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Why pH titration in lysozyme suspensions follow a Hofmeister series

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It is a pleasure to dedicate this paper to Prof. J.B. Rosenholm on his 60th birthday.

Abstract

We present theoretical results that provide new insights into the Hofmeister effects observed in protein suspensions. With a buffered solution at a supposedly fixed pH, measurements of that pH with glass electrodes in protein suspensions depend strongly on both ionic species and concentration of background salt and protein. The observed Hofmeister series cannot be explained with standard electrostatic theories. While purely electrostatic limiting laws can be used to obtain partial understanding of some nonspecific trends in buffer and protein solutions, it has long been clear that they fail to explain such ion specificity. The reasons, as explored in a number of our previous papers, have to do with the neglect in these theories of electrodynamic fluctuation (dispersion) forces between ions and proteins. We here use a Poisson–Boltzmann cell model that takes these ionic dispersion potentials between ions and protein into account. The observed ion specificity can then be accounted for.

Keywords: Hofmeister effect; Polarizability; Ionic dispersion potentials; Lysozyme; Poisson–Boltzmann equation

1. Introduction

In the present paper we discuss how one can understand ion-specific measurements with pH meter using a glass electrode. More than 100 years ago Franz Hofmeister and some of his co-workers demonstrated that salts with a common cation, but differing in anion, have different effectiveness in stabilizing protein suspensions [1–3]. The salts could be arranged in a sequence that later seemed to be universal. Depending on the choice of salt, different concentrations are required to precipitate a given concentration of proteins from a whole hen egg white dispersion. Hofmeister, specific ion effects, now refer to the relative effectiveness of anions or cations on a very wide range of phenomena. These effects appear, for instance in double layer force measurements [4–7], pH in different buffer solutions [8,9], cutting-efficiency of DNA by restriction enzymes [10], solubility of lysozyme [11,12], charge of lysozyme [13,14] and cytochrome c [15], pH in buffer free solution [16], activity coefficients of electrolytes [17], and surface tension of electrolytes [18].

The only ionic parameters included in textbook descriptions of pH measured in protein (or buffer) and salt solutions are the ionic charges and the ionic radii of the interacting species. Theory based on these quantities does not account for the experimentally observed ion specificities. There is nothing in the theory that can properly explain why pH measured in lysozyme suspension depends strongly on the choice of background salt. e.g., Experiments discussed recently reveal that very similar results are obtained when the proteins are in a 0.1 M NaSCN solution or in a 0.5 M NaCl solution. The measured pH increases with salt concentration. Significantly, and a strong hint, it also increases with increasing anion polarizability. We will use a Poisson–Boltzmann cell model to demonstrate that this and other phenomenon observed in different protein and buffer solutions can be better understood once ionic dispersion potentials acting between ions and proteins (buffers) are included in the theoretical formalism. The concept of pH is usually central to experiments in biology and biochemistry. Thus, if (apparent) pH as measured by say a glass electrode depends on the buffer or protein and on the nature and concentration of electrolyte, and theory says it should not, we are in trouble at the most basic level. Until the matter is unraveled and understood, then for instance the inference of pK_as of membrane proteins, and

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even the meaning of membrane potentials or ion pumps is in disarray! We will here demonstrate that the effects can most likely be traced to an interplay between changes in solution pH (that depend on species and concentration of buffer and salt) and local changes in the electrochemical potential near the glass electrode. The competition depends on molecular forces that most certainly exist but are missing from existing theories.

The theoretical framework of the Poisson–Boltzmann cell model that we shall need will be described in Section 2. In Section 3 we give several numerical examples obtained from the cell model for charges, solution pH, and surface pH in hen-egg-white lysozyme suspensions. We end in Section 4 with some general conclusions about pH measurements in buffer and protein solutions.

2. Theory

In several preceding papers we have studied some properties of an aqueous solution of anions and cations, of bulk concentration c and charge e, outside a single globular protein [14,15]. This is a somewhat artificial case as in solution of course there is never a single protein present. Even for an apparently dilute suspension of multicharged proteins the electrostatic screening is a highly nonlinear affair and this affects surface ion distributions and local pH. We use a Poisson–Boltzmann cell model [19] to investigate protein charge and solution pH in a suspension with a protein concentration c_p. The globular protein and the buffer anion are modeled as a homogeneously charged spheres with ionizable charge groups (i.e., as a charge regulated sphere as described in Refs. [14,15]). In the cell model the charge-regulated sphere occupies a spherical volume equal to the inverse protein concentration. The same will be assumed when we consider effects of buffer on pH. Since the solutions that we consider are electroneutral the following relationship holds:

$$Z_p + n_{H^+} + n_+ z_+ + n_- z_- - n_{OH^-} = 0, \tag{1}$$

where Z_p is the effective number of charges on each protein (which, depending on pH, can be positive or negative), n_{H^+} and n_{OH^-} are the total number of free hydronium and hydroxide ions in the cell. $n_\pm$ and $z_\pm$ are the amount of and charge number of all salt ions in solution. Since we focus here on systems with pH less than 5, we can safely ignore the extremely low concentration of hydroxide ions. This cell model enables us to determine how many of the hydronium ions are present in solution and how many are bound to proteins.

