Medium Effects on Deprotonation of Phthalic and Biphthalic Acids in Aqueous Binary Mixtures of Some Protic, Aprotic, and Dipolar Aprotic Cosolvents

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Deprotonation constants of phthalic acid (H_2A), $(K_a)_{H_2A}$, and biphthalic acid (HA^-), $(K_a)_{HA^-}$, have been determined at 25 °C by measuring the e.m.f.s of galvanic cells comprising glass and Ag–AgCl electrodes in aqueous mixtures of organic cosolvents of different chemical nature, *viz.* protic glycerol (GL), aprotic dioxane (D), protophobic dipolar aprotic acetonitrile (ACN), and protophilic dipolar aprotic dimethyl sulphoxide (DMSO). Medium effects on deprotonation of the acids: $\delta(\Delta G^\circ_{diss}) = 2.303\ RT\ [p(_sK_a) - p(_wK_a)]$ have been dissected into transfer free energies ΔG°_t of the species involved by evaluating ΔG°_t of the uncharged acid (H_2A) from the measured solubilities of the acid and using ΔG°_t of H^+ based on the widely used tetraphenylarsonium tetraphenylboride (TATB) reference electrolyte assumption, as reported earlier for the solvents. The contributions of the different species involved in the protolytic equilibria, *viz.* H^+, acids (H_2A or HA^-), and their respective conjugate bases (HA^- or A^{2-}) are discussed in terms of their solvation behaviour as guided by the 'acid–base', dispersion, structural, and electronic characteristics of the acid–base species and of the cosolvent molecules and their aqueous mixtures, besides the Born-type electrostatic interactions on the ionic acid–base species.

Despite extensive studies[1–8] the medium effects on deprotonation or protolytic equilibria of weak Brønsted acids of different charge types can hardly be taken as completely understood. Previously these effects were believed to be chiefly guided by the change of dielectric constant of the solvents. But with the recent observation that the extent of some protolytic reactions is found to differ in different isodielectric solvent systems,[8] it has been recognized that the dielectric constant cannot be the sole factor but the chemical nature of the cosolvents also plays an important role in dictating the overall solvent effects. But since the estimation of the dielectric constant or 'Born-type electrostatic effect'[4] is still a difficult task, the 'chemical' effect is hard to discern. Consequently, the true understanding of the effect of changing solvents on protolytic equilibria remains an intriguing problem.

Recently however, it has been increasingly recognized[8] that another way of estimating the medium effect on protolytic equilibria of acids and bases is to dissect the contributions of different species involved in the reaction and to understand the behaviour of the individual species in the light of physicochemical properties like acidity, basicity, dispersion, structural, and electronic characteristics of the cosolvents. Evidently, one of the essential prerequisites for understanding the protolytic equilibria is the evolution of solvation energies or at least transfer free energies ΔG°_t, of the involved species from the reference solvent to the solvents concerned.

Thus, as has been indicated earlier,[8] understanding of the solvent effects on the deprotonation of acids (A^{z+}) of different charge types becomes easier if we consider the protolytic equilibria of the acid–base system (A^{z+}–$B^{(z-1)+}$) in a particular solvent SH with respect to that in the reference solvent, water,

$$A^{z+}(s) + B^{(z-1)+}(w) + SH(s) + H_3O^+(w) \longrightarrow A^{z}+(w) + B^{(z-1)+}(s) + H_2O(w) + SH_2{}^+(s) \quad (1)$$

i.e. process (1) where (w) and (s) denote that the respective species are in the standard state in the reference solvent water (H_2O) and the solvent (SH), respectively.

Consequently, the standard free energy change $\delta(\Delta G^\circ_{diss})_{A^{z+}}$ accompanying process (1) is given by equation (2) where

$$\delta(\Delta G^\circ_{diss})_{A^{z+}} = \Delta G^\circ_t(H^+) + \Delta G^\circ_t(B^{(z-1)+}) - \Delta G^\circ_t(A^{z+}) \quad (2)$$

$\Delta G^\circ_t(H^+)$ stands for the free energy change of process (3) and

$$SH(s) + H_3O^+(w) \longrightarrow H_2O(w) + SH_2{}^+(s) \quad (3)$$

$\Delta G^\circ_t(i)$ is the Gibb's energy change accompanying the transfer of the species (i) from the standard state in the reference solvent water (w) to that in the solvent (s), *i.e.* of the process i(w)→i(s).

