Theory of Electrosorption of Water from Ionic Liquids

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Abstract

We propose and develop a classical density functional theory for the description of a minor amount of water dissolved in ionic liquid in the vicinity of an electrode. In addition to the electrostatic energy and lattice-gas mixing entropy terms, the utilised grand canonical potential contains several phenomenological terms/parameters that describe short-range interactions between ions of ionic liquid, water molecules and the electrode. Some of these have been earlier introduced in the theory of electrical double layer in pure ionic liquids. Based on this, we investigate the role of the remaining 'specific interaction' parameters – those that characterize possible (i) specific interaction of ions and molecules with the electrode, which are responsible for their specific adsorption; and (ii) hydrophilicity/hydrophobicity of ions. As a result we obtain water electrosorption isotherms as a function of the potential drop across the electrical double layer, investigate its asymmetry with respect to the sign of electrode potential, and establish the relationship between the sign of this asymmetry and hydrophobicity/hydrophilicity of cations and anions. We also calculate the effect of water electrosorption on the double layer differential capacitance which brings clear new features

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to its voltage dependence, some of which have been already experimentally observed.

Keywords: Ionic liquid, water, electrical double layer, electrosorption, differential capacitance

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1. Introduction

For a long time physical chemists were busy with dilute or moderately concentrated electrolytes, in which every dissolved ion is surrounded by a vast number of solvent molecules [1]. Solvent-in-salt, small additions of solvent molecules to an otherwise solvent-free electrolyte, is a relatively new, growing area of electrochemistry [2, 3, 4]. Consideration of solvent-in-salt came from the study of ionic liquids (ILs), which in their pure form are solvent-free electrolytes. ILs, however, rarely exist in their pure form. Indeed, they are good solvents that easily dissolve numerous solutes [5, 6]; with small additions of dipolar organic molecules being standard to 'lubricate' ILs, facilitating the mobility of ions, relevant in applications in which ion transport limitations are critical [5, 6]. But one may not even add any solvents; ILs may absorb molecules from the environment, e.g. water from humid air [5]. Thus, the fact that ILs are almost too good of a solvent could potential be a pitfall, because it might make the properties of ILs less controllable, lead to batch dependence, subject to fluctuations in air humidity, and alike.

Most concerned about it could be electrochemists. Indeed one of the advantages of ILs is their potentially large 'electrochemical window' [7]. Confined between two electrodes the IL is supposed not to take part in electrochemical reactions, if it is used as an inert electrolyte for running electrocatalytic reactions of molecules dissolved in it. But if there is a water impurity in the IL, water molecules may take part in electrolysis, which will lead to hydrogen and oxygen evolution, on the corresponding electrodes, obscuring other processes with reactants that we otherwise want to take place at those electrodes.

Similar phenomena could take place in electrochemical capacitors [8]; if we do not speak about hybrid supercapacitors, but pure double layer capacitors, we do not want to have any reactions at electrodes, i.e. of impurity water, because this will lead to discharge of the capacitor at voltages that could turn-on water electrolysis [9].

Recently, however, there were reports that water-in-salt, has much reduced reaction ability [2, 3]; interpretation of this observation is still ambiguous. On the other hand there are other reports where water starts to clearly react at electrodes, dramatically reducing the electrochemical window of the mixture.

To avoid this potential complication, experimentalists tend to perform investigations in super-refined systems: in ultra-dry atmosphere and with strongly hydrophobic ILs. But in reality, we may wish to deal with very different ILs – their enormous variety being itself one of the main advantages of this booming field [5, 6, 10]. We furthermore want to assemble our gadgets in normal room atmosphere and operate it in similar conditions. Such practically oriented scientist would be keen to know how water absorbed in IL will be distributed near the electrode. Will it adsorb onto the electrode surface and how does the adsorption depend on electrode polarization?

The first systematic computational study of these questions was reported by Feng *et al.* [11]. The main goal of that work was to find the distribution of water molecules near the electrode as a function of electrode polarization and the amount of dissolved water. The method of choice was molecular dynamics computer simulations, using well tested force field for ions, water, and the electrode [11]. It was anticipated that water, as a dipole, must be 'sucked' into the location of the peaks of electrical field, and several of such are present in the electrical double layer due to the overscreening effect [10]. Yet water is not a point dipole, but a molecule, which although small, has finite size and interaction preferences. Thus, it did not go exactly there, but was distributed nearby.

For the simulated ILs ([Bmim][PF_6] and [Bmim][Tf_2N])[11] it was found that close to the potential of zero charge, the concentration of water molecules at the interface (within 0.35 nm from it) is depleted relative to the bulk concentration. For positive surface charges, the interfacial water concentration monotonically increases with the magnitude of the charge, reflecting its propensity to stay close to hydrophilic anions that are in abundance near the positively polarized electrode. This causes the water concentration at the interface to transition from being depleted to enriched, but only above a certain value of the positive charge. When we polarize the electrode more negatively we enter water-depletion zone, and only after a certain value of the negative charge, the concentration of water at the interface starts to grow again, finally entering water enrichment zone.

There is currently intensive work going in both experimental characteri-

sation of these systems and further, more detailed, molecular dynamics simulations. In the meantime it would be good to have an elementary statistical mechanical theory that would allow to simulate effects of different specific interactions in the system on water electrosorption isotherms. Such theory is developed here.

