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SOLVENT EFFECTS ON THE DISSOCIATION OF 2,2′-BIPYRIDINE AND 1,10-PHENANTHROLINE IN AQUEOUS BINARY MIXTURES OF 2-METHOXYETHANOL AND 1,2-DIMETHOXYETHANE

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ABSTRACT

The thermodynamic dissociation constants for isoelectric reactions of the type $LH^+ \rightleftharpoons L + H^+$ (where L = 2,2′-bipyridine or 1,10-phenanthroline) have been determined pH-metrically and spectrophotometrically at 298 K in aqueous binary mixtures of 2-methoxyethanol and 1,2-dimethoxyethane (0–90 wt% of organic solvent). The pK values were found to decrease gradually and pass through minima at around 70–80 wt% of the organic solvents. The effect of the solvent on the dissociation of the protonated forms of the ligands is discussed in terms of the standard Gibbs energy of transfer of H^+ $\Delta G_t^{\ominus}(H^+)$ from water to the mixed solvents, and also in terms of the individual species involved in the dissociation process. The overall dissociation behaviour was found to be governed by specific solute–solvent interactions in the solvent media besides the relative solvent basicities.

INTRODUCTION

As part of our comprehensive studies [1–4] on dissociation equilibria in different aquo-organic mixtures we report in this communication on the results of our measurements of the dissociation constants for protonated forms of 2,2′-bipyridine and 1,10-phenanthroline in 2-methoxyethanol (ME) + water and 1,2-dimethoxyethane (DME) + water mixtures at 298 K. Studies such as these give important insights into the role of the solvent in dissociation equilibria and ion–solvent interactions, as well as providing information regarding the acid–base properties of these solvents and their structural features.

Both ME and DME (monomethyl and dimethyl ethylene glycols) are well known for their various industrial uses [5–7]. ME is quasiaprotic in nature and DME is a wholly aprotic solvent. The present work reports on a study of the behaviour of these two closely related co-solvents in aqueous mixtures in terms of dissociation equilibria and other thermodynamic parameters.

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EXPERIMENTAL

2,2′-Bipyridine (bipy) and 1,10-phenanthroline (phen) (G.R., E. Merck) were used without further purification. 2-Methoxyethanol (G.R., E. Merck) was distilled twice before use. The boiling point (124 ° C) and density (0.9602 g cm^{-3} at 25 ° C) compare well with literature values [8]. 1,2-Dimethoxyethane (Fluka) was shaken well with $FeSO_4$ (A.R., BDH) for 1–2 h, decanted and distilled. The distillate was refluxed for 12 h and distilled over metallic sodium (b.p. = 83.5 ° C, density = 0.8626 g cm^{-3}).

All other reagents were of analytical grade. The solutions were prepared using triply distilled water.

The ME + water and DME + water mixtures employed in the study were prepared by appropriate mixing of the solvents by weight.

The solubilities of 2,2′-bipyridine and 1,10-phenanthroline in ME + water and DME + water mixtures at 298 K were determined using a method reported previously [9,10].

The pK values of the ligands were determined pH-metrically and spectrophotometrically as described in our previous communications [1–4]. Molar absorption measurements were taken at 280, 295 and 300 nm for 2,2′-bipyridine and at 260, 270 and 275 nm for 1,10-phenanthroline. A Shimadzu UV-240 spectrophotometer maintained at 298 K was used for the spectrophotometric measurements. The pH was measured using a ECIL pH meter with an accuracy of ± 0.01.

The dielectric constant values of ME + water and DME + water mixtures were taken from the works of Sadek et al. [11] and Renard and Justice [12], respectively.

Calibration of glass electrode

Determining the dissociation constants for the acids requires accurate values of H^+ ion concentration. The glass–calomel electrode combination has been employed successfully for the determination of H^+ ion concentrations in various mixed and non-aqueous solvents. However, no report of H^+ ion concentration measurements in ME + water and DME + water mixtures came to our notice. A glass electrode has been reported to function satisfactorily in various dipolar aprotic solvents though the response is not always Nernstian, particularly in pure solvents [13]. Nevertheless, a glass electrode has been found to work reversibly in ME + water and DME + water mixtures, and reproducible values of H^+ ion concentration have been obtained.

Calibration of the glass electrode was achieved and ‘correction factors’ for the various percentages of the mixed solvents determined according to the method suggested by van Uitert and Haas [14], Bates [15], Irving and Manhot [16], and Lahiri, Aditya and co-workers [17–19].

The correction factors have been found to depend to a small degree on the nature of the solvents, and on the ageing and asymmetry potential of the glass electrode, but consistent and reproducible results are obtained if the correction factors are determined before each set of measurements.

