Ion Pairing in the Analysis of Voltammetric Data at the ITIES: RbTPB and RbTPBCl in 1,2-dichloroethane

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The association of rubidium-tetraphenylborate (RbTPB) and rubidium-tetrakis(-chlorophenyl)borate (RbTPBCl) ion pairs in the organic solvent 1,2-dichloroethane (DCE) have been obtained from condutivity and voltammetric data. Conductivity measurements given $K_{RbTPBCl} = 43\,100\,M^{-1}$ and yield a lower bound for K_{RbTPB} ($K_{RbTPB} > 70\,000\,M^{-1}$). The latter association constant is at variance with the previously accepted value. A method for analysing voltammetric data which allows for the determination of the association constants is presented. The positive polarization limit where the transfer of Rb^+ takes place is shifted by ca. 200 mV when changing the anion of the organic base electrolyte from TPB^- to $TPBCl^-$. If we interpret this shift in terms of the association constant, then $K_{RbTPB} = 7.4 \cdot 10^7\,M^{-1}$. The values of K_{RbTPB} and K_{RbTPCl} are discussed in terms of the classical theories by Bjerrum and Fuoss. Finally, we consider if the preferential solvation of p-chlorophenyl rings of $TPBl^-$ could account for the observed difference between the values of the association constants.

Introduction

The organic solvents most frequently used in the study of the electrochemical properties of the Interface between Two Immiscible Electrolyte Solutions (ITIES) are 1,2-dichloroethane (DCE) and nitrobenzene (NB) [1]. The low relative permittivity of these solvents, especially in the case of the DCE ($\varepsilon_r = 10.23$), leads to considerable ion pairing. However, the consequences of ion pairing are not usually remarked with sufficient emphasis. For instance, ion pairs have a contribution to the total interfacial charge which affects the structure and the capacitive properties of the ITIES [2]. Corrections for ion pairing are also necessary when determining the standard potential of ion transfer from the formal potential; this is probably the reason for the widely scattered transfer potential data in the literature.

In a recent work, the transfer of Rb^+ across the water/DCE interface placed at the tip of a micro-pipette was studied with cyclic voltammetry [3], and it was observed that the positive polarization limit was increased by 210 mV when changing the organic base electrolyte from tetrabutylammonium tetraphenylborate (TBATPB) to tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl). When Rb^+ ion transfers from water into DCE, it forms an ion pair with the organic anion in the oil phase. If this voltage shift were due to the difference of the association constants K_{RbTPB} and $K_{RbTPBCl}$ (provided that the other quantities remain constant), it follows that their ratio should be of the order of 10^3. However, this unexpected difference in the association constants is very difficult to rationalize in terms of distances of closest approach in the classical theories for ion association of Bjerrum and Fuoss. The association constant of RbTPB in DCE has been estimated as $1700\,M^{-1}$ [4], but no value for the association constant of

RbTPBCl in DCE has been reported so far. Should this value of K_{RbTPB} be correct, the saturated solution of RbTPB would have detectable conductivity, which has not been observed, though [3].

In this paper the values of K_{RbTPB} and $K_{RbTPBCl}$ are determined. First, the degree of ion pairing of Rb^+ with $TPBCl^-$ in DCE is obtained from conductivity measurements. The method suits to the evaluation of $K_{RbTPBCl}$, but yields only a lower bound for K_{RbTPB} due to the low solubility of RbTPB in the organic phase. Also, we estimate the ionic diffusion coefficients from the limiting molar conductivities. Second, the transfer of Rb^+ ion at the water/DCE interface is studied with cyclic voltammetry using a conventional four-electrode set-up with different concentrations of the organic base electrolyte TBATPBCl. A method for analysing voltammetry data which allows for the determination of the association constant is presented. Finally, we discuss about the importance of the ion pairing when TBATPB and TBATPBCl are used as base electrolytes in the organic phase, interpret the values obtained in terms of the classical theories by Bjerrum and Fuoss, and give some semiquantitative arguments for the observed difference between the K_{RbTPB} and $K_{RbTPBCl}$ values.

