Polarization phenomena at the water | o-nitrophenyl octyl ether interface. Part 1. Evaluation of the standard Gibbs energies of ion transfer from the solubility and voltammetric measurements [1]

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Abstract

Standard Gibbs energies of ion transfer from water to o-nitrophenyl octyl ether are evaluated for a series of ions from voltammetric and solubility measurements by using the tetraphenylarsonium tetraphenylborate hypothesis. Thermodynamic scales derived from these measurements are consistent with each other and with analogous scales for ion transfer to nitrobenzene and 1,2-dichloroethane.

Keywords: Polarization; Water | o-nitrophenyl octyl ether interface

1. Introduction

Thermodynamic and kinetic transfer functions of ionic species from water to organic solvents are of considerable interest because of their importance in the theory of ion extraction [1], phase-transfer catalysis [2] and ion-selective electrodes [3]. Their measurements can also be of relevance to biological transport phenomena, e.g. physiological effects of drugs correlate with the drug partition coefficient between water and oil phases [4].

Ion transfer to polar organic solvents of low miscibility with water can be investigated most conveniently by electrochemical methods, which are based on the polarization of the interface between two immiscible electrolyte solutions (ITIES) [5,6]. Systematic thermodynamic and kinetic studies have been focused on the water | nitrobenzene (NB) and water | 1,2-dichloroethane (DCE) interfaces, though some thermodynamic data have also been reported for ion transfer from water to chloroform [7], acetophenone [8], nitroethane [9], benzonitrile [10], o-nitrotoluene [11] and o-nitrophenyl octyl ether (o-NPOE) [12].

The purpose of this work was to study in detail the thermodynamics and kinetics of ion transfer across the water | o-NPOE interface. A comparison of the ion transfer to o-NPOE, NB and DCE is likely to throw some light on the factors underlying the structure and dynamics of an ITIES, inasmuch as some physico-chemical properties of o-NPOE are rather exceptional, see Table 1. Firstly, the miscibility of o-NPOE with water, as characterized by its solubility c_s^w in water, and the solubility c_{aq}^o, of water in o-NPOE, is by far the lowest. Secondly, owing to the smallest density ρ and the greatest molar mass M, o-NPOE has the largest molar volume V_0 or effective solvent radius $r = (1/2)(V_0/N_A)^{1/3}$ [18]. The miscibility and the size of the solvent molecules, together with their structure-related lateral interactions, should influence the structure of the ITIES. However, o-NPOE shows by far the highest kinematic viscosity η. Hence, a considerably slower ion transport, both in the bulk of o-NPOE and across the water | o-NPOE interface, is foreseen.

In this paper, we report the solubilities and association constants for a series of electrolytes in o-NPOE, and a relative scale of the standard Gibbs energies of ion transfer, based on the voltammetric measurements of ion transport across the water | o-NPOE interface. An attempt is also made to evaluate the absolute scale for ion transfer by using the solubility data for tetraphenylarsonium tetraphenylborate, and the non-thermodynamic hypothesis that the standard Gibbs energies of transfer of tetraphenylarsonium cation and tetraphenylborate anion are equal [19]. We shall show that the absolute scales based on the solubility or voltammetric measurements are consistent with each other and with those evaluated previously for the water | NB and water | DCE interfaces [20,21].
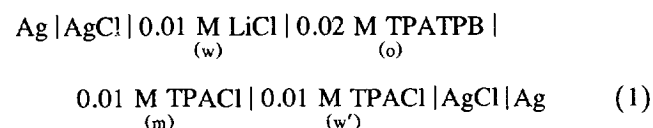

The structure of the water | o-NPOE interface and the ion transfer kinetics will be dealt with in a future communication.

