Some theoretical considerations concerning ion hydration in the case of ion transfer between water and 1,2- dichloroethane.

C. Sánchez and E. Leiva
Unidad de Matemática y Física, Facultad de Ciencias Químicas Universidad Nacional de Córdoba. Agencia Postal 4, C.C. 61 5000 Córdoba, Argentina

S.A. Dassie and A.M. Baruzzi
Depto. de Físico Química, Facultad de Ciencias Químicas Universidad Nacional de Córdoba. Agencia Postal 4, C.C. 61 5000 Córdoba, Argentina

June 28, 2021

Abstract

Some aspects of direct ion transfer across the water/1,2- dichloroethane are analyzed using a very simple model based on thermodynamic considerations. It was concluded that ion solvation by water molecules may occur in some particular cases in the organic phase, delivering an important contribution to the Gibbs free energy of ion transfer between the aqueous and the organic phase. In general terms, this particular type of transfer should be favored in the case of highly charged small ions at interfaces with a relatively low surface tension and a large difference between the reciprocal of the corresponding dielectric constants.

*Corresponding author, e.mail: eleiva@fcq.uncor.edu
1 Introduction

The understanding of charge transfer processes across liquid / liquid interfaces is particularly important in many areas of chemistry, physical chemistry and biology. In the last decades a variety of electrochemical methods have been adapted to study these processes. Cyclic voltammetry, chronopotentiometry, impedance spectroscopy applied to macro and more recently to microinterfaces between two immiscible liquids are currently being used [1]-[5]. Nevertheless, interpretation of the experimental data requires in many cases a proper knowledge of the interface [6][7]. In recent years new experimental techniques have been developed, which allow to obtain molecular level information concerning the interface. Second harmonic generation at the liquid / liquid interface provides information about the state of molecules, especially the surfactants adsorbed at the interface [8][9][10]. Scanning electrochemical microscopy studies of charge transfer processes across ITIES are in progress [11][12]. The concentration profiles on both sides of the phase boundary can be probed and the thickness of the mixed solvent layer can be evaluated by scanning the ultramicroelectrode tip [13]. More recently, IR reflection spectroscopy [14] and specular reflection of neutrons [15] have been applied yielding information at the molecular level. Theoretical calculations should provide an important contribution to give insight into interfacial structure and the mechanism of transfer across ITIES; several authors have used molecular dynamics to model the interface, the ion transfer [16][17] and the water/oil interface in the presence of micelles [18] or in the presence of a monolayer of amphipatic molecules [19]. Benjamin [20] has employed equilibrium free energy calculations and equilibrium dynamics trajectories to provide a detailed microscopic picture of the ion transfer processes. He showed that the transfer into the organic phase is accompanied by a hydration shell of water molecules and may also involve ion-pairing. A lattice gas model has been recently used by Pereira et al. [21] and Schmickler [22] to clarify a number of experimental features of liquid-liquid interfaces, including capacity and ion transfer. On the other hand, continuum models have also been employed to understand ion transfer between immiscible liquids. A review on this topic has been given by Markin and Volkov [23], where the Born model, non-linear dielectric effects and the use of non-local electrostatic methods were analyzed. Although quantitatively poor, the Born theory was found to provide a qualitative understanding of ion transfer processes from an aqueous
to an organic phase, concerning the effect of static permittivity and ion size. Among continuum models, it is also worth mentioning the contribution of Abraham et al. in a sequence of papers [24][25][26][27][28], where calculations of free energies and entropies of solvation were performed for a number of systems. We shall refer to these papers as A&Ln, the number n denoting the number with which each part was originally labelled.

It is the purpose of the present work to revive and shear new light on one of the aspects considered in A&L5, which is that of ion hydration in the organic phase. We add a new feature to their model that introduces an extra term to the free energy of transfer which was previously ignored. This accounts for the interaction between the water layer surrounding the ion in the organic phase and the organic solvent. We also use the Born model to discuss some qualitative features of the present formulation.

2 The model

We consider the direct transfer of alkaline and alkaline earth ions, indicating this process as:

\[ M^{+z}(aq) \rightleftharpoons M^{+z}(org) \]  

As pointed out in A&L5 [28] in their calculation of partition coefficients, the free energy of transfer \( \Delta G^t \) of the ion from water to the organic solvent contains in principle neutral and electrostatic terms. Since the former contributes to \( \Delta G^t \) only to a minor extent, we shall ignore it in most of the discussion given below.

