Electrochemistry

Medium Effects in Water–Ethylene Carbonate Mixtures

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Electromotive force measurements of the cell of the type:

$$\mathrm{Pt, H_2(1\ atm)/HCl}\ (m), \mathrm{EC}(x), \mathrm{H_2O}\ (100-x)/$$
$$/\mathrm{AgCl, Ag}$$

in the temperature range 25 °C to 45 °C at 5 °C intervals have been used to derive the change in the standard free energy (ΔG_t°), enthalpy (ΔH_t°), and entropy (ΔS_t°) of transfer of HCl from water to water–EC mixtures. Figure 1 shows that at 25 °C, ΔG_t° changes its sign from negative values at concentration of the organic solvent less than 40 wt.%, to positive values at higher percentages of EC. This behaviour is explained on the basis of the change in the internal structure of the mixed solvent.

The electrostatic contribution of the Gibbs free energy of transfer is evaluated according to Born's model. The results show that the electrostatic part of the free energy change plays an important role in the total value of ΔG_t° at concentration of EC < 27 wt.%. At higher percentages, the nonelectrostatic free energy change start to have an appreciable effect on ΔG_t°.

Values of the standard entropy and enthalpy of transfer are found to be always negative and decrease with increasing EC content. This clarifies that the net effect is to increase the entropy loss, and suggests that, in the transfer process, the net amount of order created by HCl as a solute is more marked in the mixed solvent than in pure water. The entropy change of mixed hydration and solvation $\Delta S^\circ_{h,s,H^+}$, is evaluated in each mixed solvent. It can be divided into a hydration component $\Delta S^\circ_{h,H^+}$, and a solvation component $\Delta S^\circ_{s,H^+}$, according to the relation:

$$\Delta S^\circ_{h,s,H^+} = x_2 \Delta S^\circ_{h,H^+} + x_1 \Delta S^\circ_{s,H^+}$$

where, x_2 and x_1 are the mole fractions of water and EC respectively.

TABLE I. Hydration and Solvation Numbers in H_2O–Ethylene Carbonate Solvent Mixtures.

EC wt%	$\Delta S^\circ_{h,s,H^+}$	$\Delta S^\circ_{h,H^+}$	n_h	$\Delta S^\circ_{s,H^+}$	n_s
0.00	−32.03	−32.03	5.4	–	–
9.50	−32.49	−31.46	5.2	−1.90	0.3
20.16	−35.49	−30.46	5.1	−4.41	0.7
28.98	−34.92	−29.56	4.9	−6.93	1.2
39.96	−38.49	−28.19	4.7	−10.80	1.8
49.75	−40.46	−26.62	4.4	−15.21	2.5
61.35	−43.34	−24.15	4.0	−22.14	3.7
78.12	−56.85	−18.42	3.1	−38.24	6.4
100.00	–	–	–	−89.98	(15.0)

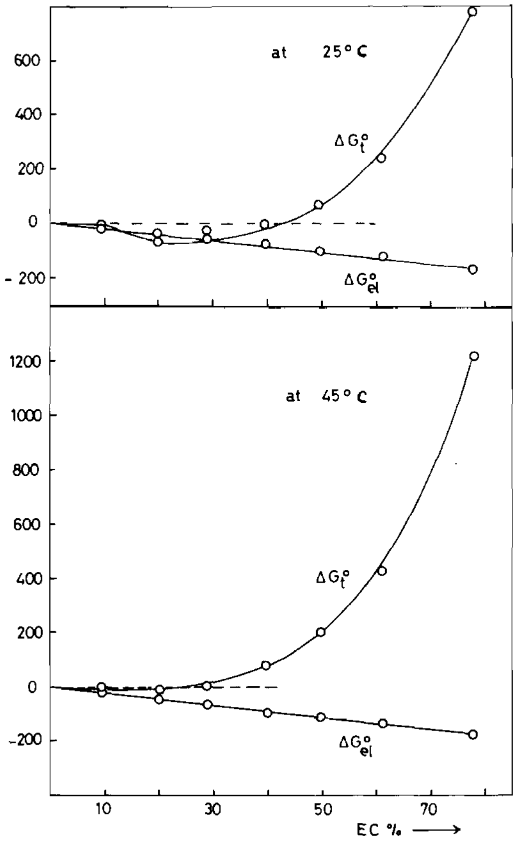

Fig. 1. Variation of ΔG_t° and ΔG_{el}° with the wt.% of ethylene carbonate.

