



UNIVERSITÀ
DEGLI STUDI
FIRENZE

FLORE

Repository istituzionale dell'Università degli Studi di Firenze

The solvation of anions in propylene carbonate

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

The solvation of anions in propylene carbonate / Peruzzi, Niccolò; LO NOSTRO, Pierandrea; Ninham, B. W.; Baglioni, Piero. - In: JOURNAL OF SOLUTION CHEMISTRY. - ISSN 0095-9782. - STAMPA. - 44:(2015), pp. 1224-1239. [10.1007/s10953-015-0335-z]

Availability:

This version is available at: 2158/947564 since: 2015-12-08T12:27:59Z

Published version:

DOI: 10.1007/s10953-015-0335-z

Terms of use:

Open Access

La pubblicazione è resa disponibile sotto le norme e i termini della licenza di deposito, secondo quanto stabilito dalla Policy per l'accesso aperto dell'Università degli Studi di Firenze (<https://www.sba.unifi.it/upload/policy-oa-2016-1.pdf>)

Publisher copyright claim:

(Article begins on next page)

The solvation of anions in propylene carbonate

Niccolò Peruzzi,¹ Pierandrea Lo Nostro,^{1,*} Barry W. Ninham,² Piero Baglioni¹

¹ Department of Chemistry “Ugo Schiff” and CSGI, University of Florence, 50019 Sesto Fiorentino (Firenze) - Italy

² Research School of Physical Sciences and Engineering, Canberra, ACT0200 - Australia

* Corresponding author. e-mail: PLN@csgi.unifi.it. Tel.: +39 055 457-3010. Fax: +39 055 457-3036.

Abstract

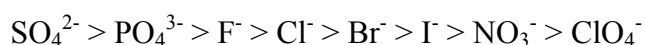
The solubility of some univalent potassium salts (KF, KCl, KBr, KI, KClO₄, KSCN, and KCNO) in propylene carbonate (PC) was determined at different temperatures through Flame Emission Spectroscopy. From the solubility measurements, the thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 of solution were calculated. Measurements were carried out via conductimetry and FTIR to investigate the formation of ion pairs, and the ion-solvent interactions. This study was motivated by the open question of whether specific ion (Hofmeister) effects are related to the structure of the solvent (i.e. hydrogen bonding). As for water the effects are due to solute induced solvent structure changes not accounted for by electrostatic forces.

Keywords

Hofmeister series; propylene carbonate; specific ion effects; ion solvation; solvent structure.

1 Introduction

The expression “Hofmeister effect” refers to the specificity that ions exhibit on a plethora of phenomena. Some examples are colloidal interactions, surfactant dispersions, microemulsions stability, polymers, and biomacromolecules (proteins, enzymes, nucleic acids, etc.) [1, 2]. The ion effect is usually quantified and organized in a specific trend, which may parallel one or more ion properties such as the size, charge, polarizability, partial molar volume, etc. In particular, Hofmeister studied the precipitation of egg yolk albumin from aqueous dispersions upon the addition of some sodium salts, and discovered that their effect can be ordered according to the following ranking for anions (at fixed cation) [1, 2]:



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 [3], the physico-chemical properties of ionic liquids [4, 5], the bubble-bubble coalescence in different organic liquids [6], and the activity of enzymes in non-aqueous media [7].

In a previous study we reported on the solubility of some potassium salts in ethylene carbonate (EC) [8], and showed that the solubility increases with temperature and with the size of the anions according to the following series:



Like EC, propylene carbonate (PC) is a polar aprotic solvent, and bears a methyl group on the lactone ring (see Fig. 1). Possessing a large dipole moment (4.81 D), a large dielectric constant (64.9 at 25°C) [9], and a significant donor number (63.2 kJ·mol⁻¹), PC solubilizes strong electrolytes and, for this reason, it is used in a variety of syntheses and applications.

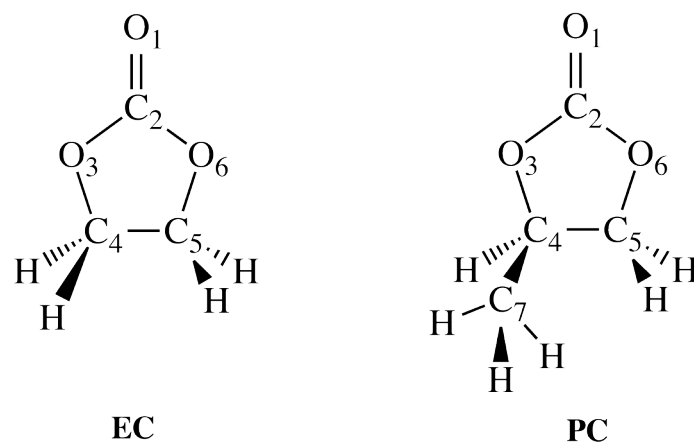


Fig. 1 Chemical structure and atom numbering for ethylene carbonate (EC) and propylene carbonate (PC)

For example, it is possible to obtain sodium, potassium and other alkali metals by electrolysis of their chlorides [10]. PC is used as a co-solvent in cleaning systems to remove naturally aged polymeric acrylic layers from the surface of wall paintings [11, 12]. Alkylene carbonates are also used as “safe” solvent substitutes in agriculture and as carrier solvents in therapeutic and cosmetic preparations [13]. The electrochemical stability and the high dielectric constant of propylene carbonate make it a prime choice for solvents studied for application in lithium-ion batteries [14]. This liquid, and its mixtures with EC and/or dimethyl carbonate (DMC), has proved to be among the most efficient solvents in terms of battery cyclability [15]. Because the electrolyte defines how fast the energy can be released [16], by controlling the rate of mass flow within the battery, the solvation properties of the selected solvent play an important role.

Our choice of PC lies further in studying the effect of an additional methyl group to EC, and of the different solvent structuredness on the thermodynamic parameters of solvation. More than that a comparison of electrolyte solubilities in different aprotic organic liquids should help in clarifying whether Hofmeister phenomena are driven by a specific ion induced perturbation of the three dimensional structure of the solvent or not.

Prompted by this motivation we measured the solubility of KF, KCl, KBr, KI, KClO₄, KSCN, and KCNO in PC at 25°, 30°, 35°, 40°, and 45° C through Flame Emission Spectroscopy (FES). FTIR measurements were performed in order to detect any modification of the solvent infrared spectral properties upon addition of the salts, and conductivity measurements were carried out to detect the presence of ion pairs.

2 Experimental Section

2.1 Materials

Anhydrous propylene carbonate (purity > 99.7%), potassium fluoride (purity ≥ 99.5%), chloride (purity ≥ 99.0%), bromide (purity ≥ 99.0%), iodide (purity ≥ 99.5%), perchlorate (purity ≥ 99%), thiocyanate (purity ≥ 99.0%) and cyanate (purity 96%) were purchased from Sigma-Aldrich-Fluka (Milan, Italy).

PC, stored in a sealed bottle (Sure/Seal), was used without any further purification, while all salts were recrystallized and purified according to literature recommendations [17]. They were stored under vacuum in a dessicator at room temperature over CaCl₂.

