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SOLVATION AND ION TRANSFER ACROSS THE WATER/2-CHLOROETHYL ETHER INTERFACE

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ABSTRACT. The transfer of several ions across the immiscible water/2-chloroethyl ether interface has been studied using cyclic voltammetry. The standard Gibbs energies of ion transfer have been determined using the tetraphenylarsonium tetraphynylborate assumption. The results have been compared with theoretical data calculated from an ionic solvation model.

INTRODUCTION

The investigation of ion transfer across immiscible water/organic solvent interfaces has attracted a great deal of interest [1-4]. The importance and application of such work in the fields of chemistry and biology have been fully described in several review articles [3,4]. The transfer of ions from one solvent to another is of particular interest to chemists dealing with diverse problems such as phase transfer catalysis in organic synthesis, solvent extraction in hydrometallurgy and electroanalytical chemistry [5]. Thermodynamic quantities for individual ionic species can be obtained from such experiments.

Due to the requirements of high dielectric constant, immiscibility with water and different density from that of water, few organic solvents have been used so far, mainly nitrobenzene and 1,2 dichloroethane. 2-Chloroethyl ether is widely used in extraction processes, scouring of textiles, purification of oils and as insecticidal soil fumigant [6]. The solvent has a fairly high dielectric constant, low solubility in water and a density higher than that of water. The most important physical properties of the liquid are compared with those of 1,2-dichloroethane in Table 1 [7]. In the present work, results for the Gibbs energy of transfer of eleven ions at the water/2-chloroethyl ether interface are presented.

EXPERIMENTAL

DC cyclic voltammetry measurements were carried out using a Hi-Tek PPR 1 waveform generator and a four electrode potentiostat with ohmic compensation.

The electrochemical cell was the same as used before [8], with an interfacial area of 0.69 cm^2. The base electrolyte in the aqueous phase was 10 mM LiCl (Aldrich). 10 mM tetraphenylarsonium tetrakis(4-chlorotetraphenyl) borate (TPAsTPBCl) and 10 mM μ-nitrido-bis(triphenylphosphorus) 3,3-como-bis (undecahydro-1,2-dicarba-3-cobalta-closododecabor)ate (PNPDCC) were employed alternatively as supporting electrolytes in the organic phase. TPAsTPB was prepared by mixing equimolar solutions of tetraphenylarsonium chloride, TPAsCl

Table 1. Some physical properties of 2-chloroethyl ether and 1,2-dichloroethane at 293 K [7].

Property	2-chloroethyl ether	1,2-dichlorethane
Density/g cm^{-3}	1.22	1.25
Viscosity/cp	2.41	0.84
Dielectric constant	21.20	10.45
Solubility in water/%(w/w)	1.02	0.84
Solubility of water in solvent/%(w/w)	0.10	0.16

(Fluka) and potassium tetrakis (4-chlorotetraphenyl) borate, KTPBCl (Fluka) from an ethanol-water mixture (1:2), followed by recrystallisation from acetone. PNPDCC (Technische Hochschule "Karl Schorlemmer" Leuna, Merseburg, Sektion Chemie, Germany) was a generous gift of Dr B. Hundhammer. To fix the zero of the Galvani potential difference of the interface, the ionic transfer of tetraphenylarsonium tetraphenylborate (TPAsTPB) was used as described in ref. 9. The salt was precipitated out by mixing equimolar aqueous solutions of TPAsCl (Fluka) and NaTPB (Fluka). The sodium salts of ClO_4^-, IO_4^-, SCN^- and picrate, the chloride and Pi^- salts of TMA^+, TEA^+, $TPrA^+$, TBA^+, methylviologen (MV^{2+}), acetylcholine (Ach^+), and choline (Ch^+), all from Aldrich Chemicals, were used. 2-Chloroethyl ether (Fluka, > 99%) was used without further purification. Millipore water was further purified by three times distillation from alkaline permanganate. The measurements were made using the cell arrangement:

Ag/AgCl/10 mM TPAsCl/10 mM TPAsTPBCl/σ /10 mM LiCl/AgCl/Ag

Before the start of each experiment the interface was allowed to equilibrate for 1 h. All the measurements were carried out at room temperature (22±2°C).