DATA ANALYSIS

The thermodynamic dissociation constants for the reaction

$$LH^+ \rightleftharpoons L + H^+ \tag{1}$$

(where L = 2,2′-bipyridine or 1,10-phenanthroline) can be written as

$$K_T = \frac{C_L C_{H^+}}{C_{LH^+}} \frac{f_L f_{H^+}}{f_{LH^+}} \tag{2}$$

When determining dissociation constants, the use of inert electrolytes should be avoided [9,10,20] and the concentrations of electrolytes kept very low so that their effects on the solvent structures are minimal—a condition essential for the determination of the 'medium effects' of ions.

The activity coefficients of f_{LH^+} and f_{H^+} have been assumed to be the same in dilute solutions though a slight variation in f_{H^+} and f_{LH^+} values is to be expected in view of the difference in the solvational characteristics and ion-size parameters of H^+ and LH^+ ions. Thus, the variations of $f_{H^+}f_L/f_{LH^+}$ will definitely be small and will not exceed experimental error limits at low ionic strengths ($3–7 \times 10^{-4}$ M using the pH-metric method, and even lower using the spectrophotometric method).

The pK_T values were calculated according to the method described in our previous communications [1–4,9,10].

Free energy of transfer of the ligands from water to mixed solvents was calculated using the relation

$$\Delta G_t^{\ominus}(L) = -2.303\,RT \log \frac{C_s}{C_w} \tag{3}$$

where C_s and C_w represent the molar concentrations of L in aquo-organic solvents and water, respectively.

Free energies of transfer for the ionization of LH^+ were calculated using the equation

$$\Delta G_t^{\ominus}(1) = 2.303\,RT[pK_s(1) - pK_w(1)] \tag{4}$$

RESULTS AND DISCUSSION

The average values of pK_T for 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) determined pH-metrically and spectrophotometrically (see Tables 1 and 2) show excellent consistency.

TABLE 1

The pK values of 2,2′-bipyridine and 1,10-phenanthroline in ME+water mixtures at 298 K

Wt.% of ME	Mole fraction of ME	$\frac{1}{\epsilon} \times 10^2$	Correction factor	pK_T of bipyridine			pK_T of phenanthroline		
				pH-metric (a)	Spectro-photometric (b)	Average of (a)&(b)	pH-metric (a)	Spectro-photometric (b)	Average of (a)&(b)
00	0	1.27	±0.00	4.49±0.01	4.47±0.01	4.48	5.07±0.01	5.05±0.01	5.06
10	0.0255	1.34	+0.11	4.32±0.01	4.29±0.01	4.30	4.83±0.01	4.81±0.02	4.82
20	0.0558	1.43	+0.15	4.14±0.01	4.13±0.01	4.14	4.66±0.01	4.61±0.01	4.64
30	0.0921	1.56	+0.19	3.99±0.01	3.94±0.01	3.97	4.55±0.01	4.52±0.02	4.54
40	0.1363	1.74	+0.27	3.92±0.01	3.88±0.01	3.90	4.49±0.01	4.46±0.01	4.48
50	0.1914	1.99	+0.31	3.69±0.02	3.66±0.02	3.68	4.34±0.01	4.33±0.02	4.34
60	0.2620	2.37	+0.35	3.59±0.01	3.58±0.02	3.59	4.21±0.02	4.19±0.01	4.20
70	0.3559	2.92	+0.38	3.41±0.01	3.37±0.01	3.39	4.02±0.01	4.03±0.02	4.03
80	0.4864	3.77	+0.48	3.23±0.01	3.18±0.01	3.21	3.89±0.01	3.91±0.02	3.90
90	0.6806	5.26	+1.07	3.37±0.01	3.33±0.01	3.35	4.16±0.01	4.20±0.02	4.18

TABLE 2

The pK values of 2,2′-bipyridine and 1,10-phenanthroline in DME + water mixtures at 298 K

