Solute–Solvent Effects in the Dissociation of Thymolsulphonephthalein (an Uncharged Acid) in Aqueous Mixtures of Protic (Methanol) and Dipolar Aprotic (Dimethylformamide) Solvents

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The thermodynamic first dissociation constants, $(_{s}K)_{H_2A}$ of thymolsulphonephthalein, an uncharged acid, have been determined spectrophotometrically at 25 °C in aqueous solutions containing 10, 30, 50, 70, and 80 wt% protic solvent (methanol) and in aqueous solutions containing 20, 40, 60, 70, and 80 wt% dipolar aprotic solvent (*NN*-dimethylformamide) (DMF). $p(_{s}K)^{N}_{H_2A}$ Increases gradually with increase in proportion of methanol in the solvent. In contrast, as DMF is progressively added to water, $p(_{s}K)^{N}_{H_2A}$ decreases sharply at the beginning followed by a very small decrease before showing a weak tendency to rise after *ca.* 40 mol% DMF. The solvent effect on the dissociation of the acid has been discussed in terms of the standard Gibbs energy of transfer of H^+ from water to the mixed solvent, $\Delta G^{\circ}_{t}(H^+)$, and the relative values of the standard Gibbs energies of transfer of HA^-, $\Delta G^{\circ}_{t}(HA^-)$, and of H_2A, $\Delta G^{\circ}_{t}(H_2A)$, in the two solvent systems. The contrasting behaviour of the indicator acid is found to be dictated by the specific solute–solvent interactions of the species involved in the ionization equilibria.

It is now a well recognized fact that the dissociation of weak acids in mixed solvents is a function not only of electrostatic effects but is also largely influenced by specific solvation of the acid, the conjugate base, and the proton. In aqueous mixtures of methanol (MeOH) and of *NN*-dimethylformamide (DMF) having almost the same dielectric constant values for similar mol% non-aqueous components, the solvent effect on dissociation will be of nearly the same magnitude so far as the Born-type electrostatic effect[1] is concerned. Therefore, a study of dissociation in these two solvent systems may be expected to reveal the specific molecular picture of solvation of the species involved in the ionization equilibria. The present paper reports a study of the dissociation of thymolsulphonephthalein, an uncharged acid, in aqueous mixtures of MeOH and of DMF.

The neutral thymolsulphonephthalein molecule can be written as H_2A since it has two ionizable hydrogen atoms, one of which undergoes ionization in the acid range (step i) and the other in the alkaline range (step ii). The two steps may be represented by equation (1). The first stage of ionization of neutral H_2A in the solvent SH is represented by equation (2).

$$\underset{\text{(red)}}{H_2A} \underset{\text{step i}}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{(yellow)}}{HA^-} \underset{\text{step ii}}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{(blue)}}{A^{2-}} \qquad (1)$$

$$H_2A + SH \rightleftharpoons HA^- + SH_2^+ \qquad (2)$$

Results

The expression for the dissociation constant of H_2A, K_{H_2A}, in the molal scale is obtained by combining the mass-law expression for equation (2) with the Debye–Huckel expression for the activity coefficients of the ions concerned. The resulting equation is (3) where $p(_{s}K')_{H_2A}$ is given by equation (4) and $m_{SH_2^+}$ is the effective molality of H^+ in the solution, A and B are the Debye–Huckel constants, I is the ionic strength ($I = m_{HCl}$), and a_0 and β are adjustable parameters of which the former is termed the 'ion size parameter'. In equation (3), $(_{s}K')_{H_2A}$ is the apparent dissociation constant which becomes equal to the thermodynamic dissociation constant, $(_{s}K)_{H_2A}$ at an ionic strength of zero. As the concentration of the ionic species obtained from dissociation of H_2A is extremely small compared with that of m_{HCl}, their contribution to the ionic strength can be neglected. As the indicator concentration is very small, the value of $m_{SH_2^+}$ is practically the same as that of m_{HCl}. Densities[1,2] and dielectric constant[1,3] values necessary for the calculation of Debye–Huckel constants were available from the literature. The values of $m_{HA^-}/m_{H_2A} = (D - D_1)/(D_2 - D)$ were obtained from absorbances D_1, D_2, and D of the completely acidic form (H_2A), completely basic form (HA^-), and the mixture of the two forms measured at an identical total concentration of the indicator in the same cell.[4,5] In the calculation of $p(_{s}K')_{H_2A}$, a_0 was taken to be zero, because, this numerical value resulted in linear plots of $p(_{s}K')_{H_2A}$ *versus* I. Other values of $a_0(=1,2,$ *etc.*) also result in straight lines with different slopes and have practically no influence on $p(_{s}K)_{H_2A}$ values.

