

Anion Effect on Single Ionic Salting-out Coefficients of Hydrophobic Electrolytes

Kyösti Kontturi,^{*,a} Lasse Murtomäki^a and David J. Schiffrin^b

KEMISK BIBLIOTEK
Den kgl. Veterinær- og Landbohøjskole

^aLaboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, Kemistintie 1 A, SF-02150 Espoo, Finland and ^bChemistry Department, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

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The effect of anions on the salting-out of hydrophobic electrolytes is studied by cyclic voltammetry at the interface between two immiscible electrolyte solutions (ITIES). The results agree with the lyotropic series, and the values of the salting-out coefficients could be explained by the scaled particle theory.

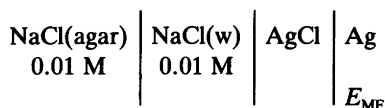
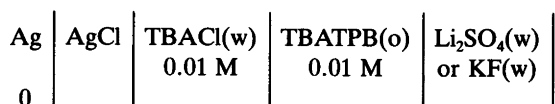
It has been recently shown that it is possible to predict the salting-out of single hydrophobic ions from the measurement of the ionic transfer potentials at the interface of immiscible electrolytes.^{1,2} The practical importance of this work has been to show that it is possible to avoid the use of tedious partition experiments by simple electroanalytical techniques. Furthermore, electrochemical ion-transfer experiments provide a direct route to the estimation of Gibbs energies of transfer for individual ions and hence to individual ionic salting-out coefficients.³

It is recognized that the anion solvation of the aqueous electrolyte is important in determining the salting-out coefficient (lyotropic series). The purpose of the present work was to extend previous results obtained with chlorides² to more strongly hydrated anions, such as fluoride and sulphate.

Experimental

The experimental details have been described elsewhere.² KF (Merck, Suprapur), Li₂SO₄ (Merck, Suprapur) and 1,2-dichloroethane, DCE (Rathburn, HPLC grade) were used without further purification. The densities of aqueous solutions needed in theoretical calculations were measured by an Anton Paar DMA 40 densitometer.

Cell (I) was used, where w refers to the aqueous phase



(I)

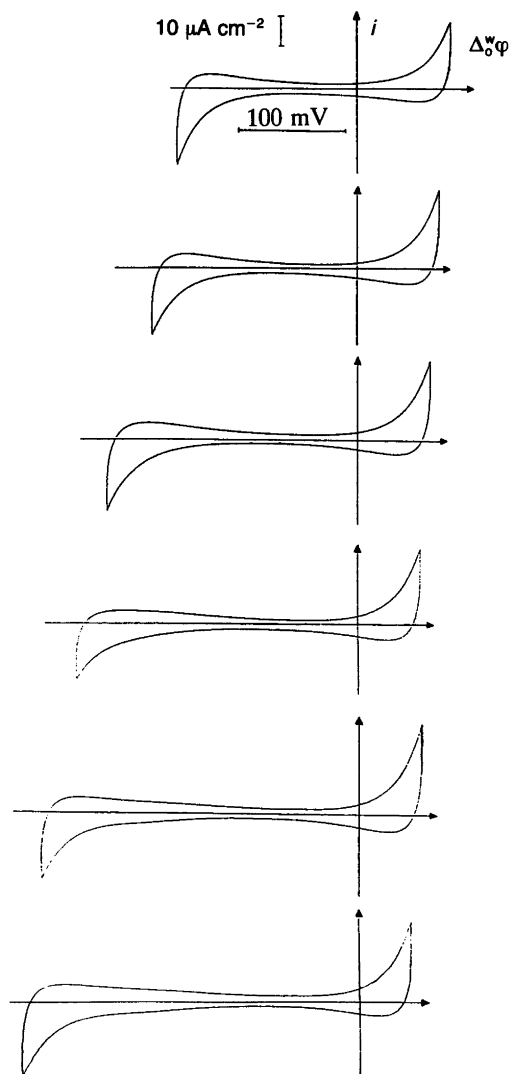


Fig. 1. Salting-out of TBA⁺ by KF at the negative polarisation limit. The concentrations of KF are (from top to bottom): 1, 2, 3, 4, 5 and 6 mol dm⁻³. The sweep rate is 25 mV s⁻¹.