Table I shows the Standard Gibbs energy \( \Delta G^0_{tr} \) of this reaction as given by Sabela et al. [29], compared with the corresponding values for several anions. In contrast to the transfer of anions, where large differences are observed, the transfer energy for the smaller alkaline ions appears to be rather size-insensitive. An interpretation of these results could be attempted in terms of a continuum model of the solvent with inclusion of non linear dielectric effects or non local electrostatic models, as proposed in an interesting review by Markin and Volkov [23]. However, we first want to draw attention here to an alternative model, which is also based on a continuum model for the solvent, but introduces a feature that has been absent in most of the previous theoretical considerations. This characteristic is the allowance for a
remaining solvation sheet belonging to the aqueous phase even after the ion has been transferred to the organic phase. In fact, although Abraham and Liszi [28] did consider the existence of a hydration sheet in the organic phase, a relevant contribution to the free energy of transfer was omitted there, as discussed below. At the very preliminary stage of development of these speculations, we will not seek a close agreement with the experiment, but rather point out under which circumstances this kind of events may occur. More sophisticated theoretical considerations and further experimental evidence will allow the confirmation or rebuttal of the present ideas.

We turn now to consider a naive but enlightening model for the transfer of ions from the aqueous to the organic phase and we later considered some improvements to it within the continuum approach. In order to avoid confusion, we want to state here what we mean when we write below the ”radius of the ion”. In the case where we use ideas related to the work of Abraham and Liszi, we shall be talking about the crystallographic radius. On the other hand, when we apply the concept developed by Rashin and Honig [31], we shall be actually referring to the cavity that the ion produces into the solvent. A detailed discussion about this point has been given by Rashin and Honig[31]. Our first simplified model is shown in Figure 1 and follows the ideas suggested in A&L5. We assume that the alkaline ion of radius \( r_o \) eventually may carry with it a solvation sheet of radius \( r_s - r_o \), so that after the transfer it is immersed in a mixed dielectric medium, constituted by a sphere of dielectric constant \( \varepsilon_1 \), the same as that of the aqueous phase, which is in turn embedded in a dielectric continuum of constant \( \varepsilon_2 \). We shall refer to this kind of ionic transfer as a transfer through a ”water peel (WP)” mechanism. If we calculate the electrostatic free energy change for this process according to the spirit of Born’s model, we get:

\[
\Delta G^{0_{\text{elec}}} = -\frac{q^2}{2r_0\varepsilon_1} + \frac{q^2}{2} \left\{ \frac{1}{\varepsilon_1} \left[ \frac{1}{r_0} - \frac{1}{r_s} \right] + \frac{1}{\varepsilon_2 r_s} \right\}
\]

(2)

where \( q \) represents charge of the ion. However, a very important element is missing in this model, as can be understood from the following argument. The presence of the aqueous solvation sheet makes the ion more stable in the organic phase, and this stability increases as \( r_s \) increases. Thus, on electrostatic grounds \( r_s \) should increase indefinitely to stabilize the ion as much as possible. The reason for this not to happen is that the creation of the water layer in the organic phase must have some cost, this depending on
the radius \( r_s \). Note that these considerations are absent in A&L5, where the water layer is somewhat arbitrarily (but very reasonably) assumed to be of one water molecular diameter. According to the previous argument, we shall write the free energy of transfer according to:

\[
\Delta G^{0w}_{\text{trans}} = -\frac{q^2}{2r_0\varepsilon_1} + \frac{q^2}{2} \left\{ \frac{1}{\varepsilon_1} \left[ \frac{1}{r_0} - \frac{1}{r_s} \right] + \frac{1}{\varepsilon_2r_s} \right\} + 4\pi \gamma r_s^2 \tag{3}
\]

where \( \gamma \) denotes the surface tension of a water/organic solvent interface. Thus, the three terms on the r.h.s. of eqn. 3 represent the solvation energy of the ion in the aqueous phase, the solvation energy in the mixed phase and the free energy required to create the new surface originated by the water sphere of radius \( r_s \), respectively. The last term looks like the solvophobic term discussed by Markin and Volkov [23] when considering the contribution of the solvophobic effect to the resolvation energy. However, it is clear that it has here quite a different meaning, since \( r_s \) is no longer the ionic radius but that of the hydrated ion.