Evidently, solvent effects on the protolytic equilibria of the acids in the solvent with respect to that in water are related to the deprotonation constant [equation (4) where the subscript s

$$\delta(\Delta G^\circ_{diss})_{A^{z+}} = 2.303\ RT[p(_sK_a)_{A^{z+}} - p(_wK_a)_{A^{z+}}] \quad (4)$$

refers to the solvent and w to water]. Consequently, as equations (2) and (4) suggest, the estimates of individual species are an aid to better understanding of the solvent effects on deprotonation of the acids, provided ΔG°_t of the neutral acid A° be determined by a suitable method and that of H^+ in the solvent be known.

Now $\Delta G^\circ_t(i)$ of single ions including H^+, though not accessible from direct measurements, have been recently evaluated in various aquo-organic solvents, including the cosolvents of our present studies, by a reasonable extrathermodynamic assumption such as the widely used tetraphenylarsonium tetraphenylboride (Ph_4AsPh_4B = TATB) reference electrolyte (RE) assumption:[9] ΔG°_t (Ph_4As^+) = ΔG°_t (Ph_4B^-) = $\frac{1}{2}\Delta G^\circ_t$ (Ph_4AsPh_4B). Moreover, if the neutral acid A° is solid, $\Delta G^\circ_t(A^\circ)$ can conveniently be determined from solubility measurements. Consequently, as equation (2) and (4) suggest, ΔG°_t (B^{-1}) of the conjugate base B^- would be accessible, if the deprotonation constants (K_a) of the acid A° is determined by suitable methods.

In this paper attempts have been made to examine the medium effects on deprotonation equilibria of the acids of different charge types but of similar structural and chemical nature such as neutral phthalic (H_2A) and negatively charged biphthalic (HA^-) acids in a series of aqueous binary mixtures of several cosolvents having different physicochemical characteristics such as protic glycerol (GL), aprotic dioxane (D), protophobic dipolar aprotic acetonitrile (ACN), and protophilic dipolar aprotic dimethyl sulphoxide (DMSO), in the light of the solvation behaviour of the individual species involved in the deprotonation equilibria. It is hoped that such analysis would help impart important information on the solvation behaviour of these acids and their respective conjugate bases, as would be guided by the influence of varying acidity, basicity, dispersion, structural, and electronic characteristics of the cosolvents and their aqueous mixtures, besides the varying Born-type electrostatic interactions on the ionic species involved.

Deprotonation constants (K_a) of the acid H_2A or HA^- were determined at 25 °C from e.m.f. measurements of a cell of type [A] at different ionic strengths (μ) of the appropriate buffer

$$\text{Glass–H}^+/\text{H}_2\text{A or HA}^-\ (m_1),\ \text{HA}^-\text{ or A}^{2-}\ (m_2),\ \text{KCl}\ (m_3),\ \text{solvent/AgCl–Ag}\quad [\text{A}]$$

solutions. The required standard e.m.f.s of cell [A] were obtained by measuring e.m.f.s of cell [B] at different molalities

$$\text{Glass–H}^+/\text{HCl}\ (m_1),\ \text{solvent/AgCl–Ag}\qquad [\text{B}]$$

(m) of HCl in each composition of the different solvent systems. Also, ΔG_t° values of the neutral acid H_2A were determined at 25 °C by measuring the saturated solubilities of the acid in different solvents at that temperature.

Experimental

The quality of the solvents and the procedures for their purification have been described.[10] Phthalic acid (GR; Merck) and potassium hydrogen phthalate (AR; B.D.H.) were dried in a desiccator for several days before use. Triply distilled water was used and mixed solvents were prepared by mass dilution. The Glass–H^+ electrode was from Elico (India), model H-51, and the Ag–AgCl electrodes were prepared by the thermal electrolytic method.[11] The reversibility of the glass–H^+ electrodes in water and in 50 wt % aqueous cosolvents was tested by comparing the differences of the measured e.m.f.s of the cell with 0.01 and 0.05M-HCl solutions and those expected from the Nernst equation after due correction for the mean activity coefficients of HCl as obtained from literature data[12] or from extended Debye–Hückel equation with ion-size parameter $a_o = 0.4$ nm. The observed results compared fairly well. Moreover, ΔG_t°(HCl) values obtained by use of cell B for 50 wt % cosolvents also agreed fairly well with the literature values.[10,13] E.m.f. values of the cells were measured by a Kiethly model-616 digital electrometer.

Cell vessels for e.m.f. measurements of cells [A] and [B] were essentially double-walled Pyrex vessels (150 ml) with provision for the circulation of water from a thermostat through the annulus space and fitted with three standard joints at the mouth which allowed air-tight insertion of the Ag–AgCl and glass–H^+ electrodes and the tip of a weight pipette. There was also a provision for passing H_2 gas presaturated with solvent vapour, near the bottom of the side wall of the vessels, which escaped through a small bubbler attached to the upper end of the vessel. The cell solutions could be stirred by a magnetic stirrer whenever necessary.

