

was obtained (eq 2). The ratio a_1^0/a_2^0 had a value of 1.1 and

$$\frac{\Delta a_1}{\Delta a_2} = \frac{a_1^0 Y_1}{a_2^0 Y_2} \quad (2)$$

was rather insensitive to the temperature and pressure. When eq 1 and 2 are combined, Δa_1 can be expressed by eq 3.

$$\Delta a_1 = \frac{\Delta a^t}{1 + \frac{a_2^0 Y_2}{a_1^0 Y_1}} \quad (3)$$

The true amount of each component adsorbed is the observed value subtracted by Δa_i .

Results

The isothermal data of adsorption for pure components which have been measured in the desorption process are well correlated in log-log form by the polynomial equation of 7th power

$$\log a = \sum_{i=0}^7 C_i (\log P)^i \quad (4)$$

where a is the amount adsorbed expressed in mmol/g of adsorbent and P is the pressure in Pa. The coefficients of the equations and the standard deviation expressed in mg/g of adsorbent are listed in Table I. The calculated adsorption isotherms essentially include the unremovable adsorptions whose values averaged over two or three runs are also listed in Table I. The equilibrium data for the binary mixtures are shown in Table II. The composition of ethylene in the adsorbed phase increases with pressure at constant vapor-phase composition. The same effect, but to a lesser degree, is shown with increasing temperature.

Registry No. Carbon, 7440-44-0; ethane, 74-84-0; ethylene, 74-85-1.

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Studies of Proton-Transfer Equilibria of Different Charge Type Acids in the Glycerol-Water Solvent System at 25 °C

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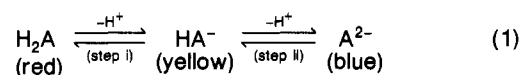
First dissociation constants of thymolsulfonephthalein (H_2A), a neutral acid, second dissociation constants of thymolsulfonephthalein (HA^-), a negatively charged acid, and dissociation constants of *m*-nitroanilinium ion (BH^+), a positively charged acid have been determined spectrophotometrically at 25 °C in glycerol-water mixtures containing 10, 30, 50, and 70 wt % glycerol. Standard Gibbs energies of transfer, $\Delta G^\circ_t(B)$, of *m*-nitroaniline (B) from water to mixed solvents have been evaluated from measurement of solubilities at 25 °C. $p(K)_{H_2A}$ increases gradually, but $p(K)_{HA^-}$ increased rapidly with increase in proportion of glycerol in the solvent. In contrast, the corresponding value of BH^+ decreases, passes through a minimum, and then rises very slowly as mole percent of glycerol increases in the solvent. The widely different nature of solvent effect $\delta(\Delta G^\circ) = 2.303RT[p(K)^N - p(wK)^N]$ for different charge type acids in this solvent system has been interpreted in terms of various types of interaction of all the species involved in the ionization equilibria with the solvent molecules.

Introduction

It is now a well-recognized fact that dissociation of acids in mixed solvent media is not only a function of the electrostatic effect but is also influenced profoundly by specific solvation of the species involved in the ionization equilibria. In order to understand solvent effect on the dissociation of acid in glycerol (GL)-water solvent system, dissociation constants of three different charge type acids have been measured at 25 °C. First dissociation constants of thymolsulfonephthalein (H_2A), a neutral

acid, second dissociation constant of thymolsulfonephthalein (HA^-), a negatively charged acid, and dissociation constants of *m*-nitroanilinium ion (BH^+), a positively charged acid, have been measured in a series of aqueous mixtures of glycerol. The contribution (1) of the base, *m*-nitroaniline (B), to the dissociation of the BH^+ acid was determined from the measurement of solubilities in water as well as in various solvent mixtures.

The neutral thymolsulfonephthalein 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 (step ii). The two steps may be represented as shown in eq 1.