Note that three of us has earlier published a theory of this kind for non-polar but polarizable molecules dissolved in ILs [12]. In the present paper we, on the contrary, neglect the electronic polarizability of water but concentrate on its permanent dipole moment which is expected to be the main effect. In addition we take into account specific interactions between ions, water molecules and the electrode. The redistribution of water, even at minute concentrations of it in the bulk, but eagerly populating the surface at large absolute values of voltage drop across the double layer, appears to affect the differential capacitance. It brings the latter new features, some of which may have been seen in the first experiments [13, 14].

The predictive power of this theory, as of any semi-phenomenological approach, should not be overestimated; it permits exploration of several main trends capable of answering certain questions. For example, the developed statistical mechanical theory of water-in-salt can answer such questions as: (i) How does the hydrophobicity of cations influence the electrosorption isotherm? (ii) How does this change the double layer capacitance curves? To a certain extent this study intends to give a framework for understanding various computer simulations, as well as for planning and interpretation of electrochemical experiments in mildly humid systems.

The structure of the article is as follows. First we outline the general formalism for an IL with dipolar solvent at a flat electrified interface. Full numerical solutions of the resulting system of equations is then obtained to study the effect of hydrophobicity/ hydrophilicity of ions and their specific interactions with the electrodes. For convenience, we included in the end a table of symbols and typical values of parameters/ variables, used in the numerical analysis.

2. Model and Basic Equations

We consider an IL with a small quantity of water homogeneously dissolved in it.[2] We assume that ions of the IL are singly charged, $\pm e$, while the water molecules carry the permanent dipole moment, p. [3] To describe the thermodynamic properties of such a system, we use the classical density functional theory with local density approximation [21, 22, 12, 23, 24, 25, 26]. We write the grand thermodynamic potential of the system as follows

$$\Omega = -\int \frac{\varepsilon_{IL}\varepsilon_0 \left(\nabla\psi(\mathbf{r})\right)^2}{2} d\mathbf{r} + \int \rho_c(\mathbf{r})\psi(\mathbf{r}) d\mathbf{r} - k_B T \int d\mathbf{r} c_0(\mathbf{r}) \ln\left(\frac{\sinh \beta p|\nabla\psi(\mathbf{r})|}{\beta p|\nabla\psi(\mathbf{r})|}\right)$$
$$-\frac{1}{2}\int d\mathbf{r} \sum_{i,j} A_{ij}^{-1}\phi_i(\mathbf{r})\phi_j(\mathbf{r}) + \int d\mathbf{r} \sum_i c_i(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r} \sum_i c_i(\mathbf{r}) W_i(\mathbf{r})$$
$$+ \int \left(f(c_+(\mathbf{r}), c_-(\mathbf{r}), c_0(\mathbf{r})) - \mu_+ c_+(\mathbf{r}) - \mu_- c_-(\mathbf{r}) - \mu_0 c_0(\mathbf{r})\right) d\mathbf{r}, \qquad (1)$$

where $\varepsilon_{IL}\varepsilon_0$ is the dielectric permittivity of pure IL (expressed in SI units) which is assumed to be a constant here, $c_\pm(\mathbf{r})$ are the local ionic concentrations, $\rho_c(\mathbf{r}) = e(c_+(\mathbf{r}) - c_-(\mathbf{r}))$ is the local charge density, $c_0(\mathbf{r})$ is the local concentration of solvent. The first two terms represent the electrostatic energy of the IL. The third term is the free energy of the ideal gas of water dipoles in electric field, $-\nabla\psi(\mathbf{r})$, in accordance with the Langevin theory,[4] where $\beta = 1/k_B T$ is inverse thermal energy with k_B and T denoting Boltzmann's constant and temperature, respectively. The fourth and fifth terms describe the regular solution free energy of short-range specific interactions between species with the matrix of the interactions, A_{ij} $(i, j = \pm, 0)$, and the fictitious auxiliary 'potentials' of the specific interactions, $\phi_j(\mathbf{r})$ $(j = \pm, 0)$,

[2]There is recent evidence which suggests that ions in ILs cannot be considered as an ideal mixture of cations and anions [15, 16, 17, 18]. However, since the system of small additions of water in IL is already considerably complex, we do not deal with the added complexity of the balance between spectating and participating states of ions [16, 19]. Such more general theory will be the topic of further investigations.

[3]Note that in present study we neglected the quadrupole moment of the water molecules, because its contribution to the local dielectric permittivity is rather small with respect to the contribution of dipole moment [20] and thus cannot qualitatively change the final results.

[4]Note that Langevin theory is expected, at least to a first approximation, to work reasonably well because the concentration of dipoles is small.

the meaning of which will become clearer later [21, 25, 27]. The sixth term is the energy of specific interactions of the ions and molecules with the 'external potentials', $W_i(\mathbf{r})$, which were introduced for generality to account for possible short-range interactions with these species and the electrode. In the seventh term, f determines the free energy density of the reference system, which in our case is the mixture without the electrostatic and short-range specific interactions between particles, and μ_j are the chemical potentials of species. We would like to stress that contributions of the electrostatic and short-range specific interactions are described by terms depending on the electrostatic potential ψ and auxiliary potentials ϕ_j.

Note that the electronic polarizability of water molecules can be easily take into account within the proposed here formalism [12]. However, making the final equations more cumbersome, its account will not change the final results, neither qualitatively nor quantitatively (due to a very small electronic polarizability of water molecules with respect to their orientational polarizability).

