A Gouy–Chapman–Stern model of the double layer
at a (metal)/(ionic liquid) interface

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Abstract

Kornyshev [A.A. Kornyshev, J. Phys. Chem. B 111 (2007) 5545] has recently modelled the (metal)/(ionic liquid) junction and predicted therefrom the capacitance of that interface as a function of the applied potential. One of the purposes of the present article is to demonstrate that, at least in one particular case, the same prediction can be made more simply by applying the principles that Gouy, Chapman and Stern adopted in their classic treatments of the double layer at a (metal)/(electrolyte solution) interface. The analysis predicts the distributions of potential, charge and ionic concentration, leading to support of Kornyshev’s finding of a capacitance that displays a maximum value at the point of zero charge, whereas a minimum is expected for a double layer at an electrode in electrolyte solution. The two systems are compared and contrasted in respect to capacitance and the distribution of ions.

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1. Introduction

The recent flurry of research activity on ionic liquids and their faradaic electrochemistry, partly spurred by their potential technological applications, have aroused interest in the interface between ionic liquids and metals. There has been debate about whether this double layer at this interface is fundamentally different from, or similar to, that at the extensively studied (metal)/(electrolyte solution) junction. Sadly, it must be admitted that, despite the extensive study, our knowledge of the latter interface is still sketchy, with close correlation between theory and experiment being the exception rather than the rule. Perhaps we should expect no better of the (metal)/(ionic liquid) interface.

For a very comprehensive review of previous work on the structure of ionic liquids and their behaviour close to interfaces, the reader is referred to the recent feature article of Kornyshev [1]. That author develops a novel chemical-physics approach to the ionic–liquid double layer, based on a statistical mechanical analysis of a lattice model. Moreover, Kornyshev references the rather sparse experimental data in the field. The present work is much more modest and is couched in a formalism familiar to electrochemists through the theories of Gouy–Chapman and Debye–Hückel. As does the treatment of Kornyshev [1], to which it is identical in outcome, the present treatment, based on analysis of a simplistic model, leads to the prediction that the double layer at a (metal)/(ionic liquid) interface will differ substantially from the picture of the (metal)/(electrolyte solution) double layer with which electrochemists are familiar.

2. Double layer models

The paradigm used to describe the structure of the equilibrium double layer at the junction of a metal with an electrolyte solution conceives the layer to have two elements, in
addition to the sheet of electronic charge on the metal surface. The inner element, known as the “compact layer” or “Helmholtz layer”, is charge-free and its width is of atomic dimension. The outer element, the “diffuse layer” or “Gouy–Chapman layer” is semiinfinite in extent and contains anions and cations distributed unequally in obedience to the laws of Poisson and Boltzmann. The theory is almost a century old, and is cited in almost all textbooks of electrochemistry [2] and in many physical chemistry texts. This dual-element concept is preserved in the present model of the (metal)/(ionic liquid) interface, as it was in Kornishev’s work.

The structure of double layers is most easily probed by studying their capacitance and the main goal here is to investigate how a very simple model predicts the value of this property and its dependence on the electrical condition of the junction. Because an understanding of the equilibrium configuration is sought, it is the so-called “specific integral capacitance” $C$ (with an F m$^{-2}$ unit) of the double layer that is the focus of attention. This is defined as the ratio of the specific charge $q$ (C m$^{-2}$) on the metal to the difference in electrical potential ($V$) in the liquid medium between the metal surface and a plane “at infinity” in the bulk liquid

$$C = \frac{q}{\phi(0) - \phi(\infty)}$$  

(1)

$\phi(x)$ being the electrical potential in the medium at a distance $x$ from the interface.