On the other hand, the transfer of an alkaline ion from the aqueous to the organic phase without the aqueous solvation sheet would involve the contribution:

\[
\Delta G^0_{\text{trans}} = \frac{q^2}{2} \frac{1}{r_0} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right] \tag{4}
\]

We are aware that we actually should use instead of this equation a similar one taking into account that the cavity radius produced by a particular ion will vary in different solvents [31], but we postpone this discussion for below.

Thus, the fact whether the ion will be transferred with an aqueous solvation sheet or not, will depend on the relative magnitudes of the processes involved in 3 and 4. Simplification of eqn. 3 yields:

\[
\Delta G^{0w}_{\text{trans}} = \frac{q^2}{2} \frac{1}{r_s} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right] + 4\pi \gamma r_s^2 \tag{5}
\]

Note that according to this expression \( \Delta G^{0w}_{\text{trans}} \) is independent of the ionic radius, in agreement with the experimental observation for the smaller alkaline ions. We will now analyze under which conditions the processes related to 4 or 5 should prevail. We illustrate this point in Figure 2, where we make a qualitative plot of \( \Delta G_{\text{trans}} \) and \( \Delta G^{0w}_{\text{trans}} \) as a function of the
radius of the aqueous sphere surrounding the ion. Three different situations may appear. In the first (Figure 2a) the curves for $\Delta G'_\text{trans}$ and $\Delta G_{\text{trans}}$ intersect in two points, and there exists an infinity of values of $r_s$ which allow the inequality $\Delta G'_\text{trans} < \Delta G_{\text{trans}}$. Alkaline ion WP transfer should be the predominant mechanism for the ion transfer in this case. In the second (Figure 2b), there is only one point in which we get $\Delta G'_\text{trans} = \Delta G_{\text{trans}}$. In the third case, we get $\Delta G'_\text{trans} > \Delta G_{\text{trans}}$ for all $r_s$, so that ion WP transfer should not occur.

The relevance of the physical parameters involved in the present model may be envisaged from the following analysis. Let us set the necessary condition for a minimum in eqn. 3 according to:

$$\frac{d\Delta G^0_{\text{trans}}}{dr_s} = -\frac{q^2}{2} \frac{1}{r_s^2} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right] + 8\pi\gamma r_s = 0 \quad (6)$$

which leads us to the value for the radius of the aqueous sphere at the minimum:

$$r_{s_{\text{min}}} = \frac{1}{2} \left[ \frac{q^2}{2\gamma \pi} \left( \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right) \right]^{(1/3)} \quad (7)$$

Substituting $r_{s_{\text{min}}}$ back into eqn. 3, we get:

$$\Delta G^0_{\text{trans}} = \frac{3}{2} \frac{q^2}{2} \frac{1}{r_{s_{\text{min}}}^3} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right] \quad (8)$$

which resembles in shape eqn. 4. Thus, the existence of a minimum for $\Delta G'_\text{trans}$ located below $\Delta G_{\text{trans}}$ (the case depicted shown in Figure 2a) will imply the condition:

$$r_0 < \frac{2}{3} r_{s_{\text{min}}} \quad (9)$$

If we now substitute $r_{s_{\text{min}}}$ into eqn. 3 and rearrange, we arrive at the inequality:

$$\frac{\gamma r_0^3}{q^2} < \frac{1}{54\pi} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right]$$