2. Experimental

CsCl, HCl, KCl, LiCl, LiClO$_4$, tetramethylammonium chloride (TMACl), tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), tetrapentylammonium chloride (TPACl), tetraphenylarsonium chloride (TPAsCl), tetrapropylammonium hydroxide (TPrAOH), tetraphenylarsonium perchlorate (TPAsClO$_4$), sodium tetraphenylborate (NaTPB) and tetrabutylammonium tetraphenylborate (TBATPB), all purchased from Fluka as reagent grade chemicals, were used as received. TPrACl was prepared by a neutralization of TPrAOH with HCl. Other tetraphenylborates, i.e. CsTPB, TEATPB, TPATPB and TPAsTPB, were precipitated from NaTPB and corresponding chlorides. The precipitates were recrystallized from acetone or water + acetone mixture. Twice distilled water and o-nitrophenyl octyl ether (Fluka, Selectophore®) were used for preparation of the solutions. Prior to use, the organic solvent was purified by passing it slowly through a column of activated alumina.

Electrochemical measurements were carried out at the ambient temperature, i.e. 295 ± 2 K, in a four-electrode microcell [22] which can be represented by the scheme

Ag | AgCl | 0.01 M LiCl | 0.02 M TPATPB |
          (w)   (o)

          0.01 M TPACl | 0.01 M TPACl | AgCl | Ag   (1)
          (m)   (w')

A flat water | o-NPOE interface with geometric area 0.166 cm^2 was formed at the top of a glass cylinder. At the bottom of the cylinder, the organic phase (o) was separated from the reference aqueous phase (w') by a membrane (m). The Nafion® membrane used in the previous setup [22] was replaced by a microporous hydrophilic filter (0,45

type RC55, Schleicher and Schuell, Germany) impregnated with the reference aqueous solution (w').

Voltammetric and impedance measurements were performed by using a four-electrode potentiostat (1287 Electrochemical Interface Solartron, Solartron Instruments, UK) and a frequency response analyser (1255 FRA Solartron, Solartron Instruments, UK) equipped with software (ZPlot/ZView, Scribner Associates, Inc.) for computer control of impedance measurements and for non-linear least-squares fitting of impedance data. In impedance measurements, a 20 mV peak-to-peak a.c. voltage was applied across the cell (1) sweeping the frequency range 1 to 1000 Hz at a constant potential, which was then changed in a step-wise manner so as to cover the potential range available.

Conductometric measurements were carried out in a glass cell with two sealed Pt wire electrodes. The volume of the cell was approximately 150 μl. The cell was immersed in a water bath, the temperature of which was maintained at 298.0 ± 0.1 K. The solution resistance was evaluated as the real component of the cell impedance by using the impedance technique described above. The cell constant of (4.075 ± 0.02) × 10^{-2} cm was determined from the slope of the linear plot of the measured conductivity of five standard aqueous solutions of KCl vs. their specific conductivity.

Saturated solutions of electrolytes in o-NPOE were prepared by agitating the solvent with an excess of the electrolyte at 298 K for one day. The mixture was then centrifuged and the aliquot portions of the saturated solution were taken for analysis. Samples of o-NPOE solutions of tetraphenylborates were dissolved in acetonitrile, and the concentration of tetraphenylborate anion was determined from the limiting diffusion current corresponding to anion oxidation at a gold rotating disc electrode in the presence of an inert base electrolyte. The concentration of the saturated solution of TPAsClO$_4$ was determined conductometrically; i.e. after a defined dilution by o-NPOE the conductivity of the solution was measured and the concentration was evaluated using a calibrated curve.

Table 1
Comparison of some properties of o-nitrophenyl octyl ether, nitrobenzene and 1,2-dichloroethane at 298 K [a]

Property	o-NPOE	NB	DCE
$M/\text{g mol}^{-1}$	251.33	123.11	98.96
$\rho/\text{g cm}^{-3}$	1.041 [b]	1.1984	1.2458
$V_0/\text{cm}^3 \text{ mol}^{-1}$	241.4	102.7	79.4
r/nm	0.368	0.277	0.254
$\eta/10^{-3}$ Pa s	13.8 [13]	1.795	0.779
ϵ_r	24.2 [13]	34.82	10.36
$\sigma/\text{mN m}^{-1}$	—	42.76	31.54
c_s^w/M	2.01 × 10^{-6}[13]	1.5 × 10^{-2} [15]	8.5 × 10^{-2} [16]
c_{aq}^0/M	4.6 × 10^{-2}[14]	0.2 [15]	0.11 [17]

[a] Taken from Ref. [1], p. 130, unless otherwise indicated.
[b] 293 K.

