Short Communication

A Preliminary Study of Transfer of Laurylsulfate Ion at the Water/Dichloroethane Interface

Anna-Kaisa Kontturi,[a] K. Kontturi[a] and Z. Samec[b]

[a]Helsinki University of Technology, Laboratory of Physical Chemistry and Electrochemistry, Kemistintie 1, SF-02150 Espoo, Finland and [b]J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, u Tovarén 254, 10200 Prague 10, Czechoslovakia

Ion transfer across the interface between two immiscible electrolyte solutions (ITIES) can be used in modelling and studying extraction processes, phase transfer catalysis and related phenomena. Many important applications of ion transfer across ITIES can be found in analytical chemistry. So far, most of the ions studied have not been surface active species, as can be seen from published tables of measured data.[1-3] However, systems containing surface active compounds are interesting because of adsorption phenomena, their ability to create instabilities of interfaces and, of course, their influence on surface tension.

In this work the transfer of a surfactant, viz. the dodecylsulfate anion (laurylsulfate), across the water/dichloroethane (DCE) interface has been studied. The transfer of this anion across the water/nitrobenzene interface has been investigated by Vanysek[4] using an electrolyte dropping electrode. Vanysek did not present any kinetic data.

Experimental

Apparatus. The cell used is described in detail elsewhere (see, e.g., Ref. 5). The diameter of the circular interface was 5.5 mm. With the cell construction used it was possible to achieve an extremely flat surface, which is necessary in order to obtain complete *IR* compensation. The four-electrode potentiostat has been described by Sa-

mec and co-workers.[5] The frequency response analyzer used in the kinetic studies was a Solartron 1250.

Materials. The water used was doubly distilled; 1,2-dichloroethane (DCE), LiCl, tetrabutylammonium chloride (TBAC) and sodium dodecylsulfate (sodium laurylsulfate) were of analytical grade and were used without further purification. Tetrabutylammonium tetraphenylborate (TBATPB) was recrystallized from acetone. The TBA salt of laurylsulfate (a liquid substance at room temperature) was synthesized from TBAC and sodium laurylsulfate. The purity of this salt was checked by comparing the peak currents of cyclic voltammograms obtained when laurylsulfate anion was transferred from water to DCE with those obtained when the transfer was from DCE to water. The results showed that the synthesized salt was TBA laurylsulfate and that it was pure.

Measurements. Cyclic voltammetry was carried out in cell (I), where the concentration of laurylsulfate, a, had the values $1.15 \cdot 10^{-4}$, $2.25 \cdot 10^{-4}$, $4.20 \cdot 10^{-4}$ and $4.90 \cdot 10^{-4}$ M. The single-sweep method was used and the starting potential was chosen to be so negative with respect to the oil phase that laurylsulfate was not transferred, i.e. the potential $E = \varphi^{Ag} - \varphi^{Ag'} = 460$ mV in the cell described above. The sweep rates used were 5, 10, 20, 50 and 100 mV s^{-1}.

Ag/AgCl	Aqueous phase 10^{-2} M LiCl a M Na laurylsulf.	Organic phase 10^{-2} M TBATPB in DCE	Aqueous sol. 10^{-2} M TBAC	AgCl/Ag' (I)

Ag/AgCl	Aqueous phase $5 \cdot 10^{-2}$ M LiCl a M Na laurylsulf.	Organic phase $5 \cdot 10^{-2}$ M TBATPB in DCE and a M TBA-laurylsulf.	Aqueous phase. $5 \cdot 10^{-2}$ M TBAC	AgCl/Ag' (II)

The impedance measurements for the determination of the rate constant k^0 for the transfer DCE/water made in cell (II), where the concentration of laurylsulfate anion, a, was varied from $2.5 \cdot 10^{-4}$ M to $8 \cdot 10^{-4}$ M. At these concentrations the laurylsulfate salts appeared to be almost completely dissociated, both in aqueous and in oil phase. Thus, the impedance measurements carried out near the half-wave potential can provide easily interpreted kinetic data (cf. Wandlowski et al.[6]). It should also be noted that when the impedance measurements are made, in the neighbourhood of the half-wave potential and with small amplitudes (± 10 mV), IR compensation is not necessary.

All measurements were made at $25\,^{\circ}$C.

