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Some Theoretical Considerations Concerning Ion Hydration in the Case of Ion Transfer between Water and 1,2-Dichloroethane

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Some aspects of direct ion transfer across water/1,2-dichloroethane have been 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.

An understanding of the charge-transfer processes across liquid/liquid interfaces is particularly important in many areas of chemistry, physical chemistry and biology. During 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, an interpretation of the experimental data in many cases requires proper knowledge of the interface.6,7) In recent years new experimental techniques have been developed, which allow one to obtain molecular-level information concerning the interface. Second-harmonic generation at a liquid/liquid interface provides information about the state of molecules, especially the surfactants adsorbed at the interface.8—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 spectroscopy14) and specular reflection of neutrons15) have been applied, yielding information at the molecular level. Theoretical calculations should provide important contributions and insight into the interfacial structure and mechanism of transfer across ITIES; several authors have used molecular dynamics to model the interface, the ion transfer16,17) and the water/oil interface in the presence of micelles18) or in the presence of a monolayer of amphipatic molecules.19) Benjamin20) has employed equilibrium free-energy calculations and equilibrium dynamics trajectories to provide a detailed microscopic picture of the ion-transfer processes. He showed that 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 recently been used by Pereira et al.21) and Schmickler22) to clarify a number of experimental features of liquid–liquid interfaces, including the capacity and ion transfer. On the other hand, continuum models have also been employed to understand ion transfer between immiscible liquids. A review of this topic has been given by Markin and Volkov,23) where the Born model, nonlinear dielectric effects and the use of nonlocal electrostatic methods were analyzed. Although quantitatively poor, the Born theory was found to provide a qualitative understanding of ion-transfer processes from an aqueous phase 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—28) where calculations of the free energies and entropies of solvation were performed for a number of systems. We refer to these paper as A&L*n*, the number *n* denoting the number with which each part was originally labelled.

It is the purpose of the present work to revive and shed new light on one of the aspects considered,28) 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.

The Model, Results and Discussion

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

$$\mathrm{M}^{+z}(\mathrm{aq}) \rightleftharpoons \mathrm{M}^{+z}(\mathrm{org}). \tag{1}$$

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

Table 1 shows the Standard Gibbs energy (ΔG^0_{tr}) of this reaction, as given by Sabela at 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 the inclusion of nonlinear dielectric effects or nonlocal electrostatic model, as proposed in an interesting review by Markin and Volkov.[23] However, we first wish to draw attention here to an alternative model, which is also based on a continuum model, but introduces a feature that has been absent in most of the previous theoretical considerations. This characteristic is an 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 the development of these speculations, we do not seek a close agreement with the experiment, but rather point out under which circumstances this kind of event may occur. More sophisticated theoretical considerations and further experimental evidence will allow either a confirmation or a rebuttal of the present ideas.

We turn now to consider a naive, but enlightening, model for the transfer of ions from the aqueous phase to the organic phase, and later considered some improvements to it within the continuum approach. In order to avoid confusion, we wish to state here what we mean by "radius of the ion". In the case where we use ideas related to the work of Abraham and Liszi, we are talking about the crystallographic radius. On the other hand, when we apply the concept developed by Rashin and Honig,[31] we are actually referring to the cavity that the ion produces into the solvent. A detailed discussion about this point has been given by Rashin Honig.[31] Our first simplified model is shown in Fig. 1, and follows the ideas suggested in A&L5. We assume that the alkaline ion of radius r_0 *may* eventually carry with it a solvation sheet of radius $r_s - r_0$, so that after a transfer it is immersed in a mixed dielectric medium, constituted by a sphere of dielectric constant ε_1, the same as that of the aqueous phase, which is in turn embedded in a dielectric continnum of constant ε_2. We 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 obtain

Table 1. Standard Gibbs Transfer Energies of Univalent Ions from Water to 1,2-Dichloroethane (as quoted in Table 2 of Ref. 29)

Ion	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
$\dfrac{\Delta G^0_{\mathrm{tr}}}{\mathrm{kJ\,mol^{-1}}}$	53	57	57	50	42	35	51	43	33

