Hofmeister Phenomena in Nonaqueous Media: The Solubility of Electrolytes in Ethylene Carbonate

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S *Supporting Information*

ABSTRACT: The solubility of some potassium salts (KF, KCl, KBr, KI, KNO₃, KClO₄, KSCN, and KSeCN) in ethylene carbonate (EC) was determined at different temperatures with an inductively coupled plasma atomic emission spectrometer. From the solubility measurements, the thermodynamic parameters ΔG, ΔH, and ΔS, of solution and of solvation, were calculated. Measurements were carried out via XRD, ATR, and FTIR to determine the effect of each salt on the properties of the solvent. The open question of whether specific ion (Hofmeister) effects are restricted to hydration peculiar to water is resolved. As for water, the effects are due to solute (ion, dipolar) induced solvent structure not accounted for by electrostatic forces. Cooperative quantum mechanical forces are necessary to understand the phenomena.
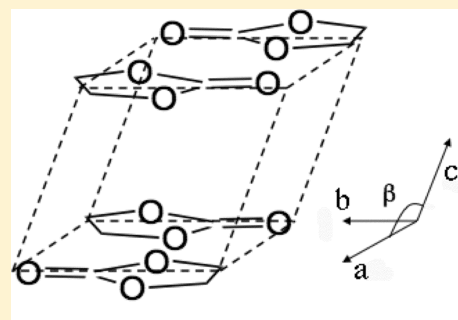
INTRODUCTION

Hofmeister effects occur universally in aqueous electrolyte systems. Examples where specific ion effects occur are in colloidal interactions, surfactant dispersions, microemulsions, polymers, and biomacromolecules (proteins, enzymes, nucleic acids, etc.). Usually the salt concentration at which specificity shows up is moderately high, e.g., above 10−100 mM.[1,2]

The effects embrace very different systems and manifestations: from the CMCs and self-assembly properties of systems involving surfactants, to the phase behavior of polymers, from the stabilization and conformational properties of proteins to the activity of enzymes, from the physicochemical properties of water bulk solutions to the growth and size of nanoparticles, from the growth of bacteria to the optical activity of chiral molecules just to mention a few. Hofmeister effects date back at least 150 years. Detailed accounts of the present state of understanding which provide a challenge to classical electrolyte theory can be found in, e.g., refs 1−6.

Indeed, Hofmeister phenomena are not restricted to aqueous environments. Some studies have shown the occurrence of specific ion effects in water-free systems, for example, the solubility of salts in organic polar solvents,[7] the physicochemical properties of ionic liquids,[8−10] the bubble−bubble coalescence in different liquids,[11,12] and the activity of enzymes in nonaqueous media.[13]

What emerges clearly from recent studies is this: the specificity of ions in an aqueous milieu that determines their behavior in solution and at interfaces can be linked, not just to ion size, electrostatic forces, and consequent hydration. It can be traced rather to the totality of quantum mechanical fluctuation forces. These non-electrostatic forces are either omitted from classical descriptions or subsumed in "effective" potential characterizations. (We remark that they are also

missing from experimental techniques that rely on theory for the interpretation of a measurement.) These forces depend on the frequency dependent polarizabilities of the solutes and ions, dielectric properties of the solvent, and temperature. The contributions include ion−dipole and dipole−dipole forces which in solution are highly non-additive, besides conventional dispersion forces proper due to fluctuation frequencies in the visible and UV. Short-range ion−solvent interactions are dominated by the geometries of solvent and ions relative to each other, and by the partial charge on each atom. However, a proper description of specificity emerges as a complex competition between ion size, properly quantified, cavity energies, and electrostatic and non-electrostatic forces. These conspire to set hydration,[14] and crucially renormalized effective potentials. These are due to interpenetration of hydration shells (variously termed Gurney potentials, chaotropic and cosmotropic, hard and soft ions).[15]

Progress, and in parallel simulation studies, is encouraging.[2,3,15] However, it would be naïve to imagine that a complete predictive understanding of the chimera of hydration, ionic association, and hydronium and hydroxide ions is around the corner. Therefore, it may be useful to explore ion specificity in simpler systems for which hydration would be absent, or in which the solute-induced solvent structure takes a different form to that in aqueous solutions. Our aim in this paper is precisely that.

Ethylene carbonate (EC, or 1,3-dioxolan-2-one, see Figure 1) is a polar aprotic solvent that possesses a significant solvent capability for inorganic salts. For example, it dissolves large
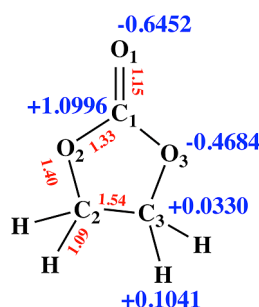
Figure 1. Chemical structure and charge density of EC. In red the interatomic distances (in Å) and in blue the partial charge q/e. From refs 19 and 20.

amounts of LiF and LiClO$_4$. It is for this reason that it is used in lithium batteries.[16] EC is also used as a cleaner and degreaser, due to its low volatility, excellent chemical compatibility, and solvent power. The solvent capability of EC is reflected by its large Hildebrand solubility parameter, $\delta \approx 30.1$ MPa$^{1/2}$. The dispersive, polar, and hydrogen bonding components of δ are 18.0, 21.3, 10.4 MPa$^{1/2}$, respectively. These parameters suggest the relevance of dispersion and dipolar interactions both in the pure liquid state and in solutions.[17] EC is completely miscible with water.[17] Interestingly, LiF does not dissociate in EC but forms ion pairs, and clusters such as (LiF)$_n$, and other species. On the other hand, NaI, KI, and CsI behave as strong electrolytes in EC, as shown by conductometric measurements.[18] Table 1 lists the main physicochemical properties of EC and for comparison those of water and hydrazine.