Rewriting the grand thermodynamic potential, Eq. (1), and using the Legendre transformation

$$P(\mu_+, \mu_-, \mu_0) = \mu_+ c_+ + \mu_- c_- + \mu_0 c_0 - f(c_+, c_-, c_0), \tag{2}$$

we obtain eventually

$$\Omega = -\int d\mathbf{r} \left(\frac{\varepsilon_{IL}\varepsilon_0 \left(\nabla\psi\right)^2}{2} + \frac{1}{2}\sum_{i,j} A_{ij}^{-1}\phi_i\phi_j \right)$$

$$-\int d\mathbf{r} P(\mu_+ - \phi_+ - e\psi - W_+, \mu_- - \phi_- + e\psi - W_-, \mu_0 - \phi_0 + \Psi - W_0), \tag{3}$$

where we introduce a new auxiliary function

$$\Psi(\mathbf{r}) = k_B T \ln\left(\frac{\sinh \beta p |\nabla\psi(\mathbf{r})|}{\beta p |\nabla\psi(\mathbf{r})|} \right). \tag{4}$$

Minimization of the functional, Eq. (3), with respect to the potentials ψ and ϕ_i, in accordance with the standard saddle-point approximation [23], yields the system of coupled equations

$$\nabla(\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})) = -e\left(\bar{c}_+(\mathbf{r}) - \bar{c}_-(\mathbf{r})\right), \tag{5}$$

and

$$\phi_i(\mathbf{r}) = \sum_j A_{ij}\bar{c}_j(\mathbf{r}), \tag{6}$$

where

$$\varepsilon(\mathbf{r}) = \varepsilon_{IL}\varepsilon_0 + \frac{p^2}{k_BT}\bar{c}_0(\mathbf{r})\frac{L(\beta p|\nabla\psi(\mathbf{r})|)}{\beta p|\nabla\psi(\mathbf{r})|} \tag{7}$$

is the local dielectric permittivity; $L(x) = \coth x - 1/x$ is the Langevin function. The equilibrium concentrations of species in the local density approximation are determined from

$$\bar{c}_\pm = \frac{\partial P}{\partial \mu_\pm}, \quad \bar{c}_0 = \frac{\partial P}{\partial \mu_0}. \tag{8}$$

Thus, if the explicit function $P = P(\mu_+, \mu_-, \mu_0)$ is known, then one can obtain the equations for the electrostatic potential $\psi(\mathbf{r})$ and potentials of specific short-range interactions ϕ_i, calculating the average concentrations of species by Eqs. (8). The bulk self-consistent potentials, $\phi_{i,b}$, can be obtained from inserting the bulk concentration of species, $c_{j,b}$, in Eqs. (6).

3. Mean-Field Theory with Entropically Independent Lattices

Let us consider the case of an IL with minor amounts of water dissolved in contact with a semi-infinite flat electrode. Placing the origin at the electrode surface, we write down the grand canonical potential per unit area as

$$\Omega[\psi, \phi_+, \phi_-, \phi_0] = -\int_0^\infty dz \left(\frac{\varepsilon_{IL}\varepsilon_0\psi'^2}{2} + \frac{1}{2}\sum_{i,j} A_{ij}^{-1}\phi_i\phi_j \right)$$

$$-\int_0^\infty dz P(\mu_+ - e\psi - \phi_+ - W_+, \mu_- + e\psi - \phi_- - W_-, \mu_0 - \phi_0 + \Psi - W_0), \tag{9}$$

where only the z dependence of fields are considered, and a prime replaces the differential operator to denote the derivative in this direction.

As a reference system we choose two entropically independent lattice gases, as depicted in Fig. 1, with equal cell volumes v, so that the mentioned above dependence of pressure on the chemical potentials can be written in the form

$$P(\mu_+, \mu_-, \mu_0) = \frac{k_BT}{v}\Big[\ln\left(1 + e^{\beta\mu_+} + e^{\beta\mu_-}\right) + \ln\left(1 + e^{\beta\mu_0}\right)\Big]. \tag{10}$$

A reference system with two independent lattices, one for the solvent and the other for IL, has been chosen for several reasons (note that this model should only work well when the ions in the IL are much larger than water, which is typically the case). Firstly, there have been reports that although the solubilities of small molecular species, such as carbon dioxide and water, are very high in ILs, the overall volume of the IL does not change significantly upon absorption of small molecules, suggesting e.g. that there could be an intercalative mechanism at action [28]. In fact, the volume between ions accounts for most of the free space in ILs, with only a vanishingly small fraction of the free space being associated to voids of the same size as ions (see Ref. 19 and references cited within for more details). Hence, a lattice-model that captures these features was required; one such model could be with two independent lattices with the same number density of occupation sites, achieved with the same volume of lattice sites. Of course, this assumes that the solvent is uniformly distributed in the IL bulk, which is not always the case [29]. Secondly, this assumption permits the resulting system of equations to be partially decoupled, simplifying matters over approaches that describe the system on a single lattice [30, 24].

Employing such a lattice model will tend to overestimate the steric interactions between water molecules and underestimate the interactions between ions and water. These deficiencies, however, can potentially be rectified through the short-range correlations. The employed lattice model saturates the water concentration at the same concentration as the maximal concentration of the IL. This does not necessarily have to be the case, since the elementary lattice volume of the water should be taken smaller than of the IL lattice. Further investigation will be required to determine if this assumptions is justified, but for qualitative trends it is certainly adequate, at least before the surface layer of water is saturated.

It is generally the case that the cations and anions in ILs are not of the same size; they might not even have the same shape. This can influence physical observables, such as the differential capacitance [21, 31]. However, since the primary concern here is the electrosorption of water, and since asymmetric steric interactions can be introduced through the short-range correlation terms, we utilise a simpler model where the ions are assumed to have the same volume.

