Inhibition of Bubble Coalescence by Electrolytes in Binary Mixtures of Dimethyl Sulfoxide and Propylene Carbonate

Guangming Liu,[†] Yi Hou,[‡] Guangzhao Zhang,[‡] and Vincent S. J. Craig^{*,†}

[†]Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia, and [‡]Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, P. R. China

Received April 5, 2009. Revised Manuscript Received May 28, 2009

We have investigated the effect of solvent composition on inhibition of bubble coalescence by electrolytes in binary mixtures of dimethyl sulfoxide (DMSO) and propylene carbonate (PC). Unlike most mixtures, combinations of DMSO and PC exhibit minimal foaming over all compositions (with the strongest effect being at 25% PC by volume); thus, the influence of electrolytes can be investigated. Both LiBr and KSCN at moderate concentrations inhibit bubble coalescence at all solvent compositions. However, the concentration of electrolyte required to inhibit coalescence was in both cases a minimum at the PC(v/v) of 25%. The surface tension of electrolyte solutions in the mixed solvents indicates that the gradient in surface tension is not correlated with coalescence inhibition and therefore inhibition cannot be attributed to surface elasticity. We have also studied the inhibition of bubble coalescence by HCl at different solvent compositions. HCl is strongly inhibitory in DMSO but only weakly so in PC. We have found that HCl exhibits strong inhibition behavior at all mixtures studied. All electrolytes studied were most effective at inhibiting bubble coalescence at the PC(v/v) of 25%, indicating that the interactions between solvent molecules strongly determine the influence of electrolyte on coalescence inhibition. We propose that the formation of solvent complexes between DMSO and PC results in an increase in surface viscosity and the presence of electrolytes further amplifies this effect.

Introduction

Electrolyte Inhibition of Bubble Coalescence in Aqueous Solutions. When waves crash at the beach, a transient foam is created. This is a result of bubble coalescence inhibition due to the high concentration of electrolyte in seawater. Indeed, for many years, it has been known that some electrolytes can inhibit bubble coalescence in water at concentrations of ~ 0.1 M.^{1,2} Notably, the identity of the ions can have a dramatic influence on the degree of coalescence inhibition: some electrolytes at concentrations up to 0.5 M have little or no effect on bubble coalescence. We note that bubble coalescence still occurs but it takes longer than in pure solution with the bubble lifetime at an interface typically being extended from less than 1 s to ~ 5 s for a bubble rising to a free interface.³ An electrolyte's coalescence inhibition behavior is described using simple combining rules that depend on empirically assigning ions a value of either α or β .^{4,5} An electrolyte formed from an α cation and an α anion (designated $\alpha\alpha$) will inhibit bubble coalescence, as will an electrolyte formed from a β cation and a β anion ($\beta\beta$). However, electrolytes formed from an α cation and a β anion ($\alpha\beta$) or a β cation and an α anion ($\beta\alpha$) will have no effect. Thus, it can be seen that coalescence inhibition depends on the partnering of the ions and not on the nature of any one ion, and that this can be codified in these simple rules, though the physical meaning of the α and β assignments is yet to be elucidated.

Electrolyte Inhibition of Bubble Coalescence in Nonaqueous Solutions. The influence of electrolytes on bubble coalescence in a range of nonaqueous solvents has recently been reported.⁶ It was found that electrolytes inhibit coalescence in nonaqueous solvents and that this coalescence inhibition behavior shows ion-specificity that can also be codified by the same combining rules that apply in aqueous systems; and further, the empirical assignments to ions (i.e., α and β) differs between solvents. In formamide, these assignments were identical to those in water, whereas in propylene carbonate (PC) combining rules applied, but the α and β assignments for some ions were different. In dimethyl sulfoxide (DMSO) and methanol, all the electrolyte combinations employed inhibited bubble coalescence, so it is uncertain whether combining rules are required in these circumstances. Notwithstanding the simplicity of these rules, a good understanding of the chemistry and physics at play in bubble coalescence inhibition remains elusive. However, it is apparent that the ion-specificity and therefore the bubble coalescence mechanism are not related to any unique property of water, as similar effects are exhibited in other solvents. Thus, studies of bubble coalescence in nonaqueous solvents can be used to understand both ion specific effects and the mechanism of bubble coalescence.