$$p(_{s}K)_{H_2A} = -\log m_{SH_2^+} - \log\frac{m_{HA^-}}{m_{H_2A}} + \frac{2A\sqrt{I}}{1 + Ba_0\sqrt{I}} - \beta I = p(_{s}K')_{H_2A} - \beta I \qquad (3)$$

$$p(_{s}K')_{H_2A} = -\log m_{SH_2^+} - \log\frac{m_{HA^-}}{m_{H_2A}} + \frac{2A\sqrt{I}}{1 + Ba_0\sqrt{I}} \qquad (4)$$

The values of m_{HCl}, spectral absorbances D, and $p(_{s}K')_{H_2A}$ are given in Tables 1 and 2. The $p(_{s}K)_{H_2A}$ values obtained in the molal scale in different solvents are given at the bottom of the column of $p(_{s}K')_{H_2A}$. The uncertainty in the $p(_{s}K)_{H_2A}$ value is *ca.* ±0.01 unit for methanol–water and ±0.02 for DMF–H_2O. ($p_{w}K$ 1.60) In water agrees excellently with that reported in the literature.[6]

Discussion

For the sake of comparison[7] in different solvents, the molal scale values of $p(_{s}K)_{H_2A}$ have been converted into the mole fraction scale $p(_{s}K)^{N}_{H_2A}$, by the relation[8] $p(_{s}K)^{N}_{H_2A} = p(_{s}K)_{H_2A} + \log(1000/M_{SH})$ where M_{SH} is the average molecular weight of the mixed solvent. The $p(_{s}K)^{N}_{H_2A}$ values are recorded in Table 3. In order to have a better understanding of the solvent

Table 1. Data for spectrophotometric determination of $p({}_sK)_{H_2A}$ of thymolsulphonephthalein in methanol–water at 25 °C

m_{HCl}	D	$p({}_sK')_{H_2A}$	m_{HCl}	D	$p({}_sK')_{H_2A}$
Water; [Indicator] 1.37×10^{-5} M			50 wt% MeOH; [Indicator] 1.12×10^{-5} M		
Completely basic	0.011		Completely basic	0.009	
0.006 219	0.087	1.601	0.005 932	0.093	1.821
0.012 44	0.136	1.611	0.011 87	0.141	1.847
0.024 85	0.196	1.618	0.017 95	0.171	1.857
0.037 46	0.235	1.629	0.023 83	0.197	1.889
0.049 93	0.261	1.638	0.035 55	0.231	1.933
0.061 50	0.281	1.652	0.047 37	0.253	1.967
0.074 82	0.296	1.663	0.059 44	0.272	2.016
0.087 07	0.308	1.663	0.071 36	0.285	2.051
0.099 51	0.318	1.671	0.083 08	0.298	2.105
Completely acidic	0.456		Completely acidic	0.377	
$p({}_wK)_{H_2A}$ 1.60			$p({}_sK)_{H_2A}$ 1.80		
10 wt% MeOH; [Indicator] 1.43×10^{-5} M			70 wt% MeOH; [Indicator] 1.38×10^{-5} M		
Completely basic	0.010		Completely basic	0.013	
0.006 160	0.095	1.645	0.005 003	0.146	2.071
0.012 33	0.147	1.651	0.007 502	0.180	2.076
0.024 72	0.214	1.670	0.010 04	0.208	2.090
0.036 84	0.255	1.689	0.014 99	0.247	2.113
0.049 17	0.283	1.702	0.020 45	0.271	2.114
0.061 75	0.307	1.726	0.025 07	0.292	2.142
0.073 96	0.324	1.744	0.030 06	0.306	2.153
0.086 49	0.337	1.756	0.035 04	0.322	2.184
0.098 58	0.346	1.762	0.040 02	0.332	2.199
Completely acidic	0.476		Completely acidic	0.461	
$p({}_sK)_{H_2A}$ 1.64			$p({}_sK)_{H_2A}$ 2.05		
30 wt% MeOH; [Indicator] 1.31×10^{-5} M			80 wt% MeOH; [Indicator] 1.72×10^{-5} M		
Completely basic	0.011		Completely basic	0.015	
0.005 619	0.097	1.753	0.003 304	0.178	2.225
0.011 25	0.147	1.761	0.004 947	0.220	2.228
0.022 46	0.211	1.795	0.006 613	0.257	2.247
0.033 87	0.249	1.816	0.009 894	0.311	2.282
0.044 92	0.275	1.839	0.013 20	0.344	2.296
0.056 29	0.297	1.874	0.016 44	0.368	2.310
0.066 10	0.309	1.888	0.019 97	0.393	2.340
0.078 94	0.323	1.913	0.023 15	0.410	2.362
0.091 03	0.335	1.943	Completely acidic	0.578	
Completely acidic	0.943				
$p({}_sK)_{H_2A}$ 1.74			$p({}_sK)_{H_2A}$ 2.20		