We introduce the specific interaction parameters between ions, $A_{++} = vA_c$, $A_{--} = vA_a$, $A_{+-} = A_{-+} = vA_{ca}$, and between water molecules $A_{00} = vA_w$. We account for the specific interactions between ions and water

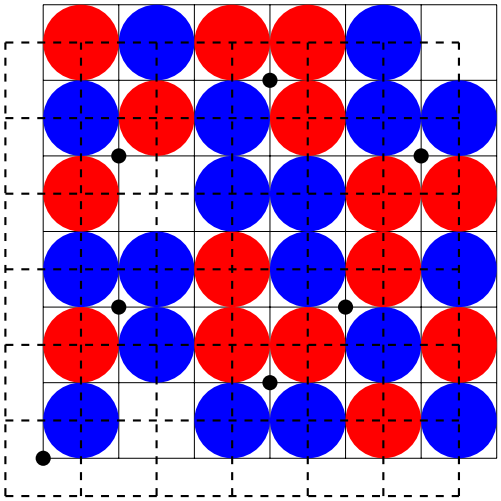


Figure 1: Representation of intercalating solvent in an IL. The red and blue circles represent cations and anions, and the smaller black circles water. The solid lines correspond to the lattice of the ions, while the dashed lines are for the water lattice.

molecules through parameters: $A_{0+} = A_{+0} = vB_{cw}$ and $A_{0-} = A_{-0} = vB_{aw}$. Thus the system of nonlinear equations on self-consistent fields takes the form

$$\phi_0 = A_w v\bar{c}_0 + B_{cw} v\bar{c}_+ + B_{aw} v\bar{c}_-, \tag{11}$$

$$\phi_+ = B_{cw} v\bar{c}_0 + A_c v\bar{c}_+ + A_{ac} v\bar{c}_-, \tag{12}$$

$$\phi_- = B_{aw} v\bar{c}_0 + A_{ac} v\bar{c}_+ + A_a v\bar{c}_-. \tag{13}$$

Solution of this system of equations gives the potentials of the specific interactions as functions of local electrostatic potential $\psi(z)$ and electric field $\mathcal{E} = -\psi'(z)$, i.e $\phi_i = \phi_i(\psi, \mathcal{E})$. The latter functions allow us to obtain the equilibrium concentrations of species as functions of electrostatic potential and electric field from the following relations

$$\bar{c}_+ v = \frac{e^{\beta(\mu_+ - \phi_+ - e\psi - W_+)}}{1 + e^{\beta(\mu_+ - \phi_+ - e\psi - W_+)} + e^{\beta(\mu_- - \phi_- + e\psi - W_-)}}, \tag{14}$$

$$\bar{c}_- v = \frac{e^{\beta(\mu_- - \phi_- + e\psi - W_-)}}{1 + e^{\beta(\mu_+ - \phi_+ - e\psi - W_+)} + e^{\beta(\mu_- - \phi_- + e\psi - W_-)}}, \tag{15}$$

$$\bar{c}_0 v = \frac{\frac{\sinh(\beta p\mathcal{E})}{\beta p\mathcal{E}} e^{\beta(\mu_0 - \phi_0 - W_0)}}{1 + \frac{\sinh(\beta p\mathcal{E})}{\beta p\mathcal{E}} e^{\beta(\mu_0 - \phi_0 - W_0)}}. \tag{16}$$

The relations (14-16), in turn, allow us to determine the relations for the chemical potentials. Indeed, in the bulk it is assumed that $W_{\pm}(\infty) = W_0(\infty) = 0$, $\psi = 0$, and $\bar{c}_i(\infty) = c_{i,b}$. The Eqs. (14)-(15) must be solved simultaneously, where the electroneutrality condition ($c_{+,b} = c_{-,b}$) holds, to afford

$$\mu_{\pm} = \phi_{\pm,b} + k_B T \ln\left(\frac{\gamma/2}{1-\gamma}\right) \tag{17}$$

the chemical potential of cations and anions in the bulk [21, 25]; where $\gamma = 2cv$ is the standard packing parameter, $c = c_{\pm,b}$ are the ionic concentrations in the bulk. The chemical potential of water can be directly obtained from Eq. (16) through algebraic manipulations

$$\mu_0 = \phi_{0,b} + k_B T \ln\left(\frac{\gamma_w}{1-\gamma_w}\right); \tag{18}$$

where $\gamma_w = c_{0,b} v$ is the packing parameter of the water molecules on its lattice.

In order to calculate the electrostatic potential profile, we have to solve the following modified Poisson-Fermi equation

$$\frac{d}{dz}\left(\varepsilon(z)\psi'(z)\right) = -\frac{e\gamma}{2v}\frac{e^{\beta\left(\phi_{+,b}-\phi_{+}-e\psi-W_{+}\right)} - e^{\beta\left(\phi_{-,b}-\phi_{-}+e\psi-W_{-}\right)}}{1-\gamma+\frac{\gamma}{2}\left[e^{\beta\left(\phi_{+,b}-\phi_{+}-e\psi-W_{+}\right)} + e^{\beta\left(\phi_{-,b}-\phi_{-}+e\psi-W_{-}\right)}\right]} \tag{19}$$

(obviously in which all variables on the right hand side depend on z). The local dielectric permittivity, namely Eq. (7), can be explicitly stated as

$$\varepsilon(z) = \varepsilon_{IL}\varepsilon_0 + \frac{p^2\gamma_w}{k_B T v}\frac{\mathcal{G}(\beta p\mathcal{E})e^{\beta\left(\phi_{0,b}-\phi_0-W_0\right)}}{1-\gamma_w\left(1-\frac{\sinh(\beta p\mathcal{E})}{\beta p\mathcal{E}}e^{\beta\left(\phi_{0,b}-\phi_0-W_0\right)}\right)}, \tag{20}$$

where an auxiliary function $\mathcal{G}(x) = (\sinh(x)L(x))/x^2$ has been introduced. This equation closes the system of equations on $\phi_{\pm,0}$ and ψ, as seen in Eqs. (11)-(16), (19) and (20).

