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The Cosolvent Effect on the Transport Parameters of HCl in Aqueous + Organic Solvent Mixtures

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The electromotive forces E_A of concentration cells with transference Ag|AgCl|HCl($m_{2,\mathrm{var}}$), (S + H_2O)||HCl($m_{1,\mathrm{fixed}}$), (S + H_2O)|AgCl|Ag, where $m_{1,\mathrm{fixed}}$ and $m_{2,\mathrm{var}}$ denote electrolyte molalities (fixed and variable, respectively), have been measured at $T = 298.15$ K in a wide range of aqueous organic solvents (S + H_2O) with both protic (methanol, ethanol, propanol, ethylene glycol, and glycerol) and aprotic cosolvents (propylene carbonate, acetonitrile, and 1,4-dioxane) of low to high permittivities, allowing the determination of infinite dilution ionic transference numbers for HCl in such solvents. Appropriate combination of the latter with limiting molar conductivity data, determined in the same media, yielded the limiting ionic mobilities. The results provide an insight on the effect of the organic cosolvents on relative and absolute transport properties of HCl. They are compared with results obtained by our group for "viscous-motion" alkali halides MeCl, discussed in terms of dielectric friction parameters. For the limiting case of pure water, the abundant transference cell data available up to very high HCl concentrations have now been reassessed along our recently improved interpretative scheme.

Introduction

Surprisingly enough, despite the importance of hydrochloric acid as an electrolyte with wide applications in nonaqueous as well as in aqueous chemistry, a large disproportion still exists between the papers dealing with the transport parameters of hydrochloric acid in pure water and those in nonaqueous solvents and aqueous−organic solvent mixtures; in fact, the latter systems explored hitherto were regrettably few.[1−5] This lack of information does not allow one to compare the organic cosolvent effect on the transport parameters of (a) cations having viscous motion vs (b) cation H^+, having in water an exceptional mobility as a result of the well-known, peculiar jump-like mechanism.[6,7]

This work attempts to reduce the above gap. In particular, transference numbers and conductivities of hydrochloric acid in eight aqueous−organic solvent systems for a total of 34 different mixtures have here been determined. Limiting ionic mobilities and Stokes radii have been derived.

The ionic transference numbers have here been determined by measuring the electromotive force (emf) E_A of concentration cells with transference of the type

$$\mathrm{Ag|AgCl|HCl}(m_2),\mathrm{Z|HCl}(m_1),\mathrm{Z|AgCl|Ag} \qquad \text{(A)}$$

where Z = (S + H_2O) represents mixtures of water with an organic cosolvent S, the HCl molalities having m_2 (varying) > m_1 (fixed). The E_A data need to be combined with the emf data E_{MAX} of the corresponding double cell without transference

$$\mathrm{Ag|AgCl|HCl}(m_2),\mathrm{Z|H_2|Pt{-}Pt|H_2|HCl}(m_1),\mathrm{Z|AgCl|Ag} \qquad \text{(B)}$$

measured on the same $m_2 > m_1$ pair of HCl molalities, to attain the H^+ transference number in terms of the key equation

$$t_{H^+} = \mathrm{d}E_A/\mathrm{d}E_{\mathrm{MAX}} \qquad (1)$$

The E_{MAX} expression is

$$E_{\mathrm{MAX}} = 2k \ln\{m_2\gamma_2/m_1\gamma_1\} \qquad (2)$$

where $k = RT/F$ and γ represents the mean molal activity coefficients of HCl at the molalities indicated by subscripts. Clearly, if accurate values of γ at the pertinent molalities m are known, then E_{MAX} could be calculated therefrom, and there is no need of direct measurement.

According to a revised[8,9] scheme of calculations, eq 1 is articulated with the following set of basic equations

$$\mathrm{d}E_A/\mathrm{d}E_{\mathrm{MAX}} = (t_{H^+})_{\mathrm{APP}} = t_{H^+} - \tau_Z M_Z m_2 \qquad (3)$$

$$E_A + E_C = E_{\mathrm{MAX}} \qquad (3a)$$

$$t_{H^+} + t_{Cl^-} = 1 = \mathrm{d}E_A/\mathrm{d}E_{\mathrm{MAX}} + \mathrm{d}E_C/\mathrm{d}E_{\mathrm{MAX}} \qquad (3b)$$

$$E_A = aE_{\mathrm{MAX}} + b - \exp(cE_{\mathrm{MAX}} + dE_{\mathrm{MAX}}{}^2 + e) \qquad (4)$$

In these equations, $(t_{H^+})_{\mathrm{APP}}$ and t_{H^+} are the *apparent* and the corresponding *true* transference numbers of H^+, respectively, τ_Z and M_Z are the transport number and the molar mass of the solvent Z, respectively,[1,2,36] *a*, *b*, *c*, *d*, and *e* are some constants, and E_C is the emf of the transference cell C

$$\mathrm{Pt|H_2|HCl}(m_1),\mathrm{Z||HCl}(m_2),\mathrm{Z|H_2|Pt} \qquad \text{(C)}$$

of configuration symmetrical to cell A. From eqs 3 and 4

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$$\mathrm{d}E_{\mathrm{A}}/\mathrm{d}E_{\mathrm{MAX}} = (t_{\mathrm{H}^+})_{\mathrm{APP}} = t_{\mathrm{H}^+} - \tau_Z M_Z m_2 = a - (c + 2dE_{\mathrm{MAX}}) \exp(cE_{\mathrm{MAX}} + dE_{\mathrm{MAX}}^2 + e) \quad (5)$$

for which it can be shown that, under the limiting conditions of infinite dilution ($m_2 = 0$, $\gamma_2 = 1$), $\tau_Z M_Z m_2 = 0$ for the solvent-transfer term, and thus one obtains $t_{\mathrm{H}^+}{}^\circ$ as the limiting slope

$$(\mathrm{d}E_{\mathrm{A}}/\mathrm{d}E_{\mathrm{MAX}})_{m=0} = a = (t_{\mathrm{H}^+}{}^\circ)_{\mathrm{APP}} = t_{\mathrm{H}^+}{}^\circ \quad (6)$$

Experimental Methods

The silver/silver chloride electrodes used for the cells were prepared according to the bielectrolytic type[10] described previously. The emf measurements were carried out by means of a Keithley model 619 differential electrometer having an input impedance higher than 10^{13} Ω. The thermostatic apparatus was described earlier.[11] The conductivity (κ) measurements at different HCl concentrations in the solvents considered were made by an AMEL model 160 conductimeter using a conductivity cell with platinized platinum electrodes of cell constant of about 1 cm^{-1}, standardized with the NIST-recommended[12] 0.01 *m* KCl solution. The working solution was placed into a double-jacketed compartment in which accurate temperature control was ensured by a HAAKE D8 thermostat with recirculating water bath. All solutions were prepared by mass from redistilled deionized water, high-performance liquid chromatorgraphy grade solvents (methanol > 99.9% from Merck; ethanol > 99.8%, Merck; 2-propanol > 99%, Carlo Erba; glycerol ≥ 99.5%, Fluka; ethylene glycol > 99.5%, Merck; acetonitrile > 99.8%, Merck; 1,4-dioxane > 99.5%, Merck), and the following compounds: HCl (Carlo Erba) and MeCl salts (LiCl >99.7% from Fluka; NaCl ≥ 99.5%, Fluka; KCl ≥ 99.5%, Fluka). The HCl and MeCl concentrations were checked by pH metric and argentometric titrations.