Table 2

Limiting molar conductivities, association constants and solubilities of electrolytes in o-NPOE at 298 K

Electrolyte	A_0 / Ω cm^2 mol^{-1} [a]	K_A /M	c_s^0 /M
TEATPB	3.52 (142.77)	~0	1.56×10^{-3}
TBATPB	3.27 (119.65)	~0	2.40×10^{-2}
TPATPB	3.08 (114.96)	39.1	—
TPAsTPB	2.45 (114.1)	485	6.17×10^{-4}
CsTPB	2.20 (145.47)	3010	2.83×10^{-4}
TPAsClO$_4$	3.73 (159.58)	~0	1.89×10^{-3}

[a] Data in parentheses represent the limiting molar conductivities in acetonitrile [24].

3. Results and discussion

3.1. Standard Gibbs energies of transfer of electrolytes

Conductometric and solubility data for several electrolytes in o-NPOE are given in Table 2. The choice of electrolytes was governed by the availability of thermodynamic data for aqueous solutions, which are necessary for the calculation of the transfer function. Ion association constants K_A and the limiting molar conductivities A_0 were calculated from the slope and intercept of the Shedlovsky plot [23]:

$$(AS)^{-1} = A_0^{-1} + K_A c \gamma_{\pm}^2 AS / A_0^2 \qquad (2)$$

where A is the molar conductivity of the electrolyte at a concentration c, $S = [(z/2) + (1 + (z/2)^2)^{1/2}]^2$ is the function of $z = (\alpha A_0 + \beta) A_0^{-3/2} (cA)^{1/2}$, $\alpha = 82.046 \times 10^4 / (\epsilon_r T)^{3/2}$ mol$^{-1/2}$ dm$^{1/2}$, $\beta = 82.487 / \eta(\epsilon_r T)^{1/2}$ Ω^{-1} cm^2 mol$^{-3/2}$ dm$^{1/2}$ [24], ϵ_r is the relative dielectric permittivity and $\gamma_{\pm}$ is the mean activity coefficient. The variables of the plot, i.e $(AS)^{-1}$ and $c \gamma_{\pm}^2 AS$, were evaluated by an iterative procedure from Eq. (2), the extended Debye–Hückel equation:

$$- \log \gamma_{\pm} = A(\alpha\, c)^{1/2} / \left[1 + aB(\alpha\, c)^{1/2} \right] \qquad (3)$$

and the equation for K_A:

$$K_A = (1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 \qquad (4)$$

where α is the degree of dissociation, $A = 2.9769$ mol$^{-1/2}$ dm$^{1/2}$ K$^{3/2}$, $B = 0.59197 \times 10^8$ cm^{-1} mol$^{-1/2}$ dm$^{1/2}$ K$^{1/2}$. Since the magnitude of the size parameter a was
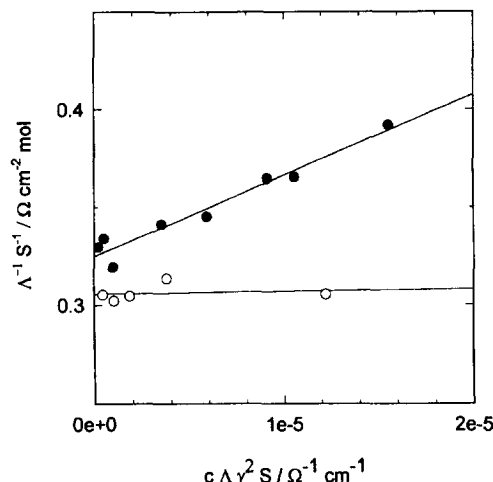

Fig. 1. Shedlovsky plot for TBATPB (O) and TPATPB (●) in o-NPOE at 298 K.

shown to have negligible effect on the calculated transfer functions of weak electrolytes [25], the value of $a = 6.6 \times 10^{-8}$ cm for TPAsTPB in DCE [25] was also adopted for all electrolytes in o-NPOE. Fig. 1 shows the Shedlovsky plots for a strong electrolyte (TBATPB) and a weak electrolyte (TPATPB).

