



The double layer potentials at the toluene–aqueous interface in the presence of CTAB/NaBr. Implications for Ion-Selective Electrodes

Kamil Wojciechowski^{a,*}, Marta Kucharek^a, Wojciech Wróblewski^a, Piotr Warszyński^b

^a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

^b Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland

ARTICLE INFO

Article history:

Received 30 September 2008

Received in revised form 5 January 2009

Accepted 30 January 2009

Available online 5 April 2009

Keywords:

Ionic surfactants

Tetraalkylammonium salts

Interfacial tension

Ion-Selective Electrodes

ABSTRACT

The interfacial tension isotherms for cetyltrimethylammonium bromide (CTAB) in the presence of sodium bromide at the aqueous–toluene interface are discussed. In accordance with previous observations for an aqueous–air interface, the presence of a non-surface active electrolyte (NaBr) has strong influence on the interfacial activity of CTAB at the aqueous–toluene interface. The results were analysed within the framework of the Surface quasi-Two Dimensional Electrolyte model (STDE), assuming that the non-surface active bromide counterions partially penetrate the Stern layer formed by cetyltrimethylammonium cations adsorbed at the interface. This analysis allowed for calculation of the electrical double layer (EDL) potentials (Stern potential and the diffuse double layer potential). The calculated EDL potentials were compared with the membrane potentials generated in the Ion-Selective Electrodes (ISE) containing neither ionophore nor ion-exchanger, when exposed to aqueous solutions of CTAB.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Tetraalkylammonium salts are major components of anion-selective membranes of the Ion-Selective Electrodes (ISE). The analytical signal of ISEs is generated through the charge separation at the interface between the ion-selective membrane and the aqueous solution. A typical anion-selective membrane is made of plasticized poly(vinyl chloride) and contains a long-chain tetraalkylammonium salt, e.g. tetradodecylammonium bromide. ISEs with such membranes display a selectivity pattern consistent with the Hofmeister series (so-called Hofmeister-selectivity pattern). In presence of additional complexing agents (ionophores) the selectivity pattern may change, depending on the selectivity of ionophore [1].

The exact mechanism of ion partitioning and charge separation across the interface is not yet well understood [2]. According to a simple classical approach based on the Nernst equation, solely the partition equilibria are responsible for the potential difference generation [3]. Generalising this approach, Sokalski, Lewenstam et al. pointed to the role of the mass and charge transport phenomena in the build-up of the potential difference across the membrane. They performed a series of simulations using the Nernst–Planck–Poisson set of equations in order to calculate both temporal and spatial dis-

tributions of ionic concentrations and electrical potentials in the membrane [4].

On the other hand, some authors [5,6] stress the importance of the interfacial phenomena in generation of the potentiometric signal in ISEs. In fact, tetraalkylammonium salts, especially with long alkyl chains, show increased surface activity and are often used as surfactants. Especially the salts belonging to the group of alkyltrimethylammonium halogenides are very popular cationic surfactants. Also the phase-transfer catalytic properties of tetraalkylammonium salts are often associated with their interfacial activity (Makosza's interfacial mechanism) [7].

The ionic surfactant character of tetraalkylammonium salts used in the membranes of ISEs with the Hofmeister-selectivity necessitates considering a possible role it may play in the generation of electrical potential difference across the ISE membrane. In this paper we aimed to estimate the double layer potentials at the model liquid–liquid interface in the presence of a typical tetraalkylammonium salt: cetyltrimethylammonium bromide (CTAB). The toluene–aqueous interface was chosen as a crude model of the ISE membrane–aqueous interface. For estimation of the double layer potential we employed the “Surface quasi-Two Dimensional Electrolyte” (STDE) model of Warszyński et al. originally developed for the aqueous–air interfaces [8,9]. Due to the low dielectric constant of toluene ($\epsilon = 2.6$) and negligible partitioning of CTAB into this solvent [10], the double layer is expected to be built only in the aqueous phase. In such a case it should be possible to use the STDE model without any modifications.