Experimental Section

The purification of the solvents glycerol (GL) and water have been described (2). Thymolsulfonephthalein (proanalysis, E. Merck) was used without any further purification. *m*-Nitroaniline (A.R.) was purified by two crystallizations from aqueous ethanol (95% v/v) and then dried in vacuo. Tris(hydroxymethyl)methylamine (Tris) (Sigma, reagent grade) was used after recrystallization from 75% methanol. HCl solution was prepared and titrated in the manner already described (3).

Since H_2A and BH^+ are relatively strong acids, a considerable variation in the degree of dissociation was achieved by varying the concentration of the added strong acid, HCl, and thermodynamic dissociation constants could be determined without recourse to buffer solutions. In both the cases, a series of solutions were prepared (total volume 10 cm³) by adding weighed amounts of HCl solutions and the solvents to weighed

Table I. Properties of Glycerol-Water Solvents at 25 °C

wt % GL	mol % GL	mean mol wt	10 ⁻³ density ^a / (kg m ⁻³)	dielec const ^b	Debye-Hückel const	
					A/(mol ^{-1/2} kg ^{1/2})	B/(Å ⁻¹ mol ^{-1/2} kg ^{1/2})
0	0	18.02	0.9971 ^c	78.33 ^c	0.5108	0.3286
10	2.12	19.60	1.0207	75.7	0.5435	0.3382
30	7.73	23.75	1.0706	70.0	0.6259	0.3602
50	16.35	30.14	1.1239	64.0	0.7336	0.3860
70	31.33	41.24	1.1784	55.6	0.9277	0.4240

^aReference 6. ^bReference 7. ^cReference 8.

amounts of indicator solutions. A simple calculation gave the molalities of HCl in different solutions. The wavelength (548 nm) used for the measurement of absorbances was that at which the absorption of the acid form H₂A (red in color) was maximum in water. The absorption of the acid form was taken in very concentrated solutions of HCl (~4 M) but that for the base form (HA⁻) was determined in respective solvents without any addition of alkali (4). The indicator solution in the pure solvent contained virtually the species HA⁻ and there was no trace of A²⁻ because absorption at 598 nm (the maximum absorption wavelength of the blue form A²⁻) was negligible. For BH⁺ acid, absorbances were taken at 360 nm which is the maximum absorption wavelength of the base form. The limiting absorbances of the acidic and basic forms were measured in concentrated HCl solution (4–6 M) and in very dilute sodium lyate (0.001 M) solution, respectively. Absorbance readings were taken at 25 ± 0.2 °C with Carl Zeiss Jena (DDR) spectrophotometer with 1-cm cells and absorbance readings were corrected, where necessary, for the identical total concentration of the indicator.

The acid HA⁻ is weak and in order to get a considerable variation of the ratio of the base and acid forms of the indicator acid, a buffer solution containing Tris and Tris H⁺Cl⁻ was used. The base Tris, or its conjugate acid has no absorption in the visible region. Solutions required for study were prepared in 10-cm³ amounts by adding weighed amounts of buffer solution, indicator solution, and the solvent. Buffer solution was prepared by adding weighed amounts of solid Tris and standard HCl solution. The ratio $m_{\text{Tris}}:m_{\text{Tris HCl}}$ was kept constant for a given solvent while the ionic strength was varied. The absorbance readings were taken in 1-cm cells at 598 nm which was the wavelength for maximum absorption of the alkaline form, A²⁻ (blue in color) in water. The absorption of the completely alkaline form was obtained in 0.1 M sodium lyate solution, but that for acid form (HA⁻) was obtained by using pure solvent without any addition of either acid or alkali. The absorption of yellow acid form (HA⁻) was zero at 598 nm.

For the determination of the solubilities of *m*-nitroaniline, a small quantity of solute was added to the appropriate solvent, shaken, and allowed to equilibrate in a thermostat at 25 ± 0.1 °C. Aliquots of each solution were withdrawn and estimated after appropriate dilution with large volume of water so that the medium was essentially aqueous. The estimation was performed spectrophotometrically at 360 nm, from the knowledge of the absorbance of standard indicator solution in water. The saturation equilibrium was reached in 7–10 days, when the concentration showed no further change.