Thermodynamically, the introduction of bubbles (i.e. the creation of an interface) in a pure liquid is unfavorable, and therefore, in the absence of an energy barrier, bubbles colliding should rapidly coalesce to minimize the interfacial area and the energy of the system. In pure liquid, there is no stabilization mechanism by which this coalescence can be opposed beyond hydrodynamic repulsion;⁷ hence, bubbles in pure liquids are unstable

*To whom correspondence should be addressed. E-mail: vince.craig@anu.edu.au.

(1) Foulk, C. W.; Miller, J. N. *Ind. Eng. Chem.* **1931**, *23*, 1283.
(2) Pollock, J. A. *Philos. Mag.* **1912**, *24*, 189.
(3) Craig, V. S. J. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 178.
(4) Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* **1993**, *97*, 10192.
(5) Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. *Nature* **1993**, *364*, 317.

(6) Henry, C. L.; Craig, V. S. J. *Langmuir* **2008**, *24*, 7979.

(7) Aveyard, R.; Binks, B. P.; Clint, J. H.; Fletcher, P. D. I. *Foams and Emulsions*; Sadoe, J. F., Rivier, N., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1999; Chapter 2, pp 21–44.

to coalescence, whereas in solutions the presence of a solute generally leads to a Gibbs elasticity of the interface.⁸ Other stabilizing mechanisms such as Gibbs–Marangoni flows, alteration of the hydrodynamic boundary conditions to that of no-slip, and repulsive surface forces can also arise, depending on the nature of the solute. Bubbles in mixtures of miscible solvents are generally also stabilized to coalescence, and many foam significantly. However, binary mixtures of solvents that have very similar surface energies do not foam.⁹ Why this is the case is not well understood. It could simply be the absence of both Marangoni effects and surface elasticity, or perhaps more importantly the similarity of the surface tension reflects the interaction between, and populations of, the different solvent molecules in the interfacial region. One such solvent couple is DMSO ($\gamma \approx 43 \text{ mN m}^{-1}$)¹⁰ and PC ($\gamma \approx 42 \text{ mN m}^{-1}$).¹¹ Thus, the DMSO/PC system allows us to investigate how bubble coalescence inhibition by electrolytes is influenced by solvent composition, for the effect cannot be studied in most solvent mixtures as the solvents themselves foam. Additionally, both these solvents solubilize electrolytes to a significant degree and have been shown to exhibit bubble coalescence inhibition in the presence of electrolytes.⁶

In the present study, we have investigated the effect of solvent composition on inhibition of bubble coalescence by LiBr, KSCN, and HCl in binary mixtures of DMSO and PC. These electrolytes were chosen, as they are soluble to a high degree in both solvents. Further, the amount of electrolyte required to inhibit bubble coalescence is in some cases similar between solvents and in other cases very different (as shown later in Table 1). We are interested in how the transition concentration may be influenced by the solvent composition; how the concentration of electrolyte required to inhibit coalescence (as characterized by the transition concentration) changes with solvent composition; and if the pure solvents or mixtures are more efficient in inhibiting bubble coalescence.

Experimental Section

Materials. Dimethyl sulfoxide (anhydrous, 99.9%) and propylene carbonate (anhydrous, 99.7%) were purchased from Sigma Aldrich and used as received. Lithium bromide (LiBr, analytical grade, 99%) and potassium thiocyanate (KSCN, analytical grade, 99%) were dried under a vacuum (~ 1 Torr) for ~ 2 h to remove adsorbed moisture before each use. Hydrochloric acid (HCl, analytical grade, 36%) was used as received.