* Corresponding author. Tel.: +48 22 234 56 31; fax: +48 22 234 56 31.
E-mail address: kamil.wojciechowski@ch.pw.edu.pl (K. Wojciechowski).

2. Experimental

Toluene (puriss. p.a. ACS reagent for UV spectroscopy) was purchased from Fluka and was used as received after checking its surface purity by measuring the dynamic interfacial tension against water for at least 1 h. Cetyltrimethylammonium bromide, CTAB (puriss p.a. $\geq 99\%$) and NaBr (purum p.a. $\geq 99\%$) were purchased from Fluka and were used without any further purification. The surface purity of NaBr was verified by measuring the dynamic interfacial tension of its $5 \times 10^{-2} \text{ mol/dm}^3$ solution against toluene. Fresh Millipore water ($18.2 \times 10^6 \Omega/\text{cm}$) was used for all the measurements.

All glassware was cleaned with acetone and Hellmanex II solution (Hellma Worldwide) and rinsed with copious amounts of Millipore water. All the experiments were performed at constant temperature (21°C) controlled with a thermostatic bath.

All interfacial tension measurements were performed using the drop profile analysis tensiometer PAT-1 (SINTERFACE, Germany). Fitting of the dynamic interfacial tension data to the Ward–Tordai equation coupled with Langmuir and Frumkin equations was performed using the WardTordai software developed by Aksenenko et al. [11]

The potentiometric electrodes contained membranes composed of polymer matrix (poly(vinyl chloride), PVC) (33%) plasticized with bis(2-ethylhexyl) sebacate (DOS) (67%) mounted into the standard Philips ISE bodies. The internal electrolyte consisted of 10^{-2} mol/dm^3 solution of NaCl. After conditioning for 1 day in distilled water, the response of the membrane electrodes to the presence of CTAB was measured against a double-junction Ag/AgCl reference electrode (Hydromet) with 1 M CH_3COOLi as a liquid junction electrolyte. Each electrode was used only once to avoid any memory effects. The measurements at each CTAB concentration were performed at least in triplicate. At a given time, an aliquot of CTAB solution was added to the beaker filled with distilled water, in which the electrodes were immersed, and the potential response was recorded.

3. Results and discussion

Fig. 1 presents the main features of the STDE model of ionic surfactant adsorption at a fluid interface. The details of the model were described in [8,9] and refs cited therein. Here only an overview of the major features is given. Adsorption of the ionic surfactants at

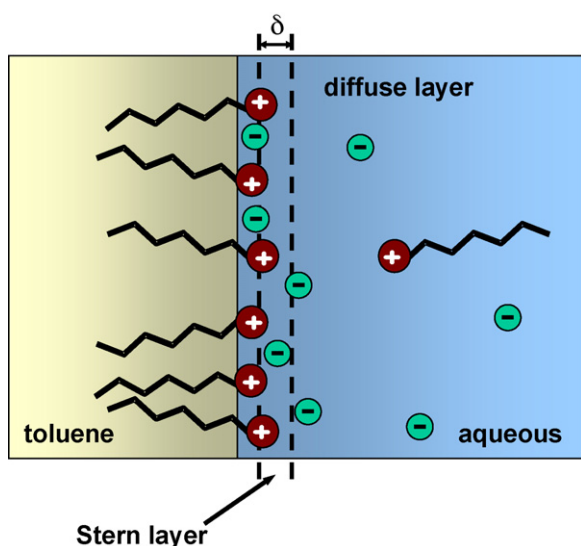


Fig. 1. Schematic representation of the structure of electrical double layer (EDL) at the aqueous–toluene interface in the presence of CTAB.

the oil–electrolyte interface leads to formation of an electric double layer (EDL). Cationic surfactant head-groups together with their counterions and anions of added electrolyte (if present) are accumulating in the Stern layer. They preserve their freedom of motion and therefore, the Stern layer can be considered as a quasi two-dimensional electrolyte, which does not fulfil the electroneutrality condition.