The model adopted here for the (metal)/(ionic liquid) interface is essentially that of Gouy [4], and independently of Chapman [5], as modified by Stern [6], to describe the (metal)/(electrolyte solution) double layer. There have been many subsequent refinements and modifications of the Gouy–Chapman–Stern model, but here use is made of the simplest possible version that captures the essentials. Each cation and anion is treated as a hard sphere, each of the same radius $r$, with its charge located at the geometric centre of the sphere. Only univalent ions are considered. In the bulk of the ionic liquid exactly one-half of the ions are positively charged, the other half being anions. Close to the metal surface however, this 50:50 composition is perturbed. With $c$ denoting the reciprocal of the molar volume of the ionic liquid, and $c_{\pm}$ the ionic concentrations, the rule

$$c_+ + c_- = 2c$$  

(2)

is taken to hold everywhere, though one might question whether it is reasonable to treat the density of the liquid as a constant in regions where the concentration parity between anions and cations is upset. The permittivity of the medium is regarded as uniform. The electrode is a planar sheet of an excellent electronic conductor, having no specific interaction with the components of the liquid phase.

In addition to $r$, there is another characteristic length that enters into double layer theory. This is the Debye length

$$\delta = \sqrt{\frac{RTc}{2F^2c}}$$  

(3)

In this definition, the permittivity ($F$ m$^{-1}$) of the medium is represented by $\varepsilon$ (sometimes unnecessarily written as the product of the dielectric constant and the permittivity $\varepsilon_0$ of space) and other symbols are standard. Note that the Debye length depends only on the properties of the liquid and is independent of the interface and its electrical state.

There are two important local electrical properties that are functions of $x$, the distance measured normally from the metal surface. These are the potential $\phi$ and the charge density $\rho$ (C m$^{-3}$); they are linked by Poisson’s law

$$\frac{d^2}{dx^2}\phi(x) = \frac{-\rho(x)}{\varepsilon} \quad 0 \leq x \leq \infty$$  

(4)

There is no charge density within the inner layer, and therefore two straightforward integrations convert Eq. (4) first into

$$\frac{d\phi}{dx} = \frac{\phi(r) - \phi(0)}{r} \quad 0 < x \leq r$$  

(5)

and thence to

$$\phi(x) = \phi(0) + \frac{x}{r} (\phi(r) - \phi(0)) \quad 0 < x \leq r$$  

(6)

In the classical Gouy–Chapman theory as applied to the outer double layer element in electrolyte solutions, Boltzmann’s law is invoked in assuming that, if $w_{A\rightarrow B}$ is the work required to carry an ion of charge $Q$ from point A in the solution to point B, then the equilibrium ionic concentrations at the two locations are in the ratio

$$\frac{c(x_B)}{c(x_A)} = \exp\left\{-\frac{w_{A\rightarrow B}}{kT}\right\} = \exp\left\{-\frac{Q(\phi_B - \phi_A)}{kT}\right\}$$  

(7)

$k$ being Boltzmann’s constant. The second equality in (7) holds on making the assumption that the only work involved is electrical. The law may also be stated in statistical parlance: the exponential term expresses the probability that an ion will be at point B compared with its probability of being at point A. Of course, in the electrolyte solution case, when the ion moves from A to B it is implied that a solvent molecule is displaced at B and that a solvent molecule fills the vacancy left at A. In the present case of an ionic liquid, there are no solvent molecules to play this role, and it is more fitting to consider the exchange of two ions. Consider the replacement of an anion, located at some plane $x$ in the diffuse layer, by a cation. In principle, this can be accomplished by carrying the anion adiabatically into the bulk medium and bringing a cation back to occupy the anion’s original location. The work expended in this exchange, again assuming that the work is solely electrical, is

$$w_{\text{exchange}} = Q_+ [\phi(\infty) - \phi(x)] + Q_- [\phi(x) - \phi(\infty)]$$

$$= 2Q_+ [\phi(x) - \phi(\infty)]$$  

(8)
Accordingly, the Boltzmannian term is
\[
\exp \left\{ -\frac{w_- - w_+}{kT} \right\} = \exp \left\{ -\frac{2Q_+ [\varphi(x) - \varphi(\infty)]}{kT} \right\}
\]  
(9)