2.2 Sample preparation

In order to measure the salt solubility in PC at different temperatures, a certain amount of liquid anhydrous PC 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*, in grams) of solution was carefully sucked from the top of the solution and transferred to a flask and diluted with Millipore water, filtered with 0.22 μm Millipore filters, up to a volume *V* (in L). Repeated sample uptakes up to 48 h did not result in a variation of the average measured concentration.

2.3 Experimental Apparatus

Potassium was determined by FES using a Perkin Elmer Analyst 100 instrument operating in emission mode at 766.5 nm. Acetylene-air in 1:2 ratio flame was used for atomization and excitation. The sample flux on the flame was regularly measured and kept constant at 9.5 mL·min⁻¹.

The reproducibility of the measure is 5% and the detection limit (calculated as the concentration corresponding to three times the standard deviation of the signal obtained by 10 replicates of a 0.05 g·L⁻¹ of K⁺ standard) is 0.020 mg·L⁻¹.

The calibration curve was obtained by six standard solutions in the concentration range between 0.05 and 13.0 mg·L⁻¹ by dilution of 400 ppm KBr with ultrapure water (MilliQ water, resistivity > 18 MΩ).

The calibration data were fitted with a linear plot with a correlation coefficient R^2 of 0.99993.

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

$$m = \frac{1000Vc_K}{1000bM_K - VMc_K} \quad (1)$$

Where M_K is the atomic mass of potassium (39.102 g·mol⁻¹), c_K is the concentration of potassium ions in mg·L⁻¹, and M is the molar mass of the salt.

Conductivity measurements were made with a Metrohm 712 conductometer equipped with a 6.0910.120 conductivity measuring cell, cell constant $C = 0.9 \text{ cm}^{-1}$, purchased from Metrohm.

The cell constant was determined before each set of measurements with a standard solution of KCl 0.0100 mol·L⁻¹, for which the tabulated specific conductivity is $\kappa_{\text{tab}} = 1412 \text{ } \mu\text{S}\cdot\text{cm}^{-1}$ [18].

Before each measurement, the solution (about 25 or 50 mL) in the cell was magnetically stirred for 10 min and then was left to equilibrate for 5 min. The measurements were carried out in a thermostatted bath at $(25.0 \pm 0.2) \text{ }^\circ\text{C}$.

FTIR analysis was carried out in transmission mode using a Bio-Rad FTS-40 spectrometer with 4 cm^{-1} resolution and 32 scans. The spectral range was $4000\text{--}1000 \text{ cm}^{-1}$. The transmission spectra were recorded using a liquid cell equipped with NaCl aperture plates.

FTIR transmission was selected to perform a qualitative analysis of pure PC and of its solutions with the salts, at room temperature, choosing a concentration of $2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ for all salts except KCl. In the latter case the spectra were recorded on a saturated solution, due to the poor solubility of potassium chloride in propylene carbonate.

3 Experimental results and discussion

3.1 Solvent structure

Like EC, PC has a large dipole moment (see Table 1), which promotes ion-dipole attractive interactions.

As the PC dipole moment is very close to that of EC, every variation of the thermodynamic functions is presumably ascribed to the steric hindrance of the methyl group.

Supposedly, the replacement of a hydrogen atom by a methyl group in the ring affects its capability to solvate the ions, modifying the entropy and the enthalpy change of solution. We will discuss this issue later.

Due to the presence of a large permanent dipole moment, the liquid molecules of EC associate in dimers. This has also been confirmed by Monte Carlo studies [19]. The presence of the methyl group makes PC a more asymmetric molecule with respect to EC, and thus a less structured solvent. In fact no dimers have been detected [9]. Dielectric measurements complemented by IR and NMR data indicate that PC behaves as a typical polar liquid with

strong dipole-dipole interactions but no association [20].

The lack of a solvent structure in PC is also suggested by the value of the Trouton constant $\Delta S_{\text{vap}}/R$ and by the Kirkwood correlation parameter g , defined as:

$$g = \frac{9k_B\epsilon_0V_m(\epsilon - 1.1n_D^2)(2\epsilon + 1.1n_D^2)}{\epsilon N\mu^2(2 + 1.1n_D^2)} \quad (2)$$

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 static dielectric constant, the Avogadro number, and the dipole moment, respectively. For PC, g comes out to be about 1.23 and $\Delta S_{\text{vap}}/R = 11.63$. According to Marcus [21], solvents with $\Delta S_{\text{vap}}/R$ lower than 13 and/or g lower than 2 should be considered as unstructured.

Table 1 lists some physico-chemical properties of PC and for comparison those of EC.

Table 1 Physico-chemical properties of PC and EC at 25 °C [9, 22]

| Property | PC | EC |
|--|--------|--------------|
| Dielectric constant, ϵ | 64.9 | 89.8 |
| Dipole moment, μ (D) | 4.81 | 4.61 |
| Viscosity, η (cP) | 2.53 | 1.90 (40 °C) |
| Density, ρ (g·cm ⁻³) | 1.200 | 1.321 |
| Molecular mass, M (g·mol ⁻¹) | 102.09 | 88.06 |
| Hildebrand parameter, δ (MPa ^{1/2}) | 27.2 | 30.1 |
| Hansen dispersion term, δ_D (MPa ^{1/2}) | 20.0 | 19.4 |
| Hansen polar term, δ_P (MPa ^{1/2}) | 18.0 | 22.4 |
| Hansen H bonding term, δ_H (MPa ^{1/2}) | 4.1 | 5.1 |
| Electrostatic factor, $f = \mu\epsilon$ (D) | 311.52 | 413.98 |
| Polarizability, α (Å ³) ^a | 8.7 | 6.8 |
| Molar polarization, P_M | 81.2 | 64.5 |
| Donor number, DN (kJ·mol ⁻¹) | 63.2 | 68.6 |
| Acceptor number, AN (ppm) | 18.3 | - |
| Kirkwood parameter, g | 1.23 | 1.60 |

^a calculated from the Clausius-Mossotti equation.

3.2 Solubility of electrolytes and ion solvation in PC

The solubility in PC (in molal units) of the equilibrated saturated solutions of the electrolytes investigated was determined as a function of temperature (Table 2).

The solubility of the electrolytes in PC is lower than that in EC. We discuss the results in terms of the ion-dipole interactions that the ions establish with the solvent molecules, of the solvent donicity for the cation, and of the solvent structuredness, and compare these data to those previously obtained in EC.

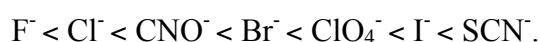
The data for KCl, KBr, KI and KClO₄ are close to those reported in previous reports [23, 24].