The protein is modeled as a dielectric, homogeneously charged, hard sphere of radius $r_p = 16.5$ Å. Such a model should hopefully capture the main features of rigid proteins with high degree of structural stability such as hen-egg-white lysozyme.

2.1. Surface versus bulk pH

Before we discuss the theory that we will use to capture the essential features of specific ion effects in pH titration, we first define exactly what we mean by the terms "surface pH" and pH. Bulk pH is equal to minus the logarithm of the chemical potential (which is constant in the entire salt solution) [21,22],

$$\mathrm{pH} = -\log[c_H \gamma_H], \tag{2}$$

where c_H is the hydronium ion concentration and the activity coefficient here is approximated with the purely electrostatic low density approximation, e.g., from Hill [23,24]:

$$\gamma_H \approx \exp\left[-\left(\frac{e^2}{8\pi\varepsilon_0\varepsilon_w kT}\right)\frac{\kappa_{eff}}{1+2r_{ion}\kappa_{eff}} + \frac{8\pi}{3}c(2r_{ion})^3\right], \tag{3}$$

Here ε_w is the dielectric constant of water, k Boltzmann's constant, T temperature, and κ_{eff} the effective inverse Debye length of the solution. We remark that the Debye length to be used is that for the whole solution, not just the electrolyte. The presence of even an extremely low concentration of highly charged species like proteins (or polymers) dramatically changes the Debye screening length. Such effects have rarely been taken into account [24–27]. This true effective inverse Debye length is approximated by the asymptotic formula derived by Mitchell and Ninham [25–27]. This formula is given in Refs. [14,27] and will not be repeated here. It has been shown to give close agreement with experiments, notably in direct force experiments on cytochrome c [26] and insulin solutions [27]. We here neglect the fact that the activity coefficients of salt solutions depend strongly on the choice of background salt solution [17]. We do so deliberately as we wish to focus on specific protein surface effects explicitly. In a later publication we will explore how these ion specific changes in activity coefficients at high concentration influence the result but we focus here on other very important surface effects. While the chemical potential is constant the electrochemical potential changes near interfaces [28]. We define surface pH to mean minus the logarithm of the electrochemical potential. This, rather than pH, is the quantity that influences the number of acid and basic charge groups on a surface. We will demonstrate that pH in solution can be quite different compared to surface pH near a protein surface, and again different near a glass electrode surface. The surface pH differs from pH by the addition of the factor $e\phi(\text{surface})/kT\ln(10)$. Mörnestam et al. [19] have demonstrated that the nonspecific concentration dependence of pH titration could be understood if one plotted protein charge against $\mathrm{pH} + e\phi(\text{surface})kT\ln(10)$ rather than against pH.

The pK_a values and other information about different charge groups of lysozyme [14,20] were taken from the literature. We will perform calculations that both include, and exclude the fact that the pK_a values depend on the protein net-charge. In an elegant paper published more than 50 years ago [29] Tanford demonstrated how one can take into account approximately the change in free energy of ionization from the electrostatic free energy in our model system. The result is:

$$\Delta \mathrm{p}K_a \approx -\frac{Z_p e^2}{4\pi\ln(10)\varepsilon_0\varepsilon_w kT r_p} \times \left[1 - \frac{\kappa_{eff} r_p}{1+\kappa_{eff}(r_p + 2.5\times 10^{-10})}\right]. \tag{4}$$

Note again that in highly charged systems one should use the effective inverse Debye length. While many improvements in theoretical calculations of pK_a values for protein charge groups have been made, this is a reasonable and convenient result to use within our approximation with a homogeneously charged globular protein. These pK_a values will be ion specific due their dependence on protein charge and on the effective inverse Debye length.

