Image Forces at a Mercury–Aqueous Electrolyte Interface

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The Onsager–Samaras theory is extended to the metal–solution interface. Surface excesses and interfacial tension values are calculated taking image forces into account.

Introduction

The existence of Coulombic repulsive forces on the ions at an air–aqueous electrolyte interface has long been recognized. The surface tension of dilute solutions can be successfully predicted on the basis of these forces alone.[2] For more concentrated solutions, it has to be assumed that an ion-free layer is present at the surface and the surface tension values, predicted using a model in which both effects are taken into account, agree remarkably well with the experimental values.[3]

In the present paper, the theory is extended to the uncharged Hg–aqueous electrolyte interface where attractive forces are present on the ions.

The Surface Tension of a Metal–Solution Interface

When the metallic surface is uncharged, the energy of an ion located at a distance x from it, due to its image and the image of its ionic atmosphere in the metal, is given by the expression obtained by Onsager and Samaras[2]

$$W(x) = -\frac{e^2}{4Dx}\exp(-2\chi x) \qquad (1)$$

where e is the charge of the ion, D is the dielectric constant, and χ is the reciprocal of the radius of the ionic atmosphere in the Debye–Hückel theory.

This expression assumes that the value of χ is constant up to the boundary of the interface. The justification for this approximation and hence of the Onsager–Samaras theory has been borne out by experiments.[3-7]

The electrolyte concentration at a distance x from the electrode is then given by

$$C_x = C_{salt}\exp\left\{\frac{e^2}{4DkTx}\exp(-2\chi x)\right\} \qquad (2)$$

where C_{salt} is the bulk concentration of the electrolyte.

Ionic surface excesses due to image forces can be calculated by integration of

$$\Gamma_{if} = \int_{x_0}^{\infty}[C_x - C_{salt}]\,dx \qquad (3)$$

where Γ_{if} is the ionic excess due to image forces and x_0 is the distance of closest approach of the hydrated ions to the metallic surface (outer Helmholtz plane, OHP) and is of the order of the radius of such an ion;[8] χ was assumed constant, and although this is not the case close to the metallic surface, this does not seem to produce large errors as can be seen from the air-solution interface results. Furthermore, some calculations were performed by an iterative method taking into account the variation of χ with distance,[9] and the results were substantially the same as those obtained using a simplified model. No correction due to the finite volume of the ions was attempted.

The calculation and integration of (2) was carried out with a Mercury Ferranti computer using a modified version of the Autocode program A-502.

Interfacial tension values were calculated by numerical integration of the surface excess values with respect to the chemical potential of the electrolyte. At the electrocapillary maximum, the Gibbs adsorption isotherm is[10]

$$\Gamma = -\left(\frac{\partial\gamma^{max}}{\partial\mu_{salt}}\right)_{P,T} = m_{salt} - m_{H_2O}\frac{n_{salt}}{n_{H_2O}} \qquad (4)$$

where γ^{max} is the interfacial tension at the ECM, μ_{salt} is the chemical potential of the electrolyte, m_{salt} and m_{H_2O} are the number of moles of salt and water forming the interface, and n_{salt} and n_{H_2O} are the number of moles of salt and water present in the bulk of the solution. The value of Γ is invariant with respect to the thickness ascribed to the interfacial layer, provided it includes all of the regions where inhomogeneities occur.[2] The

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physical meaning of the term m_{H_2O} (n_{salt}/n_{H_2O}) is the amount of electrolyte which would be associated in the bulk phase with the amount of water contained in the whole interfacial region. According to the current views on the structure of the Hg–solution interface,[11] this can be divided into two regions: the inner and the diffuse layers. In the absence of specific adsorption of ions, the inner layer consists only of solvent molecules, and as a consequence, for sufficiently concentrated solutions, the electrolyte is actually *desorbed* from the interface.[12] The degree of desorption depends on the positioning of the OHP and, hence, on the degree of hydration of the electrolyte. To simplify the analysis, differences in the degree of hydration of the cation and anion are not taken into account.

The contribution to the surface excess due to the inner layer can be conveniently expressed in terms of a thickness parameter, x_0[12]

$$m^{i}_{H_2O}\frac{n_{salt}}{n_{H_2O}} = x_0 C_{salt} \qquad (5)$$

where $m^{i}_{H_2O}$ is the amount of water present in the ion-free layer.

There is some experimental evidence that this assumption is not unrealistic[12-14] and values of distances of closest approach to the surface, calculated from thermodynamic ionic surface excess data of concentrated solutions, do not contradict values estimated from capacitance data. Also, distances of closest approach calculated from surface excess results appear to be constant over a wide concentration range.[12-14] Hence, thermodynamic surface excesses and interfacial tension values can be predicted for very dilute solutions through eq 3–5.

$$\Gamma = \Gamma_{if} - x_0 C_{salt} \qquad (6)$$

The calculated surface excess values for three different values of the parameter x_0 were numerically integrated with respect to the chemical potential of the electrolyte, using NaOH solutions as an example. The activity coefficients of the NaOH solutions were taken from tables.[15] The activity coefficient in the concentration range 0.01–0.001 M was considered to be the same as that of an NaCl solution. The activity coefficient of more dilute solution was calculated using the extended Debye–Hückel equation taking the ionic size parameter as $a = 4.0$ Å. Numerical values for the constants were taken from ref 16. The programs were set to give a final accuracy of 0.1%.