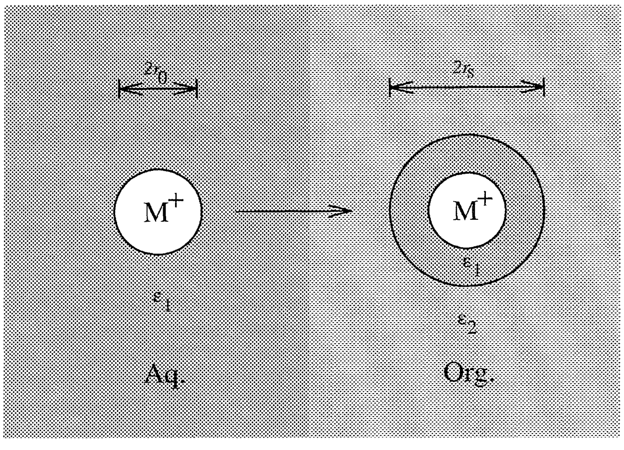

Fig. 1. Model for the direct transfer of an alkaline ion of radius r_0 through the water/organic interface. We allow for the possibility that the ion carries with it a solvation sheet which is essentially similar to that existing in the aqueous phase. The conditions under which this may occur are discussed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

$$\Delta G^{0\prime}_{\mathrm{elec}} = -\frac{q^2}{2r_0\varepsilon_1} + \frac{q^2}{2}\left\{\frac{1}{\varepsilon_1}\left[\frac{1}{r_0} - \frac{1}{r_\mathrm{s}}\right] + \frac{1}{\varepsilon_2 r_\mathrm{s}}\right\}, \tag{2}$$

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 an 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 that this does not happen is because the creation of a water layer in the organic phase must have some cost, 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 write the free energy of transfer according to

$$\Delta G^{0\prime}_{\mathrm{trans}\,f} = -\frac{q^2}{2r_0\varepsilon_1} + \frac{q^2}{2}\left\{\frac{1}{\varepsilon_1}\left[\frac{1}{r_0} - \frac{1}{r_\mathrm{s}}\right] + \frac{1}{\varepsilon_2 r_\mathrm{s}}\right\} + 4\pi\gamma r_\mathrm{s}^2, \tag{3}$$

where γ denotes the surface tension of a water/organic solvent interface. Thus, the three terms on the r.h.s. of Eq. 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 a new surface originating by the water sphere of radius r_s, respectively. We note that this free-energy change includes a contribution related to the disappearance of all interactions between the "water peel" and its surrounding water, and the energy released when this "water peel" interacts with the organic phase. That is, the energetic cost necessary to break the hydrogen bonds between the "water peel" and the surrounding water molecules is included in this surface formation energy. Since the present method is a zero-order approach, we are not considering the reorganization that the water peel suffers in its internal structure upon a transfer. 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 here it has 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 an aqueous solvation sheet would involve the contribution

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

Although we are aware that we actually should use instead of this equation a similar one which takes into account that the cavity radius produced by a particular ion varied in different solvents,[31] we postpone this discussion for below.

Thus, the fact whether the ion is transferred with an aqueous solvation sheet or not, depends on the relative magnitudes of the processes involved in 3 and 4. A simplification of Eq. 3 yield

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

Note that according to this expression $\Delta G^{0\prime}_{\text{trans}}$ is independent of the ionic radius, in agreement with the experimental observation for smaller alkaline ions. We will now analyze under which conditions the processes related to 4 or 5 should prevail. We illustrate this point in Fig. 2, where we make a qualitative plot of $\Delta G^{0}_{\text{trans}}$ and $\Delta G^{0\prime}_{\text{trans}}$ as a function of the radius of the aqueous sphere surrounding the ion. Three different situations may appear. In the first (Fig. 2a) the curves for $\Delta G^{0\prime}_{\text{trans}}$ and $\Delta G^{0}_{\text{trans}}$ intersect at two points, and there exists an infinity of values of r_s which allow the inequality $\Delta G^{0\prime}_{\text{trans}} < \Delta G^{0}_{\text{trans}}$. Alkaline ion WP transfer should be the predominant mechanism for ion transfer in this case. In the second (Fig. 2b), there is only one point in which we obtain $\Delta G^{0\prime}_{\text{trans}} = \Delta G^{0}_{\text{trans}}$. In the third case, since we obtain $\Delta G^{0\prime}_{\text{trans}} > \Delta G^{0}_{\text{trans}}$ for all r_s, an 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 Eq. 5 according to

$$\frac{\mathrm{d}\Delta G^{0\prime}_{\text{trans}}}{\mathrm{d}r_s} = -\frac{q^2}{2}\frac{1}{r_s^2}\left[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right] + 8\pi\gamma r_s = 0, \tag{6}$$