Table 2 Solubility (in molal units, mol·kg⁻¹) of electrolytes in PC as a function of temperature. The uncertainty on each measurement is calculated with the error propagation formula

| $T/(^{\circ}\text{C})$ | KF | KCl | KBr | KI |
|------------------------|--------------------------------|--------------------------------|--------------------------------|------------------|
| 25.0 | $(1.70\pm 0.20)\times 10^{-4}$ | $(3.67\pm 0.40)\times 10^{-4}$ | $(3.98\pm 0.40)\times 10^{-3}$ | 0.221 ± 0.020 |
| 30.0 | $(2.78\pm 0.30)\times 10^{-4}$ | $(3.69\pm 0.40)\times 10^{-4}$ | $(3.81\pm 0.40)\times 10^{-3}$ | 0.199 ± 0.020 |
| 35.0 | $(2.85\pm 0.30)\times 10^{-4}$ | $(3.63\pm 0.40)\times 10^{-4}$ | $(3.76\pm 0.40)\times 10^{-3}$ | 0.218 ± 0.020 |
| 40.0 | $(1.45\pm 0.15)\times 10^{-4}$ | $(4.18\pm 0.40)\times 10^{-4}$ | $(3.86\pm 0.40)\times 10^{-3}$ | 0.216 ± 0.020 |
| 45.0 | $(2.75\pm 0.30)\times 10^{-4}$ | $(5.18\pm 0.50)\times 10^{-4}$ | $(4.19\pm 0.40)\times 10^{-3}$ | 0.211 ± 0.020 |

| $T/(^{\circ}\text{C})$ | KClO ₄ | KSCN | KCNO |
|------------------------|--------------------------------|----------------|--------------------------------|
| 25.0 | $(4.57\pm 0.20)\times 10^{-2}$ | 1.09 ± 0.02 | $(1.52\pm 0.15)\times 10^{-3}$ |
| 30.0 | $(4.65\pm 0.20)\times 10^{-2}$ | 1.33 ± 0.03 | $(1.70\pm 0.17)\times 10^{-3}$ |
| 35.0 | $(5.03\pm 0.25)\times 10^{-2}$ | 1.72 ± 0.03 | $(1.92\pm 0.20)\times 10^{-3}$ |
| 40.0 | $(5.10\pm 0.25)\times 10^{-2}$ | 1.97 ± 0.04 | $(2.34\pm 0.23)\times 10^{-3}$ |
| 45.0 | $(5.21\pm 0.26)\times 10^{-2}$ | 2.10 ± 0.04 | $(2.50\pm 0.25)\times 10^{-3}$ |

The solubility increases with the size of the anion according to the trend:



These results agree with those already found for solutions in EC [8]. Moreover, also in the case of PC, KI is the only salt whose solubility decreases with temperature. The comparison between the solubilities of the same potassium salts in PC and in EC [8] shows that the investigated electrolytes are by far more soluble in ethylene carbonate, presumably due to the higher dielectric constant and donor number of this liquid (see Table 1). We note that the solubility of potassium thiocyanate is particularly large, and increases with the temperature. One possible explanation of this behavior might be the chemical reaction between the SCN⁻ ion and the C₄ carbon atom of the cyclic carbonate (see Fig. 1), leading to the formation of

episulfide, CNO^- , and CO_2 . We had already encountered this phenomenon in a previous paper, where we measured the solubility of some potassium salts in ethylene carbonate [8].

The enthalpy, Gibbs free energy and entropy changes of solution were calculated from Eqs. 3-5 [8, 25, 26], and are listed in Table 3:

$$\Delta G_{sol}^0 = -RT \ln K_{ps} = -RT \ln(\gamma_{\pm} m)^2 \quad (3)$$

$$\Delta H_{sol}^0 = -2R \left[\frac{\partial \ln(\gamma_{\pm} m)}{\partial (1/T)} \right] \quad (4)$$

$$\Delta S_{sol}^0 = \frac{1}{T} (\Delta G_{sol}^0 - \Delta H_{sol}^0) \quad (5)$$

where γ_{\pm} is the mean molal activity coefficient and K_{sp} is the solubility product of the salt in PC.

Table 3 Enthalpy (ΔH_{sol}^0 , in $\text{kJ}\cdot\text{mol}^{-1}$), Gibbs free energy (ΔG_{sol}^0 , in $\text{kJ}\cdot\text{mol}^{-1}$), entropy (ΔS_{sol}^0 , in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) changes of solution at 40 °C, experimental lattice energy (U , in $\text{kJ}\cdot\text{mol}^{-1}$) [28], enthalpy change of solvation (ΔH_{solv}^0 , in $\text{kJ}\cdot\text{mol}^{-1}$) calculated according to Eq. 10 for electrolytes in PC, and crystallographic radius of the anion (r_i , in Å)

| Salt | ΔH_{sol}^0 | ΔG_{sol}^0 | ΔS_{sol}^0 | U | ΔH_{solv}^0 | r_i |
|-------------------|--------------------|--------------------|--------------------|------------------|---------------------|-------|
| KCl | 24.7±1.2 | 40.6±2.0 | -50.8±5.1 | 715 | -690±34 | 1.81 |
| KBr | 9.2±0.5 | 29.4±1.5 | -64.5±6.5 | 682 | -673±34 | 1.96 |
| KI | -3.0±0.2 | 10.3±0.5 | -42.5±4.2 | 649 | -652±33 | 2.16 |
| KClO ₄ | 8.0±0.4 | 16.9±0.8 | -25.5±2.6 | 602 | -593±30 | 2.36 |
| KSCN | 44.3±2.2 | -0.1±0.1 | 141.6±14 | 615 | -571±28 | 2.13 |
| KCNO | 39.5±2.0 | 31.9±1.6 | 24.3±2.4 | 653 ^a | -614±31 | 2.34 |

^a calculated value [28].

The value of γ_{\pm} was estimated through the Debye-Hückel theory as [27]:

$$\log_{10} \gamma_{\pm} = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} \quad (6)$$

Here m is the molal concentration of the salt.

$$A = 1.8247 \times 10^6 \left(\frac{\rho}{\epsilon^3 T^3} \right)^{1/2} \quad (7)$$

$$B = 50.2901 \left(\frac{\rho}{\epsilon T} \right)^{1/2} \quad (8)$$

where ρ , ε and T are the density and the static dielectric constant of the solvent, and the absolute temperature, respectively. A is given in $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ and B in $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}\cdot\text{\AA}^{-1}$.

a is the distance of closest approach. For fully dissociated 1:1 electrolytes a can be taken as the Bjerrum length q :

$$q = \frac{e^2}{2\varepsilon k_B T} \quad (9)$$

where e and k_B are the elementary charge and the Boltzmann constant, respectively.

Table 4 shows the values of ε , A , ρ , q , and B as a function of temperature that were used for the calculation of the average ionic activity coefficients in PC solutions.

Table 4 Values of ρ (in $\text{g}\cdot\text{mL}^{-1}$), ε , q (in \AA), A and B as a function of temperature (T , in $^\circ\text{C}$) that were used for the calculation of γ_{\pm} in PC solutions

| $T/(^\circ\text{C})$ | ρ^a | ε^b | q | A | B |
|----------------------|----------|-----------------|--------|---------|---------|
| 30 | 1.1946 | 63.664 | 4.3294 | 0.74382 | 0.39565 |
| 35 | 1.1892 | 62.630 | 4.3294 | 0.74216 | 0.39476 |
| 40 | 1.1841 | 61.515 | 4.3389 | 0.74300 | 0.39435 |
| 45 | 1.1787 | 60.240 | 4.3597 | 0.74665 | 0.39439 |

^a from [29]; ^b from [30].