Results and Discussion

Figure 1 shows the concentration of electrolyte at a given distance from the metallic surface for various concentrations and Figure 2 shows the calculated interfacial tension changes $\gamma_c - \gamma_{0.0005\ M}$ for different values of the parameter x_0. The concentration $5 \times 10^{-5} M$ was used as a reference for the integration. The

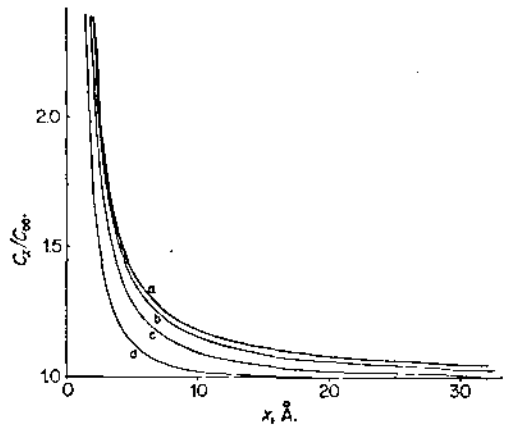

Figure 1. Ratio of concentration of electrolyte to bulk concentration as a function of distance to the electrode for different bulk concentrations: a, $10^{-4} M$; b, $10^{-3} M$; c, $10^{-2} M$; d, $10^{-1} M$.

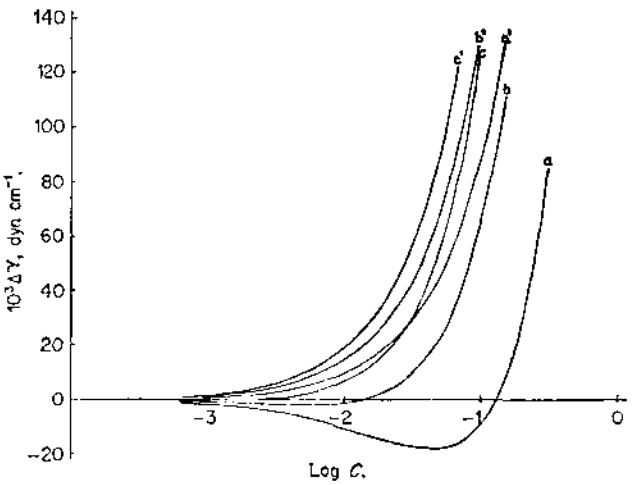

Figure 2. $\gamma_c - \gamma_{0.0005\ M}$ for various distances of closest approach. a, b, and c correspond to thicknesses of 2, 3, and 4 Å, taking image forces into account; a', b', and c' are the same but without image forces.

value of Γ for lower concentrations is so small that no appreciable change in the calculated interfacial tension values appears if a lower limit of integration is taken. At any rate, the experimental difficulties of measuring minute interfacial tension changes in very dilute solutions are such as to make this measurement impossible for concentrations lower than $10^{-4} M$.

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From Figure 1 it can be seen that the range of the image forces can be large in dilute solutions and decreases rapidly for more concentrated solutions. This is due to the more effective screening of the ionic charge by its ionic atmosphere in concentrated solutions.

The concentration of electrolyte rises sharply in the immediate neighborhood of the metallic surface, and for an ion with a distance of closest approach of 2.0-2.5 Å, its concentration at the OHP is almost twice its value in the bulk of the solution up to solution concentrations of 10^{-2} *M*. In certain cases, this effect might prove to be of importance in the study of electrode kinetics in the absence of a supporting electrolyte. The effect of this rapid increase in concentration near the electrode on the surface excess and hence on the interfacial tension can be seen in Figure 2. The concentration at which the value of the surface excess changes sign, and hence the interfacial tension curves show a minimum, is shifted to the more dilute concentrations. For example, the position of the minimum in the interfacial tension changes from 0.05 to 0.001 *M* when the position of the OHP is shifted from 2 to 4 Å. Also, the decrease in the interfacial tension values due to image forces is much less. (The maximum decrease is 0.02 dyn/cm for 2 Å and 0.0002 dyn/cm for 4 Å.) Two concurring effects produce this large change: (1) an increase of over-all adsorption due to imaging in the metal and (2) an increase of the electrolyte desorption due to the presence of an ion-free layer at the metal surface given by the term $x_0 C_{salt}$ in eq 6.

The largest expected decrease of the interfacial tension at the ECM for a 1:1 electrolyte in the absence of specific adsorption, when the concentration is varied from 10^{-4} to 5×10^{-2} *M*, would be of the order of 0.02 dyn/cm. If this were the case, it should be possible to measure this change with a sufficiently accurate differential electrometer.

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