Table 1. Some Physico-Chemical Properties of Ethylene Carbonate, Water, and Hydrazine

property	EC	H$_2$O	N$_2$H$_4$
melting point (mp, °C)	36.4°[a]	0°	2°
enthalpy change of melting (ΔH_m, kJ/mol)	13.3	6.01	12.6
liquid−solid heat capacity change (ΔC_p, J/mol·K)	17	37.5	33
normal boiling point[a] (bp, °C)	248°[a]	100°	114°
enthalpy change of evaporation[a] (ΔH_{vap}, kJ/mol)	51	44.0	44.8
density[a,b] (g/mL)	1.3214[a,b]	0.997[c]	1.0026[d]
surface tension[b] (γ, mN/m)	37.3[b]	71.97[c]	66.4[c]
dielectric constant (ε)[a,b]	89.78[a,b]	80.4[e]	52.0[e]
dipole moment[b] (μ, D)	4.81[b]	1.85	1.85
viscosity[b] (η, cP)	1.90[b]	1.002[e]	0.8725[c]
molar volume[b] (V_m, mL/mol)	67.3[b]	29.9	31.9[c]
refractive index[b] (n_D)	1.4255[b]	1.3330[e]	1.4604[f]

[a]From ref 21. [b]40 °C. [c]25 °C. [d]27 °C. [e]20 °C. [f]22 °C.

While water and hydrazine possess similar properties (except for the dielectric constant and the enthalpy change of melting), the melting point, boiling point, and dipole moment are significantly different in EC.

In the solid state, X-ray diffraction studies have shown that ethylene carbonate crystals possess a monoclinic unit cell with four molecules ($a = 8.92$ Å, $b = 6.25$ Å, $c = 6.94$ Å, and $\beta = 100.5°$).[22]

The ring of ethylene carbonate molecule is not planar, with a O−C−C−O dihedral angle of 24.8°,[21] and due to the presence of a strong permanent dipole moment, the liquid molecules associate in dimers as in γ-butyrolactone.[16,22,23] This has been

confirmed also by Monte Carlo studies, which suggest the presence of an antiparallel configuration that corresponds to the lowest energy (a), and of a parallel configuration with a local energy minimum (b), as depicted in Figure 2.[19] Although
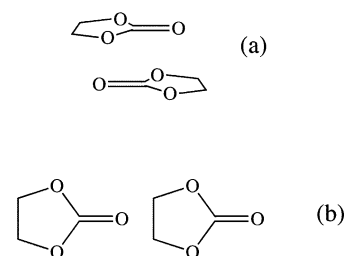

Figure 2. Self-association of ethylene carbonate.

the antiparallel orientation of the dipoles corresponds to the most energetically favorable in the gas phase, this arrangement is not predominant in the liquid EC and propylene carbonate (PC).

In this work, we determined the solubility of some potassium electrolytes in EC.

We found that the solubility in EC of the electrolytes investigated follows a Hofmeister sequence. We discuss the results in terms of the interactions that the ions establish with the solvent molecules. Since EC does not possess hydrogen bonding, the present study is important in order to tease out and elucidate the relevance of hydrogen bonding in specific ion effects.

■ MATERIALS AND METHODS

Ethylene carbonate, potassium fluoride, chloride, bromide, iodide, nitrate, perchlorate, thiocyanate, and selenocyanate were purchased from Sigma-Aldrich-Fluka (Milan, Italy).

EC was distilled twice under a vacuum (10^{-7} atm) and was stored in the dark in a desiccator under P$_4$O$_{10}$ to prevent water contamination. All salts were recrystallized and purified according to the literature[24] and stored under a vacuum in a desiccator at room temperature over CaCl$_2$. All chemicals were used within 3 days after the purification.

In order to measure the salt solubility in EC at different temperatures, a certain amount of liquid anhydrous EC was transferred in a vial and an excess of dry salt was added. The vial was sealed and kept under magnetic stirring for 2 days in a thermostatted bath at the required temperature (± 0.1 °C). Then, the stirring was stopped and the saturated solution was left to equilibrate in the presence of the salt for 24 h, before a certain amount (b) of solution was carefully sucked from the top of the solution and transferred to a flask and diluted with water up to a volume V (in L). The aqueous mixture was than analyzed through inductively coupled plasma atomic emission spectrometer (ICP-AES) in order to measure the concentration of K$^+$ (c, in mg/L). The calibration curve was built analyzing five standard solutions of dry KCl using a water+EC mixture as a solvent with approximately the same composition of the sample under investigation. The calibration data were fitted with a quadratic curve with a correlation coefficient R^2 of 0.99993. The experimental details of the ICP-AES analysis are reported in the Supporting Information (see Table S1).

