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STUDIES ON THE DISSOCIATION CONSTANTS OF 1,10-PHENANTHROLINE IN ETHANEDIOL + WATER MIXTURES AT 25°C

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ABSTRACT

The thermodynamic dissociation constants for the isoelectric reaction $LH^+ \rightleftharpoons L + H^+$ (where L = 1,10-phenanthroline) were determined pH-metrically and spectrophotometrically in ethanediol + water mixtures (0–100%). The changes in the pK values are interpreted in terms of solvent basicity and ion–solvent interactions. The free energies of transfer of the H^+ ion from water to ethanediol + water mixtures were also calculated. The results suggest that the ethanediol + water mixtures are more basic than water. The basicity increases and passes through a maximum at about 60 wt.% of ethanediol. However, the ethanediol and ethanediol-rich mixtures are less basic than water. The changes in basicity are probably related to changes in the structure of the solvent mixtures.

INTRODUCTION

In our previous reports [1–3], we have described the effect of mono-ols on the dissociation constants of 1,10-phenanthroline and 2,2′-bipyridine. The dissociation constant values were used to determine the free energy of transfer of the H^+ ion from water to mono-ol + water mixtures. As a continuation of this work the dissociation constants of 1,10-phenanthroline in water + ethanediol (or ethylene glycol (abbreviated as EG)) mixtures (0–100%) were determined pH-metrically and spectrophotometrically. The

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basicities of ethanediol + water mixtures were calculated from the free energy of transfer of the H^+ ion from water to aquo–ethanediol mixtures. The results are presented in this paper.

EXPERIMENTAL

Ethanediol (E.G., L.R., BDH) was purified using the method of Bose and Kundu [4]. The distilled solvent was used within 24 h. Triply distilled water was used for the preparation of solvent mixtures. Other experimental details are similar to those described previously [1–3].

The solvent mixtures were prepared by weight and the density values were determined using a calibrated pycnometer.

The optical density readings were recorded using a Varian Techtron (Series 634) spectrophotometer maintained at 298 K. The pH-meter readings were taken using a Systronics digital pH-meter-335 with an accuracy of ±0.01 pH unit.

RESULTS

The thermodynamic dissociation constant for the reaction

$$LH^+ \rightleftharpoons L + H^+ \qquad (1)$$

where L = 1,10-phenanthroline, is written as

$$K_T = \frac{a_L \times a_{H^+}}{a_{LH^+}} = \frac{c_L \times c_{H^+}}{c_{LH^+}} \times \frac{f_L \times f_{H^+}}{f_{LH^+}} \qquad (2)$$

The terms have their usual meanings. The ionic strength of the solution ranges between 3×10^{-4} and 7×10^{-4} M in the pH-metric method and is even less in the spectrophotometric method. In view of the low ionic strengths, $f_L \times f_{H^+}/f_{LH^+}$ can reasonably be expected to be unity.

The values of the ion-size parameters are uncertain, but those of LH^+ and H^+ are definitely different. Moreover, the solvation characteristics of H^+ and LH^+ are expected to be different, resulting in a change in the true ion-size parameters. Thus the actual values of the activity coefficients may be expected to differ slightly, particularly at higher percentages of organic solvent. However, the change in pK values due to the change in activity coefficients of H^+ and LH^+ (i.e. f_{H^+} and f_{LH^+}) will be small and will not exceed experimental error limits.

The presence of inert electrolytes or an increase in the concentration of an electrolyte usually modifies the structure of the solvent mixtures considerably and is not congenial for the determination of ion–solvent interactions. Therefore, we used a low concentration of electrolyte, a condition essential for the determination of the "medium effects" of ions.