As far as the plane at \( x \) is concerned, an anion has been changed into a cation and Eq. (8) represents the work needed to effect this alchemy. The principles of Boltzmann statistics then assert that the exponential term governs the extent of interconversion of the ions, so that
\[
c_+ = \exp \left\{ -\frac{w_- - w_+}{kT} \right\} = \exp \left\{ -\frac{2Q_+ [\varphi(x) - \varphi(\infty)]}{kT} \right\}
\]
(which corresponded to \( c_- \) in the diffuse layer, which is no longer small in magnitude, the (metal)/(electrolyte solution) double layer only by the equality of the (metal)/(electrolyte solution) double layer only by the identity disappears.

On combining Eqs. (2) and (10) one finds that
\[
c_+ = \frac{2c}{1 + \exp \{2F[\varphi(x) - \varphi(\infty)]/RT\}} = \frac{c \exp(-A)}{\cosh(A)}
\]  
(11)

whereas
\[
c_- = \frac{2c}{1 + \exp \{-2F[\varphi(x) - \varphi(\infty)]/RT\}} = \frac{c \exp(A)}{\cosh(A)}
\]  
(12)

The final expressions in these two equations arise from some algebra and from the definition
\[
A = \frac{F}{RT} [\varphi(x) - \varphi(\infty)]
\]  
(13)
of a convenient distance-dependent normalized potential parameter. Eqs. (11) and (12) may be combined into an expression for the charge density
\[
\rho(x) = F[c_+(x) - c_-(x)] = \frac{Fc \exp(-A) - F \exp(A)}{\cosh(A)}
\]  
(14)

This result differs from the corresponding expression for the (metal)/(electrolyte solution) double layer only by the hyperbolic tangent of \( A \) having replaced the hyperbolic sine of \( A \). Because both these hyperbolic functions become equal to \( A \) itself at small \( A \), this implies that the electrical properties of the two double layers are identical remote from the interface, the charge density there being proportional to the potential difference \( \varphi(x) - \varphi(\infty) \) through the proportionality constant \(-2F^2/c/RT\). Close to the interface, however, where \( A \) is no longer small in magnitude, the identity disappears.

Combining Eq. (14) with Poisson’s Eq. (3) leads to the differential equation
\[
\frac{2Fc}{\varepsilon} \tanh(A) = \frac{d^2}{dx^2} \varphi(x) = \frac{RT}{F} \frac{d^2A}{dx^2}
\]  
(15)

which may be recast as
\[
\frac{2F^2c}{RT \varepsilon} \tanh(A) = \frac{d^2A}{dx^2} \frac{dA}{dx} \frac{dA}{dx} = \frac{1}{2} \frac{dA}{dx} \left( \frac{dA}{dx} \right)^2
\]  
(16)

Recognize that the reciprocal square of the Debye length \( \delta \), defined in Eq. (3), has appeared as a coefficient in (16). The latter equation may be rearranged to
\[
\delta^2 \frac{dA}{dx}^2 = 2 \tanh(A) dA \quad r \leq x \leq \infty
\]  
(17)

and integrated once to
\[
\delta^2 \frac{dA}{dx}^2 = 2 \ln \{\cosh(A)\} \quad r \leq x \leq \infty
\]  
(18)

Taking the square root of Eq. (18) introduces a ± option, but physical arguments show the appropriate choice to be
\[
\frac{dA}{dx} = -\frac{\text{sgn}(q) \sqrt{2 \ln \{\cosh(A)\}}}{\delta} \quad r \leq x \leq \infty
\]  
(19)

where \( \text{sgn}(q) \) is the sign of the charge on the metal sheet.