The solubility (m in molal units, i.e., moles of solute per 1 kg of EC) of the salt was then calculated as

Table 2. Solubility (in Molal Units, mol/kg) of Electrolytes in EC as a Function of Temperature

T (°C)	KF	KCl	KBr	KI	KNO$_3$	KClO$_4$	KSCN
9							0.0029
15							0.0031
19							0.0033
25				0.8512			0.0034
30				0.7948			0.0037
35				0.7435			
40	0.0045	0.0115	0.0185	0.6969	0.0248	0.2779	
45	0.0113	0.0153	0.0223	0.6543	0.0304	0.3093	
50	0.0193	0.0201	0.0259	0.6153	0.0371	0.3430	
55	0.0249	0.0263	0.0314	0.5797	0.0450	0.3790	
60	0.0340	0.0341	0.0365	0.5470	0.0542	0.4175	

$$m = \frac{1000Vc}{1000M_{\mathrm{K}}b - VcM} \qquad (1)$$

where M_{K} is the atomic mass of potassium (39.102 g/mol) and M is the molar mass of the salt.

RESULTS AND DISCUSSION

Ethylene carbonate is an associated liquid, with strong intermolecular interactions in the liquid state. This is suggested by its symmetry, by the large value of the Trouton constant $\Delta S_{\mathrm{vap}}/R \approx 12.16$, and by the Kirkwood correlation parameter, g, defined as

$$g = \frac{9k_{\mathrm{B}}\varepsilon_0 V_{\mathrm{m}} T(\varepsilon - 1.1 n_{\mathrm{D}}^2)(2\varepsilon + 1.1 n_{\mathrm{D}}^2)}{\varepsilon N \mu^2 (2 + 1.1 n_{\mathrm{D}}^2)} \qquad (2)$$

Here, k_{B}, ε_0, V_{m}, T, n_{D}, ε, N, and μ are the Boltzmann constant, the vacuum permittivity, the molar volume, the absolute temperature, the refractive index, the dielectric constant, the Avogadro number, and the dipole moment, respectively.[25] For EC, g is about 1.6, a remarkably large value that should reflect the presence of associated dimers in the liquid state. We note that following the classification between "definitely structured" and "totally unstructured" solvents, based on the values of $\Delta S_{\mathrm{vap}}/R$ and g, EC should belong to the "gray zone" according to Marcus.[25] Instead, Payne concludes that EC is a non-associated solvent, based on dielectric constant data.[26] More recently, Naejus described EC as a dipole−dipole associated liquid, based on the excess thermodynamic properties of EC mixtures with trifluoroethyl methyl carbonate.[27]

Due to the remarkable dipole moment and polarizability, presumably dipole−dipole, dipole−induced dipole, and dispersion forces are all at work in determining the structural properties and solvent behavior of this liquid. FTIR experiments confirm the presence of strong intermolecular dipolar interactions. The dipolar interactions must be even more highly cooperative than those in water.

The textbook characterization of the relevant molecular forces acting in our system decomposes these into familiar (two-body) ion−dipole, ion−induced dipole, and dispersion forces. Ion−permanent dipole forces in particular are highly cooperative and temperature dependent.[1,3,28]

A discussion of intermolecular forces acting in the liquid EC in terms of classical theory is most but certainly only at best qualitative. It also ignores the significant, ion specific dispersion forces acting on ions. They are derived, we repeat, from calculations that assume only two-body interactions, which are additive. They are in reality many-body, temperature dependent forces which have a very different form in condensed media.

Thus, the inferences we make although standard can only be regarded as indicative.[1]

Not withstanding this and in any event, having a large dielectric constant (ε) and a strong dipole moment (μ), from *continuum* electrostatic theory alone (Born solvation), one expects that EC should be able to dissolve salts and to form strong solvation shells around the dissolved ions. The large static dielectric constant ε enhances the solvent capability of EC for electrolytes, while the large molecular dipole moment μ promotes ion−dipole attractive interactions.[17] The solvation of small and large cations, i.e., Li$^+$, Na$^+$, K$^+$, Cs$^+$, and tetraalkylammonium, has already been reported and discussed in the literature.[18] In contrast, the solvation of anions has been investigated only for the halides. In both cases, the solvation appears to be determined by the charge and the size of the ion, due to strong ion−dipole interactions.

In this work, we extend the investigation to other anions (nitrate, thiocyanate, perchlorate, and selenocyanate), and we show that for more polarizable anions strong solute−solvent interactions occur.

The solubility of the electrolytes in EC was determined as a function of temperature. It is reported in Table 2 as molality of the electrolyte (m) in the equilibrated saturated solution. The solubility of all salts, with the exception of KI, increases with the temperature. For KSCN, it changes only slightly. The solubility increases with the size of the anion in the order F$^-$ < Cl$^-$ < Br$^-$ < NO$_3^-$ < ClO$_4^-$ < I$^-$. This result agrees with previous reports.[29]