Table I illustrates the calculated values of the hydration and solvation numbers in each of water–

EC solvent mixture The high value of the solvation number in 100 wt % EC may be due to the primary solvation layer together with some contribution from the secndary solvation layer

An Estimation of the Volume of Restructured Water Shells around Hydrophobic Solutes

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Water is known to be a largely associated liquid The presence of non-electrolytes or large organic ions, tends to strengthen the hydrogen bonds between the water molecules near the large hydrophobic solute, and a cage or 'iceberg' is effectively formed around them This model of the hydrophobic hydration of alkyl groups is widely accepted but the thickness of restructured water shells around hydrophobic solutes has not been determined In order to estimate the volume of restructured water per mole hydrophobic solute we used the differential conductometry of carefully thermostatted (0 001 °C) solutions [1, 2] The experimental procedure consists of measuring the specific electrical conductance (χ) of a strong electrolyte solution before and after adding a small amount of hydrophobic solute Provided the equivalent conductance of the strong electrolyte ions in the restructured water shell is zero [3] the volume of the restructured water shell is given by [2, 3]

$$V_{s,o} = \frac{\Delta\chi \cdot 10^3}{\chi \cdot c} \ [\mathrm{cm^3/mol}]$$

where $\Delta\chi$ is the change in χ, corrected for the increase in volume and c is the molar concentration of the strong electrolyte

We have attempted to measure the $V_{s,o}$-values in aqueous solutions of perchloric acid for 16 alkylammonium ions The results obtained can be summarized as follows

$$V_{s,o} = n(CH_3)\cdot V(CH_3) + n(CH_2)\cdot V(CH_2) + n(NH_3^+)\cdot V(NH_3^+)$$

where n(i) is the number of groups i in the ion studied and V(i) is the specific volume of hydration shell of i-group In 10–20% $HClO_4$(w/w), $V(CH_3) \approx V(CH_2) \approx 40 \pm 10$ [cm³/n(i) mol] and $V(NH_3^+) \approx -48 \pm 10$ [cm³/n(i) mol] The negative value for $V(NH_3^+)$ reflects the negative hydration of $-NH_3^+$-group

References

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Structure of Aliphatic Alcohols in Electrical Double Layer on Electrode Surface

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The structure of solvent in the field of the electrical double layer exerts significant influence on the inner layer properties on adsorption of ions and molecules Some theoretical models considering differently the interaction of solvent dipoles in the inner layer have recently been elaborated [1–3] On the basis of the experimental data obtained by us on bismuth electrode in alcoholic solutions, mainly in ethanol, the analysis of the validity of the cluster models [1–3] for the description of the solvent structure in the inner layer has been carried out in this paper Cluster model was chosen since alcohols belong to the group of associated liquids According to cluster model solvent exists on the electrode surface in the form of separate chemisorbed molecules with constant orientation and of associates of molecules (clusters) the orientation of which depends upon electrode charge q and the composition of which varies with temperature T

By use of the equations of the cluster model [1–3] the electrode charge has been calculated for several temperatures in the interval from −15 to 50 °C The results of the theoretical calculations were compared with the experimental data in the form of the plots of the inner layer integral capacity K_{02} against q at several T Experimental values of K_{02} were found from the differential capacity of bismuth in alcoholic solutions of $LiClO_4$ at various temperatures

On the basis of the calculations it was established, that at T < 25 °C the ethanol molecules exist in the inner layer mainly in the form of two-dimensional double associates due to the hydrogen bonding