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Ion penetration into an 'unfriendly medium' and the double layer capacitance of the interface between two immiscible electrolytes

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Dedicated to Professor Roger Parsons, FRS, on the occasion of his retirement as the Editor of the Journal of Electroanalytical Chemistry and in appreciation of his outstanding contributions to electrochemistry

Abstract

We develop a theory of the double layer at electrolyte | electrolyte interfaces with account for the finite thickness of the interfacial region. This includes the distribution of ions between the two phases and smooth variation of dielectric properties across the interface. The theory offers simple laws for the dependence of the double layer capacitance on the nature of ions, ionic concentrations and potential, which are in line with experimental observations. The theory shows which parameters reflect the nature of ions and the structure of the interface, and how these parameters can be extracted from the capacitance data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electrochemistry of interfaces between two immiscible electrolyte solutions (ITIES) is a rapidly emerging interdisciplinary field where soft matter physics [1] and statistical physics of liquids [2,3] meet electrochemistry [4-7]. ITIES is a model system for reaction-kinetics, biomimetic systems, and a real medium for industrial phase transfer catalysis [5-7]. One of the solvents is usually water, and the other is a hydrophobic, low polar organic liquid. Such an interface separates hydrophilic and hydrophobic ions. When the two salts are dissolved in this system, one composed of hydrophobic and the other of hydrophilic ions, they form two 'back-to-back' electrical double layers and the interface can be polarized [5-7]. The resulting electric field across the interface affects a variety of phenomena which occur at the interface.

Since the pioneering works of Gavach and coworkers [8,9] interfaces between two immiscible electrolyte solutions have received considerable attention. Most of what is known experimentally has been obtained by classical electrochemical techniques including cyclic voltammetry and impedance measurements [5,6,10-12]. Thus one of the most basic experimental characteristics of the interface between two immiscible liquids is a double layer capacitance. Recently new experimental techniques such as second harmonic generation [13-15], time-resolved quasi-elastic laser scattering [16] and neutron scattering [17] have been applied to study these interfaces. However, in spite of numerous efforts, the structure of the ITIES is still a matter of controversy and there is no unambiguous picture for interpretation of electrochemical experimental data.

The first models of liquid | liquid interfaces in electrochemistry treated them as flat and sharp. It was proposed that the interface consists of two diffuse space-charge regions separated by a compact ion-free layer [5,6,10], though the physical origin of the latter was not obvious in the liquid | liquid system. The treatment of interfacial capacitance in terms of the capaci-

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tance of two 'back-to-back' Gouy-Chapman double layers works fairly well for some electrolytes, while it fails for the majority of others [5,6,10,12,18-20]. In contrast to the predictions of the simple Gouy-Chapman theory, it was found that the capacitance of ITIES depends on the nature of the ions [6,12,18-22]. Often the capacitance curves show a strong asymmetry as a function of the potential. The discrepancy between experimental results and the Gouy-Chapman theory has stimulated theoretical work, which went beyond the classical scheme. The first step in this direction was made in pioneering work [21-23], where the 'mixed boundary layer' was introduced and the effect of overlapping of the two space-charge regions on the double layer capacitance was considered. The authors used a quasi-chemical approximation [21,22] and Monte-Carlo simulations [23] to calculate the z-dependent (normal to the interface) density profiles of the ions. Then the Poisson-Boltzmann equation was solved numerically assuming, for computational simplicity, that the dielectric constants of the two solvents are equal to each other and do not vary with the distance from the interface. It was found that in some cases the penetration of ions from one solution into another led to an increase of the double layer capacitance with respect to Gouy-Chapman results, but in other systems the opposite effect was found.

The essentially numerical studies of capacitance [21–23] revealed the effect of the mixed layer. However, they did not disclose general laws for the capacitance of this interface. For instance a number of questions remain open.

- Which characteristics of the ionic density profiles determine the observed dependences of the capacitance on the nature of the ions?
- Which parameters control the sign of the deviation of the capacitance from the Gouy–Chapman result and the asymmetry of the capacitance curves as a function of the potential?



Fig. 1. An interface between two immiscible electrolyte solutions: dielectric profile, $\varepsilon(z)$ (upper curve) and distributions of ionic concentrations, $n_i(z)$ (lower curve).

• What information on the free energy profile of the ions across the interface can be obtained from the capacitance data?

Moreover, the smearing of the interface between two solvents may be manifest in the smooth variation of dielectric properties across the interface (even if the interface is sharp, similar effects emerge due to the non-local dielectric polarizability [24-31]). This property was not considered in Refs. [21-23].

In order to answer these questions we develop an analytical theory of the double layer at ITIES. The theory is based on a modified non-linear Poisson-Boltzmann equation, which takes into account the overlap of the two back-to-back double layers in the interfacial region and a smooth variation of dielectric properties across the interface. The analytical solution of this equation is obtained within the perturbation theory, which utilizes the smallness of the ratio of the 'mixed layer' thickness to the Gouy lengths in the adjacent solutions, an approximation which is valid for not too concentrated solutions and not too high voltage drops across the interface. Note that the most interesting results have been observed in the region of low ionic concentrations [6,10,12,18-22], and the theory is well justified there.

