

LETTERS TO THE EDITOR

A Self-Consistent Solution to the Poisson-Boltzmann Equation Including the Equilibrium of the Solvent

Standard analytic formulations of the electric double layer in a solution treat the solvent as a dielectric continuum and so the equilibrium of the solvent is not imposed as a condition. In such formulations, the ions are treated as an ideal gas—it is assumed that the ionic volume is negligible. In this letter we explicitly include the pressure in the solution and the volumes of ions and solvent, and we report self-consistent expressions for the equilibrium concentrations of counterions and solvent. Standard formulations also use expressions for the entropy of the ions which are appropriate to an ideal gas rather than a solution; in this calculation we use the expressions appropriate for dilute solutions. We show that the size of these two corrections can be comparable with that calculated for the effect of dielectric saturation.

In common derivations of the distribution of ions near a charged interface (8), the treatment of the solvent as a continuum implicitly neglects the force exerted by the solvent on the ions. The condition of electrochemical equilibrium is imposed on the ions, but the condition of chemical equilibrium for the solvent is not applied.

This omission can be important. Near the surface the (total) ion concentration varies with position, and so too must the concentration of the solvent. If the concentration of the solvent varies in space, and its chemical potential does not, then the pressure must vary; that is to say, there is a position-dependent osmotic pressure. If the ionic volume is neglected, this pressure is exactly equal to the Maxwell stress, but in a general treatment the variation in pressure must affect the distribution of both ions and solvent. Previous studies have given an expression for the osmotic pressure variation assuming a distribution of ions obtained by neglecting the solvent (e.g., Bolt and Miller (3)), but these authors did not consider the effect on the ion distribution of this pressure variation. To our knowledge there is no previous treatment which seeks self-consistent solutions for the equilibrium of both solute and solvent.

Further, in most standard formulations, the entropy term in the electrochemical potential of the ions is given as $kT \ln c$, where c is concentration expressed as the number of molecules per unit volume and k is Boltzmann's constant. $k \ln c$ is the entropy per molecule of an ideal gas, rather than that of a solute. In this analysis we use the expression from dilute solution theory in which the entropy per molecule is written as $k \ln X$ where X is the number fraction or mole fraction.¹

¹ The use of Raoult's law for solutions is empirical: Measurements of vapor pressure and freezing point

The correction due to the inclusion of pressure under the equilibrium condition and that due to the use of the solution form of the entropy are of comparable order. The aim of this study is to show the size of these corrections. For simplicity we shall ignore several other corrections to the Poisson-Boltzmann equation which have already been discussed by other authors, such as the effects of excluded volume (1), dielectric saturation (5), the ionic concentration on the dielectric constant (6), and dielectric polarization (2). These are reviewed by Demoiseau (4).

We shall consider the case of a highly charged surface in the presence of counterions only. Such a case arises when the ions are provided only by dissociation from the surfaces. A similar correction however would apply to a system containing ions of both charge. The effect of variation in pressure is large only when the Poisson-Boltzmann equation is strongly nonlinear, i.e., in the region near a highly charged surface where the co-ion concentration approaches zero.

Equilibrium of the counterion (subscript i) and water (subscript w) require

$$\mu_i = \mu_i^0 + kT \ln X_i + p v_i + q\phi \quad [1]$$

and

$$\mu_w = \mu_w^0 + kT \ln X_w + p v_w, \quad [2]$$

where p is the pressure, v is the partial molecular volume, q is the ionic charge, and ϕ is the electrostatic potential. The pressure includes the Maxwell stress and, in the limit where v_i approaches zero, our results reduce to the standard formulation and the pressure approaches $p = \frac{1}{2} \epsilon E^2$ where ϵ is the permittivity of the solution and E is the electric field.

In the absence of co-ions, Poisson's equation in one dimension becomes

$$\frac{d^2 \phi}{dy^2} = -q c_i / \epsilon, \quad [3]$$

where c_i is the concentration of ions. We assume ϵ to be independent of concentration and equal to that of water. (If the solvent molecules and the ions have different polarizabilities, then they will experience a differential force due to the inhomogeneous field. The effect of dielectric polarization has been treated by Bolt (2).)

depression are better fitted by $S = k \ln X$ than by $S = k \times \ln c$ (7).

From $c_i v_i + c_w v_w = 1$ it follows that

$$X_i = 1 - X_w = c_i v_w / \{1 + c_i(v_w - v_i)\}. \quad [4]$$

If $v_i c_i \ll 1$, c_i may be expanded as a power series about its value c at some reference position $y = 0$. Quadratic and higher order terms will be discarded. Making this approximation and using [4], [1] and [2] become

$$\mu_i = \mu_i^0 + kT \ln v_w c_i + kT c_i (v_i - v_w) + p v_i + q \phi \quad [5]$$

and

$$\mu_w = \mu_w^0 - kT v_w c_i + p v_w. \quad [6]$$

We shall put the zero of the coordinate system $y = 0$ where the field is zero, and where the counterion concentration is $c_i = c$ (to zeroth order), and the surface at $y = L$. It may be verified by substitution that the following are solutions to [3], [5], and [6], correct to first order in $v_i c_i$:

$$\exp(-q\phi/kT) = \frac{1}{\cos^2 \kappa y} - c \left(v_i - \frac{v_w}{2} \right) \frac{\tan^2 \kappa y + \kappa y \tan \kappa y}{\cos^2 \kappa y} \quad [7]$$

and

$$c_i = \frac{c}{\cos^2 \kappa y} - c^2 \left(v_i - \frac{v_w}{2} \right) \frac{3 \tan^2 \kappa y + \kappa y \tan \kappa y + 2}{\cos^2 \kappa y}, \quad [8]$$

where $\kappa = \sqrt{q^2 c / 2kT\epsilon}$ is the reciprocal of the Debye length (to zeroth order) at $y = 0$. The calculations are given in greater detail by Demoiseau (4).