We note that especially for KI and KSCN the solubility of the electrolytes is probably beyond the validity range of Eq. 6, therefore the calculated mean molal activity coefficient should be considered as a rough estimate.

The enthalpy change of solvation was obtained as:

$$\Delta H_{\text{sol}}^0 = \Delta H_{\text{sol}}^0 - U \quad (10)$$

where U is the lattice energy of each salt (see Table 3).

The data for KF were not calculated because of the low reproducibility of its solubility measurements. The dissolution process is always endothermic, except for KI. The enthalpy change of solution decreases from hard (Cl^-) to soft (I^-) anions. In the case of large, soft anions the ion-solvent interactions (ion-dipole and dispersive) overcome the weak electrostatic ion-ion interaction in the lattice.

Plotting ΔH_{sol}^0 as a function of the crystallographic ion radius we obtain the graph reported in

Fig. 2. ΔH_{sol}^0 decreases as the anion size increases. Interestingly there are two different trends for spherical (halides) and non-spherical (thiocyanate and cyanate) anions. Moreover perchlorate, although spherical, does not fall on the halide trend. There are two effects to be noted here: the effect of shape (which changes the dipolar contribution) as well as the effect of the multipoles.

Higher order multipoles may contribute as much as half of the total dispersion solvation energy of electron-rich spherical (monoatomic) ions [31]. Moreover both perchlorate and the linear polyatomic ions have a strong permanent quadrupole moments that the monoatomic species do not possess. We note that perchlorate, although spherical, has a strong quadrupole moment and deviates significantly from the behaviour of the monoatomic spherical halides. According to Parsons apparently the shape effect is of less importance than the multipolar effect [32].

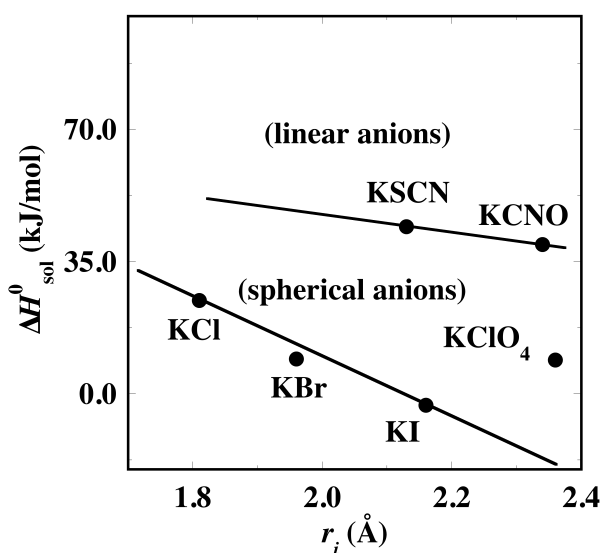


Fig. 2 Enthalpy changes of solution vs. the crystallographic radius r_i for each anion. The lines are a guide for the eye

Assuming that the contribution of K^+ to solvation is constant for all electrolytes, the solute-solvent interactions are stronger for Cl^- than for I^- , as indicated by the values of ΔH_{sol}^0 .

The sign of ΔH_{sol}^0 is due to the fact that the anion-cation interaction in the lattice is stronger in KCl than in KI for electrostatic reasons.

The free energy of solution decreases when the anion size increases, in agreement to the data reported by Muhuri [23]. The entropy change of solution increases with the size of the anion.

The comparison of the solution thermodynamic functions for PC and EC [8] shows that large differences in solubility (ΔG_{sol}^0) are found for the two alkyl carbonates in spite of their structural similarity. The dielectric constant and the dipole moment of the solvents determine the extent of molecular interactions and hence are responsible for the solubility of the electrolytes in the solvents. Table 1 lists some useful parameters to describe the solvating power of liquids [9]. We note that the dipole moments are quite similar in the liquids, 4.61 D for EC and 4.81 D for PC. The static polarizability – that determines the strength of dispersion forces – and the molar polarization are greater in PC than in EC, however their relevance in determining the salt solubility is probably negligible because dispersion forces are weaker than ion-dipole interactions. The Hildebrand parameter is larger for EC than for PC, mainly because of the higher Hansen polar contribution (δ_p), which in turn depends on the dipole moment [13]. Finally, the dielectric constant of EC is almost 40% higher than that of PC, and the donor number of EC is about 9% higher than that of PC, resulting in a larger solubility of salts in the former, that possesses a stronger solvating capability towards the K^+ ion, due to the dipolar negative side of the carbonyl group. The solubilization process is thus driven by the cation-solvent interactions due to the relevant donicity of the solvents.

Unexpectedly, the enthalpy of solution is slightly higher in EC than in PC. This result was also observed in the case of LiF [9]. The steric hindrance due to the presence of the methyl group in PC seems to suggest that the solute-solvent interaction is stronger in EC than in PC. However the dipole moment of PC is slightly higher than that of EC, allowing a stronger cation-solvent interaction. Presumably, as the dissolution process is driven by the cation (see

later), the weaker anion-solvent interaction is balanced by the stronger cation-solvent interaction.

Moreover the difference between the experimental enthalpy of solvation in EC and PC is greater for small anions. Thus, small anions can approach the PC molecule and establish stronger interactions as a consequence of its larger dipole moment, while the approach of large anions is hindered by the hanging methyl group. In fact KI and KSCN are more solvated in EC than in PC.

Presumably, the steric hindrance due to the presence of the methyl group in PC is responsible for its weaker structuredness respect to that of ethylene carbonate [33].

The addition of an electrolyte to a solvent determines a re-orientation of the solvent molecules around the ions, producing a negative entropic solute-solvent term. In the case of structured solvents there is also a solvent-solvent term which is positive, especially in the case of kosmotropic electrolytes, because the ions disrupt the solvent structure [34].

If the solvent is unstructured this positive solvent-solvent term is presumably less important in balancing the negative solute-solvent term resulting in a dissolution process which is, globally, less favourable from an entropic point of view. Thus, interestingly, the solvent structuredness seems to determine the observed inversion of the trend that describes the dependence of ΔS_{sol}^0 on r_i (see Fig. 3).

This explains why in PC the entropy change of solution is negative, except for KSCN and KCNO, and increases in passing from kosmotropic to chaotropic ions (see Fig. 3), in fact kosmotropic ions order the solvating PC molecules more tightly.

Moreover the difference between the values of ΔS_{sol}^0 in the two solvents ($\Delta\Delta S_{\text{sol}}^0$) decreases for chaotropic ions because they bind the solvent molecules more weakly, therefore their behaviour in EC and PC is similar.