Results and Discussion

Solvent Effect on Ionic Transference Numbers. To ensure homogeneous data processing when comparing different solvent mixtures Z, the emf E_{A} data for HCl in pure water[13−18] solvent, as well as those in (1,4-dioxane + water) solvent mixtures,[4,5] which long ago had been treated along with the traditional scheme, have now been reprocessed in terms of the recently revised method.[8,9] The consolidated data set for HCl in pure water, which comprises both E_{A} and E_{C} measurements by various authors, is available in Table 1B, where the E_{C} data have been preliminarily converted to E_{A} data using eqs 2 and 3a. The required E_{MAX} values have been computed by eq 2 using the activity coefficients γ of hydrochloric acid from the critical compilation by Hamer and Wu.[19] The resulting E_{A} vs E_{MAX} relation, which refers to HCl molalities up to 13.5 $\mathrm{mol{\cdot}kg^{-1}}$, is represented in the Figure 1 and complies with the general eq 4. It is a straight line that gets curved at the highest molalities, with an evident oblique asymptote. By application of eq 6, the limiting value at $m_2 = 0$ of the first derivative $\mathrm{d}E_{\mathrm{A}}/\mathrm{d}E_{\mathrm{MAX}}$ yields the sought limiting transference number in water at 298.15 K: $t_{\mathrm{H}^+}{}^\circ = a = 0.8303 \pm 0.0007$. The “apparent” transference numbers $(t_{\mathrm{H}^+})_{\mathrm{APP}}$ calculated by eq 5 at the various HCl molalities within the explored range are quoted in the Table 1. As shown by Figure 1, the consistency and coherence of the literature data to the overall set is good, as well as the fitting of the experimental points by the model, both in the asymptotic and in the exponential region.

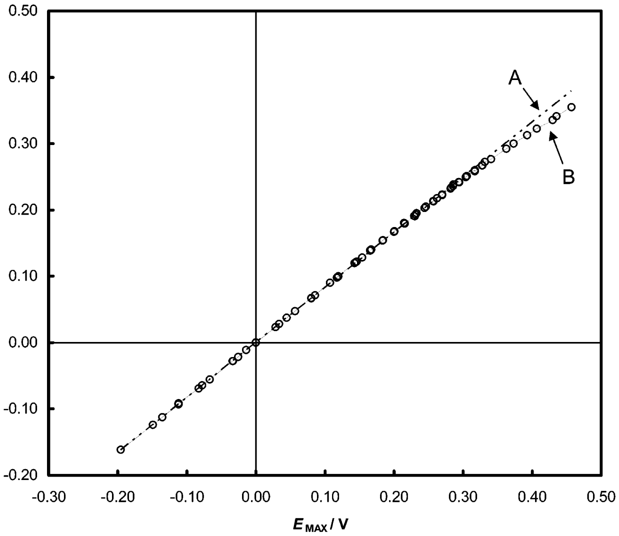

Figure 1. Experimental E_{A} vs E_{MAX} relationship at 298.15 K for HCl up to 13.5 $\mathrm{mol{\cdot}kg^{-1}}$ in water (curve B) and its limiting tangent (line A).

Table 1. Apparent Transport Numbers $(t_{\mathrm{H}^+})_{\mathrm{APP}}$ of HCl in Water at 298.15 K at Different Molalities m_{HCl}

$m_{\mathrm{HCl}}/\mathrm{mol \cdot kg^{-1}}$	$(t_{\mathrm{H}^+})_{\mathrm{APP}}$	$m_{\mathrm{HCl}}/\mathrm{mol \cdot kg^{-1}}$	$(t_{\mathrm{H}^+})_{\mathrm{APP}}$
0	0.830	6	0.790
0.001	0.830	7	0.771
0.01	0.830	8	0.747
0.10	0.830	9	0.720
1	0.830	10	0.691
1.5	0.829	11	0.663
2	0.827	12	0.637
3	0.823	13	0.616
4	0.816	14	0.600
5	0.806	15	0.589

The same basic treatment has been applied to the recalculation of Harned and Dreby’s E_{A} data,[4] which cover (1,4-dioxane + water) solvent mixtures of dioxane mass fractions $w_{\mathrm{S}} = 0.20$, 0.45, 0.70, and 0.82. (Harned and Dreby[4] had outlined the difficulties of measuring E_{A} at dioxane mass fractions greater than $w_{\mathrm{S}} = 0.82$, which corresponds to a relative permittivity as low as 9.7 at 298.15 K, but the results leave no doubt about the general trend of $t_{\mathrm{H}^+}{}^\circ$ in question.) The HCl molality ranges covered are much lower (up to 3 $\mathrm{mol{\cdot}kg^{-1}}$) than the one studied in pure water. For the computation of the pertinent E_{MAX} values through eq 2, the activity coefficients γ have been taken from the compilation by Harned and Owen.[20] The resulting E_{A} vs E_{MAX} relations are shown altogether in the Figure 1B. By proceeding as done in the case of the solvent water above, with application of eq 6, the limiting transference numbers at 298.15 K turn out to be: $t_{\mathrm{H}^+}{}^\circ = a = 0.8373 \pm 0.0009$, 0.8203 ± 0.0010, 0.7588 ± 0.0016, and 0.7131 ± 0.0036, respectively. The dependence of $t_{\mathrm{H}^+}{}^\circ$ on the dioxane mole fraction x_{S} is shown in the Figure 2 and on the dioxane volume fraction $\varphi_{\mathrm{S}}{}^{\mathrm{V}}$ in Figure 2B and shows a characteristic maximum at $x_{\mathrm{S}} \approx 0.05$, which may be due to an increase of the H^+ mobility caused by some solvent destructuration phenomenon in this mixture.