Limiting molar conductivities in o-NPOE and acetonitrile are compared in Table 2. Low values of A_0 in the former case are obviously due to high kinematic viscosity of o-NPOE, cf. Table 1. Indeed, the ratio of the limiting equivalent conductivities of electrolytes in acetonitrile and o-NPOE varies from 37 to 47, which corresponds to the ratio of 41 of the kinematic viscosities of these two solvents (Walden rule). The behaviour of CsTPB is somewhat exceptional and seems to reflect an unexpectedly low ion conductivity of Cs$^+$ ion in o-NPOE.

From the solubilities c_s^0 and the association constants K_A it is possible to calculate the solubilities $c_i^0 = \alpha\, c_s^0$ of ionic species and the standard Gibbs energy $\Delta G_s^{0,o}$ of solution (on the molar scale) [26]:

$$\Delta G_s^{0,o} = -2RT \ln(\gamma_{\pm}^0 c_i^0) = -2RT \ln(\gamma_{\pm}^0 \alpha\; c_s^0) \qquad (5)$$

The standard Gibbs energy $\Delta_w^o G_s^0$ of transfer of an electrolyte from water to o-NPOE, which is the sum of the standard Gibbs energies of transfer of cation and anion, $\Delta_w^o G_+^0$ and $\Delta_w^o G_-^0$ respectively, is then obtained as the

Table 3

Calculation of the standard Gibbs energies $\Delta_w^o G_s^0$ of transfer (on the molar scale) from water to o-NPOE for various electrolytes at 298 K

Electrolyte	c_s^0/M	α	$\gamma_{\pm}^0$	$\Delta G_s^{0,o}$/kJ mol^{-1}	$\Delta G_s^{0,w}$ [a] /kJ mol^{-1}	$\Delta_w^o G_s^0$/kJ mol^{-1}
TEATPB	1.56×10^{-3}	0.99	0.794	33.2	60.9[27]	−27.7
TBATPB	2.40×10^{-2}	0.99	0.536	21.6	75.2	−53.6
TPAsTPB	6.17×10^{-4}	0.84	0.866	38.2	98.7	−60.5
CsTPB	2.83×10^{-4}	0.68	0.914	42.9	50.2	−7.3
TPAsClO$_4$	1.89×10^{-3}	0.99	0.775	32.3	47.3	−14.9

[a] Ref. [25] unless otherwise indicated.

Table 4

Calculation of the standard Gibbs energies of ion transfer from water to o-NPOE at 298 K from solubility and voltammetric measurements

Ion	E^0/V	$\delta\Delta_o^w\varphi^0$/V	$\Delta_w^o G_i^0$/kJ mol^{-1}	
			Solubility	Voltammetry
Cs$^+$	0.534	0.192	23.0	21.0
TMA$^+$	0.427	0.085	—	10.7
TEA$^+$	0.342	0	2.6	2.6 [a]
TPrA$^+$	0.226	−0.116	—	−8.7
TBA$^+$	—	—	−23.3	—
TPA$^+$	−0.008	−0.350	—	−31.3
TPAs$^+$	—	—	−30.3	—
TPB$^-$	0.642	0.300	−30.3	−31.5
ClO$_4^-$	0.180	−0.162	15.4	13.1

[a] An assumption.

difference of the standard Gibbs energies of the organic and aqueous solutions:

$$\Delta_w^o G_s^0 = \Delta_w^o G_+^0 + \Delta_w^o G_-^0 = \Delta G_s^{0,o} - \Delta G_s^{0,w} \qquad (6)$$

Results of the calculation of $\Delta_w^o G_s^0$ are summarized in Table 3.