and ϕ to the organic phase, TBATPB is the tetrabutylammonium tetraphenylborate electrolyte and TBACl is the tetrabutylammonium chloride. The Galvani potential differences correspond to $\Delta_o^w\phi = \phi(w) - \phi(o)$ (ϕ is the Galvani potential) and were calculated from the measured potentials (E_{MF}) as described before.² KCl was measured in the cell presented earlier.^{1,2}

Results

Fig. 1 shows the cyclic voltammetry for the KF(aq)/TBATPB(o) interface. A clear shift in the potential limits is observed. The effect of the anion can be seen in Fig. 2, where the voltammetry for Cl^- , F^- and SO_4^{2-} solutions is compared. (Unfortunately lithium sulphate must be used because of limited solubility of potassium sulphate.) Qualitatively, it can be seen that the ionic salting-out of the TBA^+ ion increases with the degree of hydration of the anion.

Discussion

The ionic salting-out coefficient, K_i , is given by² eqn. (1),

$$K_i = \frac{F}{2.303RT} \left(\frac{\partial \Delta_o^w\phi_i}{\partial c} \right)_{\text{at TBATPB}, i} \quad (1)$$

where $\Delta_o^w\phi_i$ is the limit of potential at constant current for the transfer of the organic ion i to the aqueous phase; c is

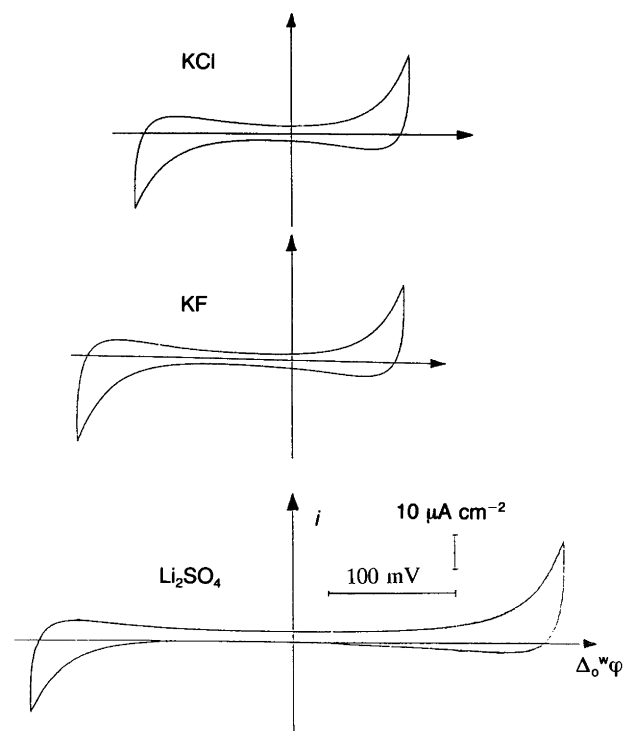


Fig. 2. Comparison of the salting-out electrolytes are 1.0 mol dm^{-3} . The sweep rate is 25 mV s^{-1} .

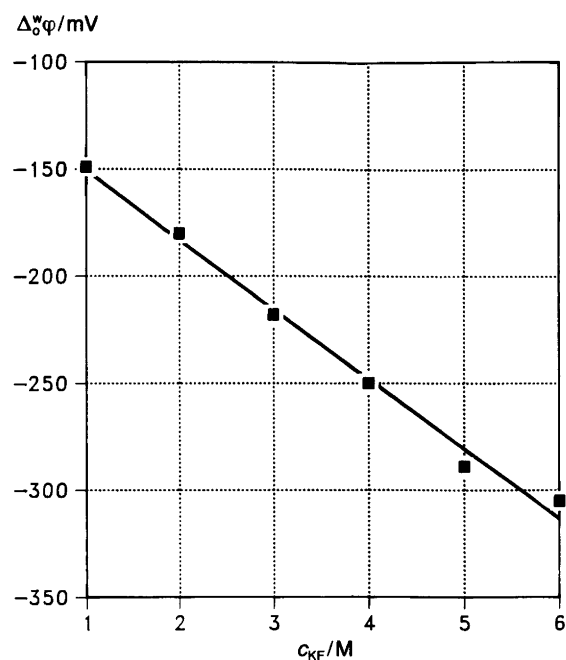


Fig. 3. The change of the negative polarisation limit with the concentration of KF.