This is a very simple mathematical formulation emphasizing the relevance of the physical magnitudes which will allow a WP transfer of ions from an
aqueous phase to an organic one: the surface tension of the corresponding water/organic interface, the ionic radius and the charge of the ion. Thus, for a given water/organic interface, the ionic transfer through the WP mechanism will be favored for interfaces with the lower surface tension and ions with the smaller radii and the higher charges. In order to make a quantitative test of these ideas, we have plotted in Figure 3 the standard Gibbs energies for the transfer of some univalent ions from water to 1,2-dichloroethane, obtained from electrochemical measurements\[29]\[30] as a function of the reciprocal of the ionic radius. In Figure 3a we used the ionic radius as usually reported in textbooks\[34]\, and in Figure 3b we employed the corrected radius as quoted by Rashin and Honig \[31]\. This corresponds to the choice of ionic radii for anions and covalent radii for cations, all increased by 7%. Although there remain some differences between anions and cations, the latter choice seems to be more adequate for this representation. In the case of all the anions and the bigger cations, an increase of $\Delta G_{\text{trans}}$ with $1/r_0$ is found, a fact which was predicted by eqn. 4. The differences observed between cations and anions may be attributed to the fact of using the same $r_0$ irrespective of the solvent. It has been pointed out in the literature that different radii for the cavity surrounding the ions are expected, especially when the solvents involved have a different polarity \[31]\. On the other hand, a remarkable deviation from the linear behavior is found in the case of the smaller cations $\text{Li}^+$ and $\text{Na}^+$. Furthermore, the experimental $\Delta G_{\text{trans}}$ is not found to change with the ionic radius, a feature which was anticipated in the discussion given above by eqn. 8. Due to the simplicity of the present model, only a qualitative description of the direct transfer can be pursued here. However, we can attempt an improvement in terms of dielectric saturation effects as proposed in A&L3. Thus, eq. 3 can be replaced by:

$$
\Delta G_{\text{trans}}^0 = \frac{q^2}{2} \int_0^\infty \frac{1}{r^2} \left[ \frac{1}{\varepsilon_2(r)} - \frac{1}{\varepsilon_1(r)} \right] \, dr + 4\pi \gamma r_s^2
$$

(10)

where $\varepsilon_1(r)$ and $\varepsilon_2(r)$ are now electric field dependent functions as given in A&L3. These can be calculated numerically by solving the equation $\varepsilon = n^2 + \frac{4\pi \rho \mu}{E} \left( \coth \left( \frac{3\mu E}{2kT} \right) - \frac{2kT}{3\mu E} \right)$ along with $E = \frac{q}{\varepsilon r^2}$, where $n$ denotes internal refractivity of the liquid, $\rho$ the number density, $\mu$ the dipole moment and $kT$ has the usual meaning. The integral can also be performed numerically and numerical minimization of $11$ provides an estimation of $r_s^{\text{min}}$ and $\Delta G_{\text{trans}}^{\text{min}}$.
These are given in Table 2 along with the more approximate values stemming from Born’s theory. These values point towards a hydration sheet close to a molecular diameter, as suggested in A&L5 and the value for $\Delta G'_{\text{trans}}$ reasonably agrees with the experimental finding for $Li^+$ and $Na^+$, where we expect WP transfer to take place. Since there is theoretical evidence that the surface tension of small drops should decrease with increasing curvature[33], we expect from eq. 10 that the hydration extent in the organic phase should be somewhat larger than what we calculate here. However, the minimum described by this equation is relatively flat so that important changes in the hydration extent should not appreciably change the values of $\Delta G'_{\text{trans}}$ we report here. A further comment is also relevant concerning the accuracy of eq. 10. We expect the values obtained from it for WP transfer to be much more accurate that any estimation of transfer free energy that can be made for ion transfer without hydration. In fact, if we assume that the structure of the hydration sheet remains essentially unaltered in the organic phase, this equation reduces to:

$$\Delta G^0_{\text{trans}} = \frac{q^2}{2} \int_{r_s}^{\infty} \frac{1}{r^2} \left[ \frac{1}{\varepsilon_2(r)} - \frac{1}{\varepsilon_1(r)} \right] dr + 4\pi\gamma r_s^2$$  \hspace{1cm} (11)

the integral being extended over regions relatively far from the ion. This would naturally not be the case for an analogous extension of eq. 4 to consider dielectric saturation, which would result in:

$$\Delta G^0_{\text{trans}} = \frac{q^2}{2} \int_{r_0}^{\infty} \frac{1}{r^2} \left[ \frac{1}{\varepsilon_2(r)} - \frac{1}{\varepsilon_1(r)} \right] dr$$  \hspace{1cm} (12)

The value of integral is here according to our experience extremely sensitive to assumptions made concerning the structure of the dielectric media in the neighborhood of the ion.