The same general behavior is shown by the H^+ transference numbers of HCl in the other water mixtures Z = W + S with seven organic cosolvents S experimentally explored in the present study. These cosolvents were, of course, selected so as to cover a variety of typologies (e.g., protic, aprotic, polar, nonpolar). The relevant E_{A} values measured are quoted in Tables 2B−8B and cover HCl molalities mostly ≤0.2 $\mathrm{mol{\cdot}kg^{-1}}$. For the quantification of the E_{MAX}

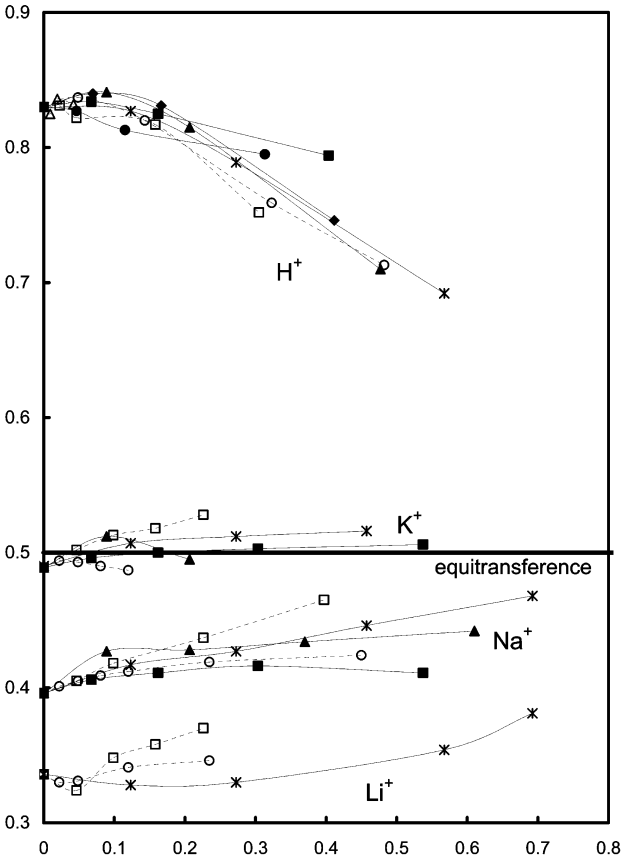

Figure 2. Limiting cationic transference numbers $t_+°$ at 298.15 K for HCl, KCl, NaCl, and LiCl in different aqueous mixtures with organic cosolvents S at various mole fractions x_S. ○, 1,4-dioxane; ●, glycerol; □, acetonitrile; ■, ethylene glycol; ▲, ethanol; ◆, 2-propanol; *, methanol; △, propylene carbonate.

values, the required mean molal activity coefficients γ have been obtained from former studies of HCl thermodynamics in the pertinent aqueous mixtures with cosolvents S (i.e., methanol,[21] ethanol,[22] 2-propanol,[23] ethylene glycol,[24] glycerol,[25] propylene carbonate,[26] and acetonitrile)[27,28] and also, for sake of comparison, computed by the Debye–Hückel equation, $\log \gamma = -A\sqrt{m}/(1 + a_0B\sqrt{m})$ using the values of the ion-size parameter a_0 quoted in the pertinent tables cited above. The E_A vs E_{MAX} relations are linear for each solvent mixture explored; the resulting respective limiting transference numbers $t_{H^+}°$ are quoted at the bottom of the relevant Tables 2B–8B (plus in the cumulative Table 2). The same transference numbers are visualized in the looking over Figures 2 and 2B together with those formerly determined by our research group for the first three alkali chlorides in the same solvent mixtures.[9,29–32]

The effect of the mixed solvent composition on the transference numbers (and the derived key quantities, see later) have been analyzed and visualized (Figure 2) as a function of the cosolvent mole fraction x_S. It is worthwhile to note that analyzing them alternatively in terms of the cosolvent volume fractions φ_S^V (Figure 2B) would be equally justified as was outlined earlier,[33–35] because the components of the solvent mixtures studied earlier had wide different molar volumes (by the way, it could be noted that numerically the volume fraction scale turns out to be rather similar to the very popular "macroscopic" mass fraction scale). However, the conclusions that can be drawn do not change significantly, as shown by comparison of the figure sequences (Figure 2 vs Figure 2B).

The general trend of the electrolytes explored is an evident approach to $t_+° = 0.5$ (i.e., a condition corresponding to equitransference) with increasing mole fraction x_S of cosolvent. Now, as a matter of fact, the transference number represents the relative speed of the considered ion with respect to the partner ion. Accordingly, the most equitransferent electrolytes in water are those having an anion and a cation of similar softness, charge-to-radius ratio, and (consequently) hydration sphere, a condition which is actually achieved in terms of little or no hydration sphere, as in the KCl case and, much better, in the RbX and CsX cases.[36–38]

In this context, the above trend in the explored aqueous organic solvent mixtures implies, with respect to the Cl^- partner:

- *A gradual deceleration of the proton H^+* (sometimes featuring a maximum in the t_{H+} vs x_S characteristics at $w_S \approx 0.1$), which is consistent with the proton gradually losing that peculiar "aqueous" jump mechanism which justifies its exceptional mobility in water.[6,7]
- *Vice-versa, a gradual acceleration of the alkali cations.*

Solvent Effect on Ionic Mobilities. The features of the moving solvated ion are better accounted for by such an absolute transport property as the ion mobility u; to this purpose, the overall set of $t_{H^+}°$ values, and the related transference numbers of the chloride ion ($t_{Cl^-}° = 1 - t_{H^+}°$), could be used to split the relevant limiting molar conductivities $\Lambda_{HCl}°$ into the ionic parts $\lambda_{H^+}°$ and $\lambda_{Cl^-}°$, for the final computation of the relevant ionic mobilities $u_{H^+}° = \lambda_{H^+}°/F$ and $u_{Cl^-}° = \lambda_{Cl^-}°/F$. However, not all the pertinent infinite-dilution molar conductivities $\Lambda°$ were available in the literature; therefore, it was necessary to experimentally determine them by systematic measurements of the conductivity κ at different HCl concentrations in the solvents considered. The concentrations were chosen in the high-dilution range so that, in terms of molar conductivities Λ, the Onsager equation

$$\Lambda = \Lambda° - (B_1\Lambda° + B_2)c^{1/2}/(1 + Ba_0\,c^{1/2}) \qquad (7)$$

could be applied for linear extrapolation of the infinite-dilution molar conductivity $\Lambda°$ values. The results for the HCl conductivities in the different solvent series considered are collected in Table 9B together with the relevant $\Lambda°$ values obtained by extrapolation through Onsager's equation. Furthermore, achieving a full comparison of the proton and alkali cation mobilities has required completion of the $\Lambda°$ values already available in the literature for MeCl electrolytes in the solvents considered with some new determinations concerning LiCl and KCl, which are quoted in Tables 10B and 11B. The infinite-dilution, single-ion mobilities $u_+°$ in the aqueous–organic solvents so determined are represented in Figures 3 and 3B, contrasting the H^+ mobility with those of the three smaller alkali metal cations.