the concentration and i is the electric current density. For the transfer of TBA^+ , the potential at a constant current density of $7 \mu\text{A cm}^{-2}$ for the different concentrations of KF and Li_2SO_4 studied are shown in Figs. 3 and 4. The expected linear dependences of $\Delta_o^w\phi_i$ on the concentration are observed. Values of $K_{\text{TBA}^+} = 0.55 \text{ M}^{-1}$ for KF and $K_{\text{TBA}^+} = 1.23 \text{ M}^{-1}$ for Li_2SO_4 are obtained.

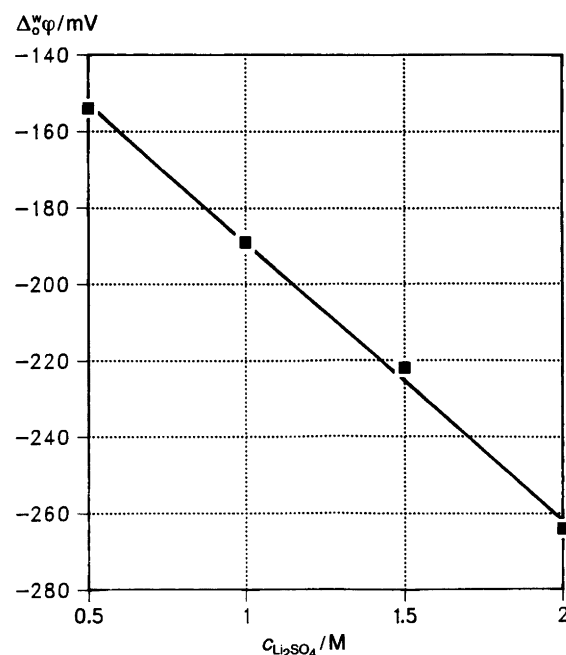


Fig. 4. The change of the negative polarisation limit with the concentration of Li_2SO_4 .

There have been many theoretical approaches to the calculation of salting-out coefficients,⁴ but the most promising modern approaches have been based on Kirkwood's method and on the scaled-particle theory.^{2,5-7}

For a molecule with no permanent dipole Kirkwood's approach leads to eqn. (2), where N is Avogadro's con-

$$K_i = \frac{2\pi N e^2}{2.303 \epsilon k T} \frac{b^3 \alpha(b/a)}{a} \quad (2)$$

stant, e is the elementary charge, ϵ is the dielectric constant, k is Boltzmann's constant, T is the thermodynamic temperature, b is the radius of the organic molecule, a is the distance of closest approach, and $\alpha(b/a)$ is a function having values comprised between 1.00 and 1.96 for values of b/a between 0 and 0.9.⁵ A value of $b = 0.75$ nm was calculated by taking the effective hydrated radius of the F^- ion as 0.4 nm (ionic radius = 0.136 nm;⁸ diameter of a water molecule = 0.275 nm⁶). Using the crystallographic radius of F^- the result is $b = 0.6$ nm. Both of these values are clearly too large when compared with the values calculated by other methods as discussed in Ref. 2. A calculation for the sulfate anion leads to the same conclusion. Using a value of b of 0.41 nm obtained by other methods the calculations according to Kirkwood's treatment yield a value for the parameter of closest approach, a that is much less than the sum of crystallographic radii, indicating the unsatisfactory applicability of this theory in the present case.