It is most natural to solve the system of equations with the following boundary conditions

$$\psi(0) = \Phi,\ \psi(\infty) = 0, \tag{21}$$

where Φ is the total potential drop across the double layer.

The electrode surface charge density can be calculated by the standard relation

$$\sigma = \varepsilon_s \mathcal{E}_s, \tag{22}$$

where $\varepsilon_s = \varepsilon(0)$ and $\mathcal{E}_s = \mathcal{E}(0)$ are, respectively, the dielectric permittivity and the electric field values on the electrode. The double layer differential capacitance can be calculated from

$$C = \frac{d\sigma}{d\Phi}. \tag{23}$$

For the numerical calculations we assume $W_{\pm}(z) = W_{c/a}H(l-z)$ and $W_0(z) = W_0 H(l-z)$, where $H(z)$ is the Heaviside step-function and $W_{c/a} \leq 0$ are the energy of the specific adsorption of the ions onto the electrode; $W_0 > 0$ is the electrode hydrophobicity, and $W_0 < 0$ is electrode hydrophilicity; l is the effective thickness of the layer in which the specific interactions of ions and water molecules with the electrode take place.

For the sake of simplicity, we neglect the specific interaction (hydrogen bonding) between the water molecules, i.e assume $A_w = 0$. The latter assumption is motivated by the fact that, in the presented study, the water concentration is small ($\gamma_w << 1$). Although, when a dense monolayer of water molecules adsorbed at the electrode surface, hydrogen bonding may take place between them; such situation only occurs at large electrode polarizations, however. Thus the error related with neglecting short-range correlations for water may manifest itself only within the a narrow range of potentials, just before the formation of the complete monolayers ($v\bar{c}_0 = 1$).

Before the numerical calculations are presented, it is insightful to perform linear response analysis to obtain simple equations for trends near the potential of zero charge. Here we are concerned with the behaviour of small quantities of water absorbed in IL, so we shall do such analysis only for the water concentration. To simplify matters, we assume that $A_c = A_a = A_{ac} = 0$ and that $W_i = 0$ for all i, and thus focus on the effect of hydrophobicity/hydrophilicity of cations and anions (including correlations between ions will not change the qualitative results since they appear through rescaling the charge which multiplies the electrostatic potential [25]). Under these assumptions it is reasonable to take $\phi_{\pm,b} - \phi_{\pm} \approx 0$. The lowest order expansion is then

$$v\bar{c}_0 = \gamma_w \Big[1 + \frac{\gamma}{2}\beta(B_{cw} - B_{aw})\beta e\psi\Big]. \tag{24}$$

When there are no short-range correlations between ions and water, or if they are the of same sign and magnitude ($B_{cw} = B_{aw}$), then, at linear response, to the lowest order, the water concentration does not change. Otherwise water gets expelled or invited into the double layer. At linear response, cations and anions are exchanged, with no compression of the double layer [25]. Hence, if water has an energetic preference for one ion, it would be expected that water is enriched in the double layer when that ion accumulates in the double layer, and is diminished when it is depleted. This is exactly what Eq. (24) states.

To investigate the case of symmetric hydrophobicity/hydrophilicity constants ($B_{cw} = B_{aw} = B$) we need to take the next order expansion

$$v\bar{c}_0 = \gamma_w \Big[1 + \frac{1}{6}(\beta p \mathcal{E})^2 - \beta B \frac{\gamma}{2} (\beta e \psi)^2 \Big]. \tag{25}$$

When there are no short-range correlations between ions and water, then solvent concentration only increases, owing to dipoles response to electric field. Whereas, for sufficiently large hydrophobicity constants between water and ions, the response differs: solvent is expelled from the double layer. At sufficiently large potentials, water would overcome this repulsion and accumulate in the double-layer again. Thus, creating a highly non-monotonic W-shaped curve.

4. Numerical Results and Discussions

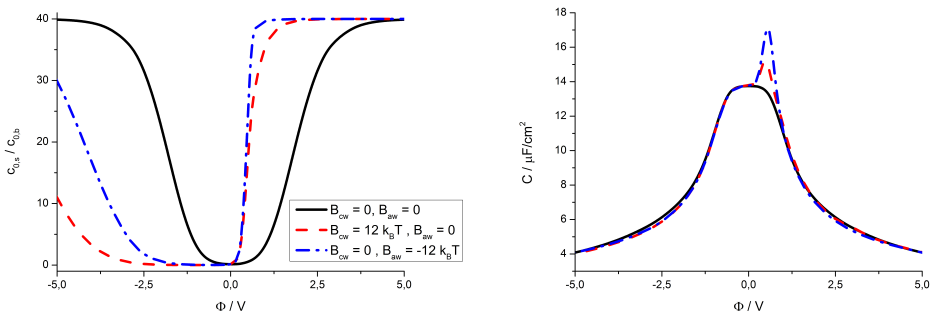
Turning to the numerical solutions of the system of equations, we assume that the thickness in which the specific attraction of the cations to the electrode takes place is $l \simeq v^{1/3}$ (i.e. of the order of the molecular scale), and we consider the following values: $\varepsilon_{IL} = 3.5$, $p = 1.8$ D, $T = 338$ K,[5] $v^{1/3} = 0.7$ nm, $\gamma = 0.8$, $\gamma_w = 0.025$, $A_c = A_a = 50$ $\mathrm{k_B T}$[6] and $A_{ca} = 0$. For further details of parameters/variables see Tab. 1.

