R}_{S}y_0 + \ln {}^{S}_{S}y \tag{E3.2}$$

species i is dissolved, left hand superscripts indicate to which medium the standard state of infinite dilution refers, and right hand subscripts are used to designate the concentration of species i. In this latter connexion, the subscript 0 represents infinite dilution, and the absence of a subscript denotes an unspecified finite concentration. Of course, an analogous equation can also be written for dissolution of species i in the reference solvent R. Equation E3.3 is in fact an identity relationship because ${}^{R}_{R}y_0$ is equal to unity by the original choice and definition of the reference standard state. Subtraction of equation E3.3 from

$$\ln {}^{R}_{R}y = \ln {}^{R}_{R}y_0 + \ln {}^{R}_{R}y \tag{E3.3}$$

equation E3.2, followed by combination of terms leads to equation E3.4 in which the first term on the right hand side reflects the effect of the solvent on the activity coefficient of species i and the second term reflects the effect of the concentration of species i. Hence, these

$$\ln \frac{{}^{R}_{R}y}{{}^{R}_{R}y} = \ln \frac{{}^{R}_{S}y_0}{{}^{R}_{R}y_0} + \ln \frac{{}^{S}_{S}y}{{}^{R}_{R}y} \tag{E3.4}$$

terms have been called the meduim activity coefficient and the salt activity coefficient, respectively.[2]

Since the activity coefficients, and thus the activities, of a single species in various solvents can be meaningfully compared relative to a single standard state in a reference solvent, it should be possible to do the same for the partial molar free energies of the species. Equation E3.5 expresses the partial molar free energy of a species *i* in solvent S in terms of its partial molar free energy under standard conditions in S and its activity in S referred to a standard state of infinite dilution in S. In equation E3.5, *T* is the absolute temperature, and *R* is the ideal gas constant. Equation E3.6 expresses

$${}_{\mathrm{S}}G = {}_{\mathrm{S}}G^{\circ} + RT \ln {}^{\mathrm{S}}_{\mathrm{S}}a \qquad \text{E3.5}$$

${}_{\mathrm{S}}G$ for species *i* in solvent S relative to standard conditions and a standard state in reference solvent R. Combination of equations E3.5

$${}_{\mathrm{S}}G = {}_{\mathrm{R}}G^{\circ} + RT \ln {}^{\mathrm{R}}_{\mathrm{S}}a \qquad \text{E3.6}$$

and E3.6, together with substitutions from equations E3.1 and E3.4, yields the relationship between the standard partial molar free energy of species *i* in solvents S and R and the medium activity coefficient as shown in equation E3.7. Thus, in principle, it is possible to compare

$${}_{\mathrm{S}}G^{\circ} - {}_{\mathrm{R}}G^{\circ} = RT \ln \frac{{}^{\mathrm{R}}_{\mathrm{S}}y}{{}^{\mathrm{S}}_{\mathrm{S}}y} = RT \ln \frac{{}^{\mathrm{R}}_{\mathrm{S}}y_0}{{}^{\mathrm{R}}_{\mathrm{R}}y_0} \qquad \text{E3.7}$$

the standard partial molar free energies of a single species in various solvents, all referred to one standard state in one reference solvent.

Throughout the foregoing discussion, all of the equations presented are equally valid whether the 'single species' in the various solvents be a neutral molecule, a complete electrolyte, or a single ionic species. In practice, however, measurements can only be made on uncharged molecules or electrically neutral combinations of ions in solution; with conventional experimental techniques it is impossible rigorously to determine the contributions of the individual ions to the variables which characterise the solvation of complete electrolytes in various solvents.[3,4] The relationship between the experimentally accessible solvation and solution data for a representative complete electrolyte and the experimentally inaccessible data for the ionic components of the electrolyte is presented schematically in figure F3.1. The solution to this classical problem is of paramount importance to the complete understanding of ion solvation phenomena, and a number of methods, all of which rely on invoking 'extrathermodynamic' arguments and assumptions, have been proposed for the estimation of the values for the individual ions.

3.2 Extrathermodynamic Assumptions

Several reviews comparing various extrathermodynamic assumptions for estimating single ion solvation energies and medium effects have appeared in the recent chemical literature.[2,5-7] The essential features of some of the more widely used methods are outlined below both for the sake of completeness and to facilitate subsequent discussion of experimental data compared for the various assumptions (*cf.* chapter 5). As Popovych has noted, the assumptions can be divided into two major groups: those based upon an assumed negligible liquid junction potential being established between contiguous dissimilar solvents, and those based upon correlations between the size and the solvation energy of a solute.[2]

3.2.1 Assumed Negligible Liquid Junction Potential. Perhaps the first-used,[2,8] historically, and certainly the simplest,[2,9] experimentally, of the extrathermodynamic assumptions proposed for estimating single ion medium effects or solvent activity coefficients is the negligible liquid

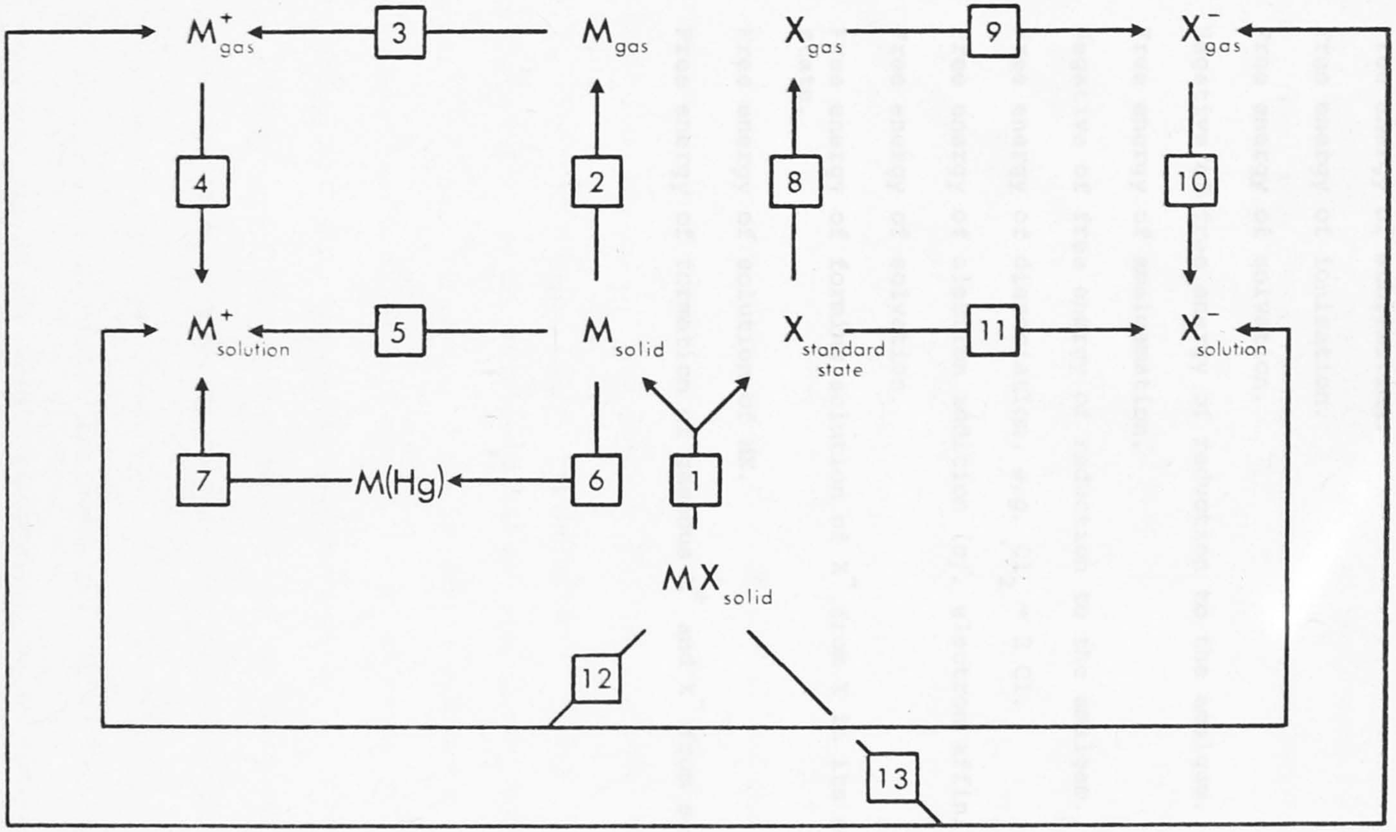

FIGURE F3.1 : Relationship between the free energy of solvation and of solution of an electrolyte (represented for simplicity by an alkali metal halide MX). See following page for legend.

FIGURE F3.1 (Continued)

LEGEND:

1. Negative of the free energy of formation of the electrolyte.
2. Free energy of sublimation.
3. Free energy of ionisation.
4. Free energy of solvation.
5. Negative of free energy of reduction to the amalgam.
6. Free energy of amalgamation.
7. Negative of free energy of reduction to the amalgam.
8. Free energy of dissociation, *e.g.* $Cl_2 \rightarrow 2\,Cl$.
9. Free energy of electron addition (*cf.* electron affinity).
10. Free energy of solvation.
11. Free energy of forming solution of X^- from X in its standard state.
12. Free energy of solution of MX.
13. Free energy of formation of gaseous M^+ and X^- from solid MX.

junction potential assumption (abbreviated NLJP assumption). In an electrochemical cell such as cell C3.1, in which the electrode processes are reversible and the concentration of M^+ is the same in both solvents, the measured cell potential reflects not only the medium and salt effects for M^+, but also the potential present at the junction between the two solvents. This latter potential, the so-called liquid junction

$$\mathrm{M}\ \Big|\ \begin{matrix}\mathrm{M}^{+}\\ \text{solvent R}\end{matrix}\ \Big\|\ \begin{matrix}\mathrm{M}^{+}\\ \text{solvent S}\end{matrix}\ \Big|\ \mathrm{M} \qquad \text{C3.1}$$

potential, arises from the migration or diffusion of charged species across the liquid-liquid boundary.[10] (*N.B.* Parker, *et al.*, have pointed out that account must also be taken of solvent molecules which traverse the boundary region as part of the 'solvation sheath' of the ion charge carriers.[11]) If the time dependence of the diffusion process is discounted, the junction potential can be approximated by the Henderson or Planck equation in terms of the charges, transport numbers, and activities of ions throughout the boundary region. However, an explicit solution to the Henderson or Planck equation depends upon a knowledge of the variation of the ion transport numbers and activities upon traversing this region.[10-13] This knowledge is not presently available. Nevertheless, it is possible under certain conditions to suppress, or otherwise to render negligible, this liquid junction potential. In practice this is done by interposing a salt bridge between the two solutions of cell C3.1, but separated from them by means of porous plugs allowing electrical contact without significant mass transport. If the electrolyte concentration in the bridge greatly exceeds the concentration of M^+ in solvents R and S, then the ions of the bridge electrolyte can be considered the major charge carriers. The liquid junction potential is then suppressed provided the cation and the anion of the bridge electrolyte have nearly equal mobilities and nearly equal activities in each boundary region.[9,14,15]

Evidently, the successful application of this assumption rests upon finding a bridge electrolyte to satisfy these criteria. Several authors have pointed out that this is no simple task. However, Parker, *et al.*, have demonstrated that this assumption, using tetraethylammonium picrate as the bridge electrolyte, gives much the same results as several other types of assumption provided that the two solvents of cell C3.1 are of essentially the same type, *i.e.* either both protic or both dipolar aprotic solvents.[9] If the liquid junction potential established in cell C3.1 can be neglected, then the overall cell potential is simply related to the medium effect for M^+ in solvents R and S (assuming negligible salt effects).[2,6,16]

3.2.2 Correlations between Size and Solvation Energy of Solute. This second category of extrathermodynamic assumption can be further subdivided into applications of the Born equation, extrapolation methods, and empirical relationships for reference solutes.[2]

3.2.2.1 Born treatment. Through the Born equation, the difference in the solvation energies of a single type of ionic species in two solvents R and S can be related to the number of ions involved (N), to the ion radius (r), to the ion charge (ze), and to the dielectric constants of the two solvents (D_S and D_R), as shown in equation E3.8. The Born

$$G^o_S - G^o_R = \Delta G^o_{tr} = \frac{N(ze)^2}{2r}\left(\frac{1}{D_S} - \frac{1}{D_R}\right) \qquad \text{E3.8}$$

theory treats the ion as a rigid sphere in a dielectric continuum with all ion-solvent interactions being electrostatic and nonspecific in nature.[17] Although the Born theory is successful in accounting for the major part of ion solvation energies, it is insufficiently sensitive to reflect the relatively small energy changes which accompany 'transfer' of an ion from one solvent to another.[2,5,12] The neglect of solvent structural considerations, of electrostriction, of changes in ion radius upon solvation, and of dielectric saturation in the immediate ion vicinity are all recognised shortcomings of the simple Born theory. Some progress has been achieved by modifying the Born equation to allow specifically for dielectric saturation and changes in the ion radius in solution.[2,6]

3.2.2.2 Extrapolation methods. The extrapolation technique originally proposed by Izmailov[18,19] for determining single ion solvation free energies consists of plotting the experimental free energies of solvation of a series of acids HX, where X is a halide ion, against the reciprocal radius of the halide ion. Extrapolation to infinite halide ion radius was assumed to give a value for the free energy of solvation of the proton. Alternatively, the difference in solvation energies of MCl and HCl, where M is an alkali metal ion, could be plotted against the reciprocal alkali metal ion radius. Extrapolation to infinite alkali metal ion radius could again be assumed to yield the free energy of solvation of the proton. In a more recent proposal, Izmailov suggested that the solvation free energy difference for isoelectronic alkali metal and halide ions should tend to zero with increasing principal quantum number n of the orbital formed upon bonding the solvent lone pair electrons to the ions.[20-22] Thus, plotting the experimentally accessible values of $-G_i^\circ + [(G_\mathrm{M}^\circ - G_\mathrm{X}^\circ)/2]$, where M and X are isoelectronic alkali metal and halide ions, against $1/n^2$ led Izmailov to values of G_i° for $i = \mathrm{H}^+$, Li^+, and Ag^+. Once a value for the solvation free energy for any single ionic species was obtained in this manner, it could be combined with solvation data for complete electrolytes to obtain the single ion values for other ionic species.

Several variations of the Izmailov method have also been used.[2,6,7] Feakins, *et al.*, have determined single ion free energy values from plots of free energies of transfer of electrically neutral combinations of ions, with one ion constant, against the reciprocal radius of the variable ion.[23,24] De Ligny, *et al.*, in their extrapolations against reciprocal ion radius, have included a neutral component as well as the electrostatic contribution to the overall solvation energy of an ion.[12,25] The neutral part of the ion solvation energy could be estimated from either solvation or transfer free energies of isoelectronic noble gases or other uncharged molecules of analogous size.

Determinations of relative single ion solvation free energies by means of extrapolation techniques have met with only limited success. Popovych has pointed out that different extrapolation methods often do not even yield consistent signs for a specific comparison of ion solvation in two solvents.[2] Errors undoubtedly arise from the long (possibly nonlinear) extrapolations required.[2,6] The future success of the method evidently depends on more accurate estimations of the neutral contributions to the total ion solvation energies.

3.2.2.3 Reference solutes. In view of the inadequacies of the abovementioned techniques for determining single ion free energies of solvation, many workers have resorted to empirical methods based upon assumed values for the solvation free energies of suitably chosen reference solutes.

3.2.2.3.1 Solvent independent redox couple potentials. It is evident from figure F3.1 that the partial molar free energy of solvation of a representative metal ion consists of the partial molar free energies (with appropriate signs) of ionisation, sublimation, amalgamation, and reduction.[26-28] Of these quantities, only the reduction free energy is affected by a change of solvent. Furthermore, the standard reduction free energy G°_{red} is directly proportional to the standard electrode potential E° of the reducible ion (assuming a reversible electrode couple) through equation E3.9 in which z is the ion charge and F is the Faraday constant. It follows that the partial molar free energy of

$$G^{\circ}_{\mathrm{red}} = -zFE^{\circ} \qquad \text{E3.9}$$

solvation for a single ion species could be determined unambiguously if its redox potential were measured against another redox couple whose potential is solvent independent.[6,29] Indeed, it was this realisation that led Pleskov to propose that the redox potential of the Rb^+/Rb couple is solvent independent.[30] The proposal was based on the condition that the reference ion be large, be of low charge and polarisability, and be involved in no strong or specific solute-solvent interactions in order to ensure nearly constant solvation energies of the reference ion in all solvents. This approach was promising but seemed limited by the insufficiently large size of the rubidium cation and by the failure to make explicit allowance for the effect of a large uncharged solute on the solvent structure.[6]

Strehlow, *et al.*, recognised the significance of solvent independent redox couple potentials and undertook a study of a number of redox reactions to find a more suitable reference electrode couple.[31] They investigated several large, spheroidal, organometallic ion-molecule structural analogues in which the central, charge-carrying, metal atoms lay 'buried' beneath insulating organic ligands. Both ion and molecule were expected to be solvated in a similar manner and to much the same extent. The ferrocene/ferricinium system appeared best to fulfil most of the requirements used as criteria for assessing the suitability of such redox couples as solvent independent reference electrodes.[6] The applicability of the ferrocene assumption seems quite general except when used for determining single ion free energies of transfer to or from water or formamide. Parker, *et al.*,[9,32,33] have interpreted this failing as an indication of competitive solvation of the first and second kinds[34] in these highly structured[35] solvents. The organic ligands are expected to favour formation of a 'surface' of ordered solvent molecules around both the ion and molecule of the redox couple (solvation of the second kind) whereas only the not-so-large ferricinium ion, because of its charge, can be expected to cause direct orientation of solvent dipoles (solvation of the first kind). Thus, in such solvents a fundamental difference can be expected in the type of solvation of ion-molecule structural analogues if the ion and the molecule are insufficiently large and inadequately shielded to obviate these complications of electrostatic origin. Such criticisms could also apply to a number of other popular redox couples used as reference electrode systems.[36-39]

3.2.2.3.2 Reference electrolytes. The use of reference electrolytes in the estimation of single ion medium effects or solvent activity coefficients retains most of the advantages of the solvent independent redox couple potential method whilst avoiding the possibility of differing solvation mechanisms for charged and uncharged structural analogues in the same solvent. The method consists essentially of choosing a suitable reference electrolyte, determining its solubility products in the solvents of interest, and dividing the resulting free energies of transfer into equal contributions from the cation and the anion of the reference electrolyte. Possible differing solvation energies arising from the expected opposite orientations of solvent dipoles interacting electrostatically with the cation and the anion can be minimised by choosing a reference electrolyte such that both ionic components consist of a central charged atom surrounded by organic ligands, such that both ions are large and of nearly equal size, and such that both ions are as nearly spherical and as nearly structurally equivalent as possible. If these criteria (*cf.* the criteria used to determine the suitability of a reference redox couple) are met, the electrostatic contributions to the ion solvation energies should be significantly decreased. Of course, once the single ion free energies of transfer are known for one ion, those for other single ionic species can be determined from free energies of transfer of whole electrolytes (as derived from, say, solubility data). Convincing arguments have also been advanced advocating the extension of this assumption to apply to the enthalpies and entropies of transfer of the reference electrolyte ions between solvents.[32,49] The most popular reference electrolytes currently being used include tetraphenylphosphonium tetraphenylboride,[40] tetraphenylarsonium tetraphenylboride,[40,41] and triisoamyl-*n*-butylammonium tetraphenylboride[42,43,44].

3.3 The Tetraphenylarsonium Tetraphenylboride (TATB) Assumption

Because most of the experimental data reported in this thesis have been collected and analysed on the basis of the assumed equality of the solvation free energies, enthalpies, and entropies of the tetraphenylarsonium cation and the tetraphenylboride anion in each solvent, it is appropriate to comment on the validity of this assumption.

The similar large sizes and shapes of both the tetraphenylarsonium and tetraphenylboride ions, together with the fact that their respective central charge-carrying atoms are surrounded by aryl groups, make these ions seem excellent candidates for a reference electrolyte to be used in estimating single ion free energies of solvation. Indeed, for these reasons both ions are expected to be solvated equally in a particular solvent (*i.e.* similar solvation energies and ion-imposed solvent structures for the two ions). These expectations have found a significant degree of experimental support insofar as medium effects for several reference electrolytes (including tetraphenylarsonium tetraphenylboride) are in close agreement with twice the value of the medium effects calculated by combining the Born type electrostatic component of the solvation energy with the neutral component estimated from similarly sized molecular structural analogues.[2,44,45] The expectations are not always upheld when the medium effects involve 'transfer' of ions between dissimilar solvent types, such as between a dipolar aprotic and a protic solvent.[46] As Parker, *et al.*, have noted, this apparent failing possibly arises from the complication of solvation of the second kind occurring in highly structured protic solvents capable of hydrogen bonding (*cf.* chapter 2).[32]

Popovych has summarised a number of objections to the use of the TATB assumption.[2] The most serious criticisms centre around uncertainties in the radii of the reference electrolyte ions (estimates ranging from 4.2 to 5.5 × 10^{-10} m), suggestion of stronger solvation of the cation than the anion of the reference electrolyte in dipolar aprotic solvents, and possibilities of specific solvent-reference ion interactions. Certainly significant differences in the radii of the reference cation and anion would be expected to contribute to differences in their solvation energies in a particular solvent. However, for a number of solvent systems the solvation energies of the ions appear to be equal within experimental error. Nevertheless, the uncertainty in the size of the ions does need to be resolved. Although dipolar aprotic solvents do discriminate in their solvation of small cations and anions, they are not expected to do so for very large ions; furthermore, the experimental data generally support the view of similar solvation of the reference ions.[44,45] Unquestionably, the most serious objection to the TATB assumption is the possibility of specific interactions of solvent molecules with either the cation or the anion of the reference electrolyte. The nuclear magnetic resonance and infrared studies of Coetzee, *et al.*,[47] indicate that the tetraphenylarsonium and tetraphenylboride ions may be involved in specific solvation interactions in some solvents, but as several authors[2,48-50] have noted, it is difficult to quantify chemical shifts in terms of the energetics of proposed ion-solvent interactions. Moreover, there is some uncertainty attending the assumptions that Coetzee, *et al.*, used, namely that the tetraethylammonium cation causes no solvent chemical shift in any of the solvents studied (including water) and that the perchlorate anion causes no solvent chemical shift in the dipolar aprotic solvents. Jolicoeur, *et al.*, have found near infrared spectral evidence to indicate that water discriminates between the solvation of the cation and the anion of the tetraphenylarsonium tetraphenylboride reference electrolyte, the anion apparently acting as a structure maker and the cation evidently not appreciably affecting the water structure.[51] Millero has found evidence for differing molal expansivities and differing rates of change of the expansivities with temperature for these two ions, these findings again suggesting different ion-solvent interactions for the reference cation and anion.[52,53] Jolicoeur, *et al.*, also reported markedly different effects for these two ions on the electron paramagnetic resonance behaviour (spin relaxation) of *2,2,6,6*-tetramethyl-*4*-piperidine-*1*-oxyl which is a stable nitroxide radical in aqueous solution.[54] They were unable to determine, however, whether the effect resulted from a greater hydrophobic interaction of the anion with water or from some other effect. In a later study of molal volumes, heat capacities, and viscosities, Jolicoeur, *et al.*, noted only slight differences in the behaviour of the two ions upon transfer from water to methanol.[55] The enthalpies of transferring the reference ions between solvents have been interpreted by Friedman[56] and by Friedman, *et al.*,[57] as indications of possible specific interactions between the reference ions and solvent molecules, although the specific effects apparently are not reflected in the ion transfer free energy data.[56] The validity of the assumptions and the extrapolation method used by Friedman, *et al.*, can be questioned, and one author[50] feels that Friedman's conclusions hardly seem justified in light of a range of other chemical evidence.[49] The specific effects envisaged in these various studies have not been specified, but they can be considered to result either from opposite orientations of solvent dipoles around the oppositely charged reference cations and anions, or from orientation of solvent dipoles about one ion and not the other of the reference electrolyte. Such orientation in either scheme implies some degree of 'leakage' of the central atom charge into the surrounding phenyl rings, but charge dispersal over four phenyl rings should minimise strong interactions.[45] Several authors have cautioned that the planar structure of each of the phenyl rings of the reference electrolyte ions is not entirely consistent with an effectively spherical shielding layer between the respective central atoms of the ions and the surrounding solvent molecules.[40,45,47] Indeed, from their spectral studies, Long, *et al.*, have suggested the possible inclusion of a water molecule in the coordination sphere of tetraphenylarsonium ions in aqueous media.[58] Water was thought to occupy an axial position in trigonal bipyramidal coordination of pentavalent arsenic, but Long, *et al.*, freely admit that the evidence taken as support for this view is ambiguous. No similar findings were reported for methanol, in which the arsenic of the tetraphenylarsonium cation apparently remains tetracoordinate. Clearly, more substantiating experimental work is required before the claims of either the advocates or the critics of the TATB assumption can catagorically be accepted or denied. The bulk of existing experimental data, however, points to the reliability (as judged by comparisons with data based on other assumptions) of the TATB assumption in estimating single ion solvent activity coefficients or medium effects, but due caution should be exercised in its application both for obtaining and for interpreting new data.

It should be noted, however, that the reference electrolyte assumption in general, and the TATB assumption in particular, constitutes a sound basis for recording data for the behaviour of various species in solution regardless of whether the original assumption is valid or not. For example, if the contributions of the ionic components of a reference electrolyte are unequal for transfer between solvents, then the 'error' in the reference cation value (for the free energy, enthalpy, or entropy) must be equal in magnitude but opposite in sign to the corresponding 'error' in the reference anion value. These (constant) errors will, of course, be reflected in all other single ion values determined on the basis of the original assumption. However, the errors cancel when a cation value is combined with an anion value to yield a value for a complete electrolyte. Similarly, provided the same assumption is used throughout, comparisons between cations (or between anions) are exact because, once again, the errors cancel.[9,49]

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CHAPTER 4

EXPERIMENTAL METHODS

In this chapter the apparatus and general techniques employed for the collection of the experimental data are presented and discussed. In addition, the purification and handling of reagents common to work reported in all subsequent chapters are described. The instances requiring these methods to be altered for specific systems are noted in appropriate places in the relevant chapters.

4.1 Single Ion Free Energies of Transfer Determined from Potentiometric Measurements

As noted from figure F3.1 in chapter 3, the free energy of solvation of a metallic cationic species (the chemical solvation free energy as defined by the difference in the free energies of the cationic species in solution and in the gas phase[1-4]) is related to its standard free energy of reduction to a pure metallic state or to an amalgam of the metal with mercury.[5] Furthermore, this standard reduction free energy is related to the standard electrode reduction potential of the cation in the solvent being considered as shown in equation E3.9 of chapter 3. Comparison of the solvation of a single ionic species in two different solvents, R and S, then leads to equation E4.1. The term ${}^{R}\Delta^{S}G_{tr}\ M^{+}$

$$ {}^{R}\Delta^{S}G_{tr}\ M^{+} = -nF\Delta E \qquad \text{E4.1} $$

represents the difference in the standard chemical free energies of solvation of M^{+} in the two solvents and is called the single ion free energy of transfer of M^{+} from solvent R to solvent S. The factor ΔE represents the difference in the standard electrode reduction potentials of the ionic species in the two solvents. The right hand superscript ^{o} for denoting standard quantities (*cf.* chapter 3) has been omitted for the sake of clarity. Thus, if one assumes negligible salt effects and a negligible liquid junction potential at the solvent-solvent interface, a simple potential measurement on cell C4.1 leads directly to a value of the free energy of transfer of M^{+} from reference solvent R to solvent S. In cell C4.1 a vertical line represents a phase boundary,

$$ M \left| \begin{matrix} M^{+} \\ \text{solvent R} \end{matrix} \right\| \begin{matrix} M^{+} \\ \text{solvent S} \end{matrix} \right| M \qquad \text{C4.1} $$

and a double line indicates a liquid junction potential assumed to be negligible.

4.1.1 Apparatus. The apparatus used for this work was designed to enable measurements of the potential of cell C4.1 for various solvents R and S.[6] Both for the sake of safety (in the case of the alkali metals) and for experimental convenience, metal-mercury liquid amalgam electrodes were used instead of solid pure metals. The apparatus consisted essentially of three major parts (*cf.* figure F4.1): an amalgam generating cell, an amalgam receiving reservoir in which concentrated amalgams could be diluted with pure mercury, and a liquid junction electrochemical bridge cell. These components were arranged vertically to allow for gravity feed of the amalgam from one cell to that below. All cells could be flushed simultaneously and continuously with oxygen-free dry nitrogen. The cells, as well as the gas and electrolyte delivery and exhaust tubes, were constructed of Pyrex glass. Teflon stop-cocks were used throughout the assembly. A nylon Swagelok union was used for joining the amalgam generating cell to the receiving reservoir; Teflon Swagelok unions were used for connecting this latter cell to the liquid junction bridge cell. Platinum wires sealed through the glass walls of the cells and capillaries served to establish electrical contact between the amalgam and external leads.

Although the basic cell design resembles that described by Bennetto and Willmott,[7] several aspects of the liquid junction cell design are of particular interest. Amalgam delivery to each side of the cell was by means of 0.4 millimetre internal diameter capillaries of 18 centimetre length. Stop-cocks for control of amalgam flow and removable glass cups at the capillary tips provided several choices of amalgam electrode configuration: streaming, dropping, spilling pool, or stationary pool. In the streaming and dropping configurations, contact time of the amalgam with solution was reduced to a minimum by allowing the spent amalgam to fall free of the solution into a separate waste chamber beneath each side of the cell. A bridge compartment

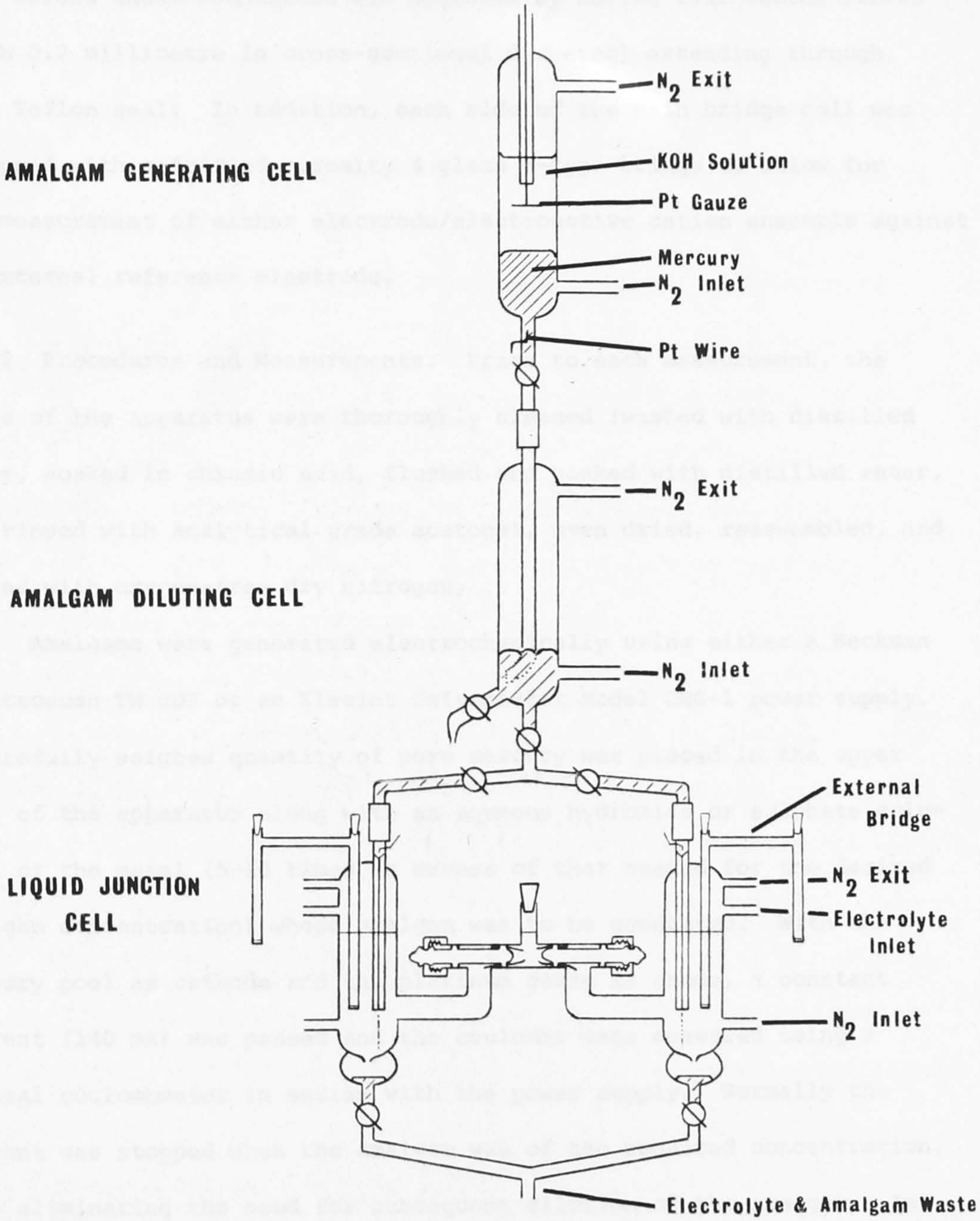

FIGURE F4.1 : Apparatus for the potentiometric determination of free energies of transfer. The case for generation and use of potassium amalgam electrodes is illustrated.

separated the two sides of the cell, with the bridge solution being isolated from the electrolytes in the two side chambers by means of removable Teflon seals. Electrical contact with minimal mass transport across these boundaries was achieved by having four cotton fibres (each 0.2 millimetre in cross-sectional diameter) extending through each Teflon seal. In addition, each side of the main bridge cell was equipped with a fritted porosity 4 glass H-type bridge to allow for the measurement of either electrode/electroactive cation ensemble against an external reference electrode.