Experimental

a) Conductivity Measurements

Conductivity measurements were carried out using a Philips PW9527 conductivity meter and a Radiometer CDC114 conductivity cell, the cell constant of which is $1.0\,cm^{-1}$. This value was checked by calibration with aqueous KCl solutions ($0.1 - 100\,mM$) and it remained constant within 3% accuracy in this concentration range. It must be emphasized, though, that the conductivity of the most diluted calibration solution is at least ten times higher than the conductivity of the DCE solutions to be measured.

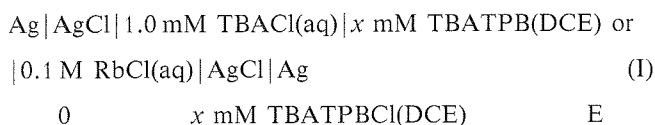*) To whom correspondence should be addressed.

More diluted calibration solutions could not be used due to the conductivity of water itself which was purified by distillation and use of Millipore MilliQ apparatus. The conductivity of pure DCE (M & B spectroscopic grade) was zero, exactly.

TBATPBCl was precipitated from the ethanolic solution of KTPBCl (Lancaster Synthesis) with the aqueous solution of TBACl (Aldrich) and recrystallized from p.a. acetone (M & B). TBATPB was precipitated from the aqueous solutions of NaTPB (Aldrich) and TBACl. KTPBCl, NaTPB and TBACl were all of analytical grade. RbTPBCl was also precipitated from the ethanolic solution of KTPBCl with a 100 fold excess of aqueous RbCl (suprapur, Sigma) solution. After recrystallization from acetone the salt was analyzed with Varian Atomic Absorption Spectrophotometer. The Rb contents of the salt was 3% lower than calculated from the molecular formula. Therefore, the existence of possible impurities or other reaction product was checked with NMR analysis according to which these impurities were aromatic aldehydes and alcohols which do not contribute to the conductivity.

The concentration of the saturated solution of RbTPBCl in DCE was found to be 0.137 mM while TBATPBCl dissolves up to ca. 0.3 M concentration. From the saturated solution of RbTPBCl a series of solutions were diluted and their conductivities were measured at $25.00 \pm 0.01\,°C$. After each measurement the cell was washed with pure DCE until zero conductivity was obtained.

b) Linear Sweep Voltammograms

The cell potential E corresponds to the following cell:

$Ag|AgCl|1.0\,mM\ TBACl(aq)|x\ mM\ TBATPB(DCE)$ or

$|0.1\,M\ RbCl(aq)|AgCl|Ag$ (I)

$\quad$ 0 $\qquad\qquad$ x mM TBATPBCl(DCE) $\qquad$ E

where x was 0.5, 1.0, 5.0 and 10. The all-glass four electrode cell is described elsewhere [5]. The signal generator was HI-TEK PPR1 and the four electrode potentiostat Sycopel Rix-Räx-Pum. The voltammograms were stored into Advantest R 9211E Digital Spectrum Analyser from which the data was easily transferrable to convolution analysis on a PC.

Cyclic voltammograms were measured at the sweep rates of 5, 10, 25, 50 and 100 mV s^{-1}. The compensation of the solution resistance was first carried out in the potentiostat by the conventional positive feed-back techniques but it appeared to work unsatisfactorily. Therefore, the solution resistance was calculated afterwards from uncompensated voltammograms, which were then corrected for the iR drop. (The calculation of the solutions resistance is based on the fact that at the foot of the polarization wave, where current is less than 10% of the peak current, current raises exponentially according to Butler-Volmer equation, but with the charge transfer coefficient $\alpha = 1$. This can be checked from the classical solution of Nicholson and Shain, presented in, e.g., Ref. [6]).

