

Short Communication

Monovalent Cations at the Water/1,2-Dichloroethane Interface

Anna-Kaisa Kontturi,^{a,*} Kyösti Kontturi,^a Lasse Murtomäki^b and Bernadette Quinn^b

^aLaboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, Kemistintie 1, FIN-02150 Espoo, Finland and ^bDepartment of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland

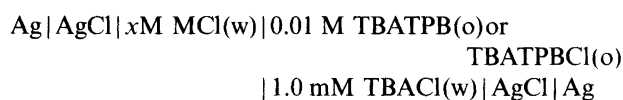
Kontturi, A.-K., Kontturi, K., Murtomäki, L. and Quinn, B., 1996. Monovalent Cations at the Water/1,2-Dichloroethane Interface. – Acta Chem. Scand. 50: 640–642 © Acta Chemica Scandinavica 1996.

Ion transfer across the interface between two immiscible electrolyte solutions (ITIES) has lately appeared to be more complicated than anticipated in the advent of this field of electrochemistry ca. 20 years ago.^{1–5} In addition to the usual difficulty always present in electrochemistry of establishing consistent sets of ionic quantities, the low relative permittivity of the organic phase causes extensive ion-pairing.⁶ These problems are reflected, for instance, in the scattered values of ionic standard potentials of transfer reported in literature, or in disagreements concerning the mechanism of the ion transfer.^{7–11} Also, the kinetics of ion transfer can be inferred by the homogeneous reaction kinetics in the organic phase.¹²

In this paper we investigate problems associated with ion transfer using monovalent cations, H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and NH₄⁺, as examples at the water/1,2-dichloroethane (DCE) interface, and show that even in these simple systems several possibilities exist which are responsible for the observed behaviour. Two anions, tetraphenylborate (TPB[−]) and *p*-[4-chlorotetrakis]tetraphenylborate (TPBCl[−]), were used as the organic base electrolyte. In spite of their structural similarity, the latter anion is much more hydrophobic, which changes the transfer mechanism at the positive polarization limit completely for certain cations. An obvious explanation of this behaviour was shown to be preferential solvation¹³ of TPBCl[−].

Experimental

The four-electrode cell and experimental procedures used have been described elsewhere.¹⁴ The measured potentials correspond to the cell



where M corresponds to the cation and $x=0.1, 0.2, 0.5, 1.0$ or 2.0 ; TBA = tetrabutyl ammonium, TPB = tetraphenylborate and TPBCl = *p*-[4-chlorotetrakis]tetraphenylborate. The concentration dependence of the potential at constant current which corresponds to a Tafel slope was determined using this four-electrode cell as reported previously.¹⁵

To determine which ion is crossing the interface at the positive polarization limit, cyclic voltammograms were measured with micropipette techniques described earlier.¹³ The sweep rate was 25 mV s^{-1} . The cell was the same as above with $x=0.1 \text{ M}$. In all the measurements potentials were corrected for the absolute Galvani potential scale as before.¹⁴

TBATPB and TBATPBCl were prepared as previously described.^{16,17} Chloride salts MCl were of analytical grade (Merck). TBACl (Fluka) and 1,2-dichloroethane (Rathburn HPLC) were used without further purification. Water was purified with a Millipore Milli-Q system.

Results and discussion

Micropipette techniques provide a versatile means to deduce which ion is crossing the interface at the polarization limits.¹⁸ When using TPBCl[−] as an anion of the organic base electrolyte all the ions investigated here were crossing at the positive polarization limit, because the free energy of transfer of TPBCl[−] from DCE to water is higher than the free energies of transfer of these cations. However, when TPB[−] was used it was transferred before Na⁺ or Li⁺. Nevertheless, this result does not mean that the free energies of transfer of K⁺, Rb⁺, Cs⁺, H⁺ or NH₄⁺ are necessarily lower than the free

* To whom correspondence should be addressed.

energy of TPB^- ; however, they are transferred as a result of ion-pairing in the organic phase, which lowers the formal potential of transfer:

$$\Delta_o^w \Phi_{M^+}' = \Delta_o^w \Phi_{M^+}^\circ - \frac{RT}{F} \ln(1/\gamma_{M^+}^\circ + K_a \alpha_{\text{TPB}^-, \text{TPBCl}^-}^\circ) \quad (1)$$

$\Delta_o^w \Phi_{M^+}'$ and $\Delta_o^w \Phi_{M^+}^\circ$ are the formal and standard potentials of ion transfer, K_a is the association constant of the reaction between the cation transferred and TPB^- or TPBCl^- ; $\gamma_{M^+}^\circ$ is the ionic activity coefficient of the transferred cation in the oil phase, and $\alpha_{\text{TPB}^-, \text{TPBCl}^-}^\circ$ is the activity of TPB^- or TPBCl^- . In Fig. 1 the transfer of NH_4^+ is shown in the both cases, while in Fig. 2 either Na^+ or TPB^- is transferred, depending on the organic base electrolyte anion.