Wt.% of DME	Mole fraction of DME	Correction factor	$\frac{1}{\epsilon} \times 10^2$	pK_T of bipyridine			pK_T of phenanthroline		
				pH-metric (a)	Spectro-photometric (b)	Average of (a)&(b)	pH-metric (a)	Spectro-photometric (b)	Average of (a)&(b)
10	0.0217	−0.04	1.40	4.18 ± 0.01	4.17 ± 0.02	4.18	4.69 ± 0.01	4.68 ± 0.02	4.69
20	0.0475	−0.03	1.56	3.92 ± 0.02	3.90 ± 0.01	3.91	4.54 ± 0.01	4.53 ± 0.01	4.54
30	0.0788	−0.02	1.75	3.73 ± 0.01	3.71 ± 0.01	3.72	4.37 ± 0.02	4.35 ± 0.01	4.36
40	0.1175	−0.01	2.01	3.50 ± 0.02	3.47 ± 0.01	3.48	4.19 ± 0.01	4.16 ± 0.02	4.18
50	0.1666	±0.00	2.35	3.29 ± 0.01	3.25 ± 0.02	3.27	4.02 ± 0.01	4.01 ± 0.01	4.01
60	0.2308	+0.02	2.79	3.15 ± 0.01	3.12 ± 0.01	3.14	3.82 ± 0.01	3.78 ± 0.01	3.80
70	0.3182	+0.11	3.58	3.03 ± 0.02	3.01 ± 0.01	3.02	3.56 ± 0.02	3.54 ± 0.01	3.55
80	0.4445	+0.52	4.79	3.14 ± 0.02	3.10 ± 0.01	3.12	3.63 ± 0.01	3.59 ± 0.02	3.61
90	0.6428	+1.48	7.42	3.38 ± 0.02	3.34 ± 0.01	3.36	4.06 ± 0.02	4.03 ± 0.01	4.05

The pK_T values of the ligands were found to decrease on the addition of organic solvent to the ME + water and DME + water mixtures. The minima were found at around 80 and 70 wt.% of ME and DME, respectively. Similar behaviour has been observed for other solvents.

When plotted against mole-fraction of organic solvents the pK_T values show linearity at best up to 70 wt.%; beyond this considerable deviations occur.

Tables 1 and 2 show that the effects of the solvent on the dissociation equilibrium of LH^+-type acids (isoelectronic in nature) are more or less similar in aqueous ME and DME solutions. The $\Delta G_t^\ominus(1)$ values for both solvent systems pass through minima on the addition of a non-aqueous component, the variation being more marked for DME than for ME. The appearance of such minima can be attributed to (1) increased solubility leading to greater dissociation of LH^+; (2) changed solvational properties of the ligands and their conjugate acids; (3) enhanced basicity of the solvent mixtures up to 70–80% of organic solvents, and subsequent decrease in basicity.

No useful conclusion can be derived from the analysis of $(\Delta G_t^\ominus(LH^+) - \Delta G_t^\ominus(L))$ values, as this implies increasingly positive values of $\Delta G_{t(el)}^\ominus$ (LH^+). This is an inherent limitation, arising from the assumption $\Delta G_t^\ominus$ $(LH^+) = \Delta G_t^\ominus(L) + \Delta G_{t(el)}^\ominus$ (LH^+).

It should be noted that the relative affinities of water or the non-aqueous component towards the base (L) or its conjugated acid (LH^+) may be expected to arise from the relative bonding capacities of solvent dipoles, exerted largely through the formation of hydrogen bonds. However, their contributions to values of $\Delta G_t^\ominus(1)$ cannot be calculated.

Values of $\Delta G_t^\ominus(L)$ can be obtained from the solubility values of the ligands at 298 K (see Tables 4 and 5 below). The accuracy of the solubility values is within 0.5–1.0%. The solubility values increase with the increase in hydrophobic character of the solvent mixtures. The solubility values for bipy and phen in water at 298 K have been determined to be 0.0347 and 0.0136 mol dm^{-3}, respectively. While this solubility value for bipy is in agreement with values reported previously, a considerable discrepancy is observed in the case of the values for phen [9,10].

In order to understand the structural complexities, ion–solvent interactions and basicities of the solvent mixtures, attempts were made to determine values of $\Delta G_t^\ominus(H^+)$ in aquo-organic mixtures, using the method suggested by Lahiri and co-workers [9,10]. Values of $\Delta G_t^\ominus(H^+)$ give a quantitative measure of the free energy of transfer, or 'medium effects', when H^+ is transferred from water to mixed solvents, and is regarded as being the best measure of solvent basicity compared to that of water.

Thus we have for reaction (1)

$$\Delta G_t^\ominus(1) = \Delta G_t^\ominus(L) + \Delta G_t^\ominus(H^+) - \Delta G_t^\ominus(LH^+) \qquad (5)$$

or

$$\Delta G_t^{\ominus}(\mathrm{H}^+) = \Delta G_t^{\ominus}(1) + \Delta G_{t(el)}^{\ominus}(\mathrm{LH}^+) \tag{6}$$

since

$$\Delta G_t^{\ominus}(\mathrm{LH})^+ = \Delta G_t^{\ominus}(\mathrm{L}) + \Delta G_{t(el)}^{\ominus}(\mathrm{LH}^+)$$