2.2. Ion-specific Poisson–Boltzmann cell model

The net protein charge, surface pH, solution pH, and ion distributions can be determined self-consistently via the non-linear Poisson–Boltzmann equation:

$$\frac{\varepsilon_w \varepsilon_0}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) = -e[c_+(r) - c_-(r) + c_{H^+}(r)], \quad (5)$$

with the ion concentrations given by:

$$c(r) = c\ \exp(-[\pm e\phi + U_\pm(r)]), \quad (6)$$

Here ϕ is the self-consistent electrostatic potential and $U_\pm$ the interaction potential experienced by the ions. This interaction potential receives contributions from different sources (e.g., hard-core interaction, images, and ion–ion interactions) but here we only include the ionic dispersion potential between ion and protein. The boundary conditions follow from global charge neutrality and we have no charges at the cell boundary. The electric field at the protein surface is related to the solution charge as follows:

$$(r_p + r_{ion})^2 \left.\frac{d\phi}{dr}\right|_{r=r_p+r_{ion}} = -\sum_i \frac{q_\pm^i}{4\pi\varepsilon_0\varepsilon_w}. \quad (7)$$

In this approach we can only consider cases where the protein concentration is sufficiently low that the mean separation between two proteins is much larger than the Debye length. For typical protein concentrations this is not a major restriction. If the opposite condition applies $\kappa R < 0.5$ the Debye length has to be calculated by taking into account with the background salt only the "bound" counterions [5]. One should observe that there is a very good agreement between ion distributions obtained from the ion-specific Poisson–Boltzmann equation above and results obtained from Monte Carlo simulations [30].

The above equations are solved in a standard way [14] with the additional complication that we now give the total amount of hydronium ions in the system as input data. Following an initial guess for the hydronium ion concentration at the cell boundary one obtains a certain amount of bound hydronium ions. Since the total amount in the system is specified we can then iterate in a straightforward way until the sum of free and bound hydronium ions is equal to what we specified initially. This method gives accurate results.

The dispersion potential between a point particle (ion) and a sphere (protein) is approximated as [14],

$$U_\pm(r) \approx \frac{B_\pm}{(r - r_p)^3[1 + (r - r_p)^3/(r_p)^3]}, \quad (8)$$

where the dispersion coefficient ($B_\pm$) will be different for different combinations of ion and spherical protein. By the term dispersion forces we mean the totality of many body electrodynamic fluctuation forces embraced by extensions of Lifshitz theory (including those from infrared and microwave, which reflect ion induced hydration and bulk water hydration induced by ions, even though we here only consider high frequency contributions). Using ionic polarizabilities and dielectric properties described elsewhere [14,17] we estimate that the dispersion coefficients are around $-0.454 \times 10^{-50}\,\mathrm{Jm}^3$, $-3.574 \times 10^{-50}\,\mathrm{Jm}^3$, $-10 \times 10^{-50}\,\mathrm{Jm}^3$ for sodium, chloride, and thiocyanate like ions. Although the values presented may deviate slightly from the correct values for a specific ion and a specific protein they are of the right order of magnitude. Our results are quite general since many proteins (such as lysozyme and cytochrome c) should all have very similar dielectric properties in the visible and UV frequency range. A point to note is that the values used for the ionic excess polarizabilities and dispersion potentials give consistency between theory and experiment in a number of different systems. For example: surface tension changes and surface potentials in electrolytes [18]; salt dependence of protein charge [14]; and activity coefficients of electrolytes [17].

3. Numerical results: pH and charge in protein solutions

The purpose of this section is to demonstrate how it is possible to go beyond our recent work that considered an isolated globular protein in a salt solution [14,15]. We use the cell model, which enables us to consider protein charge and solution pH in a solution with finite protein concentration.

It is known that the lysozyme net charge in both potassium chloride [13] and sodium chloride [19] increases with concentration, and that both charge and pH (see references in [14]) in protein solutions depend on the choice of background salt (the lysozyme charge is for instance larger in 0.1 M KSCN than in 0.1 M KCl). While results obtained using electrostatic estimates sometimes can be used to explain the nonspecific concentration dependence it cannot accommodate any such ion specificity. We will here demonstrate how the Poisson–Boltzmann cell model, with ionic dispersion potentials included, can capture the essential features of the experimental ion specificity.

We first consider the properties of a 5 g/l lysozyme protein solution with constant total (bound plus free) hydronium concentration and a varying salt concentration. In this case, the task of theoretical modeling is to find out how much of the added hydronium ions are in solution (changing pH directly) and how much is bound to the protein (so changing the protein charge and hence Debye length, activity, and indirectly the pH). In other words we are interested in how well the solution is buffered against pH changes as more acid is added to the solution. The buffer capacity depends, e.g., on the amount of hydronium ions present in the cell, the volume of the cell, and the concentration and species of the background salt solution. The protein will obviously be better buffered in pH regimes where the protein charge changes rapidly (i.e., in pH regimes where many charge groups release or take up hydronium ions).

