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Solubilities of Some Alkali-Metal Salts, Tetraphenylarsonium Chloride, and Tetraphenylphosphonium Bromide in Propylene Carbonate at 25 °C Using the Ion-Selective Electrode Technique

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The solubilities of 15 alkali-metal salts, MX (M^+ = Li, Na, K, Rb, and Cs; X^- = Cl, Br, and ClO_4), tetraphenylarsonium chloride, and tetraphenylphosphonium bromide are reported in propylene carbonate (PC) at 25 °C, and the free energies of solution for these electrolytes in this solvent have been determined. Combination of these values with solubility results in water yields the free energies of transfer of the electrolytes from water to propylene carbonate. Transfer activity coefficients for the electrolytes have also been computed from their solubility products in water and in the nonaqueous solvent. The results indicate that the perchlorates are more soluble in propylene carbonate compared to the corresponding chloride or bromide salts.

Introduction

Propylene carbonate (4-methyl-1,3-dioxolan-2-one, PC), a dipolar aprotic solvent with high dielectric constant (64.40 at 25 °C) and dipole moment (4.94 D) has been assumed to be an "ideal structureless dielectric" solvent for studies of electrolytes (*1, 2*). The chemical properties of this solvent have given it an important place in the development of high-energy batteries (*3*), and thus there has been a growing interest to study various electrochemical reactions in this medium (*4, 5*). Solubility offers one of the most obvious ways of studying ionic solvation, but in PC these values in general are not available, except of a very few alkali-metal halides (*2, 6*). It is therefore desirable to obtain the useful solubility data particularly for the salts containing Ph_4As^+ or Ph_4P^+ ions and thus to have an idea of solute–solvent interactions in this nonaqueous medium.

Hence, we have measured the solubilities of a number of 1:1 electrolytes in PC at 25 °C using the ion-selective electrode technique, and from these the solubility products and free energies of solution for the salts have been determined. The free energies of transfer of the electrolytes from water to PC or the corresponding transfer activity coefficients, $_m\gamma$'s, have been evaluated and compared with the previous values obtained mainly from emf measurements (*7*).

Experimental Section

Materials. Propylene carbonate (E. Merck, Germany; >99% pure) was purified as reported earlier (*8*); the viscosity and density were 2.4711 mPa s and 1.1988 g cm^{-3} at 25 °C, respectively. Solutions were always prepared with the freshly distilled solvent.

All salts were of Fluka's either purum or puriss grade.

The alkali-metal chlorides and bromides were dried in vacuo for a long time immediately prior to use and were used without further purification.

Lithium perchlorate was recrystallized three times from distilled water and then heated under vacuum for several days (*2*). Sodium perchlorate was heated under vacuum over silica gel and calcium chloride for 5–7 days. These were tested with silver nitrate solution to detect any chloride before use. Other alkali-metal perchlorates were prepared by mixing equimolar solutions of the corresponding alkali-metal chloride and sodium perchlorate (*9*), washed with a 1:1 methanol–water mixture, recrystallized three times from water, and dried in vacuum over calcium chloride and silica gel for several days.

Tetraphenylarsonium chloride (Fluka) was recrystallized from absolute ethanol solution by dry ether and dried in vacuum (*10*). Tetraphenylphosphonium bromide (Fluka, puriss grade) was dissolved in absolute ethanol, reprecipitated by the addition of dry ether, and vacuum dried at 100 °C (*10*).