We derive a formula for capacitance, which demonstrates that the dependence of the capacitance on the nature of the ion is controlled by three integral parameters. These parameters are independent of the potential and ionic concentrations. They are expressed through z-dependent profiles of the short-range contribution to the free-energy of ion transfer across the interface and through the dielectric profile of the solvent solvent interface. The dependences of these integral parameters on the type of ion can be disclosed on the basis of a microscopic model of the interface [21-23] or molecular dynamics simulations [4]. On the other hand these parameters can be extracted from the capacitance measurements, and their dependence on the nature of the ion can be traced. Thus the theory suggests a new framework for the treatment of the capacitance data and establishes a relationship between experimental results and the microscopic structure of ITIES.

2. Double layer theory

Consider a contact between two immiscible electrolyte solutions (Fig. 1) characterized by dielectric constants, ε_1 and ε_2 , and Debye lengths, κ_1^{-1} and κ_2^{-1} , respectively. For 1–1 binary electrolyte solutions $\kappa_i^{-1} = (\varepsilon_i k_{\rm B} T / 8 \pi n_i^0 e^2)^{1/2}$, where n_i^0 is the bulk electrolyte concentration in the corresponding phase (*i* = 1,2), *e* is the charge of a proton, *T* is the temperature, and $k_{\rm B}$ is the Boltzmann constant. In the present paper we assume that the ions that have affinity to one solution

cannot penetrate into the *bulk* of the other solution, in other words the system 'stays inside' the potential window over which the interface is ideally polarizable. Then the bulk of solvent 1 ($z \ll 0$), contains only anions and cations of sort 1, $\binom{1}{1}$, while the bulk of solvent 2 ($z \gg 0$) contains ions of sort 2 ($\frac{1}{2}$). Here we also assume that the interface is flat and all properties of the system are functions of the distance from the interface, z, only.

2.1. Free energy functional

Density profiles of the ions and electric field distribution at the interface can be calculated using the functional of the free energy of two contacting electrolyte solutions.

We use the functional which contains the following generic terms: the *electrostatic energy*, $F_{\rm e}$, the short range contribution to the *free-energy of ion transfer* across the interface, $F_{\rm tr}$, and the *entropy* of diluted electrolytes, $F_{\rm s}$:

$$F = F_{\rm e} + F_{\rm tr} + F_{\rm s} \tag{1}$$

where

$$F_{e} = -\frac{1}{8\pi} \int_{-\infty}^{+\infty} dz \varepsilon(z) [\nabla \phi(z)]^{2} + e \sum_{i=1}^{2} \int_{-\infty}^{+\infty} dz \phi(z) (n_{i}^{+}(z) - n_{i}^{-}(z)) - EQ$$
(2)

$$F_{\rm tr} = \sum_{i=1}^{2} \int_{-\infty}^{+\infty} dz [f_i^+(z) n_i^+(z) + f_i^-(z) n_i^-(z)]$$
(3)

and

$$F_{\rm s} = k_{\rm B}T \sum_{i=1}^{2} \left\{ \int_{-\infty}^{+\infty} dz [n_i^+(z) \log(n_i^+(z)v_i) + n_i^-(z)\log(n_i^-(z)v_i) - (n_i^+ + n_i^-)] \right\}$$
(4)

The notation used is as follows: $\phi(z)$ and $n_i^{\pm}(z)$ are the electrostatic potential and concentrations of positive and negative ions of the kind *i*, v_i is a volume per molecule of the solvent (*i*), $\varepsilon(z)$ represents a dielectric profile at the interface between two solvents, functions $f_i^{\pm}(z)$ describe the free-energy profiles for a transfer of positive and negative ions of kind *i* across the interface, *E* is the overall potential drop across the interface, and *Q* and -Q are the overall charges in the first and second phases, respectively.

The last term EQ in the expression for electrostatic energy is the extra work needed to maintain the overall potential difference E. This term should be included in the free energy functional if the overall potential drop between two phases is given [32].

The diffuseness of the interface between the two liquids as well as the microscopic structure of the liquids lead to a smooth variation of dielectric properties across the interface. Thus the dielectric function $\varepsilon(z)$ can be written in the form

$$\varepsilon(z) = \varepsilon_0(z) + \delta\varepsilon(z) \tag{5}$$

where a step-wise dielectric function $\varepsilon_0(z) = \varepsilon_1 \theta(-z) + \varepsilon_2 \theta(z)$ corresponds to an idealized sharp interface, and a smearing function $\delta \varepsilon(z)$ differs from zero only in the microscopically thin interfacial layer of thickness λ .

Under the assumption of ideal polarizability of the interface, the free energy profile functions $f_i^{\pm}(z)$ must meet the following conditions:

$$f_1^{\pm}(z) \to 0 \text{ for } z \to -\infty \text{ and } f_1^{\pm}(z) \to \infty \text{ for } z \to \infty$$

$$f_2^{\pm}(z) \to \infty \text{ for } z \to -\infty \text{ and } f_2^{\pm}(z) \to 0 \text{ for } z \to \infty$$

$$(6)$$

and differ from the corresponding limiting values only in the microscopic interfacial regions of thicknesses λ_i^{\pm} . Introduction of the finite smearing lengths λ_i^{\pm} gives rise to a 'mixed boundary layer' where the overlapping of the two space-charge regions occurs. Recently numerical simulations [4,23,33] and mean field approximations [21,22] have been employed to calculate the free energy profile functions, and to study the dependence of the thickness of the mixed layer on the nature of the ions. Within the model of a sharp interface [5,6], where each sort of ion is either in water or in oil, all smearing lengths are equal to zero, $\lambda_i^{\pm} = 0$. Note also that a helpful simplifying assumption of $f_i^{\pm}(z)$ varying from zero to ∞ , first introduced in Ref. [21], is a good approximation only when the free energies of ion transfer are much larger than thermal energies. However, in the opposite case the interface is not polarisable.