We are now in a position to calculate the total charge in the diffuse layer, which is \(-q\), because \( q \) is the charge on the metal surface and overall electroneutrality must prevail. Starting from Eq. (14), and incorporating Eq. (19), the lengthy development

\[
-q = \int_r^\infty \rho(x) \, dx = -2Fc \int_r^\infty \tanh(A) \, dx
\]

\[
= -2Fc \int_{\lambda_r}^0 \frac{\tanh(A)}{(dA/\delta) \, d\lambda}
\]

\[
= \frac{\sqrt{2Fc\delta}}{\text{sgn}(q)} \int_{\lambda_r}^0 \frac{\tanh(A)}{\sqrt{\ln \{\cosh(A)\}}} \, d\lambda
\]

\[
= \frac{-F\delta}{\text{sgn}(q)} \sqrt{8 \ln \{\cosh(A_r)\}}
\]  
(20)

leads to a succinct expression. Here \( A_r \) is the value of \( A \) at \( x = r \), namely \( F[\varphi(r) - \varphi(\infty)]/RT \). Eq. (20) may be inverted to provide the formula
\[
A_r = \text{sgn}(q) \arccosh \left\{ \exp \left( \frac{q^2}{8F^2c^2\delta^2} \right) \right\}
\]

\[
= \text{sgn}(q) \arccosh \left\{ \exp \left( \frac{q^2}{4RT\varepsilon c} \right) \right\}
\]  
(21)

expressing the value of the undimensionalized potential at the junction between the compact and diffuse elements of the double layer. Alternatively, one may directly combine Eqs. (19) and (20) into
\[
\frac{dA}{dx} (r) = -q \left( \frac{F\varepsilon}{2F^2c} \right) = -\frac{Fq}{RT \varepsilon}
\]  
(22)

to express the undimensionalized potential gradient at that junction. On dispensing with the \( A \) abbreviation, the last two equations may be rearranged respectively to
\[
\frac{\varphi(r) - \varphi(\infty)}{q} = \frac{RT}{F |q|} \arccosh \left\{ \exp \left( \frac{q^2}{4RT\varepsilon c} \right) \right\}
\]  
(23)

and, in the light of Eq. (6)
\[
\frac{\varphi(0) - \varphi(r)}{q} = -\frac{r}{\varepsilon} \frac{d\varphi}{dx} (r) = \frac{r}{\varepsilon}
\]  
(24)
This provides explicit expressions for the (potential difference)/charge ratios for the two elements of the ionic–liquid double layer.

Finally, addition of Eqs. (23) and (24) leads to

$$\frac{\varphi(0) - \varphi(\infty)}{q} = \frac{r}{e} + \frac{RT}{F|q|} \text{arcosh} \left( \exp \left( \frac{q^2}{4RT\varepsilon} \right) \right) \quad \text{(ionic liquid)}$$

as the equation relating the electrical potential difference across the entire ionic–liquid double layer to the charge density $q$ on the metal sheet. This equation is the ionic–liquid analogue of the equation

$$\frac{\varphi(0) - \varphi(\infty)}{q} = \frac{r}{e} + \frac{2RT}{Fq} \text{arsinh} \left( \frac{q}{\sqrt{8RT\varepsilon}} \right) \quad \text{(electrolyte solution)}$$

which is the corresponding result for the (metal)/(electrolyte solution) interface according to the same Gouy–Chapman–Stern model.

The derivation of Eq. (25), the major result of this analysis, from the model is exact. This equation is of the form expected for capacitors in series; thus the reciprocal of the overall capacitance can be written

$$\frac{1}{C} = \frac{\varphi(0) - \varphi(\infty)}{q} = \frac{\varphi(0) - \varphi(r)}{q} + \frac{\varphi(r) - \varphi(\infty)}{q}$$

as the sum of two components, each representing one of the elements of which the double layer is comprised. The inner capacitance is, of course, just $\varepsilon/r$. The final term in expression (25) is evidently the reciprocal of the outer capacitance, so that, factoring out the reciprocal Debye length

$$C_{\text{outer}} = \frac{\varepsilon}{\delta} \left[ \frac{|q|}{\sqrt{2RT\varepsilon \text{arcosh} \left( \exp \left( \frac{q^2}{4RT\varepsilon} \right) \right) \right]} \right]$$