EC, which does not contain donor sites for hydrogen bonding, solvates cations and anions, presumably and mainly through ion−dipole interactions. At 40 °C, the solubilities of potassium salts in EC follow the sequence

$$KF < KCl < KBr < KNO_3 < KClO_4 < KI$$

For small anions such as fluoride, chloride, and bromide, the ion−dipole interactions are stronger. Because of the partial charges distribution (see Figure 1) and of the geometry features of EC, larger and more polarizable anions such as perchlorate and iodide are probably too large to establish strong attractive interactions with C$_1$, due to the presence of the partially negative oxygens O$_2$ and O$_3$, and dispersion forces can contribute in enhancing the salt solubility.[29] In solution, the cation competes with the solvent molecules for the same anion, especially when the cation is relatively large and electrostatic interactions are less significant, as is the case for potassium. This explains why KI and KClO$_4$ are much more soluble than the other salts.[18]

Figure 3 shows the molal solubility versus T for the different salts in EC. The enthalpy, Gibbs free energy, and entropy
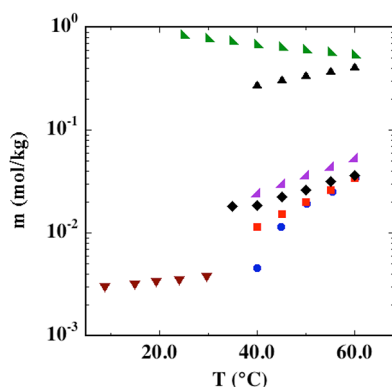

Figure 3. Plots of m versus T for the different electrolytes dissolved in EC: KF (blue circles), KCl (red squares), KBr (black diamonds), KI (green triangles), KNO$_3$ (purple triangles), KClO$_4$ (black triangles), and KSCN (maroon triangles).

changes of solution were calculated from eqs 3−5,[31,32] and are listed in Table 3:

$$\Delta G_{sol} = -RT \ln K_{sp} = -RT \ln(\gamma_\pm m)^2 \tag{3}$$

$$\Delta H_{sol} = -2R \left[\frac{\partial \ln(\gamma_\pm m)}{\partial(1/T)} \right] \tag{4}$$

$$\Delta S_{sol} = \frac{\Delta H_{sol} - \Delta G_{sol}}{T} \tag{5}$$

Table 3. Enthalpy (ΔH_{sol}, in kJ/mol), Gibbs Free Energy (ΔG_{sol}, in kJ/mol), Entropy (ΔS_{sol}, in J/K·mol) Changes of Solution at 40° C, Lattice Energy (U, in kJ/mol), and the Experimental Enthalpy Change of Solvation (ΔH_{solv}^{exp}, in kJ/mol) Calculated According to eq 6 for the Investigated Electrolytes in EC

salt	ΔH_{sol}	ΔG_{sol}	ΔS_{sol}	U^b	ΔH_{solv}^{exp}
KF	115.1	28.4	286	820.1	−705.0
KCl	88.7	23.7	208	715.1	−626.4
KBr	54.8	19.2	107	682.0	−627.2
KI	−19.0	4.3	−74	649.0	−668.0
KNO$_3$	62.7	20.0	136	686.2	−623.5
KClO$_4$	30.5	8.5	70	602.5	−572.0
KSCN	14.9^a	27.3^a	−44^a	615.0	−600.1

^{a}Value extrapolated at 25 °C.

In the equations, $\gamma_\pm$ is the mean molal activity coefficient (see text and Table S2 in the Supporting Information) and K_{sp} the solubility product of the salt in EC. The dissolution of all salts, with the exception of KI, is endothermic. The values of ΔS_{sol} suggest that the solubilization process is entropy driven. The entropy changes are positive (with the exception of KI and KSCN), indicating that the addition of an electrolyte induces a strong perturbation in the liquid.

Figure 4 shows the enthalpy and entropy changes of solution as a function of the anionic polarizabilities in EC (α_{EC}, see Table 4). Both values decrease with α_{EC}. For all salts, the value of ΔH_{sol} is positive (endothermic), and is negative (exothermic) only for KI. The differences between the
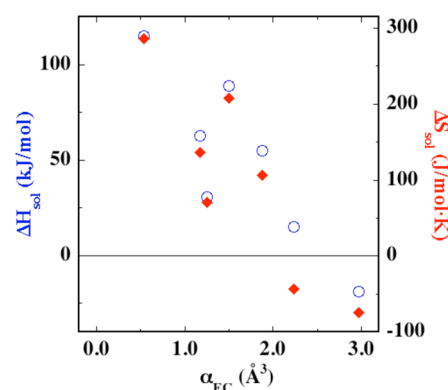

Figure 4. ΔH_{sol} (O) and ΔS_{sol} (◆) for the different salts in EC, calculated from eqs 4 and 5.

Table 4. Calculated Ion Solvation Free Energy (ΔG_{solv}^{calc}, in kJ/mol), Entropy (ΔS_{solv}^{calc}, in J/mol·K), and Enthalpy (ΔH_{solv}^{calc}, in kJ/mol) Changes (see eqs 7−9) at 40° C, Crystallographic Radius (r_i in Å), Experimental Best Fitting δ_i^{exp} (in Å), and Polarizability (α_{EC}, in Å^3) of Ions in EC

ion	ΔG_{solv}^{calc}	ΔS_{solv}^{calc}	ΔH_{solv}^{calc}	r_i	δ_i^{exp}	α_{EC}
K$^+$	−371	−18	−377	1.33		
F$^-$	−354	−17	−356	1.36	0.76	0.54
Cl$^-$	−287	−14	−289	1.81	0.98	1.50
Br$^-$	−271	−13	−272	1.96	0.82	1.88
I$^-$	−279	−13	−253	2.16	0.23	2.97
NO$_3^-$	−271	−13	−280	1.89	0.94	
ClO$_4^-$	−204	−10	−234	2.36	1.21	
SCN$^-$	−228	−11	−255	2.13	0.99	2.24

cation−anion and solvent−ion interactions, which determine the ΔH_{sol}, decrease with the polarizability, producing a less endothermic dissolution process. In the case of KI, ion−solvent interactions overcome the ion−ion interaction in the lattice. An increase of α determines a reduction in ΔS_{sol}.