Results

a) Conductivity Measurements

The association constant of the organic base electrolyte is required when evaluating the activities of free ions in the oil phase, which will be used later in the analysis of the voltammetry data. Also, some interesting information on ionic molar conductivities can be derived from it. In Ref. 7, the association constant and limiting molar conductivity at infinite dilution of TBATPB in DCE were determined, with the results $K_{TBATPB} = 1715\,M^{-1}$ and $\Lambda_0 = 50.14\,\Omega^{-1}\,cm^2\,mol^{-1}$. We determined $K_{TBATPBCl}$ from the conductivity measurements, as shown in Fig. 1, and the points were fitted to Eq. (1)
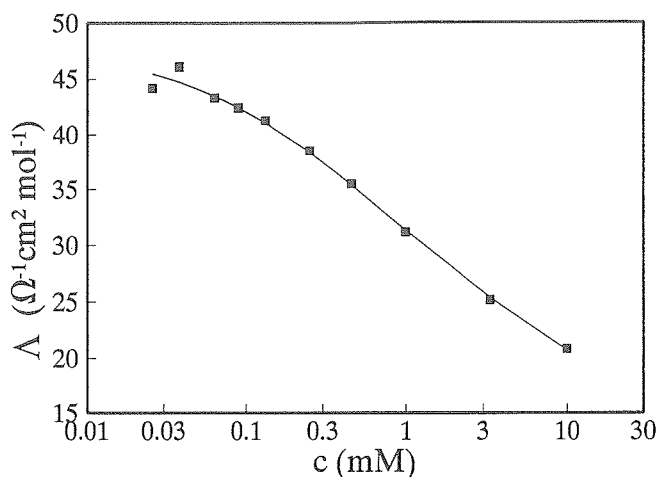

Fig. 1
Molar conductivity of TBATPBCl at different concentrations c. The solid line represents the best fit to Eq. (1) with $K_{TBATPBCl} = 1770\,M^{-1}$ and $\Lambda_0 = 47.7\,\Omega^{-1}\,cm^2\,mol^{-1}$

$$\Lambda = \alpha\,(\Lambda_0 - \sqrt{\alpha\,c})$$ (1)

with

$$\Lambda_0 = \frac{F^2}{RT} \sum |z_i|\,D_i$$ (2)

and

$$\alpha = \frac{\sqrt{1 + 4K\gamma_\pm^2\,c} - 1}{2K\gamma_\pm^2\,c}\,.$$ (3)

In Eqs. (1)–(3), α is the degree of dissociation, S is the slope of theoretical limiting tangent, and c is the salt concentration; z_i and D_i are the charge number and the diffusion coefficient of the i-th ion, respectively, and constants $F, R,$ and T have their usual meaning. The mean activity coefficient $\gamma_\pm$ was iterated at each fitting round from the extended Debye-Hückel theory, while the activity coefficient of the ion pair is unity. The results of the fit were $K_{TBATPBCl} = 1770\,M^{-1}$ and $\Lambda_0 = 47.7\,\Omega^{-1}\,cm^2\,mol^{-1}$, thus confirming the similarity of TBATPB and TBATPBCl.

The efforts to measure the conductivity of RbTPB in DCE were unsuccessful [3] due the low solubility of the salt [4] and the apparently high value of the association constant. Since this conductivity was under the detection limit of 0.1 µS, the association constant of RbTPB should be higher than 70000 M^{-1}. The solubility of RbTPBCl appeared to be one order of magnitude higher. In Fig. 2 the measured conductivities are presented along with the fit into Eq. (1), and the results of the fit are $K_{RbTPBCl} = 43\,100\,M^{-1}$ and $A_0 = 61.5\,\Omega^{-1}\,cm^2\,mol^{-1}$.
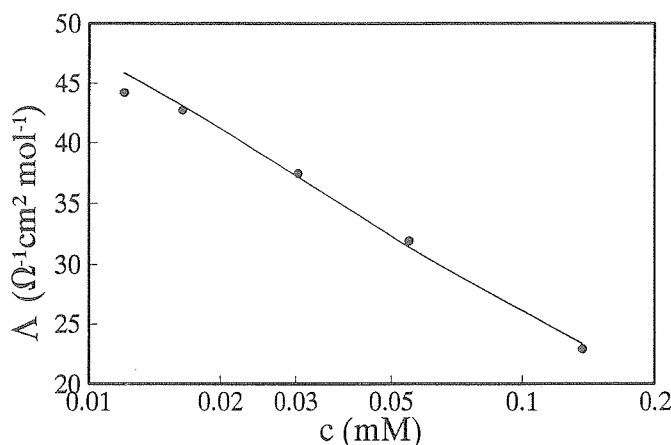

Fig. 2

Molar conductivity of RbTPBCl at different concentrations c. The solid line represents the best fit to Eq. (1) with $K_{RbTPBCl} = 43\,100\,M^{-1}$ and $A_0 = 61.5\,\Omega^{-1}\,cm^2\,mol^{-1}$

The limiting molar conductivities obtained above can be used to estimate the ionic diffusion coefficients. These magnitudes will be relevant to the calculation of the convolution integrals below [5] and they are also of more general interest.