RESULTS AND DISCUSSION

Figure1 compares the dc voltammograms of the base electrolytes obtained at the water/2-chloroethyl ether interface for 10 mM LiCl in the aqueous phase and 10 mM TPAsTPB (a), TPAsTPBCl (b), and PNPDCC (c) in the organic phase. As can be seen from the figure the largest potential window is observed for the electrolyte couple LiCl(w)/PNPDCC(o). The polarisation obtained range is reasonably wide to detect the transfer of many ions which have been previously studied at the water/nitrobenzene or 1,2-dichloroethane interface [9,10]. The extent of polarisability of the water/2-chloroethyl ether interface is however smaller than those of the above mentioned systems. This might be due to slightly higher solubility of 2-chloroethyl ether in water.

Figure 2 and 3 show the dc voltammograms for the transfer of ClO_4^-, SCN^-, and MV^{2+} ions from water to organic and back to water. The reversibility of the ion transfer was checked from the 59/z mV (z = ionic charge) peak to peak separation. This was also apparent from the sweep rate (2-100 mV/s) and concentration (0.01-0.1 mM) independence of the peak potentials.

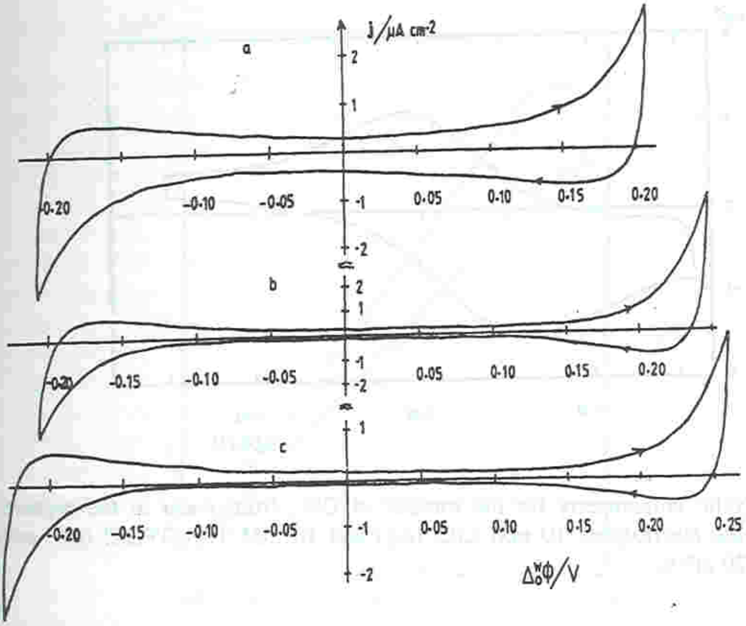

Figure 1. Comparisons of the cyclic voltammograms of 10 mM LiCl in water and 10 mM TPAsTPB (a), TPAsTPBCl (b), and PNPDCC (c) in 2-chloroethyl ether at a sweep rate of 10 mV/s.

Figure 4 shows the plots of peak current (I_p) vs square root of the sweep rate ($v^{½}$) for the transfer of methylviologen dication and acetylcholine ions from water to 2-chloroethyl ether respectively. In both cases linear dependence is observed. From the slopes of the plots, the diffusion coefficients of the ions in water were obtained using the Randles-Sevick equation [11]

$$I_p = 0.4463\ Z^{3/2} FAC(F/RT)\ (\nu D)^{1/2} \qquad (1)$$

The calculated values of the diffusion coefficients were 3.7×10^{-6} cm^2 s^{-1} and 13×10^{-6} cm^2 s^{-1} for MV^{2+} and ACh^+ respectively. The results obtained for acetylcholine is comparable with the value reported in the literature $D_W = 10 \times 10^{-6}$ cm^2 s^{-1}) [12]
From the half-wave potentials $\Delta^w_o\phi_{1/2}$ of the voltammograms, the standard Galvani potential differences $\Delta^w_o\phi^o$ were determined from [11]

$$\Delta^w_o\phi_{1/2} = \Delta^w_o\phi^o + (RT/ZF)\ln(D_W/D_o)^{½}(\Upsilon_o/\Upsilon_w) \qquad (2)$$

In equation 2, the ratio of the activity coefficients was assumed to be unity for the electrolyte concentrations used in these experiments (0.01-0.1 mM) and ion association was not considered. The diffusion coefficients of the ions in the organic phase were calculated according to the method of Coetzee and Cunningham [13]. The evaluation was based indirectly on tetraisoamylammonium tetraisoamyl borate as a reference electrolyte and assuming that Walden's product holds for the reference electrolyte in the solvent. Table 2 lists the diffusion coefficients of the ions in 2-chloroethyl ether estimated from reference 14 together with those calculated from the sweep rate dependence of the current density. As can be seen, the agreement between