In the absence of any suitable and reliable equation for the unambiguous calculation of $\Delta G_{t(el)}^{\ominus}$, we were forced to use the Born equation [21] despite its limitations when calculating $\Delta G_{t(el)}^{\ominus}$ in going from water of relative permittivity ϵ_w to a solvent of relative permittivity ϵ_s. Thus

$$\Delta G_{t(el)(Born)}^{\ominus} = \frac{NZ^2e^2}{2r_{\mathrm{LH}^+}}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right) \tag{7}$$

where r_{LH^+} is taken to be 3.70 A [9,10]. It is to be expected that considerable uncertainties in values of $\Delta G_{t(el)}^{\ominus}$ will arise from the use of the Born equation in cases of unsymmetrical ions like phenH$^+$, as results are found to be defective even in cases of spherical ions such as Na$^+$, K$^+$, Cl$^-$, etc. Moreover, it is to be expected that the ions will lose their sphericity in solution. Therefore, the use of the Born equation assuming spherical orientation of phenH$^+$ with the solvent molecules can be taken to be in order.

However, in calculating $\Delta G_{t(el)}^{\ominus}$, we consider 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) [22–24], etc. Charge-transfer and other weak interactions are usually neglected.

Thus

$$\Delta G_{t(el)}^{\ominus} = \Delta G_{t(el)}^{\ominus}(\mathrm{B}) + \Delta G_t^{\ominus}(\text{i–d}) + \Delta G_t^{\ominus}(\text{i–i-d}) + \Delta G_t^{\ominus}(\text{i–q})$$

Owing to a lack of knowledge of the accurate values of the quadrupole moments of the solvents, the $\Delta G_t^{\ominus}(\text{i–q})$ term will also be neglected.

The expressions for the energy terms are

$$\Delta G_t^{\ominus}(\text{i–d}) = -\frac{nNZ_ie\mu}{(r_i + r_s)^2} \tag{8}$$

$$\Delta G_t^{\ominus}(\text{i–i-d}) = -\frac{nN\alpha(Z_ie)^2}{2(r_i + r_s)^4} \tag{9}$$

where n, μ and r_s represent the solvation number, dipole moment polarizability and radius of the solvent, respectively.

The polarizability α of the ME and DME values was calculated using the relation

$$\alpha = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d}\frac{3}{4\pi N} \tag{10}$$

The n_D values for ME and DME were taken from the literature [25]. The radii of the solvent mixtures were calculated from their molar volumes. The values of $\Delta G^{\ominus}$(i–d) and $\Delta G^{\ominus}$(i–i-d) in water, ME and DME were calculated using the following parameters

$\mu_w = 1.86 \times 10^{-18}$ e.s.u., $\alpha_w = 1.47 \times 10^{-24}$ cm^3, $r_w = 1.38 \times 10^{-8}$ cm
$\mu_{ME} = 2.18 \times 10^{-18}$ e.s.u., $\alpha_{ME} = 7.62 \times 10^{-24}$ cm^3, $r_{ME} = 3.14 \times 10^{-8}$ cm
$\mu_{DME} = 1.71 \times 10^{-18}$ e.s.u., $\alpha_{DME} = 9.57 \times 10^{-24}$ cm^3, $r_{DME} = 3.45 \times 10^{-8}$ cm

The values for $\Delta G_t^{\ominus}$(i–d) and $\Delta G_t^{\ominus}$(i–i–d) in the aquo-organic mixtures were calculated assuming the solute to be distributed in the binary mixtures in the ratio of their mole-fractions X_1 and X_2. Thus we have

$$\Delta G_t^{\ominus}(\text{i–d}) = \left[X_1\, \Delta G^{\ominus}_{\text{i–d(w)}} + X_2\, \Delta G^{\ominus}_{\text{i–d(org.solv.)}}\right] - \Delta G^{\ominus}_{\text{i–d(w)}} \tag{11}$$

and so on.

The values of $\Delta G^{\ominus}_{t(el)}$(B) and $\Delta G^{\ominus}_{t(el)}$ (B + i–d + i–i-d) assuming monosolvation of the LH$^+$ ions, are recorded in Columns I and II of Table 3. Column III gives $\Delta G^{\ominus}_{t(el)}$ values based on a 'one-layer solvation model' [26].

$$\Delta G^{\ominus}_{t(el)} = \frac{NZ^2e^2}{2}\left(\frac{1}{\epsilon_1} - 1\right)\left(\frac{1}{r_{LH^+}} - \frac{1}{b}\right) + \frac{NZ^2e^2}{2}\left(\frac{1}{\epsilon_0} - 1\right)\left(\frac{1}{b}\right) \tag{12}$$

where $b = r_{LH^+} + r_s$, r_s is the radius of the solvent molecules, $\epsilon_1 = 2$, and ϵ_0 is the bulk dielectric constant. The mean molar mass of each solvent is determined from the relation

$$M_s = 100\left\{\frac{w}{M} + \frac{100 - w}{18.02}\right\}^{-1} \tag{13}$$

where M is the molecular weight for ME or DME, respectively. The density values were determined experimentally.