4.1.2 Procedures and Measurements. Prior to each measurement, the cells of the apparatus were thoroughly cleaned (washed with distilled water, soaked in chromic acid, flushed and soaked with distilled water, and rinsed with analytical grade acetone), oven dried, reassembled, and purged with oxygen-free dry nitrogen.

Amalgams were generated electrochemically using either a Beckman Electroscan TM 30P or an Elscint Galvanostat Model CHG-1 power supply. A carefully weighed quantity of pure mercury was placed in the upper cell of the apparatus along with an aqueous hydroxide or sulphate solution of the metal (5-10 times in excess of that needed for the desired amalgam concentration) whose amalgam was to be generated. With the mercury pool as cathode and the platinum gauze as anode, a constant current (140 mA) was passed and the coulombs were measured using a digital coulombmeter in series with the power supply. Normally the current was stopped when the amalgam was of the required concentration, thus eliminating the need for subsequent dilution of the amalgam. In such cases, the amalgam diluting cell served the alternative purpose of separating the freshly-prepared amalgam from the aqueous electrolyte in the generating cell. Nitrogen was bubbled upwards through the mercury during amalgam generation and through the amalgam stored in the receiving reservoir.

The two side cells of the liquid junction bridge were filled with their complements of electrolytes in appropriate solvents by using a nitrogen pressure loading system. Once within the side cells, the solutions were purged with purified nitrogen. The bridge was filled manually, using a pipette. After the amalgam was generated and the solutions were purged with nitrogen, the electrodes were set in operation by manipulating the stop-cocks to establish amalgam flow through the capillaries.

All measurements were conducted at a constant temperature of 298 ± 1 K. Potentials were monitored using a high impedance Radiometer pH Meter 26 and were recorded as soon as amalgam flow was established through the electrolyte solutions. Values were generally stable to better than ±5 mV over 5 minutes, but slow drifts in potential with time were occasionally observed, probably arising from diffusion of bridge electrolyte into the side cell solutions or, in the case of pool electrodes, from possible amalgam decomposition. As expected, the cell potential was found to be independent of the concentration of metal in the amalgam since the same dilute amalgam, split into two streams, flowed simultaneously into the electrolyte solutions in each side of the liquid junction bridge cell. Somewhat unexpectedly, however, the cell potential was dependent, in some cases, on the polarity of the electrodes relative to that of the potentiometer. This effect became evident only as the solvent purification and handling techniques improved sufficiently to achieve lower solvent conductivities than those obtained initially (*cf.* table T4.1 and chapters 5 and 6) and to maintain water content below 2.5×10^{-3} *M* for all solvents (*cf.* table T4.1 and chapter 7). The anomalous potentiometer response was traced to a higher solution resistance which apparently became comparable to that of the potentiometer itself. In such a case, the potentiometer is incapable of sensing the relative potentials of the two electrodes

TABLE T4.1

DATA RELEVANT TO PURITY OF SOLVENTS

SOLVENT[a]	WATER CONTENT mol dm^{-3} × 10^{3}		CONDUCTIVITY S m^{-1} × 10^{4}		BOILING POINT K	PRESSURE Pa × 10^{-2}
	minimum[b]	maximum[c]	experimental	literature		
E		2.78	0.41	0.001-391.0[d]	351	953.1
TFE		11.00	0.39		347	953.1
HMPT	1.00	12.79	0.19		357	2.7
NMP		11.11	0.39	0.01-0.02[d]	313	0.3
M	2.28	2.78	2.64	0.002-1.5[d]	337	953.1
NM		2.73	2.70	0.005-0.656[d]	372	953.1
DMF	3.62	11.51	0.32	0.03-9.75[d]	307	4.3
AN	1.67	3.28	0.19	0.01-1.0[d]	354	953.1
DMA		4.84	0.71	0.08-0.20[d]	331	12.0
TMS		8.05	0.052	0.002-0.023[d]	353	0.7
DMSO	2.22	2.22	0.37	0.02-0.03[d]	329	4.0
SDMF	2.50	19.45	2.32	0.19[e]	343	1.3
PC		2.00	0.15	1.0-2.0[d]	369	4.0
W			0.20	0.03-0.08[f]	372	953.1
F	3.34	34.85	34.74	0.2-8700.0[d]	341	1.3

a. Abbreviations are as in table T2.1.

b. Used for work reported in chapter 7.

c. Used for work reported in chapters 5 and 6.

d. Data taken from reference 19.

e. Data taken from reference 20.

f. Data taken from reference 21.

in an 'open circuit' equilibrium configuration, because a significant net current flows in the cell. According to the Tafel[8,9] simplification of the more general Butler-Volmer[9-13] relationship, this current is related to the deviation of the measured potential from the true reversible potential of the electrodes. This 'overpotential' was suppressed, experimentally, by the addition of 10^{-2} *M* tetraethylammonium perchlorate as supporting electrolyte in the side cell solutions of the liquid junction cell. When this was done, the cell resistance was sufficiently lower than that of the potentiometer for normal potentiometer behaviour to be observed for either polarity of the electrodes. Instances which required this procedure to be followed are noted in subsequent chapters (*cf.* chapter 7).

4.2 Single Ion Enthalpies of Transfer Derived from Calorimetric Measurements

Whereas single ion free energies of transfer are directly accessible experimentally from potentiometric measurements, corresponding enthalpies of transfer are derived quantities. They are obtained from directly measurable enthalpies of solution of complete electrolytes in the various solvents of interest, in conjunction with the assumption that the enthalpy of transferring tetraphenylarsonium tetraphenylboride from one solvent to another consists of equal contributions from the tetraphenylarsonium cation and the tetraphenylboride anion (the TATB assumption).

All enthalpies of solution determined in this work were measured at 298.15 ± 0.05 K using an LKB 8700-1 Precision Calorimetry System supplied commercially by LKB-Produkter AB, Stockholm, Sweden. The 0.1 dm^3 reaction vessel used was that supplied by the manufacturer. The instrumental design was similar to that described by Sunner and Wadsö,[15] and the experimental technique followed was that of Hedwig and Parker.[16] Rather than plotting resistance *versus* time curves manually, the voltage output from the Wheatstone bridge was monitored on a Hitachi QPD 54 chart recorder. The operating conditions were those suggested by the manufacturer, and the recorder sensitivity was adjusted to correspond to a 50 millimetre pen deflection for a 0.1 Ω thermister resistance change. Results were analysed either using the Dickinson[17,18] method for calculating the corrected temperature change accompanying salt dissolution when reaction times were short (less than 5 minutes), or using the Regnault-Pfaundler[17,18] method when dissolution times were protracted (more than 5 minutes).

4.3 Materials

4.3.1 Solvents. All of the solvents studied in this work were dried and fractionally distilled at least twice before use. Measurements of the conductivity of the purified solvents (using a Wayne Kerr Universal Bridge B221 with a conductivity cell of cell constant 193 m^{-1}) and Karl Fischer titrimetric determinations of their water content (using a Radiometer Titration Assembly Type TTA 1c in conjunction with a Titrator 11 and a pH Meter 26) were used to gauge the efficacy of the purification methods, as indicated in table T4.1. Ethanol, E (Ajax Univar analytical reagent), was dried by refluxing the solvent over a quantity of magnesium ethoxide generated according to the method of Vogel.[22] The dry solvent was then fractionally distilled twice at atmospheric pressure. *2,2,2*-Trifluoroethanol, TFE (Eastman Kodak), was dried by stirring with potassium carbonate, followed by two successive fractional distillations at atmospheric pressure. Hexamethylphosphorotriamide, HMPT (Aldrich), was first fractionally distilled under a reduced pressure of nitrogen, and then fractionally crystallised twice, prior to stirring over Linde 4A activated (by heating to

800 K in air) molecular sieves. The dry solvent was then again fractionally distilled under the initial conditions. *N*-Methyl-2-pyrrolidone, NMP (Aldrich), was dried by stirring over calcium sulphate and then twice fractionally distilled under a reduced pressure of dry nitrogen. Methanol, M (Ajax Univar analytical reagent), was purified in a manner analogous to that used for ethanol; however, the drying agent was magnesium methoxide as generated by the method of Vogel.[22] Nitromethane, NM (Ajax Unilab laboratory reagent), was dried on calcium sulphate, passed successively through columns of basic, acidic, and neutral alumina, and then refluxed over silver perchlorate for several hours. *N,N*-Dimethylformamide, DMF (Mallinckrodt analytical reagent), after drying over Linde 4A activated molecular sieves, was passed through a basic alumina column as recommended by Moe,[23] prior to redrying and fractional distillation under a reduced pressure atmosphere of dry nitrogen. Acetonitrile, AN (Ajax Univar analytical reagent) was subjected to the benzoyl chloride-potassium permanganate treatment described by Mann, *et al.*[24] *N,N*-Dimethylacetamide, DMA (Aldrich), was dried on Linde 4A activated molecular sieves prior to fractionation under a reduced pressure atmosphere of dry nitrogen. Tetramethylenesulphone or sulpholane, TMS (Eastman Kodak), was purified by the hydrogen peroxide-sulphuric acid treatment followed by granular sodium hydroxide as described by Jones.[25] Two final fractionations from powdered calcium hydride under a reduced pressure atmosphere of dry nitrogen completed the procedure. Dimethylsulphoxide, DMSO (Merck), was also fractionally distilled under a reduced pressure atmosphere of dry nitrogen after the solvent had been dried by stirring over calcium hydride. *N,N*-Dimethylthioformamide, SDMF, was prepared from purified *N,N*-dimethylformamide (as described above) and phosphorus pentasulphide (BDH laboratory reagent) according to the method of Willstatter and Wirth.[26] Further purification was by drying on molecular sieves and vacuum distillation.

Propylene carbonate, PC (Aldrich), was dried on calcium sulphate and then vacuum distilled. The water, W, used in these experiments was deionised and distilled in an all glass apparatus. Formamide, F (Ajax Unilab laboratory reagent), was initially dried on calcium sulphate followed by fractional distillation under vacuum. The resulting material was further purified by the method of Notley and Spiro.[27]

4.3.2 Mercury. The mercury used for amalgam preparations was first washed with dilute nitric acid followed by prolonged rinsing with distilled water. The mercury treated in this manner was further purified by successive ultrasonic cleansings, once under a layer of Freon TF, twice under a layer of 10% nitric acid, and thrice under a layer of distilled water, in the order stated.[28]

4.3.3 Silver. Silver electrodes were in the form of silver wires of purity greater than 99.99% and were mechanically abraded to give a bright surface before each use.

4.3.4 Nitrogen. Nitrogen (CIG, high purity and dry) for purging the cells and degassing solutions was purified by passage through the following sequence of columns: Pyrex glass cotton, Linde 4A activated molecular sieves, soda lime, copper foil ribbons maintained at 600 K, soda lime, molecular sieves, and glass cotton.

4.3.5 Salts. Silver perchlorate (BDH laboratory reagent) for use in preparing Pleskov type reference electrodes in the various solvents was dried at 350 K under vacuum for 24 hours. Tetraethylammonium picrate for use in the salt bridges was prepared by neutralising 10% aqueous tetraethylammonium hydroxide (Eastman Kodak) with picric acid (Ajax Univar analytical reagent) in methanol.[29] The resulting tetraethylammonium picrate was recrystallised from methanol three times. Tetraethylammonium perchlorate for use as a supporting electrolyte was prepared by neutralising 10% aqueous tetraethylammonium hydroxide with perchloric acid (BDH laboratory reagent) using a phenolphthalein indicator.[29] The resulting perchlorate salt was recrystallised from water four times. All salts were vacuum dried and stored in a desiccator containing silica gel. The infrared spectra of the respective salts mulled with paraffin oil showed no detectable OH stretching frequency absorptions characteristic of water. The preparation of other specific salts is described in appropriate places in subsequent chapters.

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CHAPTER 5

SOLVATION OF POTASSIUM CATION

In this chapter the free energies of transfer of potassium cation from water to various nonaqueous dipolar solvents are reported. The values are derived from measurements in an electrochemical cell assumed to have a negligible liquid junction potential, and are compared with new and already existing literature values based on the TATB and various other assumptions. The essentially electrostatic character of its solvation behaviour allows the potassium cation to be used as a model for nonspecific ion-solvent interactions.

5.1 Introduction

As with other simple spherical monovalent cations of closed electron shells, the solvation of potassium cation is best described in terms primarily of the electrostatic interactions between the ion and polar solvent molecules.[1,2] The ion-solvent interactions, of course, are influenced somewhat by the effect of the ion on the solvent-solvent interactions (*i.e.* by solvent 'structure', *cf.* chapter 2).[3] In addition, although covalent interactions are expected to be of relatively minor importance,[1] their possible contribution to solvent interactions with potassium cation must be recognised.[4] However, because of the possibility of describing its solvation in simple terms, potassium cation may, through comparisons with other cations, serve favourably both in modelling some of the more important nonspecific electrostatic and structural effects which generally influence the solvation of cations, and in indicating certain instances in which specific interaction effects may affect the solvation of other cations. For example, it is well known that the silver cation, a Lewis acid with completely filled outer d-electron orbitals, experiences strong specific covalent interactions with certain basic solvents such as acetonitrile.[1,3,5-7] Because this generally is not the case with the potassium cation, deviations from linearity of a plot of the standard chemical free energy of silver ion *versus* that of potassium for transfer from a reference solvent to a variety of other solvents (ΔG_{tr} Ag^+ *versus* ΔG_{tr} K^+) can be used to indicate the contribution of specific ion-solvent interactions to the overall solvation free energy of silver cation in certain solvents. Thus, it is of interest to determine and to interpret the change in the standard chemical free energy (molar scale) of potassium cation, ΔG_{tr} K^+, on transfer from water to other solvents at 298 K.

Several values of $\Delta G_{\mathrm{tr}}\ \mathrm{K}^+$ have been calculated by applying the TATB assumption to appropriate solubility data.[3,8-10] (The general procedure for this method is outlined in chapter 3.) Solubility measurements, however, are often subject to uncertainties arising from possible crystal solvate formation, ion association in saturated solutions, and ionic strength or salt concentration effects.[11] Values of $\Delta G_{\mathrm{tr}}\ \mathrm{K}^+$ can also be determined by polarographic techniques if a suitable reference electrode whose potential is solvent independent (*cf.* chapter 3) can be found.[1] The method usually involves measuring the half-wave potential for the reversible reduction on mercury of the cation of interest. To a first approximation, this half-wave potential can be equated to the reversible standard electrode potential of the metal/metal cation couple in the solvent of interest, but for more precise work, account must be taken of the diffusion coefficients and activity coefficients of the oxidised and reduced species.[12] This knowledge is scant or, more often, nonexistent for the systems studied here. Furthermore, the relatively high concentration of supporting electrolyte required to suppress the migration current of the reducible species often engenders complications arising from ion association and salt effects.

An alternative approach which avoids many of these problems was used in this work. A direct measurement of the potential of half-cell C5.1 in a particular solvent S *versus* a suitable reference electrode at 298 K was made. In this half-cell, TEAPIC represents tetraethyl-

$$\mathrm{K(Hg)}\ \left|\ \begin{array}{c} 0.01\ M\ \mathrm{KClO_4} \\ \text{solvent S} \end{array}\ \right\|\ \begin{array}{c} 0.1\ M\ \text{TEAPIC} \\ \text{solvent S} \end{array} \qquad \text{C5.1}$$

ammonium picrate. The half-cell consisted of a dilute potassium amalgam (potassium mole fraction 2.3×10^{-3}; potassium activity coefficient taken as unity) in contact with a dilute solution ($1.0 \times 10^{-2}\ M$; M

represents units of mol dm^{-3}) of a selected potassium salt in the solvent of interest. The preferred potassium salt, subject to solubility limitations, was the perchlorate so that formation of stable metal complexes or other ion aggregates could be avoided.[6] Ample evidence attests to the general behaviour of perchlorates as strong electrolytes in most of the solvents considered.[13-15] Even for the solvents of relatively low dielectric constant, such as acetonitrile, existing data suggest that ion association is unlikely to be a major complicating factor at the low salt concentrations used.[16] The choice of tetraethylammonium picrate as the salt bridge electrolyte was made because of the high solubility of this salt in most of the solvents studied, because of the apparent absence of strong specific interactions between its constituent ions and the solvent molecules, and because of the assumed similar solvation numbers and transport numbers of the tetraethylammonium cation and the picrate anion in the various solvents.[9,10,17] Although other supporting evidence is scarce, the similarity of the ion transport numbers as calculated from conductance data is evident (*cf.* table T5.1).[9,16,18,19] The fulfilment of all these conditions is required if a liquid junction potential is to be suppressed by the interposition of a salt bridge.[17]

The possible choices of a reference electrode to be coupled with half-cell C5.1 were complicated by several considerations. The saturated calomel electrode in water was unsuitable because of the uncertainty in the liquid junction potential between the saturated aqueous potassium chloride solution and the nonaqueous tetraethylammonium picrate solution in the various solvents. The oxidation-reduction potential of the ferrocene molecule/ferricinium cation couple on platinum metal in the same solvent as half-cell C5.1 could be used as a reference point insofar as solvent junctions would be eliminated, but the utility of such an electrode for potentiometric cells is compromised by the ferricinium cation instability in several of the solvents considered.[9,20]

TABLE T5.1

EQUIVALENT CONDUCTANCE AND TRANSPORT NUMBERS[a] FOR TETRAETHYLAMMONIUM (TEA^+) AND PICRATE (PIC^+) IONS IN VARIOUS SOLVENTS AT 298 K

SOLVENT[b]	Λ_o S $m^2 \times 10^4$	λ (TEA^+) S $m^2 \times 10^4$	λ (PIC^-) S $m^2 \times 10^4$	t (TEA^+)	t (PIC^-)
E	54.2	27.9	26.3	0.51	0.49
M	107.4	58.2	49.2	0.54	0.46
NM	93.5	49.5	44	0.53	0.47
DMF	79	43	36	0.54	0.46
AN	163.8	86.1	77.7	0.53	0.47
DMA[c]	74.2	32.7	41.5	0.44	0.56
DMSO[d]	34.4	17.1	17.3	0.50	0.50
W[e]	63.0	32.6	30.4	0.52	0.48

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a. All data are from reference 16 unless noted otherwise.

b. Abbreviations are as in table T2.1.

c. Data are from references 9 and 18.

d. Data are from reference 9.

e. Data are from reference 19.

Ultimately, two reference electrodes were chosen. One, the Pleskov electrode ($\mathrm{Ag}|0.01\ M\ \mathrm{AgClO_4}||$) in the same solvent as half-cell C5.1, overcame the difficulty of an uncertain liquid junction potential between contiguous dissimilar solvents.[21,22] The experimental cell was that represented by cell C5.2, and comparison of the cell potentials in various solvents *versus* that in a reference solvent led to values for the difference in the free energies of transfer of the two ions, $\Delta G_{\mathrm{tr}}\ \mathrm{K}^+ - \Delta G_{\mathrm{tr}}\ \mathrm{Ag}^+$. Furthermore, since values of $\Delta G_{\mathrm{tr}}\ \mathrm{Ag}^+$, based on the TATB assumption, had already been reported,[3,8,9] corresponding values of $\Delta G_{\mathrm{tr}}\ \mathrm{K}^+$ on the same assumption could be obtained. Some problems in obtaining reproducible potentials for this cell were expected because of the reported susceptibility of the Pleskov electrode to trace impurities which interact strongly with silver cation in certain solvents[9,20] and because of difficulty in obtaining amalgams of invariant concentration. Although the former reservations proved to be of minor concern, variations of up to 10 mV in the potential of cell C5.2 were obtained using amalgams of nominally the same potassium concentration. The other reference electrode used was merely half-cell C5.1 itself in acetonitrile as reference solvent. The overall cell was that represented by cell C5.3. Because the same dilute amalgam was streamed through each potassium salt solution, the difficulties in reproducing the amalgam concentration were circumvented. The cell potential, of course, included a liquid junction potential, but other evidence suggested that its magnitude was often small and that it could often be neglected.[9,17] Alternatively, its value could be estimated

$$\begin{array}{c|c||c||c|c} \mathrm{Ag} & 0.01\ M\ \mathrm{AgClO_4} & 0.1\ M\ \mathrm{TEAPIC} & 0.01\ M\ \mathrm{KClO_4} & \mathrm{K(Hg)} \\ & \text{solvent S} & \text{solvent S} & \text{solvent S} & \end{array} \qquad \text{C5.2}$$

$$\begin{array}{c|c||c||c|c} \mathrm{K(Hg)} & 0.01\ M\ \mathrm{KClO_4} & 0.1\ M\ \mathrm{TEAPIC} & 0.01\ M\ \mathrm{KClO_4} & \mathrm{K(Hg)} \\ & \text{solvent AN} & \text{solvent AN} & \text{solvent S} & \end{array} \qquad \text{C5.3}$$

on the TATB assumption from the difference between the ΔG_{tr} K^+ values derived from measurements in cells C5.2 and C5.3 together with the already existing ΔG_{tr} Ag^+ (TATB assumption) values. So that liquid junction potentials estimated in this manner could be compared with those derived directly from differences in the ΔG_{tr} Ag^+ values on the TATB and negligible liquid junction potential (abbreviated NLJP) assumptions, measurements of the potential of cell C5.4, analogous to cell C5.3, were also made.

$$\begin{array}{c|c||c||c|c} \text{Ag} & 0.01\ M\ \text{AgClO}_4 & 0.1\ M\ \text{TEAPIC} & 0.01\ M\ \text{AgClO}_4 & \text{Ag} \\ & \text{solvent AN} & \text{solvent AN} & \text{solvent S} & \end{array} \qquad \text{C5.4}$$

5.2 Experimental Details

The apparatus and solvents used were described in chapter 4. Potassium hydroxide (Ajax Univar analytical reagent) for amalgam preparation was used without further purification. Potassium iodide (BDH analytical reagent) was dried under vacuum at 400 K for 24 hours prior to use. Potassium perchlorate (Merck) was recrystallised from water and dried under vacuum at 405 K for 72 hours. Potassium tetraphenylboride was prepared by metathesis of potassium chloride (Ajax Univar analytical reagent) with sodium tetraphenylboride (Fluka) and then recrystallised from acetone-water.[23] The amalgams were generated to be nominally of 2.3×10^{-3} mole fraction potassium. Slight variations in this concentration from one amalgam to another did occur as judged by the amalgam potential *versus* that of the saturated calomel electrode in water, but corrections for these variations were made by normalising all potentials to a single amalgam composition. The amalgam electrodes were used in a streaming configuration (amalgam flow 0.8×10^{-5} dm^3 sec^{-1}) in order to provide a continuously regenerated electrode surface.

In cells C5.2, C5.3, and C5.4, salts other than perchlorates were occasionally used if the perchlorates were insufficiently soluble.

Thus, in cell C5.2 0.01 *M* $KBPh_4$ was used in SDMF and PC (solvent abbreviations are as in table T2.1). In cell C5.3 0.01 *M* KI was used in E and TFE, and 0.01 *M* $KBPh_4$ was used in NMP, NM, TMS, SDMF, and PC. Use of 0.0004 *M* $KClO_4$ in SDMF (and in AN as reference) produced results identical with those obtained using 0.01 *M* $KBPh_4$. For M and W 0.001 *M* $KClO_4$ was used (with 0.001 *M* $KClO_4$ in AN also). In cell C5.4 0.001 *M* $AgClO_4$ was used in TFE and NM (as well as in the AN reference). In all other cases 0.01 *M* perchlorate salts were used.

All potentiometric measurements were conducted at 298 K except when TMS was one of the solvents being used. In such cases the measurements were performed at 303 K.

5.3 Results

The measured potentials E_x, E_y, and E_z of cells C5.2, C5.3, and C5.4, respectively, for various solvents are listed in table T5.2 using the I.U.P.A.C. sign convention.[24] Values of $E_y - E_z$ and values of E_x (S) - E_x (AN) for each solvent S are also included to facilitate calculations of ΔG_{tr} K^+ - ΔG_{tr} Ag^+. The close correspondence of the values for $E_y - E_z$ and for E_x (S) - E_x (AN) indicates that the liquid junction potentials in cells C5.3 and C5.4 are identical within experimental error. Thus, the contributions to the liquid junction potentials by transport of potassium, silver, and perchlorate ions across the dissimilar solvent boundaries can be neglected. In cell C5.2 the junction potential is minimal because of the use of a single solvent throughout and because of the nearly equal transport numbers of the tetraethylammonium and picrate ions in the solvents studied here (*cf.* table T5.1).[9,10,17]

Using values for ΔG_{tr} Ag^+ (TATB) expressed as potentials[3] together with values of E_x (S) - E_x (AN), estimates of various solvent

TABLE T5.2

MEASURED CELL POTENTIALS

SOLVENT[a]	E_x[b] V	E_y[b] V	E_z[b] V	$E_y - E_z$[b] V	E_x (S) - E_x (AN)[b] V
E		0.051[c]	0.243	-0.192	
TFE		0.267[c]	0.686[c]	-0.419	
HMPT	-2.370	-0.320	-0.230[d]	-0.090	-0.089
NMP		-0.207[c]	-0.026	-0.181	
M		0.026[c]	0.265[d]	-0.239	
NM		0.102[c]	0.423[c]	-0.321	
DMF	-2.527	-0.207	0.043	-0.250	-0.246
AN	-2.281	0.000	0.000	0.000	0.000
DMA		-0.235	-0.030	-0.205	
TMS[e]		-0.068[c]	0.288	-0.356	
DMSO	-2.382	-0.256	-0.152[d]	-0.104	-0.101
SDMF	-1.288	0.130[c]	-0.855	0.985	0.993
PC	-2.748	-0.043[c]	0.440	-0.483	-0.467
W	-2.595	-0.139[c]	0.185[d]	-0.324	-0.314
F		-0.120	0.068[d]	-0.188	

---

a. Abbreviations are as in table T2.1.

b. *Cf.* text for description of cells.

c. *Cf.* text for experimental conditions.

d. Data are from reference 9.

e. Measurements were conducted at 303 K.

S/AN liquid junction potentials on the TATB assumtion can be obtained. Similarly, the potentials of cell C5.4 can be compared directly with ΔG_{tr} Ag^+ (TATB) values expressed as potentials in order to obtain estimates for the same junctions. These values are listed in table T5.3 along with ones from the literature.[25]

Using the cell potentials given in table T5.2, the standard free energies of transfer of potassium cation from acetonitrile to other solvents S and from water to other solvents S on both the NLJP and the TATB assumptions were calculated. (The transfers from acetonitrile correspond to directly measured values of the cell potentials. The transfers from water were calculated not only to facilitate comparisons with literature values on different assumptions, but also because of the historical use of water as a reference solvent.) These values appear in table T5.4. Corresponding values for silver cation transfer appear in table T5.5 The ΔG_{tr} values derived from the measured cell potentials were converted to standard ΔG_{tr} values by considering the salt activity coefficients.[11] Correction factors, calculated from the Davies[26,27] modification of the Debye-Hückel equation[19,27,28] but using a value of 0.3 for the adjustable parameter b as subsequently suggested by Davies,[27] were always less than 0.5 kJ mol^{-1} for the electrolyte concentrations and solvents used. As this was less than the estimated experimental precision of ±2 kJ mol^{-1}, the measured cell potentials could be used straightaway for calculating standard free energies of transfer. (*N.B.* In those solvents for which data are available, potassium cation reduction is known to be reversible,[29] and the potential characterising this reduction is not complicated by large overpotentials caused by rate factors.[6] Hence, measured potentials correspond to equilibrium potentials, allowing immediate calculation of standard free energies of transfer.)

In table T5.6 the solvation free energies (differences in the free energy of an ion in solution and in the gas phase) of potassium

TABLE T5.3

COMPARISON OF LIQUID JUNCTION POTENTIAL ESTIMATES BASED ON THE TATB ASSUMPTION

JUNCTION[a]	ORIGIN OF ESTIMATE		
	Potassium Solvation Study[b]	Silver Solvation Study[c]	Literature[d]
E/AN		-0.065	-0.046
HMPT/AN	-0.062	-0.061	-0.057
M/AN		-0.039	-0.060
NM/AN		-0.063	+0.043
DMF/AN	-0.009	-0.005	-0.008
TMS/AN[e]		+0.101	+0.113
DMSO/AN	-0.034	-0.031	-0.030
PC/AN	+0.034	+0.049	+0.023
W/AN	-0.051	-0.041	-0.040
F/AN		+0.003	+0.010

a. Abbreviations are as in table T2.1. Potentials quoted in volts.

b. Using E_x (S) - E_x (AN) from table T5.2 with ΔG_{tr} K^+ (NLJP) from table T5.4 and ΔG_{tr} Ag^+ (TATB) from reference 3, the liquid junction potential (*LJP*) was calculated from the relationship

$$LJP = \frac{\Delta G_{tr}\ K^+\ (\mathrm{NLJP})}{nF} - \left(E_x\ (\mathrm{S}) - E_x\ (\mathrm{AN}) + \frac{\Delta G_{tr}\ Ag^+\ (\mathrm{TATB})}{nF}\right).$$

c. Using E_z from table T5.2 with ΔG_{tr} Ag^+ (TATB) from reference 3, the liquid junction potential (*LJP*) was calculated from the relationship

$$LJP = E_z - \frac{\Delta G_{tr}\ Ag^+\ (\mathrm{TATB})}{nF}.$$

d. Data are from reference 25. Note that all signs reported here are opposites of those in the original reference so that consistent use of the I.U.P.A.C. convention is maintained.

e. Measurements were conducted at 303 K.

TABLE T5.4

FREE ENERGIES OF TRANSFER OF POTASSIUM CATION BETWEEN SOLVENTS

SOLVENT[a]	ΔG_{tr} K^+ kJ g-ion^{-1}			
Assumption:	NLJP		TATB[b]	
Reference Solvent:	AN	W	AN	W
E	+4.9	+18.3	+11.2	+20.7
TFE	+25.8	+39.2	+25.8[c]	+39.2[c]
HMPT	-30.9	-17.5	-25.0	-15.5
NMP	-20.0	-6.6	-25.0	-15.5
M	+2.5	+15.9	+6.2	+15.7
NM	+9.8	+23.2	+15.9	+25.4
DMF	-20.0	-6.6	-19.5	-10.0
AN	0.0	+13.4	0.0	+9.5
DMA	-22.7	-9.3	-21.4	-11.9
TMS[d]	-6.6	+6.8	-16.4	-6.9
DMSO	-24.7	-11.3	-21.7	-12.2
SDMF	+12.5	+25.9	+12.5[c]	+25.9[c]
PC	-4.1	+9.3	-8.9	+0.6
W	-13.4	0.0	-9.5	0.0
F	-11.6	+1.8	-11.8	-2.3

---

a. Abbreviations are as in table T2.1.

b. With AN as reference, ΔG_{tr} K^+ (TATB) was calculated from $E_y - E_z$ in table T5.2 and from ΔG_{tr} Ag^+ (TATB) in table T5.5 according to the relationship

$$\Delta G_{tr}\ K^+\ (\text{TATB}) = +nF(E_y - E_z) + \Delta G_{tr}\ Ag^+\ (\text{TATB}).$$

With W as reference, ΔG_{tr} K^+ (TATB) was calculated according to ΔG_{tr} K^+ (TATB) W→S = ΔG_{tr} K^+ (TATB) AN→S - ΔG_{tr} K^+ (TATB) AN→W.

c. ΔG_{tr} K^+ (TATB) is defined as equal to ΔG_{tr} K^+ (NLJP) for this solvent because of experimental difficulties attending the determination of ΔG_{tr} K^+ (TATB) in the solvent (*cf.* references 2 and 9).

d. Measurements were conducted at 303 K.