(1) Proton Mobilities. The most evident feature in Figure 3 (as in Figure 3B) is the dramatic decay of the proton mobility with increasing amount of organic cosolvent tending to mobility values that are typical of "viscous-motion" cations in the pure organic solvent where the Grotthus mechanism is impossible, or at least more difficult than in water (e.g., with short-chain alcoholic cosolvents such as methanol and ethanol, which result in some smoothing of the mobility decrease at high cosolvent percentages with respect to aprotic cosolvents). The diminutive trend of $u_{H^+}°$ persists upon approaching the highest cosolvent mole fractions x_S in agreement with Krumgalz's[39] estimated $u_{H^+}°$ values in some 100% pure S

Table 2. Limiting Transport Properties (t_i°, Λ°, Λ_i°, u_i°) at 298.15 K for HCl and Its Single Ions in (Water + Organic Cosolvent S) Mixtures of Cosolvent Mass Fractions w_S, Mole Fractions x_S, and Volume Fractions $\varphi^V{}_S$[a]

					Λ°	λ_+°	λ_-°	u_+°	u°	η°
cosolvent	w_S	x_S	φ_S^V	t_+°	$S\cdot cm^2\cdot mol^{-1}$	$S\cdot cm^2\cdot mol^{-1}$	$S\cdot cm^2\cdot mol^{-1}$	$cm^2\cdot s^{-1}\cdot V^{-1}$	$cm^2\cdot s^{-1}\cdot V^{-1}$	mPa·s
methanol	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.123	0.241	0.827	276.8[a]	229	47.9	0.0024	0.00050	1.413
	0.4	0.273	0.458	0.789	191.1[a]	151	40.3	0.0016	0.00042	1.559
	0.7	0.567	0.747	0.692	121.9[a]	84	37.5	0.0009	0.00039	1.230
ethanol	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.089	0.211	0.841	273.3	230	43.5	0.00238	0.00045	1.811
	0.4	0.207	0.416	0.815	164.6	134	30.4	0.00139	0.00032	2.368
	0.7	0.477	0.714	0.710	91.8	65	26.6	0.00068	0.00028	2.002
2-propanol	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.070	0.242	0.840	302.0	254	48.3	0.00263	0.00050	1.836
	0.4	0.167	0.460	0.831	176.8	147	29.9	0.00152	0.00031	2.497
	0.7	0.412	0.749	0.746	77.2	58	19.6	0.00060	0.00020	2.594
ethylene glycol	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.068	0.183	0.834	302.4	252	50.2	0.00261	0.00052	1.712
	0.4	0.162	0.375	0.825	201.6	166	35.3	0.00172	0.00037	2.269
	0.7	0.404	0.677	0.794	44.8	36	9.2	0.00037	0.00010	5.615
glycerol	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.047	0.193	0.827	278.3	230	48.1	0.00239	0.00050	1.235
	0.4	0.115	0.389	0.813	171.3	139	32.0	0.00144	0.00033	3.373
	0.7	0.313	0.690	0.795	44.8	36	9.2	0.00037	0.00010	18.727
propylene carbonate	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.05	0.009	0.042	0.825	377.5	311	66.1	0.00323	0.00068	0.905
	0.1	0.019	0.085	0.836	355.6	297	58.3	0.00308	0.00060	0.922
	0.2	0.042	0.173	0.832	311.5	259	52.3	0.00269	0.00054	0.959
acetonitrile	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.05	0.023	0.063	0.831	406.6	338	68.7	0.00350	0.00071	0.935
	0.1	0.046	0.125	0.822	395.3	325	70.4	0.00337	0.00073	0.962
	0.3	0.158	0.355	0.817	320.6	262	58.7	0.00271	0.00061	0.939
	0.5	0.305	0.562	0.752	252.3	190	62.6	0.00197	0.00065	0.774
1,4-dioxane	0	0.000	0.000	0.830	426.1[a]	354	72.4	0.00369	0.00075	0.890
	0.2	0.049	0.195	0.837	303.2[a]	254	49.4	0.00263	0.00051	1.266
	0.45	0.143	0.443	0.820	180.4[a]	148	32.5	0.00153	0.00034	1.824
	0.7	0.323	0.694	0.759	93.3[a]	71	22.5	0.00074	0.00023	1.932
	0.82	0.482	0.816	0.713	58.2	41	16.7	0.00042	0.00017	1.651

[a] Λ° data marked *a* from ref 5. Ancillary quantities from ref 40.

cosolvents. In particular, in the alcohol series, the proton mobility decay with respect to water follows the very regular sequence methanol < ethanol < propanol < ethylene glycol ≈ glycerol, which is fully justified by the consideration that the more waterlike the cosolvent is the less should it hamper the typical aqueous proton motion. Anyway, surprisingly enough, the highest proton mobilities are obtained with the aprotic cosolvent acetonitrile, at least up to cosolvent mole fraction 0.226 (the accessible experimental range). These features observed with the alcoholic cosolvents and with acetonitrile can be considered a partial resemblance of the "viscous" ion cases for which, as we will see, they are much more conspicuous.

(2) Monovalent Cation Mobilities. All the ions considered in this work, excepting the proton, can be assumed to have the so-called "viscous" motion. Such motion actually shows strong deviations from the classical Stokes' law about viscous motion (implying D proportional to r^{-1}) and the related Walden rule (implying $u^\circ\eta^\circ$ = constant), especially in the case of small, "hard" cations having high charge-to-radius ratios and therefore being highly solvated, such as Na^+ and Li^+, which have dramatically lower mobilities than the predicted ones. This feature has been traditionally justified considering not the radius of the bare ion but the radius of the much larger solvated one (postulating that the solvent molecules adjacent to the ion remain rigidly bound to it during its motion, according to the so-called "solvent-berg model").[40] Accordingly, the resistance encountered by the moving solvated ion was described as

$$R = 6\pi\eta r_{ST} \tag{8}$$

i.e., in terms of Stokes' law, under "stick" boundary conditions, considering the so-called Stokes radius of the solvated ion, r_{ST}.[40] However, as we recently pointed out,[41] the motion of this kinetic entity should be interpreted not only in terms of dimensions but also in terms of type and extent of the solvent/solvent interactions between the outer surface of the solvation sphere and the surrounding bulk solvent.

Unfortunately, this very intuitive "static" model cannot afford satisfactory quantitative calculations. Therefore, an alternative, "dynamic" approach, hinging on the concept of "dielectric friction", has been proposed and gradually developed, initially considering the solvent as a continuum (especially by Born,[42] Fuoss,[43] Boyd,[44] Zwanzig,[45] and Hubbard and Onsager[46]) and finally considering instant-by- instant orientation/deorientation of the solvent dipoles around the (bare) moving ion (Wolynes),[47−49] requiring us to take into account all possible modes of solvent relaxation in order to achieve good agreement with the experimental data (Bagchi).[50−53] This approach considers a total "friction" ζ, inversely proportional to the ion mobility