Results

Cyclic voltammetry. The cyclic voltammograms showed clearly that the difference in peak potentials at different sweep rates was ca. 60 mV. Fig. 1 shows the peak currents as a function of the square root of the sweep rate and as can be seen, the result confirms the reversible behaviour. From the slopes of these straight lines the diffusion coefficient for laurylsulfate ion in water, $D(\text{w})$, can be evaluated when the surface area of the interface is known accurately enough. The precision of the determination of the diffusion coefficient by this method is strongly dependent on the diameter (d) of the surface (note that the error in $D \propto d^{-4}$). Therefore we determined the surface area of the cell also with the aid of a separate measurement, viz. the determination of the transfer of picrate ion across a water/nitrobenzene interface by cyclic voltammetry using the same supporting electrolytes as in cell (I). Since the diffusion coefficient of picrate is known in this system,[6] the surface area of the cell could be evaluated.

From our measurements the diffusion coefficient for laurylsulfate ion in water was calculated to be:

$$D(\text{w}) = (0.73 \pm 0.02) \cdot 10^{-5} \text{ cm}^2\text{s}^{-1}.$$

From the cyclic voltammograms, the values for the half-wave potential and Gibbs energy of transfer can also be estimated. Our measurements gave the following values:

$E_{1/2} = 310$ mV and $\Delta G_{\text{tr}}^{0,\,\text{w}\to 0} = 7.7$ kJ mol^{-1} or the standard potential difference $\Delta_0^{\text{w}}\varphi^0 = 80$ mV.
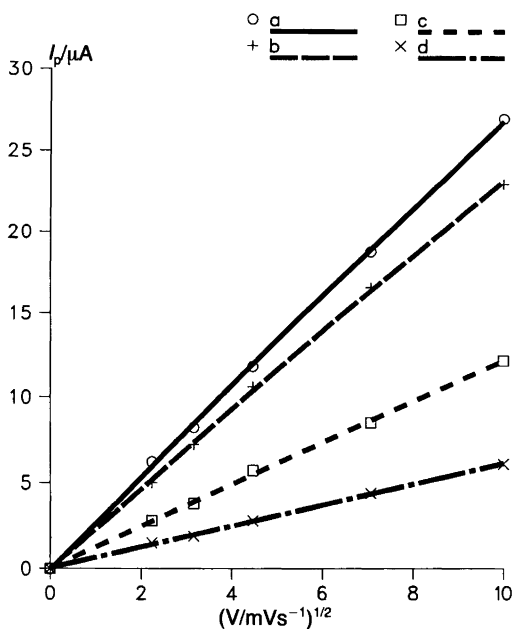

Fig. 1. Peak current (I_p) as a function of square-root of sweep rate (v). Concentration of laurylsulfate in the aqueous phase: a: $4.90 \cdot 10^{-4}$ mol dm^{-3}, b: $4.20 \cdot 10^{-4}$ mol dm^{-3}, c: $2.25 \cdot 10^{-4}$ mol dm^{-3}, d: $1.15 \cdot 10^{-4}$ mol dm^{-3}.

193

Impedance measurements. The problem in impedance measurements is the high ohmic resistance (ca. 700 Ω) in the cell. Because of this ohmic resistance the kinetic measurements are bound to be relatively inaccurate. However, with careful analysis, including the substraction of the effect of supporting electrolyte, reasonable and reproducible values for the charge transfer resistance can be obtained. The substraction of the effect of the supporting electrolyte was carried out using the so-called analytical method based on conversions between equivalent series and parallel *RC* networks.[6]

The transfer of laurylsulfate ion across the water/DCE interface appeared to be very fast: The rate constant was estimated to be $k^0 = 0.3$ cm s^{-1} and the exchange current density $j_0 = 22$ mA cm^{-2}. These results are preliminary. A great deal of work is still needed to obtain more realiable values for k^0 and j_0. Furthermore, surface tension measurements and an analysis based on such data are necessary to complete this study. These measurements are in progress.

References

1. Koryta, J. *Electrochim. Acta 29* (1984) 445.
2. Vanýsek, D. *Electrochemistry in Liquid/Liquid Interfaces, Lecture Notes in Chemistry 39,* Springer, Heildelberg.
3. Koryta, J., Marecek, V. and Samec, Z. *Adv. Colloid Surface Sci. In press.*
4. Vanýsek, P. *J. Electroanal. Chem. 121* (1981) 149.
5. Samec, Z., Marecek, V. and Weber, J. *J. Electroanal. Chem. 100* (1979) 841.
6. Wandlowski, T., Marecek, V. and Samec, Z. *J. Electroanal. Chem.* (1988). *In press.*