TABLE T5.5

FREE ENERGIES OF TRANSFER OF SILVER CATION BETWEEN SOLVENTS

SOLVENT[a]	ΔG_{tr} Ag^+ kJ g-ion^{-1}			
Assumption:	NLJP[b]		TATB	
Reference Solvent:	AN	W	AN	W
E	+23.4	+5.5	+29.7[c]	+7.9[c]
TFE	+66.2	+48.3	+66.2[c,d]	+48.3[c,d]
HMPT	-22.2	-40.1	-16.3[c]	-38.1[c]
NMP	-2.5	-20.4	-7.5[c]	-29.3[c]
M	+25.6	+7.7	+29.3[e]	+7.5[e]
NM	+40.8	+22.7	+46.9[c]	+25.1[c]
DMF	+4.1	-13.8	+4.6[e]	-17.2[e]
AN	0.0	-17.9	0.0[e]	-21.8[e]
DMA	-2.9	-20.8	-1.6[c]	-23.4[c]
TMS[f]	+27.8	+9.9	+18.0[e]	-3.8[e]
DMSO	-14.7	-32.6	-11.7[e]	-33.5[e]
SDMF	-82.5	-100.4	-82.5[c,d]	-100.4[c,d]
PC	+42.5	+24.6	+37.7[e]	+15.9[e]
W	+17.9	0.0	+21.8[e]	0.0[e]
F	+6.6	-11.3	+6.3[e]	-15.5[e]

---

a. Abbreviations are as in table T2.1.

b. Data are from table T5.2.

c. Data are from reference 9.

d. ΔG_{tr} Ag^+ (TATB) is defined as equal to ΔG_{tr} Ag^+ for this solvent because of experimental difficulties attending the determination of ΔG_{tr} Ag^+ (TATB) in the solvent (*cf*. footnote *c* of table T5.4 and references 2 and 9).

e. Data are from reference 3.

f. Measurements were conducted at 303 K.

TABLE T5.6

SOLVATION FREE ENERGIES AND STANDARD ELECTRODE REDUCTION POTENTIALS OF POTASSIUM AND SILVER CATIONS IN VARIOUS SOLVENTS

SOLVENT[a]	$\Delta G_{\text{solv}}\text{K}^+$(TATB) kJ g-ion^{-1}	$\Delta G_{\text{solv}}\text{Ag}^+$(TATB) kJ g-ion^{-1}	$E^{\circ}\text{K}^+/\text{K}$(TATB) V	$E^{\circ}\text{Ag}^+/\text{Ag}$(TATB) V
E	-316.5	-471.2	-2.709	+0.882
TFE	-298.0	-430.8	-2.518	+1.301
HMPT	-352.7	-517.2	-3.085	+0.405
NMP	-352.7	-508.4	-3.085	+0.496
M	-321.5	-471.6	-2.761	+0.878
NM	-311.8	-454.0	-2.661	+1.060
DMF	-326.7	-496.3	-3.028	+0.622
AN	-327.7	-500.9	-2.826	+o.574
DMA	-349.1	-502.5	-3.047	+0.557
TMS[b]	-344.1	-482.9	-2.996	+0.761
DMSO	-349.4	-512.6	-3.050	+0.453
SDMF	-311.3	-579.5	-2.656	-0.240
PC	-336.6	-463.2	-2.918	+0.965
W	-337.2	-479.1	-2.924	+0.800
F	-339.5	-494.6	-2.948	+0.639

a. Abbreviations are as in table T2.1.

b. Measurements were conducted at 303 K.

and silver cations are listed. They were calculated using equation E5.1 where M^+ represents K^+ or Ag^+ and the subscripts $_{solv}$ and $_{hyd}$ represent solvation and hydration, respectively. The hydration free

$$\Delta G_{solv}\ M^+ = \Delta G_{hyd}\ M^+ + \Delta G_{tr}\ M^+ \qquad \text{E5.1}$$

energies are derived from those reported by Rosseinsky.[30] Also listed in table T5.6 are the standard electrode potentials of potassium and silver cation reductions in various solvents (TATB assumption) *versus* the normal hydrogen electrode potential in water. These potentials were calculated using equation E5.2, in which all terms have their usual significance.

$$E^{o}\ M^+/M \text{ in S (TATB)} = E^{o}\ M^+/M \text{ in W} + \frac{\Delta G_{tr}\ M^+ \text{ (TATB)}}{nF} \qquad \text{E5.2}$$

In table T5.7, the $\Delta G_{tr}\ K^+$ (TATB) values determined in this work are compared with various literature values based on other assumptions. Of all values previously reported, those presented in table T5.7 are selective rather than exhaustive. Collectively, the values indicate that the estimate of a particular $\Delta G_{tr}\ K^+$ value evidently may differ in magnitude and in sign according to both the assumption used and the experimentalist performing the measurement!

5.4 Discussion

5.4.1 Cells with Liquid Junction Potentials. One of the objectives of the present study was to determine the practical suitability of the NLJP assumption for estimating single ion free energies of transfer in cells such as C5.3 and C5.4. From the data in table T5.3 it is apparent that the liquid junction between different dipolar solvents is often quite significant, as determined using the TATB assumption. However, the generally close agreement among various experimental estimations

TABLE T5.7

COMPARISON OF ΔG_{tr} K^+ VALUES BASED ON VARIOUS ASSUMPTIONS

SOLVENT[a]	ΔG_{tr} K^+ kJ g-ion^{-1}						
Reference:	2[b]	9	8	31	Misc.	32	3
Assumption:	TATB	NLJP	TATB&ITI[c]	Pleskov[d]	Pleskov[d]	TATB	TATB
E	+20.7	+23.9					
TFE	+39.2[e]	+44.4					
HMPT	-15.5	-8.5	-18.8				
NMP	-15.5						-13.8
M	+15.7	+19.3	+8.5			+10.3	+10.0
NM	+25.4	+29.6					
DMF	-10.0	-0.6	-12.5	-2.9	-2.9[f]	-9.7	-9.6
AN	+9.5	+18.2	-0.6	+1.9	+2.9[g]	+7.9	+7.9
DMA	-11.9	-5.7		-3.8			
TMS[j]	-6.9			+1.0	+1.9[h]		-4.2
DMSO	-12.2	-5.7	-17.1	-4.8	-1.9[i]	-12.0	-12.1
SDMF	+25.9[e]						
PC	+0.6			+12.6			+5.9
W	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F	-2.3	+8.0					-6.3

---

a. Abbreviations are as in table T2.1.

b. This work. Data are from table T5.4.

c. ITI signifies the assumption that the free energies of transfer of iodine and triiodide ion are equal as proposed in reference 8.

d. The assumption that rubidium cation is similarly solvated in all solvents (*cf.* chapter 3 and reference 21).

e. *Cf.* table T5.4.

f. Data are from reference 33.

g. Data are from reference 6.

h. Data are from reference 34.

i. Data are from reference 35.

j. Measurements were conducted at 303 K.

of the liquid junction potentials suggests that a correction factor can be determined for each solvent junction. Then, if the contribution of the liquid junction to the overall cell potential is specifically taken into account, measurements on cells such as C5.3 and C5.4 provide the simplest means for determining experimental single ion free energies of transfer.

5.4.2 Solvation of Potassium Cation

5.4.2.1 Free energy considerations. Most of the solvents investigated in this study interact electrostatically with potassium cation through partial negative charge residing primarily on their respective oxygen atoms,[36] although acetonitrile and *N*,*N*-dimethylthioformamide are exceptions which interact through their nitrogen[37] and sulphur[38] atoms, respectively. The solvents studied, then, can be divided for discussion purposes into three categories: oxygen electron donors, nitrogen electron donors, and sulphur electron donors.

5.4.2.1.1 Oxygen electron donor solvents. From the data listed in table T5.4 it is immediately apparent that the oxygen electron donor solvents can conveniently be further divided into two groups: those which are stronger solvators of potassium cation than is water, and those whose solvating ability towards this cation is weaker than or comparable to that of water. The former group includes the solvents hexamethylphosphorotriamide, *N*-methyl-*2*-pyrrolidone, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, dimethylsulphoxide, and formamide. These solvents each contain a single oxygen atom which carries extensive localised negative charge and which is relatively 'exposed' or free of groups which might sterically interfere with its direct interaction with the potassium cation.[39] The phosphorus-oxygen, sulphur-oxygen, and carbon-oxygen bonds in these phosphoramides, sulphoxides, and amides have less than full double bond character; indeed, their structures in the first solvation shell around potassium cation may well more resemble the species represented by (b), (d), and (f) in figure F5.1 than those depicted by (a), (c), and (e). The other group of oxygen electron donor solvents includes ethanol, *2,2,2*-trifluoroethanol, methanol, nitromethane, tetramethylenesulphone, propylene carbonate, and water. These relatively weaker solvators of potassium cation either have their partial negative charge dispersed over more than one oxygen atom (as in nitromethane, tetramethylenesulphone, and propylene carbonate) or have a single oxygen atom which is partially shielded sterically through its bonding to two other atoms or groups (as in ethanol, *2,2,2*-trifluoroethanol, methanol, and water).[36] In both cases this set of solvents is expected, as observed, to solvate potassium cation more weakly than the phosphoramides, sulphoxides, and amides discussed earlier.

Some of the ΔG_{tr} K^+ (TATB) values from table T5.4 deserve special comment. A degree of ambiguity surrounds the reliability of the tetramethylenesulphone result. As seen from the comparisons with literature values in table T5.7, there is uncertainty not only in the magnitude of the ΔG_{tr} K^+ value for transfer from water to tetramethylenesulphone, but also in its sign. The available data are derived both from polarographic and from solubility experiments. For the solubility determinations it is not unlikely that some uncertainty attends the composition of the solid phase in equilibrium with the liquid electrolyte on which measurements were made.[11] The solubility behaviour of the electrolytes is likely to be further complicated by the fact that measurements were conducted at temperatures only marginally above the solvent melting point (*cf.* table T2.1). In view of these possibilities and considering the dispersal of partial negative charge over two oxygen atoms, it appears reasonable to class tetramethylenesulphone either as having

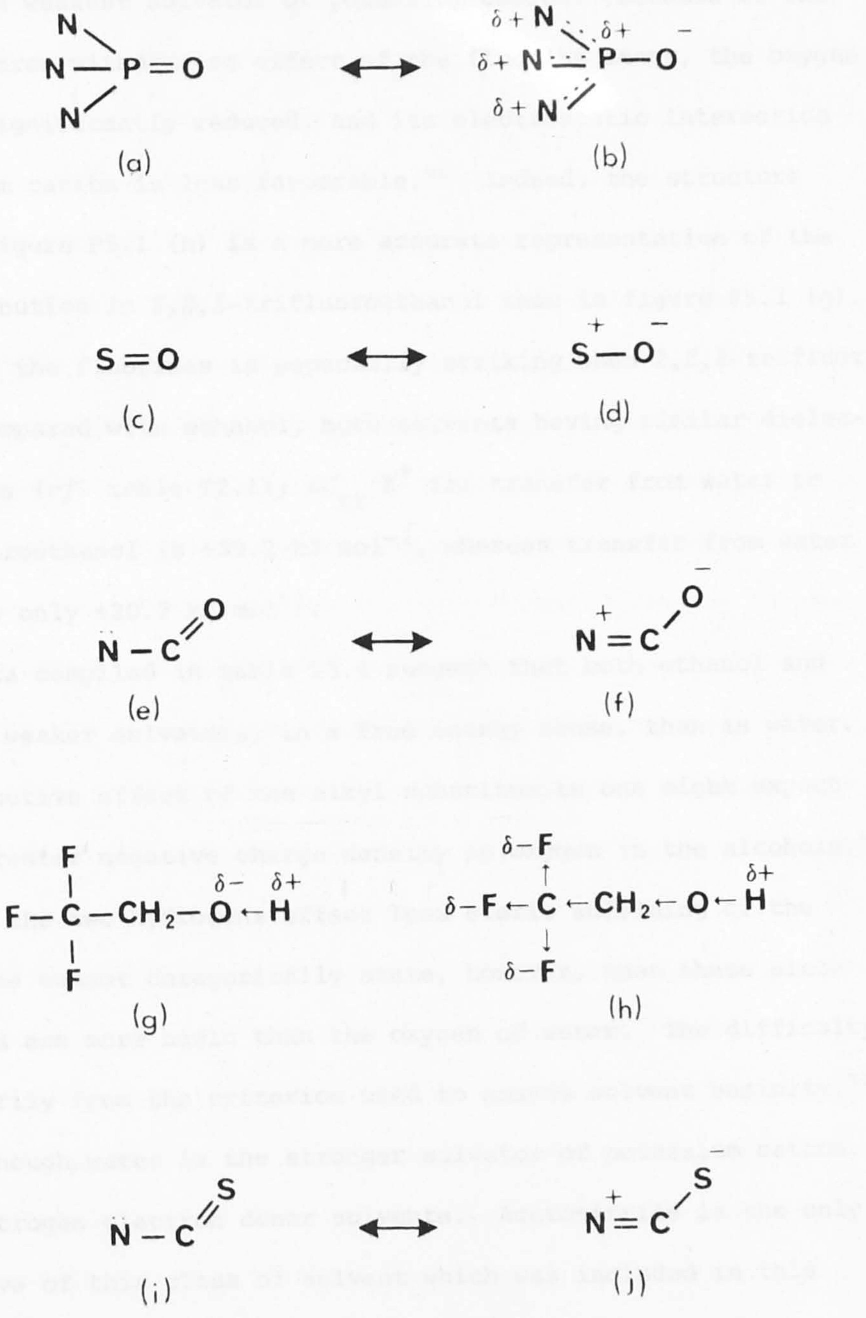

FIGURE F5.1 : Representation of charge distribution in neutral solvent molecules. In this figure (a) and (b), (c) and (d), (e) and (f), and (i) and (j) represent contributions to resonance hybrids, whereas (g) and (h) represent differing inductive and electron withdrawing effects.

intermediate solvating capabilities towards potassium cation or as being comparable to the relatively weaker solvators of this ion.[7]

Of the oxygen electron donor solvents studied, *2,2,2*-trifluoroethanol is the weakest solvator of potassium cation. Because of the powerful electron withdrawing effect of the fluorine atoms, the oxygen basicity is significantly reduced, and its electrostatic interaction with potassium cation is less favourable.[40] Indeed, the structure depicted in figure F5.1 (h) is a more accurate representation of the charge distribution in *2,2,2*-trifluoroethanol than is figure F5.1 (g). The effect of the fluorines is especially striking when *2,2,2*-trifluoroethanol is compared with ethanol, both solvents having similar dielectric constants (*cf.* table T2.1); $\Delta G_{tr}\ K^+$ for transfer from water to *2,2,2*-trifluoroethanol is +39.2 kJ mol^{-1}, whereas transfer from water to ethanol is only +20.7 kJ mol^{-1}.

The data compiled in table T5.4 suggest that both ethanol and methanol are weaker solvators, in a free energy sense, than is water. From the inductive effect of the alkyl substituents one might expect a somewhat greater negative charge density on oxygen in the alcohols,[41] but in water the two hydrogens effect less steric shielding of the oxygen.[36] One cannot categorically state, however, that these alcoholic oxygens are more basic than the oxygen of water. The difficulty arises primarily from the criterion used to assess solvent basicity.[42] Evidently, though, water is the stronger solvator of potassium cation.

5.4.2.1.2 Nitrogen electron donor solvents. Acetonitrile is the only representative of this class of solvent which was included in this study. Spectroscopic evidence is unambiguous in indicating that it is, indeed, through the nitrogen atom that this solvent interacts with cations.[7] Relative to the oxygen electron donor solvents, acetonitrile is generally a poorer solvator of potassium cation, as judged from the data in table T5.4. This observation is entirely consistent with

Ahrland's classification of nitrogen as being a 'softer' donor than oxygen;[43] hence, interactions of the nitrogen atom with the relatively 'hard' potassium cation are generally expected to be less favourable than corresponding oxygen atom-potassium cation interactions.[44]

5.4.2.1.3 Sulphur electron donor solvents. *N*,*N*-Dimethylthioformamide is the only sulphur electron donor solvent which was included in this investigation. Although no direct spectroscopic evidence for its interaction through the sulphur atom with potassium ion is known to be available, there is other evidence for similar interactions between the thio analogue of *N*,*N*-dimethylacetamide and suitable acceptors.[4,45] The likelihood that a considerable degree of negative charge is centred on sulphur (*cf*. representations (i) and (j) in figure F5.1) notwithstanding, the *N*,*N*-dimethylthioformamide-potassium cation interaction is demonstrated to be significantly weaker than the formally similar interaction between the oxygen electron donor *N*,*N*-dimethylformamide and the cation. According to Pearson's Hard and Soft Acids and Bases principle,[44] the former interaction, being soft-hard, is considerably less favourable than the latter interaction which is hard-hard. Furthermore, as sulphur is a considerably softer donor than nitrogen,[43] *N*,*N*-dimethylthioformamide is expected, as observed, to be an even poorer solvator of the relatively hard potassium cation than is acetonitrile.

5.4.2.1.4 Summary. The discussion of the relative 'solvating abilities' of the various oxygen, nitrogen, and sulphur electron donor solvents studied is incomplete unless mention is made of the role played by other atoms in the various solvent molecules. Thus, in *N*,*N*-dimethylformamide, for example, electron donation from nitrogen enhances the basicity of the oxygen. In dimethylsulphoxide the oxygen being bound to sulphur gives the oxygen a greater electron donor ability than might otherwise be expected (in, for example, acetone[9]). Analogous effects enhance the oxygen electron donor properties of hexamethylphosphorotriamide and

N,*N*-dimethylacetamide, and the sulphur electron donor properties of *N*,*N*-dimethylthioformamide. In acetonitrile, however, there is no suitable donor group to enhance the basicity of the nitrogen, and as a result, this solvent appears to be a remarkably poor electron donor in comparison with several of the oxygen electron donor solvents. In general, predictions of relative donor abilities among oxygen, nitrogen, and sulphur electron donor solvents cannot be made solely on the basis of which atom is primarily involved in interactions with the cation.

5.4.2.2 Enthalpy and entropy considerations. The foregoing discussion centred around free energy considerations. The interpretation of observed free energies of transfer exclusively in terms of physical-organic chemical arguments relating to steric effects and to basicities of various atoms is a rather simplistic approach to the understanding of ion-solvent interactions at the molecular level. Although this approach is quite useful for interpreting free energies of transfer of ions from one dipolar aprotic solvent to another, it is generally inadequate for discussing transfers in which one or both solvents have significant solvent-solvent interactions (*e.g.* water, formamide, methanol; *cf.* chapter 2). In such cases, the results presented can be better understood if combined with previously reported single ion enthalpies of transfer[3] to obtain single ion entropies of transfer as compiled in table T5.8.

For all of the solvents for which data are available, the enthalpies of transfer of potassium cation from water are exothermic. This exothermicity reflects not only the strong electrostatic interaction between potassium cation and the various solvents, but also the fact that water is quite different from the other solvents studied. Because of the extensive three-dimensional polymeric hydrogen bonded structure of liquid water, and the more poorly developed structures of the other solvents (*cf.* chapter 2), transfer of potassium cation from water to the other solvents is accompanied by an exothermic enthalpy change. Part of this

TABLE T5.8

FREE ENERGIES, ENTHALPIES, AND ENTROPIES OF TRANSFER OF POTASSIUM CATION FROM WATER TO OTHER SOLVENTS AT 298 K (TATB ASSUMPTION)

SOLVENT[a]	ΔG_{tr} K^+ (TATB)[b] kJ g-ion^{-1}	ΔH_{tr} K^+ (TATB)[c] kJ g-ion^{-1}	ΔS_{tr} K^+ (TATB) J K^{-1} g-ion^{-1}
NMP	-15.5	-43.9	-95
M	+15.7	-18.4	-114
DMF	-10.0	-39.3	-98
AN	+9.5	-22.6	-108
TMS[d]	-6.9	-25.1	-60
DMSO	-12.2	-34.7	-75
PC	+0.6	-20.9	-72
F	-2.3	-16.7	-48

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a. Abbreviations are as in table T2.1.

b. Data are from table T5.4.

c. Data are from reference 3.

d. Measurements were conducted at 303 K.

change is associated with incorporating into the bulk water structure the water molecules which had previously been in the potassium cation solvation shells, whilst the remainder of the exothermic change arises from the favourable electrostatic interactions between the potassium cation and the nonaqueous solvent molecules. Counteracting these exothermic changes are the endothermic processes of disrupting both the water molecule-potassium cation electrostatic interactions and the nonaqueous solvent structure. The opposing enthalpic changes are not altogether compensatory, primarily because the endothermicity of disrupting the nonaqueous solvent structure is usually small. Hence, the overall enthalpy of transfer of potassium cation from water to the other solvents is exothermic.[3]

When combined with the free energies of transfer determined in this work, the previously reported[3] enthalpies of transfer can be used for determining the single ion entropies of transfer listed in table T5.8. In all cases for which data are available, the entropy changes for the transfers from water to other solvents are negative. The entropic changes parallel those for the enthalpies. Thus, removal of potassium cation from water is accompanied by a significant gain in entropy resulting from the disruption of the interactions between the potassium cation and the water molecules from its solvation shells. However, accomodating these molecules from the solvation shells into the bulk water structure results in a substantial loss of entropy. Hence, removal of potassium cation from water is accompanied by a smaller positive entropy change than would be expected if liquid water were completely unstructured. When the potassium cation is transferred into a relatively unstructured nonaqueous solvent, the entropy loss upon formation of one or more solvation shells predominates over the insignificant entropy gain associated with disruption of the inherent solvent structure. Thus, just as is the case for the enthalpies, the entropies of transfer from water to the other solvents are negative for the potassium cation.

The full implications of such enthalpic and entropic changes on transferring single ionic species from water to various nonaqueous solvents have been discussed by Parker, *et al.*,[3] in terms of a solvation model similar to that proposed by Frank and Evans[46] (*cf.* the case for divalent metal cations in chapter 7).

5.4.3 Comparison of the Solvation of Potassium and Silver Cations. It is necessary to distinguish between those ion-solvent interactions which are essentially electrostatic in nature and those which are primarily of covalent character.[4] As noted previously, potassium cation, with its closed electron shells and moderate size (crystallographic radius 1.33 $\times\ 10^{-10}$ m), is expected to respond almost exclusively to electrostatic solvation effects,[1] whereas silver cation, as a transition metal with filled outer d-electron orbitals, is expected to be capable of experiencing a variety of covalent interactions including back bonding to suitable ligands.[36] Because of its smaller size (crystallographic radius 1.26×10^{-10} m), and thus greater formal surface charge density, silver cation may also have stronger electrostatic interactions with all the solvents studied than has potassium cation. Such an interpretation is certainly consistent with the data in table T5.6; all $\Delta G_{\mathrm{solv}}\ \mathrm{K}^+$ values listed are less in magnitude than -375 kJ g-ion^{-1}, but all values of $\Delta G_{\mathrm{solv}}\ \mathrm{Ag}^+$ are greater in magnitude than -425 kJ g-ion^{-1}.

The comparison between the free energies of transfer of silver cation and of potassium cation from water to nonaqueous solvents is summarised in figure F5.2, a plot of $\Delta G_{\mathrm{tr}}\ \mathrm{Ag}^+$ (TATB) *versus* $\Delta G_{\mathrm{tr}}\ \mathrm{K}^+$ (TATB). There is a reasonable linear correlation between these quantities for transfer to solvents which interact through oxygen with the cations. The gradient of 1.32 being greater than unity indicates that, as expected on electrostatic grounds, silver cation is more responsive to solvent transfer than is potassium.

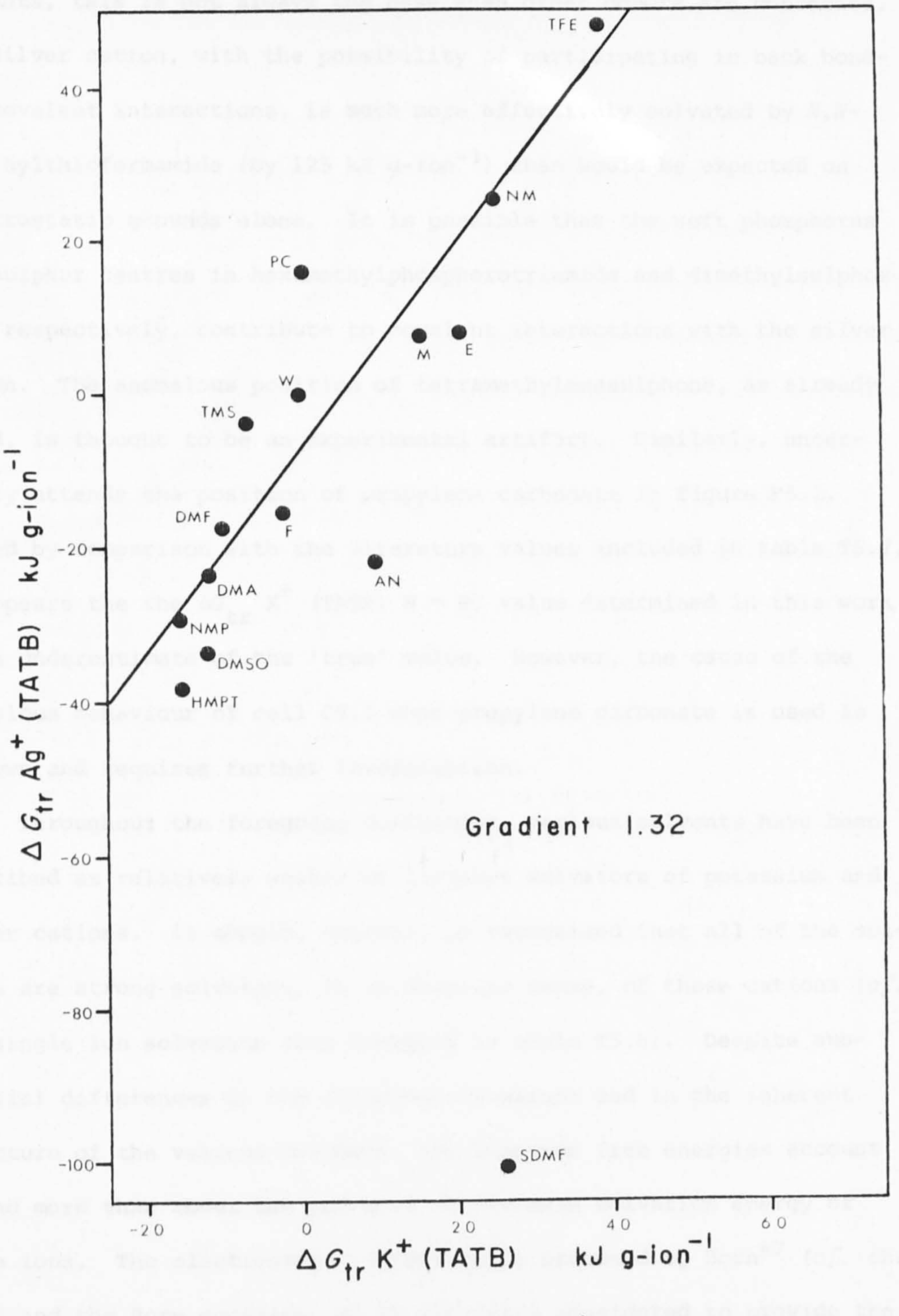

FIGURE F5.2 : ΔG_{tr} Ag^+ (TATB) *versus* ΔG_{tr} K^+ (TATB) for transfers from water to other solvents at 298 K (molar scale).

Although nonspecific electrostatic interactions seem to govern the solvation of potassium and silver cations by oxygen electron donor solvents, this is not always the case when other donors are concerned. The silver cation, with the possibility of participating in back bonding covalent interactions, is much more effectively solvated by *N*,*N*-dimethylthioformamide (by 125 kJ g-ion^{-1}) than would be expected on electrostatic grounds alone. It is possible that the soft phosphorus and sulphur centres in hexamethylphosphorotriamide and dimethylsulphoxide, respectively, contribute to covalent interactions with the silver cation. The anomalous position of tetramethylenesulphone, as already noted, is thought to be an experimental artifact. Similarly, uncertainty attends the position of propylene carbonate in figure F5.2. Judged by comparison with the literature values included in table T5.7, it appears the the ΔG_{tr} K^+ (TATB) W → PC value determined in this work is an underestimate of the 'true' value. However, the cause of the anomolous behaviour of cell C5.3 when propylene carbonate is used is unknown and requires further investigation.

Throughout the foregoing discussion, various solvents have been described as relatively weaker or stronger solvators of potassium and silver cations. It should, however, be recognised that all of the solvents are strong solvators, in an absolute sense, of these cations (*cf.* the single ion solvation free energies in table T5.6). Despite substantial differences in the dielectric constant and in the inherent structure of the various solvents, the transfer free energies account for no more than about ten per cent of the mean solvation energy of these ions. The electrostatic interactions proposed by Born[47] (*cf.* chapter 3 and the Born equation, E3.8) are still considered to provide the major contribution to the energetics of ion solvation. For example, the dielectric constants of the solvents used in this study range from 24.33 (ethanol) to 109.5 (formamide), with most being in the range 25 to 50.

For a given cation, the Born equation shows that transfer from ethanol to formamide (in equation E3.8, $\frac{1}{D_S} - \frac{1}{D_R} = \frac{1}{109.5} - \frac{1}{24.33} = -0.032$) is only three per cent of the solvation free energy of the cation (unspecified) in ethanol (in equation E3.8, $\frac{1}{D_S} - 1 = \frac{1}{24.33} - 1 = -0.959$). Thus, although the Born theory is known to overestimate the absolute values of ion solvation free energies,[11] often by as much as fifty per cent (*cf.* the solvation free energy of potassium cation in ethanol calculated to be -500 kJ g-ion^{-1} *via* the Born equation, but experimentally determined to be -317 kJ g-ion^{-1} as shown in table T5.6), it is nevertheless quite successful in attributing solvation effects primarily to electrostatic phenomena and in suggesting that changes in single ion free energies upon transfer between solvents of moderate dielectric constant should constitute only a slight energetic effect relative to the total solvation free energy in either of the solvents.

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CHAPTER 6

COMPARATIVE SOLVATION OF SELECTED MONOVALENT CATIONS BY VARIOUS SOLVENTS INCLUDING *N*,*N*-DIMETHYLFORMAMIDE AND *N*,*N*-DIMETHYLTHIOFORMAMIDE

The use of the potassium cation as a model for nonspecific ion-solvent interactions, as proposed in chapter 5, is demonstrated in this chapter. Free energies of transfer for the other alkali metal cations, when compared with those for the potassium cation, demonstrate that the solvation of these cations is influenced primarily by non-specific electrostatic ion-solvent interactions. Similar comparisons of representative monovalent d^{10} cations with the potassium cation, however, reveal the influence of specific ion-solvent interactions in some instances. These specific interactions are especially striking when *N*,*N*-dimethylformamide is compared with its thio analogue *N*,*N*-dimethylthioformamide. Interactions are discussed in terms of the concept of Hard and Soft Acids and Bases. The tetraphenylarsonium cation is demonstrated to be relatively insensitive to solvent transfer unless one of the solvents involved is highly structured, in which case specific ion-solvent interactions play a significant role.

6.1 Introduction

Although ion solvation free energies, of which Born[1] type electrostatic interactions constitute the major part,[2-6] vary only slightly according to which dipolar solvent is being considered, differences in the smaller free energies of transfer of single ionic species often reflect quite spectacular differences in the chemical behaviour of the ions in various solutions.[7,8] A striking illustration of such effects is afforded by a comparison of cation solvation in *N*,*N*-dimethylformamide and its thio analogue *N*,*N*-dimethylthioformamide.