From the limiting molar conductivity of TBATPB, $A_0 = 50.14\,\Omega^{-1}\,cm^2\,mol^{-1}$, it can be calculated that $D_{TBA^+}^{DCE} + D_{TPB^-}^{DCE} \approx 1.33 \cdot 10^{-5}\,cm^2\,s^{-1}$. If it is assumed that these diffusion coefficients are inversely proportional to the ionic radii, which can be estimated as 0.40 nm for TBA$^+$ and 0.49 nm for TPB$^-$ [8], it is found that $D_{TBA^+}^{DCE} \approx 7.4 \cdot 10^{-6}\,cm^2\,s^{-1}$ and $D_{TPB^-}^{DCE} \approx 5.9 \cdot 10^{-6}\,cm^2\,s^{-1}$.

Now, by using the diffusion coefficient of TBA$^+$ calculated above and the limiting molar conductivity of TBATPBCl, $A_0 = 47.7\,\Omega^{-1}\,cm^2\,mol^{-1}$, the diffusion coefficient of TPBCl$^-$ can be estimated to be $D_{TPBCl^-}^{DCE} \approx 5.3 \cdot 10^{-6}\,cm^2\,s^{-1}$. Finally, from this value and the limiting conductivity of RbTPBCl, $A_0 = 61.5\,\Omega^{-1}\,cm^2\,mol^{-1}$, the diffusion coefficient of Rb$^+$ in DCE results to be $D_{Rb^+}^{DCE} \approx 1.11 \cdot 10^{-5}\,cm^2\,s^{-1}$.

It is interesting to note that $D_{Rb^+}^{DCE}$ is about one half of the diffusion coefficient of Rb$^+$ in water, $D_{Rb^+}^{W} = 2.04 \cdot 10^{-5}\,cm^2\,s^{-1}$ [9]. Again, we have been unsuccessful in finding a value for $D_{Rb^+}^{DCE}$ in the literature, and the common practice of using Walden's rule is not applicable here because the product $\lambda_i\eta$ is ca. 0.3 for several solvent-ion couples, but ca. 0.7 for water-ion couples (see

Fig. 3). The limiting ionic conductivities λ_i were taken from Ref. 9 and the solvent dynamic viscosities η from Ref. 10. Thus, the diffusion coefficients evaluated here from limiting conductivities could be reasonable.
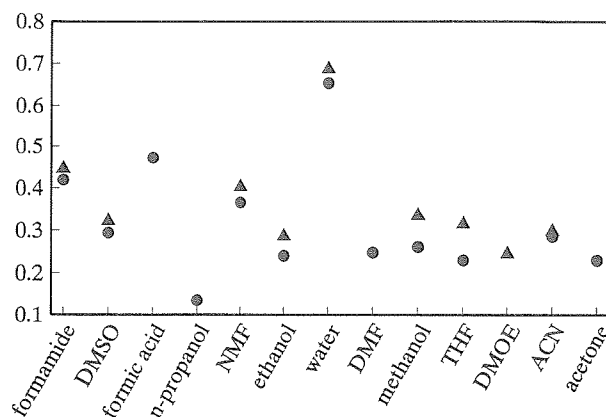

Fig. 3

Walden's product $\lambda_i\eta$ for K$^+$ (●) and Cs$^+$ (▲) and different solvents; DMSO stands for dimethylsulphoxide, NMF for n-methylformamide, DMF for dimethylformamide, THF for tetrahydrofuran, DMOE for dimethoxyethane, and ACN for acetonitrile

b) Linear Sweep Voltammograms

In Ref. 3, the difference between the positive polarization limits for TPB$^-$ and TPBCl$^-$ was found to be 210 mV. This result was obtained using a micropipette, with 0.01 M TBATPC or TBATPBCl in the organic phase, and 0.1 M RbCl in the aqueous phase. The sweep rate was 100 mV/s. Due to the important implications of this large difference, it was reasonable to confirm this result by using a four-electrode cell [5] and a difference of 190 mV was found. The reason for the discrepancy of 20 mV is probably that it is quite difficult to reproduce the exact position of the interface at the tip of a micropipette.