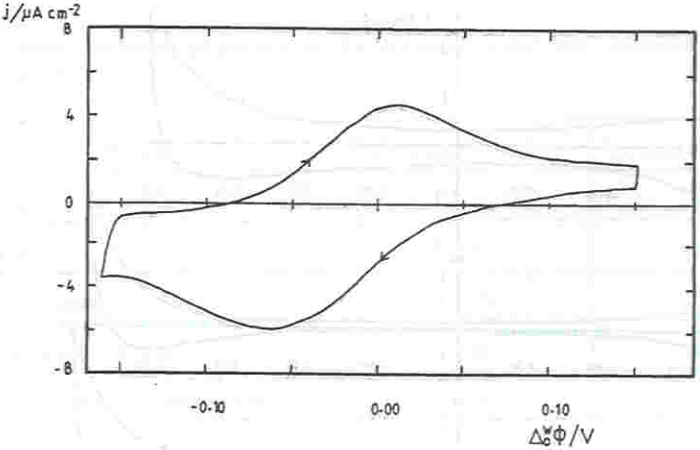

Figure 2. Cyclic voltammetry for the transfer of $Cl0_4^-$ from water to the organic phase. Base electrolytes: 10 mM LiCl (aq.) and 10 mM TPAsTPBCl (o), sweep rate = 20 mV/s.

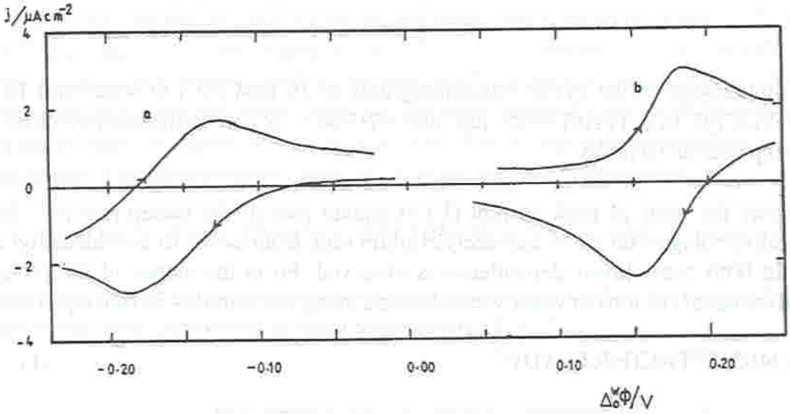

Figure 3. Cyclic voltammetry for the transfer SCN^- and MV^{2+} from water to the organic phase. Base electrolytes: 10 mM LiCl (aq.) and 10 mM TPAsTPBCl (o), sweep rate = 20 mV/s.

Table 2. Diffusion coefficient of ions in 2-chloroethyl ether.

Ion	TMA^+	TEA^+	$TPrA^+$	TBA^+	$I0_4^-$	ClO_4^-	Pi^-	SCN^-
D^i $10^{-6(a)}$	3.9	3.5	2.9	2.6	4.2	4.3	3.2	4.7
D^i $10^{-6(b)}$	4.2	3.1	2.4		3.3	3.7	3.7	5.5

[a] Values estimated from reference 14.

[b] Calculated from the voltametric measurements.

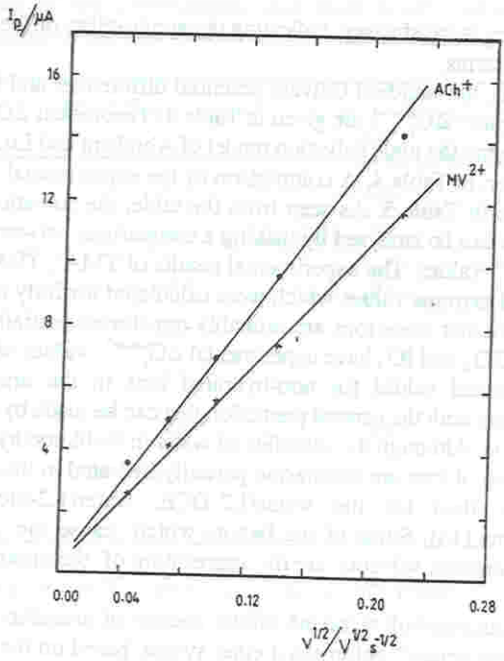

Figure 4. Peak current (Ip) vs square root of the sweep rate for 0.05 mM methylviologen (MV^{+2}) and 0.2 mM acetylcholine (ACh$^+$). Base electrolytes as in Figure 2.

