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Adsorption of ions at the interface oil|aqueous electrolyte and at interfaces with adsorbed alcohol

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ABSTRACT

We investigate the applicability of the Schmutzer's model for three types of interfaces: aqueous electrolyte|alkane, aqueous electrolyte|long chained alcohol phase, and aqueous electrolyte|alkane with adsorbed alcohol. The model predicts a strong decrease of the electrolyte desorption at water|alcohol interface in comparison with water|alkane, in quantitative agreement with the tensiometric data. The effect is related to the penetration of the alcohol –OH group into the surface layer of the aqueous solution. The same model predicts a decrease with the electrolyte concentration of the chemical potential of the alcohol molecules adsorbed at the water|oil interface, which results in an increase of the adsorption activity of oil-soluble alcohols, again in quantitative agreement with the experiment. The analysis of the deviations of Schmutzer's model predictions from the experimental data for large polarizable anions allows making qualitative conclusions for the magnitude of the ion-specific hydrophobic and dispersion forces at water|gas and water|oil interfaces.

1. Introduction

All properties of the interface between aqueous electrolyte and an oil phase (W|O) depend on the salt concentration C_{el} and the nature of the ions. Examples are the interfacial tension σ [1–7], the electrokinetic ζ-potential of oil droplets [8–10], the adsorption of nonionic [11] and ionic [12] surfactants at the W|O interface, etc.

There are several large classes of interfaces, which would interact with the electrolyte differently. Here we investigate the simplest case: the interface is between immiscible aqueous electrolyte and oil, and oil does not dissolve salt (class I). Another class is the interface between two electrolyte solutions (e.g., the oil phase is polar and dissolves electrolyte) where ion partition and Galvani potential plays an important role for most interfacial properties [13–16,5]. A third class of interfaces is the one where water and oil are partly miscible, and the electrolyte either increases or decreases the mutual solubility of the two phases [17]. Class II and III have more complex features and require a separate study.

An example for a simple interface of class I is water|alkane (W|alkane). Its interfacial tension increases with the addition of inorganic salt, exception being made for salts with large anions and certain acids. The dependence of the interfacial tension increment $\Delta\sigma$ on C_{el} is ion-specific. Often, the $\Delta\sigma(C_{el})$ isotherms are almost indiscernible for W|alkane and W|gas (W|G) [1,2,7]. Aveyard and Saleem found that most oils are similar to alkanes with respect to the effect of the electrolyte on σ [2]. A notorious exception is the interface between water and a long-chained alcohol phase (W|alcohol): the increment $\Delta\sigma$ is always significantly smaller compared to W|alkane in this case [11]. This fact points at a difference in the structures of the interfaces W|alcohol and W|alkane: the reason is the –OH groups of the alcohol which are able to penetrate into the water surface layer and thus to alter its properties.

Consider now an interface between aqueous electrolyte solution and alkane with an adsorbed monolayer of alcohol onto it. The alcohol can be water-soluble or oil-soluble [11]. For this 4-component system, the structure of the interface will be something in between W|alkane and W|alcohol. At low adsorption of alcohol, the electrolyte will behave as if the interface is W|alkane, while if dense alcohol monolayer is formed, the electrolyte will interact with it as with W|alcohol. In such a tunable system, the adsorption of alcohol Γ_{OH} serves as a fine instrument for the investigation of the structure of water surface layer, as demonstrated in the remarkable work of Aveyard et al. [11].

There are few theoretical studies investigating the adsorption of inorganic salts at simple W|O [18–20]. Some molecular dynamics [21], dissipative particle dynamics [22] and Monte Carlo [23]

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simulations are also available. These studies test existing models for the W|G surface of an electrolyte solution by extending it to W|O interface and comparing the results with the experimental data. These tests are very useful, especially in view of the ongoing discussion whether large ions are attracted to the W|G interface due to van der Waals forces [24], hydrophobic interactions or for another reason [18]. A short review on the topic is present in Ref. [25]. None of these works deal with the W|alcohol interface, which is the most interesting W|O in view of its peculiar behavior [11] and its natural relation to interfaces with adsorbed layers of surfactants.

Our first aim in the current study is to use the available experimental data for the effect of inorganic salts on the interfacial tension of various W|O interfaces [1–7,11] for testing a model of the interface previously used successfully for W|G surfaces of brines. We refer to this model as *modified Schmutzer's model* [26–28]. This classical model of the surface of brines involves a depletion layer free of ions and image forces [28], and fully neglects hydrophobic and van der Waals ion-surface interactions. This makes it inapplicable to salts with large monovalent anions. The modification [26,27] of the original theory involves a contribution from the diffuse electric layer and an explicit model for the depletion layer thickness, which is related to the ion–solvent correlation function and the so-called thickness of the hydrophobic gap [29]. The modified model will be considered briefly in Section 2. Schmutzer's model predicts without adjustable parameters the surface tension of scores of 1:1, 1:2 and 2:1 electrolyte with high accuracy up to very high electrolyte concentrations (C_m = 5–10 mol/kg [26,27]). It also predicts correctly the surface $\Delta\chi$-potential of Z_+:Z_- electrolytes provided that no large anions are present [26]. The comparison of Schmutzer's model with experiment revealed that the Hofmeister effect on these *surface* characteristics is, at least for small ions, a direct consequence [26,27] from the ion-specificity of *bulk* properties such as activity coefficient (discussed also by others [30,31]) and dielectric permittivity. Checking the accuracy of Schmutzer's model against data for the W|O interfacial tension can bring insight into the structure of the surface layer of water molecules, as well as into the nature of the Hofmeister series.