The pK_T values are calculated using the equation

$$\begin{aligned} pK_T &= pc_{H^+} + \log\frac{c_{LH^+}}{c_L} \\ &= B + \log U_H + \log\frac{c_{LH^+}}{c_L} \\ &= B + \log U_H \pm \log\frac{d-d_M}{d_I - d} \end{aligned}$$

where B represents the pH-meter reading of the experimental solution, and d_M, d_I and d are the molar absorptivities of the molecular form, the ionic form and the mixtures of ionic and molecular forms of the ligand, respectively. The calibration of the pH-meter in aquo-binary mixtures and the correction factors for the measurement of H^+ ions in different mixed solvents were determined as described previously [5–8].

The concentrations of free L and LH^+ can be determined from the relationships

$$[L]_{total} = [L]_{free} + [LH^+]$$

and

$$[H^+]_{total} = [H^+]_{free} + [LH^+]$$

The average values of pK_T for 1,10-phenanthroline using pH-metric and spectrophotometric methods are recorded in Table 1. The results are accurate to within ±0.02 pK units.

DISCUSSION

The values of pK_T for 1,10-phenanthroline determined pH-metrically agree very well with those determined spectrophotometrically. The pK value of 1,10-phenanthroline decreases and passes through a minimum at about 65 wt.% of ethanediol. Similar trends (i.e. a minimum) have also been observed in other solvents [2,3]. The pK values show a linear relationship with $1/\epsilon$ and the mole fraction of organic solvent up to approximately 70 wt.%, beyond which slight deviations occur.

Since the reactions are isoelectric in nature, the decrease in pK values with increasing organic solvent content can be ascribed to greater solubilities and basic character of the solvent mixtures leading to greater dissociation of LH^+ molecules. However, the basicity probably decreases above approximately 60 wt.% EG, resulting in an increase in pK values.

Bates and Robinson [9] have analysed the free energy changes of the ligands in terms of electrostatic and non-electrostatic contributions, i.e.

$$\Delta G_t^{\ominus} = \Delta G_{el}^{\ominus} + \Delta G_{nonel}^{\ominus}$$

TABLE 1

pK values for 1,10-phenanthrolium ion in ethanediol + water mixtures at 298 K, free energy of transfer values and deviations of $\epsilon_r(X)$ from ideal values

Organic solvent EG (wt.%)	Mole fraction of EG	$1/\epsilon \times 10^2$	pK_T values for the reaction $PhH^+ \rightleftharpoons Ph + H^+$			$\Delta G_t^\ominus(1)$ (kJ mol^{-1})	$\Delta G_{t(el)}^\ominus$ (kJ mol^{-1})	$\Delta G_{t(nonel)}^\ominus$ (kJ mol^{-1})	Deviations of $\epsilon_r(X)$ from ideal values
			Spectro-photo-metri-cally	pH-metri-cally	Average				
0.0	0.000		5.05						
11.8	0.038	1.33	4.92	4.92	4.92	−0.74	0.37	−1.11	0.48(10 wt.%)
21.8	0.075	1.38	4.82	4.82	4.82	−1.31	0.68	−1.99	1.47(20 wt.%)
32.3	0.122	1.45	4.77	4.75	4.76	−1.65	1.12	−2.77	1.74(30 wt.%)
42.7	0.178	1.52	4.69	4.68	4.69	−2.11	1.55	−3.66	2.03(40 wt.%)
52.7	0.245	1.60	4.64	4.63	4.64	−2.34	2.05	−4.39	2.68(50 wt.%)
62.6	0.327	1.72	4.59	4.58	4.59	−2.62	2.79	−5.41	2.23(60 wt.%)
72.2	0.430	1.87	4.68	4.69	4.69	−2.11	3.72	−5.83	1.39(70 wt.%)
81.7	0.564	2.06	4.83	4.82	4.82	−1.31	4.96	−6.27	−0.44(80 wt.%)
90.9	0.745	2.3	4.96	4.95	4.96	−0.57	6.51	−7.08	−1.66(90 wt.%)
100.0	1.000	2.4	5.15	5.15	5.15	+0.57	8.56	−7.99	

We calculated $\Delta G^{\ominus}_{t(el)}$ terms using the Born equation [10]

$$\Delta G^{\ominus}_{t(el)} = \frac{Ne^2}{2}\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_W}\right)\left(\frac{1}{r_{H^+}} - \frac{1}{r_{LH^+}}\right)$$

taking $r_{H^+} = 0.086$ mm [11,12] and $r_{LH^+} = 0.370$ mm [1].