Table 3. Half-wave potentials $\Delta_o^w\phi_{1/2}$, standard Galvani potential differences,$\Delta_o^w\phi^o$ and standard Gibbs energies of transfer of ions, $\Delta G_t^{o\ w\text{->}0}$, obtained experimentally for the water/2-chloroethyl ether system.

Ion	$\Delta_o^w\phi_{1/2}$/V	$\Delta_o^w\phi^o$ /V	$\Delta G_t^{o\ w\text{->}0}$ /kJmol^{-1}
TMA$^+$	0.109	0.123	11.9
TEA$^+$	0.034	0.045	4.3
TPrA$^+$	-0.061	-0.051	-4.9
TBA$^+$	-0.176	-0.167	-16.1
MV^{2+}	0.164	-0.169	32.6
ACh$^+$	0.134	0.145	14.0
Ch$^+$	0.204	0.215	20.7
ClO$_4^-$	-0.056	-0.074	7.1
IO$_4^-$	-0.081	-0.099	9.6
SCN$^-$	-0.161	-0.178	17.2
Pi$^-$	0.044	0.032	-3.1

calculation and measurement is satisfactory, indicating the applicability of the method described in reference 13 to these systems.

The half-wave potentials, the standard Galvani potential differences and the standard Gibbs energies of transfer of the ions, $\Delta G_t^{o\,w\text{->}0}$, are given in Table 3. Theoretical $\Delta G_t^{o\,w\text{->}0}$ values of the ions were calculated employing the ionic solvation model of Abraham and Liszi [14, 15] . Details of the calculations are given in Table 4. A comparison of the experimental and the theoretical results of $\Delta G_t^{o\,w\text{->}0}$ is made in Table 5. As seen from the table, the solvation state of the ions during the transfer process can be analysed by making a comparison between the experimental and the theoretical $\Delta G_t^{o\,w\text{->}0}$ values. The experimental results of TMA^+, TEA^+, SCN^- and Pi^- lie between the two theoretical extreme values which were calculated for fully hydrated ions in the organic phase. This implies that these ions are probably transferred partially hydrated. On the other hand $TPrA^+$, TBA^+, ClO_4^- and IO_4^- have experimental $\Delta G_t^{o\,w\text{->}0}$ values which are very close to the theoretically calculated values for non-hydrated ions in the organic phase. These observations are in agreement with the general prediction that can be made by taking only the size of the ions into consideration. Although the solubility of water in 2-chloroethyl ether is very small (see Table 1), a large number of ions are transferred partially hydrated in this system, and this is a more general feature, than for the water/1,2-DCE, water/1,2-dichlorobenzene and water/nitrobenzene systems [14]. Some of the factors which cause the co-transfer of H_2O molecules with ions into organic solvents are the aggregation of the organic

Table 4. Theoretical calculation of standard Gibbs energy of transfer of ions $\Delta G_t^{o\,w\text{->}0}$ (kJ.. mol^{-1}) for the water/2-chloroethyl ether system based on the model of Abraham and Liszi [14.15]

	a				b		
ion	ΔG_e^o	ΔG_n^o	ΔG_s^o	$\Delta G_t^{o\,w\text{->}0}$	ΔG_e^o	ΔG_n^o	$\Delta G_t^{o\,w\text{->}0}$
TMA^+	-191.3	6.0	-185.3	22.1	-211.3	-205.3	2.1
TEA^+	-163.8	-4.7	-168.5	9.6	-180.1	-184.7	-6.7
$TPrA^+$	-147.1	-15.1	-162.2	-4.2	-161.1	-176.2	-18.4
TBA^+	-136.9	-22.6	-159.5	-17.9	-149.5	-172.1	-30.4
ClO_4^-	-199.0	7.8	-191.2	11.9	-226.9	-219.1	-15.9
IO_4^-	-193.8	6.5	-187.3	9.8	-214.1	-207.6	-10.5
SCN^-	-242.0	14.7	-227.3	34.0	-268.6	-253.9	7.4
Pi^-	-168.4	0.2	-168.2	3.4	-185.3	-185.1	13.5