2.2. Basic equations

The free energy Eq. (1) is a functional of two types of independent fields, ϕ and n_i^{\pm} . Relationships between these fields arise under equilibrium conditions. In order to derive equations for the electrostatic potential and ionic concentrations we minimize the grand potential, Ω

$$\Omega = F - k_{\rm B} T \sum_{i=1}^{2} \mu_i \int_{-\infty}^{+\infty} dz (n_i^+(z) + n_i^-(z))$$
(7)

with respect to ϕ and n_i^{\pm} . Here *F* is given by Eqs. (1)–(4) and μ_i is the chemical potential of positive and negative ions of the kind *i*, which is related to the bulk concentration of the corresponding electrolyte through the equation

$$\mu_i = k_{\rm B} T \ln(n_i^0 v_i) \tag{8}$$

In this way we obtain a Poisson–Boltzmann equation for the potential

$$\frac{\mathrm{d}}{\mathrm{d}z}\,\varepsilon(z)\frac{\mathrm{d}}{\mathrm{d}z}\,\psi(z) = -\frac{4\pi e^2}{k_{\mathrm{B}}T}\,N(\psi(z))\tag{9}$$

and expressions for the ionic concentrations through the potential and free energy profile functions

$$n_{1}^{\pm}(z) = n_{1}^{0} \exp[\mp (\psi(z) + g_{1}^{\pm}(z) - V)]$$

$$n_{2}^{\pm}(z) = n_{2}^{0} \exp[\mp (\psi(z) + g_{2}^{\pm}(z))]$$
(10)

Here we introduce the total charge density of ions

$$eN(\psi(z)) = e \sum_{i=1}^{2} [n_i^+(\psi(z)) - n_i^-(\psi(z))]$$
(11)

and dimensionless potentials, $\psi = e\beta\phi$, $V = e\beta E$, and free energy profile functions $g_i^{\pm} = \beta f_i^{\pm}$, where $\beta = (k_{\rm B}T)^{-1}$.

The potential obeys standard boundary conditions

$$\psi \to V \text{ as } z \to -\infty \text{ and } \psi \to 0 \text{ as } z \to \infty$$
 (12)

Within the model of a sharp interface $\exp[-g_1^{\pm}(z)] = \theta(-z)$ and $\exp[-g_2^{\pm}(z)] = \theta(z)$, which excludes penetration of ions through the interface, z = 0.

In order to solve Eq. (9), it is convenient to rewrite it in the form

$$\frac{\mathrm{d}}{\mathrm{d}z} \varepsilon_0(z) \frac{\mathrm{d}}{\mathrm{d}z} \psi(z) + \frac{4\pi e^2}{k_{\mathrm{B}}T} N_0(\psi(z))$$

$$= -\frac{\mathrm{d}}{\mathrm{d}z} \delta \varepsilon(z) \frac{\mathrm{d}}{\mathrm{d}z} \psi(z) - \frac{4\pi e^2}{k_{\mathrm{B}}T} [N(\psi(z)) - N_0(\psi(z))]$$
(13)

where $eN_0(\psi(z))$ is the total ionic charge density at the sharp interface

$$N_0(\psi(z)) = -2\theta(-z)n_1^0\sinh(\psi(z) - V)$$

-2\theta(z)n_2^0\sinh(\psi(z)) (14)

Equating the left-hand side of Eq. (13) to zero gives an equation which describes the potential distribution at the sharp interface. It has an exact analytical solution, which is nothing other than the Gouy–Chapman result for two back-to-back ionic double layers [5,6]. The right-hand side of Eq. (13) prescribes a correction to the Gouy–Chapman result due to diffuseness of the liquid | liquid interface and the possibility for ions to penetrate into the interfacial region of the 'unfriendly' medium. The diffuseness of the molecular and ionic profiles is localized [4,21–23,33] in a microscopically thin layer of not more than several molecular diame-

ters. The right-hand side of Eq. (13) is localized within this layer, the scale of which is determined by the largest of the smearing lengths,
$$\lambda, \lambda_i^{\pm}$$
.

In what follows we assume that the thickness of the mixed layer is much smaller than the Gouy lengths of both sides of the interface, i.e.

$$\lambda, \lambda_i^{\pm} < (\kappa_i^2 + (2\pi L_{\rm B}^{(i)}Q/e)^2)^{-1/2}$$
(15)

where $L_{\rm B}^{(i)} = e^2/\varepsilon_i k_{\rm B}T$ is the Bjerrum length for the solvent (*i*). This assumption is well justified for not too concentrated solutions and not too high voltage drops across the interface [4,21–23,33]. Then Eq. (13) can be solved analytically within the perturbation theory, which utilizes the smallness of the ratio of the intermediate layer thickness to the Gouy–Chapman lengths. The known analytical result for the potential distribution at a sharp interface, impermeable for ions serves as a zero-order approximation. The details of the perturbation approach for calculating the potential distribution are given in Appendix A.