Making a power-series expansion of the bracketed expression in Eq. (28) is informative. The first few terms are

$$C_{\text{outer}} = \frac{\varepsilon}{\delta} \left[ 1 - \frac{q^2}{24RT\varepsilon} + \frac{7q^4}{5760(RT\varepsilon)^2} - \frac{17q^6}{967680(RT\varepsilon)^3} + \cdots \right] \quad \text{(ionic liquid)}$$

This expansion should be compared with the corresponding expansion

$$C_{\text{outer}} = \frac{\varepsilon}{\delta} \left[ 1 + \frac{q^2}{48RT\varepsilon} - \frac{17q^4}{23040(RT\varepsilon)^2} + \frac{367q^6}{7741440(RT\varepsilon)^3} - \cdots \right] \quad \text{(electrolyte solution)}$$

for the (metal)/(electrolyte solution) interface. In each case, when the polarization of the interface is small – that is, close to the potential of zero charge – the outer capacitance has a parabolic dependence on the charge, whereas the point of zero charge corresponds to a local minimum in the capacitance of an electrolyte solution double layer, it corresponds to a maximum in the capacitance of the ionic–liquid double layer, as found by Kornyshev [1]. At the point of zero charge itself, the total capacitance is

$$C = \frac{1}{(1/C_{\text{inner}}) + (1/C_{\text{outer}})} = \frac{1}{(r/e) + (\delta/e)} = \frac{\varepsilon}{r + \delta} \quad q \rightarrow 0$$

for both the ionic–liquid and electrolyte solution double layers. The concept of a “Debye length” is grounded in dilute electrolyte solution theory and it is interesting to note that it also appears to play a similar role in ionic liquids, despite the chemical dissimilarity.

Expansion (29) can provide a good approximation for small or moderate values of the quantity $q^2/RT\varepsilon$. At the other extreme, when this quantity is large, the approximation

$$C_{\text{outer}} \approx \frac{\sqrt{2RT\varepsilon^3 c}}{\delta|q|} \quad |q| \gg \sqrt{RT\varepsilon}$$

becomes valid. Worthy of comment is how nonideally the “capacitance” behaves in this limit. A capacitor is supposed to store charge proportionally to the voltage across it. The element that obeys Eq. (32) stores charge proportionally only to the square root of the applied voltage. That this is so is shown by taking the large-charge limit of Eq. (23).

To this point, we have treated the charge $q$ as the independent electrical variable, but potential commonly plays that role. In discussions of the outer capacitance, the natural potential variable is the potential difference $\varphi(r) - \varphi(\infty)$ across the outer region. This potential difference is related to $q$ through Eq. (23) and thereby one derives the expression

$$C_{\text{outer}} = \frac{RT\varepsilon}{F\delta[\varphi(r) - \varphi(\infty)]} \times \sqrt{2 \ln \left\{ \cosh \left( \frac{F}{\delta[A_r] \varphi(r) - \varphi(\infty)] \right) \right\}}$$

as an equivalent alternative to Eq. (28). Its series expansion is

$$C_{\text{outer}} = \frac{\varepsilon}{\delta} \left[ 1 - \frac{A_r^2}{12} + \frac{3A_r^4}{160} - \frac{209A_r^4}{40320} + \cdots \right]$$

$$A_r = \frac{F}{RT} [\varphi(r) - \varphi(\infty)]$$

2.1. A numerical example for the (metal)/(ionic liquid) double layer

To exemplify the relationships developed in the previous section, the following numerical choices
\[ \varepsilon = 1.77 \times 10^{-10} \text{ F m}^{-1} \quad (\text{a dielectric constant of } 20) \]

and

\[ r = 1.00 \times 10^{-9} \text{ m} = 0.100 \text{ nm} \]

will be made. They are considered to be physically realistic for many ionic liquids. These parameters imply that the capacitance of the inner layer is

\[ C_{\text{inner}} = 0.177 \text{ F m}^{-2} = 17.7 \mu \text{F cm}^{-2} \]

according to the model.