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

$$r_s^{\min} = \frac{1}{2}\left[\frac{q^2}{2\gamma\pi}\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right)\right]^{(1/3)}. \tag{7}$$

Substituting $r_s^{\min}$ back into Eq. 5, we obtain

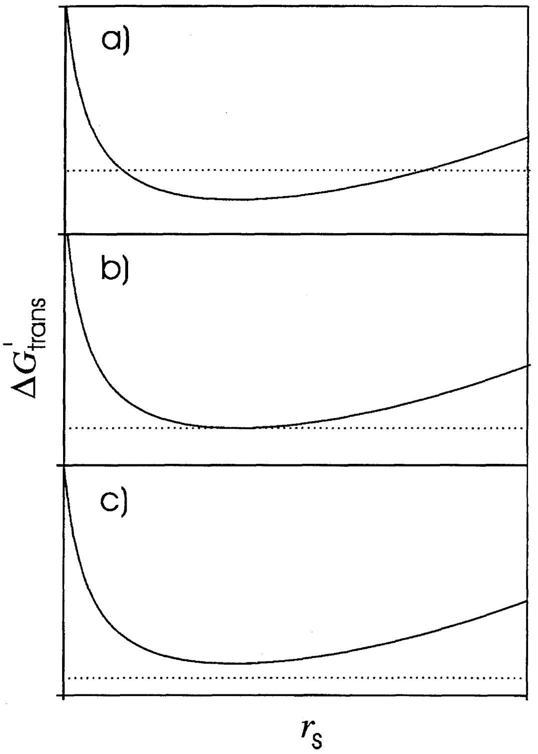

Fig. 2. Qualitative plot of the transfer free energy of an ion with an aqueous solvation sheet ($\Delta G^{0\prime}_{\text{trans}}$), as a function of the radius r_s of a sphere containing the ion+aqueous layer. a) The horizontal line labelled ($\Delta G^{0}_{\text{trans}}$) indicates the transfer free energy of an ion without the aqueous layer. These schemes correspond to the conditions: a) $\frac{\gamma r_0^3}{q^2} < \frac{1}{54\pi}[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}]$; b) $\frac{\gamma r_0^3}{q^2} = \frac{1}{54\pi}[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}]$; c) $\frac{\gamma r_0^3}{q^2} > \frac{1}{54\pi}[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}]$.

$$\Delta G^{0\prime/\min}_{\text{trans}} = \frac{3}{2}\frac{q^2}{2}\frac{1}{r_s^{\min}}\left[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right], \tag{8}$$

which resembles in shape Eq. 4. Thus, the existence of a minimum for $\Delta G^{0\prime}_{\text{trans}}$ located below $\Delta G^{0}_{\text{trams}}$ (the case depicted shown in Fig. 2a) implies the condition

$$r_0 < \frac{2}{3}r_s^{\min}. \tag{9}$$

If we now substitute $r_s^{\min}$ into Eq. 9 and rearrange, we arrive at the inequality

$$\frac{\gamma r_0^3}{q^2} < \frac{1}{54\pi}\left[\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right]. \tag{10}$$

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 a lower surface tension and ions with smaller radii and higher charges. In order to perform a quantitative test of these ideas, we have plotted in Fig. 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