It has been suggested that the concept of Hard and Soft Acids and Bases (the HSAB principle)[9] extends to the interactions between solvents and ions.[10-12] According to this scheme the oxygen electron donor solvent *N*,*N*-dimethylformamide is classed as a hard solvent, whilst its sulphur electron donor analogue *N*,*N*-dimethylthioformamide is classed as a soft solvent. On the basis of several of their physical properties (*cf.* table T2.1), both solvents are expected to be relatively strong cation solvators. Indeed, because *N*,*N*-dimethylthioformamide has higher values for its molecular polarisability (14.7×10^{-30} m^3), dielectric constant (47.5), and dipole moment (14.6×10^{-12}C m), it might be expected generally to be a stronger cation solvator than is *N*,*N*-dimethylformamide whose values for these properties are 7.9×10^{-30} m^3, 36.7, and 12.9×10^{-12} C m, respectively.[13] Certainly when potassium cation solvation is considered (*cf.* chapter 5), the opposite is true. Furthermore, Drago and Wayland have compared the base behaviour of the oxygen electron donor *N*,*N*-dimethylacetamide and the analogous sulphur electron donor *N*,*N*-dimethylthioacetamide towards the Lewis acids phenol and iodine.[14] Covalent base parameters, C_B, of 3.00 for *N*,*N*-dimethylacetamide and 9.06 for *N*,*N*-dimethylthioacetamide towards iodine were reported, whilst electrostatic base parameters, E_B, towards phenol were 1.00 and 0.064 for these solvents, respectively. Drago stated the results to be consistent with the HSAB principle.[15] Evidently the soft sulphur electron donor interacts (covalently) more strongly with the soft acid iodine than does the hard oxygen electron donor. On the other hand, the hard oxygen electron donor interacts (electrostatically) more strongly with the hard acid phenol than does the soft sulphur electron donor. A similar relationship should exist between the relative electrostatic contributions, and between the relative covalent interactions, for *N,N*-dimethylformamide and *N,N*-dimethylthioformamide towards cations as Lewis acids.

Although the closed electron shell alkali metal cations are all considered to be hard,[16] or of Class A character,[17] their radii, polarisabilities, and degrees of softness increase in regular fashion from lithium to caesium.[10,11,18-20] They have strong but decreasing electrostatic interactions with polar solvents and weak but increasing dispersion force interactions with soft, polarisable solvents. Covalent interactions between solvents and these cations are weak.[21] In contrast, however, the soft, polarisable Class B silver and thallous cations do interact covalently, and do have strong dispersion force interactions, with soft, polarisable solvents. Taken collectively, these cations can be arranged in qualitative order of decreasing softness as follows: $Ag^+ >> Tl^+ >> Cs^+ > K^+ > Na^+ > Li^+$. On the basis of the HSAB principle, the free energies of transfer from *N,N*-dimethylformamide to *N,N*-dimethylthioformamide should become successively more positive (the indicated transfer becomes energetically less favourable) as each cation of the series is considered in the above order.

6.2 Experimental Details

The experimental apparatus (the liquid junction potentiometric cell) and the general operating procedures were described in chapter 4. Measurements were made of the potential of cell C6.1 in which M represents the metal being investigated, X represents the anion, and TEAPIC represents the bridge electrolyte tetraethylammonium picrate. For

$$\mathrm{M(Hg)}\ \left|\ \begin{array}{c}0.001\ M\ \mathrm{MX}\\ \mathrm{DMF}\end{array}\ \right\|\ \begin{array}{c}0.1\ M\ \mathrm{TEAPIC}\\ \mathrm{SDMF}\end{array}\ \left\|\ \begin{array}{c}0.001\ M\ \mathrm{MX}\\ \mathrm{SDMF}\end{array}\ \right|\ \mathrm{M(Hg)} \qquad \mathrm{C6.1}$$

measurements involving lithium or silver, the perchlorate salts were used to prepare the electrolyte solutions, whilst for thallium the nitrate was used. For the other alkali metals the tetraphenylboride salts were used. Alkali metal amalgams for electrodes were generated from appropriate aqueous metal hydroxide solutions by electroreducing the cation at a mercury pool cathode (*cf.* chapter 4). In the case of thallium, the amalgam was similarly generated from an aqueous nitrate solution. All amalgams contained the appropriate complement of metal at 0.025% (by weight) concentration. The amalgam electrodes were used in a streaming configuration (except in the case of lithium, for which a slowly spilling pool was used). For cell C6.1 involving silver, the silver perchlorate concentration was 0.01 *M*, and pure silver wires were used as electrodes. Solutions were purged with oxygen-free dry nitrogen, and cell potentials, measured at 298 K, were stable to within 10 mV.

Observed dependence of cell potential on amalgam electrode configuration (*i.e.* whether streaming, dropping, spilling pool, or stationary pool) in *N*,*N*-dimethylformamide (DMF) for lithium but not for the other alkali metals was investigated concurrently with the free energy determinations. The investigation was aimed at finding conditions for which the lithium amalgam electrode in DMF would behave reversibly. A Princeton Applied Research Electrochemistry System Model 170 with iR compensation was used to record cyclic voltammograms at various voltage scan rates (5-500 mV s^{-1}) for alkali metal cation behaviour (using 0.001-0.005 *M* perchlorate solutions) at a hanging mercury drop in *N*,*N*-dimethylformamide. Measurements were carried out in a standard double-H cell using a Pleskov[22] reference electrode ($Ag|0.01\ M\ AgClO_4||$) in *N*,*N*-dimethylformamide. The supporting electrolyte was 0.1 *M* tetrabutylammonium tetrafluoroboride.

The preparation, purification, and handling of solvents were described in chapter 4. All *N*,*N*-dimethylthioformamide, because of its photosensitivity and ease of oxidation, was stored in the dark under an atmosphere of oxygen-free dry nitrogen, and was used immediately after purification by reduced pressure fractional distillation. Lithium perchlorate (Fluka, analytical reagent) was vacuum dried at 393 K for 24 hours. Sodium tetraphenylboride (BDH, laboratory reagent) was purified by recrystallisation from acetone-toluene.[6] Potassium and caesium tetraphenylborides were prepared by metathesis of the chloride and bromide salts, respectively, with sodium tetraphenylboride and were recrystallised from acetone-water. Thallium nitrate (BDH, laboratory reagent) was vacuum dried at ambient temperature and stored in an evacuated desiccator containing silica gel. The treatment of other salts and solvents was described in detail in chapter 4.

6.3 Results

The potentials of cell C6.1 along with corresponding values of $\Delta G_{tr}\ M^+$ (NLJP) for transfer from *N*,*N*-dimethylformamide to *N*,*N*-dimethylthioformamide are listed in table T6.1. With the same amalgam being used for both sides of cell C6.1, cell potentials were observed to be

TABLE T6.1

DATA RELEVANT TO THE FREE ENERGIES OF TRANSFER OF VARIOUS CATIONS FROM *N*,*N*-DIMETHYLFORMAMIDE TO *N*,*N*-DIMETHYLTHIOFORMAMIDE AT 298 K

CATION	$E_{\text{cell C6.1}}$ [a] V	ΔG_{tr} M^+ (NLJP) DMF→SDMF[b] kJ g-ion^{-1}	$k_{c\ \text{rel}}$ DMF[c]
Li^+	+0.660	+63.7	1
Na^+	+0.518	+50.0	4
K^+	+0.386	+37.2	6
Cs^+	+0.245	+23.3	9
Tl^+	-0.045	-4.3	-
Ag^+	-0.837[d]	-80.8	-

a. See text for experimental details.

b. Abbreviations are as in table T2.1.

c. Relative standard electron transfer heterogeneous rate constants for cation reduction to the amalgam in DMF as measured by J.W. Diggle (*cf.* reference 34).

d. From data in reference 37.

independent of electrolyte concentration in the range 0.0001-0.01 *M*. Also, as noted in chapter 5, effects attributable to salt activity coefficients were neglected since these were less than the experimental precision for the particular solvents and electrolyte concentrations used. The ΔG_{tr} M^+ values were calculated directly from the cell potentials as described in chapters 4 and 5.

For all of the streaming amalgams used, except lithium, reversible behaviour has been reported in *N,N*-dimethylformamide[23] and was assumed to extend to *N,N*-dimethylthioformamide. Indeed, the potentials of cell C6.1 were observed to be independent of amalgam configuration except when lithium was used. In other systems in which cell potentials have been noted to depend on the configuration of amalgam electrodes (*i.e.* whether streaming or dropping),[24-26] it has been suggested that kinetic factors retard the attainment of equilibrium in the electrode process.[25] Thus, for lithium in cell C6.1 the anomalous behaviour was thought to result from slow kinetics of the electrode processes. By analogy to similar behaviour in dimethylsulphoxide,[27,28] the extent of ion-centred ordering of *N,N*-dimethylformamide around a cation in solution (*cf*. chapter 7) decreases through the series of alkali metals from lithium to caesium.[29] The energy required for solvent reorganisation decreases in the same manner, with a corresponding increase in the electron transfer rate (solvent reorganisation being prerequisite for electron transfer).[30,31]

From the cyclic voltammograms, the separation of the anodic and cathodic peaks was observed to vary with voltage scan rate. Using the Nicholson equations,[32,33] Diggle[34] estimated the relative magnitudes of the standard electron transfer heterogeneous rate constants for the alkali metal cations in *N,N*-dimethylformamide. These values are also reported in table T6.1. Electron transfer is evidently slowest for lithium.

Reversible behaviour of an amalgam electrode requires that the ratio of the exchange current density to the diffusion limited current density at the amalgam surface be at least 10 to 1.[35] For a streaming lithium amalgam in *N*,*N*-dimethylformamide, this ratio has been estimated to be 4 to 1, whereas for streaming sodium, potassium, and caesium amalgams the ratios have been estimated to be 16 to 1, 24 to 1, and 36 to 1, respectively.[34] Thus, lithium amalgam in a streaming configuration in *N*,*N*-dimethylformamide fails to exhibit reversibility. However, the diffusion limited current density can be decreased by an order of magnitude by changing from a streaming to a stationary pool amalgam (tantamount to changing from a stirred to a still solution).[36] The decreased diffusion limited current density arises from an increased diffusion layer thickness and results in an increase, by as much as an order of magnitude, of the ratio of exchange current density to diffusion limited current density. Thus, a stationary or slowly spilling amalgam pool was employed for the lithium measurements reported in table T6.1.

6.4 Discussion

The data reported in table T6.1 are based on the NLJP rather than the TATB assumption. (The problems attending the application of the TATB assumption in *N*,*N*-dimethylthioformamide[5,18,37,38] were outlined in chapter 5.) Although liquid junction potentials between contiguous dissimilar solvents have been demonstrated to be significant for some solvent pairs[39] (*cf.* table T5.3), the liquid junction potential contribution to the overall potential of cell C6.1 is likely to remain constant throughout a series of measurements in which only the electroactive cation (at 0.001 M concentration) is changed. Hence, inferences regarding the relative values of $\Delta G_{tr}\ M^+$ (NLJP) in table T6.1

are not significantly qualified by the validity or invalidity of the NLJP assumption.

6.4.1 Alkali Metal Cations. From the ΔG_{tr} M^+ values reported in table T6.1 it is apparent that the free energies of transfer for the alkali metal cations from *N,N*-dimethylformamide to *N,N*-dimethylthioformamide become less positive (increasingly favourable, energetically) with increasing ion size and polarisability. This behaviour is, indeed, consistent with the predictions of the HSAB principle. The relative solvation of the extremes of this set of cations can be compared concisely by means of a hypothetical equilibrium in which $Cs^+{\cdot}DMF$ represents caesium cation solvated by *N,N*-dimethylformamide, $Li^+{\cdot}SDMF$ represents lithium cation solvated by *N,N*-dimethylthioformamide, *etc*. The

$$Cs^+{\cdot}DMF + Li^+{\cdot}SDMF \rightleftarrows Cs^+{\cdot}SDMF + Li^+{\cdot}DMF$$

equilibrium constant for the process, calculated from the free energies of transfer listed in table T6.1, is $10^{7\cdot 1}$. Caesium, being somewhat softer than lithium, is expected to be more strongly solvated by the softer sulphur electron donor solvent *N,N*-dimethylthioformamide than is lithium. Conversely, lithium, being rather harder than caesium, is expected to be more strongly solvated by the harder oxygen electron donor solvent *N,N*-dimethylformamide than is caesium.

Alternatively, the behaviour of the alkali metal cations towards these two solvents can be accounted for, at least qualitatively, in terms solely of electrostatic interactions governed by size and charge density effects. Lithium cation, because of its smaller size, has a greater formal surface charge density than does caesium; hence, lithium cation is always expected to have stronger electrostatic interactions with all solvent molecules and to be more responsive to solvent transfer than is caesium. For transfer from *N,N*-dimethylformamide to *N,N*-dimethylthioformamide, or indeed, for any transfer to a weaker solvator of alkali metal cations, the ΔG_{tr} Li^+ values are expected to be more positive than the ΔG_{tr} Cs^+ values. The only exceptions to this generalisation occur when transfers are to or from highly structured solvents such as methanol, formamide, or water. In such instances, entropic effects are known to play an important role (*cf.* chapters 2, 5, and 7) and to constitute a significant fraction of the free energies of transfer of the ions.[29]

The standard electrode reduction potentials of the alkali metal cations (determined from the standard values in water,[40] the free energies of transfer from water to *N,N*-dimethylformamide,[29] and the free energy data in table T6.1) in the solvents considered can be used to compare their relative interactions with solvents as shown in figure F6.1. The separation between the reduction potential in *N,N*-dimethylformamide and in *N,N*-dimethylthioformamide decreases in regular fashion from lithium through to caesium in accord with the expected order of decreasing sensitivity to solvent transfer. The separation between the potential in water and that in the other two solvents cannot be so simply interpreted because of the above-mentioned entropic complications which occur in water.

6.4.2 Thallous and Silver Cations. The ΔG_{tr} M^+ values in table T6.1 indicate that both thallous and silver cations behave much differently from the alkali metal cations for solvation by soft *N,N*-dimethylthioformamide and by hard *N,N*-dimethylformamide. Although the former solvent is a weaker solvator of the alkali metal cations than is the latter solvent, it is a slightly stronger solvator of the monovalent thallium cation and a much stronger solvator of silver cation. The soft, Class B, monovalent thallium and silver cations are indeed expected, on the basis of the HSAB principle, to exhibit the observed behaviour. The nature of the interaction, which cannot be predicted on the basis of the HSAB principle, is believed to involve interaction of the completely filled d-electron orbitals of the cation (5d orbitals for thallium

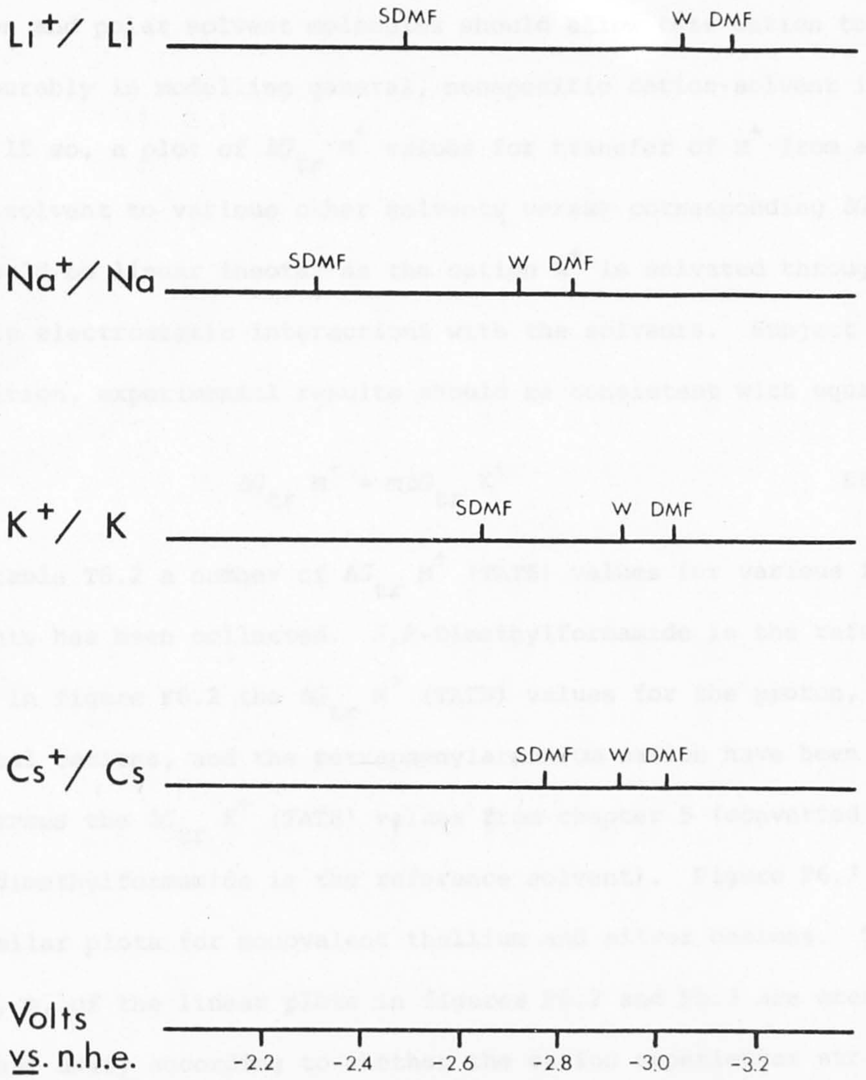

FIGURE F6.1 : Standard electrode reduction potentials (*versus* the normal hydrogen electrode in water) on the TATB assumption for representative alkali metal cations in *N*,*N*-dimethylformamide and in its thio analogue *N*,*N*-dimethylthioformamide.

and 4d orbitals for silver cation) with unfilled d-electron orbitals on sulphur.[41,42]

6.4.3 Comparisons with Potassium Cation. In chapter 5 it was suggested that the essentially electrostatic nature of interactions between potassium cation and polar solvent molecules should allow this cation to serve favourably in modelling general, nonspecific cation-solvent interactions. If so, a plot of ΔG_{tr} M^+ values for transfer of M^+ from a reference solvent to various other solvents *versus* corresponding ΔG_{tr} K^+ values should be linear insofar as the cation M^+ is solvated through nonspecific electrostatic interactions with the solvents. Subject to this condition, experimental results should be consistent with equation E6.1.

$$\Delta G_{tr}\ M^+ = m\Delta G_{tr}\ K^+ \qquad \text{E6.1}$$

In table T6.2 a number of ΔG_{tr} M^+ (TATB) values for various ions and solvents has been collected. *N,N*-Dimethylformamide is the reference solvent. In figure F6.2 the ΔG_{tr} M^+ (TATB) values for the proton, the alkali metal cations, and the tetraphenylarsonium cation have been plotted *versus* the ΔG_{tr} K^+ (TATB) values from chapter 5 (converted so that *N,N*-dimethylformamide is the reference solvent). Figure F6.3 includes similar plots for monovalent thallium and silver cations. The gradients, *m*, of the linear plots in figures F6.2 and F6.3 are greater or less that unity according to whether the cation experiences stronger or weaker electrostatic ion-solvent interactions than potassium cation. Larger gradients reveal greater sensitivity of the cation to solvent transfer. The gradients are included in the figures.

In the plots of figures F6.2 and F6.3 instances of specific ion-solvent interactions produce deviations from the linear relationship expressed by equation E6.1. Most notable in this regard in figure F6.2 are the data for the tetraphenylarsonium cation in the highly structured

TABLE T6.2

FREE ENERGIES OF TRANSFER (TATB ASSUMPTION) OF VARIOUS CATIONS FROM *N,N*-DIMETHYLFORMAMIDE TO OTHER SOLVENTS AT 298 K

SOLVENT[a]	ΔG_{tr} M^+ (TATB)[b] kJ g-ion^{-1}							
M^+:	K^+[c]	H^+	Li^+	Na^+	Cs^+	Ph_4As^+	Ag^+[c]	Tl^+
E	+30.7						+25.1	
TFE	+49.2						+65.5	
HMPT	-5.5						-20.9	
NMP	-5.5			-5.9		-1.7	-12.1	
M	*+25.7*	*+25.1*	*+13.4*	*+18.8*	*+18.8*	*+14.6*	*+24.7*	*+15.9*[d]
NM	+35.4						+42.3	
DMF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AN	+19.5	+60.7	+39.3[d]	+24.3	+14.2[d]	+5.4	*-4.6*	+20.9[d]
DMA	-1.9						-6.2	
TMS (303 K)	*+3.1*			*+7.5*	*-0.8*	*+2.5*	*+13.4*	
DMSO	-2.2	-4.6	-5.0	-3.3	-3.3	+1.3	-16.3	*-13.4*[d]
SDMF[e]	+37.2		+63.7	+50.0	+23.3		*-80.8*	*-4.3*
PC	*+10.6*		*+33.5*	*+25.5*	*-2.9*	*+2.5*	*+33.1*	*+20.1*[d]
W	+10.0	+14.2	+9.6	+10.5	+9.2	*+38.1*	+17.2	+11.7[d]
F	+7.7		*0.0*	+2.5	+1.7	*+14.2*	+1.7	

---

a. Abbreviations are as in table T2.1.

b. All values are from data reported in reference 29 unless noted otherwise. Italicised values were omitted from the calculations to determine gradients of the lines in figures F6.2 and F6.3 (*cf.* text).

c. From data in tables T5.4 and T5.5 (*cf.* reference 5).

d. From data in reference 53 (preprint kindly supplied by B.G. Cox).

e. All values are from table T6.1 (*cf.* reference 18). ΔG_{tr} (NLJP) = ΔG_{tr} (TATB) by definition for SDMF (*cf.* chapter 5).

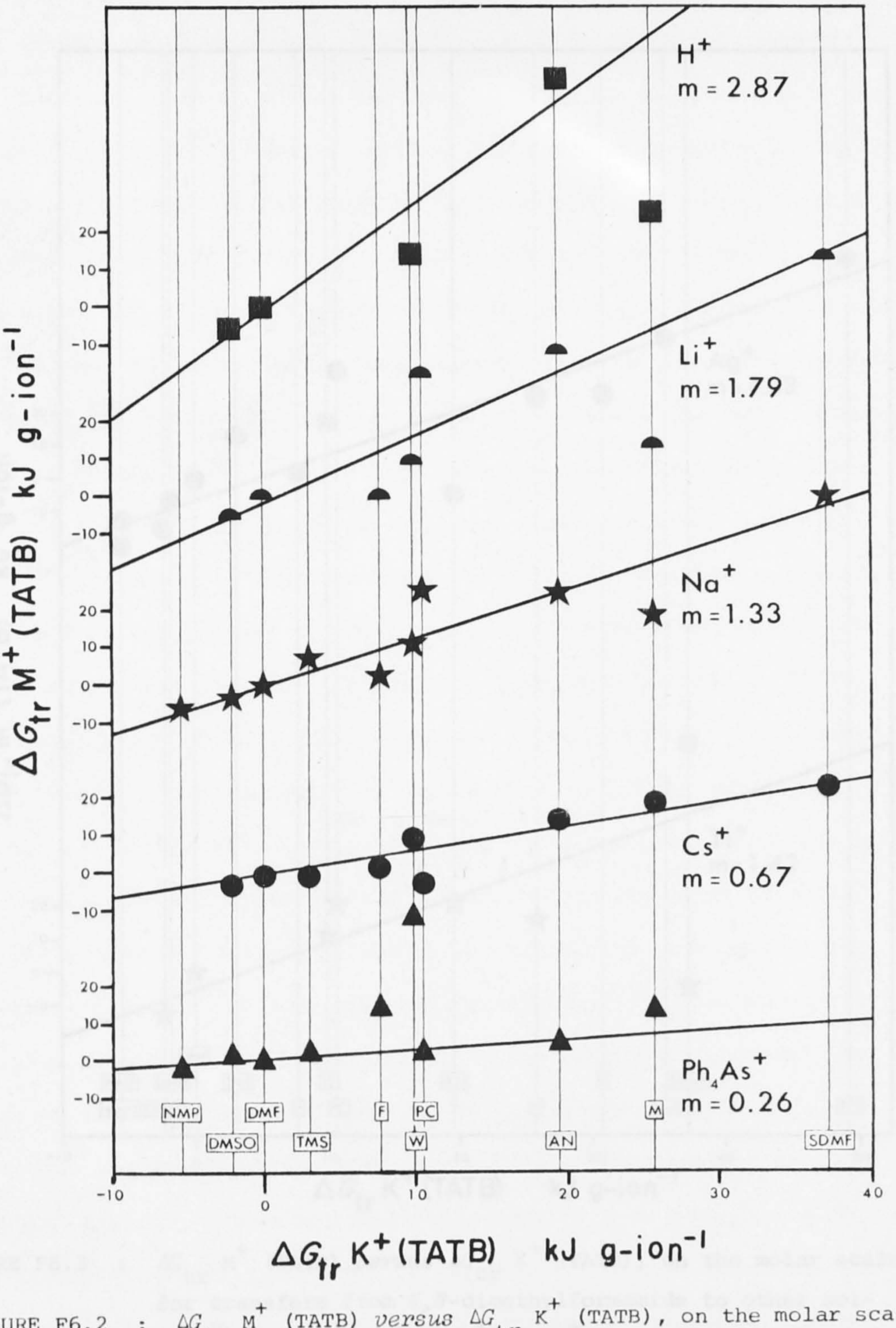

FIGURE F6.2 : ΔG_{tr} M$^+$ (TATB) *versus* ΔG_{tr} K$^+$ (TATB), on the molar scale, for transfers from *N*,*N*-dimethylformamide to other solvents at 298 K. M$^+$ = Ph$_4$As$^+$, Cs$^+$, Na$^+$, Li$^+$, and H$^+$.

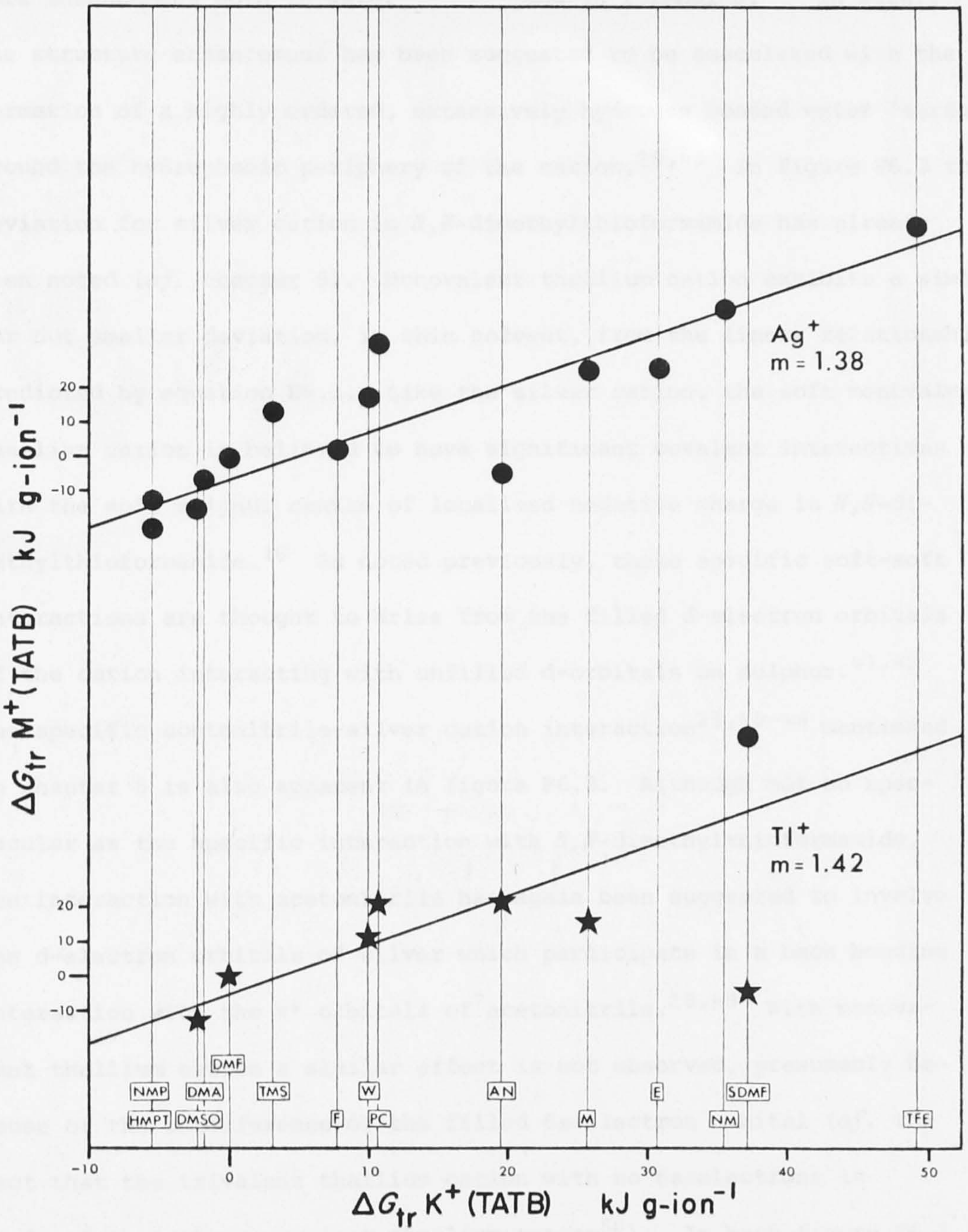

FIGURE F6.3 : ΔG_{tr} M$^+$ (TATB) *versus* ΔG_{tr} K$^+$ (TATB), on the molar scale, for transfers from *N,N*-dimethylformamide to other solvents at 298 K. M$^+$ = Tl$^+$ and Ag$^+$.

solvents water and formamide (*cf.* chapter 2). It has been recognised that this ion and structurally similar ones cause significant structure enhancement both in water[29,43,44] and in formamide.[29] In water, the structure enhancement has been suggested to be associated with the formation of a highly ordered, extensively hydrogen bonded water 'surface' around the hydrophobic periphery of the cation.[29,45] In figure F6.3 the deviation for silver cation in *N,N*-dimethylthioformamide has already been noted (*cf.* chapter 5). Monovalent thallium cation exhibits a similar but smaller deviation, in this solvent, from the linear relationship predicted by equation E6.1. Like the silver cation, the soft monovalent thallium cation is believed to have significant covalent interactions with the soft sulphur centre of localised negative charge in *N,N*-dimethylthioformamide.[16] As noted previously, these specific soft-soft interactions are thought to arise from the filled d-electron orbitals of the cation interacting with unfilled d-orbitals on sulphur.[41,42] The specific acetonitrile-silver cation interaction[29,45-48] mentioned in chapter 5 is also apparent in figure F6.3. Although not so spectacular as the specific interaction with *N,N*-dimethylthioformamide, the interaction with acetonitrile has again been suggested to involve the d-electron orbitals of silver which participate in a back bonding interaction with the π^* orbitals of acetonitrile.[29,49] With monovalent thallium cation a similar effect is not observed, presumably because of the interference of the filled 6s-electron orbital (*cf.* the fact that the trivalent thallium cation with no 6s-electrons is 'softer' than the monovalent thallium cation[50]). In both figure F6.2 and figure F6.3 deviations from the predicted linear relationship of equation E6.1 are generally observed for propylene carbonate, tetramethylenesulphone, and methanol. For the former two solvents the uncertainty lies in the ΔG_{tr} K^+(TATB) value, as already noted in chapter 5. For methanol the uncertainty is believed to arise from the questionable validity of the TATB assumption itself in this solvent (*cf.* chapter 3).[51,52]

Throughout the foregoing discussion the relative solvation behaviour of the potassium cation has been used for correlating a large amount of data for other cations through equation E6.1. 'Anomalous' behaviour for any of the cations in any of the solvents studied is, indeed, an indication of probable specific solvation effects. The correlation scheme does not, however, identify the nature of the specific interactions indicated. Nevertheless, the scheme provides a useful starting point for the further investigation of specific cation-solvent interactions.