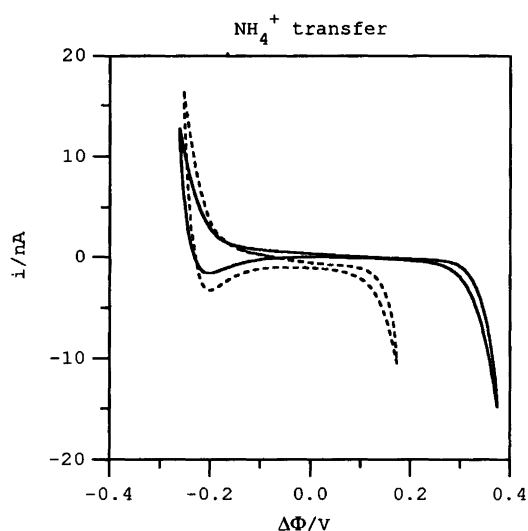


Fig. 1. Voltammograms of $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}(\text{w})$ – $0.01 \text{ mol dm}^{-3} \text{ TBATPB}(\text{o})$ (---) and $0.1 \text{ mol cm}^{-3} \text{ NH}_4\text{Cl}(\text{w})$ – $0.01 \text{ mol dm}^{-3} \text{ TBATPBCl}$ (—). The sweep rate is 25 mV s^{-1} and the diameter of the micropipette is $20 \mu\text{m}$.

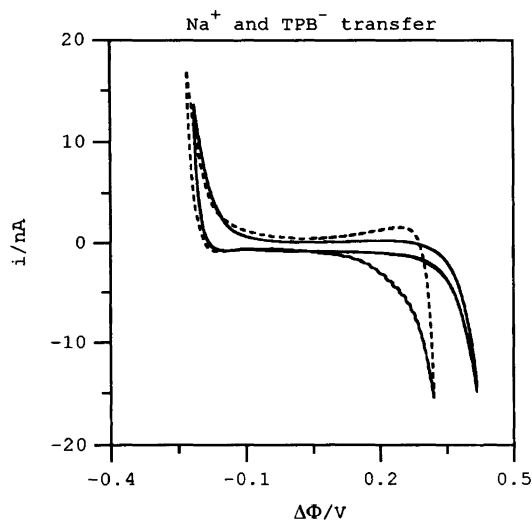


Fig. 2. As in Fig. 1 but for $\text{NaCl}(\text{w})$.

Apparent Tafel slopes were determined for those cations which were transferred across the interface, as shown in Figs. 3a and 3b. In the case of TPBCl^- all the slopes were approximately 60 mV per decade, indicating Nernstian behaviour. Using TPB^- as an anion a slope of ca. 40 mV per decade was observed for the transfer of K^+ and H^+ , which corresponds to the formation of an interfacial ion pair.^{12,15} Small deviations from the slope of 60 mV per decade in the case of Cs^+ and Rb^+ together with TPB^- are due to the narrow potential window. Also, the evaluation of ionic activities is subject to small errors. Interestingly, none of the cations showed a Tafel slope of 120 mV per decade related to Butler–Volmer kinetics.

In a recent study¹³ the shift of the transfer potential of Rb^+ at the positive polarization limit was found to be due to preferential solvation of TPBCl^- phenyl rings.