It can be seen that the contributions due to ion–dipole and ion–induced-dipole interactions are high. It should also be noted that the values for $\Delta G^{\ominus}_{t(el)}$ (B + i–d + i–i-d) and $\Delta G^{\ominus}_{t(el)}$ (one-layer) differ considerably in most cases. The nature of the uncertainties in the $\Delta G^{\ominus}_{t(el)}$ values from the different equations can be ascertained from the results.

$\Delta G_t^{\ominus}(H^+)$ values in ME + water and DME + water mixtures using bipyridine, phenanthroline and their averages are recorded in Tables 4 and 5. The conversion factors to obtain values for $\Delta G_t^{\ominus}(H^+)_N$ (in mole-fraction scale) are determined from the relationship

$$\Delta G_t^{\ominus}(H^+) = \Delta G_t^{\ominus}(H^+)_C + 5.7 \log \frac{M_w d_s}{d_w M_s} \tag{14}$$

The $\Delta G_t^{\ominus}(H^+)$ values using bipy and phen show excellent consistency both qualitatively and quantitatively at low percentages, but vary consider-

TABLE 3

Values of $\Delta G^{\ominus}_{t(el)(Born)}$, $\Delta G^{\ominus}_{t(el)}(B+i\text{-}d+i\text{-}i\text{-}d)$, $\Delta G^{\ominus}_{t(el)(Total)}$ and $\Delta G^{\ominus}_{t(el)(one\text{-}layer)}$ (kJ mol^{-1}) from water to ME + water and DME + water mixtures at 298 K

ME					DME				
	I	II		III		I	II		III
Wt.% of ME	$\Delta G^{\ominus}_{t(el)(Born)}$	$\Delta G^{\ominus}_{t(el)[B+i-d+i-i-d]}$	$\Delta G^{\ominus}_{t(el)(Total)}$	$\Delta G^{\ominus}_{t(el)(one\text{-}layer)}$	Wt.% of DME	$\Delta G^{\ominus}_{t(el)(Born)}$	$\Delta G^{\ominus}_{t(el)[B+i-d+i-i-d]}$	$\Delta G^{\ominus}_{t(el)(Total)}$	$\Delta G^{\ominus}_{t(el)(one\text{-}layer)}$
10	0.13	(0.19 + 0.02)	0.34	7.08	10	0.24	(0.24 + 0.01)	0.49	7.15
20	0.29	(0.40 + 0.05)	0.74	7.71	20	0.54	(0.52 + 0.05)	1.11	7.97
30	0.54	(0.65 + 0.08)	1.27	8.58	30	0.91	(0.90 + 0.08)	1.89	8.91
40	0.88	(1.0 + 0.12)	2.00	9.48	40	1.38	(1.10 + 0.12)	2.60	10.00
50	1.35	(1.4 + 0.17)	2.92	10.63	50	2.02	(1.80 + 0.17)	3.99	11.33
60	2.07	(1.9 + 0.23)	4.20	12.00	60	2.85	(2.50 + 0.23)	5.58	12.83
70	3.09	(2.53 + 0.32)	5.94	13.76	70	4.33	(3.50 + 0.32)	8.15	14.91
80	4.69	(3.5 + 0.43)	8.62	16.02	80	6.60	(4.90 + 0.45)	11.95	17.59
90	7.48	(4.8 + 0.61)	12.89	19.29	90	11.53	(7.00 + 0.65)	19.18	22.11

TABLE 4

Free energies of transfer [H$^+$] and related ions in ME + water mixtures at 298 K