2.3. Capacitance

The net result for the charge density in the first phase reads:

$$Q = en_{1}^{0} \int_{-\infty}^{+\infty} dz \{ \exp[-(\psi(z) + g_{1}^{+}(z) - V)] - \exp[\psi(z) - g_{1}^{-}(z) + V] \}$$

$$= \frac{k_{\rm B}T}{e} C_{\rm GC}^{0} \{ U_{0}(V) + U_{1}(V)L_{1} + U_{2}(V)L_{2} + U_{3}(V)L_{3} \}$$
(16)

Here C_{GC}^0 is the Gouy–Chapman capacitance of the two back-to-back ionic double layers separated by a sharp interface at the point of zero charge [5,6]

$$C_{\rm GC}^{0} = \frac{\varepsilon_1 \kappa_1 \varepsilon_2 \kappa_2}{4\pi (\varepsilon_1 \kappa_1 + \varepsilon_2 \kappa_2)} \tag{17}$$

 $U_0(V)$, $U_1(V)$, $U_2(V)$ and $U_3(V)$ are the functions of the overall potential drop and the bulk properties of the contacting electrolyte solutions (dielectric constants and ionic concentrations):

(18)

$$\begin{split} U_0(V) &= \frac{2\sinh(V/2)}{[1 + (8\pi C_{GC}^0/(\varepsilon_1\kappa_1 + \varepsilon_2\kappa_2))(\cosh(V/2) - 1)]^{1/2}} \\ U_1(V) &= \frac{2\pi u_1(V)}{\varepsilon_1} \Biggl[\frac{2C_{GC}^0\sinh^2(V/2)\varepsilon_2\kappa_2}{(\varepsilon_1\kappa_1 + \varepsilon_2\kappa_2) + 8\pi C_{GC}^0(\cosh(V/2) - 1)} + \frac{\varepsilon_1\kappa_1}{4\pi} \Biggr] \\ U_2(V) &= -\frac{2\pi u_2(V)}{\varepsilon_2} \Biggl[\frac{2C_{GC}^0\sinh^2(V/2)\varepsilon_1\kappa_1}{(\varepsilon_1\kappa_1 + \varepsilon_2\kappa_2) + 8\pi C_{GC}^0(\cosh(V/2) - 1)} + \frac{\varepsilon_2\kappa_2}{4\pi} \Biggr] \\ U_3(V) &= 8\pi C_{GC}^0 u_1(V)u_2(V)\sinh(V/2) \end{split}$$



Fig. 2. Potential dependences of the functions dU_1/dV , dU_2/dV and $10^{-1}dU_3/dV$. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $\kappa_1 = \kappa_2 = 0.3$ nm⁻¹.



Fig. 3. The effect of dielectric profile on the potential dependence of the normalized capacitance, $C/C_{\rm GC}^0$, for the interface impermeable for ions, $L_1 = L_2 = 0$. Curves correspond to the indicated values of L_3 in nanometers. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $\kappa_1 = \kappa_2 = 0.3$ nm⁻¹.

where

$$u_{1}(V) = \frac{(\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}) + \varepsilon_{1}\kappa_{1}(\cosh(V/2) - 1)}{(\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}) + 8\pi C_{GC}^{0}(\cosh(V/2) - 1)}$$

$$u_{2}(V) = \frac{(\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}) + \varepsilon_{2}\kappa_{2}(\cosh(V/2) - 1)}{(\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}) + 8\pi C_{GC}^{0}(\cosh(V/2) - 1)}$$
(19)

The integral parameters L_1 , L_2 and L_3 , which appear in Eq. (16) do not depend on potential and electrolyte concentrations. The parameters L_1 and L_2 depend only on the specific interaction of ions of the 'first' and the 'second' salt with the contacting solvents.

$$L_1 = \int_{-\infty}^{+\infty} dz \left[\exp(-g_1^+(z)) - \exp(-g_1^-(z)) \right]$$
(20)

$$L_2 = \int_{-\infty}^{+\infty} dz [\exp(-g_2^+(z)) - \exp(-g_2^-(z))]$$
(21)

In addition to L_1 and L_2 , the nature of ions enters the 'combined' parameter L_3 , which is also affected by the profiles of the dielectric constant across the interface:

$$L_{3} = \int_{-\infty}^{+\infty} dz \left[\frac{1}{2} \left(\frac{1}{\varepsilon_{1}} \exp(-g_{1}^{+}(z)) + \frac{1}{\varepsilon_{1}} \exp(-g_{1}^{-}(z)) + \frac{1}{\varepsilon_{2}} \exp(-g_{2}^{-}(z)) + \frac{1}{\varepsilon_{2}} \exp(-g_{2}^{-}(z)) \right) - \frac{1}{\varepsilon(z)} \right]$$
(22)

All three integrals, L_1 , L_2 and L_3 have the dimensions of length. If the profiles of $g_i(z)$ and $1/\varepsilon(z)$ have a common point of inversion, $L_1 = L_2 = L_3 = 0$. For 'asymmetric' integrands in Eqs. (20)–(22), the absolute values of these lengths may be of the order of the corresponding smearing lengths, λ, λ_i^{\pm} , but their sign can be positive or negative depending on the profiles of the integrands. The length L_3 is typically ε_2 -times smaller than L_1 and L_2 . However, L_3 enters into Eq. (16) with the coefficient, U_3 , which is ε_1 (ε_2)-times larger than U_1 (U_2). Thus the contribution of L_3 to the charge density is of the same order as the contributions of L_1 and L_2 .

