Standard Electrode Potential of Alkali Metal Electrodes from Transfer Free Energies of Ions - in PC and PC + DMF.

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The transfer free energies (ΔG°_{t}) of Li^{+}, Na^{+} and K^{+} ions from PC to PC + DMF mixtures have been determined from precise solubility data of alkali metal picrates (obtained by spectrophotometric method) and activity (evaluated using Pitzer equation). The sign and magnitude of ΔG°_{t} in different mixed solvents indicate that the alkali metal ions are more stabilized in the mixed solvents. The results are explained in terms of cation stabilizing effect on the co-solvent. Standard electrode potential, E°, of M/M^{+} (M = Li, Na or K) have been evaluated. The higher E° values observed in mixed media indicate possible application of mixed media as non-aqueous battery solvents.

We have recently described [1] a simple colorimetric method of obtaining standard electrode potential E° of M/M^{+} (M = Li, Na, K) electrode in propylene carbonate and its mixture with dimethyl sulphoxide (DMSO). The method has been extended in this paper to the estimation of E° values of these active alkali metals in PC + DMF mixture. A knowledge of E° of these active metals in mixed solvents will help development of non-aqueous batteries in these media.

EXPERIMENTAL

Propylene carbonate (PC), dimethyl formamide (DMF) of analytical reagent grade were dried and distilled under reduced pressure as described previously [2,3]. The specific conductance of the purified DMF was 3-6 x 10^{-8} S cm^{-1}.

Lithium picrate, sodium picrate and potassium picrate were prepared and purified as before [1]. The purity of the salts have been examined by IR spectra using KBr windows.

The determination of saturated solubilities of alkali metal picrates in PC and in the PC + DMF mixtures were performed as described previously using spectrophotometer [1].

RESULTS

Transfer Free Energy of Salts

ΔG°_{t} (Mpic) values are determined from precise solubility measurement of Mpic and activity co-efficient . Saturated solubilities of the salts - Lipic, Napic and Kpic - in different PC + DMF mixtues at 27°C are shown in Table 1. The activity co-efficients ($\gamma_{\pm}$) were evaluated using Pitzer's equation with appropriate Pitzer

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Table 1

Solubilities on molar scale (S), mean molal activity coefficient ($\gamma_\pm$), standard free energy of solvation (ΔG°_s), standard free energy of transfer (ΔG°_t) of alkali metal picrate from PC to PC + DMF mixtures at 27°C.

Mixed solvent	S mol dm^{-3}	$\gamma_\pm$	ΔG°_s kJ. mol^{-1}	ΔG°_t kJ. mol^{-1}
Lipic				
0 % DMF	0.089	0.729	14.63	
20 % DMF	0.649	0.548	6.43	-8.20
40 % DMF	1.380	0.459	3.97	-10.66
Napic				
0 % DMF	0.666	0.589	6.41	
20 % DMF	1.300	0.461	4.45	-1.96
40 % DMF	2.400	0.366	3.26	-3.15
Kpic				
0 % DMF	0.041	0.773	18.20	
20 % DMF	0.125	0.622	13.53	-4.67
40 % DMF	0.361	0.450	9.89	-8.31

parameters for these salts. The $\gamma_\pm$ values are also shown in Table 1. Free energies of solvation (ΔG°_s) of these salts in these solvents are obtained [4] using

$$\Delta G^\circ_s = 2RT \ln (m \gamma_\pm)_{Sat} \quad \ldots\ldots (1)$$

Transfer free energies ΔG°_t were calculated by the difference between the ΔG°_s values in required and reference solvents.

Transfer Free Energy of Ions

The transfer free energies of alkali metal ions from PC to PC + DMF mixtures were calculated by using extrapolation method [5]. $\Delta G^\circ_t(Pic^-)$ values are the intercepts of the plots of $\Delta G^\circ_t(Mpic)$ *vs* $1/r_{M^+}$ (r_{M^+} = radius of metal ions). Here, the extra thermodynamic assumption is that solvation free energies of a hypothetical large ion is assumed as zero. $\Delta G^\circ_t(M^+)$ values are obtained by subtrating $G^\circ_t(Pic^-)$ from $\Delta G^\circ_t(MPic)$. These values are shown in Table 2. Finally E° of M/M^+ are determined using the relationship

$$\Delta G^\circ_t(M^+) = - zF (E^\circ_s - E^\circ_r) \quad \ldots\ldots (2)$$

where z is the number of electrons transfered and F is 96,500 coulombs; s refers to desired solvent and r refers to reference solvent. E° values obtained through equation 2 are also shown in Table 2.