3.2. Standard Gibbs energies of transfer of ions

Thermodynamic studies of ion transfer usually refer to the Parker non-thermodynamic convention [19] that the standard Gibbs energies of transfer of TPAs$^+$ cation and TPB$^-$ anion are equal for any pair of solvents, $\Delta_w^o G_{TPAs^+}^0 = \Delta_w^o G_{TPB^-}^0$. By applying this convention, it is possible to calculate $\Delta_w^o G_{TPAs^+}^0$ and $\Delta_w^o G_{TPB^-}^0$ from the standard Gibbs energy of transfer of TPAsTPB, cf. Eq. (6). Subsequently, the experimental values of $\Delta_w^o G_s^0$ for various electrolytes comprising TPAs$^+$ and TPB$^-$ ions can be used to evaluate the standard Gibbs energy of transfer of the counter ion. Results of these calculations are given in Table 4.

An original electrochemical method for the evaluation of $\Delta_w^o G_{TPAs^+}^0$ and $\Delta_w^o G_{TPB^-}^0$ has been proposed by Koryta and coworkers [12]. The method is based on the measurement of the standard potential $E_{TPB^-}^0$ of the TPB$^-$ anion:

$$E_{TPB^-}^0 = \Delta_o^w\varphi_{TPB^-}^0 - \Delta_o^w\varphi_{TPAs^+}^0 \qquad (7)$$

from the current–potential curve of the TPB$^-$ ion transfer from an organic solvent containing TPAsTPB as the base electrolyte. Since the standard potential difference $\Delta_o^w\varphi_i^0$ of an ion is related to the standard Gibbs energy $\Delta_w^o G_i^0$ of ion transfer

$$\Delta_o^w\varphi_i^0 = \Delta_w^o G_i^0/zF \qquad (8)$$

where z is the charge number of the ion, $E_{TPB^-}^0$ is given by the standard Gibbs energy of transfer of TPAsTPB, i.e. $E_{TPB^-}^0 = -(\Delta_w^o G_{TPB^-}^0 + \Delta_w^o G_{TPAs^+}^0)/F$. Then, either the TPAsTPB hypothesis is used or, more simply, the centre of symmetry of the current potential curve (i.e. the middle of the potential range) is determined, which should correspond to the zero point of the potential scale after Parker.

The technical difficulty with this approach is that the solubility of TPAsTPB is very low and its association is high in most polar solvents, so that it is necessary to correct the current–potential curve for a rather large ohmic potential drop due to the low concentration of ions.

Therefore, we used instead TPATPB as the base electrolyte for the organic phase and evaluated the reversible half-wave potentials $E_{1/2}^{rev}$ for a series of ions from their cyclic voltammograms at the ITIES. By taking into account the ion association in the organic phase, the value of $E_{1/2}^{rev}$, as inferred from measurements in the cell (1), can be expressed as [20,28]

$$E_{1/2}^{rev} = \Delta_o^w\varphi_i^0 - \Delta_o^w\varphi_{TPA^+}^0 \pm (RT/F) \ln(\gamma_i^o/\gamma_i^w)$$

$$\pm (RT/2F) \ln(D_i^w/D_i^o) \mp (RT/F)$$

$$\times \ln\left[1 + K_A\alpha c^o(\gamma_\pm^o)^2(D_A^o/D_i^o)^{1/2}\right]$$

$$-(RT/F) \ln(a_{TPA^+}^o/a_{TPA^+}^{w'}) + (RT/F)$$

$$\times \ln(a_{Cl^-}^{w'}/a_{Cl^-}^w) \qquad (9)$$

where the upper or lower sign applies to the transfer of a cation or anion respectively, $\Delta_o^w\varphi_{TPA^+}^0$ is the standard potential difference of the reference TPA$^+$ cation, γ_i is the ion activity coefficient, a_i is the ion activity, D_i is the ion diffusion coefficient, K_A is the constant of association between the transferred ion and the counter ion of the organic base electrolyte, D_A^o is the diffusion coefficient of the ion pair, α is the degree of dissociation of the organic base electrolyte, c^o is its concentration and $\gamma_\pm^o$ the mean activity coefficient. Obviously, the measured values of $E_{1/2}^{rev}$ can be used to calculate the standard potential difference for an ion transfer relative to the standard potential difference of TPA$^+$ cation, $E^0 = \Delta_o^w\varphi_i^0 - \Delta_o^w\varphi_{TPA^+}^0$.