Differentiation of Eq. (16) over E gives an expression for the potential dependent non-linear capacitance

$$C = \frac{dQ}{dE} = C_{GC}^{0} \left[\frac{dU_{0}}{dV} + L_{1} \frac{dU_{1}}{dV} + L_{2} \frac{dU_{2}}{dV} + L_{3} \frac{dU_{3}}{dV} \right]$$
(23)

The first term in Eq. (23) defines the Gouy–Chapman capacitance of two back-to-back ionic double layers separated by a sharp interface, and the three other terms are caused by the overlap of the double layers in the interfacial region and a smooth variation of dielectric properties across the interface.

3. Results and discussion

Let us summarize our findings.

3.1. Dependence of the capacitance on the nature of the ions

This is controlled by *length parameters*, L_1 , L_2 and L_3 (Eqs. (20)–(22)). These lengths are independent of the potential and ionic concentrations. They are expressed through z-dependent profiles of the free energy of ion transfer across the interface and through the dielectric profile of the solvent | solvent interface. The parameters $L_{1,2}$ represent differences in zero moments of cation and anion distributions across the interface for the salts that prefer phase '1' or '2', respectively. The parameter L_3 characterizes the combined effect of the variation of the dielectric properties and the smearing of ionic distribution across the interface.

3.2. Potential dependence of the capacitance

This is determined by the functions $dU_1(V)/dV$, $dU_2(V)/dV$ and $dU_3(V)/dV$, as exemplified in Fig. 2.

The functions $dU_0(V)/dV$ and $dU_3(V)/dV$ are symmetric in potential with a minimum at V = 0, while $dU_1(V)/dV$ and $dU_2(V)/dV$ are asymmetric functions of the potential. Thus the parameter L_3 influences the symmetric part of the capacitance, and L_1 and L_2 control the asymmetry. Figs. 3–6 illustrate this, showing the effects of the ionic nature and dielectric profile on the potential dependence of the capacitance. C(E)curves presented here exhibit the main features observed experimentally of the electrical capacitance of ITIES [12,18,19].



Fig. 4. The effect of penetration of a hydrophilic positive ion into the organic phase on the potential dependence of the normalized capacitance, C/C_{GC}^0 . Curves correspond to Gouy–Chapman results obtained for $L_1 = L_2 = L_3 = 0$, and to the values indicated of the parameter $L_1^+ = \int_{-\infty}^{+\infty} dz [\exp(-g_1^+(z)) - \theta(-z)]$ in nanometers. The figure is plotted for the case of no penetration of other ions through the interface and no smearing of the dielectric profile. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $\kappa_1 = \kappa_2 = 0.3$ nm⁻¹.



Fig. 5. The effect of penetration of a hydrophobic positive ion into the aqueous solution on the potential dependence of the normalized capacitance, C/C_{GC}^0 . Curves correspond to Gouy–Chapman results obtained for $L_1 = L_2 = L_3 = 0$, and to the values indicated of the parameter $L_2^+ = \int_{-\infty}^{+\infty} dz [\exp(-g_2^+(z)) - \theta(z)]$ in nanometers. The figure is plotted for the case of no penetration of other ions through the interface, and no smearing of the dielectric profile. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $\kappa_1 = \kappa_2 = 0.3$ nm⁻¹.



Fig. 6. The combined effect of smearing of the dielectric profile and the penetration of a hydrophobic positive ion into the aqueous solution on the potential dependence of the normalized capacitance, C/C_{GC}^0 . (1) Gouy–Chapman result; (2) the effect of ionic penetration only, $L_2^+ = \int_{-\infty}^{+\infty} dz [\exp(-g_2^+(z)) - \theta(z)] = 0.3$ nm; combined effects (3) $L_2^+ = 0.3$ nm and $\Delta \varepsilon = \int_{-\infty}^{+\infty} dz [(1/\varepsilon_1)\theta(-z) + (1/\varepsilon_2)\theta(z) - (1/\varepsilon(z))] = 0.02$ nm, and (4) $L_2^+ = 0.3$ nm and $\Delta \varepsilon = -0.02$ nm. The figure is plotted for the case of no penetration of other ions through the interface. $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $\kappa_1 = \kappa_2 = 0.3$ nm⁻¹.

3.3. Deviation from the Gouy–Chapman result

The microscopic parameters L_1 , L_2 and L_3 can take either positive or negative values depending on the shape of the free energy profiles and dielectric function. As a result the capacitance of ITIES can be higher as well as lower than that predicted by Gouy-Chapman theory for two back-to-back double layers (see Figs. 3-6). Both types of behavior have been observed experimentally [12,18,19] and through numerical simulations [21,23].

3.4. Role of the dielectric constants of the liquids in contact

Eqs. (18)–(23) and Figs. 2 and 4 show that the influence of the nature of the ion on the capacitance is inversely proportional to the dielectric constant of the phase where the corresponding ion is dissolved. Since the dielectric constant of water is much higher than that of an organic solvent, the effect discussed here should be mainly determined by the nature of the ion dissolved in the organic phase. As expected, the influence of the nature of the cation (anion) from the aqueous phase is observed only at positive (negative) potentials (see Fig. 4), but the nature of the cation (anion) in the organic phase is manifested predominantly in the negative (positive) range of potentials (see Fig. 5).

3.5. Effect of electrolyte concentration

Eqs. (18)–(23) suggest that deviations from the Gouy–Chapman capacitance and differences between

capacitances measured for different ions should increase with increasing ionic concentrations. Experimentally the effect of concentration on the C(E) curves has usually been assessed by using equally concentrated solutions of the electrolytes in each phase, $n_1^0 = n_2^0$. Our theory predicts that in this case the deviations should be proportional to the square root of the concentration. This behavior has been observed experimentally [12].