In Fig. 4, the linear sweep voltammograms at 5 mV/s for different concentrations of the organic base electrolyte TBATPBCl are presented. This set of data was chosen for analysis to avoid the correction for capacitive current which would be necessary at higher sweep rates [5]. The measured cell potential E is corrected for the absolute Galvani potential scale $\Delta_0^W \Phi = \Phi^W - \Phi^0$ through Eq. (4)

$$\Delta_0^W \Phi = E - \Delta_0^W \Phi_{TBA^+}^0 + \frac{RT}{F} \ln \frac{a_{Cl^-}^W a_{TBA^+}^0}{a_{TBACl}^2} . \tag{4}$$

The standard transfer potential of TBA$^+$ was taken as $-225\,mV$ [1], and the activity of free TBA$^+$ in the oil phase is evaluated from the association constant of the organic base electrolyte as before [8].

Assuming reversible Nernstian behavior, the Galvani potential difference across the ITIES is given by

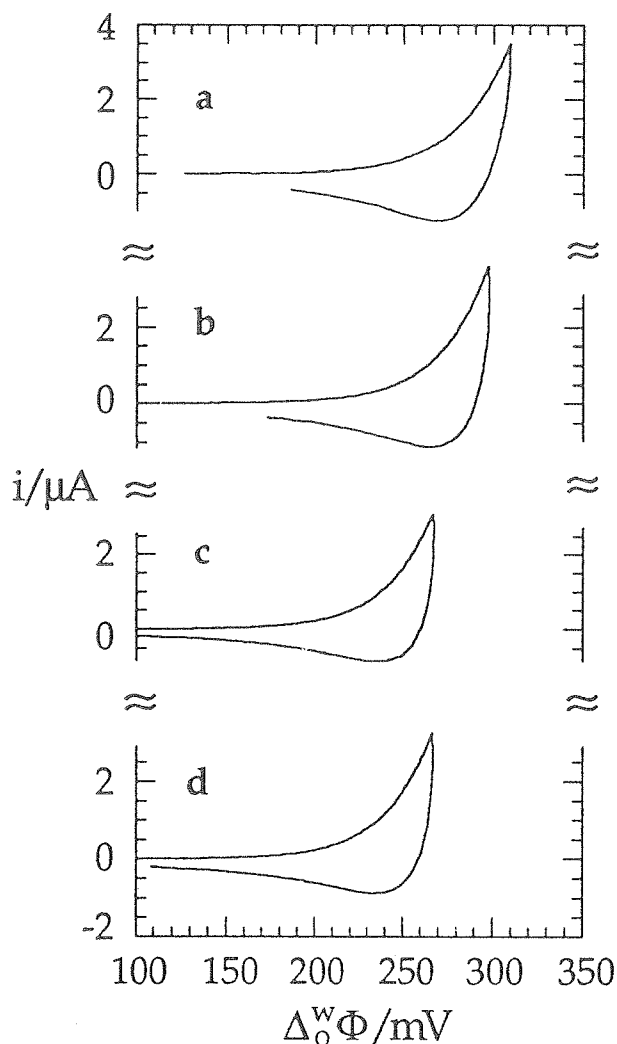$$\Delta_0^W \Phi = \Delta_0^W \Phi_{Rb^+}^0 + \frac{RT}{F} \ln \frac{a_{Rb^+}^0}{a_{Rb^+}^W} , \tag{5}$$