A known amount of the solvent was first placed in the cell vessel. Electrodes were then inserted at their respective positions and then known amounts of a stock concentrated buffer or HCl solution of ionic strength *ca.* 0.3 were added from a weight pipette. After allowing sufficient time for thermal equilibrium by circulating water from a thermostat at 25 °C, the e.m.f. readings were noted at fixed intervals. Initial readings were found to drift with time but with decreasing rates, for *ca.* 10 min or more. Equilibrium e.m.f. values as judged by the constancy of 0.5 mV were attained within 15—20 min, which were found to remain constant for *ca.* 30 min, when tested for some readings in each case. Successive additions of the stock solutions were made so as to get e.m.f. data for the respective cells for different ionic strengths which varied between 0.01 and 0.1. The equilibrium e.m.f.s E_A and E_B of the cells [A] and [B] respectively were recorded after each addition of the electrolyte in each case.

Solubilities (S) of phthalic acid were determined by a method essentially similar to that described earlier.[8] Sufficient amounts of solid acid (H_2A) were added to 30—40 ml solvents taken in a series of well stoppered Jena bottles, and shaken in a mechanical shaker at a low speed for *ca.* 12 h at room temperature (25—28 °C). The bottles were then thermostatted at 25 ± 0.1 °C for a few days with occasional shaking. Portions of each solution were withdrawn at 2 day intervals, using specially constructed pipettes fitted with G_3-Gooch discs, weighed, and then estimated by titrating with a standard KOH solution using phenolphthalein as indicator. The operations were repeated until successive readings agreed with ±1%. The observed solubilities S are listed in Table 2.

Results

The equilibrium e.m.f. values E_B of cell [B] for different molalities (m) of HCl in each solvent mixture were used to evolve E°_{cell} of cells [A] and [B] from the usual relation (5)

$$E^{\circ'} = E_B + 2k\log {}^{m}\text{HCl} - 2k\,S_f m^{\frac{1}{2}} = (E^\circ_{\text{cell}})_B + bm \qquad (5)$$

where $k = 2.303\,RT/F$ and S_f = the Debye-Hückel constant as given by $S_f = 1.824 \times 10^6/(\varepsilon T)^{\frac{3}{2}}$ and computed by taking dielectric constant values of the solvents from the literature.[10a—d] Plots of $E^{\circ'}$ against m were found to be linear, and on extrapolation to $m = 0$ yielded E°_{cell} which is the same for both cells [A] and [B].

As phthalic acid (H_2A) is moderately strong in most of the solvent mixtures, $p(K_a)_{H_2A}$ values were obtained by plotting $p(K'_a)_{H_2A}$ values against μ and extrapolating to $\mu = 0$, where $p(K'_a)_{H_2A}$ values are given by equation (6)[12] and the apparent H^+ concentration (m'_H) by equation (7) where $\mu = m_2 + m_3 + m_H'$ and d_o is the density of the mixed solvent.

$$p(K'_a)_{H_2A} = -\log\frac{(m_2 + m'_H)\,m'_H}{m_1 - m'_H} + 2\,S_f\,(\mu d_o)^{\frac{1}{2}} \qquad (6)$$

$$-\log m'_H = \frac{E_A - E^\circ_{\text{cell}}}{2.303\,RT} + \log m_{Cl^-} - 2\,S_f\,(\mu d_o)^{\frac{1}{2}} \qquad (7)$$

Biphthalic acid (HA^-) being moderately weak in most of the solvent mixtures, $p(K_a)_{HA^-}$ values for the acid were evaluated in the solvents by plotting the usual extrapolation function $p(K'_a)_{HA^-}$, defined by equations (8) and (9), against μ to $\mu = 0$.

$$p(K'_a)_{HA^-} = \frac{(E - E^\circ_{\text{cell}})\,F}{2.303\,RT} + \log m_{Cl^-} + \log m_{HA^-}/m_{A^{2-}} \qquad (8)$$

$$= p(K_a)_{HA^-} + b\mu \qquad (9)$$

The deprotonation constants of the acids $(K_a)_{H_2A}$ and $(K_a)_{HA^-}$ (on molal scale) correct up to ±0.02 unit are listed in Table 1. The solvent effect on deprotonation constants of the acids relative to that in water, $\delta(\Delta G^\circ_{\text{diss}})$, was computed on mole fraction scale using relation (10) where M_w and M_s are the

$$\delta(\Delta G^\circ_{\text{diss}}) = 2.303\,RT\,[p({}_sK_a) - p({}_wK_a)] + 2.303\,RT\log M_s/M_w \qquad (10)$$

molar (or mean molar) mass of water and the mixed solvents respectively. These values are presented in Table 1.