Returning to our discussion above, it seems that hydration in the organic phase should only occur for the smaller ions. However, the model given above is only adequate to describe a complete solvation layer, and hydration by one or a couple of water molecules may occur. A rough estimation of the free energy decrease $\Delta G_{\text{repl}}$ that accompanies the replacement of part of the organic solvation layer by a single water molecule may be made according to the following argument. We divide the free energy change related to this
hydration process in two parts. One corresponding to the ion-dipole interactions $\Delta G_{i-dip}$ and another one corresponding to dipole-dipole interactions $\Delta G_{dip-dip}^0$. The change related to the ion-dipole interactions can be written as:

$$\Delta G_{ion-dip}^0 = -\frac{q^2}{n_H^2 \rho H_2O r_{i-H_2O}^2} \mu_{H_2O} < \cos \Theta_{H_2O}> + \rho_{DCE} \frac{q^2}{n_{DCE}^2 r_{i-DCE}^2} \mu_{DCE} < \cos \Theta_{DCE}>$$

where $n$ labels the refractive index, $\mu$ the dipole moment, $\rho$ the number density and $< \cos \Theta >$ the average orientation of water ($H_2O$) and 1,2-dichloroethane (DCE) dipoles respectively. The ion-dipole distances denoted as $r_{i-H_2O}$ and $r_{i-DCE}$ can be taken to be equal to the sum of the ionic radius plus the corresponding molecular radius. The average orientation can be estimated using Langevin’s equation $L(x) = \coth(x) - 1/x$ with $x = E\mu/kT$. Thus, the first term on the r.h.s of eq. (13) represents the free energy decrease when the ion is solvated by a water dipole, and the second term represents the corresponding free energy increase due to desolvation of the corresponding part of the organic solvent. The values obtained from this equation are shown in Table 3 for the different ions considered here. As an estimation for the $\Delta G_{dip-dip}^0$ term we consider the free energy change corresponding to the dissolution of water in 1,2-dichloroethane at the saturation concentration, that can in principle be obtained from solubility data of $H_2O$ in 1, 2 – DCE. Since these solubility values reported in the literature [30] vary between 0.1 M and $10^{-3}$M, we estimated $\Delta G_{dip-dip}^0$ to be in the range $10 - 30KJ/mol$. Whatever the accurate value, we see that within the present approximation practically all the ions considered in Table 3 should prefer solvation with one water molecule to be anhydrous in the organic solvent. Moreover, since the resulting values for $\Delta G_{repl} = \Delta G_{ion-dip}^0 + \Delta G_{dip-dip}^0$ are of the same order of magnitude that a reasonable calculation or free energy of transfer without hydration would yield, we expect that even solvation with a single water molecule should deliver a meaningful contribution to this process.

A more quantitative approach would require a simulation based on realistic potentials describing the ion-water, ion-1,2-DCE and all the intermolecular interactions. In this respect, it is worth mentioning here the interesting results of the simulation performed by Benjamin[20] concerning the transfer of an ion from a nonpolar to a polar phase. In the case where the liquid-liquid
interface is not forced to be sharp but a wider transition region is allowed, an important part of the polar solvent solvation shell is already formed around the ion when it is still on the nonpolar side of the liquid-liquid interface. It would be thus worthwhile to perform this type of simulation with more specific potentials for the different ions. This would provide an important test to the present ideas. Determination of standard free energies for the transfer of alkaline-earth ions will be also helpful to distinguish between a WP or a "dry" transfer. In fact, any electrostatic estimation of the standard Gibbs energies of the dry transfer should scale in a first approximation with $q^2$, as predicted by Born’s equation. On the other hand, replacing eqn. 7 into eqn. 8 yields:

$$
\Delta G_{\text{trans}}^{0y, \text{min}} = \frac{3}{2} q^{(4/3)} (2\gamma\pi)^{1/3} \left[ \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right]^{(2/3)}
$$

(14)

Thus, the WP transfer free energies are expected to scale with $q^{(4/3)}$, which is much weaker than the $q^2$ dependence given above.

We can summarize the present results saying that we have clarified some aspects of direct ion transfer across the water/1,2 dichloroethane by using a very simple model based on thermodynamic considerations. We believe that ion solvation by water molecules may occur in some particular cases in the organic phase, delivering an important contribution to the Gibbs free energy of ion transfer between the aqueous and the organic phase. This particular type of transfer should be favored in the case of highly charged small ions, at interfaces with a relatively low surface tension and a large difference between the reciprocal of the corresponding dielectric constants.