The increasing negative values of $\Delta G^{\ominus}_{t(nonel)}$ suggest increasing basicities of the ethanediol + water mixtures. In view of the limitations of the calculations, the results can only be regarded as qualitative.

It has been stressed that the basicity of the solvent mixtures and the ion–solvent interactions can best be determined from the free energy of transfer of the H^+ ion from water to aquo-organic mixtures. The free energies of transfer for reaction (1) were used to determine the free energy of transfer of the H^+ ion, i.e. $\Delta G_t^{\ominus}(H^+)$.

It is seen that [1–3]

$$\begin{aligned}\Delta G_t^{\ominus}(1) &= \Delta G_t^{\ominus}(L) + \Delta G_t^{\ominus}(H^+) - \Delta G_t^{\ominus}(LH^+)\\ &= \Delta G_t^{\ominus}(L) + \Delta G_t^{\ominus}(H^+) - \left(\Delta G_t^{\ominus}(L) + \Delta G^{\ominus}_{t(el)}\right)\end{aligned}$$

or

$$\Delta G_t^{\ominus}(H^+) = \Delta G_t^{\ominus}(1) + \Delta G^{\ominus}_{t(el)}$$

The calculations of $\Delta G^{\ominus}_{t(el)}(\mathrm{PhenH}^+)$ pose a problem. The limitations of the Born equation are well known [10]. Even in the case of spherical ions, such as Na^+, K^+, Cl^- etc., the results are found to be defective. Therefore, it is reasonable to assume that the equation will be defective in the case of unsymmetrical ions such as PhenH^+. Unfortunately, there is no equation which can be used unequivocally even in the case of spherical ions. Therefore we are forced to use the Born equation, assuming a spherical orientation of PhenH^+ with the solvent molecules.

Thus $\Delta G^{\ominus}_{t(el)}$, on going from water of relative permittivity ϵ_W to a solvent of relative permittivity ϵ_S, can be calculated using the Born equation [10]

$$\Delta G^{\ominus}_{t(el)(Born)} = \frac{Nz^2e^2}{2r_{LH^+}}\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_W}\right)$$

However, the calculation of the solvation energy involves not only the energy of interactions arising from Born charging (B), but also the energy of interactions such as ion–dipole (i–d), ion–induced-dipole (i–i-d), ion–quadrupole (i–q), charge transfer (CT) and other weak interactions [13–15].

According to Muirhead-Gould and Laidler [14], the electrostatic terms associated with the different charging processes are strictly free energy terms. Thus, $\Delta G^{\ominus}_{t(el)}$ can be written as

$$\Delta G^{\ominus}_{t(el)} = \Delta G^{\ominus}_{t(el)(B)} + \Delta G^{\ominus}_{t(i-d)} + \Delta G^{\ominus}_{t(i-i\text{-}d)} + \Delta G^{\ominus}_{t(i-q)}$$

However, we have omitted the term due to ion–quadrupole interactions owing to the non-availability of reliable quadrupole moment data for ethanediol.

The expressions for the energy terms are [15]

$$\Delta G^{\ominus}_{(i-d)} = -\frac{nNZ_i e\mu}{(r_i + r_S)^2}$$

$$\Delta G^{\ominus}_{(i-i-d)} = -\frac{nN\alpha(Z_i e)^2}{2(r_i + r_S)^4}$$

where n, μ, α and r_S are the solvation number, the dipole moment, the polarizability and the radius of the particular solvent, respectively.