$$u_i = q_i/\zeta \tag{9}$$

being the sum of two components

$$\zeta = \zeta^H + \zeta^D \tag{10}$$

of which the superscripts H and D denote the "hydrody-

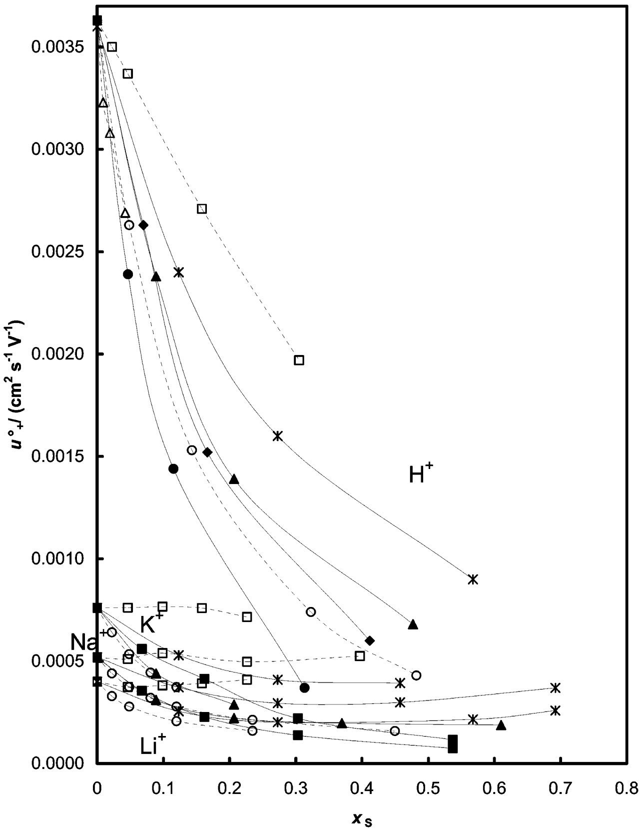

Figure 3. Limiting cationic mobilities $u_+°$ at 298.15 K in aqueous mixtures with different organic cosolvents S at various mole fractions x_S. ○, 1,4-dioxane; ●, glycerol; □, acetonitrile; ■, ethylene glycol; ▲, ethanol; ◆, 2-propanol; *, methanol; △, propylene carbonate.

namic" and "dielectric" character, respectively. In particular, the hydrodynamic friction ζ^H is a nonpolar, short-range effect roughly corresponding to the viscous motion of the entirely bare ion and well accounted for by the Stokes law written under "slip" boundary conditions

$$\zeta^H = 4\pi\eta r_{\mathrm{bare}} \qquad (11)$$

while the dielectric friction ζ^D originates from long-range ion−dipole interactions and is inversely proportional to the difficulties in solvent relaxation, of which one must consider all the possible modes in order to achieve convergency between the experimental characteristics and the calculated ones.[50−53] An oversimplified but elegant expression for ζ^D (well reproducing the shape of the non monotonic experimental u vs r^{-1} patterns, although only qualitatively, since the u values are systematically underestimated) is provided by the Zwanzig model[45]

$$\zeta^D = \frac{3q^2}{ur^3}\left(1 - \frac{\epsilon_\infty}{\epsilon_0}\right)\frac{\tau_D}{2\epsilon_0 + 1} \qquad (12)$$

where ϵ_0 and ϵ_∞ are the static and infinite-frequency dielectric constants of the solvent. In particular, it is evident that the dielectric friction increases (a) *with increasing charge-to-radius ratio of the moving ion* (accounting for its capacity of solvent coordination in the solvent-berg model) and (b) *with increasing relaxation time of the solvent* as a dipolar liquid (accounting for the peripheric solvent/solvent interactions in the same model).

Looking at the infinite-dilution cationic mobilities $u°_+$ of LiCl, NaCl, and KCl in the mixed solvents examined, collected in Tables 3−5 and visualized in Figure 3, it is evident that the general mobility sequence typical of alkali cations in water, $K^+ \gg Na^+ \gg Li^+$ (which is consistent with both the solvent-berg model and the dielectric friction model, the smallest ion actually being the slowest one since it is by far the most hydrated), also applies to the cases of acetonitrile, methanol, and ethanol cosolvents, resulting in remarkably parallel characteristics for the different cations with a given cosolvent, while they collapse to similar, low values with the very viscous cosolvent ethylene glycol and with the low affinity cosolvent dioxane. The case of the cosolvent acetonitrile, resulting in the highest mobilities, is even more impressive than the proton case, since the mobilities appear not to decrease at all upon addition of organic cosolvent for the three smallest alkali cations considered. Another similarity with the proton case concerns the smoothing effect on the mobility decrease in the cases of short, low-viscosity alcoholic cosolvents (methanol and ethanol); again, the effect is even sharper than that in the proton case, featuring a minimum for intermediate cosolvent mole fractions. It is notable that not only is methanol, like water, protic and capable of hydrogen bonding but it also has, after acetonitrile, the lowest viscosity among the cosolvents considered (0.551 mPa·s, while for cosolvents ethanol, ethylene glycol, and 1,4-dioxane the viscosities are 1.083, 16.9, and 1.028 mPa·s, respectively).[54] Similar considerations apply also to the limiting mobilities of the anion chloride (Tables 3−5, Figures 4 and 4B). It is worthwhile to notice that in this case more than one curve is available for each cosolvent, since different mobility series were obtained with different cation partners (the proton and the alkali cations), but they look nearly coincident for a given cosolvent (in the case of cosolvent acetonitrile, the high mobility values probably account for the higher dispersions), which constitutes a good consistency test on our determinations of both transference numbers and molar conductivities. As for the trends with increasing mole fractions of organic cosolvent, they appear very similar to the cases of the largest alkali cations examined, although there is some little mobility decrease upon addition of cosolvent acetonitrile, and in the case of alcoholic cosolvents, little or no increase is perceivable after the typical minimum in the wide solvent range explored. The chloride case is also important since it is the only ion, excepting the proton, for which data are available for all the cosolvents considered. It appears that:

(1) the aprotic cosolvent acetonitrile, having the lowest viscosity, results in the highest mobilities;

(2) the low-viscosity alcohols result in similar characteristics featuring a minimum;

(3) the minimum is lost with highly viscous alcohols (ethylene glycol, 16.9 mPa·s; glycerol, 1412 mPa·s);

(4) in the alcohol series, the higher the cosolvent viscosity (methanol, 0.551 < ethanol, 1.083 < propanol, 1.943 < ethylene glycol, 16.9 < glycerol, 1412 mPa·s), the lower the relevant anion mobility characteristics; and

(5) the curves referring to the cosolvent dioxane, yet without a minimum, are situated between the ethanol and the propanol ones, consistently with the dioxane viscosity of 1.087 mPa·s (similar to the ethanol one) and its lower affinity for the ion considered.