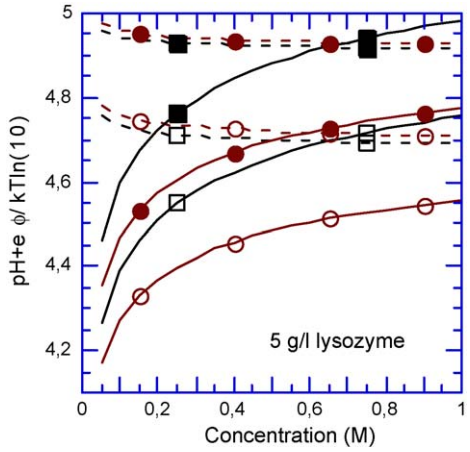

Fig. 1. Calculated pH of lysozyme solutions as functions of salt concentration are shown as solid curves. The "surface pH" (or more accurately: minus the logarithm of the electrochemical potential of a hydronium ion at the lysozyme–solution interface) are shown as dotted lines. Squares and circles correspond to model calculations for "NaSCN" and "NaCl" salt. Open symbols or filled symbols correspond to the cases when the Tanford electrostatic shifts in pK_a values have been taken into account or not been taken into account, respectively.

As can be seen in Fig. 1 the solution pH increases with added salt and also with increasing ion polarizability. This means that one obtains the same pH in a system with larger concentration of NaCl as one does in a system with a smaller concentration of NaSCN. This trend is in excellent agreement with the experimental results presented recently for cytochrome c. One should note that the local electrochemical potential near the protein is very well buffered. Very similar ion-specific trends are also observed for the net protein charge in Fig. 2. The reason for this connection between ion specificity observed for pH and for protein charge is clear. More polarizable anions are more strongly attracted towards the protein surface. This in turn leads to more hydronium ions near the surface (or strictly speaking a higher surface electrochemical potential) and more bound hydronium ions (higher charge). There are then fewer hydronium ions present in solution, and a higher bulk pH.

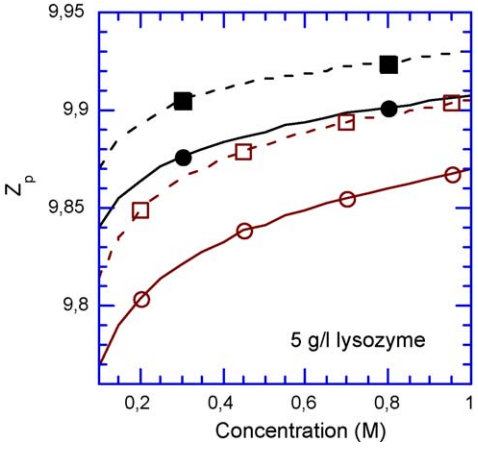

Fig. 2. Calculated charge of a hen-egg-white lysozyme protein as functions of salt concentration. (We used in this figure the same symbols and the same constant hydronium concentration as in Fig. 1.)

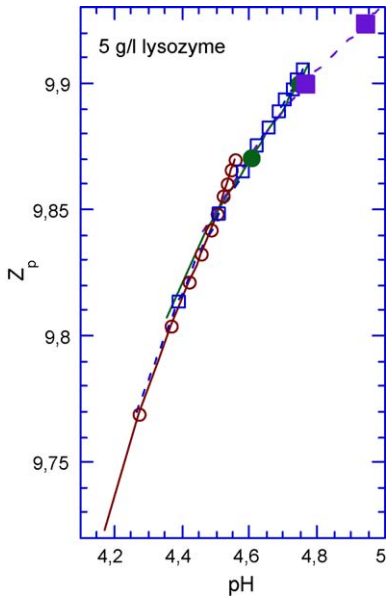

Fig. 3. The concentration dependent charge of a hen-egg-white lysozyme protein from Fig. 2 is shown as a function of the corresponding pH in solution from Fig. 1. The circles (squares) are for "NaCl" ("NaSCN") salt and the open (filled) symbols are for the case when the Tanford electrostatic shifts in pK_a values have been taken into account (not been taken into account). The symbols represent from left to right a concentration of 0.1 M, 0.2 M, 0.3 M, and so on.

One should also observe in the Figs. 1 and 2 that electrostatic shifts in the pK_a values can give important corrections to pH and charge. Since the pK_a values depend on the protein charge and on the Debye length, and these quantities are ion specific, so too are the pK_a values ion specific.