The $\Delta G^{\ominus}_{(i-d)}$ and $\Delta G^{\ominus}_{(i-i-d)}$ values in water and ethanediol were calculated using the dipole moment μ, polarizability α and radii values of the solvents from the literature [13]. These are $\mu_W = 1.85 \times 10^{-18}$ e.s.u., $\alpha_W = 1.47 \times 10^{-24}$ cm^3 and $r_W = 1.38 \times 10^{-8}$ cm for water, and $\mu_{EG} = 2.34 \times 10^{-18}$ e.s.u., $\alpha_{EG} = 5.7 \times 10^{-24}$ cm^3 and $r_{EG} = 2.24 \times 10^{-8}$ cm for ethanediol.

The values $\Delta G^{\ominus}_{t(i-d)}$ and $\Delta G^{\ominus}_{t(i-i-d)}$ in mixed solvents were calculated assuming the solute to be distributed in the solvent in the ratio of their mole fractions X_1 and X_2. Thus, $\Delta G^{\ominus}_{t(i-d)} = (X_1 \Delta G^{\ominus}_{(i-d)(\text{water})} + X_2 \Delta G^{\ominus}_{(i-d)(\text{org.solv.})}) - \Delta G^{\ominus}_{(i-d)(\text{water})}$, etc. $\Delta G^{\ominus}_{t(i-d)}$ and $\Delta G^{\ominus}_{t(i-i-d)}$ in mixed solvents appear to be small and almost cancel each other out.

In calculating $\Delta G^{\ominus}_{t(el)}$ for Ph_4As^+ and Ph_4B^-, Kim [13] assumed tetrahedral solvation. The basis of the reference electrolyte method lies in the fact that the ions are large and spherically symmetrical and the charge is buried in the centre so that no appreciable solvation can occur. It is unlikely that large ions such as Ph_4As^+ or Ph_4B^- will be solvated to the same extent as Na^+ and K^+. However, the effective charge of Ph_4As^+ and Ph_4B^- has been calculated as 0.447.

The values of $\Delta G^{\ominus}_{t(el)(B)}$ and $\Delta G^{\ominus}_{t(el)(B+i-d+i-i-d)}$ (assuming mono-solvation and tetrahedral solvation) are recorded in columns 2, 3 and 4 of Table 2. Column 5 contains the $\Delta G^{\ominus}_{t(el)}$ values based on a one-layer solvation model [16]

$$\Delta G^{\ominus}_{t(el)} = \frac{Nz^2e^2}{2}\left(\frac{1}{\epsilon_1} - 1\right)\left(\frac{1}{r} - \frac{1}{b}\right) + \frac{Nz^2e^2}{2}\left(\frac{1}{\epsilon_0} - 1\right)\left(\frac{1}{b}\right)$$

where r is the radius of the bare ion, $b = r + r_S$, r_S is the radius of the solvent molecules, ϵ_1 is 2 and ϵ_0 is the bulk dielectric constant. The radii of the aquo–organic mixtures were calculated from the radii of the solvents.

The $\Delta G^{\ominus}_t(H^+)$ values in $EG + H_2O$ mixtures calculated using different $\Delta G^{\ominus}_{t(el)}$ values are recorded in Table 3. The $\Delta G^{\ominus}_{t(el)}$ values calculated using the one-layer model appear to be rather high; we do not favour this model.

It is apparent that the various methods of calculation of $\Delta G^{\ominus}_{t(el)}$ give different results; however, the results clearly provide an estimate of devia-

TABLE 2

The electrostatic free energy of transfer of PhenH^+ ion from water to $\text{EG} + \text{H}_2\text{O}$ mixtures ($\Delta G^{\ominus}_{t(el)}(\text{PhenH}^+)$ in kJ g-ion^{-1})