Bubble Coalescence Measurements. The change in bubble coalescence due to addition of electrolytes was measured using the change in turbidity in a custom-built bubble column (Figure 1).^{4,6,12} In each experiment, a quantity of solvent (40.0 mL) was placed into a cylindrical glass tube with a sintered glass frit at the bottom. A stable flow of N_2 gas ($\sim 12 \text{ mL s}^{-1}$) into the tube through the frit results in a bubble stream rising in the column. Turbulent bubble flow was increased via a constriction in the bubble column, to encourage bubble collisions. A concentrated electrolyte solution was then titrated into the solvent. A beam of light from a diode laser (670 nm) was expanded and passed through the bubbling solvent before being condensed onto a photodiode detector. A filter placed over the photodiode detector excluded light at all other wavelengths. When coalescence is readily taking place, the amount of light reaching the detector is

Figure 1. Bubble coalescence apparatus. Small bubbles are produced at the frit and rise in the column passing through the constriction that promotes bubble collisions. In solvents without electrolytes, they rapidly coalesce such that the bubbles breaking the laser beam are large and few in number. In this case, most of the light is transmitted and strikes the detector. When coalescence is inhibited, the bubbles remain small and numerous, resulting in a large amount of scattering and low light intensity at the detector.

high as is the measured voltage. For solvent without electrolyte, this is defined as the 100% coalescence level. As bubble coalescence inhibition occurs, the small bubbles created at the frit remain small and more light is scattered, lowering the voltage at the detector. At a sufficiently high concentration of a coalescence-inhibiting electrolyte, the voltage stabilizes at a minimum level. This is defined as 0% coalescence. Intermediate voltages are converted to bubble coalescence using a linear conversion. The transition concentration (TC) is defined at 50% coalescence. For each electrolyte concentration, data were averaged over at least 30 data points, each of which was an average of the detector voltage acquired over 3 s. All the experiments were conducted at $\sim 22^\circ\text{C}$.

Surface Tension Measurements. The surface tensions of electrolyte solutions were determined using a KSV (Helsinki, Finland) CAM 200 surface tension meter via pendant drop shape analysis. The shape of a drop hanging from a syringe tip is determined by the balance of gravitational and surface tension forces. Therefore, the surface tension (γ) of the liquid can be related to the drop shape through the following equation:¹³

$$\gamma = \frac{(\rho_{\text{liquid}} - \rho_{\text{air}})gR_0}{\beta} \quad (1)$$

where g is the gravitational constant; R_0 is the radius of drop curvature at apex; β is the shape factor; and ρ_{liquid} and ρ_{air} are liquid density and air density, respectively. Therefore, the density of liquid should be determined first to obtain the liquid surface tension. In the present work, the densities of electrolyte solutions were determined using an Anton Paar (Graz, Austria) DMA 4500 density meter. The values determined are given in the Supporting Information (Table S-1). Each value of surface tension reported was obtained by averaging at least 30 data points from three different liquid drops, and all the experiments were conducted at $\sim 22^\circ\text{C}$.

Results and Discussion

In Figure 2, it can be seen that the surface tension of the binary mixture gradually decreases upon increasing the amount of propylene carbonate (PC% (v/v)) in the mixture, within a small range of between ~ 42.7 and $\sim 41.1 \text{ mN m}^{-1}$. The low gradient in surface tension indicates that mixtures of these solvents should

(8) Gibbs, J. W. *The Collected Works*; Longmans Green and Co.: New York, 1928; Vol. I, p 300.

(9) Syeda, S. R.; Afacan, A.; Chuang, K. T. *Chem. Eng. Res. Des.* **2004**, 82, 762.

(10) Clever, H. L.; Sneed, C. C. *J. Phys. Chem.* **1963**, 67, 918.

