

CHAPTER-III

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

Solubility offers one of the most obvious ways of studying ionic solvation and ion-solvent interactions and it finds unique application particularly for those electrolytes which are poorly soluble in a solvent medium so that the other more conventional methods like viscometry and conductometry can hardly be applied, but in PC these values in general are not available, except of very few alkali metal halides^{1,2}. 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 non-aqueous medium.

Here, 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 e.m.f. measurements³.

Experimental

Propylene carbonate (E. Merck, Germany; >99% pure) was purified as reported in Chapters II and VI.

All salts were of Fluka's either purum or puriss grade and were purified as described in Chapter II.

Saturated solutions were prepared by shaking the solid with the solvent in a glass-stoppered bottle at 27°C for 24 hours. The bottle was then placed in a thermostatic bath for further two days maintained at 25 ± 0.01 °C. Finally, the solution was transferred to a Campbell solubility apparatus⁴ fitted with a sintered disc and fine tube and allowed to equilibrate at 25°C. At regular intervals, the solutions were filtered by inverting the apparatus (while keeping it within the thermostat), 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 $\pm 0.1\%$. A solution was considered saturated when two successive analysis at 2-3 days 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 Cl^- and ClO_4^- ion electrode. However, for measuring ClO_4^- ion concentrations, the outer chamber of the reference electrode was filled with $(\text{NH}_4)_2\text{SO}_4$ 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 Nernstian response. In order to check the correctness of the data, 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 1.

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

$$\Delta G_{\text{Solution}}^{\circ} = -RT \ln K \quad (1)$$

where, K is the equilibrium constant for the reaction, $\text{MX} \rightleftharpoons \text{M}^+ + \text{X}^-$. Upon introduction of the Debye-Hückel expression for the mean activity coefficient, one obtains⁵ :

$$\Delta G_{\text{Solution}}^{\circ} = 2.303 RT \left[-\nu \log m - \log \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-} + \nu \delta_{\nu} d_0^{\frac{1}{2}} m^{\frac{1}{2}} \right) \right] \quad (2)$$

In equation (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 equation (2) to obtain the standard free energies of solution; further these were combined with the free energies of formation of the respective crystalline salts⁶ to obtain the corresponding standard free energies of formation for the alkali metal salts. Results of these calculations have been listed in Tables 1 and 2.

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

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

where, $m\gamma_{\pm}$ is the transfer activity coefficient (medium effect) and subscript w and s denote aqueous and non-aqueous solvent respectively. The values have been given in Table 2. The standard free energies of solution in water, $\Delta G_{\text{Soln}}^{\circ}(\text{H}_2\text{O})$, except for the tetraphenyl salts, have been taken from the literature^{3,7}. We have measured the solubilities of Ph_4AsCl and Ph_4PBr in water at 25°C (0.81M and 0.047M for Ph_4AsCl and Ph_4PBr respectively). Abraham *et al*⁸ have reported the free energies of solution for the tetraphenyl salts (3.48 and 4.38 for Ph_4AsCl and Ph_4PBr respectively) based on the osmotic pressure and activity coefficient data of Kalfoglou and Bowen⁹, which on comparison with the values reported in Table 2 would seem to be in error.

Single ion free energies of transfer from water to PC based on $\text{Ph}_4\text{AsBPh}_4$ convention have been reported in Table 3. The ΔG_t° values for Ph_4As^+ and Ph_4P^+ ions from water to PC have been taken from the literature³. Ionic transfer free energy values together with ionic transfer activity coefficients have been reported in Table 3. Following Latimer, Pitzer and Slansky¹⁰, we have also calculated the single ion free energies of solvation by the modified Born equation,

$$\Delta G_{\text{solv}}^\circ = -\frac{Nz^2e^2}{2} \left[1 - \frac{1}{\epsilon} \right] / (r_i + \delta) \quad (4)$$

taking $\delta_c = 0.85\text{\AA}^\circ$ and $\delta_a = 1.00\text{\AA}^\circ$ as taken by Criss et al in DMF medium⁵. The values thus obtained have been reported in Table 3.

An examination of the solubilities of the alkali metal salts (Table 1) show that most electrolytes are much less soluble in propylene carbonate than in water³ and also in some other dipolar aprotic solvents like DMSO² and DMF^{2,5}. Lithium salts are found to be more soluble in PC compared to other alkali metal salts, 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: $\text{Cl}^- < \text{Br}^- < \text{ClO}_4^-$ as in water and other dipolar aprotic solvents. The poor solubility of these salts in such a high dielectric media may be due to the dipolar aprotic nature of this solvent medium. The perchlorates, we see, have a much higher

solubility than the halide ones. 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 or highly 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 2 we see that in general, the standard free energies of transfer, ΔG_t^0 , of the electrolytes from water to PC are positive and so the transfer process is not favourable. Notable exception is Ph_4PBr . The negative sign reflects the fact that the distribution of its ions favours the non-aqueous phase, compared to the positive medium effects for most electrolytes. Cox and his coworkers³ have presented ΔG_t^0 values of some common salts from water to PC by taking the basic data from the literature. Our reported ΔG_t^0 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. Salomon¹¹ has also reported ΔG_t^0 values of LiCl and LiBr from water to PC as 14.74 and 12.98 K Cal mol⁻¹ from potentiometric study, whereas we have found it to be 14.47 and 12.89 K Cal mol⁻¹ respectively from direct solubility measurements.