Table 1. Values of $p(K_a)$ and $\delta(\Delta G^\circ_{diss})$ of phthalic (H_2A) and biphthalic acid (HA^-) in aqueous binaries of GL, D, ACN, and DMSO at 25 °C

Cosolvent	Wt % cosolvent	Mole % cosolvent	$p(K_a)_{H_2A}$	$\delta(\Delta G^\circ_{diss})_{H_2A}$/ kJ mol^{-1}	$p(K_a)_{HA^-}$	$\delta(\Delta G^\circ_{diss})_{HA^-}$/ kJ mol^{-1}
GL	0	0	2.89[a]	0	5.51[a]	0
	30	7.73	3.29	1.57	5.89	1.51
	50	16.36	3.51	2.24	6.19	2.61
	70	31.54	3.54	1.63	6.38	2.93
D	20	4.86	3.46	2.81	5.88	1.67
	40	12.00	3.60	3.13	6.63	5.47
	60	23.47	4.04	4.94	7.53	9.91
ACN	20	9.89	3.61	3.83	5.86	3.06
	40	22.64	3.62	3.55	5.63	4.81
	50	30.50	3.69	3.72	7.64	11.34
DMSO	30	8.99	3.92	5.22	6.38	4.30
	50	18.74	4.14	5.93	7.23	8.61
	70	34.98	4.64	8.08	8.75	16.59

[a] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, The Chemical Rubber Co., Cleveland, 52nd edn., 1971–72, p. D 120.

Table 2. Values of solubility S of H_2A and ΔG°_t of H_2A, HA^-, and A^{2-} in aqueous binary mixtures of GL, D, ACN, and DMSO at 25 °C

Cosolvent	Mole % cosolvent	S/mol kg^{-1}	$\Delta G^\circ_t(H_2A)$/ kJ mol^{-1}	$\Delta G^\circ_t(H^+)^a$/ kJ mol^{-1}	$\Delta G^\circ_t(HA^-)$/ kJ mol^{-1}	$\Delta G^\circ_t(A^{2-})$/ kJ mol^{-1}
GL	0	0.0425	0	0	0	0
	7.73	0.0428	−1.21	1.3	−1.0	−0.8
	16.36	0.0561	−2.30	2.3	−2.4	−2.1
	31.54	0.0733	−3.77	3.9	−6.1	−7.1
D	4.86	0.1498	−3.95	−4.1	3.0	8.7
	12.00	0.5505	−7.77	−6.6	2.0	14.0
	23.47	1.0828	−10.13	−5.2	0.0	15.0
ACN	9.89	0.2344	−4.97	−3.1	2.0	8.7
	22.64	0.5623	−7.51	−4.8	0.8	10.5
	30.50	0.6926	−8.21	−5.0	0.5	16.9
DMSO	8.99	0.1587	−4.35	−5.5	6.3	16.1
	18.74	1.124	−9.86	−11.8	7.8	28.2
	34.98	2.996	−12.98	−22.6	17.7	56.8

[a] $\Delta G^\circ_t(H^+)$ values are taken from refs. 10*a—d*, but slightly modified due to the involved computational error in the previous data.

Standard transfer free energies of the neutral phthalic acid (H_2A) from water to the mixed solvents were obtained by the method of Bates *et al.*[6,8] using relation (11) where α stands for

$$\Delta G^\circ_t(H_2A) = 2.303\,RT\log(1-\alpha_w)S_w/(1-\alpha_s)S_s + 2.303\,RT\log M_s/M_w \quad (11)$$

the degree of ionization of the acid in its saturated solution in the respective solvents. α Values were obtained by use of expression (12) and taking $(K_a)_{H_2A}$ values from Table 1 and $\gamma_\pm$

$$\alpha = \frac{-(K_a)_{H_2A} \pm \sqrt{(K_a)^2_{H_2A} + 4(K_a)_{H_2A} S\gamma_\pm{}^2}}{2\,S\gamma_\pm{}^2} \quad (12)$$

values computed by use of the limiting form of the Debye–Hückel equation. $\Delta G^\circ_t(H_2A)$ values so obtained are presented in Table 2.

Values of $\Delta G^\circ_t(HA^-)$ and $\Delta G^\circ_t(A^{2-})$ were then evaluated with the help of an equation analogous to equation (2), taking the required $\Delta G^\circ_t(H^+)$ values for the solvents from previous papers.[10a–d] These values are listed in Table 2.