The second aim of the study is to provide an explanation for the lower surface tension increment when the electrolyte solution is in contact with alcohol instead of alkane [11]. We will show that for W|alkane, the available tensiometric data is in agreement with Schmutzer's model, and it needs no modifications in comparison with the theory for W|G [26,27]. For W|alcohol, however, attention must be taken for the penetration of –OH groups into the surface layer of the water phase. As discussed in Section 2.2, this penetration results into a shift of the Gibbs equimolecular surface towards the aqueous solution. Every –OH group replaces a water molecule, which can be effectively described as desorption of water; the process does not alter the ion distribution profile significantly. Schmutzer's model remains valid for W|alcohol – only the location of the dividing surface is different.

Having a model which works for both W|alkane and W|alcohol allows the understanding of the effect of the inorganic salt dissolved in the water phase on a monolayer of adsorbed alcohol [11]. We will consider the effect of the electrolyte on the adsorption energy of oil-soluble alcohol in Section 3.1, and water-soluble alcohol will be discussed in Section 3.2. The effect of the electrolyte on the properties of an insoluble monolayer of long-chained alcohol at W|G will be considered briefly in Section 3.3. All types of monolayers considered are analyzed based on a single simple explicit relation between the standard chemical potential of a surfactant adsorbed at the interface and the electrolyte concentration, Eq. (35), which follows from Schmutzer's model.

In cases where no large ions are present, Schmutzer's model shows high precision in predicting the role of the electrolyte in nominally different phenomena (interfacial tension increment, adsorption constant of alcohols) without free adjustable parameters. Large adsorbing ions such as I$^-$ and SCN$^-$, and to a lesser extent Br$^-$ and NO$_3^-$, show negative deviations from the theoretical predictions. Even with them, Schmutzer's model can be used for some interesting qualitative observations based on the deviations between the experimental data and the theoretical predictions – an approach used previously for 1:1 electrolytes at W|G [27].

2. Model of the interface between an electrolyte solution and a hydrophobic phase (oil or gas)

2.1. Ion-surface interactions and ion adsorption

2.1.1. The image force

The image potential $u_{\mathrm{im}\pm}$ of an ion of charge $Z_\pm e$ at a distance z from the interface of an electrolyte solution is given by [32–34]:

$$u_{\mathrm{im}\pm} = \frac{Z_\pm^2 e^2}{16\pi\varepsilon|z|}\exp(-2|z|/L_\mathrm{D}), \tag{1}$$

where subscripts "+" and "−" refer to the cation and the anion respectively; for Z_+:Z_- electrolyte, the Debye length L_D is defined with $L_\mathrm{D}^2 = \varepsilon T/2e^2 k_\mathrm{is} C_\mathrm{el}$; C_el is the electrolyte concentration (in units m^{-3}); ε is the absolute dielectric permittivity of the aqueous solution [F/m]; e is the elementary charge; T denotes the thermodynamic temperature (T[J] = $k_\mathrm{B}T$[K]); $k_\mathrm{is} = (\nu_+ Z_+^2 + \nu_- Z_-^2)/2$ is the ratio between ionic strength and C_el; $\nu_\pm$ are the stoichiometric numbers of the cation and the anion (for the convenience of the reader, a full list of symbols is provided in Supplementary materials S5). Sometimes, a correction factor $(\varepsilon - \varepsilon^\mathrm{H})/(\varepsilon + \varepsilon^\mathrm{H})$ is introduced in Eq. (1), where ε^H is the absolute dielectric permittivity of the hydrophobic phase [34]. Our analysis showed that this correction can be neglected in all cases investigated below. We will also neglect the effect of the electrolyte concentration on the value of ε and the correction of Onsager and Samaras for the steric ion-ion interaction at the interface [27].

2.1.2. Hydration forces

The second ion-surface interaction in Schmutzer's model is the hydration potential $u_{\mathrm{hydr}\pm}$, modeled with a hard wall potential disallowing the ion to approach the interface at a distance of less than the thickness $R_\pm$ of the "depletion layer" [28], i.e., $u_{\mathrm{hydr}\pm} = \infty\cdot\eta(z + R_\pm)$, where η is the Heaviside step function. The precise value of $R_\pm$ is a problematic question for most modern theories of ion adsorption [12,18,19,24,30,34–38]. The thickness $R_\pm$ represents the minimal possible distance at which an ion can approach the water surface without losing water molecules from its hydration shell. To define $R_\pm$, one must first define carefully the position of the water surface. It is well known that the last one or two layers of water molecules at the surface are of decreased density. Let us define the *physical surface* of the water as the tangent plane to the top layer of water molecules ($z = +R_\mathrm{hg}$ in Fig. 1). An ideal solid (structureless, no long-ranged interactions with water) can approach the aqueous solution from the gas phase side to this position without interaction, and further advance will be impossible due to the repulsion. We assumed in Refs. [26,27] that an ion can approach this surface from the water phase side to a minimal distance equal to the hydration radius $R_{\mathrm{h}\pm}$. Next we define the *surface of discontinuity of density* of *pure* water ($z = 0$ in Fig. 1) as the position at which the Gibbs excess of the water is zero, that is:

$$\int_{-\infty}^{0}(C_\mathrm{w}(z) - C_\mathrm{w}(\infty))\mathrm{d}z + \int_{0}^{\infty} C_\mathrm{w}(z)\mathrm{d}z = 0, \tag{2}$$

where $C_\mathrm{w}(z)$ is the water concentration profile and $C_\mathrm{w}(\infty)$ is the density of the bulk liquid phase ($z < 0$). Since the dielectric