In the case of water, the solubility sequence at 40 °C is[30]

$$\mathrm{KClO_4 < KCl < KBr \approx KNO_3 < KI \ll KF < KSCN}$$

ΔH_{sol} is always positive and much lower than the corresponding value in EC (see Table S3 in the Supporting Information), except for KSCN. The entropy change of solution of the salts in water is significantly lower than the corresponding value in EC.

The thermodynamic parameters obtained for EC suggest that the dissolution of the electrolyte requires more energy than that involved in the orientation of the solvent dipole around the dissolved ions. By contrast for KI, the interactions between the anion and EC are stronger and the enthalpy gain becomes negative.

The enthalpy change of solvation, ΔH_{solv}, was calculated through a thermodynamic cycle (see Figure 5) as

$$\Delta H_{solv} = \Delta H_{sol} - U \tag{6}$$

where U is the lattice energy of each solid.

Assuming that the contribution of K$^+$ to solvation energies is constant, the solute−solvent interactions are stronger for F$^-$ (which is a kosmotropic ion in water) than for I$^-$ (which is a chaotropic ion in water), as described by ΔH_{solv}. The sign of ΔH_{sol} is due to the fact that the anion−cation interaction in the lattice is stronger in KF than in KI for electrostatic reasons. The
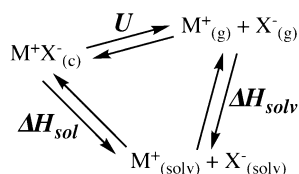
Figure 5. Thermodynamic cycle for the calculation of the enthalpy change of solvation.

results suggest the presence of a balance between the ion size and the ion polarizability in the solvent. In fact, there is a competition between K^+ and EC for the same anion: as the lattice energy decreases, the anion is more available to interact with the solvent (particularly with large cations).

According to the literature, the value of ΔH_{sol} of LiF in EC (36.8 kJ/mol) shows it to be less endothermic than that of KF (82.3 kJ/mol).[33] Ion−dipole interactions are then more favored with Li^+ because of its high charge density, and can overcome the loss of the enormous lattice energy of this salt.

The Gibbs free energy, the enthalpy, and the entropy changes of solvation can be roughly estimated with the modified Born equations:[34]

$$\Delta G_{solv,i} = -\frac{e^2 N(\varepsilon - 1)}{8\pi\varepsilon_0\varepsilon(r_i + \delta_i)} \tag{7}$$

$$\Delta H_{solv,i} = -\frac{e^2 N}{8\pi\varepsilon_0(r_i + \delta_i)}\left(1 - \frac{1}{\varepsilon} - \frac{T}{\varepsilon^2}\frac{\partial\varepsilon}{\partial T}\right) \tag{8}$$

$$\Delta S_{solv,i} = \frac{e^2 N}{8\pi\varepsilon_0\varepsilon^2(r_i + \delta_i)}\left(\frac{\partial\varepsilon}{\partial T}\right)_p \tag{9}$$

Assuming that δ_i is temperature independent, $(\partial\varepsilon/\partial T)_p$ is about -0.3761 K^{-1} for EC and was estimated from the values of ε measured at different temperatures between 40 and 70 °C.[26] The calculated solvation thermodynamic parameters are listed in Table 4, by assuming $\delta_i = 0.52$ Å for K^+ and 0.60 for all anions, following the procedure used by Criss and Luksha in their study of the solvation of alkali halides in dimethylforma-mide (DMF),[32] and by Salomon.[34] The values of δ_i^{exp} (see Table 4) were determined through the experimental values of ΔH_{solv}. Similarly to what occurs in other polar aprotic solvents like DMF, the entropy changes of solvation for the anions in EC are all negative. This means that the disordering perturbation induced by the ion on the solvent is small, while the ordering orientation of the solvating EC molecules around the ion is much more significant, bringing about a significant decrement in the entropy. The most effective ion, besides K^+, is F^-, while ClO_4^- has the least effect.