Discussion

$\delta(\Delta G^\circ_{diss})$–Composition profiles of both acids H_2A and HA^- for different solvent systems are illustrated in Figure 1. Notably, despite marked differences in the chemical nature of the cosolvents the profiles for either acid are more or less similar in nature in all the solvent systems. This apparent similarity of the overall behaviour of the deprotonation equilibria of the acids in these cosolvent systems is possibly indicative of the intrinsic similarity of the relative behaviour of the respective species involved in these deprotonation equilibria. So, reasonable analysis of the solvent effects on the individual species in each of the solvent systems should be rewarding. Figures 2—5 illustrate

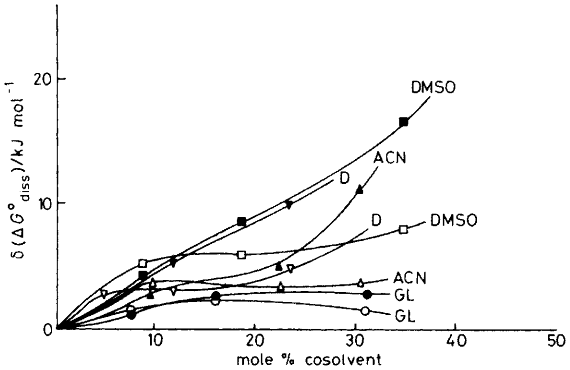


Figure 1. Variation of $\delta(\Delta G^\circ_{diss})$ of phthalic acid (H_2A) (empty notations) and of biphthalic acid (HA^-) (filled notations) with cosolvent composition in aqueous mixtures of glycerol (○,●), dioxane (△,▼), acetonitrile (△,▲), and DMSO (□,■) at 25 °C

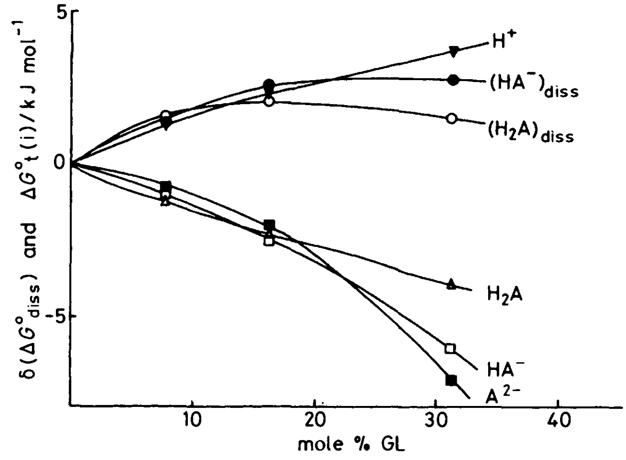


Figure 2. Variation of $\delta(\Delta G^\circ_{diss})$ of phthalic acid (H_2A) (○), biphthalic acid (HA^-) (●), and $\Delta G^\circ_t(i)$ of H^+ (▼), H_2A (△), HA^- (□), and A^{2-} (●) with cosolvent compostion in GL–water mixtures at 25 °C

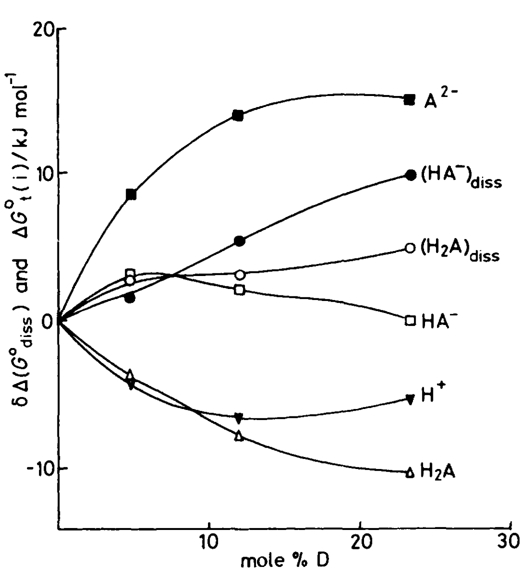


Figure 3. Variation of $\delta(\Delta G^\circ_{diss})$ of phthalic acid (H_2A) (○) and biphthalic acid (HA^-) (●) and ΔG°_t of H^+ (▼), H_2A (△), HA^- (□), and A^{2-} (■) with cosolvent composition in D–water mixtures at 25 °C

the same in the aqueous mixtures of GL, D, ACN, and DMSO, respectively.