The scaled-particle theory divides the salting-out coefficient into three parts: $k_s = k_\alpha + k_\beta + k_\gamma$, where the electro-

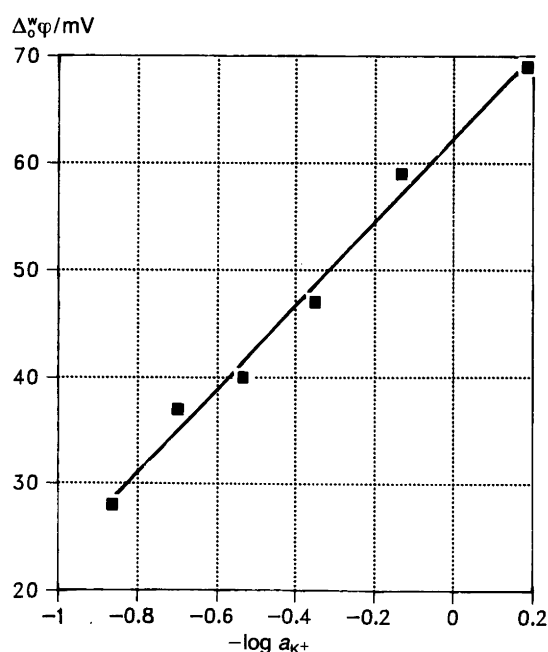


Fig. 5. The change of the positive polarisation limit with the activity of K^+ showing the kinetic control of the transfer of potassium ion.

Table 1. Salting-out coefficients obtained by scaled particle theory.^a

| Salt | k_γ/M^{-1} | k_β/M^{-1} | k_α/M^{-1} | k_s/M^{-1} |
|---------------------------------|-------------------|------------------|-------------------|--------------|
| KCl | 0.0029 | -0.313 | 0.442 | 0.131 |
| KF | 0.0086 | -0.226 | 0.803 | 0.586 |
| Li ₂ SO ₄ | 0.0127 | -0.390 | 1.686 | 1.309 |

^aCalculations were carried out at a salt concentration of 1 M, and without an electrostatic contribution.

static contribution has not been included. k_α describes the energy of cavity formation for the solute, k_β the energy of introducing the solute into the cavity, and k_γ changes the concentration scale into the number-density scale. For further details see Refs. 2, 6 and 7. Applying the scaled-particle theory as presented previously,² ionic radii of 0.19 and 0.28 nm were found for the fluoride and sulfate, respectively. These values can be regarded as reasonably good estimates for hydrated anions when compared with the crystallographic radii.

In Fig. 1 it can be seen that the positive polarisation limit decreases with increasing KF concentration. As discussed before, K^+ ion transfer determines the behaviour of the system:⁹ Fig. 5 shows the dependence of transfer potential at $i = 7 \mu A cm^{-2}$ on the activity of the potassium ion. As observed before, a slope of 39 ± 2 mV/decade was observed, confirming that the positive potential limit is determined by K^+ transfer,⁹ and hence no information on the salting-out coefficient for TPB^- can be obtained.

The effect of the anion on salting-out can be clearly seen in Fig. 2. The transfer potential of TBA^+ is shifted by 46 mV going from SO_4^{2-} to F^- and 41 mV from F^- to Cl^- . This is the expected behaviour from the lyotropic series.¹⁰ The difference between the anions can be simply rationalized in terms of scaled-particle theory, where three contributions to the salting out coefficient as discussed above, are considered. In Table 1 the calculated contributions of k_α , k_β and k_γ are presented for KCl, KF and Li₂SO₄. As can be seen, the change in the energy of cavity formation, i.e. in k_α , has the major effect on the salting-out coefficient. Furthermore, a separate calculation for LiCl shows that k_α is only slightly influenced by the cation.

Conclusions

It has been shown that single ionic salting-out coefficients can be experimentally measured from electrochemical experiments at the interface of immiscible electrolytes. Kirkwood's theory appears to be unsuitable in predicting ionic salting-out coefficients. However, the salting-out coefficients can be analyzed using scaled-particle theory. Interestingly, scaled-particle theory confirms the known fact that the salting-out phenomenon is mainly due to the anion.¹⁰

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