Table 2. Data for spectrophotometric determination of $p({}_sK)_{H_2A}$ of thymolsulphonephthalein in *NN*-dimethylformamide–water solvents at 25 °C

m_{HCl}	D	$p({}_sK')_{H_2A}$	m_{HCl}	D	$p({}_sK')_{H_2A}$
20 wt% DMF; [Indicator] 1.46×10^{-5} M			70 wt% DMF; [Indicator] 1.29×10^{-5} M		
Completely basic	0.012		Completely basic	0.011	
0.015 49	0.103	1.321	0.026 99	0.072	1.083
0.031 01	0.156	1.339	0.053 87	0.101	1.106
0.046 42	0.190	1.346	0.080 94	0.126	1.160
0.061 93	0.214	1.350	0.1095	0.140	1.180
0.092 81	0.259	1.400	0.1336	0.156	1.229
0.1238	0.278	1.397	0.1612	0.166	1.255
0.1541	0.304	1.444	0.1880	0.179	1.300
Completely acidic	0.488		0.2166	0.186	1.323
			Completely acidic	0.432	
$p({}_sK)_{H_2A}$ 1.31			$p({}_sK)_{H_2A}$ 1.04		
40 wt% DMF; [Indicator] 1.51×10^{-5} M			80 wt% DMF; [Indicator] 1.42×10^{-5} M		
Completely basic	0.012		Completely basic	0.012	
0.027 96	0.094	1.058	0.029 20	0.095	1.220
0.055 86	0.144	1.106	0.058 31	0.126	1.237
0.083 86	0.176	1.130	0.087 77	0.153	1.298
0.1110	0.205	1.174	0.1175	0.172	1.347
0.1395	0.223	1.189	0.1442	0.179	1.362
0.1681	0.245	1.232	0.1776	0.198	1.431
0.2036	0.265	1.270	0.2041	0.202	1.448
0.2235	0.274	1.288	0.2334	0.217	1.510
Completely acidic	0.509		Completely acidic	0.475	
$p({}_sK)_{H_2A}$ 1.03			$p({}_sK)_{H_2A}$ 1.17		
60 wt% DMF; [Indicator] 1.41×10^{-5} M					
Completely basic	0.011				
0.028 84	0.080	1.049			
0.057 50	0.121	1.107			
0.086 47	0.146	1.135			
0.1149	0.162	1.150			
0.1451	0.187	1.216			
0.1743	0.201	1.248			
0.2026	0.212	1.275			
0.2308	0.227	1.322			
Completely acidic	0.468				
$p({}_sK)_{H_2A}$ 1.02					

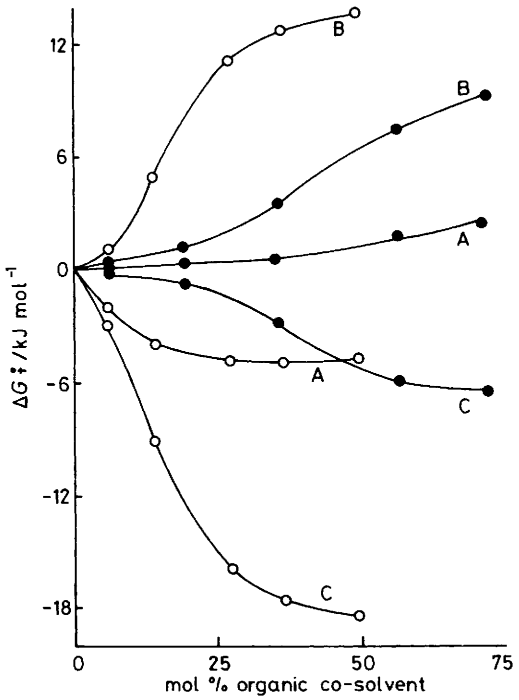
Table 3. Values of $p({}_sK)^N_{H_2A}$ and $\partial(\Delta G^o)$ for thymolsulphonephthalein in MeOH–water and DMF–water solvents at 25 °C [$\partial(\Delta G^o)$ values in kJ mol^{-1} (mole fraction scale)]