Voltammetric data were obtained for the transfer of Cs$^+$, TMA$^+$, TEA$^+$, TPrA$^+$, TPA$^+$, TPB$^-$ and ClO$_4^-$ ions. The contributions of the various terms on the right-hand side of Eq. (9) were estimated by using the values of the parameters derived in part from conductometric measurements, i.e. $\gamma_i^o = 0.5519$, $\gamma_i^w = 0.89$, $\alpha = 0.86$, $a_{TPA^+}^o/a_{TPA^+}^{w'} = \alpha\ \gamma_i^o\ c^o/\gamma_i^{w'}c^{w'} = 0.95$, $a_{Cl^-}^{w'}/a_{Cl^-}^w = 1$, $D_i^w/D_i^o = 15.5$ (Walden rule). The magnitude of the term accounting for the ion association was found to be negligible for most ion transfer reactions, except for Cs$^+$, in which case $(RT/F) \ln[1 + K_A\alpha c^o(\gamma_\pm^o)^2(D_A^o/D_i^o)^{1/2}] = 58$ mV, by taking $D_A^o/D_i^o = 0.3$ [20].

The range of polarization of the water|o-NPOE interface is apparent from Fig. 2, which shows the cyclic voltammogram of the base electrolytes in the cell (1). In general, the electric current is the sum of the faradaic and capacitance current, $I = I_F + I_C$. In order to estimate the latter contribution, we measured the interfacial capacitance C by impedance spectroscopy, cf. Fig. 3. The capacitance current I_C was then calculated for the particular sweep rate v as $I_C = C\ v$. As can be seen from Fig. 2, at low sweep rates the capacitance current represents a relatively small
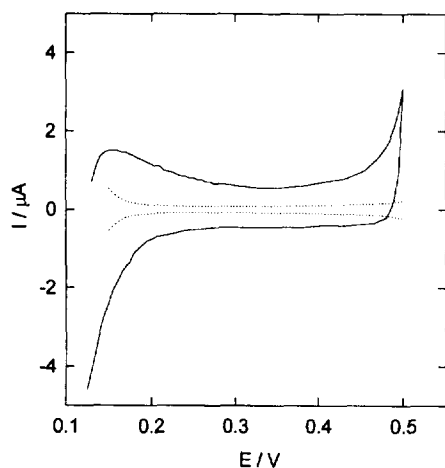
Fig. 2. Cyclic voltammogram of 0.01 M LiCl in water and 0.02 M TPATPB in o-NPOE (————) compared with the capacitance current (· · · · ·) which was calculated from the capacitance data displayed in Fig. 3. Sweep rate 0.08 V s^{-1}.

Fig. 4. Cyclic voltammogram of the tetrapropylammonium ion transfer across the water|o-NPOE interface (————) after correction for the base electrolyte current (· · · · ·), compared with the theoretical voltammogram for a reversible ion transfer (— — —) calculated using simulation software [29] for $D_i^w = 1.09 \times 10^{-5}$ cm^2 s^{-1}. Ion concentration 5×10^{-4} mol dm^{-3}, sweep rate 0.08 V s^{-1}.

portion of the current measured, cf. the dotted line in Fig. 2. Hence, the onset current I at the negative and positive limit of the cyclic voltammogram can be used to evaluate $E_{1/2}^{rev}$ for the base electrolyte ions, presumably TPA$^+$ and TPB$^-$ respectively [12]:

$$I = -zFA(\mid z \mid F D_i^o v/RT)^{1/2} c^o$$
$$\times \exp\left[-zF\left(E - E_{1/2}^{rev}\right)/RT\right] \quad (10)$$