Wt.% of ME	$-\Delta G_t^\ominus(1)$ (kJ mol^{-1})		$-\Delta G_t^\ominus(\mathrm{H}^+)_\mathrm{C}$ based on[a] (kJ mol^{-1})			Conversion factor ($-Ve$) to be added to get $\Delta G_t^\ominus(\mathrm{H}^+)_\mathrm{N}$ (mole-fraction)	Solubility (mol dm^{-3})		$-\Delta G_t^\ominus$ [b] (kJ mol^{-1})	
	bipy	phen	bipy	phen	Average		bipy	phen	bipyH$^+$	phenH$^+$
10	1.03	1.37	0.90 (0.69)	1.24 (1.03)	1.07 (0.86)	0.19	0.0812	0.0431	2.15 (1.94)	2.56 (2.35)
20	1.94	2.40	1.65 (1.20)	2.11 (1.66)	1.88 (1.43)	0.40				
30	2.91	2.97	2.37 (1.64)	2.43 (1.70)	2.40 (1.67)	0.60	0.2163	0.1478	4.02 (3.29)	5.34 (4.61)
40	3.31	3.31	2.43 (1.31)	2.43 (1.31)	2.43 (1.31)	0.88				
50	4.56	4.11	3.21 (1.64)	2.76 (1.19)	2.99 (1.42)	1.17	0.7326	0.2559	5.99 (4.42)	6.13 (4.56)
60	5.08	4.91	3.01 (0.88)	2.84 (0.71)	2.93 (0.80)	1.50				
70	6.22	5.88	3.13 (0.28)	2.79 (−0.06)	2.96 (0.11)	2.00	1.0998	0.8124	5.30 (2.45)	7.21 (4.36)
80	7.25	6.62	2.56 (−1.37)	1.93 (−2.00)	2.25 (−1.69)	2.34				
90	6.45	5.02	−1.03 (−6.44)	−2.46 (−7.87)	−1.75 (−7.16)	2.94				

[a] Values in parentheses are based on $\Delta G^\ominus_{t(el)(Total)}$.

[b] Values in parentheses are from eqn. (5).

TABLE 5

Free energies of transfer of [H^+] and related ions in DME+water mixtures at 298 K

Wt.% of DME	$-\Delta G_t^{\ominus}(1)$ (kJ mol^{-1})		$-\Delta G_t^{\ominus}(H^+)_C$ based on [a] (kJ mol^{-1})			Conversion factor ($-Ve$) to be added to get $\Delta G_t^{\ominus}(H^+)_N$ (mole-fraction)	Solubility (mol dm^{-3})		$-\Delta G_t^{\ominus}$ [b] (kJ mol^{-1})	
	bipy	phen	bipy	phen	Average		bipy	phen	bipyH^+	phenH^+
10	1.71	2.11	1.47 (1.22)	1.87 (1.62)	1.67 (1.42)	0.21	0.1077	0.0629	2.77 (2.52)	3.36 (3.11)
20	3.25	2.97	2.71 (2.14)	2.43 (1.86)	2.57 (2.00)	0.45				
30	4.34	3.99	3.43 (2.45)	3.08 (2.10)	3.26 (2.28)	0.71	0.3499	0.2206	4.65 (3.67)	6.17 (5.19)
40	5.71	5.02	4.33 (3.11)	3.64 (2.42)	3.99 (2.77)	1.01				
50	6.90	5.99	4.88 (2.91)	3.97 (2.00)	4.43 (2.46)	1.34	0.9256	0.3255	5.67 (3.48)	6.31 (4.12)
60	7.65	7.19	4.80 (2.07)	4.34 (1.61)	4.57 (1.84)	1.73				
70	8.33	8.62	4.00 (0.18)	4.29 (0.47)	4.15 (0.33)	2.20	1.4539	0.9028	5.08 (1.26)	5.93 (2.11)
80	7.76	8.27	1.16 (−4.19)	1.67 (−3.68)	1.42 (−3.94)	2.76				
90	6.39	5.76	−5.14 (−12.79)	−5.77 (−13.42)	−5.46 (−13.11)	3.44				

[a] Values in parentheses are based on $\Delta G^{\ominus}_{t(el)(Total)}$.

[b] Values in parentheses are from eqn. (5).

TABLE 6

Comparison of $-\Delta G_t^\ominus(H^+)$ (kJ mol^{-1}) values determined in the present work with those reported by Kundu and co-workers

Wt.% of ME or DME	ME		DME	
	Present work [a]	Kundu and co-workers [28]	Present work [a]	Kundu and co-workers [29]
10	1.3 (1.2)	0.2	1.9 (1.6)	2.0
30	3.0 (2.3)	2.3	4.0 (3.0)	5.9
50	4.2 (2.6)	4.4	5.8 (3.8)	10.5
70	5.0 (2.1)	5.3		

[a] Values in parentheses are based on $\Delta G^\ominus_{t(el)(Total)}$.

ably at higher percentages. However, an error to the extent of 0.5 kJ mol^{-1} can be assumed owing to errors in the determination of pK values in mixed solvents, and other extraneous factors. This is particularly reassuring when we consider that an error to the extent of 8–12 kJ (g ion)$^{-1}$ is usually associated with single ion free energies [27].