(11) Guerrero, I.; Bocanegra, R.; Higuera, F. J.; Fernandez, J. *J. Fluid Mech.* **2007**, 591, 437.

(12) Henry, C. L.; Dalton, C. N.; Scruton, L.; Craig, V. S. J. *J. Phys. Chem. C* **2007**, 111, 1015.

(13) Hansen, F. K.; Rødsrud, G. *J. Colloid Interface Sci.* **1991**, 141, 1.

Figure 2. Surface tension (γ) and the percentage of bubble coalescence of binary mixtures of DMSO and PC expressed as PC% (v/v). Inset: Dependence of change in the square of surface tension gradient [SSTG or $(d\gamma/dc)^2$] for the mixtures of DMSO and PC expressed as PC% (v/v).

not foam significantly. This can be examined by measuring bubble coalescence upon the addition of DMSO into PC or vice versa as shown in Figure 2. We find that mixtures of DMSO and PC do not exhibit strong bubble coalescence inhibition over the whole solvent composition range. However, a slight minimum in bubble coalescence is observed at the PC(v/v) of 25%. If the inhibition of bubble coalescence is dominated by the surface elasticity or Marangoni effects, the surface tension gradient should exhibit a maximum at the PC(v/v) of 25%. However, the inset in Figure 2 shows that the square of surface tension gradient (SSTG), or $(d\gamma/dc)^2$ (which is proportional to surface elasticity), gradually decreases upon increasing PC% (v/v), indicating that either elasticity or Marangoni effects are not the sole source for inhibition in these solvent mixtures. Here, $d\gamma/dc$ is obtained by fitting the PC concentration dependent change in surface tension with a third order polynomial least-squares fit and differentiating. Note that the physical properties including relative permittivity, density, viscosity, donor numbers, refractive index, and heat capacity of this binary mixture all exhibit monotonic changes with the solvent composition,^{14–16} implying that the inhibition of bubble coalescence is not strongly influenced by these properties. Also, the investigation of heat of mixing for DMSO and PC indicates that there are no hydrogen bonds in this system and the decisive roles in the intermolecular interactions are those of orientation and induction interactions of the two polar molecules.¹⁷ Accordingly, a possible explanation for the minimum in bubble coalescence is that DMSO and PC form complexes at a certain solvent composition due to the dipolar interactions. Such complexes at the air–liquid interface may reduce the film thinning and rupture between bubbles, thereby leading to inhibition of bubble coalescence. We

Figure 3. Inhibition of bubble coalescence by LiBr and KSCN in binary mixtures of DMSO and PC as a function of electrolyte concentration ($C_{\text{electrolyte}}$). 100% coalescence is defined in solvents without electrolytes; 0% coalescence is a stable, low voltage signal in inhibiting electrolytes.

will explore this in more detail below. Indeed, similar observations of complexes in different solvents have already been used to explain other solvent composition related phenomena.^{18–21}

In Figure 3, the inhibition of bubble coalescence by LiBr and KSCN for different solvent compositions as a function of electrolyte concentration ($C_{\text{electrolyte}}$) is shown. Both LiBr and KSCN exhibit strong bubble coalescence inhibition over all solvent compositions, and inhibition is more efficient in mixed solvents than in pure solvents. This can be seen more clearly from the comparison of transition concentrations (defined as the concentration at which 50% of the total reduction in turbidity is achieved) at different solvent compositions shown in Figure 4. LiBr inhibits bubble coalescence more efficiently in DMSO than in PC, whereas KSCN exhibits similar efficiencies in inhibition of bubble coalescence for the pure solvents. It is notable that for both electrolytes there is a minimum in transition concentration at PC (v/v) $\approx$ 25% (this corresponds to a mole fraction of PC of $\sim$ 22%). Note that the solvent composition of the minimum in this figure is the same as that observed in Figure 2, indicating that the inhibition of bubble coalescence by electrolytes in binary mixtures is possibly influenced by interactions between the solvents that take place in the absence of electrolytes. To test whether the inhibition of bubble coalescence is determined by the Marangoni effect or Gibbs elasticity, we have measured the surface tensions of electrolyte solutions for LiBr and KSCN at different solvent compositions; these are shown in Figure 5. The surface tensions were measured over a wide range of electrolyte concentration (from 0 to 0.6 M) so that the accuracy of the surface tension gradient can be improved. It is apparent that the surface tension increases linearly with electrolyte concentration for all solvent compositions, indicating that the electrolytes are completely dissociated, as if neutral molecules existed in these solvents, the surface activity of the neutral molecules would lead to a nonlinear