[5]Such slightly elevated temperature was used to be consistent with MD-simulations of Ref. 11, with which we compare our results.

[6]Such a value might seem large, but estimates for ILs suggest that it is well within the range which could be expected for an ion repelling a full coordination shell of coions. Moreover, such value gives good agreement with experiments [19].

Water Electrosorption

Fig. 2a shows the dependences of water concentration on the electrode, expressed in units of the bulk water concentration c_{0s}/c_{0b}, as a function of the applied voltage (electrosorption isotherms) for three different cases: (i) IL without specific interactions with water ($B_{cw} = B_{aw} = 0$), (ii) hydrophobic cations ($B_{cw} > 0$, $B_{aw} = 0$), and (iii) hydrophilic anions ($B_{cw} = 0$, $B_{aw} < 0$). In all considered cases we turned on the electrode hydrophobicity effect (it is assumed that $W_0 = 2.5$ k$_B$T), so that water is depleted with respect to the bulk at zero potential drop.



(a) (b)

Figure 2: (a) - **The hydrophobicity/hydrophilicity of the ions has a strong influence on the behaviour and symmetry of electrosorption curves.** Calculated dependence of water concentration at the surface of the electrode (c_{0s}), scaled to its bulk value (c_{0b}), as a function of potential drop across the double layer. The curves are shown for three cases of short-range correlations between water and ions: (i) IL without specific interactions with water (solid black), (ii) IL with hydrophobic cations (dashed red), and (iii) IL with hydrophilic anions (dot-dashed blue). The plots are shown for $W_0 = 2$ k$_B$T; refer to the first paragraph of this section for the other parameters. (b) - **An IL with hydrophobic cations or hydrophilic anions can introduce sattelite maximum on the differential capacitance profile.** Differential capacitance as a function of potential drop across the double layer shown for the three cases considered in (a) of this figure. All parameters and colour coding are the same as in (a) of this figure.

As is seen, in the absence of the specific ion-water interactions, the electrosorption curve is symmetric. In that case, the electric field gradient, taking place due to the electrode charge screening, leads to attraction of water molecules to it (so-called, dielectrophoretic force [32]), so that increase in the

potential drop always results in the monotonic increase in the water concentration.

However, the effects of cationic hydrophobicity or anionic hydrophilicity make the electrosorption curves strongly asymmetric, as indicated by Eq. (24). Indeed, in a positive voltage region, water concentration grows abruptly in both cases, whereas at the negative voltages, water concentration decreases, attains a minimum, and, further, slowly grows.

In case of the hydrophobic cations and water-neutral anions, at the positive voltages, the number of the latter in the electrical double layer exceeds the number of hydrophobic cations. Thereby, even small applied voltage leads to a substantial water concentration enhancement on the electrode. On the other hand, at the negative voltages, prevailing numbers of the hydrophobic cations over the water-neutral anions tends to expel the water molecules from the electrical double layer. These described trends at linear response can be easily understood from Eq. (24). Two competing factors – dielectrophoretic force and cationic hydrophobicity – lead to non-monotonic water concentration dependence on the potential drop in the region of its negative values, in qualitative agreement with the first simulation [11].

For the case of hydrophilic anions, we have also the sudden increase in the water concentration on the electrode at positive voltages and a minimum on the electrosorption curve at negative voltages. The water concentration behavior at the positive voltages can be explained by the following arguments: prevailing numbers of hydrophilic anions over the water-neutral cations in the electric double layer causes, even at linear response, abrupt increase in the water concentration on the electrode, as rationalised by Eq. (24). In that case both factors, the dielectrophoretic force and the anionic hydrophilicity, lead to effective attraction of the water molecules to the electrode at positive voltages.

At the negative potential drops, electrostatic repulsion between the negatively charged electrode and the hydrophilic anions tends to first decrease the number of the latter in the electric double layer. Thereby, the anions leave the electric double layer together with the water molecules attracted to them due to the anionic hydrophilicity. That is why, as indicated by Eq. (24), the water concentration initially decreases at the small negative voltages (to see this in Fig. 2a one has to zoom into the potential of zero charge). Increase of the potential drop in its absolute value leads to dielectrophoretic attraction of water to the electrode. At negative voltages this becomes comparable with the anionic hydrophilicity effect, leading to minimum of the

water concentration and its subsequent growth.

The Effect of Water Electrosorption on Differential Capacitance

It is very important to understand how the water concentration on the electrode manifests itself in the differential capacitance. Fig. 2b displays the differential capacitance profiles for the three cases mentioned above using the same colour coding. When anion-water and cation-water specific interactions are absent, the differential capacitance profile has a standard bell-shape form. However turning on the strong specific interactions between the ions and the water molecules qualitatively changes the differential capacitance curve. In both the hydrophobic cation and hydrophilic anion cases, there is a pronounced maximum on the differential capacitance profile at positive voltages. Its origin is clear in view of the curves shown in Fig. 2a, if we keep in mind that the presence of water in the double layer reduces Coulomb repulsion between the ions and eases their accumulation there, and also directly increases the differential capacitance through the dielectric constant at the interface.