The magnitude of the bulk concentration \( c \) is closely related to the value chosen for \( r \). If spheres of radius \( r \) are closely packed in a cubic arrangement, each will commandeer a space of \( 8r^3 \) and their molar concentration will be \( 1/(8Lr^3) = 208 \text{ mol m}^{-3} \) (\( L \) is Avogadro’s constant). This could be the concentration of an ionic liquid in the solid state. The concentration in the liquid state will be somewhat smaller, say

\[ c = 180 \text{ mol m}^{-3} = 0.180 \text{ M} \]

The Debye length can now be calculated from formula (3). At 298 K, it turns out to be

\[ \delta = 3.62 \times 10^{-10} \text{ m} = 0.362 \text{ nm} \]

smaller than, but of a magnitude comparable to, \( r \). Another important quantity is

\[ \sqrt{RTe} = 8.89 \times 10^{-3} \text{ C m}^{-2} = 0.889 \mu \text{C cm}^{-2} \]

In this section, numerical values are cited to three digits and are given in both SI and traditional units. For these data, the overall capacitance of the unpolarized double layer is

\[ C = \frac{e}{r + \delta} = 0.130 \text{ F m}^{-2} = 13.0 \mu \text{F cm}^{-2} \]

the majority of which is contributed by the inner layer. Table 1 lists the outer-layer capacitance predicted in the unpolarized state and at a variety of polarizations. Only positive polarizations are tabulated; the capacitance at a negative voltage exactly duplicates that at a positive value of the same magnitude.

Based on the same trial values, the full lines in Fig. 1 show how the overall and component capacitances vary with charge. These graphs have been calculated with the aid of Eqs. (28), (37) and (27). Note that the outer capacitor has a tenfold range of capacitance, whereas the overall capacitance varies by a factor of less than three. For small charges, the overall capacitance is dominated by the charge-independent inner capacitor, but for larger charges, the outer capacity assumes the dominant role.

The dashed lines in Fig. 1 show how the outer and overall capacitances would behave according to the electrolyte solution version of the Gouy–Chapman–Stern model. That is, these dashed curves are based on Eqs. (26) and (27). The inner capacitance has the same constant value, \( e/r \), for each system, according to the model. The minimum predicted by the classical model at the point of zero charge contrasts markedly with the maximum that the new treatment predicts.

The same ionic–liquid capacitance data represented by the solid lines in Fig. 1 are again plotted in Fig. 2, but this time versus voltage. Kornyshev [1] reports a similar graph. The outer capacitance curve is somewhat more peaked in this representation. Note that, even though \( C_{\text{outer}} \) is defined as \( q/|\varphi(r) - \varphi(\infty)| \), the abscissa is \( |\varphi(0) - \varphi(\infty)| \) for all three curves, because this quantity, being measurable, is the usual choice of an independent variable in electrochemistry. The outer capacitance is significantly more peaked in Fig. 2 representation. This noncongruence reflects the non-ideality of the capacitance and the artificiality of treating the system as two capacitors in series.
Now, the relationship of the integral capacitance of the outer element of the ionic–liquid double layer to the corresponding differential capacitance is

\[
C_{\text{outer}} = \frac{-q}{\varphi(r) - \varphi(\infty)} = \frac{-F}{RTA_r} \int_0^q dq = \frac{1}{A_r} \int_A^{A_r} \tilde{C}_{\text{outer}} dA_r
\]

and when this relation is applied to Kornyshev’s formula (43), the integration is identical to that in (20), and Eq. (32) is recovered exactly. Thus the present treatment agrees perfectly with the limiting case of Kornyshev’s theory, as it should inasmuch as the two models are effectively the same.