Fig. 4
Voltammograms of 0.1 M RbCl in water and (a) 0.5 mM, (b) 1 mM, (c) 5 mM, and (d) 10 mM TBATPBCl in DCE. Sweep rate was 5 mV s^{-1}. The cell used is described in Experimental section

where $\Delta_0^w \Phi_{Rb^+}^0$ is the standard transfer potential of the cation and $a_{Rb^+}^w (a_{Rb^+}^0)$ is its activity in the aqueous (oil) phase. The activity of Rb$^+$ ion in the oil phase is $a_{Rb^+}^0 = \alpha \gamma_{Rb^+}^0 c_T$, where c_T is the total concentration of the cation constituent at the interface and $\gamma_{Rb^+}^0$ is the activity coefficient of the free cation in the oil phase. From the definition of the association constant

$$K = \frac{a_{ip}^0}{a_{Rb^+}^0 \cdot a_-^0} = \frac{(1-\alpha)c_T}{\alpha \gamma_{Rb^+}^0 + c_T a_-^0} = \frac{(1-\alpha)}{\alpha \gamma_{Rb^+}^0 + a_-^0} \tag{6}$$

the degree of dissociation can be written as $\alpha = (1 + K\gamma_{Rb^+}^0 a_-^0)^{-1}$. The formal potential $\Delta_0^w \Phi_{Rb^+}^{0'}$ is now introduced from Eq. (5) as

$$\Delta_0^w \Phi_{Rb^+}^{0'} \equiv \Delta_0^w \Phi_{Rb^+}^0 - \frac{RT}{F} \ln (1/\gamma_{Rb^+}^0 + Ka_-^0)$$

$$= \Delta_0^w \Phi - \frac{RT}{F} \ln \frac{c_T}{a_{Rb^+}^w} . \tag{7}$$

On the right side of Eq. (7), $\Delta_0^w \Phi$ is an arbitrary potential chosen as close as possible to the positive polarization limit in order to have higher accuracy in the calculations. The value of c_T corresponding to this potential is found from the convolution analysis [5]. In our case the separation of two subsequent data points was only ca. 19 ms and a straightforward algorithm in Ref. 6 (Eq. 6.7.10 therein) could be used for the calculation of the convolution integral. $a_{Rb^+}^w$ was taken as the bulk value in the aqueous RbCl solution because the aqueous side of the interface was polarized by only 0.01%, as can be calculated from the convolution integral; $\gamma_{Rb^+}^0$ and a_-^0 were calculated at each concentration using the extended Debye-Hückel theory along with the known value of $K_{TBATPBCl}$. In practice, the current driven across the ITIES is so small that the amount of the ions transferred cannot shift the ionic equilibrium in the oil phase significantly, and then a_-^0, $\gamma_{Rb^+}^0$ and, consequently, α remain constant during the experiment. Table 1 shows the results of these calculations. Note that the activity coefficient $\gamma_{Rb^+}^0$ depends entirely on the ionic strength of the organic base electrolyte because of the tiny amount of Rb$^+$ transferred during a sweep.

Table 1
Voltammetric data used in Eqs. (7) and (8)

c_b^0/mM	a_-^0/mM	γ_+^0	$\Delta_0^w \Phi^0$/mV	$I(t,u)$/µA s$^{1/2}$	c_T^0/mM
0.5	0.2520	0.6389	308.2	18.26	0.2542
1.0	0.4052	0.5553	296.2	17.67	0.2460
5.0	1.0818	0.3438	266.2	14.26	0.1985
10.0	1.5825	0.2564	265.4	14.32	0.1994

$I(t,u)$ is the convolution integral

$$I(t,u) = \int_0^t \frac{i(t,u)\,du}{\sqrt{t-u}}$$

Eq. (7) can be arranged into the form

$$\frac{1}{\gamma_{Rb^+}^0 + a_-^0} = \exp\left(\frac{F}{RT} \Delta_0^w \Phi_{Rb^+}^0\right)$$

$$\exp\left(\frac{-F}{RT} \Delta_0^w \Phi_{Rb^+}^{0'}\right)/a_-^0 - K . \tag{8}$$