(14) Srivastava, A. K.; Shankar, S. L. *J. Chem. Eng. Data* **1998**, *43*, 25.

(15) Rzeszutarska, J.; Ranachowski, P.; Kalinowski, M. K. *Collect. Czech. Chem. Commun.* **1994**, *59*, 2201.

(16) Comelli, F.; Francesconi, R.; Bigi, A.; Rubini, K. *J. Chem. Eng. Data* **2006**, *51*, 665.

(17) Shcherbina, E. I.; Tenenbaum, A. É.; Gurarii, L. L.; Bashun, T. V. *Chem. Technol. Fuels Oils* **1973**, *9*, 759.

(18) Zhang, G. Z.; Wu, C. J. *Am. Chem. Soc.* **2001**, *123*, 1376.

(19) Liu, G. M.; Zhang, G. Z. *Langmuir* **2005**, *21*, 2086.

(20) Dixit, S.; Crain, J.; Poon, W. C. K.; Finney, J. L.; Soper, A. K. *Nature* **2002**, *416*, 829.

(21) Guo, J. H.; Luo, Y.; Augustsson, A.; Kashtanov, S.; Rubensson, J. E.; Shuh, D. K.; Agren, H.; Nordgren, J. *Phys. Rev. Lett.* **2003**, *91*, 157401.

Figure 4. Transition concentration for bubble coalescence inhibition (TC) for LiBr and KSCN in binary mixtures of DMSO and PC expressed as the percentage of PC by volume [PC% (v/v)].

Figure 5. Surface tension (γ) versus electrolyte concentration ($C_{\text{electrolyte}}$) for LiBr and KSCN in binary mixtures of DMSO and PC. The surface tension was determined using the pendant drop method. Ten repeat determinations were performed on three different drops. The average of these 30 measurements is reported, and the error bars have been set at 3 standard deviations. The surface tensions were measured over a wide range of electrolyte concentrations (from 0 to 0.6 M), in order to improve the accuracy of determining the surface tension gradient.

response of surface tension to electrolyte concentration.¹² For LiBr, it is apparent that the gradient of the surface tension plot as a function of electrolyte concentration increases as the fraction of DMSO increases. In comparison, for KSCN, a similar gradient is observed for all solvent compositions. These data must be interpreted with some caution, as one cannot be sure that the solvent composition in the surface layer is unaffected by the electrolyte addition. If this is the case, it appears as though the depletion level of KSCN is independent of solvent composition whereas LiBr is more depleted from the interfacial region as the DMSO proportion of the mixture.

Figure 6. Square of surface tension gradient [SSTG or $(d\gamma/dc)^2$] in binary mixtures of DMSO and PC expressed as PC% (v/v). The error bars were determined by evaluating the maximum and minimum gradients that could be fit within the error bars to the surface tension data presented in Figure 5.

Figure 7. Correlation between the square of surface tension gradient [SSTG or $(d\gamma/dc)^2$] and transition concentration (TC) for LiBr and KSCN in a range of binary mixtures of DMSO and PC. The line is a least-squares fit with a correlation coefficient of ~ 0.8 .