In order to get a better feeling for how a certain concentration of a salt with highly polarizable anions can mimic the effects with a larger concentration of less polarizable ions we plot in Fig. 3 the net charge (from Fig. 2) as a function of the solution pH (from Fig. 1). The symbols in this figure represent from left to right a concentration of 0.1 M, 0.2 M, 0.3 M, and so on. It is certainly clear that it is the quantity that we refer to as "surface pH" that determines the protein net charge. But it is remarkable that the different curves presented in this figure shows that often, to a quite good approximation, one can plot, with overlapping curves for the different salt solutions, the charge as a function of solution pH. According to this model calculation one would obtain approximately the same charge and solution pH if one replaces 0.2 M NaSCN with slightly less than 0.6 M NaCl. Since the exact magnitudes of ionic dispersion potentials are not well known we can only use these results for qualitative comparison with experiments. For instance, the concentrations of one salt that can replace another salt are certainly not predicted exactly. This shows that occasionally it is possible to take into account the salt dependence of protein charge (or of enzymatic activity) in an approximate way through changes in the solution pH. Loeb observed exactly this kind of apparent dependence on bulk pH many years ago but the origin was never understood [31].

We consider next the pH titration curves of hen-egg-white lysozyme protein in Fig. 4. We see that one to a reasonable approximation can replace 0.2 M NaSCN with 0.5 M NaCl. It

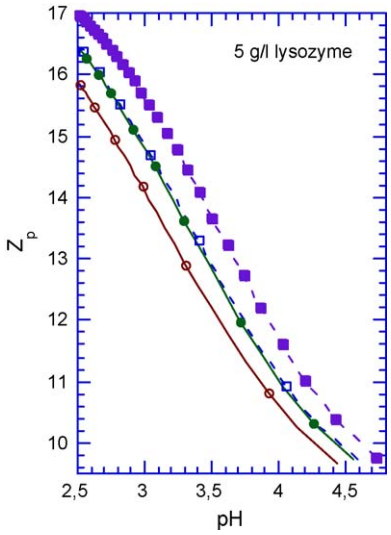

Fig. 4. The charge of a hen-egg-white lysozyme protein is shown as a function of pH (for different total hydronium ion concentrations. The circles (squares) are for "NaCl" ("NaSCN") salt, and the open (filled) symbols correspond to a salt concentration of 0.2 M (0.5 M). In these curves the electrostatic shifts in pK_a values have been included within the Tanford formalism.

is important again to stress that since the exact ionic dispersion potentials are not known in great detail we can only use these results to describe general trends.

4. Conclusions

The reversal of Hofmeister sequences in protein solutions has been known since at least 1901 [32]: "These observations apply only to a neutral or slightly alkaline reaction of the proteins and their solutions as it was found later that the order is reversed in acidic medium". We recently demonstrated that the reversal of the Hofmeister sequence of protein interaction could be understood once ionic dispersion potentials are taken into account [33]. An equally important problem is that of the role of buffer molecules and protein acting as buffers that regulates pH. Measurement of pH with glass electrode is the standard way to determine the pH of a solution. However, it has not been understood why the measured pH depends on the choice of salt, salt concentration and notably on the choice of buffer or protein. Supposedly irrelevant choice of buffer can reverse the Hofmeister sequence for the cutting efficiency of DNA with restriction enzymes and in pH measurements [8]. This has been impossible to explain within the standard theories that only account for electrostatics. We have here demonstrated the important role of ionic dispersion forces behind the ion specificity observed in pH measurements performed with a glass electrode in protein solutions. While it is clear that ionic dispersion forces and ionic polarizabilities in general have vital roles behind the experimentally observed Hofmeister series there may also be other things that influence ion specificity: e.g., ionic size (however, it is important to note that in many cases the influence of ion sizes is too small, negligibly small when the anions are co-ions, and often give trends that go in the wrong direction compared with experiments [33]), the interaction between polarizable ions and water molecules [2], and for an air–water interface also changes in the ionic solvation energies as ions moves into the interface region with its profile of water molecules and dissolved gases [18]. At very low salt and buffer concentrations dissolved gases (e.g., CO_2) may also influence pH, chemical reactivity, and many other phenomenon in solutions [34,35]. The essential point to note is that when ionic dispersion and electrostatic potentials are treated together in a nonlinear theory they give consistency between theory and experiment in a large number of systems. A few examples include: surface tension changes and surface potentials in electrolytes [18]; salt dependence of protein charge [14]; activity coefficients of electrolytes [17]; the reversed and direct Hofmeister sequences observed in protein solubility experiments and with small angle X-ray scattering [33]; pH measurements in buffer and protein solutions; and reversal of Hofmeister sequences with changes in buffer.

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