**Acknowledgments**

Financial support from the Secretaría de Ciencia y Tecnología de la Universidad Nacional de Córdoba and the Consejo Nacional de Investigaciones Científicas y Técnicas, language assistance from Pompeya Falcon and a fellowship (C.S.) from the Consejo de Investigaciones de la Provincia de Córdoba are gratefully acknowledged.
Table 1. Standard Gibbs transfer energies of univalent ions from water to 1,2-dichloroethane (as quoted in Table 2 of ref. [29]).

| Ion | $\Delta G_{tr}^{\ddagger}/kJ \ mol^{-1}$ |
|-----|-----------------------------------|
| H$^+$ | 53 |
| Li$^+$ | 57 |
| Na$^+$ | 57 |
| K$^+$ | 50 |
| Rb$^+$ | 42 |
| Cs$^+$ | 35 |
| Cl$^-$ | 51 |
| Br$^-$ | 43 |
| I$^-$ | 33 |

Table 2. Calculated radii of solvated ion and standard Gibbs energies for ion transfer surrounded by a layer of water. The values labelled with (Born) were calculated using Born’s solvation model while the values labelled with (Sat) were calculated taking into account dielectric saturation through eqn. [10]. The parameters employed in the numerical minimization of eq. [10] were: $n_{H_2O} = 1.3329$, $n_{DCE} = 1.4448$, $\varepsilon_{H_2O}(bulk) = 78.54$, $\varepsilon_{DCE}(bulk) = 10.23$, $\gamma_{H_2O/DCE} = 25.5$ dyn/cm,

| Valence / Z | $r_s$ $(Born)$ | $r_s$ $(Sat)$ | $\Delta G_{trans}^{\min}/kJ \ mol^{-1}$ $(Born)$ | $\Delta G_{trans}^{\min}/kJ \ mol^{-1}$ $(Sat)$ |
|-------------|----------------|----------------|---------------------------------|---------------------------------|
| 1           | 2.48           | 3.44           | 35.6                            | 45.6                            |
| 2           | 3.94           | 5.22           | 89.7                            | 108.8                           |

Table 3. Ion-dipole contribution to the free energy associated with the replacement of part of the organic solvation layer of an ion by a single water molecule. All values are in $kJ \ mol^{-1}$. 
| Ion  | $\Delta G_{\text{ion-dip}}/kJ \text{ mol}^{-1}$ |
|------|------------------------------------------|
| Li$^+$ | -117.4                                    |
| Na$^+$ | -91.1                                     |
| K$^+$  | -69.0                                     |
| Rb$^+$ | -62.4                                     |
| Cs$^+$ | -54.5                                     |
| F$^-$  | -69.0                                     |
| Cl$^-$ | -49.9                                     |
| Br$^-$ | -45.5                                     |
| I$^-$  | -39.5                                     |

**Figure captions**

**Figure 1:** Model for the direct transfer of an alkaline ion of radius $r_0$ through the water/organic interface. We allow for the possibility that the ion carries with it a solvation sheet which is essentially similar to that existing in the aqueous phase. The conditions under which this may occur are discussed in the text.

**Figure 2:** Qualitative plot of the transfer free energy of an ion with an aqueous solvation sheet ($\Delta G'_{\text{trans}}$), as a function of the radius $r_s$ of a sphere containing the ion+aqueous layer. a) The horizontal line labelled ($\Delta G_{\text{trans}}$) indicates the transfer free energy of an ion without the aqueous layer. These schemes correspond to the conditions: $a) \frac{\gamma r_0^2 q^2}{4} < \frac{1}{54 \pi} \left[ \frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right]$; $b) \frac{\gamma r_0^2 q^2}{4} = \frac{1}{54 \pi} \left[ \frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right]$; $c) \frac{\gamma r_0^2 q^2}{4} > \frac{1}{54 \pi} \left[ \frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right]$.

**Figure 3:** Electrochemical standard free energies for the transfer of univalent ions from water to 1,2-dichloroethane. Empty circles indicate cations, while filled circles denote anions. The reciprocal radii were calculated from a) ionic radii as reported in [34]; b) corrected radii as reported by Rashin and Honig [31].
References

[1] V. Marecek, Z. Samec, J. Koryta, Adv. Coll. Interface Sci. 29 (1988) 1.

[2] J. Koryta, Electrochim. Acta, 33 (1988) 189.

[3] P. Vanysek, Electrochimica Acta, 40(1995)2841.

[4] H.H. Girault, Electrochim. Acta, 32 (1987) 383.