It is apparent that the different equations give different results, and slight fluctuations in $\Delta G_t^\ominus(H^+)$ are to be expected in view of the inherent limitations involved in any method of calculation of single ion values involving extrathermodynamic assumptions. The agreement between the $-\Delta G_t^\ominus(H^+)$ values (mole-fraction scale) determined in the present work with those reported by Kundu and co-workers [28,29] using the TATB method (see Table 6) is very good (except at 50 wt.% DME), despite the widely divergent methods used.

The values of $\Delta G_t^\ominus(H^+)$ become increasingly negative in going from water to ME + water or DME + water mixtures, indicating that the binary mixtures are more basic than water. The basicity reaches a maximum at 80 wt.% of ME (ME : $H_2O \approx 1:1$) and at 70 wt.% DME (DME : $H_2O \approx 1:2$). Thereafter, basicity decreases and ultimately reaches a level less than that of water, at about 90 wt.% of organic solvent.

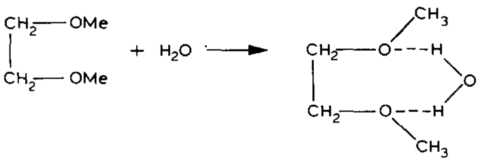
The results suggest that ME and DME are probably less basic than water. It is also apparent that DME + water mixtures are comparatively more basic than ME + water mixtures.

These findings can be easily understood in terms of structural considerations.

ME, with one methoxy group, is quasiprotic in character and is less acidic than water owing to restricted availability of the hydrogen-bonded acidic H atom. Since the acidity of the co-solvents is likely to be relayed through the co-operative structure of hydrogen-bonding between the co-solvent and water molecules in the aqueous solutions [28,30,31], the possible hydrogen-bonded co-solvent water complex should make the ME + water mixture less acidic than water. This explains the increase in basicity and consequent decrease in pK values with increasing ME content. The dipolar aprotic DME, having no acidic hydrogen atom, is highly hydrophilic, and more basic than ME owing to the presence of two flexible electron-rich ethereal O atoms. The changes in basicity are reflected in the free energy of transfer of the H^+ ion ($\Delta G_t^{\ominus}(H^+)_{ME} > \Delta G_t^{\ominus}(H^+)_{DME}$) and the p$K$ values of the ligands ($pK_{ME+water} > pK_{DME+water}$).

Addition of an organic solvent to water usually enhances the three-dimensional structure of the water molecules. However, owing to the presence of $-OCH_3$ groups the addition of ME or DME induces an initial breakdown of the three-dimensional structure of water, followed by a possible structure promoting the effect of hydrogen-bonded ME + water and DME + water complexation, which increases to 80 wt.% ME and 70 wt.% DME. However, the basicity of ME is considerably reduced, owing to intramolecular hydrogen bonding.

In the case of DME, a transition takes place in the region 70–82 wt% where DME, $2H_2O$ is converted to a DME, H_2O complex. Intermolecular hydrogen bonding may also occur in this region, leading to the decrease in basicity.



The changes in pK values and the decrease in basicity at higher compositions can be attributed to breaking up of the structure of the solvent complexes and the consequent formation of a pure solvent structure. Pure ME and DME appear to be less basic than water, contrary to expectations based on their structures. It should be noted that the basicity of a solvent in the gaseous state is a microscopic property, being determined by the intrinsic properties of individual molecules in relation to their structures; but the basicity of a solvent in the liquid state is a macroscopic property, being determined by hydrogen bonding, molecular associations, polarizability, dipole moment, and a host of other factors. Thus, for solvents in the liquid state the acidic and basic properties belong to the entire phase [32] and have less localized meaning.

Therefore, the order in the basicity of the gaseous state [32] $Bu^tOH > EtOH > MeOH > H_2O$ can be explained in terms of an increase in the electron density on the O atom owing to the inductive effect of the alkyl group. This order reverses in the liquid state, owing to structural complexities, though MeOH + water and EtOH + water mixtures are more basic than water because of the structural breakdown of water molecules.

Thus, ME and DME may be more basic than water in the gaseous phase but the order of basicity probably changes in the liquid state. It should be noted that the basicity of the solvent molecules usually arises from the attachment of H^+ ions to the oxygen or nitrogen atoms (with a lone pair of electrons) of these solvent molecules.

The basicity, being a macroscopic property, should change from solvent to solvent as there are approximately 55.5 mol of water, 31 mol of CH_3OH, 22 mol of C_2H_5OH, 16 mol of ethylene glycol (EG), 13 mol of ME, and 11 mol of DME in 1000 g of solvent. The number of O atoms (determining cation–O-centre interacting capacities) and other bulk properties change drastically in the liquid state. Thus, water is more basic than ME and DME in the liquid state, but diprotic DME with two electron-rich O atoms should be more basic than ME. This is corroborated by the trends in our $\Delta G_t^\ominus(H^+)$ values for ME + water and DME + water.