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CHAPTER 7

COMPARATIVE DIVALENT CATION SOLVATION AND SINGLE ION ENTROPIES OF TRANSFER

In this chapter single ion free energies and enthalpies of transfer for the divalent metal cations barium, zinc, and cadmium are reported on the basis of the TATB assumption. From these data corresponding single ion entropies of transfer are calculated both for transfer between real solvents and for transfer from hypothetical ideal solvents (with the same molecular weights and densities as the corresponding real solvents but with no specific ion-ion or ion-solvent interactions) to corresponding real solvents. The behaviour of these divalent cations in solution is compared with that of the silver and alkali metal cations. Results are discussed in terms of qualitative models of ion solvation.

7.1 Introduction

In chapters 5 and 6 efforts towards the characterisation of non-aqueous electrolyte solutions centred on the relative chemical solvation free energies (free energies of transfer) of cations in various solvents. Through the Gibbs equation, equation E7.1, the free energy of transfer is seen to consist of enthalpic (ΔH_{tr}) and entropic (ΔS_{tr}) contributions.

$$\Delta G_{tr} = \Delta H_{tr} - T\Delta S_{tr} \qquad \text{E7.1}$$

Combination of the experimentally accessible single ion free energies and enthalpies of transfer based on the TATB assumption (*cf.* chapters 3 and 4) allows calculation of corresponding single ion entropies of transfer on the same assumption. Knowledge of single ion enthalpies of transfer gives information regarding the relative strength of ion-solvent interactions; knowledge of single ion entropies of transfer provides insight into ion-imposed solvent structural changes.

To date, most of the existing data and models of cation solvation have been based upon studies of monovalent ions.[1-8] Despite the desirability of extending data to multivalent cation systems in order to examine the general applicability of existing solvation models,[9] efforts in this direction have been discouraged by problems of assessing the extent of ion association, particularly in solvents of low dielectric constant, of determining salt activity effects, and of preparing anhydrous electrolytes for the measurements.[10] In this work, experimental conditions were chosen to overcome or to minimise these difficulties, insofar as possible.

The need to take explicit account of the discrete structure of the solvent in order more fully to understand ion solvation and solution phenomena has been recognised.[11] It is in this connexion that single ion entropy changes upon solvation and upon solvent transfer are especially useful. The standard single ion free energies of solvation (the difference between the standard free energy of an ion in solution and in the gaseous phase) of divalent cations in polar solvents are usually much more negative than those for the monovalent cations (*e.g.* ΔG_s M^{2+} typically -1000 to -2000 kJ g-ion^{-1} whilst ΔG_s M^+ typically -250 to -500 kJ g-ion^{-1}).[12] This behaviour is primarily a consequence of the stronger electrostatic and covalent enthalpic interactions between divalent metal cations and polar solvent molecules.[13] Counteracting this effect somewhat is a more negative entropy change associated with the more extensive structuring of polar solvent molecules within ion-centred solvation shells around divalent cations than occurs with monovalent cations.[8] Both effects are intimately associated with the generally smaller size and significantly greater formal surface charge density of the divalent cations compared with the monovalent ones.

7.2 Experimental Details

7.2.1 Free Energies of Transfer. The potentiometric cell used for determining free energies of transfer was described in chapter 4. The potentials of the various amalgam electrodes were measured against the potential of the Pleskov electrode in the same solvent as described in chapter 5. The method was altered for the divalent metal cations only insofar as a stationary amalgam pool rather than a streaming amalgam electrode was used for cell C7.1 in which M represents barium, zinc, or cadmium, TEAP represents tetraethylammonium perchlorate, and TEAPIC represents tetraethylammonium picrate. Although earlier data compiled by Mann

$$\begin{array}{c|c||c||c|c} \mathrm{Ag} & 0.01\ M\ \mathrm{AgClO_4} & 0.1\ M\ \mathrm{TEAPIC} & 0.001\ M\ \mathrm{M(CF_3SO_3)_2} & \mathrm{M(Hg)} \\ & & & 0.01\ M\ \mathrm{TEAP} & \\ & \text{solvent S} & \text{solvent S} & \text{solvent S} & \end{array} \qquad \text{C7.1}$$

and Barnes[14] suggest reversible behaviour for barium, zinc, and cadmium reductions on mercury in several of the solvents considered in this study, more recent evidence suggests that these reductions (especially that for barium) may be slow in dimethylsulphoxide.[15,16] The rate determining step in the electron transfer process was suggested to be solvent reorganisation in the ion solvation sphere.[17,18] Solvated species in the stronger electron donor solvents were generally observed to have slower apparent rates for the electron transfer process. Hence, behaviour similar to that observed in dimethylsulphoxide might be expected in the strong cation solvators *N,N*-dimethylformamide and hexamethylphosphorotriamide. In order to provide the most favourable experimental conditions for equilibrium at the electrode surface (*cf.* the conditions for reversible lithium reduction in *N,N*-dimethylformamide as discussed in chapter 6), dilute amalgam pool electrodes (metal concentration in mercury 0.0289 mole per cent) were used throughout this study for all solvents and all cations considered. Several independent measurements at 298 K of the potential of cell C7.1 were made for each cation in each solvent. Reproducibility of better than two per cent was consistently achieved. For barium the anhydrous perchlorate and trifluoromethanesulphonate gave identical results. Normal Nernstian concentration dependence of the cell potential was observed in the electroactive ion concentration range 0.01 to 0.0005 *M*.

7.2.2 Enthalpies of Solution. Enthalpies of solution of anhydrous salts in hexamethylphosphorotriamide were determined using the apparatus described in chapter 4. For other solvents data were taken from the literature.[10] Calorimetric samples of the divalent metal trifluoromethanesulphonates were handled in a glove box being purged continuously with dry nitrogen. Because of the long dissolution times for the divalent metal trifluoromethanesulphonates (30 minutes for cadmium and 10 minutes for barium and zinc), calorimetric output had to be analysed by the Regnault-Pfaundler method. For other salts with shorter dissolution times (less than 5 minutes), analysis by both the Regnault-Pfaundler and the Dickinson method gave identical results. Reproducibility of the enthalpies of solution in hexamethylphosphorotriamide as assessed by the standard deviation from the mean of several measurements was within 5 kJ mol^{-1}, with the greatest difficulty being encountered in the case of cadmium trifluoromethanesulphonate (±5 kJ mol^{-1} for the cadmium salt and ±2 kJ mol^{-1} for the barium and zinc salts).

7.2.3 Solvents and Salts. The purification of solvents was described in chapter 4 and solvent water contents were listed in table T4.1 (the minimum values listed). Tetraphenylarsonium tetraphenylboride was prepared by metathesis of tetraphenylarsonium chloride (L. Light and Co.) with sodium tetraphenylboride (Fluka, analytical reagent). The product was washed with water and recrystallised from *N*,*N*-dimethylacetamide/water.[19] Zinc trifluoromethanesulphonate was prepared by neutralising zinc carbonate (BDH, analytical reagent) with trifluoromethanesulphonic acid (3M Company), recrystallising three times from water, and vacuum drying at 420 K for 48 hours. All other salts were kindly supplied by G.R. Hedwig.

7.3 Results

7.3.1 Free Energies of Transfer. Measurement of the potential of cell C7.1 in a particular solvent leads, through equation E3.9, to the difference between the free energy of the divalent metal cation in solution and twice the free energy of the silver cation in solution as shown in equation E7.2.

$$G\ M^{2+} - 2G\ Ag^{+} = 2FE_{cell} \qquad E7.2$$

The G M^{2+} value is a function of both the divalent metal cation concentration in solution and the metal concentration in the amalgam. Similarly, the G Ag^{+} value is a function of the silver cation concentration in solution. If the potential of cell C7.1 be measured both in a reference solvent (*e.g.* in water) and in another solvent of interest, then the difference in the two cell potentials is simply related to the difference in the standard partial molar free energies of transfer of the two cations, provided that in both solvents identical amalgams are used, the silver cation concentrations used are the same, and the divalent metal cation concentrations used are the same. It is also necessary to assume unit activity coefficient of the metal complement in the amalgam and negligible Debye-Hückel salt effects for the electrolyte concentrations used. Fulfilment of the former condition is assured by the low concentration of metal complement in the amalgam, whilst salt effects are expected to be small and to cancel in cell C7.1 for the solvents, salts, and ionic strengths used. Ion association is also of minor concern at the low salt concentrations used.[10] Kinetic evidence suggests that the trifluoromethanesulphonate anion, as well as the perchlorate anion, is a very weak coordinator of metal cations.[20] Available conductance data suggest that the divalent metal perchlorates are essentially completely dissociated in the media studied.[21] Thus, comparison of the potential of cell C7.1 in two solvents leads directly to equation E7.3 relating the free energies of transfer of the divalent metal and silver cations from one solvent to the other. Values of $\Delta G_{\text{tr}}\ \text{Ag}^{+}$ based on the TATB assumption[22]

$$\Delta G_{\text{tr}}\ \text{M}^{2+} - 2\Delta G_{\text{tr}}\ \text{Ag}^{+} = 2F\Delta E_{\text{cell}} \qquad \text{E7.3}$$

have been compiled in table T5.5 and can be used to determine $\Delta G_{\text{tr}}\ \text{M}^{2+}$ (TATB). Table T7.1 lists values of $\Delta G_{\text{tr}}\ \text{M}^{2+}$ calculated from the potentials of cell C7.1 for transfer from water to various other solvents. In addition to data for the divalent metal cations barium, zinc, and cadmium, data for the silver and alkali metal cations are included in the table. All data were determined at 298 K and are based on the TATB assumption. Also, for the sake of comparison with figures F5.2, F6.2, and F6.3, plots of $\Delta G_{\text{tr}}\ \text{M}^{2+}$ *vs.* $\Delta G_{\text{tr}}\ \text{K}^{+}$ are presented in figure F7.1 for M^{2+} representing barium, zinc, and cadmium.

TABLE T7.1

SINGLE ION FREE ENERGIES OF SOLVATION AND OF TRANSFER FROM WATER TO NONAQUEOUS SOLVENTS[a]

CATION	PROCESS[b]	ΔG (kJ g-ion^{-1})[c]					
	SOLVENT:[b]	HMPT	M	DMF	AN	DMSO	W
Li^+	G → S		-507.1	-520.5		-525.5	-510.9
	W → S		+3.8	-9.6		-14.6	0.0
Na^+	G → S		-402.5	-421.4	-397.1	-424.7	-410.9
	W → S		+8.4	-10.5	+13.8	-13.8	0.0
K^+	G → S	-352.7	-321.5	-347.2	-327.7	-349.4	-337.2
	W → S	-15.5	+15.7	-10.0	+9.5	-12.2	0.0
Rb^+	G → S		-305.9	-325.9	-309.2	-326.8	-315.9
	W → S		+10.0	-10.0	+6.7	-10.9	0.0
Cs^+	G → S		-274.1	-292.9		-296.3	-283.7
	W → S		+9.6	-9.2		-12.6	0.0
Ag^+	G → S	-517.2	-471.6	-496.3	-500.9	-512.6	-479.1
	W → S	-38.1	+7.5	-17.2	-21.8	-33.5	0.0
Ba^{2+}	G → S	-1299.8[d]	-1300.0	-1339.7	-1261.1	-1343.5	-1318.4
	W → S	+18.6[d]	+18.4	-21.3	+57.3	-25.1	0.0
Zn^{2+}	G → S	-2071.2	-2000.0	-2057.3	-1959.0	-2076.6	-2027.6
	W → S	-43.6	+27.6	-29.7	+68.6	-49.0	0.0
Cd^{2+}	G → S	-1843.0	-1768.6	-1834.7	-1758.9	-1854.8	-1801.2
	W → S	-41.8	+32.6	-33.5	+42.3	-53.6	0.0

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a. Data are reported on the molar scale at 298 K using the TATB assumption.

b. G → S is solvation in solvent S and W → S is transfer from water to the specified solvent. Solvent abbreviations are as in table T2.1.

c. Transfer free energies for potassium and silver are from chapter 5, whilst for the other monovalent cations they are from reference 8. Transfer free energies for the divalent cations are calculated from the potentials of cell C7.1 and free energies of transfer of silver as described in the text. Free energies of solvation in water are from reference 12, and those for the other solvents were obtained by adding the appropriate free energies of transfer to the solvation free energies in water.

d. It is believed that this value is in error because of the nonequilibrium behaviour of the barium amalgam electrode in HMPT (*cf.* text).

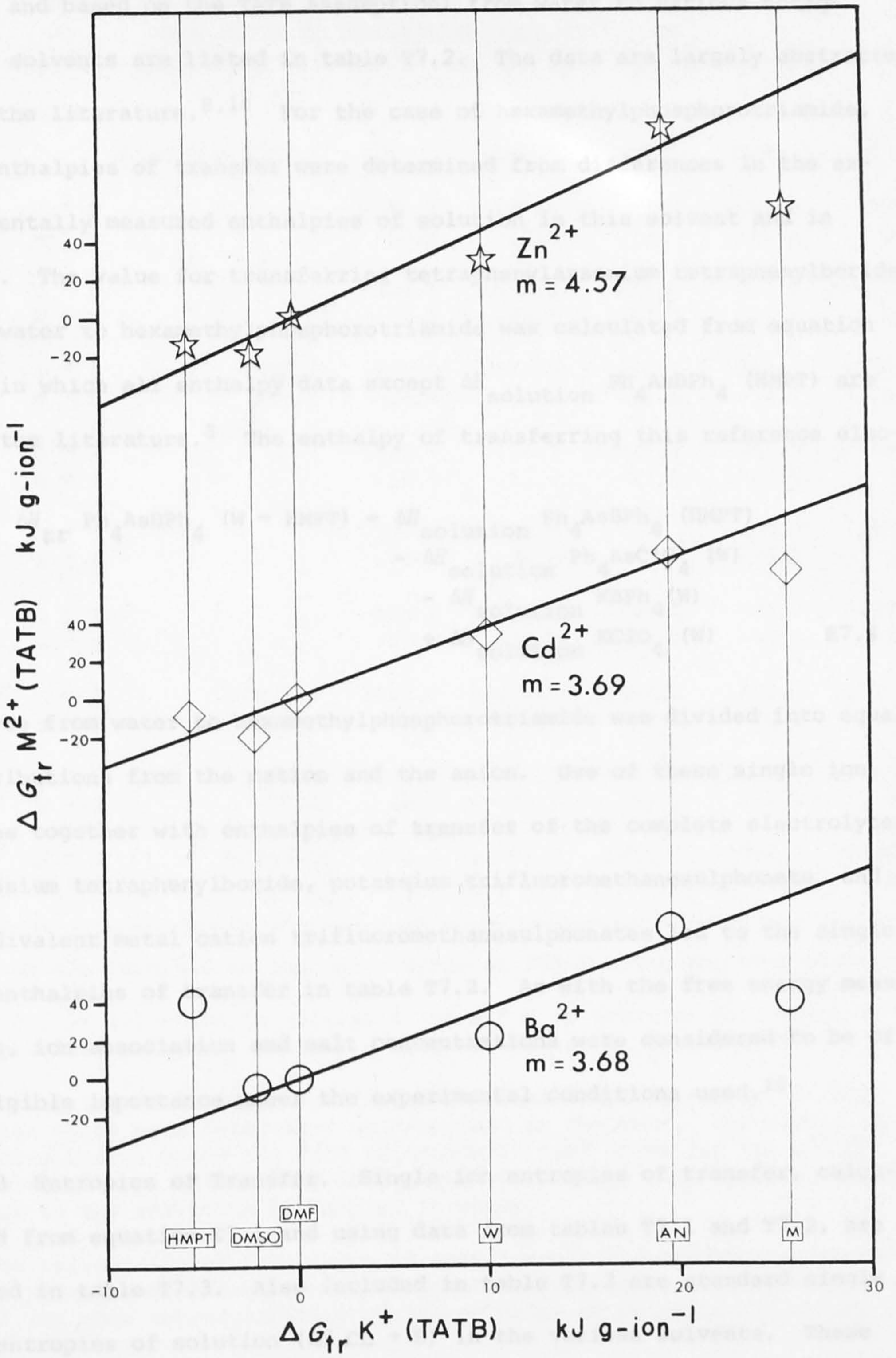

FIGURE F7.1 : ΔG_{tr} M^{2+} (TATB) *versus* ΔG_{tr} K^{+} (TATB), on the molar scale, for transfers from *N*,*N*-dimethylformamide to other solvents at 298 K. $M^{2+} = Ba^{2+}$, Cd^{2+}, and Zn^{2+}.

7.3.2 Enthalpies of Transfer. Single ion enthalpies of transfer (at 298 K and based on the TATB assumption) from water to various nonaqueous solvents are listed in table T7.2. The data are largely abstracted from the literature.[8,10] For the case of hexamethylphosphorotriamide, the enthalpies of transfer were determined from differences in the experimentally measured enthalpies of solution in this solvent and in water. The value for transferring tetraphenylarsonium tetraphenylboride from water to hexamethylphosphorotriamide was calculated from equation E7.4 in which all enthalpy data except $\Delta H_{\text{solution}}\ Ph_4AsBPh_4$ (HMPT) are from the literature.[8] The enthalpy of transferring this reference electrolyte from water to hexamethylphosphorotriamide was divided into equal contributions from the cation and the anion. Use of these single ion values together with enthalpies of transfer of the complete electrolytes potassium tetraphenylboride, potassium trifluoromethanesulphonate, and the divalent metal cation trifluoromethanesulphonates led to the single ion enthalpies of transfer in table T7.2. As with the free energy measurements, ion association and salt concentrations were considered to be of negligible importance under the experimental conditions used.[10]

$$\begin{aligned}\Delta H_{\text{tr}}\ Ph_4AsBPh_4\ (W \rightarrow HMPT) = {} & \Delta H_{\text{solution}}\ Ph_4AsBPh_4\ (HMPT)\\ & - \Delta H_{\text{solution}}\ Ph_4AsClO_4\ (W)\\ & - \Delta H_{\text{solution}}\ KBPh_4 (W)\\ & + \Delta H_{\text{solution}}\ KClO_4\ (W) \qquad \text{E7.4}\end{aligned}$$

7.3.3 Entropies of Transfer. Single ion entropies of transfer, calculated from equation E7.1 and using data from tables T7.1 and T7.2, are listed in table T7.3. Also included in table T7.3 are standard single ion entropies of solution (ΔS CL → S) in the various solvents. These result from adding previously reported[9] standard single ion entropies of solution in water (ΔS CL → W, the molar entropy change accompanying transfer of ions from crystal lattice to aqueous solution) to the standard

TABLE T7.2

SINGLE ION ENTHALPIES OF SOLVATION AND OF TRANSFER FROM WATER TO NONAQUEOUS SOLVENTS[a]

CATION	PROCESS[b]	ΔH (kJ g-ion^{-1})[c]					
	SOLVENT:[b]	HMPT	M	DMF	AN	DMSO	W
Li^+	G → S		-549.4	-559.4		-553.6	-527.2
	W → S		-22.2	-32.2		-26.4	0.0
Na^+	G → S		-438.5	-451.1	-431.0	-445.6	-418.0
	W → S		-20.5	-33.1	-13.0	-27.6	0.0
K^+	G → S	-391.4	-351.9	-372.8	-356.1	-368.2	-333.5
	W → S	-57.9	-18.4	-39.3	-22.6	-34.7	0.0
Rb^+	G → S		-323.9	-346.1	-331.4	-341.9	-308.4
	W → S		-15.5	-37.7	-23.0	-33.5	0.0
Cs^+	G → S		-289.5	-312.5		-307.9	-275.7
	W → S		-13.8	-36.8		-32.2	0.0
Ag^+	G → S		-508.8	-526.4	-540.6	-542.7	-487.9
	W → S		-20.9	-38.5	-52.7	-54.8	0.0
Ba^{2+}	G → S	-1472.2	-1386.8	-1413.1	-1336.1	-1406.1	-1327.6
	W → S	-144.6	-59.2	-85.5	-8.5	-78.5	0.0
Zn^{2+}	G → S	-2166.8	-2115.0	-2132.1	-2049.3	-2131.6	-2069.4
	W → S	-97.4	-45.6	-62.7	+20.1	-62.2	0.0
Cd^{2+}	G → S	-1947.0[d]	-1871.3	-1894.2	-1822.7	-1901.7	-1830.9
	W → S	-116.1[d]	-40.4	-63.3	+8.2	-70.8	0.0

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a. Data are reported on the molar scale at 298 K using the TATB assumption.

b. G → S is solvation in solvent S and W → S is transfer from water to the specified solvent. Solvent abbreviations are as in table T2.1.

c. Enthalpies of transfer are from references 8 and 10 except the HMPT data which were determined as described in the text. Enthalpies of solvation in water are from reference 12, and those for the other solvents were obtained by adding the appropriate enthalpies of transfer to the solvation enthalpies in water.

d. The reliability of this value is questionable because of the long dissolution time of cadmium trifluoromethanesulphonate in HMPT and because of the poor reproducibility of the enthalpy of solution (±5 kJ mol^{-1}, *cf.* text).

TABLE T7.3

SINGLE ION ENTROPIES OF SOLUTION,
OF TRANSFER FROM WATER TO NONAQUEOUS SOLVENTS,
AND OF TRANSFER FROM IDEAL TO CORRESPONDING REAL SOLVENTS[a]

CATION	PROCESS[b]	ΔS (J K^{-1} g-ion^{-1})[c]					
	SOLVENT:[b]	HMPT	M	DMF	AN	DMSO	W
Li^+	CL → S		-106.7	-95.4		-59.0	-19.7
	W → S		-87.0	-75.7		-39.3	0.0
	I → R		-146.0	-129.3		-93.7	-65.7
Na^+	CL → S		-82.9	-61.5	-75.8	-32.2	+14.2
	W → S		-97.1	-75.7	-90.0	-46.4	0.0
	I → R		-122.2	-95.4	-113.0	-66.9	-31.8
K^+	CL → S	-97.4	-69.6	-53.5	-62.9	-30.7	+44.8
	W → S	-142.2	-114.4	-98.3	-107.7	-75.5	0.0
	I → R	-124.5	-109.0	-87.1	-100.2	-65.5	-1.3
Rb^+	CL → S		-28.1	-34.8	-41.9	-18.0	+57.7
	W → S		-85.8	-92.5	-99.6	-75.7	0.0
	I → R		-67.4	-68.6	-79.1	-52.7	+11.7
Cs^+	CL → S		-11.3	-32.3		-5.9	+60.2
	W → S		-71.5	-92.5		-66.1	0.0
	I → R		-50.6	-66.1		-40.6	+14.2
Ag^+	CL → S		-88.3	-64.4	-96.7	-64.4	+7.1
	W → S		-95.4	-71.5	-103.8	-71.5	0.0
	I → R		-127.6	-98.3	-133.9	-99.2	-38.9
Ba^{2+}	CL → S	-606.4[d]	-319.3	-274.3	-279.7	-238.1	-59.0
	W → S	-547.4[d]	-260.3	-215.3	-220.7	-179.1	0.0
	I → R	-633.5[d]	-358.7	-308.2	-317.0	-272.9	-105.1
Zn^{2+}	CL → S	-310.6	-409.9	-275.1	-327.1	-208.7	-164.4
	W → S	-146.2	-245.5	-110.7	-162.7	-44.3	0.0
	I → R	-337.7	-449.3	-309.0	-364.4	-243.5	-210.5
Cd^{2+}	CL → S	-381.0[d]	-376.6	-231.7	-246.2	-189.5	-131.8
	W → S	-249.2[d]	-244.8	-99.9	-114.4	-57.7	0.0
	I → R	-408.1[d]	-416.0	-265.6	-283.5	-224.3	-177.9

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a. Data are reported on the molar scale at 298 K using the TATB assumption.

b. CL → S is solution of one mole of a hypothetical solid ion lattice in solvent S, W → S is transfer from water to the specified solvent, and I → R is transfer from an ideal to a corresponding real solvent as described in the text. Solvent abbreviations are as in table T2.1.

c. Entropies of solution (CL → S) were obtained by adding the entropies of transfer (W → S) to the entropies of solution in water given in reference 9. Entropies of transfer (W → S) were obtained using equation E7.1 and the data from tables T7.1 and T7.2. Entropies of transfer (I → R) were obtained using equation E7.5 and the entropies of solution (CL → S. Values of $R \ln [(1000\rho)/MW]$ (J K^{-1} g-ion^{-1}) are as follows: HMPT, 14.5; M, 26.8; DMF, 21.3; AN, 24.7; DMSO, 22.2; W, 33.5.

d. The reliability of these data is questionable because of uncertainty in the free energy and enthalpy data (*cf.* text and tables T7.1 and T7.2).

single ion entropies of transfer from water to the other solvents (ΔS_{tr} W → S) as shown in equation E7.4. All data are based on the TATB assumption.

$$\Delta S \text{ CL} \rightarrow \text{S} = \Delta S \text{ CL} \rightarrow \text{W} + \Delta S_{tr} \text{ W} \rightarrow \text{S} \qquad \text{E7.4}$$

The extent and nature of ion-imposed solvent structural changes, however, are difficult to assess from standard single ion entropies of transfer or of solution. From the former entropies it is difficult to determine unambiguously whether structural changes in the reference solvent or in the partner solvent (or both) account for observed entropic behaviour. For the latter entropies there is the inherent difficulty of using a solid as the reference state for an ion in solution. To overcome these difficulties, it has been proposed that a hypothetical ideal solvent of the same structure, density, and molecular weight as the corresponding real solvent be used as the reference state for ions in each real solvent considered.[8,9] Standard entropies of transfer of ions from each ideal solvent to its corresponding real solvent (ΔS_{tr} I → R) can be calculated from equation E7.5, and these results are also listed in table T7.3. Again, the data are based on the TATB assumption.

$$\Delta S_{tr} \text{ I} \rightarrow \text{R} = \Delta S \text{ CL} \rightarrow \text{S} - 12.6 - R \ln \frac{1000\rho}{MW} \qquad \text{E7.5}$$

The first term on the right hand side of equation E7.5 is taken from equation E7.4. The second term represents the entropy change (12.6 J K^{-1} g-ion^{-1}) for the change of state upon forming a unit mole fraction melt of ions from a hypothetical solid lattice of single ions, whilst the final term reflects the entropy change ($R \ln \frac{1000\rho}{MW}$, expressed in units of J K^{-1} g-ion^{-1}) for this hypothetical melt to be diluted with the solvent to form one cubic decimetre of solution having no ion-ion or ion-solvent interactions. Taken together, the terms on the right hand side of equation E7.5 represent the entropy change associated with transferring one mole of single ions from an ideal solution to a corresponding real solution of the same structure (*cf.* chapter 2), density (ρ), and molecular weight (*MW*). The hypothetical ideal solution is not 'ideal' in exactly the same sense implied by Raoult's law, for it is not defined as having complete uniformity of cohesive forces.[23] In the sense intended here, 'ideal' denotes the absence of specific ion-ion and ion-solvent interactions, but solvent-solvent interactions (*i.e.* the solvent 'structure' - *cf.* chapter 2) persist. Hence, with this definition, the entropy change upon transferring an ion from an ideal to a corresponding real solvent (*cf.* equation E7.5) must be attributable exclusively to the ion-imposed structural changes in the real solution. Implicit in the application of equation E7.5 are the assumption that the contributions to the entropy of solution (and hence to the entropy of solvent transfer) are equal for the tetraphenylarsonium cation and the tetraphenylboride anion,[9] and the Eastman-Latimer assumption that the entropy of an ion in a real ionic lattice is independent of the counterion present.[24] The general significance of the function ΔS_{tr} I → R for monovalent cations in water[9] and in nonaqueous solvents[8] has been described previously; essentially the same concepts are believed to extend to the behaviour of divalent cations in solution.

7.4 Discussion

7.4.1 Free Energies of Transfer. The data listed in table T7.1 reveal that, although there are some exceptions, the solvation free energies of a given monovalent or divalent cation generally decrease in the following order: HMPT > DMSO > DMF > W > M > AN. This order cannot be predicted solely on the basis of solvent bulk dielectric constants (*cf.* table T2.1) and the Born equation (*cf.* equation E3.8), but it can be understood in terms of the chemical properties (*e.g.* basicities, structures, donor abilities, *etc.*) of the solvents (*cf.* chapter 5).[13,25-28] Nevertheless, as with the monovalent cations, the magnitudes of the divalent cation solvation energies are largely governed by Born-type electrostatic interactions in all of the solvents studied.[29-31] Variations of ion solvation energies in different solvents (*cf.* the free energies of transfer in table T7.1) arising from chemical or specific ion-solvent interactions usually comprise less than ten percent of the mean solvation energy of an ion.

Compared with the monovalent cations, the divalent cations are considerably more sensitive to solvent transfer. The values of ΔG_{tr} M^+ for transfer between any two solvents listed in table T7.1 range over no more than 50 kJ g-ion^{-1}, whilst for ΔG_{tr} M^{2+} the range is up to 120 kJ g-ion^{-1}. This behaviour can be attributed to the divalent cations being stronger Lewis acids[32] and to their having a significantly greater formal surface charge density that the monovalent cations. If electrostatic interactions alone are considered, the sensitivity of the divalent cations to solvent transfer is expected to be $Zn^{2+} > Cd^{2+} > Ba^{2+}$. The experimentally observed order of $Cd^{2+} \gtrsim Zn^{2+} > Ba^{2+}$ arises from the stronger covalent interactions of cadmium than of zinc.[33]

In chapters 5 and 6 the specific back bonding interaction between the filled d-electron orbitals of silver cation and the π-bond system of acetonitrile[8,34,35] was noted to result in an unusually favourable (relative to the case for potassium cation) free energy of transfer from water. Although a similar interaction might be expected involving the filled d-electron orbitals of divalent zinc and cadmium, the data in table T7.1 for ion transfer from water to acetonitrile show that the effect is absent (for zinc) or significantly reduced (for cadmium). A greater formal surface charge density is known to reduce the proclivity of an ion to participate in back bonding interactions.[36] The observed behaviour of these ions, having filled d-electron orbitals, is also consistent with the HSAB principle (*cf.* chapters 5 and 6).[37] Silver cation is very much softer than the soft divalent cadmium cation, which is softer than the borderline (between the soft and hard categories) divalent zinc cation.[38] Thus, free energies of transfer from water to acetonitrile for these ions decrease in exothermicity in the order $Ag^{+} \gg Cd^{2+} > Zn^{2+}$.

The 'anomalous' free energy of transfer of the divalent barium cation from water to hexamethylphosphorotriamide is thought to result from nonequilibrium of the barium amalgam electrode in hexamethylphosphorotriamide. It has been noted (*cf.* chapter 6) that solvent reorganisation is required prior to electron transfer in the reduction of a solvated cation, and that the energy required for solvent reorganisation is greater in cases of strongly solvating solvents. It has also been observed that Group IIA cations are generally less likely to exhibit reversible electrode behaviour (*i.e.* more likely to exhibit slow electrode kinetics) than are Group IIB cations.[14,15]

7.4.2 Enthalpies of Transfer. Most aspects of the enthalpy data presented in table T7.2 have been discussed in the literature.[8,10] It should be noted here, however, that the reported single ion enthalpies of solvation (enthalpies of ions in solution relative to in the gaseous phase) in a particular solvent reflect the expected relative strengths of electrostatic interactions between the solvent and the various ions. Thus, in a given solvent, the magnitudes of the enthalpies of solvation of the divalent cations decrease in accord with decreasing formal surface charge density in the order $Zn^{2+} > Cd^{2+} > Ba^{2+}$. For a particular divalent metal cation, the enthalpies of solvation generally decrease in the order HMPT > DMF ≃ DMSO > M > W > AN.

7.4.3 Entropies of Transfer from Water to Solvent S. The data in table T7.3 indicate that a significant decrease in entropy accompanies the transfer of cations from water to each of the nonaqueous solvents included in this study. It is also apparent that the entropy losses (typically -100 to -250 kJ g-ion^{-1}) for transferring divalent cations from water are generally greater than for monovalent cations (typically -50 to -100 kJ g-ion^{-1}). Evidently, there is no simple correlation between the strength of a particular ion-solvent interaction (as judged by the appropriate enthalpy datum in table T7.2) and the attendant entropy change (*cf.* table T7.3) for the process. For example, when silver and potassium cations (crystallographic radii 1.26 and 1.33 × 10^{-10} m, respectively) are compared, their entropies of transfer from water are similar in dimethylsulphoxide and in acetonitrile, whilst they are significantly different in *N,N*-dimethylformamide and in methanol. The especially favourable acetonitrile-silver cation enthalpic interaction is not reflected in the entropy data. Apparently, single ion entropies of transfer reflect not the strength of ion-solvent interactions, but rather the number of solvent molecules whose freedom of movement is restricted upon formation of an ion-centred solvation shell (or shells). The entropy loss associated with the loss of translational freedom as a solvent molecule enters the solvation shell of a cation predominates over the entropy effects arising from changes in vibrational or rotational degrees of freedom of the solvent molecule.[8,23] Hence, to a first approximation, these latter effects can be neglected.