where z is the charge number of the ion and A is the interfacial area. Fig. 4 shows a typical cyclic voltammogram of a semi-hydrophobic ion transfer across the water|o-NPOE interface. For all the ions studied, the peak current was proportional to the ion concentration (0.1 to 1.0 mM) and to the square-root of the sweep rate (2 to 100 mV s^{-1}) and the peak potential difference $\Delta E_p = E_p^+ - E_p^- \approx 59$ mV. Hence, the ion transfer reactions are con-
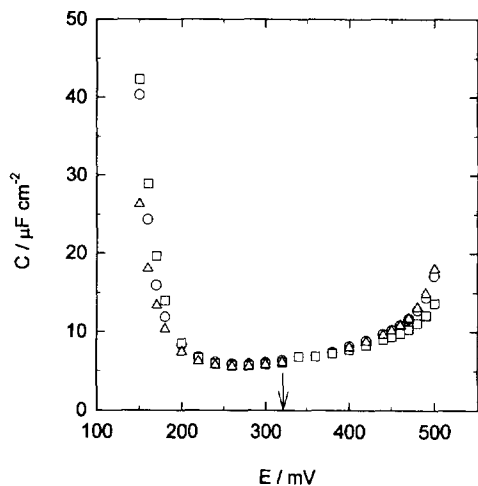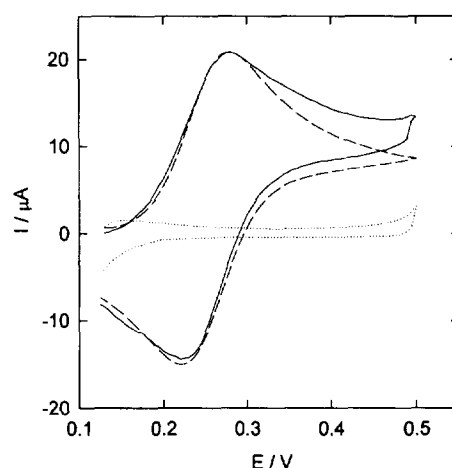

Fig. 3. Capacitance of the interface between 0.01 M LiCl in water and 0.02 M TPATPB in o-NPOE from three independent impedance measurements. The arrow indicates the potential E at which $\Delta_0^w \varphi = 0$.

trolled by the linear diffusion. Indeed, the shape of the theoretical voltammogram of a reversible ion transfer, as calculated using simulation software [29], and the parameters estimated according to the Nicholson–Shain theory [30], fits well the experimental curve corrected for the base electrolyte current, cf. the solid and dashed lines in Fig. 4. The reversible half-wave potential was then estimated as $E_{1/2}^{rev} = (E_p^+ + E_p^-)/2$ [30].

Table 4 summarizes the values of the standard potentials E^0 calculated by using Eq. (9). On the basis of Eq. (8), these data can be transformed into a relative scale of the standard Gibbs energies of ion transfer, with TPA$^+$ as the reference ion. However, it is more convenient to adopt as the reference an ion for which the value of $\Delta_w^o G_i^0$ is known, e.g. from solubility or partition measurements, and which can also be used for a calibration of the potential scale. Consequently, the thermodynamic data obtained from voltammetric measurements were related to the TEA$^+$ ion and, by using the value $\Delta_w^o G_i^0 = 2.6$ kJ mol^{-1} derived from the solubility measurements, the absolute scale of the standard Gibbs energies was also evaluated from voltammetric data, cf. Table 4. Obviously, the two absolute scales are mutually consistent, cf. the very good agreement between the values of $\Delta_w^o G_i^0$ for Cs$^+$, TPB$^-$ and ClO$_4^-$ ions.

Standard Gibbs energies of transfer of several ions to o-NPOE were also evaluated from voltammetric measurements by Koryta and coworkers [12]. However, as we have mentioned previously [22], there was an error in the formula for $E_{1/2}^{rev}$ used by the authors [12]. By correcting the latter results, one gets the values of 13.8, -2.5 and 15.8 kJ mol^{-1} for the transfer of TMA$^+$, TEA$^+$ and ClO$_4^-$ respectively, which are close to the values given in Table 4.
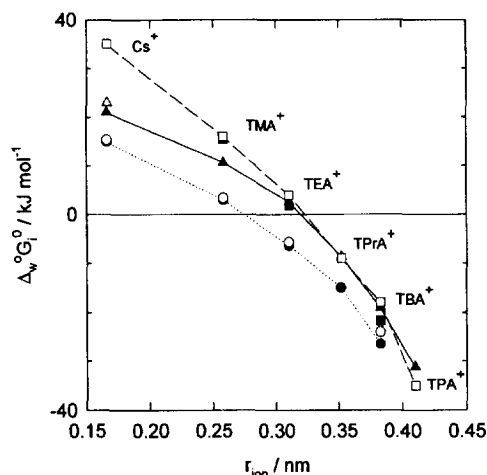
Fig. 5. Standard Gibbs energy of ion transfer vs. the ion radius from water to nitrobenzene (●, ○) [6,20,40], o-nitrophenyl octyl ether (△, ▲) and 1,2-dichloroethane (□, ■) [21] from solubility or partition (open symbols) and voltammetric (closed symbols) measurements. Ion radii taken from Ref. [18].