Solubility Measurements. Saturated solutions were prepared by shaking the solid with the solvent in a glass-stoppered bottle at 27 °C for 24 h. The bottle was then placed in a thermostatic bath maintained at 25 ± 0.01 °C for 2 days. Finally, the solution was transferred to a Campbell solubility apparatus (*11*) fitted with a sintered disk and fine tube and allowed to equilibrate at 25 °C. At regular intervals, the solution was filtered by inverting the apparatus (while keeping it within the thermostat) and appropriately diluted with the solvent (if necessary), and then the concentration was measured by using an Orion ion analyzer (model EA 920) having an accuracy of ±0.01%. A solution was considered saturated when two successive analyses at 2–3-day intervals indicated no change in concentration. Thus, the concentrations of Cl^-, Br^-, and ClO_4^- ions were determined by using specific Orion ion-selective electrodes. A double junction reference electrode was used with each of the Cl^- and ClO_4^- ion electrodes. However, for measuring ClO_4^- ion concentrations, the outer chamber of the reference electrode was filled with $(NH_4)_2SO_4$ solution as suggested in the brochure. A single junction reference electrode was used in conjunction with the Br^- ion electrode. Each ion-selective electrode was tested for a Nernstian response. In order to check the correctness of the data, a known concentration of the sample solution was measured by using the specific ion-selective electrode and the results were compared. At least two trials were given for all the solutions which were under study.

Results and Discussion

Solubility data for the electrolytes in PC at 25 °C (molar scale) are reported in Table I along with their standard deviations.

The standard free energy of solution for a solute on the molar scale is usually given by the relation

$$\Delta G^\circ_{\text{soln}} = -RT \ln K \qquad (1)$$

where K is the equilibrium constant for the reaction $MX \rightleftarrows M^+ + X^-$. Upon introduction of the Debye–Hückel expression

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Table I. Solubilities *S*, Standard Free Energies of Solution ΔG°_{soln}, and Standard Free Energies of Formation ΔG°_f and Solvation ΔG°_{solv} of the Electrolytes in Propylene Carbonate at 25 °C

salt	S/ (mol L^{-1})	ΔG°_{soln}/ (kJ mol^{-1})	$-\Delta G^\circ_f$/ (kJ mol^{-1})	$-\Delta G^\circ_{solv}$/ (kJ mol^{-1})
LiCl	0.019 ± 0.002	19.12	364.55	824.79
NaCl	0.00017 ± 0.00002	42.97	341.08	726.47
KCl	0.00058 ± 0.00004	36.82	371.50	667.35
RbCl	0.0033 ± 0.0006	28.07	376.94	653.08
CsCl	0.0076 ± 0.0007	23.85	380.33	633.88
Ph_4AsCl	0.50 ± 0.02	1.51		
LiBr	1.10 ± 0.008	−2.97	342.71	802.11
NaBr	0.0036 ± 0.0010	27.66	320.03	706.64
KBr	0.0030 ± 0.0006	28.58	350.62	643.79
RbBr	0.0099 ± 0.0005	22.51	355.64	634.80
CsBr	0.0098 ± 0.0007	22.55	360.70	610.07
Ph_4PBr	0.120 ± 0.003	9.37		
$LiClO_4$	1.40 ± 0.03	−4.35		
$NaClO_4$	2.50 ± 0.08	−7.70	264.60	
$KClO_4$	0.017 ± 0.001	19.71	284.47	
$RbClO_4$	0.025 ± 0.002	17.70	288.53	
$CsClO_4$	0.052 ± 0.003	13.85	292.75	

Table II. Free Energies of Transfer, ΔG°_t, and Transfer Activity Coefficients, log mγ, of the Electrolytes from Water to Propylene Carbonate at 25 °C

salt	$\Delta G^\circ_{soln}(H_2O)$/ (kJ mol^{-1})	ΔG°_t/ (kJ mol^{-1})	log mγ
LiCl	−41.42	60.54	10.61
NaCl	−8.79	51.76	9.07
KCl	−5.02	41.84	7.33
RbCl	−8.37	36.44	6.39
CsCl	−9.20	33.05	5.79
Ph_4AsCl	−0.59	2.09	0.37
LiBr	−56.90	53.93	9.45
NaBr	−17.15	44.81	7.85
KBr	−5.86	34.43	6.04
RbBr	−6.69	29.20	5.12
CsBr	−1.67	24.23	4.25
Ph_4PBr	14.64	−5.27	−0.92
$LiClO_4$	very soluble		
$NaClO_4$	very soluble		
$KClO_4$	11.30	8.41	0.52
$RbClO_4$	14.23	3.47	0.61
$CsClO_4$	13.81	0.04	0.007

for the mean activity coefficient, one obtains (*12*)

$$\Delta G^\circ_{soln} = 2.303RT[-\nu \log m - \log (\nu_+^{\nu_+}\nu_-^{\nu_-} + \nu\delta_\nu d_0^{1/2}m^{1/2})] \quad (2)$$