The entropy of transfer of an ion from water to a nonaqueous solvent is qualitatively interpretable in terms of solvent structural considerations.[39-42] In the solvent to which and from which the cation is being transferred, both the inherent solvent structure and the ion-induced structure enhancement (or disruption) must be considered. Early attempts to describe the structural environment of a cation in water postulated the existence of several concentric regions centred around the cation.[43-45] The first such region includes those water molecules whose dipoles are oriented favourably to interact with or to solvate the central cation. Beyond this region is a region containing water molecules of random orientational distribution. This second region separates the ion-centred solvation sphere from a third region in which the water molecules retain the structural characteristics and behaviour of normal bulk water. Recently, an analogous model has been proposed for nonaqueous solvents.[8]

The above-mentioned model for solvent structure in the vicinity of a solvated cation serves as the basis for interpreting single ion entropies of transfer from water to nonaqueous solvents. An entropy change accompanies 'desolvation' or removal of a cation from water. The water molecules from the cation's solvation shell(s) and from the disordered region separating the hydrated ion from bulk water must all be incorporated into the highly developed bulk water structure (*cf.* chapter 2). The magnitude and size of the attendant entropy change depend both upon the relative degrees of structure of water molecules in the disordered region and in the ion-centred solvation shell(s) when compared with the normal bulk water structure, and upon the number of water molecules whose structural environment changes.[46,47] For transferring a cation into a nonaqueous solvent, entropy changes accompany both the structure disrupting process of accomodating a cation in the solvent and the structure enhancing process of forming one (or more) ion-centred solvation shell(s). The latter process is expected to predominate in terms of entropic effects, because these solvents are generally considered to have rather poorly developed bulk solvent structures (*cf.* chapter 2), at least when compared with water. Hence, a net negative entropy change accompanies cation transfer to the nonaqueous solvents considered.[48] However, 'poorly developed bulk solvent structure' does not imply the absence of bulk solvent structure. Indeed, the evidence presented in chapter 2 suggests the occurrance of significant specific molecule-molecule interactions in the liquid state for methanol and dimethlysulphoxide, whilst for hexamethylphosphorotriamide, *N,N*-dimethylformamide, and acetonitrile, the solvent structure is less extensive.

When compared with those for the monovalent cations, the entropies of transfer from water to the nonaqueous solvents are generally more negative for the divalent cations. This behaviour arises largely from the much greater formal surface charge density of the divalent cations.

The polarisation of water molecules in the first solvation layer around a divalent cation greatly enhances the acidity of the peripheral hydrogens (*cf.* the greater acidity of the species $M{\cdot}W_n^{2+}$ than that of $M{\cdot}W_n^{+}$, where W represents a first solvation shell water molecule)[16] so that a second shell of water molecules, hydrogen bonded to the first shell, becomes involved in the cation-solvent interactions.[49-54] It is even conceivable that hydrogen bonding between successive shells extends beyond the second to higher order shells.[49] A two-dimensional representation of this behaviour appears in figure F7.2(a). For simplicity, only four water molecules in the first solvation layer are considered.

A certain degree of 'open-ness' has been postulated for liquid water structure.[55] This open-ness persists in the solvation layers around a solvated cation, and can be considered to represent the 'space' between adjacent solvating molecules. It is important to note that the open-ness, or available space, becomes relatively more important for higher order solvation shells. For example, if it is assumed (for simplicity) that formation of a second solvation layer doubles the radius of a solvated ion, it is apparent that the volume of this second shell is seven times that of the first layer [*i.e.* $\frac{4}{3}\pi(2r)^3 - \frac{4}{3}\pi r^3$ where r is the *diameter* of a solvent molecule, and the size of the ion itself is neglected]. However, the maximum possible occupancy of oriented molecules in the second layer is twice that of the first layer, since each

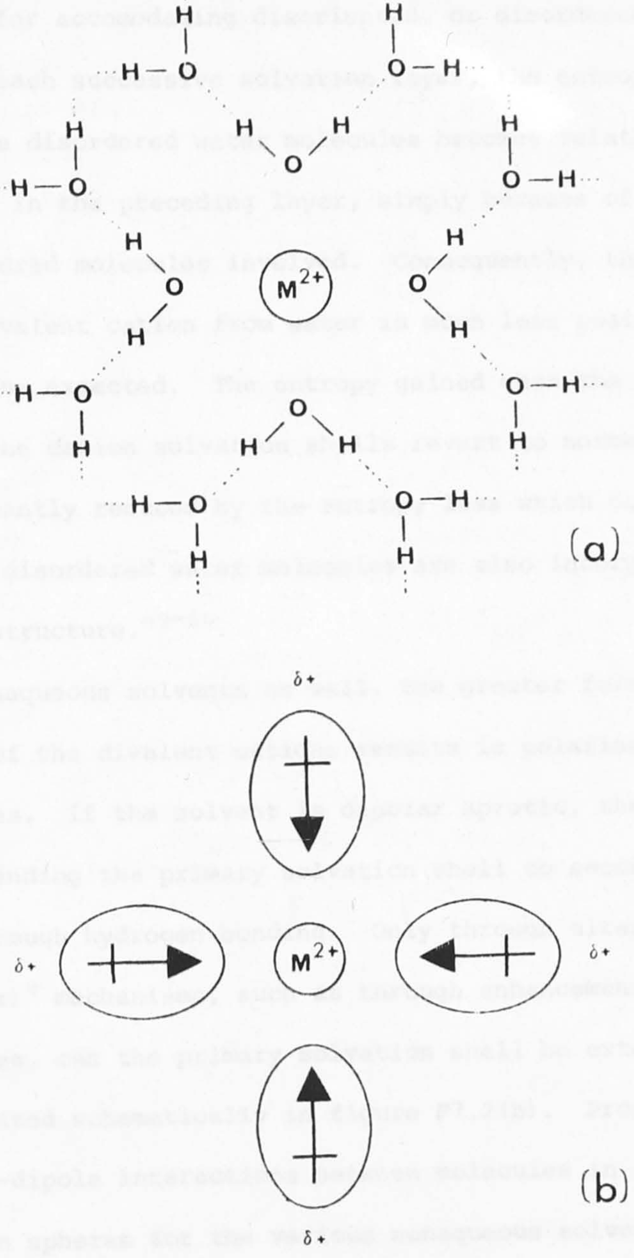

FIGURE F7.2 : Solvation of divalent metal cations in (a) water and in (b) dipolar aprotic solvents.

water molecule of the first layer can hydrogen bond to no more than two molecules in the second layer. The remaining space is available (subject to the limitations of molecular geometries and intermolecular repulsion forces) for accomodating disoriented, or disordered, water molecules. For each successive solvation layer, the entropic contribution from these disordered water molecules becomes relatively more significant than in the preceding layer, simply because of the greater number of disordered molecules involved. Consequently, the entropy of transfer of a divalent cation from water is much less positive than otherwise might be expected. The entropy gained when the oriented molecules from the cation solvation shells revert to normal water structure is significantly reduced by the entropy loss which occurs when the large number of disordered water molecules are also incorporated into the bulk water structure.[49-54]

In the nonaqueous solvents as well, the greater formal surface charge density of the divalent cations results in polarisation of the solvent molecules. If the solvent is dipolar aprotic, there is no possibility of extending the primary solvation shell to second and higher order layers through hydrogen bonding. Only through alternative (and generally weaker)[4] mechanisms, such as through enhancement of solvent permanent dipoles, can the primary solvation shell be extended. This case is represented schematically in figure F7.2(b). Proposed geometries of dipole-dipole interactions between molecules in the first and second solvation spheres for the various nonaqueous solvents are presented in figure F7.3 (*cf.* the remarkable similarity of these dipolar interactions and corresponding interactions which give rise to the inherent structure of these solvents as discussed in chapter 2). In terms of the steric 'accessibility' of the centre(s) of partial positive charge in the first solvation sphere dipoles, the general order of the nonaqueous solvents (in decreasing order of accessibility) is

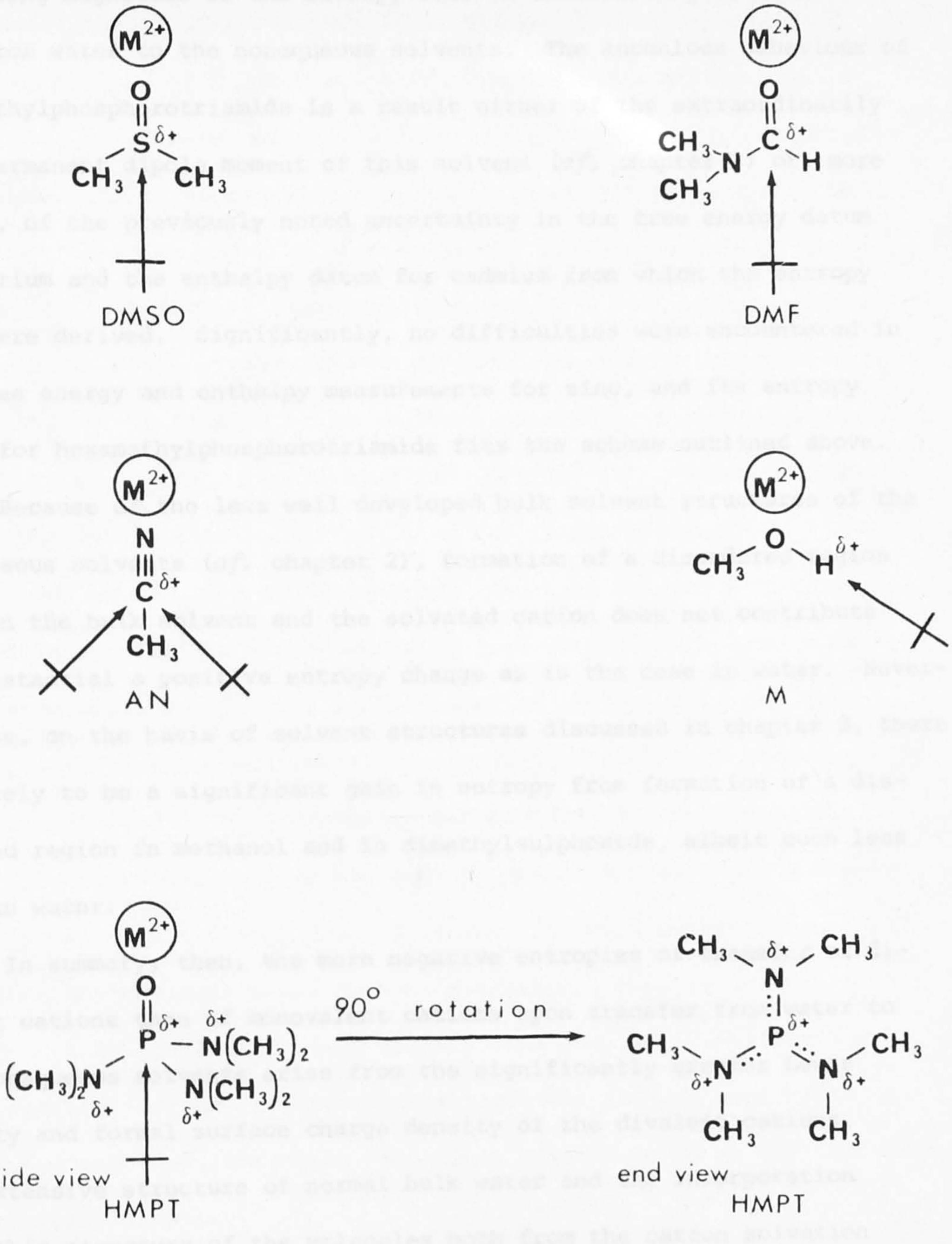

FIGURE F7.3 : 'Accessibility' of first solvation layer molecules for dipolar interaction with second solvation layer molecules for the case of divalent metal cation solvation in various nonaqueous solvents.

M.AN > DMF,HMPT > DMSO. With the exception of hexamethylphosphorotriamide, this order is consistent with that of the experimentally observed decreasing magnitude of the entropy loss on transferring divalent cations from water to the nonaqueous solvents. The anomalous behaviour of hexamethylphosphorotriamide is a result either of the extraordinarily high permanent dipole moment of this solvent (*cf.* chapter 2) or, more likely, of the previously noted uncertainty in the free energy datum for barium and the enthalpy datum for cadmium from which the entropy data were derived. Significantly, no difficulties were encountered in the free energy and enthalpy measurements for zinc, and its entropy datum for hexamethylphosphorotriamide fits the scheme outlined above.

Because of the less well developed bulk solvent structures of the nonaqueous solvents (*cf.* chapter 2), formation of a disordered region between the bulk solvent and the solvated cation does not contribute so substantial a positive entropy change as is the case in water. Nevertheless, on the basis of solvent structures discussed in chapter 2, there is likely to be a significant gain in entropy from formation of a disordered region in methanol and in dimethylsulphoxide, albeit much less than in water.

In summary, then, the more negative entropies of transfer of divalent cations than of monovalent cations upon transfer from water to the nonaqueous solvents arise from the significantly greater Lewis acidity and formal surface charge density of the divalent cations. The extensive structure of normal bulk water and the incorporation into this structure of the molecules both from the cation solvation shells and from the disordered region results in a less positive entropy of transfer of a divalent cation from water than might otherwise be expected. Upon transfer to a nonaqueous solvent, the entropy loss upon forming solvation shell(s) around a divalent cation is not so significantly reduced by the formation of a region of disordered molecules because the nonaqueous solvents considered all have much more poorly developed bulk structures than does water.[48]

7.4.4 Entropies of Transfer from Ideal Solvent S to Real Solvent S and the Estimation of Minimum Solvation Numbers.

The interpretation of entropies of transfer of single ions between solvents is complicated by the necessity of considering structural effects and changes in both the solvent to which and from which transfer is occurring. If, however, entropies of transfer are expressed as being to a real solvent from an ideal solvent in which there are no specific ion-ion or ion-solvent interactions, but in which the same solvent structure, molecular weight, and density as in the corresponding real solvent are preserved, then many of the interpretative difficulties are circumvented.[8,9]

Values of ΔS_{tr} for monovalent and divalent cations being transferred from an ideal to a corresponding real solvent have been calculated using equation E7.5 and are included in table T7.3. The data suggest that, as expected, there are substantial decreases in entropy attending transfer of divalent cations from ideal to real solvents, whilst for monovalent cations the entropy losses are smaller in magnitude. Indeed, for transfer from ideal water to real water, some of the monovalent cations experience a gain in entropy. This behaviour is consistent with the lesser Lewis acidity (and smaller formal surface charge density) of the larger monovalent cations and has been taken as support for the view that these monovalent cations serve as net 'structure breakers' in water.[8]

For the divalent cations and for the smaller monovalent cations, the order of decreasing loss of entropy on transfer from ideal to real solvents is always M > AN > DMF > DMSO > W. (The position of HMPT varies, probably as a result of uncertainty in the original free energy and enthalpy data.) The above order is consistent with several expectations: that both the inherent solvent structure and the formation of a region of disorder reduce the magnitude of the entropy loss upon solvation of a cation in water;[48] that in dimethylsulphoxide, the difficulty of extending the first solvation shell and the significant inherent solvent structure also reduce the magnitude of the entropy loss upon solvation of a cation in this solvent; that acetonitrile and *N,N*-dimethylformamide, with little inherent solvent structure and with relatively accessible centres of partial positive charge in the first solvation shell dipoles (*cf.* chapter 2 and reference 57 of chapter 2), favour large entropy losses for cation solvation; and that methanol, with a much less extensive solvent structure than water and with the possibility of extending the first solvation shell through strong hydrogen bond interactions, promotes quite large entropy losses attending cation solvation. In the above entropy of transfer order, the position of methanol is perhaps most questionable because all data from which these conclusions were drawn are based on the validity of the TATB assumption. Reservations regarding its reliability in methanol have already been noted (*cf.* chapter 3).

The entropy losses associated with orienting dipolar solvent molecules around a cation are due mainly to losses of translational freedom of movement of the solvent molecules, and are highly dependent on the number of solvent molecules favourably oriented for interaction with the cation. This number is influenced by several factors including the coordination requirements of the cation, the cation size and charge, the steric requirements of solvent molecules, and the strength of the solvent dipoles.[56,57] If the solvent freezing point is near 298 K, then its molar entropy of freezing can be used to approximate the maximum loss of entropy expected upon transferring one mole of solvent from the bulk liquid to the ion solvation shells of a unimolar cation solution (*cf.* the Ulich[58,59] method of estimating solvation numbers from entropy data). The ratio of the total entropy change upon transfer of one mole of cations from an ideal to a corresponding real solvent, to the molar entropy of freezing the real solvent, then gives a minimum estimate of the number of solvent molecules in the cation solvation shells as shown in equation E7.6. This number is defined here as the 'solvation

$$n \;=\; (\Delta S_{tr}\ \mathrm{I} \rightarrow \mathrm{R}) \times (\Delta S_{f}\ \mathrm{R})^{-1} \qquad \text{E7.6}$$

number' and denotes the average number of solvent molecules whose dipoles are oriented favourably for interaction with the central cation. It is a minimum estimate of the number of molecules oriented to solvate the central cation both because the factor ΔS_{tr} I → R includes the entropy contribution from the molecules in the region of disorder between the bulk solvent and the cation solvation shells (especially significant for water and less so for methanol and dimethylsulphoxide), and also because the entropy of freezing is likely to be an overestimation of the entropy change associated with forming an ion-centred solvation shell from the bulk liquid. Values of n from equation E7.6 are listed in table T7.4.

Of the solvents studies, only water, dimethylsulphoxide, and hexamethylphosphorotriamide have freezing points in the vicinity of 298 K at atmospheric pressure; *N*,*N*-dimethylformamide, acetonitrile, and methanol freeze at much lower temperatures (*cf.* table T2.1). Insufficient solid and liquid heat capacity data are available to allow estimation of the entropy change associated with the hypothetical liquid to solid phase transition at 298 K for these latter three solvents. Nevertheless, at least for *N*,*N*-dimethylformamide and acetonitrile, the entropies of freezing are typical of those for relatively unstructured dipolar aprotic solvents. From data compiled by Riddick and Bunger,[60] it appears that such solvents usually have entropies of freezing in the range -35 to -45 J K^{-1} mol^{-1} despite large variation in freezing points. Hence, the entropy of fusion at the normal freezing point is probably a reasonable

TABLE T7.4

MINIMUM ESTIMATES OF SOLVATION NUMBERS FOR REPRESENTATIVE CATIONS IN VARIOUS SOLVENTS[a]

SOLVENT:[b]	HMPT	M	DMF	AN	DMSO	W
CATION	MINIMUM SOLVATION NUMBER n[c]					
Li^+		7.9	3.5		2.0	3.0
K^+	2.1	5.9	2.4	2.8	1.4	0.1
Cs^+		2.7	1.8	2.2	0.9	-0.6
Ba^{2+}	10.5[d]	19.5	8.3	8.9	5.7	4.7
Zn^{2+}	5.6	24.4	8.4	10.2	5.1	9.5
Cd^{2+}	6.8[d]	22.6	7.2	8.0	4.7	8.0
PROPERTY	ANCILLARY SOLVENT DATA					
ΔH_{fusion}[e] (kJ mol^{-1})	16.95	3.21	7.88	8.17	13.93	6.01
Freezing Point (K)[e]	280.4	175.5	212.7	229.3	291.7	273.2
ΔS_{fusion}[f] (J K^{-1} mol^{-1})	-60.4	-18.4	-37.0	-35.6	-47.7	-22.2

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a. Data are for solvation behaviour at 298 K.

b. Abbreviations are as in table T2.1.

c. Calculated as described in the text.

d. Especial uncertainty attends these estimates because of the uncertainty in the ΔS_{tr} I → R values (*cf*. text and tables T7.1, T7.2, and T7.3).

e. Taken from table T2.1.

f. Calculated from $(-\Delta H_{\text{fusion}}) \times (T_{\text{freezing point}})^{-1}$.

approximation to that expected for the hypothetical liquid to solid phase transition at 298 K.

Several points should be noted in analysing the data presented in table T7.4. Because of the completely filled d-electron orbitals of divalent cadmium and zinc cations, there are no ligand field stabilisation effects to consider.[61] The solvation behaviour of these cations, like that of barium, is determined by the relative importance of covalent and electrostatic forces, both being affected by the ion size. On size considerations alone, octahedral coordination in the first solvation shell is more likely for barium, whilst tetrahedral is more likely for zinc and cadmium (although coordination numbers of six also occur for these latter two cations).[61] From the data listed in table T7.4, it is evident that for the divalent cations in all solvents considered the minimum solvation number estimates are greater than four, and in most cases are greater than six. It appears that in all solvents (except possibly dimethylsulphoxide) there is extension of the first solvation layer to outer layers. As already mentioned, the minimum solvation numbers for water are thought to be gross underestimates because of the significant positive entropy contribution from the disordered region of solvent molecules. As expected on the basis of the strength of hydrogen bonding interactions, the solvation numbers are most sensitive to the Lewis acidity of the cations in water and in methanol. When the dipolar aprotic solvents are considered, extension of the first solvation shell is by means of weaker dipole-dipole interactions (*cf.* figure F7.3). Thus, there is less sensitivity to the Lewis acidity of the cations, and solvation number estimates for each of the divalent cations are generally similar in a particular dipolar aprotic solvent. In methanol, the minimum estimates seem abnormally high, but the questionable validity of the TATB assumption itself in this solvent has already been mentioned. In hexamethylphosphorotriamide, the unusual trend and individual entropy values are thought to arise from uncertainty in some of the original data. In general, though, it is clear that extension of the first solvation layer is more favourable in the protic than in the dipolar aprotic solvents. Also, it is evident that the Lewis acidity of the divalent cations is sufficient to cause orientation of solvent dipoles beyond the first solvation layer in both protic and dipolar aprotic solvents.

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CHAPTER 8

CONCLUSIONS

In this chapter, the results and conclusions of the preceding chapters are summarised. Subjective comments regarding proposed directions of continuing and future endeavours are made.

The work presented in this thesis demonstrates the utility of considering the single ion contributions to the free energies, enthalpies, and entropies of transfer of complete electrolytes between solvents. Estimates of such single ion values, although undeterminable through rigorous thermodynamics, provide meaningful insight into the behaviour of ions in solution.

From the evidence presented on the 'validity' or 'reliability' of the various extrathermodynamic methods of estimating the single ion contributions to the thermodynamic variables characterising the solvation behaviour of electrolytes, it appears that the TATB assumption is generally the most sound. It does, of course, have its critics (*cf.* chapter 3), and certainly its weaknesses should not be overlooked (indeed, they should be exhaustively characterised).[1] However, the TATB assumption successfully establishes single ion solvation data with sufficient accuracy to allow qualitative and semi-quantitative comparison of results for different ions in various solvents.[2] Hence, it seems wise to avoid the needless proliferation of additional extrathermodynamic assumptions, in favour of allowing attention to centre on the interpretation of existing data.

The study of potassium cation solvation in various media revealed that the liquid junction potential between dissimilar solvents is frequently not negligible. Its value, however, can be estimated on the basis of the TATB assumption, and correction for its contribution to the potential of cells with liquid junction can be made.[3] Thus, meaningful single ion data can be derived from cells with liquid junctions. Experimentally, the method is among the simplest and most facile ways of obtaining such data. In addition, the potassium cation solvation study demonstrated the usefulness of potassium as a model cation for general nonspecific electrostatic cation-solvent interactions. As such, its behaviour provides a basis for qualitative predictions of the relative solvation behaviour of other ions, whilst deviations from the predicted behaviour serve to isolate instances of specific ion-solvent interactions.[4]

The comparative study of the relative solvation behaviour of representative monovalent cations in various solvents including *N,N*-dimethylformamide and its thio analogue *N,N*-dimethylthioformamide further illustrated this use of the potassium cation. Specific interactions between monovalent silver and thallium cations and the thio solvent *N,N*-dimethylthioformamide, as well as between the tetraphenylarsonium cation and water, were identified.[5] When simple cations alone are considered, observed behaviour is generally consistent with the Hard and Soft Acids and Bases principle.[6] Although the HSAB principle is not essential to the explanation of the observed behaviour, it is especially useful in allowing one to catalogue and to correlate a vast quantity of chemical data. It is inadequate, however, for predicting or explaining certain specific effects such as 'solvation of the second kind' which occurs for tetraphenylarsonium cation interactions with water.[7]

The investigation of the enthalpic and entropic contributions to the relative single ion free energies of solvation of representative divalent cations in various media provided not only a test of the general applicability of solvation models developed for monovalent cations, but also a means of plumbing the solvent structural changes which attend cation solvation. The results obtained are consistent with expectations based upon knowledge of the solvation behaviour of monovalent cations.[7] The observed behaviour of the divalent cations can be attributed to their generally smaller size, greater formal surface charge density, and enhanced Lewis acidity when compared with monovalent cations. It is especially interesting to note that the divalent cations studied are evidently capable of extending their first solvation shell to form a second layer (and possibly, higher order layers as well), even in the dipolar aprotic solvents.[8,9]

When the work presented in this thesis is viewed, collectively, in retrospect, it is evident that a number of old questions remains unanswered and a number of new questions has been engendered. It is believed that future efforts should be directed at these. To date, solvent structure in the liquid state has been only poorly characterised. Even less is known about structure in the immediate vicinity of a solvated cation (although useful information is emerging for the first solvation layer in various solvents). Ultimately, the complete understanding of cation solvation phenomena must take explicit account of the intramolecular and intermolecular solvent structure as well as of the fluxional or dynamic nature of the cation-solvent interactions. Holtzer and Emerson have criticised the seemingly ubiquitous arguments relating to solvent structure which are often used in the 'explanation' of solvation phenomena. Certainly some arguments previously advanced are specious, or equivocal at best, but this should stimulate further interest rather than be cause for dismay.[10]

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APPENDIX

REPRINTS

D.A. Owensby, A.J. Parker, and J.W. Diggle, *J. Amer. Chem. Soc.*, 96, 2682 (1974).

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Solvation of Ions. XXI.[1] Solvation of Potassium Cation in Nonaqueous Solvents

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Abstract: The free energies of transfer of potassium cation from water to 14 nonaqueous solvents are reported. The values are derived from measurements in an electrochemical cell assumed to have a negligible liquid junction potential and are compared with existing literature values based on the assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(BPH_4^-)$. The essentially electrostatic nature of its solvation allows potassium cation to be used as a model for nonspecific solvent–ion interactions. A comparison of $\Delta G_{tr}(Ag^+)$ with $\Delta G_{tr}(K^+)$ detects some specific interactions of the silver cation with solvents. Especially noteworthy in this regard is the striking difference between $\Delta G_{tr}(Ag^+)$ of -23.8 kcal mol^{-1} and $\Delta G_{tr}(K^+)$ of $+6.4$ kcal mol^{-1} for transfer from water to dimethylformthioamide at 25°.

As with other simple spherical univalent cations of closed electron shells, the solvation of potassium cation is best described in terms of the electrostatic interaction between the ion and polar solvent molecules, modified by the effect of the ion on solvent–solvent interactions (solvent structure). The potassium cation is "hard" in the Pearson sense,[2] having a size ($r_c = 1.33$ Å) intermediate between that of the very small lithium ion ($r_c = 0.68$ Å) and the large cesium ion ($r_c = 1.67$ Å). The ion–solvent interactions, of course, are modified somewhat by the effect of the ion on the solvent–solvent interactions, *i.e.*, by the solvent structure. Because covalent interactions between potassium cation and sol-

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vent molecules are of relatively minor importance,[3] this ion may serve favorably in modeling some of the more important nonspecific electrostatic and structural effects which influence the general solvation of cations. Thus it is of interest to determine and to interpret $\Delta G_{\mathrm{tr}}(\mathrm{K^+})$, the change in the standard chemical free energy (molar scale) of potassium cation on transfer from water to a variety of other solvents at 25°.[4]

Values of $\Delta G_{\mathrm{tr}}(\mathrm{Ag^+})$ for transfer of silver cation from water to other solvents have been reported previously.[5,6] It is well known that the silver cation, a Lewis acid of d^{10} electronic configuration, experiences strong specific covalent interactions with certain basic solvents[4] (*e.g.*, acetonitrile). Because potassium cation does not have specific interactions with most solvents, deviations from linearity of a plot of $\Delta G_{\mathrm{tr}}(\mathrm{Ag^+})$ *vs.* $\Delta G_{\mathrm{tr}}(\mathrm{K^+})$ for a series of solvents will indicate the contribution of specific ion–solvent interactions to the over-all solvation free energy of silver cation.

Several values of $\Delta G_{\mathrm{tr}}(\mathrm{K^+})$ have been calculated by applying to solubility data the assumption that $\Delta G_{\mathrm{tr}}(\mathrm{Ph_4As^+}) = \Delta G_{\mathrm{tr}}(\mathrm{Ph_4B^-})$ (assumption abbreviated as TATB).[5] Solubility measurements are subject to uncertainties because of possible solvate formation, ion association in saturated solutions, and ionic strength effects.[6]

An alternative approach to solubility measurements which avoids these problems has been used in this work. This involves direct measurement of the potential of half-cell A in a particular solvent *vs.* a suitable reference

$$\mathrm{K(Hg)}\left|\begin{matrix}\mathrm{KClO_4}\\ 0.01\ M\end{matrix}\right\|\begin{matrix}\mathrm{NEt_4Pic}\\ 0.01\ M\end{matrix}$$

A

electrode at 25°. The half-cell consists of a dilute potassium amalgam in contact with a dilute solution of a selected potassium salt in the solvent of interest. The preferred potassium salt, when solubility permits, is the perchlorate, so that ion association is minimized. The choice of tetraethylammonium picrate as the salt bridge electrolyte is made because of the high solubility of this salt in most of the solvents studied, because of the absence of strong specific interactions between the ions and the solvent molecules, and because of the similar mobility of the tetraethylammonium cation and the picrate anion.[7]

The choice of a reference electrode to be coupled with half-cell A presents some problems. The saturated calomel electrode in water is unsuitable without prior knowledge of the liquid junction potentials between aqueous saturated KCl and 0.1 M $\mathrm{NEt_4Pic}$ in the various nonaqueous solvents.[8] Although the ferrocene electrode (Pt|ferrocene, 0.02 M $\mathrm{NEt_4ClO_4}$|) in the same nonaqueous solvent as half-cell A would eliminate solvent junctions, its use is precluded by its instability over the extended time period required to make a potentiometric measurement.[1] However, the Pleskov electrode (Ag|0.01 M $\mathrm{AgClO_4}$|) in the same solvent as half-cell A would overcome both difficulties.[8] Measurements on cell B in a variety of solvents S would yield values of

$$\mathrm{K(Hg)}\left|\begin{matrix}0.01\ M\ \mathrm{KClO_4}\\ \text{solvent S}\end{matrix}\right\|\begin{matrix}0.1\ M\ \mathrm{NEt_4Pic}\\ \text{solvent S}\end{matrix}\left\|\begin{matrix}0.01\ M\ \mathrm{AgClO_4}\\ \text{solvent S}\end{matrix}\right|\mathrm{Ag}$$

B

$\Delta G_{\mathrm{tr}}(\mathrm{K^+}) - \Delta G_{\mathrm{tr}}(\mathrm{Ag^+})$. Furthermore, since values of $\Delta G_{\mathrm{tr}}(\mathrm{Ag^+})$ (based on the TATB assumption) are known independently,[5] the values of $\Delta G_{\mathrm{tr}}(\mathrm{K^+})$ based on the TATB assumption would be readily calculable.