The SSTG which is proportional to the Gibbs elasticity is plotted versus the volume fraction of PC in Figure 6. It is evident that for LiBr $(d\gamma/dc)^2$ gradually decreases with increasing PC% (v/v), whereas for KSCN no clear trend can be discerned from the $(d\gamma/dc)^2$ data. We note that these plots do not exhibit a maximum in $(d\gamma/dc)^2$ at a PC(v/v) of 25%, which would be expected if the inhibition was due to surface elasticity. To evaluate the correlation between $(d\gamma/dc)^2$ and transition concentration, the plot of $(d\gamma/dc)^2$ versus transition concentration (TC) for both electrolytes is shown in Figure 7. The line is a least-squares fit with a correlation coefficient of 0.8, indicating that the correlation between $(d\gamma/dc)^2$ and transition concentration is poor. From these observations, we can conclude that surface elasticity or Marangoni effects cannot account for the effects of electrolytes on the inhibition of bubble coalescence in binary mixtures.

We have also investigated the inhibition of bubble coalescence by HCl at different solvent compositions as a function of electrolyte concentration. HCl was added into the bubble column as a concentrated aqueous solution. Note that the addition of a small amount of water into DMSO or PC does not have a significant influence on bubble coalescence.⁶ HCl is categorized as a “less inhibiting agent” in PC, as it shows no strong bubble coalescence inhibition up to significantly higher concentrations (~ 0.5 M),

Figure 8. Inhibition of bubble coalescence by HCl in binary mixtures of DMSO and PC as a function of electrolyte concentration ($C_{\text{electrolyte}}$). 100% coalescence is defined in solvents without electrolytes; 0% coalescence is a stable, low voltage signal in inhibiting electrolytes.

Table 1. Comparison of Electrolyte Transition Concentrations for Bubble Coalescence Inhibition in the DMSO/PC Mixtures

	LiBr	KSCN	HCl
DMSO	0.056 M	0.083 M	0.095 M
PC 10%/DMSO 90% (v/v)	0.028 M	0.033 M	0.041 M
PC 25%/DMSO 75% (v/v)	0.022 M	0.024 M	0.031 M
PC 50%/DMSO 50% (v/v)	0.040 M	0.056 M	0.075 M
PC 75%/DMSO 25% (v/v)	0.068 M	0.073 M	0.120 M
PC	0.103 M	0.089 M	0.477 M

whereas HCl has a strong inhibition of bubble coalescence in DMSO at concentrations around 0.1 M.⁶ Therefore, it is interesting to determine what happens if we use HCl as an agent to inhibit the bubble coalescence in a DMSO/PC mixture. In particular, will the minimum in the plot of TC versus PC still be present at 25% (v/v)? The results for HCl are shown in Figure 8. For all mixtures studied, HCl is seen to inhibit bubble coalescence at relatively low concentrations similar to the behavior in pure DMSO. Additionally, HCl is seen to inhibit bubble coalescence more efficiently in mixed solvents, as was found for LiBr and KSCN. The plot of TC versus PC% (v/v) for HCl is shown in Figure 9. Again, there is a minimum in transition concentration at PC(v/v) = 25%, as was observed for LiBr and KSCN. This indicates that the effect of solvent composition on inhibition of bubble coalescence by electrolytes in the binary mixtures is independent of the electrolyte species, and it therefore must be determined by the solvents. Finally, we have tabulated the influence of the different electrolytes on the transition concentration in Table 1.