Solvent Effect on Dielectric Friction Parameters. A deeper insight on the solvent effect on the ionic mobilities can be achieved within the frame of the dielectric friction theory, calculating *experimental* ζ^D dielectric friction terms from our experimental limiting ionic mobilities combined by eq 9 and 10 with the ζ^H values univocally determined

Table 3. Limiting Transport Properties (t_i°, Λ°, Λ_i°, u_i°) at 298.15 K for LiCl and Its Single Ions in (Water + Organic Cosolvent S) Mixtures of Cosolvent Mass Fractions w_S, Mole Fractions x_S, and Volume Fractions φ_S^V [a]

cosolvent	w_S	x_S	φ_S^V	t_+° [b]	Λ° $S \cdot cm^2 \cdot mol^{-1}$	λ_+° $S \cdot cm^2 \cdot mol^{-1}$	λ_-° $S \cdot cm^2 \cdot mol^{-1}$	u_+° $cm^2 \cdot s^{-1} \cdot V^{-1}$	u° $cm^2 \cdot s^{-1} \cdot V^{-1}$	η° $mPa \cdot s$	$10^{16}\,\zeta_+^H$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_+^D$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_-^H$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_-^D$ $J \cdot s \cdot cm^{-2}$
methanol	0	0.000	0.000	0.336	114.7	39	76	0.000400	0.000789	0.890	0.67	3.33	2.02	0.01
	0.2	0.123	0.241	0.328	75.0	25	50	0.000255	0.000522	1.413	1.07	5.22	3.21	−0.14
	0.4	0.273	0.458	0.330	59.0	19	40	0.000202	0.000410	1.559	1.18	6.76	3.55	0.36
	0.6	0.458	0.655	0.354	58.7	21	38	0.000216	0.000393	1.397	1.05	6.36	3.18	0.90
	0.8	0.692	0.835	0.381	65.6	25	41	0.000259	0.000421	1.021	0.77	5.42	2.32	1.48
	1	1	1					0.000410		0.551	0.42	3.49		
1,4-dioxane	0	0.000	0.000	0.336	114.7	39	76	0.000400	0.000789	0.890	0.67	3.33	2.02	0.01
	0.1	0.022	0.097	0.330	96.3	32	65	0.000329	0.000669	1.048	0.79	4.08	2.38	0.01
	0.2	0.049	0.195	0.331	80.9	27	54	0.000278	0.000561	1.266	0.95	4.81	2.88	−0.02
	0.4	0.120	0.393	0.341	58.7	20	39	0.000207	0.000401	1.730	1.30	6.44	3.93	0.06
	0.6	0.235	0.593	0.346	44.7	15	29	0.000160	0.000303	1.981	1.49	8.52	4.51	0.78
acetonitrile	0	0.000	0.000	0.336	114.7	39	76	0.000400	0.000789	0.890	0.67	3.33	2.02	0.01
	0.1	0.046	0.125	0.324	111.3	36	75	0.000374	0.000780	0.962	0.73	3.56	2.19	−0.13
	0.2	0.099	0.243	0.348	105.6	37	69	0.000381	0.000714	0.974	0.73	3.47	2.22	0.03
	0.3	0.158	0.355	0.358	105.4	38	68	0.000391	0.000701	0.939	0.71	3.39	2.14	0.15
	0.4	0.226	0.461	0.370	106.6	39	67	0.000409	0.000696	0.868	0.65	3.26	1.97	0.33

[a] Ancillary quantities from ref 40. [b] Reference 9.

Table 4. Limiting Transport Properties (t_i°, Λ°, Λ_i°, u_i°) at 298.15 K for NaCl and Its Single Ions in (Water + Organic Cosolvent S) Mixtures of Cosolvent Mass Fractions w_S, Mole Fractions x_S, and Volume Fractions φ_S^V[a]

cosolvent	w_S	x_S	φ_S^V	t_+° [b]	Λ° $S \cdot cm^2 \cdot mol^{-1}$	λ_+° $S \cdot cm^2 \cdot mol^{-1}$	λ_-° $S \cdot cm^2 \cdot mol^{-1}$	u_+° $cm^2 \cdot s^{-1} \cdot V^{-1}$	u° $cm^2 \cdot s^{-1} \cdot V^{-1}$	η° $mPa \cdot s$	$10^{16}\,\zeta_+^H$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_+^D$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_-^H$ $J \cdot s \cdot cm^{-2}$	$10^{16}\,\zeta_-^D$ $J \cdot s \cdot cm^{-2}$
methanol	0	0.000	0.000	0.396	126.51	50	76	0.000519	0.000792	0.890	1.06	2.02	2.02	0.00
	0.2	0.123	0.241	0.417	86.0	36	50	0.000372	0.000520	1.413	1.69	2.62	3.21	−0.13
	0.4	0.273	0.458	0.427	66.7	29	38	0.000295	0.000396	1.559	1.86	3.57	3.55	0.50
	0.6	0.458	0.655	0.446	64.7	29	36	0.000299	0.000371	1.397	1.67	3.69	3.18	1.14
	0.8	0.692	0.835	0.468	76.2	36	41	0.000370	0.000420	1.021	1.22	3.11	2.32	1.49
	1	1	1					0.000469		0.551	0.66	2.76		
ethanol	0	0.000	0.000	0.396	126.5	50	76	0.000519	0.000791	0.890	1.06	2.02	2.02	0.00
	0.2	0.089	0.211	0.427	70.29	30	40	0.000311	0.000418	1.811	2.16	2.99	4.12	−0.29
	0.4	0.207	0.416	0.428	50.1	21	29	0.000222	0.000297	2.368	2.83	4.39	5.39	0.01
	0.6	0.370	0.616	0.434	43.79	19	25	0.000197	0.000257	2.235	2.67	5.46	5.08	1.15
	0.8	0.610	0.811	0.442	40.98	18	23	0.000188	0.000237	1.725	2.06	6.46	3.92	2.84
ethylene glycol	0	0.000	0.000	0.396	126.45	50	76	0.000519	0.000791	0.890	1.06	2.02	2.02	0.00
	0.2	0.068	0.183	0.406	84.3	34	50	0.000355	0.000519	1.712	2.04	2.47	3.89	−0.81
	0.4	0.162	0.375	0.411	53.5	22	32	0.000228	0.000327	2.269	2.71	4.32	5.16	−0.26
	0.6	0.303	0.574	0.416	31.9	13	19	0.000138	0.000193	3.904	4.66	6.95	8.88	−0.58
	0.8	0.537	0.782	0.411	17.4	7	10	0.000074	0.000106	8.181	9.77	11.88	18.61	−3.49
acetonitrile	0	0.000	0.000	0.396	126.5	50	76	0.000519	0.000792	0.890	1.06	2.02	2.02	0.00
	0.1	0.046	0.125	0.405	121.8	49	73	0.000511	0.000752	0.962	1.15	1.99	2.19	−0.06
	0.2	0.099	0.243	0.418	124.3	52	72	0.000539	0.000750	0.974	1.16	1.81	2.22	−0.08
	0.4	0.226	0.461	0.437	109.8	48	62	0.000497	0.000641	0.868	1.04	2.19	1.97	0.53
	0.6	0.397	0.658	0.465	108.9	51	58	0.000525	0.000604	0.667	0.80	2.26	1.52	1.14
	1	1	1					0.000796		0.341	0.41	1.61		
1,4-dioxane	0	0.000	0.000	0.396	126.45	50	76	0.000519	0.000791	0.890	1.06	2.02	2.02	0.00
	0.1	0.022	0.097	0.401	105.9	42	63	0.000440	0.000658	1.048	1.25	2.39	2.38	0.05
	0.2	0.049	0.195	0.405	89.2	36	53	0.000374	0.000550	1.266	1.51	2.77	2.88	0.03
	0.3	0.081	0.294	0.409	75.8	31	45	0.000321	0.000465	1.505	1.80	3.19	3.42	0.02
	0.4	0.120	0.393	0.412	65.1	27	38	0.000278	0.000397	1.730	2.07	3.70	3.93	0.10
	0.6	0.235	0.593	0.419	49.2	21	29	0.000213	0.000297	1.981	2.36	5.16	4.51	0.89
	0.8	0.450	0.795	0.424	36.1	15	21	0.000159	0.000216	1.718	2.05	8.03	3.91	3.51