3.6. Linear capacitance and Parsons-Zobel plots

Eqs. (16) and (23) for the charge density and capacitance are simplified in the region of small potential drops across the interface, $|E| < k_{\rm B}T/e$. In this case the capacitance can be written in the form

$$C = C_{\rm GC}^0 (1 + 4\pi C_{\rm GC}^0 L_3) \tag{24}$$

Thus for small potentials the deviation of the capacitance of ITIES from the Gouy–Chapman result is determined by the length L_3 (which includes the effects of the microscopic structure of the interface and the nature of the ions). This parameter can be found from the Parson–Zobel plot (plotting the measured inverse capacitance 1/C versus $1/C_{GC}^{0}$), which according to Eq. (24) is described by the equation

$$\frac{1}{C} = \frac{1}{C_{\rm GC}^0} - 4\pi L_3 \tag{25}$$

Thus the value of L_3 is given by the intercept of the Parson-Zobel plot at $1/C_{GC}^0 \rightarrow 0$.

3.7. Apparent compact layer contribution

Formally, Eq. (25) can be written in terms of an apparent 'compact layer contribution',

$$\frac{1}{C} = \frac{1}{C_{\rm GC}^0} + \frac{1}{C_{\rm H}}$$
(26)

where the 'compact layer capacitance'

$$C_{\rm H} = -1/(4\pi L_3) \tag{27}$$

can be positive or negative. There is no reason to expect in this system a true 'compact layer' for the interface which is permeable for both salts. Our result thus rationalizes a long-standing puzzle: the meaning of the apparent compact layer contribution, its appearance for some systems and its absence in others. All in all, it clarifies the nature of the intercept of the Parsons–Zobel plot.

3.8. Deviation of the Parsons–Zobel plots from linearity

Within the present model, a distortion of the Parsons–Zobel plot from a straight line at high concentration is controlled by a term of the second order in the ratio of the mixed layer thickness to the Gouy-Chapman lengths, similarly to what takes place at the metal | electrolyte interface [34,35]. This requires a higher order perturbation theory, in the manner of Refs. [30,34], not considered here. Within the framework of this theory there is no deviation from the linear unit slope Parsons-Zobel behavior in the limit of low concentrations.

3.9. Effect of the nature of the ion on the pzc

The theory developed predicts also a dependence of the potential of zero charge (pzc) on the nature of the ions. From Eq. (16) at Q = 0 we obtain a very simple law

$$E_0 = \frac{k_{\rm B}T}{2e} (\kappa_2 L_2 - \kappa_1 L_1) \tag{28}$$

In contrast to the low voltage capacitance, which is determined by the length L_3 (see Eq. (24)), the position of the pzc depends on L_1 and L_2 . We see that the shift of the pzc with changing one of the ions is coupled (proportional) to the square root of the ionic strength of the salt this ion belongs to. This law deserves a systematic comparison with experimental data. The simplest test will be to plot $2eE_0/k_BT$ versus the inverse Gouy length κ_2 . Within the framework of our theory, we should obtain a straight line with a slope L_2 and the intercept $-\kappa_1L_1$.

3.10. The effect of ion replacement on the capacitance

Eqs. (20)–(23) show that replacing an ion A_i^{\pm} in the phase *i* by another ion B_i^{\pm} leads to the following change of capacitance

$$C(\mathbf{B}_i^{\pm}) - C(\mathbf{A}_i^{\pm}) = F_i^{\pm}(V)\Delta L_i^{\pm}$$
⁽²⁹⁾

Here the potential dependent functions,

$$F_{1}^{\pm}(V) = C_{\rm GC}^{0} \kappa_{1} \frac{\varepsilon_{2} \kappa_{2}(\varepsilon_{1} \kappa_{1} \cosh(V/2) + \varepsilon_{2} \kappa_{2})}{[\varepsilon_{2} \kappa_{2}(\exp(\mp V/2)) + \varepsilon_{1} \kappa_{1} + \varepsilon_{2} \kappa_{2}]^{2}}$$
(30)

$$F_{2}^{\pm}(V) = C_{\rm GC}^{0} \kappa_{2} \frac{\varepsilon_{1} \kappa_{1}(\varepsilon_{2} \kappa_{2} \cosh(V/2) + \varepsilon_{1} \kappa_{1})}{[\varepsilon_{1} \kappa_{1}(\exp(\pm V/2)) + \varepsilon_{1} \kappa_{1} + \varepsilon_{2} \kappa_{2}]^{2}}$$
(31)

and the lengths

$$\Delta L_{i}^{\pm} = \int_{-\infty}^{\infty} dz [\exp(-g_{i}^{\pm}(\mathbf{B}_{i}^{\pm},z)) - \exp(-g_{i}^{\pm}(\mathbf{A}_{i}^{\pm},z))]$$
(32)

are determined by the free energy profile functions $g_i^{\pm}(\mathbf{A}_i^{\pm},z)$ and $g_i^{\pm}(\mathbf{B}_i^{\pm},z)$ for ions \mathbf{A}_i^{\pm} and \mathbf{B}_i^{\pm} , respectively.

Eqs. (29)-(32) show explicitly that the effect of substitution of an anion (cation) in phase 1 should be observed only at negative (positive) potentials, the substitution of an anion (cation) in phase 2 influences the capacitance in the positive (negative) range of potentials.