DISCUSSION

Solubility, mean ionic activity coeffcient ($\gamma_\pm$) and transfer free energies of the alkali metal pictrates in PC + DMF mixtures are shown in Table 1. It is to be noted that while the solubilities of these pictrate salts increased significantly in the

Table 2

Free energies of transfer of ions $\Delta G^{\circ}_{t}(M^{+})$ and Standard Electrode potential E° of M/M^{+} systems (in Volts) in PC, PC + DMF mixtures with reference to the NHE at 27°C.

Solvent	$\Delta G^{\circ}_{t}(M^{+})$ kJ. mol^{-1}			E° vs NHE (V)		
	Li^{+}	Na^{+}	K^{+}	Li/Li^{+}	Na/Na^{+}	K/K^{+}
Water				2.959[c]	2.714[c]	2.929[c]
PC[Ref14]	23.7	14.3	4.6	2.719	2.564	2.874
[Ref 5]	13.4	2.4	8.2	2.820	2.689	3.009
20 % DMF	-22.30	-16.06	-18.77	2.950	2.730	3.063
40 % DMF	-27.46	-19.95	-25.11	3.003	2.770	3.134

c = standard literature data.

mixed solvents, the activity co-efficients decreased as expected from the increased salt concentration and decreased dielectric constant of the mixed medium. This is similar to the behaviour in PC + DMSO [1]. $\Delta G^{\circ}_{t}(M^{+})$ values as obtained by solubility method clearly indicate that these ions are stabilized in the mixed solvents in spite of low dielectric constant of these media. This may be due to the chemical stabilization of the alkali metal ions in the mixed solvents arising out of strong acid base type interaction with the co-solvent molecules (DMSO or DMF) having high donar number (DN PC = 63.2, DN DMSO = 124.7, DN DMF = 111.3) [6-9].

The magnitudes of free energy component due to chemical stabilization, $\Delta G^{\circ}_{t}(M^{+}_{Chem.})$, may be tentatively calculated [8] from $\Delta G^{\circ}_{t}(M^{+})$ values after substracting $\Delta G^{\circ}_{t}(M^{+}_{elect})$ obtained applying Born equation.

Among the ions, the observed order of stabilization is $Li^{+} \sim K^{+} > Na^{+}$. This trend has also been found in large number of non-aqueous solvents [7] and explained in general by the combined effect of ion dipole and soft interactions [10]. Study of the co-ordination chemistry of alkali and alkaline earth cation [11] reveals that low charge density of K, Rb, Cs ions as well as the high charge density of Li and Mg ions show facilitated interaction with electrically neutral ligands while the medium charge density of Na, Sr, Ca make these ions more anion-philic towards anionic species [12,13].

The standard potential of M/M^{+} systems in PC + DMF and PC + DMSO media are highly interesting; E° value increases as DMF or DMSO is added to PC. The trends of E° as obtained through spectrophotometric technique ($E^{\circ}_{Li/Li+} - E^{\circ}_{K/K+} > E^{\circ}_{Na/Na+}$) are similar to those obtained by electrochemical tools [7].

The observed higher E° values of alkali metals in mixed PC + DMSO indicate fair possibility of using the mixed solvents in nonaqueous battery.

REFERENCES

1. S. Ray and I. Basumallick, *J. Electrochem. Soc.* **137** (1990) 3876.
2. B.G. Cox, A.J. Parker, *J. Phys. Chem.*, **78** (1974) 1731.
3. David W. James and Reyond E. Mayes, *J. Phys. Chem.*, **88** (1984) 637.
4. R. Alexander, A.J. Parker, J.H. Shassp and W.E. Waghorne, *J.Am. Chem. Soc.*, **94** (1972) 1148.
5. J. Jorne and C.W. Tobas, *J. Phys. Chem.*, **78** (1974) 2576.
6. B.G. Cox, W.E. Waghorne and C.K. Pigott, *J. Chem. Soc. Faraday I*, **75** (1979) 227.
7. H. Strehlow in *The Chemistry of Non-aqueous Solvents*. Vol. I, ed. J.J. Lagowski, **Academic Press, New York**, (1966).
8. I. Basumallick and K.K. Kundu, *Can. J. Chem.*, **58** (1980) 78.
9. Y. Marcus, M.J. Kamlet, R.W. Taft, *J. Phys. Chem.*, **92** (1988) 3613.
10. N. Nandi and I. Basumallick, *J. Phys. Chem.*, **94** (1990) 2537.
11. N.S. Poonia, A.V. Bajoj, *Chem.Rev.*, **79** (1979) 389.
12. S. Lindenbum, J.H. Ryfting and Sterrson, in *Progress in Macrocyclic Chemistry, Vol. I*, (Ed.) N.S. Poonia, **Wiley Inter Science, New York**, (1979) Chapter 3.
13. N.S. Poonia, *J. Am. Chem. Soc.*, **96** (1974) 1012.
14. S. Glikberg and Y. Marcus, *J. Sol. Chem.* **12** (1983) 255.