In DMF, which possesses a lower dipole moment (3.86 D at 298 K), the free energies of solvation are less negative for K^+ (-355 kJ/mol), Cl^- (-269), Br^- (-256), and I^- (-236), and more negative for F^- (-379) than for EC.[26] The values of ΔS_{solv} are more negative than those in EC, indicating a stronger perturbation in the liquid upon dissolution of the salt.[32]

At this point, we can take all the data together and compare with the ideas of Collins on aqueous electrolyte solutions. The law of matching water affinities has been elaborated by Collins to explain the formation of ion pairs in water and the mechanism for the interaction between ions and an inter-face.[35,36]

Briefly, ions with similar free energies of solvation will lead to the formation of strong ion pairs, for example, in the case of LiF or CsI. This is reflected in the so-called "volcano" plot where the enthalpy change of solution is plotted as a function of the difference in heats of hydration. The center of the "volcano" contains ion pairs formed by both chaotropic or kosmotropic species, while the foot of the "volcano" comprises ion pairs formed by a chaotropic cation and a kosmotropic anion, or vice versa.[36]

Figure 6 shows ΔH_{sol} in ethylene carbonate (full circles) as a function of the difference between the anion and cation

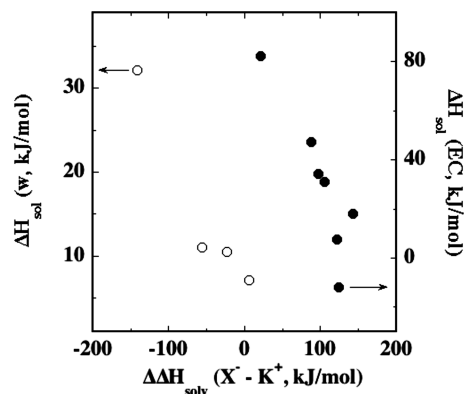**Figure 6.** ΔH_{sol} versus the difference in enthalpy of solvation of the anion and the cation ($\Delta\Delta H_{solv}$) for the electrolytes dissolved in EC at 40 °C (full circles) and in water at 25 °C (open circles).

enthalpies of solvation, $\Delta\Delta H_{solv} = \Delta H_{solv}(X^-) - \Delta H_{solv}(K^+)$. We remark that this plot is similar to the volcano graph proposed by Collins. However, in our case, we deal with saturated solutions, while Collins considered the standard heats of solution at infinite dilution. According to the law of matching solvent affinities, salts whose ions possess the same affinity with the solvent ($\Delta\Delta H_{solv}$ close to zero) show a positive ΔH_{sol}. This is the case of KF for which large electrostatic ion−ion interactions overcome the strong solvent binding to the ions. In the case of KI, the energy gained by breaking the weak iodide−solvent interaction is not enough to balance the energy cost of breaking the strong potassium−solvent interaction. Figure 6 reports also the data for potassium halides in water (open circles), that were roughly estimated (see Table S3, Supporting Information) for saturated solutions at 25 °C from the literature following the same procedure adopted for EC.[30,34] For water solutions, the data are shifted to more negative values of $\Delta\Delta H_{solv}$ because $\Delta H_{solv}(K^+)$ is more negative in ethylene carbonate than in water. In fact, EC presents a larger dipole moment and the negative side of the carbonyl dipole can approach more closely K^+. Anion solvation is poor, as a result of the fact that the positive charge is spread over all three carbon atoms of the ring, as evidenced by molecular orbital calculation.[37] Moreover, because of the steric hindrance, the interaction between an anion and the EC dipole is weaker than that between the same anion and the hydrogen atom in a water molecule.

Therefore, in EC, the solvation process is dominated by K^+, while the solvation of anions is weaker, leading to smaller values of $\Delta\Delta H_{solv}$. As a result, all the anions follow, approximately, the same line as illustrated by Figure 6. KI deviates from the general trend, presumably because of non-electrostatic interactions with the solvent.

Since liquid EC does not possess hydrogen bonding, and the solubilization of salts in EC follows qualitatively the same lyotropic series found for water, we can argue with confidence that the thermodynamic behavior mainly depends on the solvent−solute interactions rather than on hydrogen bonding.

Plotting the theoretical ΔH_{solv} calculated according to the Born equation[34] as a function of the experimental value, we obtain the graph shown in Figure 7.
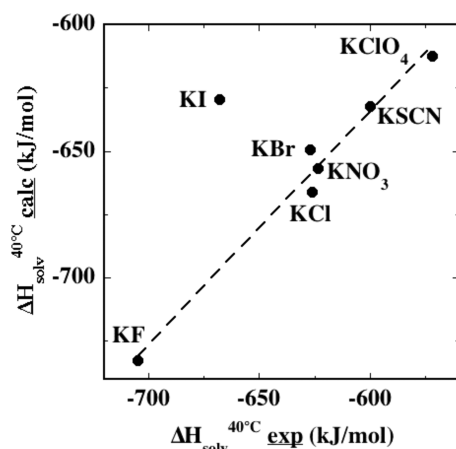

Figure 7. Calculated versus experimental ΔH_{solv} at 40 °C for the electrolytes in EC. The calculated ΔH_{solv} was obtained by summing ΔH_{solv} (K$^+$) and ΔH_{solv} (X$^-$).

The calculated ΔH_{solv} was fitted to the Born equation; thus, Figure 7 judges the goodness of that fit. The plot shows that the electrostatic Born model works quite well for all salts, except of KI that significantly deviates.