In GL–water mixtures (Figure 2) while $\Delta G^\circ_t(H^+)$ values are found to be increasingly positive indicating decreased stabilization of H^+, those for H_2A, HA^-, and A^{2-} are increasingly negative indicating increased stabilization of the species with an increased proportion of GL. Also, while their relative order is $H_2A > HA^- > A^{2-}$ at initial compositions, the reverse is true at higher compositions. These results also conform to what is expected from the effects of acidity, basicity, dielectric constant, dipolar, and dispersive forces of the solvents compared with those of water. Thus, as indicated earlier,[10a] due to the electron-withdrawing propensity of two CH_2 groups in R [$HOCH_2CH(OH)CH_2-$] of GL (= ROH) molecule, the cosolvent GL and its aqueous mixtures are less basic and more acidic than water.[14,15] The observed increased destabilization of H^+ is evidently indicative of the effect of decreased basicity of the solvents. But the observed increased stabilization of neutral phthalic acid (H_2A) suggests that dispersion-type interactions between the π-bonded aromatic nucleus of phthalic acid and the cosolvent molecule GL with large polarizability exceed the opposing decreased basicity effect of these cosolvent mixtures. Moreover, despite the fact that Born-type electrostatic interactions would impart an increased destabilization effect to HA^- and more so to A^{2-}, the observed increased stabilization of the species evidently results from the combined effects of increased dispersion and increased acidity of these solvent mixtures. As this is likely to be more effective at higher cosolvent compositions, the order of stabilization would be $H_2A < HA^- < A^{2-}$, as observed. But at initial compositions, the observed reverse

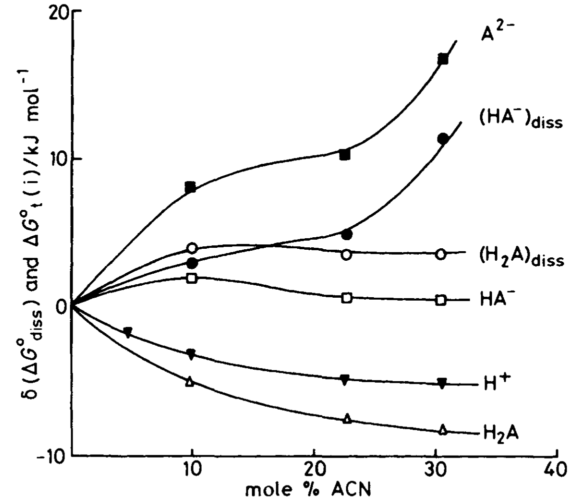


Figure 4. Variation of $\delta(\Delta G^\circ_{diss})$ of phthalic acid (H_2A) (○), and biphthalic acid (HA^-) (●), and ΔG°_t of H^+ (▼), H_2A (△), HA^- (□), and A^{2-} (■) with cosolvent composition in ACN–water mixtures

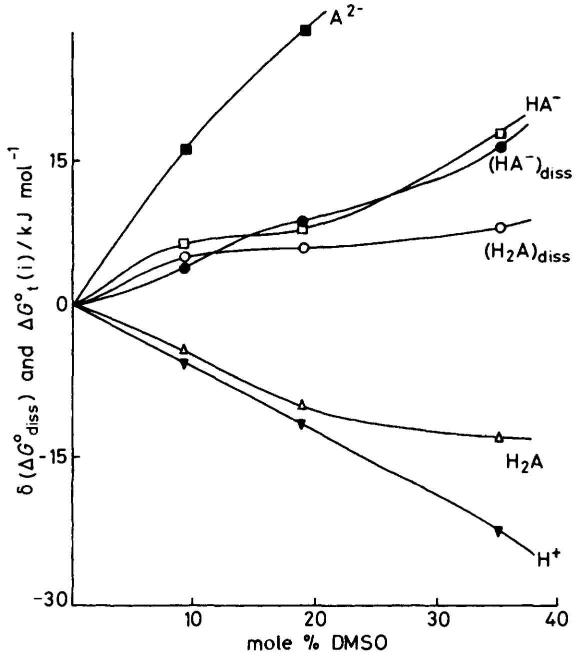
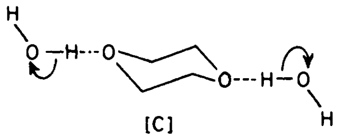
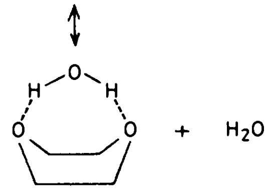