Kornyshev explores many ramifications of his theory, including unequal ionic radii. Consult the feature article [1] for details. The model adopted by Kornyshev and by myself ignores spatial gradients other than along the \(x\)-dimension. Many criticisms may be laid against such “mean field” models. At best, our theories should be considered as first steps towards an understanding of the distribution of electrical and chemical properties close to a (metal)/(ionic liquid) interface.

2.3. Ionic distributions in the double layer

The classical Gouy–Chapman–Stern treatment of the (metal)/(electrolyte solution) double layer leads [3] to the prediction that the concentration distribution for the counterion (that with a charge of sign opposite to that of \(q\)) is

\[
c_{\text{counterion}}(x) = c_c \coth \left\{ \frac{x - r}{2\delta} + \frac{1}{2} \arcsinh \left( \frac{\sqrt{RT\epsilon_c}}{q} \right) \right\}
\]

The concentration of the other ion, the coion, obeys a similar equation with the hyperbolic tangent replacing the hyperbolic cotangent. This means that

\[
c_{\text{counterion}} c_{\text{coion}} = c^2 \quad \text{(electrolyte solution)}
\]

at all points the diffuse element of the double layer. Stated otherwise, the salt concentration is everywhere the geometric mean of the anionic and cationic concentrations. This contrasts with the state of affairs at the heart of the present article, wherein Eq. (2) shows the salt concentration \(c\) to be the arithmetic mean, \((c_{\text{counterion}} + c_{\text{coion}})/2\) of the two ionic concentrations. This is a salient difference between two treatments that are elsewise very similar.

What expressions replace (45) and its congener for the ionic concentrations in the (metal)/(ionic liquid) double layer according to the present model? Eqs. (11) and (12) explicitly relate the ionic concentrations to \(A\), so all that is needed is a relationship between \(x\) and \(A\). This is provided by integrating Eq. (19)

\[
x - r = \int_r^x dx = \delta \text{sgn}(q) \int_A^{A_r} \frac{d\lambda}{\sqrt{2 \ln\{\cosh(\lambda)\}}}\]

2.2. Comparison with Kornyshev’s study

Because they commonly apply rapidly changing voltage signals to electrodes, electroanalytical chemists are less interested in the integral capacitance \(C\) of an electrode than they are in its differential capacitance \(\tilde{C}\). This is defined as the rate at which the charge changes in response to a change in the applied electrical potential difference

\[
\tilde{C} = \frac{-dq}{d(\varphi(0) - \varphi(\infty))}
\]

The model adopted in the present article is an equilibrium model and it is not equipped to deal with dynamic aspects of the ionic–liquid double layer. In the light of the high viscosity of most ionic liquids, it would be unwise to differentiate the formulas here and expect them to apply to electroanalytical experiments other than those carried out at glacially slow ramp rates or very low frequencies.

Nevertheless, results in Kornyshev’s feature article [1] are cited in terms of differential capacitance. A quantity \(\gamma\) is involved in Kornyshev’s theory; to understand its import, the original article should be read carefully. For the present purpose it suffices to note that \(\gamma\) equals unity when anions and cations are similarly sized, and when the ionic liquid is regarded as incompressible and inexpan-

sible. These being the assumptions made in this article, it is pertinent to compare the present analysis with the \(\gamma = 1\) version of Kornyshev’s prediction. The latter is embodied in Eq. (24) of Ref. [1] and, in the present notation, it is

\[
\tilde{C}_{\text{outer}} = \frac{\varepsilon}{\delta} \cosh \left( \frac{A_r}{2} \right) \frac{\sqrt{2} \left| \sinh(A_r/2) \right|}{\cosh(A_r) \sqrt{\ln\{\cosh(A_r)\}}} = \frac{\varepsilon \tanh |A_r|}{\delta \sqrt{2 \ln\{\cosh(A_r)\}}} \]