[5] H.H. Girault in ”Charge transfer accross liquid-liquid interfaces ” in Modern Aspects of Electrochemistry, Ed. J.O. Bockris, B.E. Conway and R. White, Vol. 25, Plenum, NY (1993).

[6] V. E. Kazarinov (Ed.): The Interface Structure and Electrochemical Processes at the Boundary between Two Immiscible Liquids. Springer, Berlin (1987).

[7] Z. Samec, V. Marecek, D. Homolka, J. Chem. Soc. Faraday Trans. 77 (1984) 197.

[8] J.C. Conboy, G.L. Richmond, Electrochim. Acta, 40 (1995) 2881.

[9] M.J. Crawford, J.G. Frey, Y. Zhao, J. Chem. Soc. Faraday Trans. 92 (1996) 1369.

[10] R.R. Naujok, D.A. Higgins, R.M. Corn, J. Chem. Soc. Faraday Trans. 91 (1995) 1411

[11] T.C. Richards, M.V. Mirkin, A.J. Bard, J. Phys. Chem. 97 (1993) 7672.

[12] T. Solomon, A.J. Bard, J. Phys. Chem. 99 (1995) 17487.

[13] C. Wei, M.V. Mirkin, A.J. Bard, J. Phys. Chem. 99 (1995) 16033.

[14] R.P. Sperline, H. Freiser, Langmuir, 6 (1990) 344.

[15] L.T. Lee, D. Langevin, B. Farnoux, Phys. Rev. Lett. 67 (1991) 2678.

[16] I. Benjamin, Science, 261 (1993) 1558.

[17] I. Benjamin, Chem. Phys. 180 (1994) 287.
[18] B. Smit, P.A.J. Hilbers, K. Esselink, L.A.M. Rupert, N.M. van Os, A.G. Schlijper, J. Phys. Chem. 95 (1991) 6391.

[19] T. Kakiuchi, M. Kotani, J. Noguchi, M. Nakanishi, M. Senda, J. Coll. Interface Sci. 149 (1992) 279.

[20] I. Benjamin, J. Chem. Phys. 96(1992) 577.

[21] C.M. Pereira, W. Schmickler, A.F. Silva and M.J. Sousa, Chem. Phys. Lett. 13(1997)268.

[22] W. Schmickler, J. Electroanal. Chem., in press.

[23] V.S. Markin and A.G. Volkov, Electrochimica Acta 34 (1989)93.

[24] M.H. Abraham and J. Liszi, J.C.S. Faraday I, 74, (1978)1604.

[25] M.H. Abraham and J. Liszi, J.C.S. Faraday I, 74 (1978)2858.

[26] M.H. Abraham, J. Liszi and L. Mészáros, J. Chem. Phys. 70(1979) 2491.

[27] M.H. Abraham and J. Liszi, J.C.S. Faraday I, 76 (1980)1219.

[28] M.H. Abraham and J. Liszi, J. inorg. nucl. Chem., 43 (1981)143.

[29] A. Sabela, V. Marecek, Z. Samec and R. Fuoco, Electrochimica Acta 37 (1992) 231.

[30] Z. Samec, V. Marecek and M.P. Colombini, J. Electroanal. Chem. 257 (1988) 147.

[31] A.A. Rashin and B. Honig, J. Phys. Chem. 89 (1985)5588.

[32] S.A. Dassie, L.M. Yudi and A.M. Baruzzi, Electrochimica Acta 18 (1995) 2953.

[33] D. Homolka, K. Holub and V. Marecek, J. Electroanal. Chem. 138 (1982)2959.

[34] J.O’M Bockris and A.K.N. Reedy in Modern Electrochemistry, Vol 1, p. 69, New York, Plenum Press 1970.
[35] M.P. Allen and D.J. Tildesley in *Computer Simulation of Liquids*, Ch. 11, Oxford Science Publications, Oxford, 1992.

[36] J. Czapkiewicz and B.Czapkiewicz-Tutal, J.C.S. Faraday I, **76**(1980)1663.
\[ \Delta G^0_{tr} / \text{kJ mol}^{-1} \]

\[ \frac{1}{r_0} (\text{Å}) \]

- Black circles represent one set of data points.
- Open circles represent another set of data points.

The graph shows a comparison between \( \Delta G^0_{tr} \) and \( \frac{1}{r_0} \) (Å).