The Effect of Electrode Hydrophobicity

Now we turn to discussion of the electrode hydrophobicity effect on the electrosorption curves and differential capacitance. Fig. 3a shows the electrosorption curves for different electrode hydrphobicity parameter, W_0, for the hydrophobic cation case. As is seen, increase in the electrode hydrophobicity results in the expectable behavior of the electrosorption curve – monotonic decrease in the water concentration on the electrode at all potential drop values. Fig. 3b demonstrates the capacitance profiles at the same parameters as in the Fig. 3a. It is seen that increase in the electrode hydrophobicity reduces the sattelite maximum on the differential capacitance profile, making it more symmetric. The same trends take place in the hydrophilic case of anions (see, Figs. 3c-3d). The reason for the trend is obvious: hydrophobicity of the electrode suppresses water molecules approach towards the electrode.

Electrosorption Isotherm

Figures 4a-4b demonstrate the electrosorption curves and the differential capacitance profiles at different water concentrations. As is seen, increase in the bulk water concentration leads to monotonic increase in the water concentration on the electrode and more pronounced satellite maximum in

the differential capacitance curve. The latter is in qualitative agreement with the experimental behavior of the differential capacitance presented in Refs. 13 and 14.

Specific Adsorption of Cations and Differential Capacitance

Finally, we would like to discuss how the specific adsorption of ions onto the electrode influences the differential capacitance. For the sake of simplicity, we consider below a case of pure IL, taking into account specific adsorption of the cations onto the electrode. As is seen in Fig. 5, increase of the propensity of the cations to adsorb at the electrode in the specific adsorption energy W_c causes a shift of the differential capacitance maximum to the positive voltage values. Such a behavior of the differential capacitance is in agreement with that predicted in recent theoretical study [33].

It can be seen in Fig. 5 that the differential capacitance curve is flatter near the potential of zero charge that the analytical perturbation/interpolation theory [25]. This occurs because the energetic barrier due to the short-range correlation terms to bringing additional counterions into the electrical double layer increases. This hampers the compression of electrical double layer and halts the decrease in capacitance. This feature is captured in the full numerical solution, but not the analytical perturbation/interpolation theory [25].

5. Conclusion

A statistical mechanical theory of water-in-ionic liquid at an electrified interface was developed and explored. The dipolar nature of water was described with Langevin theory; and terms were included in the grand canonical potential to describe all possible short-range correlations between ions and water, and specific interactions of ions and water with the electrode.

The effects of hydrophobicity/hydrophilicity of ions were explored in the electrosorption isotherms, where non-monotonic behavior was found.

Due to electrosorption of water the differential capacitance has a new feature: a sattelite maximum. Naturally, that peak increases with the concentration of water in the bulk because that amplifies electrosorption.

Specific interactions between water and the electrode were investigated for hydrophilic anions and hydrophobic cations. As expected, at more hydrophobic electrodes the electrosorption is relatively weaker; correspondingly, the sattelite peak gets suppressed.

Although in this paper we have focused on the electrosorption of water, the presented theory is phenomenological and could be applied to any dipolar solvent additives in an ionic liquid (provided the solvent molecules are significantly smaller than the ions). We hope that this basic theory stimulates further experimental and computational investigation into water-in-ionic liquid and will be helpful in the interpretation of future results.

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Symbols, parameters/variables, typical values

Symbol	Name	Typical Value
ε_0	Permittivity of free space	8.85 Fm^{-1}
e	Elementary charge	1.60x10^{-19} C
k_B	Boltzmann constant	1.38x10^{-23} JK^{-1}
T	Temperature	338 K
β	Inverse thermal energy	2.14x10^{20} J^{-1}
ε_{IL}	Dielectric constant of IL	3.5
p	Dipole moment of water	1.8 D [(i)]
A_c or A_a	Repulsive ion short-range correlation	50 k_BT [(ii)]
A_{ca}	Attractive ion short-range correlation	0 k_BT [(ii)]
B_{cw}	Cation-water short-range correlation	0-12 k_BT
B_{aw}	Anion-water short-range correlation	-12-0 k_BT
W_c	Cation specific interaction with electrode	-20-0 k_BT
W_a	Anion specific interaction with electrode	0 k_BT
W_0	Water specific interaction with electrode	0-4 k_BT
l	length of specific interaction with electrode	0.7 nm
$\gamma = 2vc_{\pm,b}$	Compacity of IL	0.8
$\gamma_w = vc_{0,b}$	Compacity of water	0-0.025
v	Volume of IL ion	0.343 nm^3 [(iii)]
ψ	Electrostatic potential	-5-5 V
Φ	Electrostatic potential drop across the double layer	-5-5 V
$\mathcal{E} = -\nabla\psi$	Electric field	-
C	Differential capacitance	-
σ	Surface charge density	-
ρ_c	Charge density	-
c_i or $\bar{c}_i$	Concentration	- [(iv)]
ϕ_i	Fictitious field of short-range correlations	-
μ_i	Chemical potential	-
P	Pressure	-
Ω	Grand potential	-

Table 1: (i) - Taken to reproduce bulk water dielectric constant. (ii) - Value taken to reproduce typical experimental values. It is within the range of the expected values from considering Coulomb interactions between close neighbours. [(iii)] - Bulky ions are considered here because this is when the model is most appropriate. [(iv)] - The bar denotes concentrations in the electrical double layer. General note for subscripts: s stands for surface, b for bulk, $\pm$ for cations and anions, and 0 or w for water.