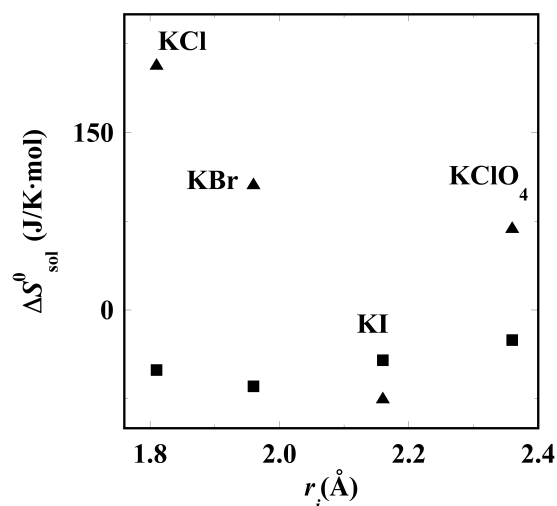


Fig. 3 ΔS_{sol}^0 in PC (black squares) and EC (black triangles) for the different salts versus the crystallographic radius r_i of the anion

We argue that K^+ is more solvated than the anions in PC. In fact, PC possesses a large dipole moment and the negative side of its carbonyl group can approach more closely and point straight toward the cation. On the other hand, anion solvation of PC is poor, as a result of the fact that the positive charge is spread over a broader set of atoms, as shown in Fig. 4 [35]. Moreover the anion solvation is prevented by the $-\text{CH}_3$ group, due to steric hindrance. We also note in this respect that, in spite of its high lattice energy, LiF is more soluble than KF in PC, as a consequence of the stronger ion-dipole interactions that Li^+ establishes with the solvent in virtue of its larger charge density [9].

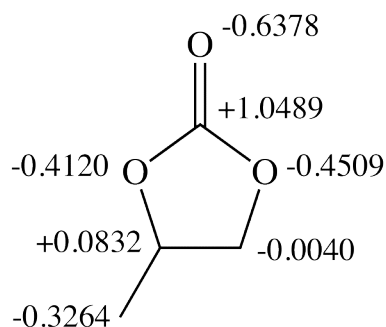


Fig. 4 Charge distribution in PC. For all hydrogens the charge is $+0.1165 \text{ \AA}$ [35]

3.3 Conductivity measurements

These data were collected in order to evaluate the tendency of the investigated salts to form ion pairs.

The ion conductivity of KF in PC is too low to obtain reproducible data.

The results of conductivity measurements on the different samples are given in Table 5 and shown in Figs. 5 and 6.

Table 5 Equivalent conductivity Λ_{eq} ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, ± 0.2) of salts as a function of the molar concentration (c , $\text{mol}\cdot\text{L}^{-1}$)

| KCl | | KBr | | KI | |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| c | Λ_{eq} | c | Λ_{eq} | c | Λ_{eq} |
| 3.05×10^{-5} | 15.7 | 2.96×10^{-5} | 31.7 | 2.96×10^{-4} | 31.1 |
| 4.60×10^{-5} | 16.5 | 6.07×10^{-5} | 31.9 | 4.47×10^{-4} | 31.5 |
| 6.10×10^{-5} | 16.1 | 8.95×10^{-5} | 31.6 | 6.74×10^{-4} | 31.7 |
| 9.20×10^{-5} | 16.1 | 3.09×10^{-5} | 30.1 | 2.50×10^{-3} | 31.1 |
| 1.22×10^{-4} | 15.4 | 6.03×10^{-4} | 29.6 | 3.73×10^{-3} | 31.3 |
| 2.14×10^{-4} | 16.7 | 8.89×10^{-4} | 29.4 | 4.46×10^{-3} | 31.3 |
| 3.05×10^{-4} | 15.0 | 1.89×10^{-3} | 28.4 | 6.71×10^{-3} | 30.9 |
| 4.60×10^{-4} | 16.0 | 2.49×10^{-3} | 28.0 | 2.48×10^{-2} | 27.2 |
| 6.10×10^{-4} | 14.2 | 4.96×10^{-3} | 27.0 | 3.73×10^{-2} | 26.0 |
| | | | | 4.48×10^{-2} | 25.7 |
| | | | | 6.73×10^{-2} | 24.5 |
| | | | | 9.09×10^{-2} | 23.4 |
| | | | | 1.09×10^{-1} | 22.5 |

| KSCN | | KClO ₄ | |
|-----------------------|-----------------------|-----------------------|-----------------------|
| c | Λ_{eq} | c | Λ_{eq} |
| 3.08×10^{-4} | 36.2 | 9.78×10^{-5} | 29.3 |
| 5.92×10^{-4} | 35.0 | 2.52×10^{-4} | 28.2 |
| 8.99×10^{-4} | 34.4 | 5.01×10^{-4} | 28.6 |
| 2.50×10^{-3} | 32.4 | 7.50×10^{-4} | 28.0 |
| 4.95×10^{-3} | 31.1 | 1.01×10^{-3} | 28.1 |
| 7.50×10^{-3} | 31.5 | 2.51×10^{-3} | 27.5 |
| 1.00×10^{-2} | 30.8 | 5.00×10^{-3} | 25.5 |
| 4.11×10^{-2} | 25.2 | | |
| 7.37×10^{-2} | 21.6 | | |
| 1.03×10^{-1} | 19.9 | | |
| 2.66×10^{-1} | 11.4 | | |
| 5.92×10^{-1} | 9.2 | | |

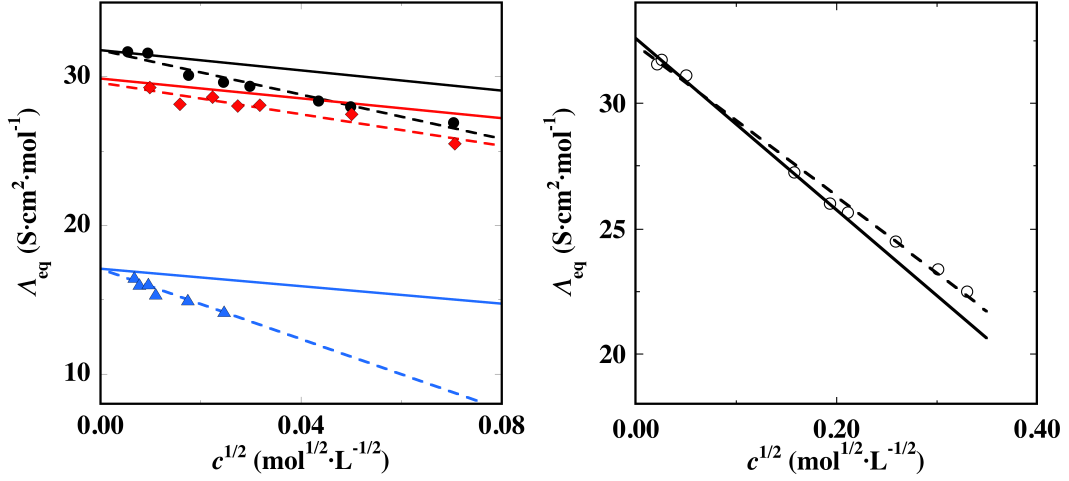


Fig. 5 Plot of Λ_{eq} vs $c^{1/2}$ at 25.0 °C. Left: KBr (black circles), KClO_4 (red diamonds), and KCl (blue triangles) in PC. Right: KI in PC. The full straight lines represent the Onsager equation, the dotted lines are a guide for the eyes