Presenting the left side of Eq. (8) as a function of $\exp\left(\frac{-F}{RT} \Delta_0^w \Phi_{Rb^+}^{0'}\right)/a_-^0$ the association constant is obtained from the intercept with the y axis and the standard transfer potential from the logarithm of the slope. The fit of the data in Table 1 into Eq. (8) gave $K_{RbTPBCl} = 45\,700$ M^{-1} and $\Delta_0^w \Phi_{Rb^+}^0 = 521$ mV, but the point corresponding to 10 mM solution had to be left out of the fit because it deviated too much from the others. A closer inspection of the fit showed that if an error or ± 0.5 mV is allowed in the determination of $\Delta_0^w \Phi$, which can easily emerge from, e.g., the correction for the absolute Galvani potential scale,

the error for the standard potential raises to some 5% but it can be as large as 200% for the intercept! Thus, this voltammetric method for the determination of K is too sensitive to small experimental errors when K and $\Delta_0^w \Phi^0$ are very large and then several very careful measurements with varying concentrations are needed. Still, the values of the association constant of RbTPBCl determined from conductivity measurements and the analysis of voltammograms are quite close (in fact, they are coincident within their experimental error) and this gives some reliability to the results.

The difference of the polarization limit with TBATPB, when choosing $\Delta_0^w \Phi$ at the same current density, was $\Delta \Phi = 190$ mV. Because the foot of the polarization wave has only a negligible contribution to the convolution integral, the same value for c_T in Eq. (7) can be considered in the two cases. It follows from Eq. (8) that the association constants have to satisfy the ratio

$$\frac{1/\gamma_{Rb^+}^0 + K_{RbTPB} a_-^0}{1/\gamma_{Rb^+}^0 + K_{RbTPBCl} a_-^0} \approx \exp\left(\frac{F\Delta\Phi}{RT}\right) \approx 1630 \ . \tag{9}$$

This equation can be used in two ways. On the one hand, if the value $K_{RbTPB} = 1700 \text{ M}^{-1}$ reported in Ref. 4 is used, then Eq. (9) predicts that $K_{RbTPBCl}$ should be negative! Once again, this casts some doubts on the value reported previously for K_{RbTPB}. On the other hand, if the more reliable value $K_{RbTPBCl} = 43\,100 \text{ M}^{-1}$ obtained from the conductivity measurements is used, K_{RbTPB} can be calculated as $7.4 \cdot 10^7 \text{ M}^{-1}$ (10 mM organic base electrolyte) which is really a high value. This will be discussed later on.

The standard transfer potential of Rb$^+$ can now be calculated from Eq. (7) using the data in Table 1 as (517.9 ± 0.1) mV which also is much higher than in our earlier studies [3, 5]. This discrepancy is due to the higher value of K_{RbTPB} obtained here and an error in the calculation of the reference junction in Refs. 3 and 5. Correction for this error gives for the standard potential ca. 450 mV when taking $K_{RbTPB} = 10^5 \text{ M}^{-1}$ as in Ref. 3. Taking into account these corrections the present value 518 mV is in accordance with the previous ones. The discrepancy with the other values in literature, e.g. [12], is also due to the different values of K_{RbTPB} there used.

Discussion

If it is accepted that the shift of the positive polarization limit is due to the difference of K_{RbTPB} and $K_{RbTPBCl}$, as calculated from Eq. (9), we are then led to the conclusion that neither Bjerrum nor Fuoss theory can explain this large difference in the association constants when the relative permittivity of the bulk solvent (DCE) is introduced. Indeed, relative permittivities lower than the bulk value (10.23) are needed to obtain realistic values of the distance of closest approch.

Ab initio calculations in Ref. 3 showed that at the minimum energy configuration the distance between Rb$^+$ and the boron atom of TPB$^-$ was 0.363 nm. This value, of course, corresponds to the configuration in vacuum but it is close to the crystallographic distance of 0.404 nm [3]. This distance requires $\varepsilon_r \approx 7$ for K_{RbTPB} from Fuoss theory. In a dilute solution of small spherical ions, the ions are surrounded by many solvent molecules and therefore the relative permittivity determining the ion-pairing should be close to that of the pure solvent. However, in our case the use of this relative permittivity must necessarily fail when attempting to estimate the electrostatic energy of the ion pair due to the expulsion of solvent at the contact zone between the ions as well as the dielectric saturation effects that experience the DCE molecules surrounding the contact ion pair.