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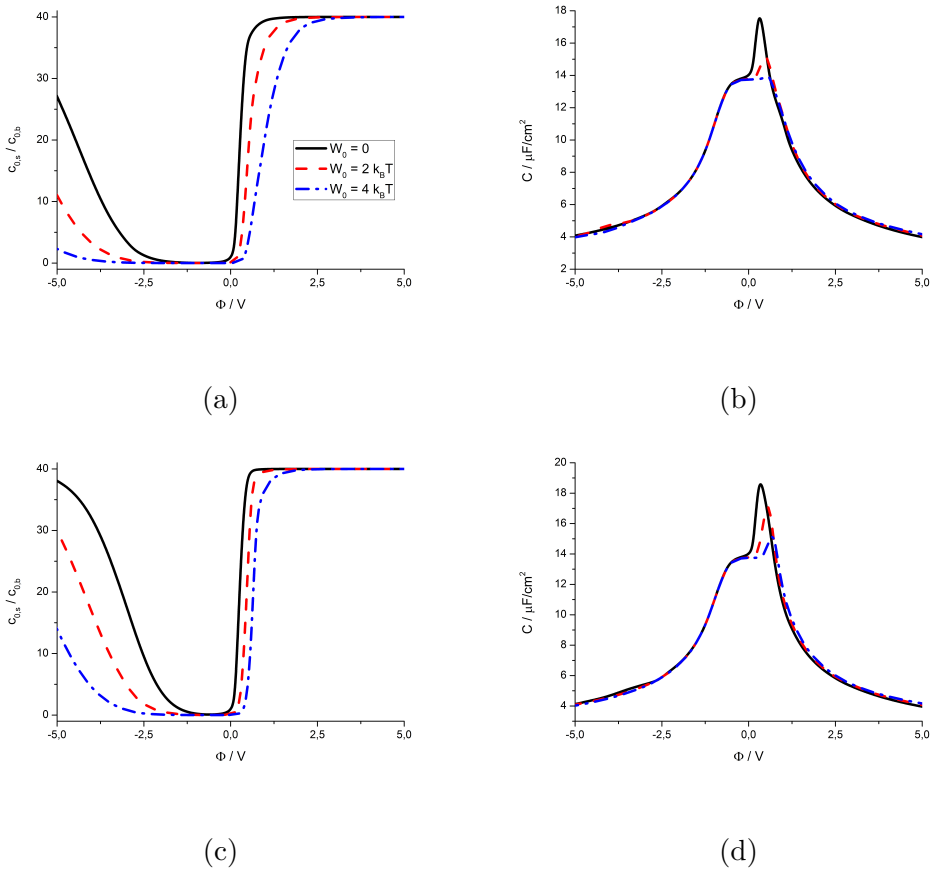
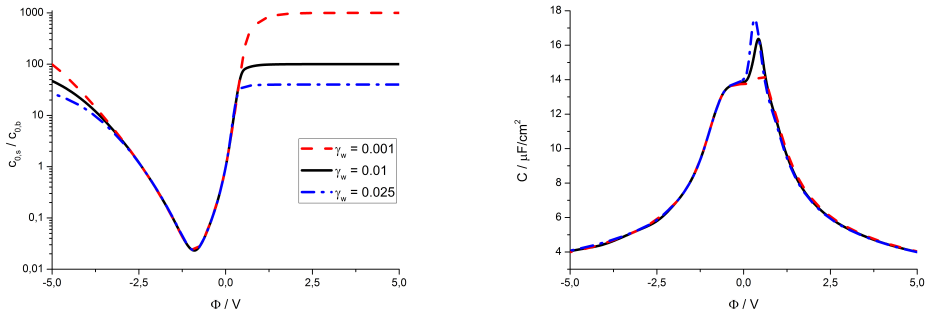


Figure 3: (a) and (c) - **Increasing electrode hydrophobicity causes the water concentration at the electrode surface to decrease, more so at negative voltages where hydrophobic cations (a) and hydrophilic anions (c) also deplete water from the surface.** Calculated dependence of water concentration at the surface of the electrode (c_{0s}), scaled to its bulk value (c_{0b}), as a function of potential drop across the double layer for hydrophobic cations (a) and hydrophilic anions (c) at different electrode hydrophobicity, W_0, as indicated in the figure. The plots are shown for $B_{cw} = 12$ k$_B$T and $B_{aw} = 0$ in (a) and $B_{cw} = 0$ and $B_{aw} = -12$ k$_B$T in (c); refer to the first paragraph of this section for the other parameters. (b) and (d) - **Increasing electrode hydrophobicity suppresses the sattelite maximum on the differential capacitance profile.** Differential capacitance as a function of potential drop across the double layer for IL with hydrophobic cations (b) and hydrophilic anions (d) at different electrode hydrophobicity, W_0. Plot (b) has the same parameters and colour coding as (a); while (d) has the same parameters and colour coding as (c).



(a) (b)

Figure 4: **Increase in the water concentration makes the satellite maximum more pronounced.** The electrosorption curves (a) and differential capacitance (b) at different bulk water concentrations, as indicated in the figure. The plots are shown for $B_{aw} = 0$, $B_{cw} = 12$ k_BT , $W_0 = W_a = W_c = 0$; refer to the first paragraph of this section for the other parameters.

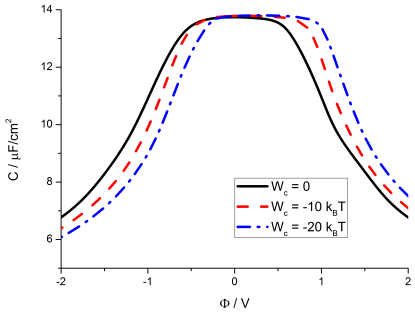


Figure 5: **Specific adsorption of ions shifts the differential capacitance curves.** Differential capacitance profiles plotted for the pure IL for different adsorption energy, W_c, of the cation onto the electrode, the values for which can be seen in the figure. The data are shown for $\gamma_w = 0$ and $W_a = 0$; refer to the first paragraph of this section for the other parameters.