THE DIFFUSE DOUBLE LAYER IN IONIC LIQUIDS

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the honoring with the Nobel Prize.

The equations used to describe the diffuse double layer in the Eigen–Wicke model of ionic liquids are presented. They are then used to estimate the potential drop across the diffuse layer and its differential capacity for two representative systems which contain monovalent ions of equal diameter. The first one is molten RbCl at 750 °C. The second system is a room temperature ionic liquid with typical parameters to describe its properties. The results of the calculations are compared with the available experimental data. It is concluded that the Eigen–Wicke model does not consider the change in local potential experienced by a given ion in the ionic liquid. The need for Monte Carlo data for the diffuse double layer in molten salt systems is emphasized.

Keywords: Electrochemistry; Monte Carlo method; Diffuse double layer; Molten salts.

Because of their potential application in batteries and electrochemical capacitors, ionic liquids have attracted considerable attention in recent years[1]. Kornyshev[2] discussed double layer properties in these systems using Fermi statistics to describe the diffuse layer. An important conclusion of this work is that the diffuse layer capacity has a maximum at the point of zero charge (pzc) in dense systems rather than the minimum which is predicted by Gouy–Chapman (GC) theory for electrolyte solutions in polar solvents[3]. However, at low densities, the diffuse layer capacity has a minimum at the pzc surrounded by maxima at positive and negative rational potentials[2].

The Kornyshev treatment of the diffuse layer in ionic liquids is based on the Eigen and Wicke theory for concentrated electrolyte solutions[4]. However, the Eigen–Wicke (EW) approach is not the only method for considering ion size effects in the diffuse double layer. Other recent contributions

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to this topic have been the Fawcett–Smagala model[5,6] which is based on the hypernetted chain integral equation, and the modified Poisson–Boltzmann theory of Outhwaite and Bhuiyan[7,8].

The purpose of the present paper is to examine the predictions of the EW model for an ionic liquid. Attention is focussed on the predictions of this model with respect to the classical GC theory, especially the question of the extrema in the diffuse layer capacity. The discussion in the present paper is limited to restricted systems, i.e., systems in which all ions have the same radius. Approximate examples on the basis of Shannon and Prewitt radii are the monoatomic systems, NaF and RbCl, at very high temperatures. Examples of room temperature systems which can be considered restricted are harder to find. Nevertheless the properties of such a system are also considered. Finally, the discussion in this paper is limited to 1:1 electrolyte systems.

THEORY

An important feature of an ionic liquid is the vacancies which provide ionic mobility. If the component ions are represented as charged hard spheres, then a significant fraction of the volume is empty because of the way that the spheres are packed. The volume of a sphere of radius r is $4\pi r^3/3$ and that of a box containing that sphere is $8r^3$. It follows that 52% of the volume is occupied if the spheres are not close packed. When the spheres all have the same radius and are close packed, the fraction of the volume which is occupied rises to 74%. Real systems with equally sized ions probably have volume occupation fractions between these limits.

Consider an ionic liquid which is made up of cations, anions and vacancies. The sizes of the cation and anion are the same, i.e., they have equal radii r_i. A vacancy is formed by removing a cation and an anion from the system, so that the volume of a vacancy is twice that of either a cation or an anion. Thus, the volume of the system is given by

$$V = (c_{+0} + c_{-0})V_i + 2c_{v0}V_i + V_{ex} \qquad (1)$$

where V_i is the volume of an ion, and c_{+0}, c_{-0} and c_{v0} are the concentrations in the bulk of cations, anions and vacancies, respectively, and V_{ex} is the excluded volume arising from the way the hard spheres are packed. The volume of a single ion is $4\pi r_i^3/3$, so that the volume of one mole of electrolyte is given by

$$V_e = \frac{8\pi N_L r_i^3}{3} \tag{2}$$

where N_L is the Avogadro constant. It follows that the hypothetical maximum concentration of the electrolyte is

$$c_m = \frac{3}{8\pi N_L r_i^3} . \tag{3}$$

The ion density is given by

$$\rho = 2N_L c_e = 2N_L c_{+0} = 2N_L c_{-0} . \tag{4}$$

The fraction of the volume occupied by the ions is

$$\gamma = \frac{4\pi\rho r_i^3}{3} = \frac{2c_e}{c_m} . \tag{5}$$

As shown by Kornyshev, the parameter γ plays an important role in determining diffuse double layer properties.