According to Eqs. (29)–(32), the ratio $(C(\mathbf{B}_i^{\pm}) - C(\mathbf{A}_i^{\pm}))/F_i^{\pm}(V)$ (i = 1,2) should be independent of the potential and concentrations. By plotting this ratio we detect the difference of zero moments, ΔL_i^{\pm} , upon the replacement of ion \mathbf{A}_i^{\pm} by ion \mathbf{B}_i^{\pm} in the salt '*i*'.

4. Conclusions

The results of Section 3 suggest a new framework for the treatment of the capacitance data and establish a relationship between experimental results and the microscopic structure of ITIES. Fitting experimental data to Eqs. (17) and (23) one may evaluate the 'integral lengths' L_1 , L_2 and L_3 and establish their dependences on the type of ion. This procedure will give us the characteristic lengths, the zero moments of ion distributions across the interface and the inverse dielectric function. This is the maximal information on the microscopic properties of ITIES that can be extracted from the capacitance measurements, because microscopic properties are integrated in these moments.

The effect of the nature of the ion on the characteristic lengths can be studied by measuring changes in potential dependence of the capacitance due to variation of one of the ions in one of the salts. In so doing the composition and ionic strength of the second salt must be kept constant. The results of such experiments have already been reported by several groups [12,20].

Before following our recommendations one should verify the general predictions of the theory. A plot of $(C(\mathbf{B}_i^{\pm}) - C(\mathbf{A}_i^{\pm}))/F_i^{\pm}(V)$ as a function of the potential and/or salt concentrations would provide an ultimate test. According to Eqs. (29)–(32) this ratio should be independent of the potential and concentrations.

In fact this conclusion, as well as all other statements based on the potential independence of L_1 , L_2 and L_3 , is correct only under the conjecture that the properties of the interfacial region do not depend on potential. In principle, this assumption may be violated at high potential drops and ionic concentrations which give rise to electric fields, capable of modifying the structure of the solvent | solvent interface. However, for potentials and electrolyte concentrations typically used in experimental studies of ITIES this assumption is warranted since the electric field generated at the interface is $\leq 10^{-1}$ V nm⁻¹.

In our previous paper we considered a model of a sharp interface which is corrugated due to spontaneous, thermally excited capillary waves [36]. The model revealed that capillary waves induced enhancement of capacitance with respect to the Gouy–Chapman result. The enhancement is stronger the larger is the potential drop, as the latter enhances the amplitudes of capillary waves [36]. The nature of electrolyte ions was not included in the model.

In contrast, in the present paper the interface is translationally invariant in the interfacial plane, but it is smeared in the z-direction, and the nature of ions enters through the moments of ion distribution across the interface.

One may envisage future development of the theory by way of combining the two effects: the finite width of the interface and its roughening due to potential drop dependent capillary waves, similarly to the theory of capillary waves at liquid | liquid interfaces [2]. In principle this would be easy to do, if all the wavelengths of capillary waves were longer than L_1 , L_2 and L_3 . However, the short wavelength part of the spectrum of capillary waves appears to give an important contribution to the capacitance, and that is why such a combination requires a special investigation.

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Appendix A

In order to solve Eq. (13) we expand the potential in powers of the ratio of the mixed layer thickness to the Gouy-Chapman lengths,

$$\psi(z) = \psi_0(z) + \psi_1(z)$$
 (A1)

The lowest order term ψ_0 satisfies the Poisson-Boltzmann equation for a sharp interface

$$\frac{d}{dz} \varepsilon_0(z) \frac{d}{dz} \psi_0(z) + \frac{4\pi e^2}{k_B T} N_0(\psi_0(z)) = 0$$
 (A2)

and the boundary conditions

$$\psi_0(z = -0) = \psi_0(z = +0)$$

$$\varepsilon_1 \frac{d\psi_0(z = -0)}{dz} = \varepsilon_2 \frac{d\psi_0(z = +0)}{dz}$$
(A3)

$$\psi_0 \to V \text{ as } z \to -\infty \text{ and } \psi_0 \to 0 \text{ as } z \to \infty$$
 (A4)

This term coincides with the Gouy–Chapman result for ITIES

$$\psi_0(z) = \begin{cases} V - 4 \operatorname{arctanh}[\exp(\kappa_1(z+z_1))], \ z \le 0\\ 4 \operatorname{arctanh}[\exp(-\kappa_2(z+z_2))], \ z > 0 \end{cases}$$
(A5)

where

$$z_{1} = -2\kappa_{1}^{-1}\operatorname{arctanh}\left[\left(\frac{\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}\exp(-V/2)}{\varepsilon_{1}\kappa_{1} + \varepsilon_{2}\kappa_{2}\exp(V/2)}\right)^{1/2}\right]$$
$$z_{2} = 2\kappa_{2}^{-1}\operatorname{arctanh}\left[\left(\frac{\varepsilon_{2}\kappa_{2} + \varepsilon_{1}\kappa_{1}\exp(-V/2)}{\varepsilon_{2}\kappa_{2} + \varepsilon_{1}\kappa_{1}\exp(V/2)}\right)^{1/2}\right]$$
(A6)