The Pleskov electrode, however, is not the one of choice because of its susceptibility to trace impurities which interact strongly with silver cation in certain solvents.[6] It is also difficult to reproduce precisely the amalgams, so that there are variations of up to 10 mV in the potential of cell B through a series of measurements. Hence, cell C was devised for the series of measurements.

$$\mathrm{K(Hg)}\left|\begin{matrix}0.01\ M\ \mathrm{KClO_4}\\ \text{solvent S}\end{matrix}\right\|\begin{matrix}0.1\ M\ \mathrm{NEt_4Pic}\\ \text{acetonitrile}\end{matrix}\left\|\begin{matrix}0.1\ M\ \mathrm{KClO_4}\\ \text{acetonitrile}\end{matrix}\right|\mathrm{K(Hg)}$$

C

In this cell, the same amalgam is streamed through the two solutions of $\mathrm{KClO_4}$, so that there is no need to reproduce precisely or to characterize the amalgam. The streaming electrode can be designed so that the amalgam has a very short contact time with the solvent, thus minimizing errors due to corrosion of the amalgam.

An alternative to potentiometry in cells B and C is to determine $E_{1/2}(\mathrm{K^+})$ by polarographic techniques.[1] In principle, $E_{1/2}(\mathrm{K^+})$ can often be equated with $E°(\mathrm{K^+})$, but the polarographic method requires that the system be reversible and that there be a relatively high concentration of some supporting electrolyte with the potassium salt. This introduces complications arising from ion association and salt effects, so that the potentiometric method in cell B or C is preferred.

Experimental Section

Apparatus. The apparatus used consisted of three major parts: (1) an amalgam generating cell, (2) an amalgam receiving reservoir in which concentrated amalgams could be diluted with pure mercury, and (3) a liquid junction electrochemical cell. These components were arranged vertically to allow for gravity feed of the amalgam from one cell to that below. Each cell could be flushed simultaneously and continuously with oxygen-free dry nitrogen (see Figure 1). The cells, as well as the gas and solution delivery tubes, were constructed of Pyrex glass. Teflon taps were used throughout. A nylon Swagelok union was used for joining the amalgam generating cell to the diluting cell; Teflon Swagelok unions were used for connecting the diluting cell to the liquid junction cell. Platinum wires sealed through the glass walls of the cells served to establish electrical contact between the amalgam and external leads.

Although the basic cell design resembles that described by Bennetto and Willmott,[9] several aspects of the liquid junction cell design are of particular interest. Amalgam delivery to each half-cell was by means of 0.4-mm i.d. capillaries of 18-cm length. Contact time of the amalgam with solution was reduced to a minimum by allowing the spent amalgam to fall free of the solution into a separate waste chamber beneath each half-cell. A bridge compartment separated the two half-cells. A removable Teflon seal on each side isolated the bridge solution from the solutions in the half-cells. Electrical contact with minimal diffusion across these boundaries was achieved by having four cotton threads (0.2-mm diameter) extending through each Teflon seal (see Figure 1). In addition, each half-cell was fitted with a glass frit type bridge to allow for the measurement of the potential of either half-cell against an external reference. (Emf values for cell B were obtained in this manner.)

Materials. (a) Solvents. All of the solvents were dried and

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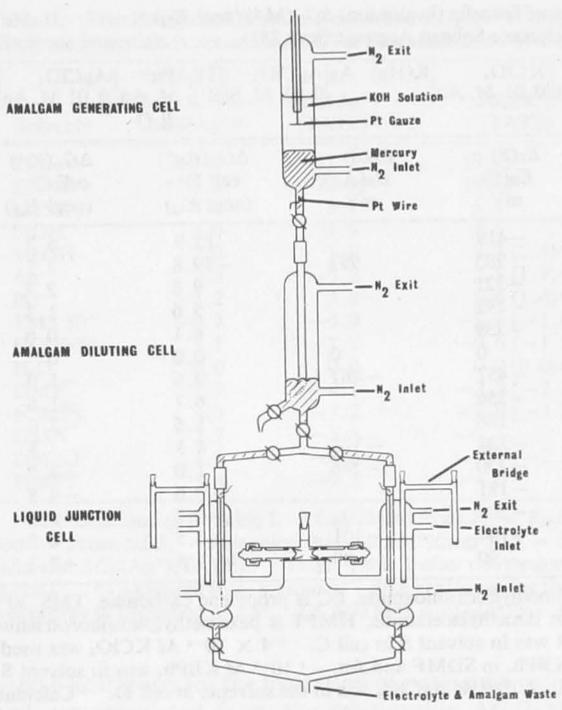

Figure 1. Amalgam cell C.

fractionally distilled at least twice before use. Karl Fischer determinations of water content and conductivity measurements were used to gauge the efficacy of the purification methods. 2,2,2-Trifluoroethanol, TFE (Eastman Kodak), was dried on potassium carbonate followed by two fractional distillations at atmospheric pressure (bp 74° at 715 Torr; water content 198 ppm; specific conductivity 3.9×10^{-7} ohm^{-1} cm^{-1}). Dimethylformthioamide, SDMF, was prepared from dimethylformamide (Mallinckrodt analytical reagent) and phosphorus pentasulfide (BDH laboratory reagent) according to the method of Willstatter and Wirth[10] (bp 70° at 1.0 Torr; water content 350 ppm; specific conductivity 2.32×10^{-6} ohm^{-1} cm^{-1}). Nitromethane, $MeNO_2$ (Ajax Unilab laboratory reagent), was dried on calcium sulfate, passed successively through columns of basic, acidic, and neutral alumina, and then refluxed over silver perchlorate for several hours. Careful distillation off the perchlorate was followed by two fractional distillations (bp 99° at 715 Torr; water content 49 ppm; specific conductivity 2.70×10^{-6} ohm^{-1} cm^{-1}). Ethanol, EtOH, and methanol, MeOH (both Ajax Univar analytical reagents), were dried by refluxing each with their respective magnesium alkoxide salts, prior to fractionally distilling each twice (EtOH, bp 78° at 715 Torr, water content 50 ppm, specific conductivity 4.1×10^{-7} ohm^{-1} cm^{-1}; MeOH, bp 64° at 715 Torr, water content 41 ppm, specific conductivity 2.64×10^{-6} ohm^{-1} cm^{-1}). Acetonitrile, An (Ajax Univar analytical reagent), was subjected to the benzoyl chloride–potassium permanganate treatment described by O'Donnell, Ayres, and Mann[11] (bp 80.5° at 715 Torr; water content 59 ppm; specific conductivity 1.9×10^{-7} ohm^{-1} cm^{-1}). Propylene carbonate, PC (Aldrich), was dried on calcium sulfate before fractional distillation (bp 96° at 3.0 Torr; water content 36 ppm; specific conductivity 1.5×10^{-7} ohm^{-1} cm^{-1}). Sulfolane, TMS (Eastman Kodak), was purified by the hydrogen peroxide–sulfuric acid treatment followed by granular sodium hydroxide as described by Jones.[12] Two final fractionations of powdered calcium hydride completed the procedure (bp 80° at 0.5 Torr; water content 145 ppm; specific conductivity 5.2×10^{-8} ohm^{-1} cm^{-1}). Formamide, $HCONH_2$ (Ajax Unilab laboratory reagent), was initially dried on calcium sulfate followed by fractional distillation. The resulting material was further purified by the method of Notley and Spiro[13] (bp 68° at 1.0 Torr; water content 627 ppm; specific conductivity 34.74×10^{-6} ohm^{-1} cm^{-1}). Deionized water was distilled from an all glass still. Dimethylformamide, DMF (Mallinckrodt analytical reagent), after drying over Linde 4A activated molecular sieves, was passed through a basic alumina column as recommended by Moe.[14] The product was subsequently fractionally distilled (bp 34° at 3.2 Torr; water content 207 ppm; specific conductivity 3.2×10^{-7} ohm^{-1} cm^{-1}). *N*-Methyl-2-pyrrolidone, NMePy (Aldrich), was dried on calcium sulfate and then twice fractionally distilled (bp 40° at 0.2 Torr; water content 200 ppm; specific conductivity 3.9×10^{-7} ohm^{-1} cm^{-1}). *N,N*-Dimethylacetamide, DMA (Aldrich), was dried on Linde 4A activated molecular sieves prior to fractionation (bp 58° at 9.0 Torr; water content 87 ppm; specific conductivity 7.1×10^{-7} ohm^{-1} cm^{-1}). Dimethyl sulfoxide, DMSO (Merck), was fractionally distilled after drying on calcium hydride (bp 56° at 3.0 Torr; water content 41 ppm; specific conductivity 3.7×10^{-7} ohm^{-1} cm^{-1}). Hexamethylphosphorotriamide, HMPT (Aldrich), was fractionally distilled without initial drying, twice fractionally crystallized (mp 7°), dried on Linde 4A activated molecular sieves, and redistilled (bp 84° at 2.0 Torr; water content 230 ppm; specific conductivity 1.9×10^{-7} ohm^{-1} cm^{-1}).

(b) Mercury. The mercury used for amalgam preparations was purified by ultrasonic cleaning once with Freon TF, twice with 10% nitric acid, and three times with distilled water.[15]

(c) Silver. Silver electrodes were in the form of silver wires (purity >99.99%) and were mechanically abraded before each use.

(d) Salts. Potassium hydroxide (Ajax Univar analytical reagent) was used without further purification. Potassium iodide (BDH analytical reagent) was dried *in vacuo* at 130° for 24 hr prior to use. Potassium perchlorate (Merck) was recrystallized from water and dried *in vacuo* at 135° for 72 hr. Potassium tetraphenylboride was prepared by metathesis of potassium chloride (Ajax Univar analytical reagent) with sodium tetraphenylboride (Fluka) and then recrystallized.[16] Silver perchlorate (BDH laboratory reagent) was used after drying *in vacuo* at 80° for 24 hr. Tetraethylammonium picrate was prepared by neutralizing 10% aqueous tetraethylammonium hydroxide (Eastman Kodak) with picric acid (Ajax Univar analytical reagent) in methanol. The resulting tetraethylammonium picrate was recrystallized from methanol.

(e) Gas. Nitrogen (CIG, high purity) was purified by passage over the following sequence of materials: Pyrex glass cotton, Linde 4A activated molecular sieves, soda lime, copper foil ribbons at 300°, soda lime, molecular sieves, and glass cotton.

Procedures and Measurements. Prior to each measurement the apparatus was thoroughly cleaned (successive rinses with distilled water, chromic acid, distilled water, analytical grade acetone), dried, and purged with oxygen-free dry nitrogen.

Amalgams were generated electrochemically using a Beckman Electroscan power supply. A carefully weighed quantity of mercury was placed in the upper cell of the apparatus along with an aqueous potassium hydroxide solution (containing 5–10 times excess potassium over that required for the desired amalgam concentration). With the mercury pool as cathode and the platinum gauze as anode, a constant current (140 mA) was passed and the coulombs were measured. Normally, the current was stopped when the amalgam was of the desired concentration (assuming 100% efficiency for the cathodic electron transfer), thus eliminating the need for diluting the amalgam. All amalgams were originally believed to contain 0.045% w/w potassium, but subsequent analysis revealed the cathodic electron transfer process to be only 50–80% efficient. Hence, amalgam concentrations were always less than 0.045% w/w potassium. Nitrogen flow was maintained through the cell during amalgam generation.

The two half-cells of the liquid junction cell were filled with their complements of electrolyte solutions in appropriate solvents by means of a nitrogen pressure loading system. Once within the half-cells, the solutions were purged with purified nitrogen. The bridge was filled manually, using a dropper. After the amalgam was generated and the solutions were purged with nitrogen, the streaming electrodes were set in operation by manipulating the taps to establish amalgam flow through the capillaries.

All measurements were conducted at a constant temperature of 25 ± 1°. Potentials were monitored using a Radiometer pH Meter 26 with an expanded scale facility. Potentials were recorded as soon as the amalgam was flowing, and values were stable to ±5 mV

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Table I. Emf (mV) of Cells B, C, and D at 25° in Solvents and Free Energies of Transfer (kcal/g-ion) $\Delta G_{tr}(M^+)$ (negl E_{1j}) Based on the Assumption of Negligible Liquid Junction in Cells C and D (Reference Solvent Acetonitrile at 25°)

$$\text{K(Hg)}^{b}\left|\begin{array}{c}\text{KClO}_4\\ 0.01\ M,\ \text{S}\end{array}\right\|\begin{array}{c}\text{TEAPic}^{a}\\ 0.1\ M,\ \text{S}\end{array}\left\|\begin{array}{c}\text{AgClO}_4\\ 0.01\ M,\ \text{S}\end{array}\right|\text{Ag}$$

cell B

$$\text{K(Hg)}^{b}\left|\begin{array}{c}\text{KClO}_4\\ 0.01\ M,\ \text{S}\end{array}\right\|\begin{array}{c}\text{TEAPic}^{a}\\ 0.1\ M,\ \text{An}\end{array}\left\|\begin{array}{c}\text{KClO}_4\\ 0.01\ M,\ \text{An}\end{array}\right|\text{K(Hg)}$$

cell C

$$\text{Ag}\left|\begin{array}{c}\text{AgClO}_4\\ 0.01\ M,\ \text{S}\end{array}\right\|\begin{array}{c}\text{TEAPic}^{a}\\ 0.1\ M,\ \text{An}\end{array}\left\|\begin{array}{c}\text{AgClO}_4\\ 0.01\ M,\ \text{An}\end{array}\right|\text{Ag}$$

cell D

Solvent[a] S	E_B(S), mV	E_C(S), mV	E_D(S), mV	E_C(S) − E_D(S), mV	E_B(S) − E_B(An), mV	$\Delta G_{tr}(Ag^+)$ cell D[i] (negl E_{1j})	$\Delta G_{tr}(K^+)$ cell C[j] (negl E_{1j})
TFE		267^{c}	686^{h}	−419		15.9	6.2
SDMF	−1.288	130^{d}	−855	985	993	−19.8	3.1
$MeNO_2$		102^{e}	423^{h}	−321		9.8	2.3
EtOH		51^{c}	243	−192		5.6	1.3
MeOH		26^{f}	265^{g}	−239		6.1	0.6
An	−2.281	0	0	0	0	0.0	0
PC	−2.748	-43^{e}	414	−457	−467	9.6	−1.0
TMS 30°		-68^{e}	288	−356		6.7	−1.6
$HCONH_2$		−120	68^{g}	−188		1.6	−3.0
H_2O	−2.595	-139^{f}	185^{g}	−324	−314	4.3	−3.3
DMF	−2.527	−207	43	−250	−246	1.0	−4.8
NMePy		-207^{e}	−26	−181		−0.6	−4.8
DMA		−235	−30	−205		−0.7	−5.5
DMSO	−2.382	−256	-152^{g}	−104	−101	−3.5	−6.0
HMPT	−2.370	−320	-230^{g}	−90	−89	−5.3	−7.3

[a] Pic is picrate, TEA is NEt_4, TFE is 2,2,2-trifluoroethanol, SDMF is dimethylformthioamide, PC is propylene carbonate, TMS 30° is tetramethylene sulfone at 30°, NMePy is *N*-methyl-2-pyrrolidone, DMA is dimethylacetamide, HMPT is hexamethylphosphorotriamide, An is acetonitrile. [b] Amalgam is −0.0445 wt % potassium. [c] 0.01 *M* KI was in solvent S in cell C. [d] 4×10^{-4} *M* $KClO_4$ was used in both SDMF and An in cell C. The same emf was obtained with 10^{-2} *M* $KBPh_4$ in SDMF and An. [e] 10^{-2} *M* $KBPh_4$ was in solvent S in cell C. [f] 10^{-3} *M* $KClO_4$ was used in S and in An in cell C. [g] Reference 6. [h] 10^{-3} *M* $AgClO_4$ was in the solvents in cell D. [i] Calculated from the emf of cell D. [j] Calculated from the emf of cell C.

over 5 min. As expected, the cell potential was found to be independent of the concentration of potassium in the amalgam since the same dilute amalgam, split into two streams, flowed simultaneously through the solvent in each half-cell. Effects attributable to decomposition of the amalgam were minimized by employing streaming capillary electrodes to provide a continually regenerated amalgam surface (see Figure 1).

Results

Values of E_B, E_C, and E_D, the emf's of cells B, C, and D, are in Table I. Values of $\Delta G_{tr}(K^+)$(negl E_{1j}) and

$$\text{Ag}\left|\begin{array}{l}0.01\ M\ \text{AgClO}_4\\ \text{solvent S}\end{array}\right\|\begin{array}{l}0.1\ M\ \text{NEt}_4\text{Pic}\\ \text{acetonitrile}\end{array}\left\|\begin{array}{l}0.01\ M\ \text{AgClO}_4\\ \text{acetonitrile}\end{array}\right|\text{Ag}$$

D

$\Delta G_{tr}(Ag^+)$(negl E_{1j}) for transfer from acetonitrile to a variety of other solvents are also in Table I. They were calculated as $23.1E_C$ and $23.1E_D$ kcal/g-ion, respectively (E, V), by assuming negligible liquid junction potential in these cells.[6]

If one accepts the TATB assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, then cells C and D do have a liquid junction potential E_{1j}(TATB).[1] However, E_{1j}(TATB) is virtually the same in cells C and D, because most of E_{1j}(TATB) is associated with the 0.1 *M* NEt_4Pic, acetonitrile–solvent S junction in each cell and the junctions only differ in having 0.01 *M* Ag^+ rather than 0.01 *M* K^+[7] in solvent S. That the junction is virtually the same is confirmed in Table I by the observation that $E_B(S) - E_B(An)$, for cell B, which has no liquid junction potential, is virtually the same as $E_C(S) - E_D(S)$, in those cases where data are available. Thus, either $E_B(S) - E_B(An)$ or $E_C(S) - E_D(S)$ can be used to calculate $\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+)$ for transfer of these cations from acetonitrile to solvent S. This difference is free of any assumptions.

Acetonitrile was chosen as reference solvent because E_{1j}(TATB) is small between acetonitrile and most solvents except water.[7] However, having obtained values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))\text{An} \rightarrow \text{S}$ it is more convenient to convert to values for transfer from water to other solvents. Thus in Table II values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \rightarrow \text{S}$ have been calculated from $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))\text{An} \rightarrow \text{S}$ in Table I through eq 1.

$$(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \longrightarrow S = (\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \longrightarrow S - (\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \longrightarrow H_2O \quad (1)$$

Values of $\Delta G_{tr}(K^+)$(TATB) for transfer from water to other solvents, based on the TATB assumption, are calculated by adding $\Delta G_{tr}(Ag^+)$(TATB), from part XIX,[5] to the values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \rightarrow \text{S}$ in Table II. $\Delta G_{tr}(K^+)$(TATB) *via* cells B and C are compared in Table II with those previously reported[5] from solubility measurements. The new values are believed more reliable.

Table II also contains $\Delta G_{tr}(K^+)$(negl E_{1j}) for transfer from water to other solvents. These values assume negligible liquid junction potential in cell C and have been algebraically manipulated from data in Table I ($\Delta G_{tr}(K^+)$(negl E_{1j}) An → S − $\Delta G_{tr}(K^+)$(negl E_{1j})An → H_2O) for transfer from water.

It was not possible to apply the TATB assumption to solvation of ions in 2,2,2-trifluoroethanol (TFE) because of the instability of the BPh_4^- anion in this acidic solvent. Nor was the TATB assumption applied to solvation in dimethylformthioamide (SDMF) because of the high solubility (>0.1 *M*) of $AgBPh_4$ in SDMF. Hence, $\Delta G_{tr}(K^+)$(negl E_{1j}) was equated to $\Delta G_{tr}(K^+)$(TATB) for transfer from water both to TFE and to SDMF. This approximation is probably valid to within 1 kcal/g-ion in view of the good correspondence between $\Delta G_{tr}(K^+)$(negl E_{1j}) and $\Delta G_{tr}(K^+)$(TATB) for the majority of other solvents in Table II.

The free energies of solvation, $\Delta G_s K^+$, for transfer of potassium cation from the gas phase to solvent S are also contained in Table II. These are based on a value of

Table II. Free Energies of Transfer from Water $\Delta G_{tr}(M^+)$ (kcal/g-ion), Free Energies of Solvation ($\Delta G_s(M^+)$), and Standard Electrode Potentials (volts *vs.* nhe, H_2O) of Potassium and Silver at 25° (Assumption $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$(TATB))

Solvent[a]	$\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+)$[b]	$\Delta G_{tr}(Ag^+)$ (TATB)[c]	$\Delta G_{tr}(K^+)$ (TATB)	$\Delta G_{tr}(K^+)$ (negl E_{1j})[f]	$-\Delta G_s(Ag^+)$ (TATB)[g]	$-\Delta G_s(K^+)$- (TATB)[g]	$E°$(Ag,S) nhe, H_2O (TATB)	$E°$(K,S) nhe, H_2O (TATB)
TFE	−2.2	(11.7)[d]	(9.5)[d]	9.5	102.8	71.1	1.31	−2.50
SDMF	+30.2	(−23.8)[d]	(6.4)[d]	6.4	138.3	74.2	−0.23	−2.64
$MeNO_2$	0.1	5.7	5.8	5.6	108.8	74.8	1.05	−2.67
EtOH	3.0	1.6	4.6	4.6	112.9	76.0	0.87	−2.72
MeOH	2.0	1.8	3.7 (2.4)[e]	3.9	112.7	76.2	0.90	−2.75
An	7.5	−5.2	2.3 (1.9)[e]	3.3	119.7	78.3	0.57	−2.82
PC	−3.2	3.8	0.6 (1.4)[e]	2.3	110.7	80.0	0.96	−2.90
TMS 30°	−0.7	−0.9	−1.6 (−1.0)[e]	1.7	115.4	82.2	6.76	−2.99
$HCONH_2$	3.1	−3.7	−0.6 (−1.5)[e]	0.3	118.2	81.2	0.64	−2.94
H_2O	0.0	0.0	0.0 (0.0)[e]	0.0	114.5	80.6	0.80	−2.92
DMF	1.9	−4.1	−2.2 (−2.3)[e]	−1.5	118.6	82.8	0.62	−3.01
NMePy	3.3	−7.2	−3.9 (−3.3)[e]	−1.5	121.7	84.5	0.49	−3.09
DMA	2.7	−5.8	−3.1	−2.2	120.3	83.7	0.55	−3.05
DMSO	5.1	−8.0	−2.9 (−2.9)[e]	−2.7	122.5	83.5	0.45	−3.05
HMPT	5.4	−9.4	−4.0	−4.0	123.9	84.6	0.39	−3.09

[a] Abbreviations as in Table I. [b] Calculated from $E_C - E_D$ in Table I after converting from acetonitrile to water as reference solvent, see text. [c] From ref 5. [d] Assuming that $\Delta G_{tr}(M^+)$(negl E_{1j}) = $\Delta G_{tr}(M^+)$(TATB), see text. [e] From ref 5, based on solubilities of potassium salts and $\Delta G_{tr}(Ag^+)$(TATB). [f] From Table I after conversion to water as reference solvent, assuming negligible liquid junction potential in cell C. [g] Calculated from a value of −80.6 kcal/g-ion for the free energy of hydration (ΔG_h) of K^+, which gives −114.5 kcal/g-ion for the free energy of hydration of Ag^+. *Cf.* $\Delta G_s(M^+) = \Delta G_h(M^+) + \Delta G_{tr}(M^+)$.

−80.6 kcal/g-ion for the hydration of potassium cation[17] and are calculated from the relationship $\Delta G_s(K^+) = -80.6 + \Delta G_{tr}(K^+)$(TATB).

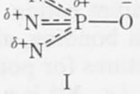
The final two columns of Table II record the standard electrode potentials, $E°$(Ag,S)(TATB) and $E°$(K,S)(TATB), of silver and potassium, respectively, *vs.* the normal hydrogen electrode (nhe) in water. These are based on the TATB assumption and are calculated from eq 2 in which M represents Ag or K and W is water.

$$E°(\mathrm{M,S})(\mathrm{TATB}) = E°(\mathrm{M,W}) + [\Delta G_{tr}(\mathrm{M}^+)(\mathrm{TATB})/23.1] \quad (2)$$

Discussion

Solvation of K⁺. Most of the solvents listed in Table II interact with potassium cation by means of their oxygen atoms. Exceptions are acetonitrile (An) and dimethylformthioamide (SDMF) which interact through N and S, respectively. The most strongly solvating solvents for potassium cation are hexamethylphosphorotriamide (HMPT), *N*-methyl-2-pyrrolidone (NMePy), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formamide, and sulfolane (TMS). In a free energy sense, all solvate potassium more strongly than does water, despite the more favorable entropic contribution to the solvation free energy in water compared to that in these less structured dipolar aprotic solvents.[5] The process of transferring potassium cation from water to each of these solvents is quite exothermic,[5] in an enthalpic sense, and this outweighs any effects due to unfavorable entropies of transfer.

The strong enthalpic interaction between potassium cation and each of the solvents HMPT, NMePy, DMA, DMSO, DMF, $HCONH_2$, and TMS and the strong ordering of solvent about potassium ion is thought to be primarily electrostatic in nature. These solvents alone, of the 15 listed in Table II, contain an oxygen atom which carries extensive negative charge and which is relatively free of groups which might interfere with its structuring about the potassium cation. The phosphorus–oxygen, sulfur–oxygen, and carbon–oxygen bonds in these phosphoramides, sulfoxides, and amides have less than full double bond character; indeed, their structures in the first solvation sphere about potassium cation may well be more like I, II, and III than IV, V, and VI. The oxygens of the alcohols, water, propylene carbonate (PC), and nitromethane ($MeNO_2$) are more shielded and carry less partial negative charge than do the oxygens of the phosphoramides, sulfoxides, and amides. Thus, the former set of solvents are weaker solvators of potassium cation than the latter, although relative to the gas phase, *i.e.*, $\Delta G_s(K^+)$ (Table II), all the solvents would be classed as strong solvators. Despite substantial differences in dielectric constant, solvent structure, and solvent polarity, values of $\Delta G_{tr}(K^+)$ and $\Delta G_{tr}(Ag^+)$, *i.e.*, the transfer free energies, account for no more than 15% of the total solvation energy of these ions in solvents of dielectric constant 25–100. Electrostatic solvation as envisaged by Born[4] is still considered the major type of solvation.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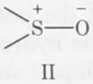
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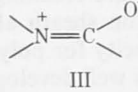
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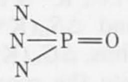
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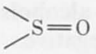
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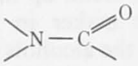
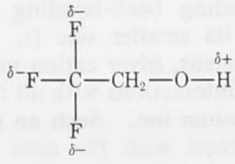

VI

Some of the $\Delta G_{tr}(K^+)$(TATB) values deserve special comment. 2,2,2-Trifluorethanol (TFE), VII, is the weakest solvator of potassium cation of the solvents studied. Although trifluoroethanol and ethanol have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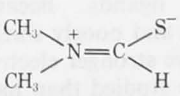
VIII

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(17) D. R. Rosseinsky, *Chem. Rev.*, 65, 469 (1965).

similar dielectric constants (26 and 24, respectively) the $\Delta G_{tr}(K^+)$(TATB) value for transfer from water to trifluoroethanol is +9.5 kcal/g-ion whereas transfer from water to ethanol is only +4.6 kcal/g-ion. The strongly electron withdrawing CF_3 group reduces the negative charge density and hence the basicity at the oxygen of trifluoroethanol, thus decreasing its ability to interact with cations.

Dimethylformthioamide (SDMF), VIII, of dielectric constant 48[18] is also a relatively poor solvator of potassium cation despite its high dielectric constant. There is considerable localized negative charge on sulfur, but this is a "soft" center in the Pearson sense.[2] According to the HSAB principle[2] the interaction between the "soft" sulfur atom of dimethylformthioamide and the "hard" potassium cation is weak. Indeed the value of $\Delta G_{tr}(K^+)$(TATB) + 8.6 kcal/g-ion for transfer "hard" dimethylformamide to "soft" dimethylformthioamide is indicative of the preference of class a cations to interact with negative oxygen, rather than sulfur, in otherwise similar coordinating solvents.

Methanol and ethanol are weaker solvators in a free energy sense of potassium cation than is water. One might expect a somewhat greater negative charge density on oxygen in the alcohols, but in water the oxygen experiences less shielding by other atoms or groups. The enthalpies of transfer favor the alcohols over water.[5] More important, though, is the more favorable entropic interaction which potassium cation has with water[5] compared to the alcohols. This favorable entropic effect arises through the unique structure of water and the structure breaking effect on this structure of forming a solvation sheath about the potassium cation. With less capacity for polymeric hydrogen bonding, alcohols have less well developed liquid structures for potassium cation to break up than does water, *i.e.*, K^+ is a strong structure maker in the alcohols and $\Delta S_{tr}(K^+)$ from water to the alcohols is negative. Thus, $\Delta G_{tr}(K^+)$ from water becomes endoenergetic, despite the more basic oxygen of the alcohols, relative to water, leading in part to an exothermic enthalpy of transfer from water to the alcohols.[5]

Comparison of K^+ Solvation and Ag^+ Solvation. It is necessary to distinguish between those ion–solvent interactions which are purely electrostatic in nature and those which are primarily of covalent character. Both types of interactions will be influenced by changes induced by the ion itself on the solvent structure (first solvation sphere effects) and by the solvent-coordinated ion on the solvent structure (second and subsequent solvation sphere effects).[5] As noted previously, potassium cation with its closed electronic shell and moderate size (r_c = 1.33 Å) is expected to respond almost exclusively to electrostatic solvation effects, whereas silver cation, as a transition metal of d^{10} electronic configuration, is expected to be capable of experiencing a variety of covalent interactions, including back-bonding to suitable ligands. Because of its smaller size (r_c = 1.26 Å) and poorly shielded nucleus, silver cation may also have stronger electrostatic interactions with all the solvents studied than has potassium ion. Such an interpretation is certainly consistent with the data in Table II; all $\Delta G_s(K^+)$ values listed are less than 85 kcal/g-ion but all values of $\Delta G_s(Ag^+)$ are greater than 100 kcal/g-ion.

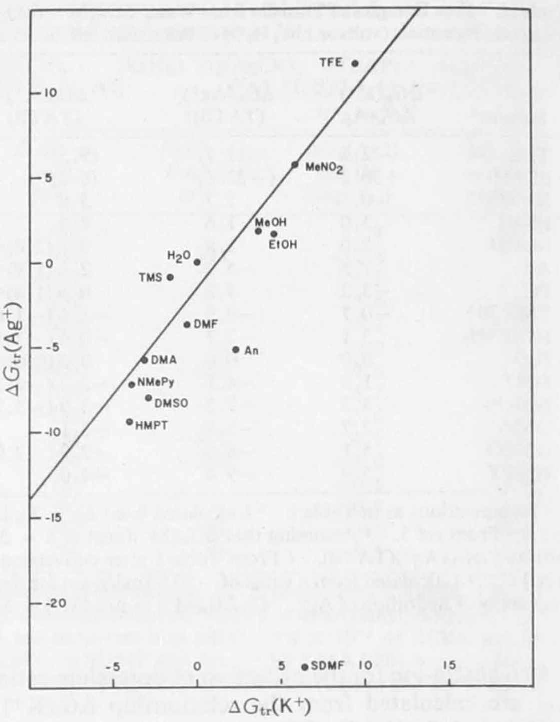

Figure 2. Plot of free energies of transfer $\Delta G_{tr}(Ag^+)$ *vs.* $\Delta G_{tr}(K^+)$ for transfer from water to other solvents at 25°. Assumption $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$.

Figure 2 is a plot of $\Delta G_{tr}(Ag^+)$(TATB) *vs.* $\Delta G_{tr}(K^+)$(TATB). There is a quite good linear correlation between these quantities for transfer to solvents which interact through oxygen with the cations. The slope of 1.24 indicates that, as expected, silver cation responds more to solvent transfer than does potassium cation. Indeed, for all of the solvents which solvate cations through oxygen, the main factors influencing solvation of potassium and silver cations seem to be nonspecific electrostatic interactions, modified by structural effects due to solvent–solvent interactions. The electrostatic interactions are greater for silver cation than for potassium cation.

A remarkably striking illustration of the effect of covalent interactions with silver cation but not with potassium cation is seen in the position of transfer to dimethylformthioamide (SDMF), VIII, in Figure 2. The silver cation is better solvated by SDMF, *i.e.*, by 30 kcal/g-ion more than would be expected from the $\Delta G_{tr}(K^+)$(TATB) plot in Figure 2. The covalent interaction of silver with the "soft" sulfur atom of SDMF is apparently responsible for the strong solvation.