[a] Ancillary quantities from ref 40. [b] References 30 and 32.

for each (ion + mixed solvent) combination by eq 11. Such friction values are reported in Tables 3−5 and visualized in Figure 5. It is worthwhile noticing that in some cases values for u_+° in the pure nonaqueous solvent were available in the literature[39] and they were included together with the relevant calculated ζ^D values in the above tables and figures, resulting in very good agreement with the experimental trend of our mixed-solvent data.

Looking at Figure 5, featuring the experimental ζ^D as full symbols and the calculated ζ^H as empty symbols (triangles for LiCl, squares for NaCl, and circles for KCl), it can be noticed that:

(1) Li^+, having the highest charge-to-radius ratio, i.e., the highest ability in coordinating polar solvents, features dielectric contributions 3−8 times higher than the hydrodynamic ones (implying a very slow solvent relaxation around the highly coordinating moving lithium ion), and this difference increases at a given cosolvent mass fraction in the cosolvent sequence ACN < MeOH < dioxane. The trend with the increasing cosolvent mole fraction is (a) almost constant with acetonitrile, having intrinsically very fast relaxation times[55] and being able to take part in ion solvation,[56] (b) strongly increasing with dioxane in the low to medium mole fraction range explored, which should be connected with the increasing difficulty of structurating/destructurating the increasingly rarer water molecules around the moving ion (while dioxane should not be involved in the solvation sphere, especially in this low mole fraction range),[57] and (c) featuring a maximum (at about $x_S = 0.3$) with methanol, for which complete characteristics

Table 5. Limiting Transport Properties ($t_i°$, $\Lambda°$, $\Lambda_i°$, $u_i°$) at 298.15 K for KCl and Its Single Ions in (Water + Organic Cosolvent S) Mixtures of Cosolvent Mass Fractions w_S, Mole Fractions x_S, and Volume Fractions φ_S^V [a]

					$\Lambda°$	$\lambda_+°$	$\lambda_-°$	$u_+°$	$u°$	$\eta°$	$10^{16}\ \zeta_+^H$	$10^{16}\ \zeta_+^D$	$10^{16}\ \zeta_-^H$	$10^{16}\ \zeta_-^D$
cosolvent	w_S	x_S	φ_S^V	$t_+°$ [b]	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$	$S \cdot cm^2 \cdot mol^{-1}$	$cm^2 \cdot s^{-1} \cdot V^{-1}$	$cm^2 \cdot s^{-1} \cdot V^{-1}$	mPa·s	$J \cdot s \cdot cm^{-2}$	$J \cdot s \cdot cm^{-2}$	$J \cdot s \cdot cm^{-2}$	$J \cdot s \cdot cm^{-2}$
methanol	0	0.000	0.000	0.490	149.93	73	77	0.000761	0.000793	0.890	1.49	0.62	2.02	0.00
	0.2	0.123	0.241	0.507	100.6	51	50	0.000529	0.000514	1.413	2.36	0.67	3.21	−0.10
	0.4	0.273	0.458	0.512	77.1	39	38	0.000409	0.000390	1.559	2.61	1.31	3.55	0.56
	0.6	0.458	0.655	0.516	73.5	38	36	0.000393	0.000369	1.397	2.33	1.74	3.18	1.16
	1	1	1					0.000543		0.551	0.92	2.03		
ethanol	0	0.000	0.000	0.489	149.85	73	77	0.000760	0.000793	0.890	1.49	0.62	2.02	0.00
	0.2	0.089	0.211	0.512	82.95	42	40	0.000440	0.000420	1.811	3.03	0.61	4.12	−0.30
	0.4	0.207	0.416	0.495	56.02	28	28	0.000288	0.000293	2.368	3.96	1.61	5.39	0.08
ethylene glycol	0	0.000	0.000	0.489	149.85	73	77	0.000760	0.000793	0.890	1.49	0.62	2.02	0.00
	0.2	0.068	0.183	0.496	108.9	54	55	0.000559	0.000569	1.712	2.86	0.00	3.89	−1.08
	0.4	0.162	0.375	0.500	79.7	40	40	0.000413	0.000413	2.269	3.79	0.09	5.16	−1.28
	0.6	0.303	0.574	0.503	42.2	21	21	0.000220	0.000217	3.904	6.52	0.76	8.88	−1.50
	0.8	0.537	0.782	0.506	22.2	11	11	0.000116	0.000114	8.181	13.67	0.14	18.61	−4.55
acetonitrile	0	0.000	0.000	0.489	149.85	73	77	0.000760	0.000793	0.890	1.49	0.62	2.02	0.00
	0.1	0.046	0.125	0.502	146.2	73	73	0.000761	0.000754	0.962	1.61	0.50	2.19	−0.06
	0.2	0.099	0.243	0.513	144.2	74	70	0.000766	0.000729	0.974	1.63	0.46	2.22	−0.02
	0.3	0.158	0.355	0.518	141.5	73	68	0.000759	0.000707	0.939	1.57	0.54	2.14	0.13
	0.4	0.226	0.461	0.528	131.0	69	62	0.000716	0.000642	0.868	1.45	0.79	1.97	0.52
	1	1	1					0.000867		0.341	0.57	1.28		
1,4-dioxane	0	0.000	0.000	0.489	149.9	73	77	0.000760	0.000794	0.890	1.49	0.62	2.02	−0.01
	0.1	0.022	0.097	0.494	125.1	62	63	0.000641	0.000656	1.048	1.75	0.75	2.38	0.06
	0.2	0.049	0.195	0.493	104.5	52	53	0.000534	0.000549	1.266	2.12	0.88	2.88	0.04
	0.3	0.081	0.294	0.490	87.6	43	45	0.000444	0.000463	1.505	2.52	1.09	3.42	0.04
	0.4	0.120	0.393	0.487	73.9	36	38	0.000373	0.000393	1.730	2.89	1.40	3.93	0.14

[a] Ancillary quantities from ref 40. [b] References 29, 31, and 32.