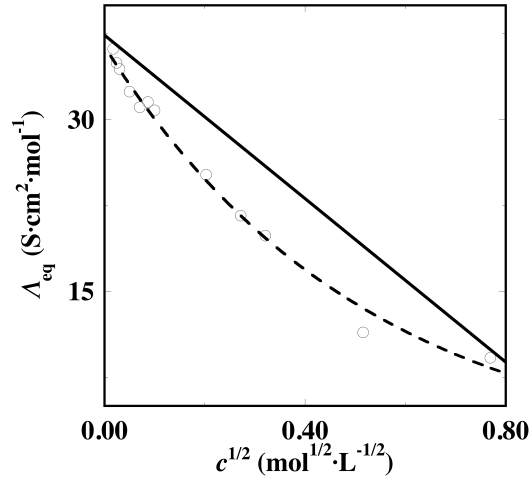


Fig. 6 Plot of Λ_{eq} vs $c^{1/2}$ for KSCN in PC at 25.0 °C. The full straight lines represent the Onsager equation, the dotted lines are a guide for the eyes

According to the Kohlrausch law the equivalent conductivity at infinite dilution (Λ_{eq}^0) (see Table 6) was determined by extrapolating the equivalent conductivity as a function of the square root of the concentration for $c < 0.01$ M.

The equivalent conductivities of KCl, KBr and KClO_4 fall on a curve which lies below the limiting tangent obtained from the Onsager equation (see Fig. 5) [36-38]:

$$\Lambda_{eq} = \Lambda_{eq}^0 - \left[\frac{8.20 \times 10^5}{(\epsilon T)^{3/2}} + \frac{82.4}{\eta(\epsilon T)^{1/2}} \right] \quad (11)$$

where Λ_{eq} is the equivalent conductivity, Λ_{eq}^0 the equivalent conductivity at infinite dilution, ϵ the dielectric constant, η the viscosity and T the absolute temperature.

The plot clearly shows that for KCl, KClO₄ and KBr ion-association takes place at a different extent. On the other hand, the plot for KI lies above the limiting tangent, suggesting that in this case ion pairs are not formed (see Fig. 5). Following the conclusions proposed by Jansen and Yeager, we argue that presumably KSCN shows that ion-pairing occurs slightly [39].

Referring to Figs. 5 and 6, the difference in slope between the experimental and the Onsager trends is larger for KCl, indicating that in comparison to KBr, KI, KClO₄, and KSCN this is the mostly associated electrolyte in PC, despite its low concentration. According to the Collins' law of matching water affinities, in the case of small anions the greater electrostatic ion-ion interactions overcome the solvent-solute ion-dipole interactions and this fact promotes ion pairing. The conductivity results seem to confirm this conclusion drawn from the thermodynamic parameters obtained from the solubility data. Moreover, the results for KI, KClO₄, and KSCN agree with those reported in the literature by Jansen and Yeager [39].

Table 6 Equivalent conductivity (Λ_{eq}^0 , S·cm²·mol⁻¹) at infinite dilution for each salt in PC at 25.0 °C (this work) in comparison to the data reported in the literature [39, 40]

| Salt | Λ_{eq}^0 | Ref. 39 | Ref. 40 |
|-------------------|-------------------------|---------|---------|
| KCl | 17.1±0.2 | | |
| KClO ₄ | 29.9±0.1 | 29.64 | 30.75 |
| KBr | 31.8±0.2 | | |
| KI | 32.6±0.2 | 29.41 | 30.75 |
| KSCN | 37.4±0.3 | 33.31 | |

The equivalent conductivity at infinite dilution increases according to the trend: Cl⁻ < ClO₄⁻ < Br⁻ < I⁻ < SCN⁻. This sequence is reversed compared to that found by Mukherjee et al. for lithium and tetrabutyl ammonium salts in PC, while it is the same as that for tetraethyl ammonium electrolytes in the same solvent [36].

Thus, the mobility of Cl⁻ is smaller than that of the other anions, suggesting that the effective size of Cl⁻ is larger than that of the other anions as a result of the stronger solvation.

These comments are in line with the results obtained by Mukherjee on the conductivity of different electrolytes in PC at 25 °C [30]. He determined the ion conductivities of different cations and anions and concluded that small cations, like Li^+ , are more solvated than larger cations.

3.4 FTIR spectra

Figure 7 shows the spectra of liquid PC at room temperature, Table 7 lists the main peak assignments [41].

Table 7 Assignments of the main FTIR peaks (see Fig. 1 for atom numbering)

| Wavenumber (cm^{-1}) | Vibration mode |
|---------------------------------|---|
| 1060 | $\text{C}_5\text{-H}$ twist + $\text{C}_4\text{-H}$ bending |
| 1120 | $\text{C}_7\text{-H}$ wag + $\text{C}_4\text{-H}$ bending |
| 1148 | $\text{C}_5\text{-C}_4 + \text{C}_2\text{-O}_6 + \text{C}_2\text{-O}_3$ stretch |
| 1177 | $\text{O}_6\text{-C}_5$ stretch + $\text{C}_7\text{-H}$ wag |
| 1337 | $\text{C}_7\text{-H}$ bending |
| 1355 | $\text{C}_7\text{-H}$ bending |
| 1391 | $\text{C}_5\text{-H}$ wag + $\text{C}_7\text{-H}$ bending |
| 1484 | $\text{C}_7\text{-H}$ umbrella |
| 1800 | $\text{C}_2\text{-O}_1$ stretching |
| 2882 | $-\text{CH}_2$ stretching |
| 2937 | $-\text{CH}_3$ stretching |
| 2990 | $-\text{CH}_3$ stretching |