Exploiting the postulate of equilibrium, i.e., assuming equal electrochemical potentials of each ion in the bulk phase and in the Stern layer, for the system of monovalent cationic surfactant solution in the presence of added monovalent salt, the adsorption equations can be written as:

$$\frac{\alpha_S}{\alpha_S} \left(-\frac{e\psi_s}{kT} \right) (1 - \theta_S - \theta_C - \theta_{C1}) = \theta_S \exp[-2H_S\theta_S] \exp\left(\frac{\phi_S}{kT}\right) \quad (1)$$

for surfactant cations, and:

$$\frac{\alpha_C}{\alpha_C} \left(\frac{e\psi_s}{kT} \right) (1 - \theta_S - \theta_C - \theta_{C1})^{g_{CS}} = \theta_C \exp\left(\frac{\phi_C}{kT}\right) \quad (2)$$

$$\frac{\alpha_{C1}}{\alpha_{C1}} \left(\frac{e\psi_s}{kT} \right) (1 - \theta_S - \theta_C - \theta_{C1})^{g_{C1S}} = \theta_{C1} \exp\left(\frac{\phi_{C1}}{kT}\right) \quad (3)$$

for surfactant counterions and anions of an added electrolyte. Here: α_S is the “surface activity” of surfactant ion, being a measure of the free energy of the adsorption after separating the contribution of the electric components, $\alpha_{C,C1}$ is the “surface activity” of the counterions, which is a measure of their penetration into the surface Stern layer resulting from the balance of dispersion forces and image forces acting on the ionic charge at the interface between the media with different dielectric properties, $\theta_S = \Gamma_S/\Gamma_{S\infty}$ is the relative surfactant surface concentration, $\Gamma_{S\infty}$ is the limiting surfactant surface concentration of the closely packed monolayer; $\theta_C = \Gamma_C/\Gamma_{C\infty}$, $\theta_{C1} = \Gamma_{C1}/\Gamma_{C1\infty}$ and $\Gamma_{C\infty}$ and $\Gamma_{C1\infty}$ are the same quantities for counterions, $g_{CS} = \Gamma_{S\infty}/\Gamma_{C\infty}$, $g_{C1S} = \Gamma_{S\infty}/\Gamma_{C1\infty}$.

H_S is the interaction parameter accounting for the attractive lateral interactions among the adsorbed surfactant hydrophobic tails.

The total charge in the Stern layer, determining the diffuse layer potential, is the sum of positive charges of the adsorbed surfactant head-groups and negative charges of the counterions. The model takes explicitly into account the finite size of head-groups and counterions and considers the lateral electric interactions between them. Consequently, the degree of penetration of the Stern layer by a given counterion depends on its effective size and interactions in the Stern layer. It is assumed that accumulation of the surfactant co-ions in the Stern layer is negligible, as a result of a strong electrostatic repulsion. The model does not take into account any ion pairing of the adsorbed ions.

The surface charge of the Stern layer is compensated by the charge of the ions accumulated in the diffuse part of the EDL, which renders the whole interface electrically neutral. The electric potential of the Stern layer can be found from:

$$\psi_s = \psi_d + \frac{\sigma\delta}{\varepsilon_0\varepsilon_s} \quad (4)$$

where the diffuse layer potential at the boundary between the Stern layer and the diffuse part of EDL can be determined from the formula:

$$\psi_d = \frac{2kT}{e} \sinh^{-1} \left(\frac{\sigma e}{2\varepsilon_0\varepsilon\kappa T} \right) \quad (5)$$

where e is the elementary charge, k is the Boltzmann constant, ε_0 is the vacuum dielectric permittivity, ε is the dielectric constant of the solution, κ is the Debye–Hückel reciprocal length, $\sigma = F(\Gamma_S - \Gamma_C - \Gamma_{C1})$ is the surface charge density, F is the Faraday constant, δ is the thickness of the Stern layer and ε_s is the dielectric constant in the Stern layer. The activity corrections for the lateral

Download English Version:

<https://daneshyari.com/en/article/595936>

Download Persian Version:

<https://daneshyari.com/article/595936>

[Daneshyari.com](https://daneshyari.com)