EG (wt.%)	Born	Born + (i–d) + (i–i–d) ($n = 1$)	Born + (i–d) + (i–i–d) ($n = 4$)	One-layer continuum model
11.8	0.11	0.06	−0.09	0.56
21.8	0.21	0.06	−0.38	0.90
32.3	0.33	0.18	−0.39	1.67
42.7	0.47	0.26	−0.37	2.29
52.7	0.62	0.34	−0.50	3.68
62.6	0.83	0.52	−0.41	4.17
72.2	1.12	0.74	−0.40	5.28
81.7	1.49	1.12	+0.01	6.74
90.9	1.97	1.73	+1.01	8.68
100.0	2.59	2.56	+2.47	11.25

tion (in kJ mol^{-1}) which can arise if we use different equations. It is observed that the $\Delta G_t^{\ominus}(\text{H}^+)$ values are in reasonable agreement at low percentages of ethanediol, but vary considerably at high percentages. The deviations appear to be small if we consider an error of 8–12 kJ g-ion^{-1} [17], usually associated with the single values. Moreover, an error of 0.2–0.3 kJ g-ion^{-1} must be allowed for the possible error of ± 0.01–0.02 pK units in the pK_T measurements.

The $\Delta G_t(\text{H}^+)$ values based on mole fraction, obtained using the relation

$$\Delta G_t^{\ominus}(\text{H}^+)_X = \Delta G_t^{\ominus}(\text{H}^+)_c + 5.7 \log \frac{M_\text{W} \times d_\text{S}}{d_\text{W} \times M_\text{S}}$$

TABLE 3

The free energy of transfer of H^+ ions and comparison of results ($\Delta G_t^{\ominus}(\text{H}^+)$ in kJ g-ion^{-1})

EG (wt.%)	Born	Born + (i–d) + (i–i–d) ($n = 1$)	Born + (i–d) + (i–i–d) ($n = 4$)	SEM	REM	FM	WM	
11.8	−0.6(−0.8)	−0.7(−0.9)	−0.8(−1.0)					
21.8	−1.1(−1.4)	−1.3(−1.4)	−1.7(−2.4)					
32.3	−1.3(−1.9)	−1.5(−2.0)	−2.0(−2.6)	−7.1	−1.2	−2.6	−1.0	30 wt.%
42.7	−1.6(−2.4)	−1.9(−2.6)	−2.5(−3.2)					
52.7	−1.7(−2.7)	−2.0(−3.0)	−2.8(−3.8)	−10.5	−1.0	−4.2	−1.9	50 wt.%
62.6	−1.8(−3.1)	−2.1(−3.4)	−3.0(−4.3)					
72.7	−1.0(−2.6)	−1.4(−2.9)	−2.5(−4.1)	−17.6	−2.2	−6.9	−1.8	70 wt.%
81.7	−0.8(−2.7)	−0.2(−2.1)	−1.3(−3.2)					
90.9	+1.4(−0.9)	+1.2(−1.2)	+0.4(−1.9)	−22.2	−0.7	−8.1	—	90 wt.%
100.0	+3.2(+0.4)	+3.1(+0.3)	+3.0(+0.2)	−18.4	5.1	−6.0	—	100 wt.%

Values in parentheses are on the basis of mole fraction.

are given in parentheses. Experimentally determined d_S values were used and

$$M_S = 100\left(\frac{W}{62.07} + \frac{100 - W}{18.02}\right)^{-1}$$

The results show that the free energy of transfer of the H^+ ion becomes increasingly negative and reaches a minimum at about 60 wt.% of ethanediol. Beyond this, $\Delta G_t(H^+)$ increases and ultimately becomes positive at about 90 wt.% of ethanediol. The results indicate increased basicity of ethanediol–water mixtures. The basicity reaches a maximum at about 60 wt.% of EG; however, the basicities of EG and EG-rich aqueous mixtures are less than that of water.

Our results, together with the values of $\Delta G_t^{\ominus}(H^+)$ in EG + H_2O mixtures determined by other workers [18–20], are given in Table 3. The previous investigations have been summarized by Das and Kundu [18]. However, the data in most cases pertain only to several percentages.