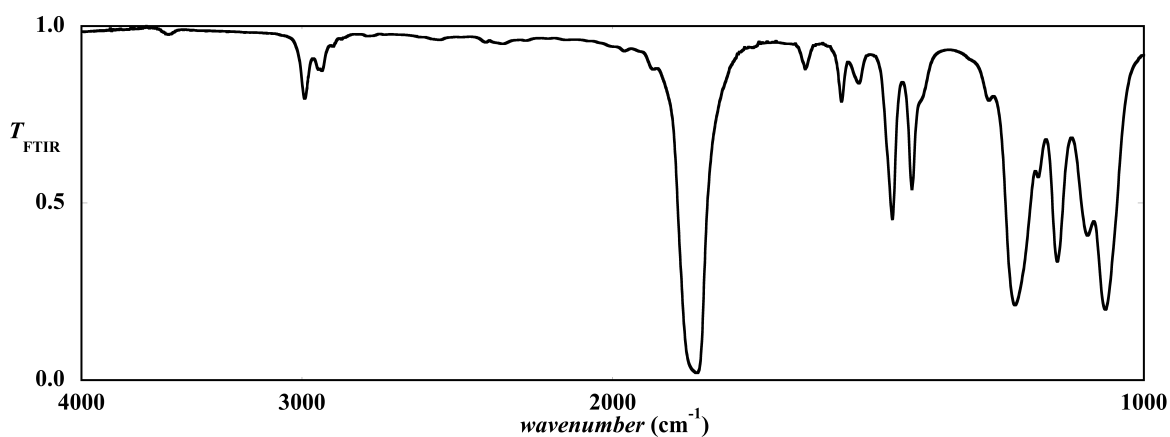


Fig. 7 FTIR spectrum of liquid PC at room temperature

The spectra were recorded also on $2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ salt solutions in PC. In the case of KCl the spectrum was collected on the saturated solution. In particular Fig. 8 shows the spectra for the wavenumber range between 1600 and 1900 cm^{-1} . The addition of the salts determines, globally, a reduction of the peak intensity, respect to the pure solvent, while there is no effect on the peak frequency. The reduction of the intensity follows the trend: $\text{KCNO} < \text{KClO}_4 < \text{KI} < \text{KBr} < \text{KSCN} < \text{KCl}$.

Since the FTIR experiment was conducted using NaCl windows, we considered the potential effect due to the dissolution of sodium chloride in the PC salt solutions. The reported solubility of NaCl in PC at 25 °C is roughly $1.7 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ [23], about one order of magnitude lower than the concentration of the electrolytes solutions in PC that we investigated in the present study by FTIR. For this reason we assume that the effect due to sodium chloride is negligible and in any case it should affect all spectra in the same way.

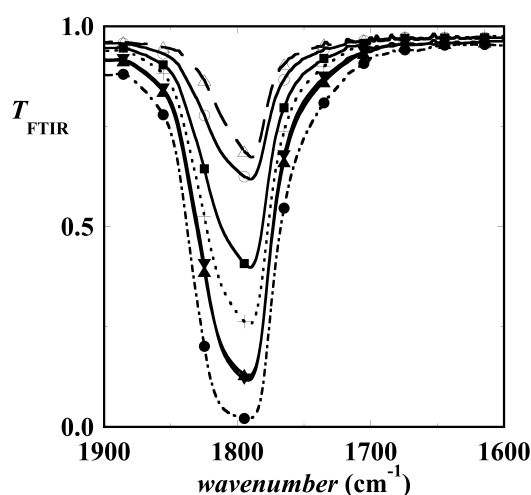


Fig. 8 FTIR spectra of salt solutions in PC between 1600 and 1900 cm^{-1} . Pure PC (●), KCl (△), KI (+), KCNO (▼), KClO_4 (▲), KBr (■), and KSCN (○)

These results suggest that smaller anions, like chloride, establish a stronger interaction with the positive side of the dipole, reducing the dipole moments changes required for the IR absorption to occur. On the other hand, large anions like CNO^- or ClO_4^- cannot approach the

positive side of the carbonyl group. KSCN shows a significant effect on the peak intensity. Presumably this effect is related to the nucleophilic activity that we discussed in our previous contribution [8].

4 Conclusions

Propylene carbonate (PC) is a polar organic solvent with a high dielectric constant and a large dipole moment, but does not possess hydrogen bonding.

We measured the solubility of some potassium salts in PC as a function of temperature and the conductivity of their solutions in PC at 25 °C. The solubility data were compared to those previously obtained in ethylene carbonate (EC). Although EC possesses about the same dipole moment and a larger donor number than PC, it has a stronger molecular structuredness. In fact, EC associates in dimers, while the presence of a methyl group in PC hinders the formation of stable dimers and significantly reduces the intermolecular interactions.

The solubility of salts in PC is lower than in EC, increases with the temperature and with the size of the anions according to the sequence: $F^- < Cl^- < CNO^- < Br^- < ClO_4^- < I^- < SCN^-$.

From the experimental data the values of the main thermodynamic functions of solution and solvation were determined. As in EC, the enthalpy change of solution (ΔH_{sol}^0) is positive for all salts in PC except for KI.

The presence of the methyl group in PC has a twofold effect: 1) it reduces the solvent structuredness, preventing the formation of dimers, and results in a negative ΔS_{sol}^0 , 2) it keeps the anion more distant from the PC ring, and lowers the anion-solvent interactions.

Comparing a structured solvent like EC with water we previously argued that the thermodynamic behaviour of salt solutions mainly depends on the solvent-solute interactions rather than on hydrogen bonding. On the other hand the data obtained with PC suggest that

the solvent structure plays a great role in the dissolution process, acting on the entropy change of solution.

The FTIR spectra confirm that small anions with low polarizability interact strongly with the PC molecule.

This fact is supported also by the conductivity measurements. The lower mobility of small anions reflects their greater solvation. Moreover these data highlight that in PC kosmotropic anions tend to form ion-pairs with K^+ , respect to chaotropic anions.

In conclusion this work shows the relevance of dielectric and donicity properties, and - more importantly - of the solvent structuredness on the solubility of salts in organic solvents.

Acknowledgements

The authors are grateful to the Prof. Enzo Ferroni Foundation (Firenze, Italy) and to CSGI (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Firenze, Italy) for partial financial support.

References

1. Ninham, B.W., Lo Nostro, P.: Molecular forces and self assembly. In colloid, nano sciences and biology. Cambridge University Press, Cambridge (2010)
2. Lo Nostro, P., Ninham, B.W.: Hofmeister phenomena: an update on ion specificity in biology. *Chem. Rev.* **112**, 2286-2322 (2012)
3. Labban, A.K.S., Marcus, Y.: The solubility and solvation of salts in mixed nonaqueous solvents. 2. Potassium halides in mixed protic solvents. *J. Solution Chem.* **26**, 1–12 (1997)
4. Yang, Z.: Hofmeister effects: an explanation for the impact of ionic liquids on biocatalysis. *J. Biotechnol.* 2009, **144**, 12–22 (2009)