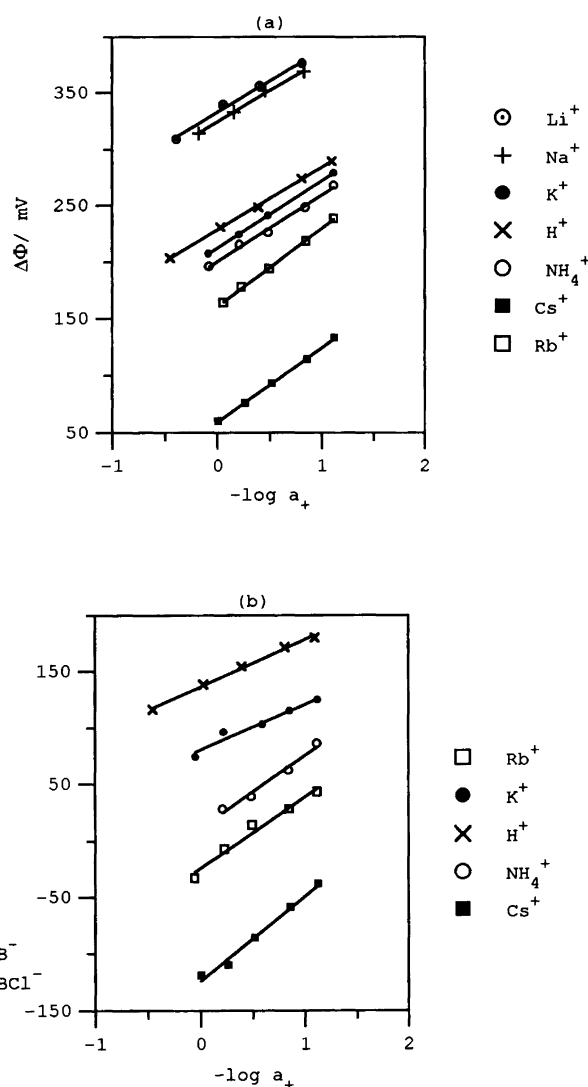


Fig. 3. The concentration dependence of the potential at constant current corresponding to a Tafel slope. (a) TPBCl^- as an organic anion and (b) TPB^- as an organic anion. The cations are as chlorides in the aqueous phase.

The same behaviour, i.e. a shift of ca. 180 mV, was observed for Cs⁺ and NH₄⁺ (Fig. 1). Also, for K⁺ and H⁺ (actually H₃O⁺) a shift of ca. 100 mV was measured indicating the existence of this phenomenon, but the difference in transfer mechanisms when changing the organic anion prevents quantitative analysis in these cases.

Acknowledgements. The support of the European Community, Human Capital and Mobility Programme and The Academy of Finland (Contract Number ERB CHRXCT 920076) is gratefully acknowledged.

References

1. Koryta, J. *Electrochim. Acta* 24 (1979) 293.
2. Koryta, J. *Electrochim. Acta* 29 (1984) 445.
3. Koryta, J. *Electrochim. Acta* 33 (1988) 189.
4. Girault, H. H. J. and Schiffrin, D. J. In: Bard, A. J., Ed., *Electroanalytical Chemistry*, Vol. 14, pp. 1–115, Marcel Dekker, New York, 1989.
5. Girault, H. H. J. In: Bockris, J. O'M., Ed. *Modern Aspects of Electrochemistry*, Vol. 25, pp. 1–62, Plenum Press, New York, 1993.
6. Kontturi, A.-K., Kontturi, K., Manzanares, J. A., Mafe, S. and Murtomäki, L. *Ber. Bunsenges. Phys. Chem.* 99 (1995) 1131.
7. Samec, Z., Marecek, V. and Colombini, M. P. *J. Electroanal. Chem.* 257 (1988) 147.
8. Wandlowski, T., Marecek, V. and Samec, Z. *Electrochim. Acta* 35 (1990) 1173.
9. Sabela, A., Marecek, V., Samec, Z. and Fuoco, R. *Electrochim. Acta* 37 (1992) 231.
10. Kontturi, A.-K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc., Faraday Trans. 86* (1990) 819.
11. Shao, Y., Stewart, A. and Girault, H. H. J. *J. Chem. Soc., Faraday Trans. 87* (1991) 2593.
12. Kontturi, A.-K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc., Faraday Trans. 91* (1995) 3433.
13. Kontturi, A.-K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc., Faraday Trans. 90* (1994) 2037.
14. Geblewicz, G., Kontturi, A.-K., Kontturi, K. and Schiffrin, D. J. *J. Electroanal. Chem.* 217 (1987) 261.
15. Kontturi, A.-K., Kontturi, K. and Schiffrin, D. J. *J. Electroanal. Chem.* 255 (1988) 331.
16. Kontturi, A.-K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc. Faraday Trans. 86* (1990) 931.
17. Kontturi, K. and Murtomäki, L. *J. Pharm. Sci.* 81 (1992) 970.
18. Taylor, G. and Girault, H. H. J. *J. Electroanal. Chem.* 208 (1986) 179.

Received September 20, 1995.