The $\Delta G_t^{\ominus}(H^+)$ values determined by us agree well with the values given by Das and Kundu [18] (using the reference electrolyte method (REM)) and Wells [20] (using the solvent-sorting equilibrium method (SSEM)). However, they differ considerably from the values determined using the ferrocene/ferricinium electrode (FM), the indicator electrode and the simultaneous extrapolation method (SEM). Rao and Kalidas [19] have observed that the maximum basicity lies in the region 90–95 wt.% of organic solvent; this is obviously erroneous as seen from the present work and from the studies of Das and Kundu [18] and Wells [20].

The basicity maximum cannot be properly correlated with other properties, such as the excess thermodynamic properties of mixing and the ultrasonic absorption maximum [21] (no maximum is observed in the case of EG + H_2O mixtures) and nothing specific can be stated regarding the structure of the solvent mixtures, although the variation in $\Delta G_t^{\ominus}$(ions) has been explained by Wells [20] in terms of excess thermodynamic properties.

Some insight into the structural properties of EG + H_2O mixtures can be obtained from the excess relative permittivities $\epsilon_r^E(X)$ of the solvent mixtures calculated using Decrooq's simplified formula [22]

$$\epsilon_r^E(X) = \epsilon_r(X) - \{(1-\phi)\epsilon_W + \phi\epsilon_{EG}\}$$

where ϕ represents the volume fraction of EG defined by

$$\phi = \frac{XV_{EG}}{(1-X)V_W + XV_{EG}}$$

and V_W and V_{EG} denote the molar volumes of water and EG respectively. The $\epsilon_r(X)$ values from the work of Akerlof [23] were used to calculate the excess values. $\epsilon_r^E(X)$ (Table 1) (Fig. 1) exhibits a positive deviation from the ideal value and passes through a maximum in the region 50–60 wt.%.