wt% MeOH	Mol%	$p({}_sK)^N_{H_2A}$	$\partial(\Delta G^o)$	wt% DMF	Mol%	$p({}_sK)^N_{H_2A}$	$\partial(\Delta G^o)$
0	0	3.344	0	0	0	3.344	0
10	5.88	3.365	0.120	20	5.81	2.983	−2.060
30	19.42	3.424	0.457	40	14.11	2.618	−4.143
50	35.99	3.438	0.536	60	27.00	2.503	−4.800
70	56.75	3.636	1.666	70	36.50	2.459	−5.051
80	72.23	3.758	2.363	80	49.66	2.474	−4.965

effect, the changes of the standard Gibbs energy accompanying the ionization of H_2A in any solvent, ${}_s\Delta G^o$, relative to that in pure water, ${}_w\Delta G^o$, have been computed at 25 °C on the mole fraction scale using equation (5). The $\partial(\Delta G^o)$ values in two solvent systems are recorded in Table 3.

$$\text{Solvent effect} = \partial(\Delta G^o) = {}_s\Delta G^o - {}_w\Delta G^o = 2.303\,RT[p({}_sK)^N_{H_2A} - p({}_wK)^N_{H_2A}] \quad (5)$$

Variation of $\partial(\Delta G^o)$ with mol% organic cosolvent (Figure) shows that solvent effect on the dissociation of H_2A is significantly different in the two solvent systems. As the



Variation of $\partial(\Delta G^\circ)$, $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ of thymolsulphonephthalein, and $\Delta G_t^\circ(H^+)$ at 298.15 K with mol % organic co-solvent: ● MeOH–water; ○ DMF–water. A, $\partial(\Delta G^\circ)$; B, $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$; C, $\Delta G_t^\circ(H^+)$

Table 4. Values of $\Delta G_t^\circ(H^+)$ and $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ in MeOH–water and DMF–water at 25 °C [ΔG°/kJ mol^{-1} (mole fraction scale)]

wt% MeOH	$\Delta G_t^\circ(H^+)^a$	$\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$	wt% DMF	$\Delta G_t^\circ(H^+)^b$	$\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$
10	−0.26	0.380	20	−2.90	0.84
30	−0.69	1.147	40	−9.10	4.957
50	−2.89	3.426	60	−15.90	11.100
70	−5.87	7.536	70	−17.60	12.549
80	−6.58	8.943	80	−18.40	13.435

[a] Ref. 20. [b] Ref. 9.

proportion of organic component increases in the solvent, $\partial(\Delta G^\circ)$ increases gradually in MeOH–water, but in DMF–water it decreases sharply at the beginning followed by a very small decrease before showing a weak tendency to rise after *ca.* 40% DMF. Many other properties of DMF–water mixtures also show an extremum or inflection point around this composition.[9,10]

In view of the fact that addition of MeOH or DMF to water produces a series of solvents of progressively decreasing dielectric constant and the values are nearly equal for the same mole fraction of the organic component it is expected from electrostatic considerations that $\partial(\Delta G^\circ)$ curves will almost coincide and increase with increasing organic mol%. The highly contrasting nature of variation of $\partial(\Delta G^\circ)$ suggests the specific nature of the interaction of the species involved in the ionization equilibria with the solvent molecules.

The solvent effect on the dissociation of H_2A is the resultant of free energy transfer values of the individual species involved in the ionization and is given[1,11,12] by equation (6) where $\Delta G_t^\circ(i)$

$$\partial(\Delta G^\circ) = \Delta G_t^\circ(H^+) + \Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A) \quad (6)$$

is the Gibbs energy change accompanying the transfer of one mole of species i from the standard state in water to the standard state in the solvent concerned, both on the mole fraction scale.