3.3. Solvent effects

Various theoretical approaches (cf. the review in Ref. [31]) suggest that the standard Gibbs energy of ion transfer can be split into an electrostatic term $\Delta_w^o G_{i,e}^0$ and a neutral term $\Delta_w^o G_{i,n}^0$:

$$\Delta_w^o G_i^0 = \Delta_w^o G_{i,e}^0 + \Delta_w^o G_{i,n}^0 \tag{11}$$

Both terms depend on the ion size, e.g. the Born formula predicts that the electrostatic contribution is inversely proportional to the ion radius r [32]:

$$\Delta_w^o G_{i,e}^0 = \left(z^2 F^2/8\pi N_A \epsilon_0 r\right)\left(1/\epsilon_r^o - 1/\epsilon_r^w\right) \tag{12}$$

where ϵ_0 is the dielectric permittivity of vacuum. The Born continuum model has been further refined by considering the dependence of the dielectric permittivity on the electric field [33,34], or by introducing the spatial correlation of the solvent polarization [35]. A more reliable physical picture of the electrostatic interactions is provided by applying the methods of liquid state physics to a discrete model represented by the mixture of the hard-sphere ions and point dipolar hard-sphere solvent molecules [36]. However, the theoretical treatment of the solvophobic interactions, which gives rise to the neutral term, is less satisfactory [31]. In the absence of a transparent theory, the value of $\Delta_w^o G_{i,e}^0$ can be estimated [31] by using a semi-empirical approach, cf. the Uhlig formula [37]:

$$\Delta_w^o G_{i,n}^0 = 4\pi r^2 \sigma^{w,o} \text{ sgn}(\sigma^o - \sigma^w) \tag{13}$$

where $\sigma^{w,o}$ is the interfacial tension between the two solvents, and σ^o or σ^w is the interfacial tension between the solvent and air. In another approach [33] the neutral term is regarded as the change in the standard Gibbs energy of solvation of a non-polar solute of the same size

and, consequently, it is assumed to be proportional to the ion radius r.

A straightforward consequence of these considerations is that for small ions the electrostatic term $\Delta_w^o G_{i,e}^0$ should prevail, i.e. the standard Gibbs energy of transfer from water to NB, DCE or o-NPOE should be negative, because $\epsilon_r^o < \epsilon_r^w = 78.3$, cf. Table 1. As the ion radius increases, the electrostatic term tends to zero, cf. Eq. (12), while the neutral term becomes increasingly negative, because $\sigma^o < \sigma^w = 71.81$ mN m^{-1} and sgn$(\sigma^o - \sigma^w) = -1$, at least for NB and DCE, cf. Table 1. Indeed, the plots of $\Delta_w^o G_i^0$ vs. ion radius shown in Fig. 5 confirm the predicted behaviour in all three solvent systems investigated. As expected, for small ions $\Delta_w^o G_i^0$ increases in the sequence DCE > o-NPOE > NB, while for large ions the values of $\Delta_w^o G_i^0$ merge as the interfacial tension $\sigma^{w,o} \approx 26$ mN m^{-1} for both the water|NB [38] and water|DCE [39] interfaces.

4. Conclusions

Absolute scales of standard Gibbs energies of ion transfer from water to o-nitrophenyl octyl ether derived from solubility and voltammetric measurements are consistent with each other and with analogous scales for ion transfer to nitrobenzene and 1,2-dichloroethane.

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