Mechanism of Coalescence Inhibition. In the absence of electrolyte, there is a minimum in bubble coalescence at PC(v/v) = 25%. This minimum cannot be attributed to changes associated with the surface tension, so we seek a molecular description. Let us now consider the formation of solvent complexes between DMSO and PC. Studies of the PC molecule indicate that the negative charge is distributed over the carbon–oxygen region whereas the positive charge is distributed over the atoms in the hydrocarbon chain.²² On the other hand, the negative center and positive center are, respectively, located on the oxygen atom and sulfur atom for the DMSO molecule.^{14,23} In addition, the intermolecular interactions in DMSO/PC mixtures are mainly dependent on the interactions between the S=O group of DMSO and

Figure 9. Transition concentration for bubble coalescence inhibition (TC) for HCl as a function of the volume fraction of propylene carbonate [PC% (v/v)].

the C=O (or C–O) group of PC.¹⁶ Accordingly, DMSO molecules and PC molecules might form solvent complexes due to the orientation and induction interactions between these two polar molecules.¹⁷ For example, three S=O groups from three DMSO molecules could be interacting with three carbon–oxygen groups from one PC molecule to form one solvent complex; that is, the mixed solvents can exactly form complexes at the PC mole fraction of 25% (this is equivalent to a volume fraction of PC of ~28%). The outer surface of such a solvent complex consisting of a hydrocarbon shell may exhibit slight solvophobic properties. This being the case, the solvent complexes would favorably adsorb at the air–liquid interface. How then might such a solvent complex contribute to bubble coalescence inhibition? We have already shown that the observed behavior cannot be attributed to surface elasticity, and recent studies on surfactant systems show that surface viscosity rather than surface elasticity is more important in stabilizing foams.²⁴ This surface viscosity arises when the interface is slow to respond to a disturbance as a result of slow exchange between the surface and the bulk. Perhaps solvent complexes are slower to exchange between the surface and the bulk than other solvent molecules (as might be expected from size considerations alone) and this then leads to an increase in surface viscosity.

In the presence of electrolytes, we have seen that less electrolyte is required to get the maximal bubble coalescence inhibition at a volume fraction of 25% PC. This strongly suggests that electrolyte is enhancing the same coalescence inhibition mechanism seen in the absence of electrolyte. One can propose two means by which this could take place. First, electrolyte could favor the formation of solvent complexes, though it is difficult to imagine how the presence of ions could do this, and therefore, we think this is unlikely. Second, it could increase the effectiveness of solvent complexes in inhibiting bubble coalescence. This could occur by making the solvent complexes more surface active (surface complexes salted out), as is observed for hydrophobic or partially hydrophobic (i.e., surfactant) molecules, or by slowing the dynamics of exchange of solvent complexes between the surface layer and the bulk and thereby increasing the surface viscosity. However, at this stage, both mechanisms appear feasible.

Conclusion

We have investigated the effect of solvent composition on inhibition of bubble coalescence by electrolytes in binary mixtures

(22) Mukherjee, L. M. *Crit. Rev. Anal. Chem.* **1975**, *4*, 325.

(23) Maxey, B. W.; Popov, A. I. *J. Am. Chem. Soc.* **1967**, *89*, 2230.

(24) Andersen, A.; Oertgen, J.; Koelsch, P.; Wantke, D.; Motschmann, H. *J. Phys. Chem. B* **2006**, *110*, 18466.

of DMSO and PC using a custom-built bubble column. The mixing of DMSO and PC does not exhibit any strong inhibition of bubble coalescence over the whole solvent composition. All the electrolytes tested in the present work inhibit coalescence more efficiently in mixed solvents than in pure solvents. The transition concentrations exhibit a minimum at the PC(v/v) fraction of 25% for all three different electrolytes. Our results demonstrate that the influence of solvent composition on inhibition of bubble coalescence by electrolytes cannot be attributed to surface elasticity or the Marangoni effect. A possible mechanism is that the formation of solvent complexes between

DMSO and PC results in an increase in surface viscosity and the presence of electrolytes further amplifies this effect.

Acknowledgment. V.S.J.C. gratefully acknowledges support from the Australian Research Council. We thank Christine L. Henry for help with bubble coalescence measurements.

Supporting Information Available: Densities of electrolyte solutions for LiBr and KSCN in binary mixtures of dimethyl sulfoxide and propylene carbonate. This material is available free of charge via the Internet at <http://pubs.acs.org>.