Figure 5. Variation of $\delta(\Delta G^\circ_{diss})$ of phthalic acid (H_2A) (○), and biphthalic acid (HA^-) (●), and ΔG°_t of H^+ (▼), H_2A (△), HA^- (□), and A^{2-} (■) with cosolvent composition in DMSO–water mixtures at 25 °C



[C]



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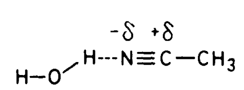
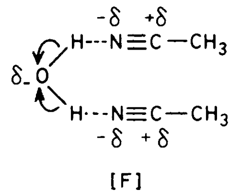


[E]



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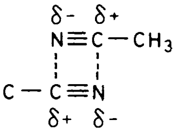

[G]

sequence of stabilization is seemingly the result of predominant dispersion interactions as the superimposed Born-type electrostatic interaction, $\Delta G^\circ_{t,el}$, in the order $\Delta G^\circ_{t,el}(A^{2-}) > \Delta G^\circ_{t,el}(HA^-) > \Delta G^\circ_{t,el}(H_2A) = 0$, partly diminishes the effects of dispersion interactions proportionately.

Unlike in GL–water mixtures, $\Delta G^\circ_t(H^+)$–composition profile in protophilic D–water mixtures (Figure 3) exhibits a minimum at *ca.* 15 mole % D and then tends to become increasingly positive. Evidently, two opposing effects are in operation. Thus, while the cosolvent-induced increased basicity[10b,15,16] of D–water mixtures imparts increased stabilization, the combined effects of Born-type electrostatic interactions and increased aproticity resulting from the shift of 'boat' to 'chair' form of the equilibrium [C] ⟷ [D] impart increased destabilization at higher compositions. Again, the ΔG°_t–composition profile for neutral phthalic acid (H_2A) suggests that solvation of H_2A is chiefly guided by increased dispersion interactions but augmented by the effect of increased basicity at initial compositions and opposed by decreased basicity at higher compositions, thus resulting in the observed near invariance of relative solvation of H_2A at those compositions. On the other hand, while the sharp destabilization of A^{2-} and the hump for HA^- at initial compositions are the proportionate effects of decreased 'acidity', the near invariance of destabilization at higher compositions is the result of opposing effects of increased dispersion interactions and the proportionate destabilizing Born-type interactions on the doubly charged A^{2-} and singly charged HA^-.

Virtually similar are the cases for the aqueous mixtures of protophobic dipolar aprotic cosolvent ACN. Thus, the observed increased solvation of H^+ can be attributed, as before,[10c] to the increased basicity of aqueous ACN resulting from the breakdown[17] of three-dimensional ice-like water structures[18] releasing more basic monomeric water molecules and the possible formation of intercomponent complexes like [E] and [F].[10c,19]

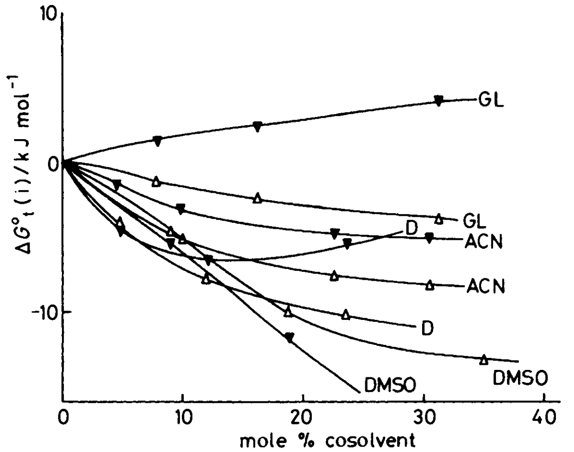

Figure 6. Variation of $\Delta G^\circ_t(i)$ of H^+ (▼) and H_2A (△) with cosolvent compositions in aqueous mixtures of different cosolvents

Also, the observed downward trend of the ΔG°_t–composition profile for neutral H_2A is evidently the effect of increased solvation of H_2A which is due partly to increased basicity and partly to increased dipolar and dispersion interactions between the acid and the cosolvent ACN molecules which have greater dipolar character and greater polarizability[20] than water. On the other hand, the observed upward trend of the ΔG°_t–composition profile of A^{2-} at initial compositions and a sharp upswing at high compositions are the result of combined effects of pronounced Born-type electrostatic interactions on the doubly charged A^{2-} and the pronounced aproticity of mixed solvents as resulted from the possible intercomponent hydrogen-bonded complexes [F] and the dimers of ACN molecules [G].[10c,21,22] The behaviour of HA^-, on the other hand, is as expected intermediate between those of H_2A and A^{2-}. Evidently, while $\delta(\Delta G^\circ_{diss})$ of H_2A is chiefly dictated by the behaviour of $\Delta G^\circ_t(HA^-)$, that for HA^- is by the corresponding behaviour of $\Delta G^\circ_t(A^{2-})$.