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REFERENCES

1 D.K. Hazra and S.C. Lahiri, Anal. Chim. Acta, 79 (1975) 335.
2 D.K. Hazra and S.C. Lahiri, J. Ind. Chem. Soc., 53 (1976) 787.
3 C.C. Deb, D.K. Hazra and S.C. Lahiri, Bull. Soc. Chim. Belg, 93 (1984) 421.
4 C.C. Deb, D.K. Hazra and S.C. Lahiri, Z. Phys. Chem. Leipzig, 266 (1985) 198.
5 J.F. Garst, in J.F. Coetzee and C.D. Ritchie (Eds.), Solute–solvent interactions, Marcel Dekker, New York, 1969, Chap. 8.
6 A.P. Kreshikov, OS Novy Analiticheskoi Khimii (Fundamentals of Analytical Chemistry), Izd. Khimiya, Moscow, 1970, Vol. 5.
7 A.G. Schwartz and J.B. Barkar, Talanta, 22 (1975) 773.
8 R.C. Weast (Ed.), Handbook of Chemistry and Physics, 67th edn., CRC Press, Boca Raton, FL, 1986–87, p. C273.
9 D. Sengupta, A. Pal and S.C. Lahiri, J. Chem. Soc., Dalton Trans., (1983) 2685.
10 A.K. Bhattacharyya, D. Sengupta and S.C. Lahiri, Z. Phys. Chem. Leipzig, 265 (1984) 372.
11 H. Sadek, Th.F. Tadros and A.A. El-Harakany, Electrochim. Acta, 16 (1971) 339.
12 E. Renard and J. Claude Justice, J. Soln. Chem., 3 (1974) 8.
13 E.J. King, in A.K. Covington and T. Dickinson (Eds.), Physical Chemistry of Organic Solvent Systems, Plenum Press, London, 1973, Chap. 3.
14 L.G. van Uitert and C.C. Haas, J. Am. Chem. Soc., 75 (1953) 451.
15 R.G. Bates, Determination of pH. Theory and Practice, Wiley-Interscience, New York, 1973, p. 276.

16 H.M.N.H. Irving and U.S. Manhot, J. Inorg. Nucl. Chem., 30 (1968) 1215.
17 U.C. Bhattacharyya and S.C. Lahiri, Z. Phys. Chem. Neue Folge, 50 (1966) 131.
18 S.K. Pal, U.C. Bhattacharyya, S.C. Lahiri and S. Aditya, J. Ind. Chem. Soc., 46 (1969) 497.
19 S.C. Lahiri and S. Aditya, J. Ind. Chem. Soc., 51 (1974) 319.
20 A. Bhattacharyya and S.C. Lahiri, J. Ind. Chem. Soc., 57 (1980) 604.
21 M. Born, Z. Phys., 1 (1920) 45.
22 J.J. Kim, Z. Phys. Chem. Neu Folge, 113 (1978) 129; J. Phys. Chem., 82 (1978) 191.
23 J.S. Muirhead-Gould and K.J. Laidler, Trans. Farad. Soc., 63 (1967) 944.
24 J.O'M. Bockris and A.K.N. Reddy, in Rosetta (Ed.), Modern Electrochemistry, Vol. I, Plenum/Rosetta, New York, 1973, Chap. 2.
25 J.A. Riddick and W.B. Bunger, Techniques of Chemistry, Vol. II: Organic Solvents, Wiley-Interscience, New York, 3rd edn., 1970, pp. 469, 213.
26 M.H. Abraham and J. Liszi, J. Chem. Soc. Faraday Trans. I, 76 (1980) 1219.
27 O. Popovych, in I.M. Kolthoff and P.J. Elving, Treatise on Analytical Chemistry, Vol. I, Wiley, New York, 2nd edn., 1978, Part I, Chap. 12.
28 A. Bhattacharyya, A.K. Das and K.K. Kundu, Indian J. Chem., 20A (1981) 347.
29 J. Datta and K.K. Kundu, Can. J. Chem., 59 (1981) 3141.
30 D. Feakins, in F. Franks (Ed.), Physico-chemical Processes in Mixed Aqueous Solvent, Heinemann, London, 1967, p. 71.
31 K.H. Khoo, J. Chem. Soc. B, (1971) 2932.
32 E.J. King, in A.K. Covington and T. Dickinson (Eds.), Physical Chemistry of Organic Solvent Systems, Plenum, London, 1973, p. 335.