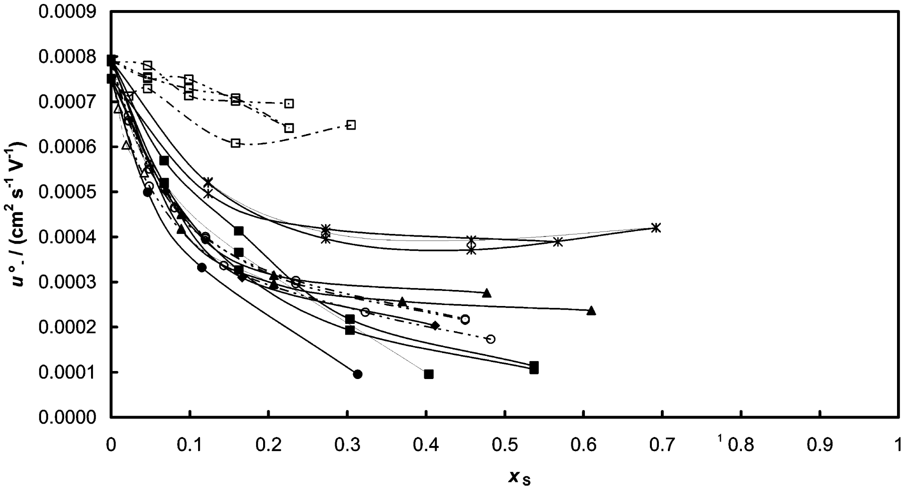

Figure 4. Limiting $u_-°$ of the Cl^- anion at 298.15 K in aqueous mixtures with different organic cosolvents S at various mole fractions x_S. ○, 1,4-dioxane; ●, glycerol; □, acetonitrile; ■, ethylene glycol; ▲, ethanol; ◆, 2-propanol; *, methanol.

are available over the whole mole fraction range, this maximum could denote that solvent structuration/destructuration around the moving ion is more difficult when both solvents are present in similar amounts (methanol being able to partially destructurate water on account of its hydrogen bonding capability) when compared to the limiting conditions of pure water and pure methanol;

(2) Na^+, having a lower charge-to-radius ratio than Li^+, features again higher dielectric contributions than the hydrodynamic ones but only by a factor of about 2, the variations with the cosolvent at a given cosolvent mole fraction, or with cosolvent mole fration with a given cosolvent, are qualitatively similar to the lithium case, but less pronounced;

(3) K^+, having the lowest charge-to-radius ratio among the three, features a remarkable inversion of tendency. In fact with all the three cosolvents considered the hydrodynamic friction is significantly higher than the dielectric one, at least up to 0.5−0.7 cosolvent mole fraction. This is in agreement with the ion moving nearly bare, exerting only a weak destructurating effect on the surrounding solvent molecules. The dielectric friction appears to become significant again only when approaching the pure organic solvent, where all the available ζ^D appear to converge;

(4) Also, Cl^- features very low dielectric friction contributions, approaching 0 (Tables 3−5); this, again, is in keeping with KCl being nearly equitransferent in all solvents considered.

Conclusions

A global, extensive view is now achieved of the modifications induced by increasing amounts of organic cosolvents (both protic and aprotic) in the ion-transport properties of HCl in aqueous−organic mixed solvents and, as a comparison, of MeCl (Me = Li, Na, K). The peculiar proton motion mechanism in water appears to be gradually lost with increasing amounts of cosolvent, the proton approaching the motion features typical of viscous-motion ions (such

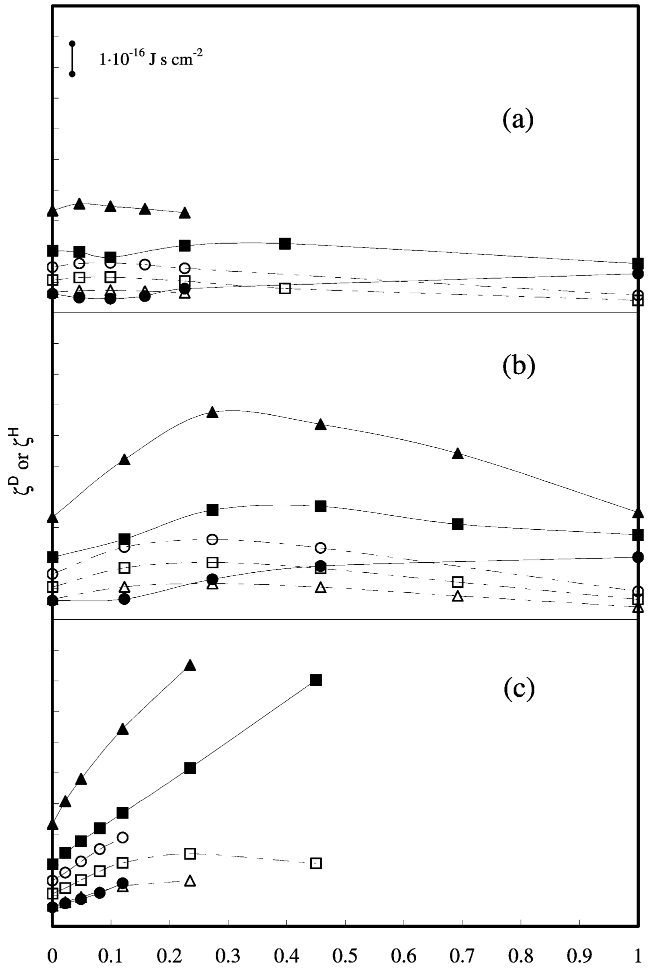

Figure 5. Dielectric and hydrodynamic friction parameters, ζ^D and ζ^H (full symbols and empty symbols, respectively), for cations Li^+ (triangles), Na^+ (squares), and K^+ (circles) in (a) (acetonitrile + water) mixed solvents, (b) (methanol + water) mixed solvents, and (c) (1,4-dioxane + water) mixed solvents at different mole fractions of organic cosolvent, x_S at 298.15 K.

as counterion Cl^- and cations Li^+, Na^+ and K^+) at cosolvent mole fractions ranging 0.2−0.5, depending on the cosolvent structure. The detailed interpretation of the proton features is conveniently achieved, distinguishing between an alcohol and a nonalcohol series, i.e., according to the cosolvent hydrogen-bonding capability, although aprotic cosolvents appear to sometimes maintain mobilities even higher than the alcohol ones. On the other hand, the experimental results for the “viscous-motion” ion cases afford very reasonable dielectric friction parameters within the frame of the “dielectric friction” theory.

In both cases, acetonitrile emerges as the cosolvent best favoring ionic motion among those tested, and to achieve structural evidence on its behavior as a cosolvent to water, we are currently performing extended X-ray absorption fine structure investigations on alkali and alkali-earth cation solvation in (water + acetonitrile) mixed solvents.

This global analysis has significant bearings, inter alia, on the contiguous electrochemical and electroanalytical fields of the acid/base equilibria and redox equilibria, and it is desirable that it be extended to the domain of such important and superpermittive solvents as the amides. This extension is currently in progress.

Supporting Information Available:

Complementary data for better understanding of the discussion terms and for enabling users to recalculate (if wanted) the present results or to duplicate them experimentally. This material is available free of charge via the Internet at http://pubs.acs.org.

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