FTIR and ATR Spectra. Figure 8 shows the FTIR spectra of liquid EC at room temperature, and Table 5 lists the main peak assignments.[23]

The spectra were recorded also on the solid samples of the EC+salt saturated solutions. The addition of salts partly modifies the frequencies of the main signals. In particular, KI

Table 5. Assignments of the Main FTIR Peaks

wavenumber (cm^{-1})	vibration mode
2998, 2933	C—H stretch
1794, 1765	C=O stretch
1481	CH$_2$ bend
1391	CH$_2$ wag
1152, 1063, 972	skeletal stretch
894	skeletal breathing
771, 716	CH$_2$ wag

and KSCN increase the wavenumber of the peaks in the C=O stretching region (Figure 9), while the other electrolytes do not
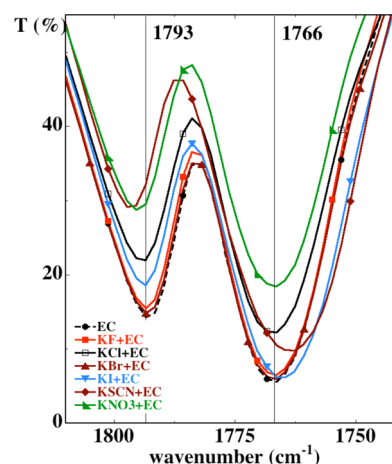

Figure 9. C=O stretching region of the FTIR spectra of EC (dotted line) and of EC+salt solutions in the solid state.

bring about significant changes. Instead, in the fingerprint region, where the skeletal stretching and breathing modes appear (between 1200 and 900 cm^{-1}, Figure 10), practically all salts induce an increment in their frequency, due to the interaction of the anion with the EC ring.
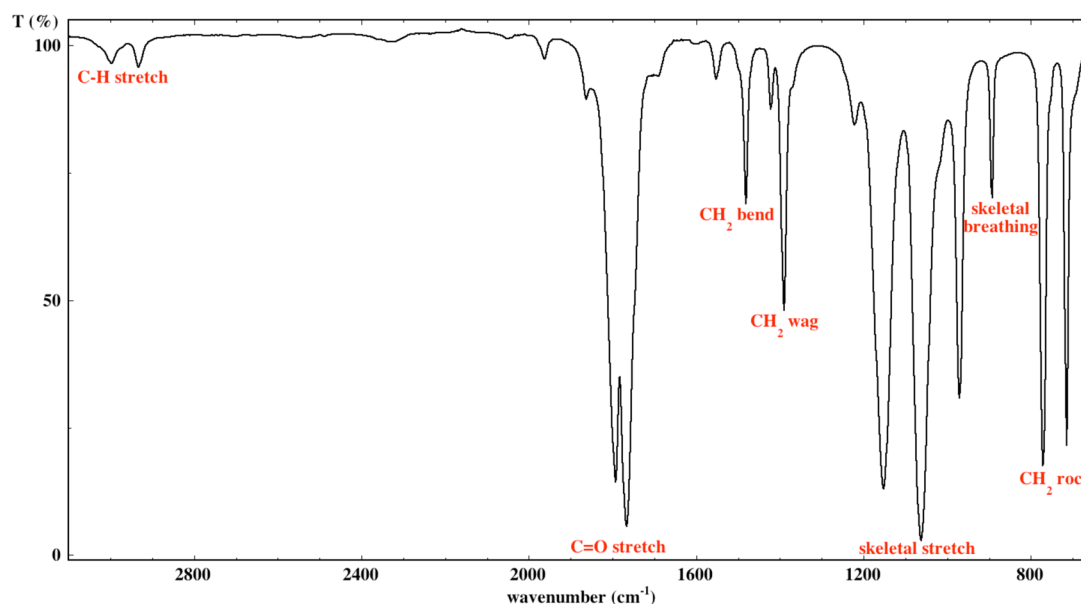

Figure 8. FTIR spectrum of EC in the solid state at room temperature. In red the main peak assignments according to ref 23.
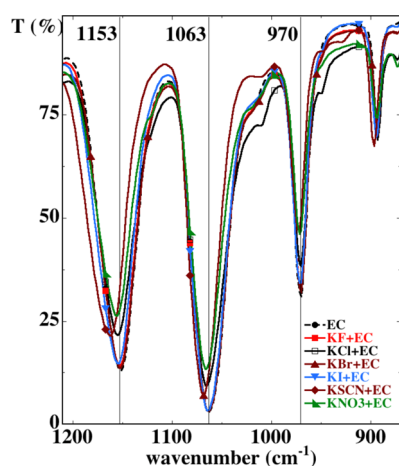
Figure 10. Skeletal stretching and breathing region of the FTIR spectra of EC (dotted line) and of EC+salt solutions in the solid state.

Figures S1a−e (Supporting Information) report the ATR spectra in the liquid state of the pure solvent and of KI and KSCN solutions in EC at the same temperature (40 °C). Interestingly, while the other salts affect only partly the C=O stretch peaks in the FTIR spectra, KI and KSCN have a greater effect on the entire ATR spectrum of liquid EC, in particular on the vibrational modes that concern the ring (skeletal stretching). This evidence suggests that I⁻ and SCN⁻ establish stronger interactions with the O—CH₂—CH₂—O residue of the ethylene carbonate molecule in the liquid state than the other anions, in agreement with the previous results.