The first-order term ψ_1 satisfies the following equations

$$\frac{\mathrm{d}}{\mathrm{d}z} \varepsilon_0(z) \frac{\mathrm{d}}{\mathrm{d}z} \psi_1(z) + \frac{4\pi e^2}{k_{\mathrm{B}}T} \psi_1 \frac{\delta N_0(\psi_0(z))}{\delta \psi}$$
$$= -\frac{\mathrm{d}}{\mathrm{d}z} \frac{\delta \varepsilon(z)}{\varepsilon(z)} \varepsilon_0(z) \frac{\mathrm{d}}{\mathrm{d}z} \psi_0(z)$$
$$-\frac{4\pi e^2}{k_{\mathrm{B}}T} [N(\psi_0(z)) - N_0(\psi_0(z))] \tag{A7}$$

with the boundary conditions

$$\psi_1(z = -0) = \psi_1(z = +0)$$

$$\varepsilon_1 \frac{d\psi_1(z = -0)}{dz} = \varepsilon_2 \frac{d\psi_1(z = +0)}{dz}$$

$$\psi_1 \to 0 \text{ as } z \to \pm \infty$$
(A8)

Here

$$\frac{\delta N_0(\psi_0(z))}{\delta \psi} = -2\theta(-z)n_1^0\cosh(\psi_0(z) - V)$$
$$-2\theta(z)n_2^0\cosh(\psi_0(z)) \tag{A9}$$

When deriving Eq. (A7) from Eq. (13) we kept in mind that the perturbation expansion Eq. (A1) is applicable to the slowly varying functions, the electrostatic potential, $\psi(z)$, and displacement, $\varepsilon(z)d\psi(z)/dz$, but not the electric field, $d\psi(z)/dz$, which varies rapidly across the interface.

The solution of Eq. (A7) can be written in the integral form

$$\psi_{1}(z) = \int_{-\infty}^{\infty} dz' G(z,z') \left\{ -\frac{d}{dz} \frac{\delta \varepsilon(z)}{\varepsilon(z)} \varepsilon_{0}(z) \frac{d}{dz} \psi_{0}(z) - \frac{4\pi e^{2}}{k_{\rm B}T} [N(\psi_{0}(z)) - N_{0}(\psi_{0}(z))] \right\}$$
(A10)

where G(z,z') is a Green function for Eq. (A7)

$$G(z, z') = -\frac{1}{2\epsilon_{2}\kappa_{2}B_{1}} [\psi_{1}^{(1)}(z)\psi_{1}^{(2)}(z')\theta(z'-z) +\psi_{1}^{(1)}(z')\psi_{1}^{(2)}(z)\theta(z-z')]$$
(A11)

functions $\psi_1^{(1)}(z)$ and $\psi_1^{(2)}(z)$ are solutions of Eq. (A7) with a zero right-hand side

$$\psi_1^{(1)}(z) = -\theta(-z) \frac{1}{\sinh[\kappa_1(z+z_1)]} + \theta(z) \\ \times \left\{ \frac{A_1}{\sinh[\kappa_2(z+z_2)]} + B_1 \left(\cosh[\kappa_2(z+z_2)] - \frac{z\kappa_2}{\sinh[\kappa_2(z+z_2)]} \right) \right\}$$

$$\psi_1^{(2)}(z) = \theta(z) \frac{1}{\sinh[\kappa_2(z+z_2)]} + \theta(-z)$$

$$\times \left\{ \frac{A_2}{\sinh[\kappa_1(z+z_1)]} + B_2 \left(\cosh[\kappa_1(z+z_1)] - \frac{z\kappa_1}{\sinh[\kappa_1(z+z_1)]} \right) \right\}$$
(A12)

and

$$A_{1} = \frac{\varepsilon_{2}\kappa_{2}}{2\varepsilon_{1}\kappa_{1}\sinh^{2}(\kappa_{2}z_{2})} [\sinh^{2}(\kappa_{2}z_{2}) - 1 -\cosh(\kappa_{1}z_{1})\cosh(\kappa_{2}z_{2})] B_{1} = \frac{\varepsilon_{2}\kappa_{2}}{2\varepsilon_{1}\kappa_{1}\sinh^{3}(\kappa_{2}z_{2})} [\cosh(\kappa_{1}z_{1}) + \cosh(\kappa_{2}z_{2})] A_{2} = \frac{\varepsilon_{1}\kappa_{1}}{2\varepsilon_{2}\kappa_{2}\sinh^{2}(\kappa_{1}z_{1})} [1 - \sinh^{2}(\kappa_{1}z_{1}) + \cosh(\kappa_{1}z_{1})\cosh(\kappa_{2}z_{2})] B_{2} = -\frac{\varepsilon_{1}\kappa_{1}}{2\varepsilon_{1}\kappa_{1}\sinh^{3}(\kappa_{1}z_{1})} [\cosh(\kappa_{1}z_{1}) + \cosh(\kappa_{2}z_{2})]$$
(A13)

Using the expansion of the potential given by Eqs. (A1), (A5) and (A6) and Eqs. (A11), (A12) and (A13) we obtain the expression for the charge density Q in the form of Eq. (16) in the text.

Calculating Q we kept only the terms of the zero and the first orders in the ratio of the mixed layer thickness to the Gouy–Chapman lengths. An essential feature of this problem that should be taken into account is a slow variation of the functions $\psi_0(z)$, $\psi_1^{(1,2)}(z)$, $\varepsilon_0(z)d\psi_0(z)/dz$ and $\varepsilon_0(z)d\psi_1^{(1,2)}(z)/dz$ over microscopic distances, λ, λ_i^{\pm} , which allows them to be factored out from the integrals containing functions localized within the microscopic interfacial layer.

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