5. Ishimatsu, R., Nishi, N., Kakiuchi, T.: Interfacial ion pairing at the interface between water and a room-temperature ionic liquid, N-tetradecylisoquinolinium bis(pentafluoroethylsulfonyl)imide. *Langmuir* **23**, 7608–7611 (2007)
6. Liu, G., Hou, Y., Zhang, G., Craig, V.S.J.: Inhibition of bubble coalescence by electrolytes in binary mixtures of dimethyl sulfoxide and propylene carbonate. *Langmuir* **25**, 10495–10500 (2009)
7. Bilanicova, D., Salis, A., Ninham, B.W., Monduzzi, M.: Specific anion effects on enzymatic activity in nonaqueous media. *J. Phys. Chem. B* **112**, 12066–12072 (2008)
8. Peruzzi, N., Ninham, B.W., Lo Nostro, P., Baglioni, P.: Hofmeister phenomena in nonaqueous media: the solubility of electrolytes in ethylene carbonate. *J. Phys. Chem. B* **116**, 14398-14405 (2012)
9. Jones, J., Anouti, M., Caillon-Caravanier, M., Willmann, P., Lemordant, D. Thermodynamic of LiF dissolution in alkylcarbonates and some of their mixtures with water. *Fluid Phase Equilib.* **285**, 62–68 (2009)
10. Jorné, J., Tobias, C.W.: Electrodeposition of the alkali metals from propylene carbonate. *J. Appl. Chem.* **5**, 279-290 (1975)
11. Grassi, S., Carretti, E., Pecorelli, P., Iacopini, F., Baglioni, P., Dei, L.: The conservation of the vecchietta's wall paintings in the old sacristy of Santa Maria della Scala in Siena: the use of nanotechnological cleaning agents. *J. Cult. Herit.* **8**, 119-125 (2007)
12. Palazzo, G., Fiorentino, D., Colafemmina, G., Ceglie, A., Carretti, E., Dei L., Baglioni, P.: Nanostructured fluids based on propylene carbonate/water mixture. *Langmuir* **21**, 6717-6725 (2005)
13. Chernyak, Y.: Dielectric constant, dipole moment, and solubility parameters of some cyclic acid esters. *J. Chem. Eng. Data* **51**, 416–418 (2006)

14. Wakihara, M., Yamamoto, O.: Lithium ion batteries fundamental and performance. Kadansha Ltd., Tokyo (1998)
15. Aurbach, D., Gofer, Y., Ben-Zion, M., Aped, C.: The behaviour of lithium electrodes in propylene and ethylene carbonate: the major factors that influence Li cycling efficiency. *J. Electroanal. Chem.* **339**, 451-471 (1992)
16. Xu, K.: Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem. Rev.* **104**, 4303-4417 (2004)
17. Perrin, D.D., Armarego, W.L.F.: Purification of laboratory chemicals. Pergamon Press, Oxford (1992)
18. Parsons, R.: Handbook of electrochemical constants. Butterworths Scientific Publications, London (1959)
19. Borges Silva, L., Gomide Freitas, L.C.: Structural and thermodynamic properties of liquid ethylene carbonate and propylene carbonate by Monte Carlo simulations. *J. Mol. Struct. THEOCHEM* **806**, 23–34 (2007)
20. Simeral, L., Amey, R.L.: Dielectric properties of liquid propylene carbonate. *J. Phys. Chem.* **74**, 1443-1446 (1970)
21. Marcus, Y.: The structuredness of solvents. *J. Solution Chem* **21**, 1217-1230 (1992)
22. Marcus, Y.: The effectivity of solvents as electron pair donors. *J. Solution Chem.* **13**, 599-624 (1984)
23. Muhuri K.P., Ghosh S.K., Hazra K.D.: Solubilities of some alkali-metal salts, tetraphenylarsonium chloride, and tetraphenylphosphonium bromide in propylene carbonate at 25 °C using the ion-selective electrode technique. *J. Chem. Eng Data* **38**, 242-244 (1993)
24. Wu Y.-C., Friedman H.L.: Heats of solution of some trifluoroacetates, tetraphenylborates, iodides, and perchlorates in water and in propylene carbonate and

- the relative enthalpies of solvation of the alkali metal ions in propylene carbonate. *J. Phys. Chem.* **70**, 501-509 (1966)
25. Strong, J., Tuttle, T.R.: Solubilities of alkali metal chlorides in some amine and ether solvents. *J. Phys. Chem.* **77**, 533–539 (1972)
 26. Criss, C.M., Luksha, E.: Thermodynamic properties of nonaqueous solutions. IV. Free energies and entropies of solvation of some alkali metal halides in N,N-dimethylformamide. *J. Phys. Chem.* **72**, 2966–2970 (1968)
 27. Hernández-Luis, F., Vazquez, M.V., Estes, M.A.: Activity coefficients of NaF in aqueous mixtures with ϵ -increasing co-solvent: ethylene carbonate–water mixtures at 298.15K. *Fluid Phase Equilib.* **218**, 295-304 (2004)
 28. CRC Handbook of chemistry and physics. Lide, D.R. (ed.) CRC, Taylor and Francis, Boca Raton (1981-1982)
 29. Barthel, J., Neueder, R., Roch, H.: Density, relative permittivity, and viscosity of propylene carbonate + dimethoxyethane mixtures from 25 °C to 125 °C. *J. Chem. Eng. Data* **45**, 1007-1011 (2000)
 30. Payne, R., Theodorou, I.E.: Dielectric properties and relaxation in ethylene carbonate and propylene carbonate. *J. Phys. Chem.* **76**, 2892–2900 (1972)
 31. Duignan, T.T., Parsons, D.F., Ninham, B.W.: A continuum solvent model of the multipolar dispersion solvation energy. *J. Phys. Chem. B* **117**, 9412-9420 (2013)
 32. Parsons, D.F., Deniz, V., Ninham, B.W.: Nonelectrostatic interactions between ions with anisotropic ab initio dynamic polarisabilities. *Colloids Surf. A* **343**, 57-63 (2009)
 33. Naejus, R., Damas, C., Lemordant, D., Coudert, R., Willmann, P.: Excess thermodynamic properties of the ethylene carbonate–trifluoroethyl methyl carbonate and propylene carbonate–trifluoroethyl methyl carbonate systems at T = (298.15 or 315.15) K. *J. Chem. Thermod.* **34**, 795–806 (2002)

34. Irudayam S.J., Richard H.H.: Prediction and interpretation of the hydration entropies of monovalent cations and anions. *Molecular Phys.* **109**, 37-48 (2011)
35. Soetesen, J.-C., Millot, C., Maigret, B.: Molecular dynamics simulation of Li^+BF_4^- in ethylene carbonate, propylene carbonate, and dimethyl carbonate solvents. *J. Phys. Chem. A* **102**, 1055-1061 (1998)
36. Mukherjee, L.M., Boden, D.P.: Equilibria in propylene carbonate. I. Viscosity and conductance studies of some lithium and quaternary ammonium salts. *J. Phys. Chem.* **73**, 3965-3968 (1969)
37. Robinson, R.A., Stokes, R.H.: *Electrolyte solutions*. Butterworths, London (1959)
38. Hammadi, A., Champeney, D.C.: Conductance of solutions of alkali-metal halides in glycerol. *J. Chem. Eng. Data* **45**, 1116-1120 (2000)
39. Jansen, M.L., Yeager, H.L.: Conductance study of 1-1 electrolytes in propylene carbonate. *J. Phys. Chem.* **77**, 3089-3092 (1973)
40. Mukherjee, L.M., Boden, D.P., Lindauer, R.: Behavior of electrolytes in propylene carbonate. II. Further studies of conductance and viscosity properties. Evaluation of ion conductances. *J. Phys. Chem.* **74**, 1942-1946 (1970)
41. Battisti, D., Nazri, A., Klassen, B., Aroca, R.: Vibrational studies of lithium perchlorate in propylene carbonate solutions. *J. Phys. Chem.* **97**, 5826-5830 (1993)