X-ray Diffraction. XRD profiles were acquired on powders of pure EC and of its mixtures with the different salts at 25 °C (see Figure 11). The profiles of pure EC and KF+EC are very similar, while the addition of KCl, KBr, and KI to the solvent induces some changes in the position of the X-ray peaks. In particular, KSCN brings about the most significant changes,
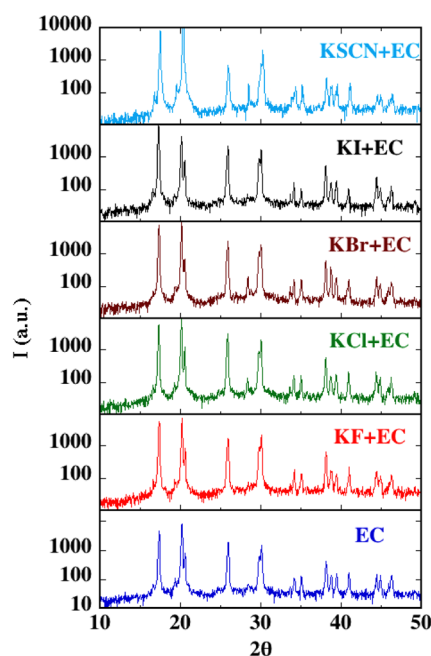

Figure 11. XRD spectra of EC, KF+EC, KCl+EC, KBr+EC, KI+EC, and KSCN+EC at 25 °C.

especially between 15 and 30°, presumably related to the deformation of the unit cell induced by this salt.

Ethylene carbonate has a monoclinic unit cell. The dimensions are shown in Table 6 and agree with the data reported in the literature.[38]

Table 6. Structural Parameters (*a*, *b*, *c* in Å and *β*) of the Unit Cells Obtained from XRD on Single Crystals of Pure EC and Its Mixtures with KF, KI, and KSCN

	EC	KF	KI	KSCN
a	8.91	8.88	8.50	8.89
b	6.23	6.36	6.36	6.32
c	7.02	6.98	7.00	6.97
β	98.7°	99.7°	99.7°	100.7°

XRD spectra on single crystals (data not shown) of pure EC and its mixtures with KF, KI, and KSCN reveal that all salts induce a slight contraction of the *a* dimension of the cell and slightly increase the *b* dimension, while the parameter *c* remains practically unchanged. The *β* angle increases, especially with KSCN. This means that, according to Figure 12, the molecules on the *ab* plane get closer, while those belonging to different cells become a little more distant, and the interlayer *c* spacing remains unaltered.
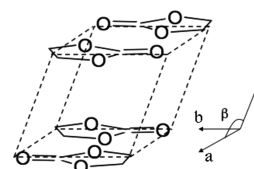

Figure 12. Arrangement of ethylene carbonate in the monoclinic unit cell.

The Case of Potassium Selenocyanate in EC. Unexpectedly, while trying to measure the solubility of KSeCN in liquid EC at 40 °C, we found out that a vigorous reaction took place, with the formation of a yellow mixture and the development of gas. It is known that anions with large polarizability, such as SCN⁻, can react with EC at about 95 °C with a yield in episulfide of 80%,[39] as depicted in Figure S2 (see the Supporting Information).

The larger polarizability of SeCN⁻ presumably lowers the temperature at which the reaction takes place, with the formation of episelenide, carbon dioxide, and a cyanate ion as in the case of SCN⁻. This is the reason why it was impossible to determine the solubility of SeCN⁻ in liquid EC.

■ CONCLUSIONS

Ethylene carbonate (EC) is a polar liquid with high dielectric constant and dipole moment and a good solvent for salts. However, it does not possess hydrogen bonding. In order to assess the relevance of hydrogen bonding in specific ion phenomena, we measured the solubility of some potassium salts in EC as a function of temperature. The solubility increases with the temperature (except for KI) and with the size of the anions according to a Hofmeister series:

$$F^- < Cl^- < Br^- < NO_3^- < ClO_4^- < I^-$$

From the experimental data, the values of the main thermodynamic functions of solution and solvation were

determined. The enthalpy change of solution (ΔH_{sol}) is positive for all salts, except for KI, indicating that the solubilization process is under entropic control. The plot of ΔH_{sol} versus the difference in heats of solvation of the anion and the cation ($\Delta\Delta H_{solv}$) for the same electrolytes dissolved in EC and in water reveals similar trends. Since water produces hydrogen bonds while EC does not, we argue that the specific ion effect that emerges in the solubilization process of electrolytes in EC does not depend on the presence of hydrogen bonding peculiar to water. It is rather due to the ion–solvent interactions that depend mainly on the ion size and on the partial charge distribution in the EC molecule.

FTIR and ATR spectra indicate that anions with a large polarizability (iodide and thiocyanate) interact strongly with the EC ring both in the liquid and in the solid state.

In the solid state, the composition of the salt may result in a slight distortion of the crystalline structure of ethylene carbonate, as FTIR and XRD experiments suggest.

What we have demonstrated in this paper is that Hofmeister effects are not limited to aqueous solutions. They exist equally in non-hydrogen-bonded fluids. It is the interplay between ion–dipole and non-electrostatic interactions that involves the ions and the solvent molecules, and that determines the solubility of electrolytes in ethylene carbonate.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

ICP-AES procedure, calculation of the mean molal activity coefficients, ATR spectra in the liquid state of the pure solvent and of KI and KSCN solutions in EC at 40 °C, and reaction scheme between thiocyanate and ethylene carbonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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