[a] Calculated for non-hydrated ions in the organic phase. [b] Calculated for fully hydrated ions in the organic phase; ΔG_n^o calculated using data for chlorobenzene (m = -3.307, c = 9.962) [15, 16]; ΔG_e^o calculated for non-hydrated ions in the organic phase using the radius of methylisobutyl ketone (r = 0.297 nm) [15, 16]; $\Delta G_t^{o\,w\text{->}0}$ obtained after adding 6.5 kJ/mol to the sum of ΔG_n^o and ΔG_h^o values (in molar scale); ΔG_h^o values were taken from reference 15.

Table 5. Comparison of the experimental and theoretically calculated values of standard Gibbs energies of transfer of selected ions from water to 2-chloroethyl ether.

ion	$\Delta G_t^{o\ w->0}$(exp.) /kJmol^{-1}	$\Delta G_t^{o\ w->0}$ (theor.) /kJ. mol^{-1}	
		(a)	(b)
TMA$^+$	11.8	22.1	2.1
TEA$^+$	4.3	9.6	-6.7
TPrA$^+$	-4.9	-4.2	-18.2
TBA$^+$	-16.1	-17.9	-30.4
ClO_4^-	7.1	11.9	-15.9
IO_4^-	9.6	9.8	-10.5
SCN$^-$	17.2	34.0	7.4
Pi$^-$	-3.1	3.4	-13.5

[a] Calculated for non-hydrated ions in the organic phase.

[b] Calculated for fully-hydrated ions in the organic phase.

electrolytes into ion-pairs, change of the nature of the organic medium by the organic salt followed by an increase in its water uptake and the formation of hydrogen bonds [16]. In this study, however, the first two effects have been minimised since the concentrations of the electrolytes were restricted to less or equal to 10 mM and the dielectric constant of 2-chloroethyl ether is high enough to dissociate the electrolytes completely. Therefore it appears that the observed enhancement in the partial hydration of the transferred ions may be due to hydrogen-bond formation between transferred water of hydration and the ether functionality in the solvent molecules.

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REFERENCES

1. Kazarinov, V.E. (Ed) *The Interface Structure and Electrochemical Process at the Boundary Between Two Immiscible Liquids,*Springer-Verlag: Berlin; 1987.
2. Koryta, J. *Electrochim Acta* **1988**, 33, 189.
3. Girault , H.H.; Schiffrin, D.J. *Electroanalytical Chemistry*, Vol. 15; Bard, A.J. (Ed), Marcel Dekker: New York,; 1989.
4. Marecek, V.; Samec, Z.; Koryta, J. *Advances in Colloid and Interface Science*, **1988**, 1, 29.
5. Marcus, Y. *Pure and Appl. Chem.*,**1983,** 55, 977.
6. Martha, Windholz (Ed) *Merck Index*, Merck & Com.: New Jersy ; 1976.

7. Riddick , J.A.; Bunger, W.B. *Organic Solvents, Physical Properties and Methods of Purification,* 3rd ed., in Techniques of Chemistry, Vol. 2 Weissberger, A. (Ed), Willey-Interscience: New York; 1970.
8. Geblewicz, G.; Kontturi, A.K.; Kontturi, K; Schiffrin, D.J. *Electro Anal. Chem.* **1987**, 217, 261.
9. Hundhammer, B.; Solomon, T. *J. Electroanal.Chem.* **1983,** 157, 19.
10. Koryta, J. *Electrochim Acta* **1984**, 29, 455.
11. Bard, A.J; Faulkner, L.R. *Electrochemical Methods, Fundamental and Applications,* Wiley: New York; 1989.
12. Samec, Z.; Marecek, V.; Homolka, D. *J. Electroanal. Chem.* **1983**, 158, 25.
13. Coetzee, J.P.; Cunningham, G.P. *J. Am Chem. Soc.***1965,** 87, 2529.
14. Abraham, M.H.; Liszi, J. *J. Inorg. Nucl. Chem.* **1981,** 43, 143.
15. Abraham , M.H.; Liszi, J. *J. Chem. Soc. Faraday Trans. I*, **1978** , 74, 1604.
16. Kenjo, T.; Diamond, R.H. *J. Inorg. Nucl. Chem.* **1974**, 36, 183.