We impose the boundary condition that all the counterions are contained in $0 < y < L$. This corresponds to the cases of

(i) two like charged surfaces at separation $2L$, in which the osmotic pressure determines the force of interaction (8); or

(ii) a film of solution on a dissociating surface whose thickness L is determined by the relative humidity of the surrounding atmosphere and the extent of dissociation at the surface (3). In this case, vapor pressure depression due to the concentration at the solution-vapor interface (where the hydrostatic pressure is zero) accounts for the relative humidity being less than 100%.

In both cases the activity of the solvent at $y = 0$ determines the chemical potential of the solvent and electroneutrality relates the surface charge density to the concentration c at $y = 0$. Integration of charge density yields

$$-\sigma/q = (c/\kappa) \tan \kappa L - \frac{v_i c^2}{4\kappa} \left(2 - \frac{v_w}{v_i} \right) (2 \tan^3 \kappa L + \kappa L \tan^2 \kappa L + 3 \tan \kappa L + \kappa L).$$

To compare the results [7] and [8] with those of the Verwey and Overbeek analysis, the partial volume of water

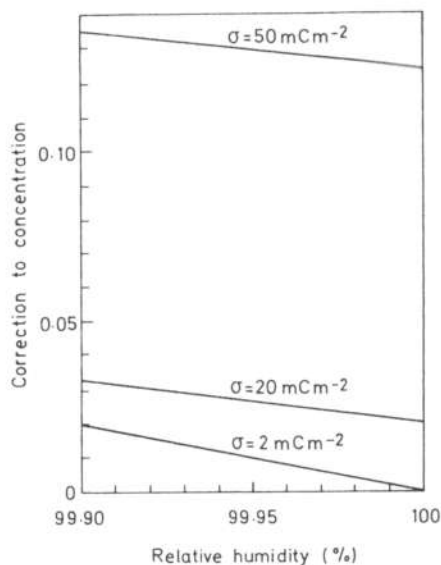


FIG. 1. The ordinate is $C/C' - 1$ where C is the concentration at the solid surface calculated using the analysis given in this paper and where C' is the same quantity calculated using standard double-layer theory. The abscissa is the relative humidity of an atmosphere in equilibrium with the solution, so the results are immediately applicable to a surface layer in equilibrium with vapor. To apply the results to the solution between two planar surfaces, the abscissa is the activity of water at the plane of symmetry.

was taken as $v_w = 3 \times 10^{-29} \text{ m}^3$, the volume of a hydrated ion as $v_i = 3 \times 10^{-28} \text{ m}^3$, and the dielectric constant of the solution as 78. Figure 1 plots the correction; i.e., it plots $(C/C' - 1)$ where C is the concentration at the $y = L$ plane as calculated above and C' is the same quantity calculated using the analysis of Verwey and Overbeek. The surface charge densities chosen are 0.05, 0.02, and 0.002 C m^{-2} .

Qualitatively, the results may be explained as follows. The high ion concentration near the surface implies a lower concentration of water near the surface. Water molecules diffuse into this region, establishing the higher pressure required for equilibrium of water. The gradient in pressure causes a small redistribution of ions away from the surface, and so the concentration of ions is lower than that calculated by ignoring this effect. The errors introduced in concentration and chemical potential by ignoring the effects considered in this study are of the order of several percent for highly charged surfaces with typical ions. This is larger than the correction introduced by the consideration of dielectric saturation effects (5). That these corrections are considerable here in one-dimensional geometry suggests that consideration of osmotic pressure and use of the entropy term from solution theory would make a substantial change to calculations in which three-dimensional

variation in concentration is permitted and where the local variation in total concentration is rather greater than that given above.

Nevertheless, for many applications, the disadvantages of using more complicated analyses (such as Eqs. [7] and [8]) will outweigh the improved accuracy, especially in view of the possibly larger errors introduced by the assumptions of mean field theory and "smeared out" charge. The knowledge that this correction is nonnegligible may be of most use in molecular dynamics or Monte Carlo calculations, where the inclusion of the pressure term would be proportionally a small complication in the algorithm.

ACKNOWLEDGMENT

We thank John Smith for helpful discussions.

REFERENCES

1. Bikerman, J. J., *Philos. Mag.* **33**, 384 (1955)
2. Bolt, G. H., *J. Colloid Sci.* **10**, 206 (1955).

3. Bolt, G. H., and Miller, R. D., *Amer. Geophys. Union Trans.* **39**, 917 (1958).
4. Demoiseau, E., B.Sc. thesis, University of New South Wales, 1987.
5. Grahame, D. C., *J. Chem. Phys.* **18**, 903 (1950).
6. Hasted, J. B., Ritson, D. M., and Collie, C. H., *J. Chem. Phys.* **16**, 1 (1948).
7. Moore, W. J., "Physical Chemistry." Longmans, Green, London, 1950.
8. Verwey, E. J. W., and Overbeek, J. G., "Theory of the Stability of Lyophobic Colloids." Elsevier, New York, 1948.

ERIC DEMOISEAU
JOE WOLFE

*School of Physics
University of New South Wales
P.O.B. 1
Kensington 2033, Australia*

Received December 29, 1987; accepted June 23, 1988