Expressions are now given for the electrochemical potentials of the ions in the diffuse layer following the treatment of concentrated electrolyte solutions by Eigen and Wicke[4]. In the case that the ions are assumed to be hard spheres which cannot penetrate one another, their electrochemical potentials are

$$\tilde{\mu}_+ = \mu_+^0 + RT \ln c_+ - RT \ln(c_m - c_+ - c_-) + F\phi \tag{6}$$

and

$$\tilde{\mu}_- = \mu_-^0 + RT \ln c_- - RT \ln(c_m - c_+ - c_-) - F\phi . \tag{7}$$

Here μ_+^0 and μ_-^0 are the standard chemical potentials of the cation and anion, respectively, and ϕ is the local electrostatic potential. The concentrations c_+ and c_- refer to the local ion concentrations in the diffuse layer. The third term on the right hand side of these expressions accounts for the change in Gibbs energy with degree of filling of the available sites in the diffuse layer.

Equating the electrochemical potential of a given ion to its value in the bulk of the solution, one eventually obtains the following expression[9] for the concentration of ion i

$$c_i = \frac{c_e \exp(-z_i \varphi)}{(1 - \gamma + \gamma \cosh \varphi)} \tag{8}$$

where $\varphi = F\phi/RT$ is the dimensionless potential. This is the Fermi equation for the ionic concentrations in the diffuse layer. When $\gamma = 0$, it reduces to the corresponding Boltzmann equation.

The equation giving the potential drop across the diffuse layer[2,9] is

$$\varphi^d = 2 \sinh^{-1}\left[\frac{\exp(\eta E^2/2) - 1}{2\gamma}\right]^{1/2} \tag{9}$$

where $E = \sigma_m/A_{GC}$ is the dimensionless electrode field and $A_{GC} = (2RT\varepsilon_0\varepsilon_s c_e)^{1/2}$ is the GC constant[3]. ε_s is the relative permittivity of the molten salt and ε_0 is the permittivity of free space.

The differential capacity of the diffuse layer C_d is given by[2,9]

$$C_d = \frac{C_{d0} \sinh \varphi^d}{E[1 + 2\gamma \sinh^2(\varphi^d/2)]} \tag{10}$$

where $C_{d0} = FA_{GC}/RT$ is the diffuse layer capacity at the pzc. These equations are essentially the same as those derived earlier by Kornyshev[2].

Keeping in mind the fact that one observes the total capacity of the double layer experimentally, it is important to consider the contribution of the inner layer C_i. In aqueous electrolyte solutions the inner layer contribution is dominant under most experimental conditions. Furthermore, potential dependence of C_i reflects the properties of the solvent in the absence of ionic specific adsorption[3]. The situation is very different in an ionic liquid. In the absence of specific adsorption, the inner layer capacity is a constant

$$C_i = \frac{\varepsilon_0 \varepsilon_s}{r_i} . \tag{11}$$

The relative permittivity of room temperature ionic liquids falls in the range from 6 to 16 (ref.[10]). Assuming that the relative permittivity is 12 and the ionic radius 0.5 nm, the value of C_i is 21.3 μF cm^{-2}. The contribution of

the diffuse layer to the total observed capacity will only be important when it is smaller or of the same order of magnitude as that of the inner layer.