The $\Delta G_t^\circ(H_2A)$ values could not be determined from solubility measurement as in the cases of very weak uncharged bases, tris,[13,14] nitroanilines,[15,16] and weak acid, benzoic acid,[17] because of experimental difficulties. Moreover, saturated solutions of H_2A contained not only neutral species (H_2A) but also appreciable amount of the dissociated form HA^-. Since the values of $\Delta G_t^\circ(H^+)$ for both the solvent systems based on the widely used[18,19] extrathermodynamic method using the reference electrolyte (Ph_4XBPh_4) assumption, $\Delta G_t^\circ(Ph_4X^+) = \Delta G_t^\circ(Ph_4B^-) = \frac{1}{2}\Delta G_t^\circ(Ph_4XBPh_4)$, are available in the literature[9,20] (X = phosphorus for MeOH–water and arsenic for DMF–water), the values of the combined term $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ could be evaluated using equation (6). Variations of $\Delta G_t^\circ(H^+)$ and $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ (Table 4) with mol% nonaqueous component are shown in the Figure.

The $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ curve passes through more positive values in DMF–water, opposite behaviour compared with that observed for $\partial(\Delta G^\circ)$ curves. In view of the fact that dispersion interactions operating both on H_2A and HA^- (each containing three benzene rings) are likely to get cancelled to a large extent in the combined term and that Born-type electrostatic effects on the large anion HA^- are small and nearly the same, it is evident that the difference for $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ in the two solvent systems must be due to the difference of the specific nature of the interaction of the species formed by the solvent molecules.

The two solvents MeOH and DMF differ in one important respect. The hydrogen-bond-donation capacity possessed by MeOH is absent[21] in DMF. The thermodynamic evidence of the well known destabilization of the anion by dipolar aprotic solvents owing to the lack of hydrogen-bond donation is provided by the large positive Gibbs energy transfer from water to aqueous mixtures of DMF for halide ion.[10] The corresponding values in MeOH–water are of smaller positive magnitude.[20] The large positive values of $\Delta G_t^\circ(HA^-) - \Delta G_t^\circ(H_2A)$ in DMF–water compared with those in MeOH–water can therefore be attributed to a large anion destabilization effect of dipolar aprotic solvent, DMF, in comparison to the protic solvent, MeOH.

The interaction of H^+ is reflected in $\Delta G_t^\circ(H^+)$ which may be taken as a measure of relative solvent basicities. The detailed interpretation of the behaviour of $\Delta G_t^\circ(H^+)$ in aqueous mixtures of MeOH and of DMF has been presented.[9,20] The overall dissociation behaviour of the acid in the two solvent systems is primarily dictated by the specific chemical nature of the solute–solvent interaction besides the effect of relative solvent basicities.

Experimental

The purification of methanol,[12] water,[22] and DMF[23] and the preparation[13] of the mixed solvent as well as the solution of HCl have been described. The HCl solution was titrated by the method described earlier.[13] Thymolsulphonephthalein (pro analysi; Merck) was used without further purification. The dissociation constants in the aqueous mixtures of MeOH and DMF were determined spectrophotometrically as in the cases of some acids described earlier.[4,5,12] Since H_2A is a relatively strong acid in the solvents studied, it is possible to achieve a considerable variation of the degree of dissociation by varying the concentration of the strong acid, HCl, and hence the thermodynamic dissociation constant can be determined without recourse to buffer solutions. A series of solutions were prepared in 10 cm^3 amounts by adding weighed amounts of HCl solution, indicator solution, and the appropriate solvent. The spectral absorbances were determined at 25 ± 0.5 °C with a Zeiss spectrophotometer with 1 cm cells at 548 nm where the absorbance shows a maximum for the acid form in water. The limiting absorbance of the acid form (H_2A) was determined in very concentrated solution of HCl (4—6M) but that for the base form (HA^-) was determined in the respective solvents without any addition of alkali.[24,25] The absorbance readings were corrected, where necessary, for the identical total concentration of the indicator. The indicator solution in pure solvent contained virtually only the species HA^- and there was no trace of A^{2-} because measurement at 598 nm (the maximum-absorption wavelength of the blue form, A^{2-}) showed no absorption at all.[4]

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