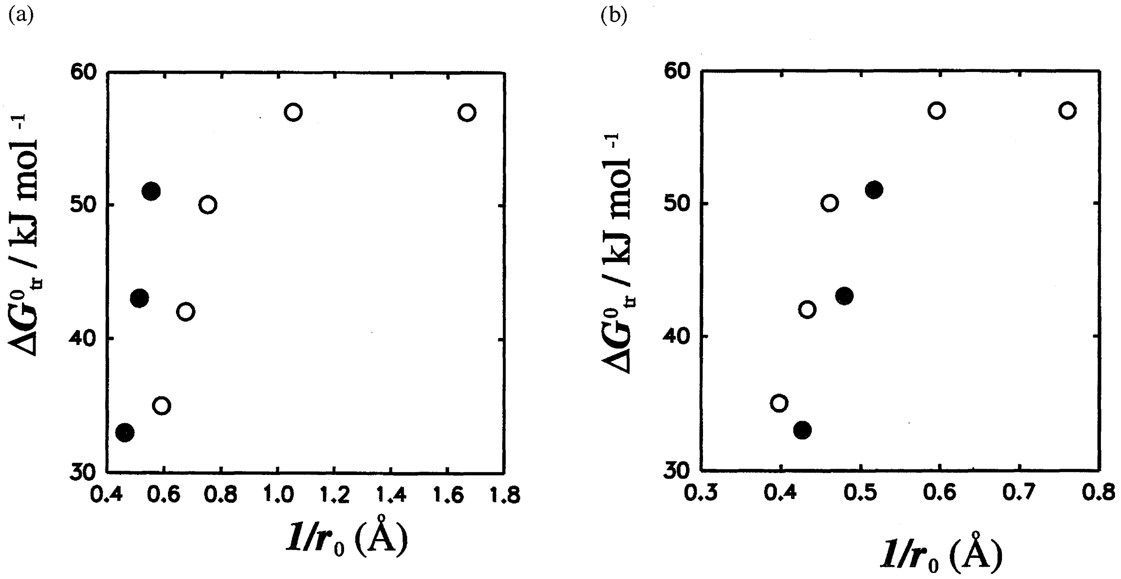

Fig. 3. Electrochemical standard free energies for the transfer of univalent ions from water to 1,2-dichloroethane. Empty circles indicate cations, while filled circles denote anions. The reciprocal radii were calculated from a) ionic radii as reported in 34 b) corrected radii as reported by Rashin and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

a function of the reciprocal of the ionic radius. In Fig. 3a we used the ionic radius, as usually reported in textbooks,[34] and in Fig. 3b we employed the corrected radius, as quoted by Rashin and Honig.[31] This corresponds to the choice of to the 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 $\Delta G^0_{\text{trans}}$ with $1/r_0$ is found, a fact which was predicted by Eq. 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 linear behavior is found in the case of the smaller cations Li^+ and Na^+. Furthermore, the experimental $\Delta G^0_{\text{trans}}$ is not found to change with the ionic radius, a feature which was anticipated in the discussion given above by Eq. 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. 5 can be replaced by

$$\Delta G^{0\prime}_{\text{trans}} = \frac{q^2}{2}\int_{r_0}^{\infty}\frac{1}{r^2}\left[\frac{1}{\varepsilon_2(r)} - \frac{1}{\varepsilon_1(r)}\right]\mathrm{d}r + 4\pi\gamma r_s^2, \tag{11}$$

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 $\varepsilon = n^2 + \frac{4\pi\rho\mu}{E}(\coth(\frac{3\mu E}{2kT}) - \frac{2kT}{3\mu E})$ along with $E = \frac{q}{\varepsilon r^2}$, where n denotes the internal refractivity of the liquid, ρ the number density, μ the dipole moment and kT has the usual meaning. The integral can also be performed numerically, and a numerical minimization of Eq. 11 provides an estimation of r_s^{min} and $\Delta G^{0/\text{min}}_{\text{trans}}$. 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; also the value for $G^{0\prime}_{\text{trans}}$ 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,[35] we expect from Eq. 11 that the hydration extent in the organic phase should be somewhat larger than what we calculate here. However, since the minimum described by this equation is relatively flat, important changes in the hydration extent should not appreciably change the values of $\Delta G^{\prime}_{\text{trans}}$ which we report here. A further comment is also relevant concerning the accuracy of Eq. 11. We expect the values obtained from it for WP transfer to be much more accurate than any estimation of the 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 es-

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 white the values labelled with (Sat) were calculated taking into account dielectric saturation through Eq. 11. The parameters employed in the numerical minimization of Eq. 11 were: $n_{\text{H}_2\text{O}} = 1.3329$, $n_{\text{DCE}} = 1.4448$, $\varepsilon_{\text{H}_2\text{O}}(\text{bulk}) = 78.54$, $\varepsilon_{\text{DCE}}(\text{bulk}) = 10.23$, $\gamma_{\text{H}_2\text{O/DCE}} = 25.5$ dyn cm^{-1},

Valence/Z	r_s		$\Delta G^{0/\text{min}}_{\text{trans}}$/kJ mol^{-1}	
	(Born)	(Sat)	(Born)	(Sat)
1	2.48	3.44	35.6	45.6
2	3.94	5.22	89.7	108.8

sentially unaltered in the organic phase, this equation reduces to

$$\Delta G^{0\prime}_{\text{trans}} = \frac{q^2}{2}\int_{r_s}^{\infty}\frac{1}{r^2}\left[\frac{1}{\varepsilon_2(r)}-\frac{1}{\varepsilon_1(r)}\right]\mathrm{d}r + 4\pi\gamma r_s^2, \tag{12}$$