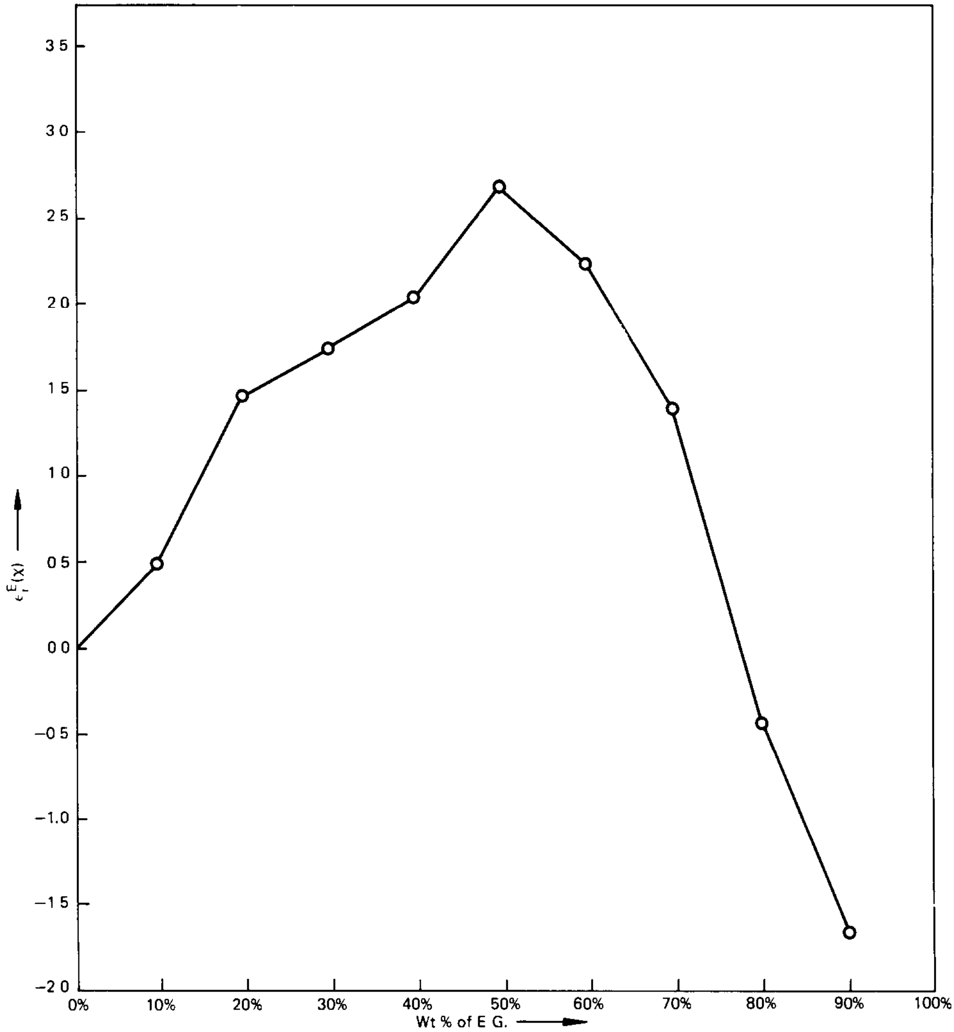

Fig. 1. Excess dielectric properties of EG + H_2 mixtures vs. wt.% of EG.

However, the positive deviation reverses beyond 80 wt.%. The results indicate structural variations in the regions 0–50 wt.% and 80–100 wt.% with an intermediate zone around 50–80 wt.% (Fig. 1).

The basicities of the solvent mixtures increase up to a region where the number of EG molecules is exactly half the number of H_2O molecules (when both the solvents have equal numbers of OH groups). However, as the number of OH groups of the organic component increases, the basicity gradually decreases, and the basicity is reversed when the number of OH groups of EG exceeds twice the number of OH groups of water, i.e. above 77 wt.% of EG. The results are usually interpreted in terms of hydrophobic interactions and consequent structural changes associated with the addition of organic solvents. An initial increase in the tetrahedral structure of water is observed due to hydrophobic interactions caused by the addition of EG; this probably attains a maximum at about 20 mass% of EG. However, the subsequent addition of EG causes depolymerization of the tetrahedral structure of water releasing the more basic monomeric water. The presence of excess OH groups with hydrogen-bonding capability probably makes EG and EG-rich mixtures more acidic than water. This is in agreement with the observations of Franks and Ives [24]. The hydrophobic hydrocarbon group is considered to resist the pull into solution exerted by the hydrophilic hydroxyl group which can hydrogen bond with the solvent molecules either as a proton donor or acceptor. The second hydroxyl group in ethanediol shifts the balance of the competing influences in favour of aqueous behaviour [24].

The inadequacies of the various methods of determination of the medium effects of ions have been well discussed by Lahiri and co-workers [1–3] and Lahiri and Aditya [25]. Wells' method, which is applicable to water-rich media, has recently been criticized by Blandamer et al. [26] on the grounds of inconsistency and thermodynamic incompatibility. They question the significance attached to the slope and intercept in Wells' method. In spite of clarifications by Sidahmed and Wells [27], the confusion prevails.

The reference electrolyte method, which is supposed to be the best available method, is not free from problems [1–3]. The single ion values based on the solubility values of Ph_4AsPi, KPi (Pi = picrate ion), etc. are to be treated with caution. The reliability of the method suffers from limitations arising from the following: hydrophobic interactions, the formation of possible micelles (particularly with water) by Ph_4 groups, the large dispersive interactions of the Ph group with organic co-solvents, the strong dispersion interactions of $-NO_2$ groups with organic solvents and the decreased hydrogen-bonding interactions in the case of picrate ions.

Considering the limitations, our method is simple and reliable, but definitely not without problems. The $\Delta G_t^{\ominus}(H^+)$ values determined by us usually come very close (within ±1 kJ, in most cases) to those obtained by the reference electrolyte method. The difference can be considered to be insignificant in view of the large errors involved in the determination of single ion values. However, we stress the need to determine single ion values using different methods, so as to obtain a reasonably consistent set of data for single ion values in different solvent media. This will enable us to extract more information regarding the structural aspects of solvent mixtures and ion–solvent interactions.

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