RESULTS AND DISCUSSION

The predictions of the EW model are now examined for the diffuse double layer in two ionic liquids. The first is a high temperature system, namely RbCl, in which the ions have nearly equal radii (165 pm) on the Shannon and Prewitt scale[3]. In fact, the interatomic distance between the two ions on the basis of X-ray data is 328.5 pm. RbCl melts at 718 °C and has a density of 2.088 g cm^{-3} at 750 °C. Assuming an ionic diameter of 328.5 pm, the fraction of the volume occupied in molten RbCl, γ, at 750 °C is 0.393. The dielectric constant for this system is 2.75 (ref.[10]).

Values of the potential drop across the diffuse layer ϕ^d estimated for the RbCl system at 750 °C according to the EW model are shown in Fig. 1. The values estimated using GC theory are also shown. It is apparent that the EW results are considerably larger than the GC values for higher charges. In fact, it was shown earlier[9] that ϕ^d estimated by the EW model is always larger than ϕ^d(GC) by expanding Eq. (*8*) to obtain an infinite series in ϕ^d(GC). In the case of concentrated 1:1 electrolytes in water, the EW estimates of ϕ^d were significantly different than Monte Carlo (MC) results. This was attributed to the fact that the EW model is a mean field theory which

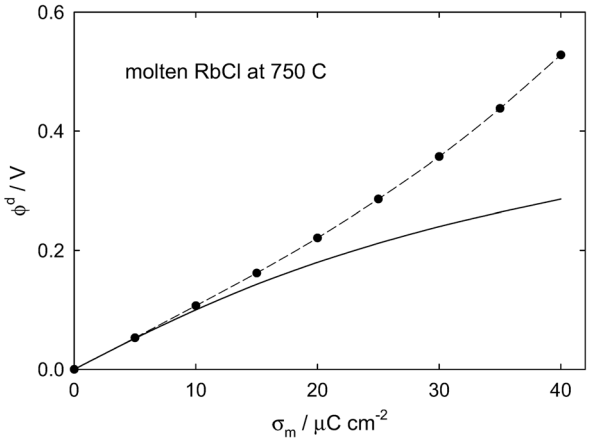

FIG. 1
Potential drop across the diffuse layer ϕ^d plotted against the electrode charge density σ_m for molten RbCl at 750 °C. The results of the Eigen–Wicke model are designated by (●) and the solid curve shows the results from Gouy–Chapman theory

does not consider the change in the local potential due to the ionic environment. Clearly MC data should be obtained for the present conditions. However, it is clear from previous MC studies[9] that ϕ^d(MC) falls below ϕ^d(GC).

The differential capacity of the diffuse layer C_d estimated by the EW model for the RbCl system is shown in Fig. 2. The interesting result is that a maximum is found in C_d at the pzc. In fact, the estimates of C_d by GC theory are very different showing a much larger magnitude for higher charges and a minimum at the pzc. The value of the inner layer capacity C_i for this system is 14.82 μF cm^{-2}. Thus, one may estimate the total capacity of the double layer using the relationship

$$C = \frac{C_i C_d}{C_i + C_d} . \qquad (12)$$

As the inner layer capacity is small, the variation in the total capacity with charge density is also small, falling from 12.8 at the pzc to 11.5 at 40 μC cm^{-2} (see Fig. 2). Finally, the diffuse layer capacity for this system follows the predictions of Kornyshev[2] for an ionic liquid with $\gamma > 1/3$.