In eq 2, d_0 is the density of PC, δ_ν is the Debye–Hückel limiting slope, ν is the total number of ions, and the other symbols have their usual significance.

We have applied eq 2 to obtain the standard free energies of solution; further, these were combined with the free energies of formation of the respective crystalline salts (*13*) to obtain the corresponding standard free energies of formation for the alkali-metal salts. Results of these calculations have been listed in Tables I and II.

The transfer activity coefficients were calculated from the solubility products by using the relationship

$$\log m\gamma_i = \log m\gamma_\pm^2 = \log_w K_s - \log_s K_s \quad (3)$$

where, mγ is the transfer activity coefficient (medium effect) and subscripts w and s denote aqueous and nonaqueous solvents, respectively. The values have been given in Table II. The standard free energies of solution in water, $\Delta G^\circ_{soln}(H_2O)$, except for the tetraphenyl salts, have been taken from the literature (*7*, *14*). We have measured the solubilities of Ph_4AsCl and Ph_4PBr in water at 25 °C (0.81 and 0.047 M for Ph_4AsCl and Ph_4PBr, respectively). Abraham et al. (*15*) have reported the free energies of solution for the tetraphenyl salts (3.48 and 4.38 for Ph_4AsCl and Ph_4PBr, respectively) on the basis of the osmotic pressure and activity coefficient data of Kalfoglou and Bowen (*10*), which on comparison with the values reported in Table II would seem to be in error.

Table III. Crystallographic Radii, r_c, Free Energies of Transfer, ΔG°_t, Transfer Activity Coefficients, log mγ_i, and Free Energies of Solvation, ΔG°_{solv}, of Single Ions in Propylene Carbonate at 25 °C

ion	r_c/Å	ΔG°_t/ (kJ mol^{-1})	log mγ_i	$-\Delta G^\circ_{solv}$/ (kJ mol^{-1})
Li^+	0.60	22.47	3.94	471.58
Na^+	0.95	13.68	2.40	379.87
K^+	1.33	3.77	0.66	313.63
Rb^+	1.48	−1.63	−0.29	293.47
Cs^+	1.69	−5.02	−0.88	269.20
Ph_4As^+	6.40	−35.98	−6.31	94.31
Ph_4P^+	6.30	−35.98	−6.31	95.65
Cl^-	1.81	38.07	6.67	243.34
Br^-	1.95	30.71	5.38	231.79
ClO_4^- [a]	2.16	5.06	0.89	216.40

[a] Calculated by using the relation $\Delta G^\circ_t(ClO_4^-) = \Delta G^\circ_t(CsClO_4) - \Delta G^\circ_t(Cs^+)$.

Single ion free energies of transfer from water to PC based on Ph_4AsBPh_4 convention have been reported in Table III. The ΔG°_t values for Ph_4As^+ and Ph_4P^+ ions from water to PC have been taken from the literature (*7*). Ionic transfer free energy values together with ionic transfer activity coefficients have been reported in Table III. Following Latimer, Pitzer, and Slansky (*16*), we have also calculated the single ion free energies of solvation by the modified Born equation:

$$\Delta G^\circ_{solv} = -\frac{Nz^2e^2}{2}[1 - 1/\epsilon]/(r_i + \delta) \quad (4)$$

taking δ_c = 0.85 Å and δ_a = 1.00 Å as taken by Criss et al. in DMF medium (*12*). The values thus obtained have been reported in Table III.