Similarly, in aqueous mixtures of DMSO, a protophilic dipolar aprotic cosolvent, the observed increased solvation of H^+ (Figure 5) is dictated by the cosolvent-induced basicity of the solvents[10d,23,24] and that of H_2A by the partial effects of basicity as well as the dipolar and dispersion interactions because of large dipolar character and polarizability of DMSO.[20] Also, the observed increased destabilization of A^{2-} and HA^- is the combined effects of increased aproticity of mixed solvents[10d,23,24] and Born-type interactions overcoming the increased stabilizing effects of dipolar and dispersion interactions. And as the destabilizing effects are pronounced for A^{2-} compared with that for HA^-, the observed ΔG°_t–composition profile for A^{2-} lies far above that for HA^-.

Referring to Figure 6, where ΔG°_t–composition profiles for H^+ and H_2A for the different cosolvent systems are compared, it can be observed that above 10 mole % cosolvent the basicity effects on H^+ are in the order: DMSO > ACN > H_2O > GL. This conforms to expectation for the relative effects of two CH_3 groups on the basic O centre in DMSO, one CH_3 group on the basic N centre in ACN, and of the R group on O centre in GL (≡ ROH) (all relative to that in water). The basicity effect of D–water mixtures, guided by the combined effects of inductive and structure-breaking effects,[15] and a shift of the chair ⟷ boat from the equilibrium[10b] between [C] and [D], leads the $\Delta G^\circ_t(H^+)$–composition profile in this solvent to behave as an 'odd man out'.

Similarly, the observed nature and order of the $\Delta G^\circ_t(H_2A)$–composition profiles, DMSO > ACN > GL > H_2O, also

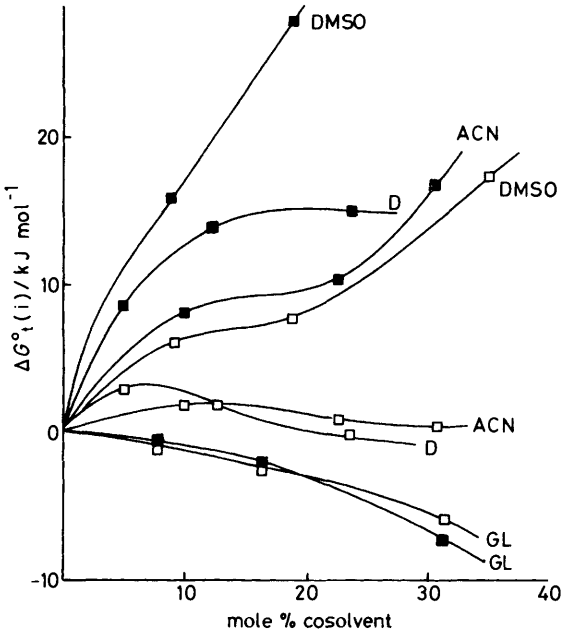

Figure 7. Variation of ΔG_t°(i) of HA$^-$ (□) and A^{2-} (■) with cosolvent composition in aqueous mixtures of different cosolvents

conform to expectations from the effects of larger polarity and polarizability of the cosolvent molecules as well as the relative basicity of their aqueous mixtures. Here as well D is behaving like an 'odd man out', for D–water mixtures behave as the strongest solvating agent at initial compositions, but second to DMSO–water mixtures at higher compositions.

On the other hand, ΔG_t°–composition profiles for HA$^-$ and A^{2-} in different solvents (Figure 7) show that the relative order of destabilization of both HA$^-$ and A^{2-} is: DMSO > ACN > H_2O > GL, D being the same 'odd man out'. These results seemingly indicate that the combined destabilizing effects of increased aproticity of the solvents and Born-type interactions of HA$^-$ and A^{2-} exceed the stabilizing effect of dipolar and dispersion interactions on these organic anions. But the reverse is true in the case of aqueous GL, for GL being protic in nature imparts increased proticity which, besides the dispersion interaction, is seemingly responsible for the enhanced solvation of these anions as is true for small anions like Cl$^-$, Br$^-$, I$^-$ *etc.* in these solvents.[10a]

Thus the foregoing analysis and discussion of the results reveal that the true understanding of the solvent effects on the overall deprotonation of acids and bases becomes relatively easier and in a sense feasible, if it is possible to dissect and understand the behaviour of the species involved in a particular solvent system and of the same species in different solvent systems of systematically varying physicochemical nature.

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