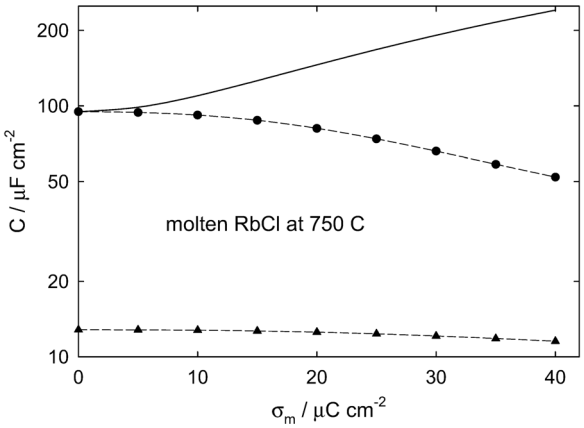

FIG. 2

Differential capacity of the diffuse layer C_d (●) and the total capacity (▲) plotted against the electrode charge density σ_m for molten RbCl at 750 °C. The diffuse layer capacity was obtained from the Eigen–Wicke model (Eq. (*10*)) and the total capacity from Eqs (*11*) and (*12*). The solid curve shows the results from Gouy–Chapman theory for the diffuse layer capacity

The second ionic liquid considered is a room temperature system. Singh and Kumar[11] have summarized the properties of various imidazolium room temperature ionic liquids (RTILs). The cation in the system considered is 1-ethyl-3-methylimidazolium and the anion tetrafluoroborate ($EtMeIMBF_4$). The molecular volume of the system is 0.229 nm^3. Assuming that the volume of the cation is equal to that of the anion, and that 50% of the volume is empty ($\gamma = 0.5$), each ion occupies 0.5725 nm^3. This corresponds to an ionic radius of 239 pm. The concentration of the RTIL calculated from its density is 6.47 mol l^{-1}. Finally the dielectric constant of the system is 15.0 (ref.[11]).

Values of the potential drop in the diffuse layer ϕ^d estimated by the EW model are shown as a function of electrode charge density in Fig. 3. ϕ^d is much larger than the GC value for higher charges reaching close to 0.5 V for a charge density of 40 μC cm^{-2} on the electrode. As pointed out above, the EW results are suspect because the model does not consider the effect of the ionic environment on the local potential. MC data for this system are expected to fall below the GC results. Data for the differential capacity of the diffuse layer are shown in Fig. 4. The RTIL also has a maximum in C_d at the pzc. The predictions of GC theory for C_d are much larger and are not shown for the entire range of charge densities for which calculations were carrried out. In assessing the above results it should be kept in mind that

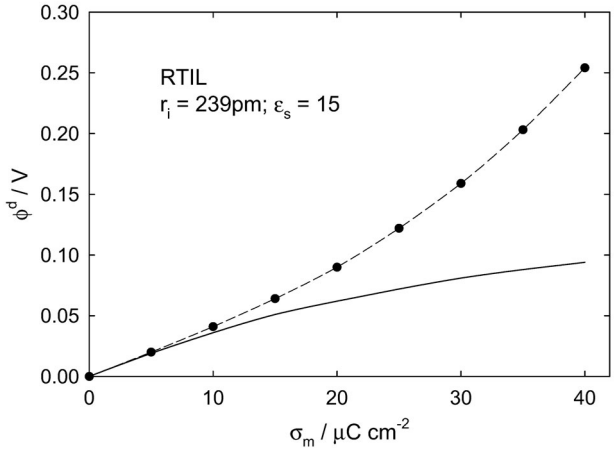

FIG. 3
As in Fig. 1 but for a room temperature ionic liquid characterized by an ionic radius r_i = 239 pm and a dielectric constant ε_s = 15 coressponding to 1-ethyl-3-methylimidazolium tetrafluoroborate

the cation in the system is only approximately spherical. In fact, for most imidazolium electrolytes, the cation is larger than the anion. Under these circumstances the electrolyte cannot be considered to be restricted. A method of treating unrestricted systems at the GC level has been described by Valleau and Torrie[12].

Some capacity data have been reported recently for RTILs [13–16]. In the case of $EtMeIMBF_4$ (ref.[13]), the capacity at the pzc is ~13 μF cm^{-2}, i.e., much smaller than the value estimated here. In experiments reported by these authors[13,14] the RTILs were saturated with nitrogen which may play some role in determining the interfacial capacity. Measurement of electrocapillary curves at a dropping mercury electrode in this system[17] showed that the curve is approximately parabolic confirming that the size of the two ions is approximately equal. Data for other RTILs with larger cations are clearly not parabolic[17].