Ionic transfer free energies and ionic transfer activity coefficients are very important parameters in non-aqueous solution

Chemistry. These two terms actually determine how the equilibrium constant and rate properties change with the nature of solvents. Ionic free energies of transfer from water to PC at 25°C have been reported in Table 3. ΔG_t° values of the ions have been calculated taking $\text{Ph}_4\text{AsBPh}_4$ as the 'reference electrolyte'³. An attempt was made to calculate ΔG_t° value of $\text{Ph}_4\text{AsBPh}_4$ 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^+ ions have a positive value of transfer free energy, whereas Rb^+ , Cs^+ , Ph_4As^+ and Ph_4P^+ have got negative ΔG_t° values. The positive values of ΔG_t° and $\log m \gamma_1$ indicate that these ions are more favourably solvated by the reference medium (water) than by the non-aqueous medium (PC) to which it is transferred. For negative values of ΔG_t° , it is just the reverse. The ΔG_t° values of alkali metal ions decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. As the size of the anion increases, its free energies of transfer from water to PC decreases ($\text{ClO}_4^- < \text{Br}^- < \text{Cl}^-$). On transferring Cl^- or Br^- ion from water to PC, there is a large increase in free energy and this increase in free energy is the cause behind the increased reactivity of these ions in this solvent medium. For example, the transfer activity coefficient of Cl^- ion in PC is 6.7 (Table 3), which means that a solution of Cl^- ion in PC has an activity of $10^{6.7}$ times greater than a solution of the same Cl^- ion concentration in water. And this causes major changes in the rate and equilibrium constants

of chemical reactions (involving Cl^- ion) in PC, compared to that in aqueous medium. Solvation of small cations is generally determined by the relative basicity of the solvents i.e. by their donor ability. Dipolar aprotic solvents containing oxygen atoms with localized negative charge e.g. DMSO, solvate cations better than water as evidenced from the negative values of free energies of transfer from water to DMSO³. DMSO is regarded to be more basic than PC^{12,13}. PC has got weakly basic oxygen and so cations are poorly solvated in this medium than DMSO resulting in positive ΔG_t° values (Table 3). 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 favourable compared to other alkali metal cations.

Table 1. Solubilities (S , mol lit $^{-1}$), Standard Free Energies of Solution ($\Delta G_{\text{soln}}^{\circ}$, kJ mol $^{-1}$) and Standard Free Energies of Formation ($\Delta G_{\text{F}}^{\circ}$, kJ mol $^{-1}$) and Solvation ($\Delta G_{\text{solv.}}^{\circ}$, kJ mol $^{-1}$) of the Electrolytes in PC at 25°C

Salt	S	$\Delta G_{\text{soln.}}^{\circ}$	$-\Delta G_{\text{F}}^{\circ}$	$-\Delta G_{\text{solv.}}^{\circ}$
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 ₄ AsCl	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 ₄ PBr	0.120 + 0.003	9.97	-----	-----
LiClO ₄	1.40 + 0.03	-4.35	-----	-----
NaClO ₄	2.50 + 0.08	-7.70	264.60	-----
KClO 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 2. Free Energies of Transfer (ΔG_t°) and Transfer Activity Coefficients ($\log m\gamma$) of the Electrolytes from Water to PC at 25°C

salt	$\Delta G_{\text{soln.}}^\circ$ (H ₂ O) kJ mol ⁻¹	ΔG_t° kJ mol ⁻¹	$\log m\gamma$
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 ₄ AsCl	-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 ₄ PBr	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

Table 3. Crystallographic Radius (r_c , Å^o), Free Energies of Transfer (ΔG_t^o , kJ mol⁻¹); Transfer Activity Coefficients ($\log m \gamma_i$) and Free Energies of Solvation ($\Delta G_{\text{solv.}}^o$, kJ mol⁻¹) of Single Ions in PC at 25°C

Ion	r_c	ΔG_t^o	$\log m \gamma_i$	$-\Delta G_{\text{solv.}}^o$
Li ⁺	0.60 ^b	22.47	3.94	471.58
Na ⁺	0.95 ^b	13.68	2.40	379.87
K ⁺	1.33 ^b	3.77	0.66	313.63
Rb ⁺	1.48 ^b	-1.63	-0.29	293.47
Cs ⁺	1.69 ^b	-5.02	-0.88	269.20
Ph ₄ As ⁺	6.40 ^c	-35.98	-6.31	94.31
Ph ₄ P ⁺	6.30 ^c	-35.98	-6.31	95.65
Cl ⁻	1.81 ^b	38.07	6.67	243.34
Br ⁻	1.95 ^b	30.71	5.38	231.79
ClO ₄ ^{-a}	2.16 ^b	5.06	0.89	216.40

^aCalculated by using the relation, $\Delta G_t^o(\text{ClO}_4^-) = \Delta G_t^o(\text{CsClO}_4) - \Delta G_t^o(\text{Cs}^+)$

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^cC.V. Krishnan and H.L. Friedman, J. Phys. Chem., 73, 3934, 1969.

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