An examination of the solubilities of the alkali-metal salts (Table I) shows that most electrolytes are much less soluble in propylene carbonate than in water (*7*) and also in some other dipolar aprotic solvents like DMSO (*6*) and DMF (*6*, *12*). Lithium salts are found to be more soluble in PC compared to other alkali-metal salts, a notable exception being $NaClO_4$, which is more soluble in PC than $LiClO_4$. Also with the exception of lithium, other alkali-metal halides appear to be sparingly soluble and the solubilities are usually in the order $Cl^- < Br^- < ClO_4^-$ as in water and other dipolar aprotic solvents. The poor solubility of these salts in such a high dielectric medium may be due to the dipolar aprotic nature of this solvent medium. The perchlorates, we see, have a much higher solubility than the halides. This indicates that ClO_4^- ion tends to increase the PC liquid structure more so than does Cl^- or Br^- ion. Further, salts having large polarizable groups, viz., Ph_4AsCl and Ph_4PBr, are found to be reasonably soluble in this medium. However, Ph_4AsCl is found to be much more soluble than Ph_4PBr. This shows that Ph_4As^+ is more polarizable than Ph_4P^+ and is preferentially solvated, most probably through a combination of dispersion and ion–dipole interactions.

From Table II we see that, in general, the standard free energies of transfer, ΔG°_t, of the electrolytes from water to PC are positive and so the transfer process is not favorable. A notable exception is Ph_4PBr. The negative sign reflects the fact that the distribution of its ions favors the nonaqueous phase, compared to the positive medium effects for most electrolytes. Cox and his co-workers (*7*) have presented ΔG°_t values of some common salts from water to PC by taking the basic data from the literature. Our reported ΔG°_t values for the alkali-metal halides are found to be in good agreement with theirs. This avoids the uncertainties in the solubility method due to ion pairing and activity coefficient measurements. Solomon (*17*) has also reported ΔG°_t values of LiCl and LiBr from water to PC as 14.74 and 12.98 kcal/mol^{-1} from a potentiometric study, whereas we have found them to be 14.47 and 12.89 kcal mol^{-1}, respectively, from direct solubility measurements.

Ionic ΔG°_t values have been calculated taking Ph_4AsBPh_4 as the "reference electrolyte" (*7*). An attempt was made to calculate the ΔG°_t value of Ph_4AsBPh_4 from water to PC by measuring the solubilities of Ph_4AsCl, NaCl, and $NaBPh_4$ in PC. But $NaBPh_4$ was found to be highly soluble in PC, and to avoid the experimental error we discarded the idea. From the table we see that among the cations, Li^+, Na^+, and K^+ have a positive value of transfer free energy, whereas Rb^+, Cs^+, Ph_4As^+, and Ph_4P^+ have negative ΔG°_t values. The positive values of ΔG°_t and log $m\gamma_i$ indicate that these ions are more favorably solvated by the reference medium (water) than by the nonaqueous medium (PC) to which it is transferred. For negative values of ΔG°_t, it is just the reverse.

Solvation of small cations is generally determined by the relative basicity of the solvents, i.e., by their donor ability. PC has weakly basic oxygen, and so cations are poorly solvated in this medium, resulting in positive ΔG°_t values (Table III). However, for Rb^+ and Cs^+ ions, the ΔG°_t values are negative in PC. From this evidence we may come to the conclusion that the transfer of Rb^+ and Cs^+ ions from water to PC is more favorable compared to other alkali-metal cations.

Conclusion

The solubilities of alkali-metal salts are comparable, although smaller than the corresponding solubilities in water as well as in other dipolar aprotic solvents. The perchlorates, however, are more soluble than the halides. The higher solubility of $NaClO_4$ compared to $LiClO_4$, somehow, tends to indicate its more compactness with the solvent dipoles than the latter. The single ion free energies of transfer from water to PC correlate well with the free energies of transfer of the ions derived by other methods.

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