The original work of Kornyshev[2] has been extended in an interesting manner by Fedorov and Kornyshev[18,19]. Using molecular dynamic simulations, they showed that the capacity is significantly overestimated when the diffuse layer component is estimated using Eq. (*10*). They attributed this result to the fact that the EW model does not treat the ionic atmosphere problem correctly. It is interesting that such a correction could account for the fact that the capacity at the pzc observed by Ohsaka et al.[13] is much smaller than predicted for the case of $EtMeImBF_4$.

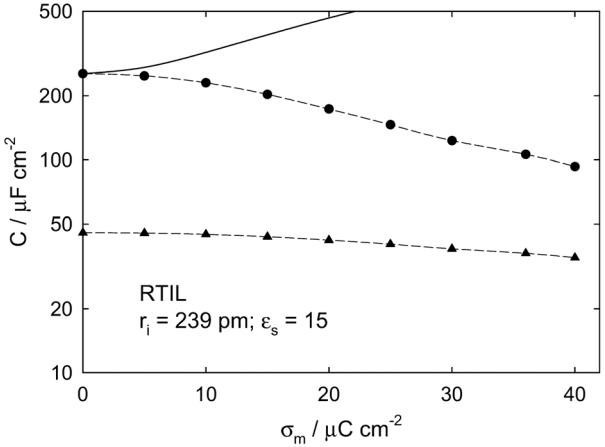

FIG. 4
As in Fig. 2 but for a room temperature ionic liquid characterized by an ionic radius r_i = 239 pm and a dielectric constant ε_s = 15

In a recent paper, Lamperski et al.[20] have described MC results for a wide range of restricted systems including RTILs. They used modified Poisson–Boltzmann theory to describe the transition between systems which have a minimum on the differential capacity curve at the pzc, and those which have a maximum. Their results covered a range of reduced densities ρ* from 0.15 to 0.45 where the reduced density is defined as

$$\rho^* = 8\rho r_i^3 . \qquad (13)$$

The systems considered here have very different reduced densities, namely 0.74 in the case of molten RbCl, and 0.11 in the case of the RTIL. The fact that a maximum is found in the value of the capacity at the pzc for RbCl appears to be in agreement with results of these authors. However, they predict a minimum for the RTIL on the basis of its low reduced density. It is clear from Eq. (*10*) that the maximum appears in our calculation because of the large value assumed for γ. Expanding the exponential terms in the hyperbolic functions in terms of the first term in their series expansion, one obtains the following expression for the dimensionless diffuse layer capacity in the vicinity of the pzc

$$Y_d = \frac{C_d}{C_{d0}} = \frac{\varphi^d}{E[1 + \gamma(\varphi^d)^2/2]} . \qquad (14)$$

When γ = 0, one obtains the GC result which is $Y_d = \varphi^d/E$. Since φ^d is equal to or larger in magnitude than E for a given value of E, the dimensionless capacity Y_d increases from its value of unity at the pzc, and a minimum is found at the pzc. However, when γ is large, as in the case in a RTIL, the denominator in Eq. (*14*) is always larger than the numerator and a maximum is found in the capacity against charge density curve. Only for very small values of γ is a minimum found at the pzc in the diffuse layer capacity, the exact transition point depending on the value of φ^d. The role of empty space in the modified Poisson–Boltzmann theory used by Lamperski et al.[20] does not appear explicitly in their equations.

It is clear from the present study that more MC simulations should be carried out for systems with properties similar to those considered here. Then it should be possible to develop an improved model for the diffuse double layer in systems with high ion densities which goes beyond the mean field approach used here. The availability of experimental double layer data for RTILs makes work in this direction more rewarding.

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