Fig. 2. As Fig. 1 but for the ionic liquid case only and with the applied potential difference \(\varphi(0) - \varphi(\infty)\) as the independent variable plotted on the abscissa.
The upper integration limit \( A \) is known from Eq. (21), but unfortunately no analytical expression for the integral appears to be known. Nevertheless, the integration may be carried out numerically, as was done in constructing Fig. 3, or the integral may be approximated through the expansion

\[
x - r = \delta \left[ \ln \left( \frac{A r}{A} \right) + \frac{A^2 - A^2}{24} - \frac{17 (A^4 - A^4)}{5760} 
\right. \\
\left. + \frac{319 (A^6 - A^6)}{725760} - \ldots \right]
\]

(48)

The full lines in Fig. 3 show how the composition of the ionic liquid varies with distance from the electrode, for the particular state of charge of the double layer reported in the legend. The curves were constructed by treating \( A \) as a parameter, then calculating \( x \) by numerical integration of Eq. (47) and the local ionic concentrations through Eqs. (11) and (12).

Also shown by dashed lines in Fig. 3 are the distributions of the ions predicted by the Gouy–Chapman–Stern theory for electrolyte solutions. The \( c^- \) dashed line reflects one serious criticism that may be levelled at the theory: that it predicts, for concentrated solutions, impossibly large concentrations of the counterion close to interelement junction. This “saturation effect” is seen to be absent in the ionic liquid case. Indeed, the “arithmetic mean” relationship places an upper limit on the concentration that any one ion can achieve, whereas no such constraint is imposed by the “geometric mean” relationship.

3. Discussion

Whereas Gouy–Chapman–Stern principles have been shown to be applicable to the double layers formed at interfaces between a metal and both dilute electrolyte solutions and ionic liquids, the two theories are not contiguous. Thus, the gradual withdrawal of solvent from an electrolyte solution leads ultimately (in principle, if rarely in practice) to an ionic liquid, but no such smooth transition occurs in the mathematic expressions that govern the ionic distributions; indeed, the “saturation effect” provides an unwelcome discontinuity between the two. The reason is not hard to find. In relating the concentrations solely to the work expended in moving a counterion from the bulk into the diffuse layer, Eq. (7) takes no cognizance of the paucity of solvent molecules that must be displaced to accommodate the immigrating counterion. If this entropic effect were to be incorporated, future work might be able to embrace the entire span from a dilute solution of a binary electrolyte through to an ionic liquid within a single framework based on the Gouy–Chapman–Stern model, or some similar statistical approach. In this context, reference may be made to the very recent work of Kilic et al. [7] who, in addressing steric effects in electrolyte solutions and without mention of ionic liquids, derive equations reminiscent of those of Kornyshev [1] and of the present work.

Returning to capacitance, it is reassuring to note the concordance between the present derivation of the integral capacitance and the differential capacitance predicted as a special case of Kornyshev’s theory. The most telling, and the most testable, prediction of both Kornyshev’s model and the present one is their predictions that the double layer should have a maximal capacitance at the zero charge point, rather than the minimum predicted (and found) for the double layers formed by electrolyte solutions. A simplistic explanation of the different behaviours of the two media follows from comparing what happens as increasing polarization causes more and more counterions to crowd in towards the interface. With an electrolyte solution, there are solvent molecules that can easily be displaced to make room for the new arrivals. For an ionic liquid, however, half the prime sites along the interface are already occupied at zero charge and the others are soon taken by immigrating counterions. Later arrivals must take up residence “in the suburbs”, where they are farther from the interface and hence contribute less to the capacitance.

My model is, of course, naïve. Perhaps the greatest lack of realism accompanies the assumption that the anions and cations have equal sizes and spherical shapes. Indeed, it is widely held that the very reason that certain salts resist crystallization and remain ionic liquids is precisely because their ions do not have similar sizes and simple shapes.

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