Similarly, acetonitrile, which is known to have specific covalent interactions with d^{10} cations, such as Cu^+, Ag^+, and Au^+,[4] solvates silver cation some 6 kcal/g-ion more strongly than might be expected from the Figure 2 correlation. Furthermore, solvation of the silver cation by dimethyl sulfoxide and by hexamethylphosphorotriamide is a little stronger than one might predict from Figure 2. This effect is thought to arise from weak covalent bonding or possibly the influence of the "soft" sulfur and phosphorus centers, respectively, in these two solvents, relative to water and related solvents.

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(18) J. W. Diggle and D. Bogsanyi, *J. Phys. Chem.*, submitted for publication.

Advocacy of Negl E_{1j} Extrathermodynamic Assumption. The assumption that there is a negligible liquid junction potential in cells C and D leads to values of $\Delta G_{tr}(M^+)$(negl E_{1j}) which in most cases are within 1 kcal/g-ion of the corresponding $\Delta G_{tr}(M^+)$(TATB) values. Considering the relative ease of performing experiments in cells C and D compared with the several steps, including solubilities, involved in applying the TATB assumption, the potentiometric measurements are to be recommended for semiquantitative estimates of $\Delta G_{tr}(M^+)$.

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Aust. J. Chem. 1974, 27, 933–41

Solvation of Ions. XXII*
Solvation of Cations by Hard *N,N*-Dimethylformamide and Soft *N,N*-Dimethylthioformamide

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Abstract

The free energies of transfer of some univalent cations from *N,N*-dimethylformamide to *N,N*-dimethylthioformamide at 25° are Li^+, 64·0; Na^+, 50·2; K^+, 37·2; Cs^+, 23·4; Tl^+, −4·2 and Ag^+, −87·0 kJ g-ion^{-1}. The values are based on the assumption of negligible liquid junction potential in an electrochemical cell. Certain ones of these values can be interpreted in terms of general interactions of hard and soft cations with hard and soft basic solvents. A linear free energy relationship, $\Delta G_{tr}(M^+) = m\Delta G_{tr}(K^+)$, is roughly obeyed by many cations for transfer to a variety of solvents. Deviations from this relationship, for example $\Delta G_{tr}(Ag^+)$ to acetonitrile, $\Delta G_{tr}(Ph_4As^+)$ to water and $\Delta G_{tr}(Ag^+)$ to *N,N*-dimethylthioformamide, allow specific solvation mechanisms to be detected.

Introduction

It is thought that the concept of hard and soft acids and bases (the HSAB principle) extends to the interactions between solvents and ions.[1–4] This paper examines the free energies of transfer, $\Delta G_{tr}(M^+)$, of hard and soft cations from a hard solvent, *N,N*-dimethylformamide ($HCONMe_2$), to its softer sulphur analogue *N,N*-dimethylthioformamide ($HCSNMe_2$). $HCSNMe_2$ has stronger covalent interactions with soft acids and is more polarizable than is $HCONMe_2$. Drago and Wayland[5] report covalent base parameters, C_B, towards soft iodine as acid, of 3·00 for *N,N*-dimethylacetamide ($MeCONMe_2$) and 9·06 for *N,N*-dimethylthioacetamide $MeCSNMe_2$. Electrostatic base parameters, E_B, towards hard phenol as acid, are 1·00 for $MeCONMe_2$ and 0·064 for $MeCSNMe_2$.[6] A similar relationship between the electrostatic and covalent parameters should apply to $HCONMe_2$ and $HCSNMe_2$, solvents which are structurally similar to $MeCONMe_2$ and $MeCSNMe_2$ respectively.

Although the alkali metal cations are of class *a* character[6] with closed electronic shell, they increase in polarizability, size, and thus softness from Li^+ to Cs^+.[2,3,7,8] They have strong but decreasing electrostatic interactions with polar solvents and

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* Part XXI, *J. Amer. Chem. Soc.*, in press.

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[5] Drago, R. S., and Wayland, B. B., *J. Amer. Chem. Soc.*, 1965, **87**, 3571.

[6] Ahrland, S., Chatt, J., and Davies, N., *Quart. Rev.* (London), 1958, **12**, 265.

[7] Pearson, R. G., and Mawby, R. J., 'Halogen Chemistry' (Ed. V. Gutman) Vol. 1 (Academic Press: London 1966).

[8] Pearson, R. G., *Surv. Progr. Chem.*, 1969, **5**, 1.

weak but increasing dispersion force interactions with polarizable solvents. However, covalent interactions between these cations and solvents, of the type envisaged by Drago and Wayland,[5] are at best weak. On the other hand, the soft, polarizable, class *b* cations Cu^+, Ag^+ and Tl^+ do interact covalently and do have strong dispersion force interactions with soft bases.[9] Most chemists would agree with the qualitative order[2,3,7,8] of increasing softness of cations

$$Li^+ < Na^+ < K^+ < Cs^+ < Tl^+ < Ag^+ < Cu^+$$

Thus, if the HSAB principle is valid as a means of estimating degrees of ion solvation, then one would expect an increasing exoenergetic free energy of transfer, i.e. $\Delta G_{tr}(M^+)$ becomes less positive, for transfer of each cation of this series from $HCONMe_2$ to softer $HCSNMe_2$ at 25°. This expectation is examined in this paper.

Experimental

The purification of solvents has been described in Part XXI.[9] Solubilities and ion pairing considerations dictated the choice of electrolytes. Lithium perchlorate (Fluka, analytical reagent) was dried in vacuum at 393 K for 24 h. Sodium tetraphenylboride (BDH, laboratory reagent) was purified by recrystallization from acetone–toluene. Potassium and caesium tetraphenylborides were prepared by metathesis of the chloride and bromide salts, respectively, with sodium tetraphenylboride and were recrystallized from acetone–water. Prior to use, thallium nitrate (BDH, laboratory reagent) was stored for several days in an evacuated desiccator containing silica gel. Cuprous salt solutions were prepared by mixing copper with cupric salts in solvents which stabilize cuprous ion (e.g. acetonitrile).[10]

For the alkali metals and thallium, the experimental procedure (outlined in Part XXI[9] along with a diagram of the apparatus) involved electrochemical generation of a dilute amalgam. The amalgam was then split into two streams, one flowing through a degassed $HCONMe_2$ solution of the appropriate dry salt at the desired concentration (10^{-2} or 10^{-3}M), and the other flowing through a degassed $HCSNMe_2$ solution of the same salt at the same concentration. The $HCONMe_2$ and $HCSNMe_2$ electrolyte solutions were joined by a bridge of 0·1M tetraethylammonium picrate (NEt_4 Pic) in $HCSNMe_2$. A similar cell was used for the silver measurements with pure silver wire rather than an amalgam contacting the $HCONMe_2$ and $HCSNMe_2$ electrolytes. Measurements involving cuprous ions were made in cell (A), the solvent being dimethyl sulphoxide (Me_2SO), acetonitrile (MeCN) or *N,N*-dimethylthioformamide.

$$\mathrm{Cu}\left|\begin{array}{c}\mathrm{CuClO_4}\\ 0{\cdot}01\mathrm{M}\\ \text{solvent}\end{array}\right\|\begin{array}{c}\mathrm{NEt_4\ Pic}\\ 0{\cdot}1\mathrm{M}\\ \text{solvent}\end{array}\left\|\begin{array}{c}\mathrm{AgClO_4}\\ 0{\cdot}01\mathrm{M}\\ \text{solvent}\end{array}\right|\mathrm{Ag} \qquad \text{(A)}$$

Measurements were conducted at 25 ± 2° under an atmosphere of dry nitrogen. The cell potentials were stable to within 1 mV during the 4–5 min time of measurement.

Results and Discussion

N,N-Dimethylthioformamide (n_D^{27} 1·5741) is more polarizable than *N,N*-dimethylformamide (n_D^{25} 1·4269)[11] and has a higher dielectric constant (47·8),[11] and greater dipole moment (4·4 D) than *N,N*-dimethylformamide (36·7, and 4·1 D),[11] and ($\leqslant 10^{-2}$M) solutions of the perchlorates or tetraphenylborides of monovalent cations behave as strong electrolytes in $HCSNMe_2$ just as in $HCONMe_2$. Although stable over short periods, $HCSNMe_2$ darkens noticeably over several days upon exposure to light

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[9] Owensby, D. A., Parker, A. J., and Diggle, J. W., *J. Amer. Chem. Soc.*, in press.

[10] Phillips, C. S. G., and Williams, R. J. P., 'Inorganic Chemistry' Vol. 1 (Oxford University Press 1966).

[11] Diggle, J. W., and Bogsányi, D., unpublished work.

and to dry air; moreover, it is readily oxidized, having a stability range between +0·15 and −2·5 V against the Pleskov electrode (Ag/Ag^+) in acetonitrile.[11] Hence care was exercised in the choice of salts (e.g. cupric salts are reduced), and freshly distilled solvent was used for all experiments.

The free energy of transfer from $HCONMe_2$ to $HCSNMe_2$, for various metal cations, was calculated from the e.m.f. of cell (B) at 25°. X represents the perchlorate, the tetraphenylboride, or the nitrate anion and M represents either silver metal or a 0·025% w/w amalgam of lithium, sodium, potassium, caesium or thallium.

$$\begin{array}{c|c||c||c|c} & \mathrm{MX} & \mathrm{NEt_4\ Pic} & \mathrm{MX} & \\ \mathrm{M} & 0\cdot01\,\mathrm{M} & 0\cdot1\,\mathrm{M} & 0\cdot01\,\mathrm{M} & \mathrm{M} \\ & \mathrm{HCSNMe_2} & \mathrm{HCSNMe_2} & \mathrm{HCONMe_2} & \end{array} \tag{B}$$

Values of $\Delta G_{tr}(M^+)$ based on the TATB assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, are at worst no more than 4 kJ g-ion^{-1} different from values based on the assumption of negligible liquid junction potential in cell (A).[1,12–14] One is unable to apply the TATB assumption with any confidence to solutions in $HCSNMe_2$ because of the very high solubility (and attendant ion pairing problems) of $AgBPh_4$ and of other tetraphenylboride salts. Hence, the $\Delta G_{tr}(M^+)$ values reported herein are based on the assumption of negligible liquid junction potential in cell (B). Moreover, even if there does exist a liquid junction potential in such a cell, it is likely to be much the same for the same pair of solvents at the junction and the series of cations studied[14] so that inferences as to the relative values of $\Delta G_{tr}(M^+)$ are not substantially qualified by the validity or otherwise of the assumption.

Values of $\Delta G_{tr}(M^+)$ for transfer from $HCONMe_2$ to $HCSNMe_2$ are reported in Table 1. The significant decrease from $\Delta G_{tr}(Li^+)$ of 64·0 kJ g-ion^{-1} to $\Delta G_{tr}(Cs^+)$ of 23·4 kJ g-ion^{-1} to $\Delta G_{tr}(Ag^+)$ of −87·0 kJ g-ion^{-1} is as expected from application of the HSAB principle. It is interesting that $HCSNMe_2$ is a weaker solvator of alkali metal cations than $HCONMe_2$, despite its greater dielectric constant, refractive index, and dipole moment.[11] The much greater value of $\Delta G_{tr}(Li^+)$ than of $\Delta G_{tr}(Cs^+)$ can be expressed in terms of a hypothetical equilibrium, where $Cs(HCONMe_2)^+$ denotes the caesium cation in $HCONMe_2$ and $Li(HCSNMe_2)^+$ denotes lithium ion in $HCSNMe_2$. The equilibrium constant for the process shown in equation (1) is $10^{7\cdot1}$:

Table 1. Free energies of transfer of cations from $HCONMe_2$ to $HCSNMe_2$ at 25°

Molar scale, calculated from the e.m.f. of cell (B) by assuming a negligible liquid junction potential

Cation	Li^+	Na^+	K^+	Cs^+	Tl^+	Ag^+
$\Delta G_{tr}(M^+)$ (negl. $E_{lj})^2$ (kJ g-ion^{-1})	64·0	50·2	37·2	23·4	−4·2	−87·0

$$Cs(HCONMe_2)^+ + Li(HCSNMe_2)^+ \rightleftharpoons Cs(HCSNMe_2)^+ + Li(HCONMe_2)^+ \tag{1}$$

Although ΔG_{tr}(alkali-metal cation) is as predicted by the HSAB principle, it can be queried whether favourable hard–hard and soft–soft interactions on the right hand side of this equilibrium, together with unfavourable soft–hard and hard–soft interactions on the left, are the real reason why equilibrium lies well to the right in (1). The

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[12] Alexander, R., Parker, A. J., Sharp, J. H., and Waghorne, W. E., *J. Amer. Chem. Soc.*, 1972, **94**, 1148.

[13] Cox, B. G., Parker, A. J., and Waghorne, W. E., *J. Amer. Chem. Soc.*, 1973, **95**, 1010.

[14] Cox, B. G., and Parker, A. J., *J. Amer. Chem. Soc.*, 1973, **95**, 402.

question cannot be answered unambiguously in the affirmative because there exists an equally plausible explanation which does not invoke the total concept of hardness and softness. The Li^+ cation has a much greater charge density and has a greater solvation energy (gas to solution)[1] than Cs^+ in all solvents. Lithium ion is expected to differentiate much more between the solvating power of polar solvents than does Cs^+. If, as is the case here, transfer is to a weaker solvator of alkali metal cations, then $\Delta G_{tr}(Li^+)$ will always be more positive than $\Delta G_{tr}(Cs^+)$ regardless of whether the transfer is to a harder or to a softer weaker solvator. Listed in Table 2 are some values of $\Delta G_{tr}(Li^+)$ and $\Delta G_{tr}(Cs^+)$ for transfer to weaker solvators, be they softer, or harder, than the reference solvent. In all cases, $\Delta G_{tr}(Li^+)$ is more positive than $\Delta G_{tr}(Cs^+)$ (cf. $Me_2SO \rightarrow$ tsul* with $HCONMe_2 \rightarrow HCSNMe_2$).

Table 2. Free energies of transfer between solvents. TATB assumption: $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$

Transfer is from solvent to solvent as shown. Solvents are classified according to their hardness or softness relative to the other partner in the transfer

Transfer (solvent → solvent)	Classification	$\Delta G_{tr}(Li^+)$ (TATB) (kJ g-ion^{-1})	$\Delta G_{tr}(Cs^+)$ (TATB) (kJ g-ion^{-1})
$HCONMe_2 \rightarrow HCSNMe_2$	H → S	64·0	23·4^A
$Me_2SO \rightarrow H_2O^B$	S → H	14·6	12·6
$Me_2SO \rightarrow$ tsul^B	S → H	26·8	2·5
$HCONMe_2 \rightarrow MeCN^B$	H → H(S?)	39·3	14·2
$HCONH_2 \rightarrow H_2O^B$	S → H	9·6	7·5

^{A} This value assumes negligible liquid junction potential in cell (B).

^{B} From Cox, B. G., Hedwig, G. R., Parker, A. J., and Watts, D. W., *Aust. J. Chem.*, 1974, **27**, 477.

The situation is further illustrated in Fig. 1, where $\Delta G_{tr}(M^+)$ is plotted against $\Delta G_{tr}(K^+)$ for the transfer of the other alkali metal cations, the proton and tetraphenylarsonium cation from $HCONMe_2$ to a variety of solvents at 25°. Linear plots of slope m are obtained which roughly obey relation (2), with some notable deviations:

$$\Delta G_{tr}(M^+) = m\Delta G_{tr}(K^+) \tag{2}$$

The slopes m of the linear plots in Fig. 1 are greater or less than unity according to whether M^+ has a greater or smaller ionic potential (charge density) than K^+. It is in this sense that Li^+ is seen to be able to discriminate more effectively between solvents upon transfer than Cs^+, as indicated by the relevant $\Delta G_{tr}(M^+)$ values in Table 2. Hence, there is no need to invoke specific hard–hard interactions favouring solvation of Li^+ by $HCONMe_2$ or soft–soft interactions favouring solvation of Cs^+ by $HCSNMe_2$. The large difference between $\Delta G_{tr}(Li^+)$ and $\Delta G_{tr}(Cs^+)$ for transfer from $HCONMe_2$ to $HCSNMe_2$ is typical of transfer from a strong to a much weaker solvator of alkali metal cations, and depends on the charge density of the cation, rather than the hardness or softness of the solvent. Similarly, the large difference between $\Delta G_{tr}(Li^+)$ (38·1 kJ g-ion^{-1}) and $\Delta G_{tr}(Cs^+)$ (5·0 kJ g-ion^{-1}) for transfer from water

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* Abbreviations used in this paper are: tsul, tetramethylene sulphone; Pic, picrate; hmpt, hexamethylphosphorotriamide; mpdn, *N*-methyl-2-pyrrolidone; pcar, propylene carbonate; tfe, trifluoroethanol.

to acetonitrile[15] is also typical of transfer from a strong to a poor solvator of alkali metal cations. It is unnecessary to develop concepts of hard water and soft acetonitrile, as Lohmann[4] has done, to explain the solvation of these cations by acetonitrile relative to that by water. Indeed, there is some doubt whether it is reasonable to class acetonitrile as a soft solvent; the classification is confusing because of the specific back-bonding interactions of acetonitrile with d^{10} cations.

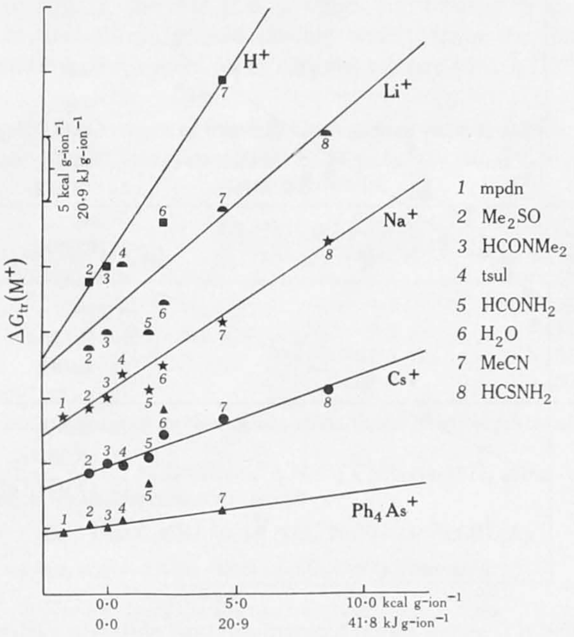

Fig. 1. $\Delta G_{tr}(M^+)$ against $\Delta G_{tr}(K^+)$ for transfer from $HCONMe_2$ to a variety of other solvents with M^+ representing H^+, Li^+, Na^+, Cs^+ or Ph_4As^+ as indicated. Note that the origins at $HCONMe_2$ are non-coincident; for graphical clarity each is separated from the one immediately below by 20·9 kJ g-ion^{-1}.

When $\Delta G_{tr}(M^+)$ values, for transfer of the soft class *b* cations[6] Ag^+ and Tl^+ from $HCONMe_2$ to $HCSNMe_2$, are examined and compared with $\Delta G_{tr}(K^+)$ there is clearly a need to employ one or more concepts, such as hardness and softness, or class *a* and class *b* character,[6] or covalent against electrostatic interactions.[5] Although $HCSNMe_2$ is a weaker solvator of the alkali metal cations than is $HCONMe_2$, it is a stronger solvator of Tl^+ and a much stronger solvator of Ag^+ (Table 1). This is illustrated in Fig. 2, where equation (2) for M^+ as Tl^+ or Ag^+ is plotted, transfer being from $HCONMe_2$ to a variety of other solvents. For transfer to those solvents which solvate through a partial negative charge, which is located on a hard oxygen atom, there is the same type of linear free energy relationship [equation (2)] between $\Delta G_{tr}(M^+)$ and $\Delta G_{tr}(K^+)$, regardless of whether M^+ is an alkali metal cation (Fig. 1) or Tl^+ or Ag^+ (Fig. 2). However, $\Delta G_{tr}(Tl^+)$ for transfer to $HCSNMe_2$ does not obey relation (2) and agreement is even worse for $\Delta G_{tr}(Ag^+)$ to $HCSNMe_2$. Both cations are very much better solvated by $HCSNMe_2$ than is predicted by $\Delta G_{tr}(K^+)$ to $HCSNMe_2$.

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[15] Cox, B. G., Hedwig, G. R., Parker, A. J., and Watts, D. W., *Aust. J. Chem.*, 1974, **27**, 477.

Values of $\Delta G_{tr}(Ag^+)$ for transfer from $HCONMe_2$ to acetonitrile also show a rather poor correlation with equation (2) in Fig. 2, in that Ag^+ is better solvated by acetonitrile than expected from $\Delta G_{tr}(K^+)$. However, $\Delta G_{tr}(Tl^+)$ for transfer of thallous ion from $HCONMe_2$ to acetonitrile is not seriously at variance with equation (2) in terms of values of $\Delta G_{tr}(Tl^+)$ for transfer from $HCONMe_2$ to other solvents.

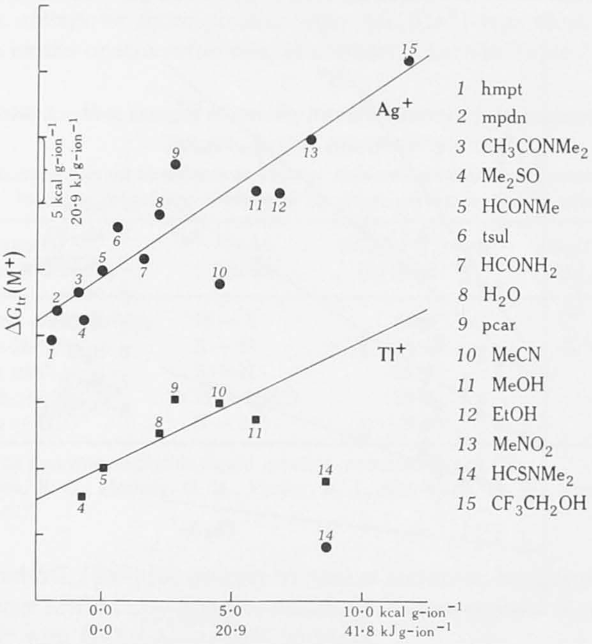

Fig. 2. $\Delta G_{tr}(Ag^+)$ and $\Delta G_{tr}(Tl^+)$ against $\Delta G_{tr}(K^+)$ for transfer from $HCONMe_2$ to a variety of other solvents. For graphical clarity the origin at $HCONMe_2$ of the $\Delta G_{tr}(Ag^+)$ data is displaced by 62·7 kJ g-ion^{-1} from the origin of the $\Delta G_{tr}(Tl^+)$ data.

It is felt that the strong interaction between acetonitrile and d^{10} cations, such as Ag^+, Cu^+ and Au^+, relative to K^+ is a specific case of synergistic electron donation and back bonding to π^* orbitals of acetonitrile. It is not a typical example of a soft–soft interaction.[4] Moreover, acetonitrile interacts weakly with iodine and with those soft acids which are not d^{10} cations and thus are not capable of strong back bonding.

The hypothetical equilibrium between solvated soft silver and hard sodium ions [equation (3)] has a calculated equilibrium constant of 1×10^{24}. This high value is

$$Ag(HCONMe_2)^+ + Na(HCSNMe_2)^+ \rightleftharpoons Ag(HCSNMe_2)^+ + Na(HCONMe_2)^+ \quad (3)$$

satisfactorily attributed, through the HSAB principle, to favourable soft–soft and hard–hard interactions on the right hand side of the equilibrium. The situation requires a somewhat different explanation from that given for equilibrium (1). Because Ag^+ is capable of much stronger covalent interactions with $HCSNMe_2$ than is Na^+, equilibrium (3) lies far to the right. It should be remembered that the Ag^+ nucleus is less effectively shielded than is Na^+ by its electrons and that Ag^+ is much more strongly solvated relative to the gas phase than is Na^+ by most solvents.[1]

Experimentally it was not possible to determine $\Delta G_{tr}(Cu^+)$ for transfer from $HCONMe_2$ to $HCSNMe_2$, because Cu^+ disproportionates in $HCONMe_2$. However, values of $\Delta G_{tr}(Cu^+)$ along with values of $\Delta G_{tr}(Ag^+)$, $\Delta G_{tr}(K^+)$, for transfer from water to $HCSNMe_2$ and to acetonitrile are reported in Table 3. The very strong covalent interaction of soft Cu^+ with soft $HCSNMe_2$ and the back bonding interaction of Cu^+, a d^{10} cation, with acetonitrile are apparent in the values. As was observed for $\Delta G_{tr}(Ag^+)$ in Fig. 2, the $\Delta G_{tr}(Cu^+)$ values for transfer from $HCONMe_2$ to $HCSNMe_2$ or to acetonitrile should deviate widely from the linear relationship [equation (2)] established for most other cations, relative to $\Delta G_{tr}(K^+)$.

Table 3. Free energies of transfer of cations from water to solvents at 25°

Values from ref. 1, TATB assumption $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ unless stated otherwise

Cation M^+	To Me_2SO	$\Delta G_{tr}(M)^+$ (kJ g-ion^{-1}) To MeCN	To $HCSNMe_2$
K^+	−12·1	9·6	26·8[A]
Tl^+	−20·5	9·2	−15·5[A]
Ag^+	−33·5	−21·8	−104·2[A]
Cu^+	−39·7[B]	−45·2[B]	−100·4[B]

[A] This work, using assumption of negligible liquid junction potential in cell (B).

[B] Waghorne, W. E., Ph.D. Thesis, A.N.U., Canberra 1972, using the TATB assumption for measurements in the cell

$$Cu|0\cdot01\text{M}\ CuClO_4||0\cdot1\text{M}\ NEt_4\ Pic||0\cdot01\text{M}\ AgClO_4|Ag$$

in one solvent, coupled with values of $\Delta G_{tr}(Ag^+)$ from ref. 1.

Although the HSAB principle has been invoked in this paper, it is believed preferable, whenever possible, to identify covalent or specific interactions between ion and solvent when considering values of ΔG_{tr}(ion). Some interactions which have been revealed include the hydrogen bonding interaction between small anions and protic solvents,[12] the back bonding interaction between d^{10} cations and nitriles or olefins with low energy π^* orbitals,[15] the acid–base interaction between H^+ and water, the covalent interactions of Ag^+ or Cu^+ with sulphur containing ligands, and the structure making interaction between Ph_4As^+ and water.[15] All of these are reflected in unusual values of ΔG_{tr}(ion) relative to 'normal' ions or relative to transfer to 'normal' solvents. If values of ΔG_{tr}(ion) can be explained in terms of well established chemical principles, then this is more satisfying than explanations based only on the HSAB principle. Despite these reservations, the value of the HSAB principle in interpreting cation solvation phenomena and in formulating qualitative predictions for new $\Delta G_{tr}(M^+)$ values should not be underestimated. The principle is especially valuable as a starting point when specific interactions cannot be identified.

The plot of $\Delta G_{tr}(Ph_4As^+)$ against $\Delta G_{tr}(K^+)$ for transfer from $HCONMe_2$ to various other dipolar aprotic solvents (Fig. 1) shows that the free energy of solution of this very large cation is quite insensitive to transfer through a series of solvents. Indeed, $\Delta G_{tr}(Ph_4As^+)$ is no more than 6·3 kJ g-ion^{-1} for transfer to any of the dipolar aprotic solvents investigated. The trend of slope m [equation (2)] decreasing from Li^+ to the larger Cs^+ is continued for the still larger Ph_4As^+ cation, when transfer is between dipolar aprotic solvents. Pleskov[16] reasoned that $\Delta G_{tr}(M^+)$ approaches zero as the radius of M^+ becomes very large and he proposed that $\Delta G_{tr}(Rb^+) = 0$. However, it is now clear that his reference ion was too small and that a larger cation than Rb^+ must be used as the reference ion, if this type of assumption is to be valid. If, however, a much larger cation than 'structure breaking' Rb^+ is used, then this type of assumption becomes suspect, if water is one of the solvents involved in the transfer. This is because of the unique structure of water and its special mechanism for solvating very large hydrophobic cations. The mechanism involves formation of a highly structured water surface about the large 'structure making' ion.[15,17] There is a change of solvation mechanism by water as one progresses from, for example, Na^+ to Ph_4As^+ in water.[17] There is not a change of mechanism from Na^+ to Ph_4As^+ in dimethylformamide or acetonitrile,[15] so that the Pleskov type of assumption ($\Delta G_{tr}(Ph_4As^+) = 0$) is reasonable for transfer of very large ions between dimethylformamide and acetonitrile. It is not reasonable for transfer from water to dimethylformamide or acetonitrile, where $\Delta G_{tr}(Ph_4As^+)$ is very exoenergetic.

The TATB assumption does not require that $\Delta G_{tr}(Ph_4As^+)$ be large or small, all it requires is that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ if the assumption is to be valid for all solvents including water. However, the fact that the assumed equality usually involves transfer energies which are small is satisfying, because the TATB assumption and the Pleskov assumption can be linked, for solvents where water is not involved in the transfer.

We have noted that there are substantial deviations from equation (2), whenever a specific ion solvent interaction, such as between Ag^+ and MeCN, or between Tl^+ and $HCSNMe_2$, is not reproduced between K^+ and the solvent. Deviations are also observed in the values of $\Delta G_{tr}(Ph_4As^+)$, for transfer from dipolar aprotic to the structured protic solvents (water and formamide). These are more positive than predicted by equation (2) (cf. Fig. 1), where M^+ are the alkali metal cations, Ag^+ or Tl^+. The deviations illustrate the special ion–solvent interaction between Ph_4As^+ and water or formamide.

The successful plots in Figs 1 and 2 suggest a linear free energy relationship [equation (2)] for predicting $\Delta G_{tr}(M^+)$ to within about 4 kJ g-ion^{-1}. The relationship employs $\Delta G_{tr}(K^+)$ as a reference in comparing cation solvation differences, and by including a sensitivity factor *m* it acknowledges that other cations will be more or less sensitive to solvent transfer than K^+. The potassium cation is chosen as the model cation, both because many values of $\Delta G_{tr}(K^+)$ are available[1] and because it is a typical cation with a closed electronic shell which is unlikely to have specific interactions with most solvents. Values of *m* for several cations, along with values of $\Delta G_{tr}(K^+)$ for transfer from $HCONMe_2$ to a variety of other solvents, are listed in Table 4.

The most useful application of equation (2) is in detecting unusual solvation mechanisms which are worthy of further investigation. In this work, deviations of other cations from the model solvation mechanism (that of K^+ in the various solvents) reveal instances of anomalous behaviour requiring an alternative explanation. Thus, anomalies for Ag^+ are successfully accounted for in terms of covalent interactions between Ag^+ and $HCSNMe_2$ or MeCN; in the case of Ph_4As^+ the deviant behaviour

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[16] Pleskov, V. A., *Usp. Khim.*, 1947, **16**, 254.

[17] Hertz, H. G., *Angew. Chem., Int. Edn*, 1970, **9**, 124.

of the ion in water and formamide is explained as resulting from the special structure making interaction of Ph_4As^+ with water and with formamide.

Table 4. Parameters for equation (2) for transfer from $HCONMe_2$ at 25°

$\Delta G_{tr}(M^+) = m\Delta G_{tr}(K^+)$

Solvent	$\Delta G_{tr}(K^+)$ [1] (kJ g-ion^{-1})	Cation M^+	m[A]	Solvent	$\Delta G_{tr}(K^+)$ [1] (kJ g-ion^{-1})
hmpt	−7·5	Li^+	1·7	pcar	11·7
Me_2SO	−2·9	Na^+	1·3	MeCN	18·8
$MeCONMe_2$	−3·8	K^+	1·0	MeOH	24·7
mpdn	−7·1	Cs^+	0·7	EtOH	28·5
$HCONMe_2$	0·0	Tl^+	1·0	$MeNO_2$	33·5
H_2O	9·2	Ag^+	1·3	$HCSNMe_2$	36·0
$HCONH_2$	6·7	H^+	3·1	tfe	49·0
tsul	2·5	Ph_4As^+	0·3		

[A] Slopes of plots in Figs 1 and 2 from least-squares analysis. Water and formamide data were elided from the calculations but are included on the plots.

The different solvent properties of $HCSNMe_2$ and water are illustrated by the relative solubilities of NaCl and AgCl in these solvents. In water AgCl is only very slightly soluble, whereas NaCl is very soluble. In $HCSNMe_2$ NaCl is only very slightly soluble ($K_s < 10^{-10}$ mol^2 l^{-2}) yet AgCl is very soluble ($K_s > 1$ mol^2 l^{-2}).[18]

Manuscript received 13 November 1973

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[18] Waghorne, W. E., Ph.D. Thesis, Australian National University, Canberra, 1972.