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

$$\Delta G^{0}_{\text{trans}} = \frac{q^2}{2}\int_{r_0}^{\infty}\frac{1}{r^2}\left[\frac{1}{\varepsilon_2(r)}-\frac{1}{\varepsilon_1(r)}\right]\mathrm{d}r. \tag{13}$$

The value of the integral is 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 (ΔG^0_{repl}) that accompanies 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 into two parts. One corresponds to the ion–dipole interactions ($\Delta G_{\text{i-dip}}$, and another one corresponds to dipole–dipole interactions ($\Delta G^0_{\text{dip-dip}}$). The change related to the ion–dipole interactions can be written as

$$\Delta G^0_{\text{ion-dip}} = -\frac{q^2}{n^2_{\text{H}_2\text{O}}r^2_{i\text{-H}_2\text{O}}}\mu_{\text{H}_2\text{O}}\langle\cos\Theta_{\text{H}_2\text{O}}\rangle + \frac{\rho_{\text{DCE}}}{\rho_{\text{H}_2\text{O}}}\frac{q^2}{n^2_{\text{DCE}}r^2_{i\text{-DCE}}}\mu_{\text{DCE}}\langle\cos\Theta_{\text{DCE}}\rangle, \tag{14}$$

where n is the refractive index, μ the dipole moment, ρ the number density and $\langle\cos\Theta\rangle$ the average orientation of water (H_2O) and 1,2-dichloroethane (DCE) dipoles respectively. The ion–dipole distances, denoted as $r_{\text{i-H}_2\text{O}}$ and $r_{\text{i-DCE}}$, 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. 14 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 $\Delta G^0_{\text{dip-dip}}$ 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[36] vary between 0.1 M and 10^{-3} M, we estimated $\Delta G^0_{\text{dip-dip}}$ to be in the range 10—30 kJ mol^{-1}. Whatever the accurate values are, we can see that within the present approximation practically all of 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 $\Delta G^0_{\text{repl}}=\Delta G^0_{\text{ion-dip}}+\Delta G^0_{\text{dip-dip}}$ are of the same order of magnitude that a reasonable calculation of the 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 respects, it is worth mentioning here the interesting results of a simulation performed by Benjamin[20] concerning the transfer of an ion from a nonpolar phase to a polar phase. In the case where the liquid–liquid interface is not force 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 thus be worth performing this type of simulation with more specific potentials for different ions. This would provide an important test to the present ideas. A determination of the standard free energies for the transfer of alkaline-earth ions would also be 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 Eq. 7 into Eq. 8 yields

$$\Delta G^{0\prime\text{min}}_{\text{trans}} = \frac{3}{2}q^{(4/3)}(2\gamma\pi)^{(1/3)}\left[\frac{1}{\varepsilon_2}-\frac{1}{\varepsilon_1}\right]^{(2/3)}. \tag{15}$$

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

Finally, we want to mention some experimental results for a system closely related to the present one that support the idea that hydration in the organic phase is important in the case of small ions. Iwachido et al.[37] have determined the number of molecules ($n_{\text{H}_2\text{O}}$) attached to different cations in nitrobenzene, finding a value of 5.6 for Li^+ and 13.0 for Ca^{+2}. The application of the present model to this solvent delivers values of 3.3 and 10.6 for Li^+ and Ca^{+2} respectively. Although in the first case our value is somewhat too low

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	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
$\dfrac{\Delta G^0_{\text{ion-dip}}}{\text{kJ mol}^{-1}}$	−117.4	−91.1	−69.0	−62.4	−54.5	−69.0	−49.9	−45.5	−39.5

because the assumption of a water annulus loses sense for such a small number of molecules, we think that the qualitative agreement is good enough to stimulate corresponding measurements for the system considered in this work, where hydration in the organic phase should be even more important due to the larger differences between the dielectric constants of the media involved (see above Eq. 7).

As stated previously, due to its simplicity, the present model is adequate only to describe a complete solvation layer. However, we expect that many of the ions may keep some of their hydration layer upon transfer. As a matter of fact, numerous experimental results indicate that almost all of the cations and anions listed in Table 1 are more or less hydrated in the organic phase.[38—42)]

We can summarize the present results by 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*.

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