Let us consider now the case of the Rb$^+$ and TPBCl$^-$ ions. It was suggested in Ref. 3 that the large differences in the transfer potential of the Rb$^+$ ion observed between organic solutions containing TPB$^-$ and TPBCl$^-$ were due to the preferential solvation of the p-chlorinated phenyl rings in TPBCl$^-$ (see Figs. 3 and 4 in Ref. 3). This was deduced from the fact that, when LiCl was used as an aqueous base electrolyte, TPB$^-$ was transferred at ca. 300 mV. Replacing TPB$^-$ with TPBCl$^-$, Li$^+$ was transferred at ca. 500 mV. (Figs. 1 and 2 were interchanged in Ref. 3.) Thus, the formal transfer potential of TPBCl$^-$ was larger than 500 mV, i.e., the free energy of transfer of TPBCl$^-$ is at least 20 kJ mol^{-1} higher (in absolute value) than that of TPB$^-$. The free energy of transfer is the difference between the free energies of solvation and hydration. If this increase of the free energy of transfer were due to the difference of the solvation energies, Rb$^+$ should transfer at the same potential in the case of TPBCl$^-$ as in the case of TPB$^-$, because the solvation energies would be the same and Rb$^+$ is interacting with a solvated anion. Thus, the solvation energy of TPBCl$^-$ has to be ca. 20 kJ mol^{-1} higher (in absolute value) than that of TPB$^-$.

Ion pairing is likely to occur with some solvent expulsion. It is clear, however, that the above preferential solvation effect should lead to a larger expulsion of solvent in the case of TPB$^-$ than in TPBCl$^-$. Therefore, Rb$^+$ should "see" a relative permittivity closer to that of the solvent in the case of the TPBCl$^-$ than in TPB$^-$. Still, this permittivity should not equal to that of bulk solvent because the DCE molecules surrounding the ion pair have partially lost their degrees of freedom due to saturation effects, i.e., they are not able to rotate freely. Moreover, the preferential solvation is expected to produce some steric effects, and then Rb$^+$ should be able to penetrate more into the TPB$^-$ structure than in the TPBCl$^-$ structure. (On intuitive grounds, we could advance that this different behavior between the TPB$^-$ and TPBCl$^-$ should not appear when the Rb$^+$ is replaced by a cation with larger size. Indeed, we have found here that $K_{TBATPB} = 1715 \text{ M}^{-1} \approx 1800 \text{ M}^{-1} = K_{TBATPBCl}$.) To put the above ideas on a more quantitative basis, we could consider, e.g., $\varepsilon_r \approx 8.5$ for RbTPBCl, which is an intermediate value between the value obtained for RbTPB, $\varepsilon_r \approx 7$, and the bulk relative permittivity of DCE, $\varepsilon_r \approx 10$.

Then, we obtain from Fuoss theory that $a = 0.6$ nm for RbTPBCl, which is not an unrealistic value, since the radius of $TPBCl^{-1}$ is ca. 0.5 nm [5] and that of Rb^+ is 0.15 nm [13].

There could be, however, an explanation for the difference observed in the association constants alternative to that of preferential solvation. It is based on the fact that the addition of chlorines into the para-position of TPB^- could cause the Rb^+ to "see" more the negative charge in outer part of the phenyl rings in the case of $TPBCl^-$ than in that of TPB^-. Accordingly, Rb^+ should penetrate less in the structure of $TPBCl^{-1}$ than in the structure of TPB^-, which leads immeadiately to $K_{TBATPB} \gg K_{TBATPBCl}$. Computations with a desktop software [14] showed that this idea could be qualitatively correct: the equilibrium position of Rb^+ was ca. 0.1 nm further away from the boron atom of $TPBCl^-$ than from that of TPB^-. For quantitative results in a more sophisticated software is needed.

Finally, it is interesting to consider practical consequencies of ion pairing. The standard potential of Rb^+ was found to be more than 500 mV, which corresponds to a free energy of transfer of ca. $+500$ kJ mol^{-1}. This means that in the absence of ion-pairing, we would not see the transfer of Rb^+ at all (it would transfer at around 600 mV) unless we used extremely hydrophobic electrolytes in the oil phase. Keeping in mind possible applications of extraction of rare metals, e.g., from waste waters, with the aid of liquid membranes, ion pairing is a versatile means to lower the energy barrier of transfer from water to oil. If the process were electrically driven, this means that lower cell voltages would be required which is benefitial because with voltage drops across a liquid membrane are bound to bring stability problems.

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