Results

The expression for the dissociation constant of BH⁺, $(\text{p}_s K)_{\text{BH}^+}$, in the molal scale is (3)

$$\begin{aligned} \text{p}_s K_{\text{BH}^+} &= \\ &= -\log m_{\text{SH}_2^+} - \log (\alpha / (1 - \alpha)) - \log (\gamma_{\text{SH}_2^+} \gamma_{\text{B}} / \gamma_{\text{BH}^+}) \\ &= \text{p}_s K'_{\text{BH}^+} - \log (\gamma_{\text{SH}_2^+} \gamma_{\text{B}} / \gamma_{\text{BH}^+}) \\ &= \text{p}_s K'_{\text{BH}^+} - f(I) \end{aligned} \quad (2)$$

The expression for the dissociation constant of H₂A, $(\text{p}_s K)_{\text{H}_2\text{A}}$ in the molal scale is obtained by combining the mass-law ex-

pression for the dissociation equilibrium of H₂A with the Debye-Hückel expression for the activity coefficients (γ_i) of the ions concerned. The resulting equation is (5)

$$\begin{aligned} \text{p}_s K_{\text{H}_2\text{A}} &= \\ &= -\log m_{\text{SH}_2^+} - \log (\alpha / (1 - \alpha)) - \log (\gamma_{\text{SH}_2^+} \gamma_{\text{HA}^-} / \gamma_{\text{H}_2\text{A}}) \\ &= -\log m_{\text{SH}_2^+} - \log (\alpha / (1 - \alpha)) + \\ &\quad 2AI^{1/2}(1 + Ba_0I^{1/2})^{-1} - f(I) \\ &= \text{p}_s K'_{\text{H}_2\text{A}} - f(I) \end{aligned} \quad (3)$$

In the above equations, $m_{\text{SH}_2^+}$ is the effective molality of H⁺ in the solution, α and $1 - \alpha$ are the fractions of the indicator species present in basic form and acid form, respectively, $A = 1.824 \times 10^6 d_s^{1/2} (\epsilon_s T)^{-3/2} \text{ mol}^{-1/2} \text{ kg}^{1/2}$, $B = 50.29 d_s^{1/2} (\epsilon_s T)^{-1/2} \text{ \AA}^{-1} \text{ mol}^{-1/2} \text{ kg}^{1/2}$ are Debye-Hückel constant, a_0 is the adjustable ion-size parameter, and I is the ionic strength being equal to the molality of hydrochloric acid (m_{HCl}) in the solution. The concentration of the ionic species obtained from dissociation of acid (H₂A) being extremely small with respect to m_{HCl} , their contribution to ionic strength can be neglected. Density (d_s) and dielectric constant values (ϵ_s) necessary for calculation of Debye-Hückel constants (A and B) were available from literature (6–8) (Table I). $\text{p}_s K_{\text{HA}^-}$ was determined by using a buffer solution of Tris H⁺ and Tris(B₁). Since both the dissociation equilibria $\text{HA}^- + \text{SH} \rightleftharpoons \text{A}^{2-} + \text{SH}_2^+$ and $\text{B}_1\text{H}^+ + \text{SH} \rightleftharpoons \text{B}_1 + \text{SH}_2^+$ exist in the same solution, the expression for $\text{p}_s K_{\text{HA}^-}$ in the molal scale was obtained by combining the mass-law equations and Debye-Hückel expression for the activity coefficient of the ions concerned. The resulting expression is

$$\begin{aligned} \text{p}_s K_{\text{HA}^-} &= \text{p}_s K_{\text{B}_1\text{H}^+} + \log (m_{\text{B}_1} / m_{\text{B}_1\text{H}^+}) - \\ &\quad \log (\alpha / (1 - \alpha)) + 4AI^{1/2}(1 + Ba_0I^{1/2})^{-1} - f(I) \\ &= \text{p}_s K'_{\text{HA}^-} - f(I) \end{aligned} \quad (4)$$

where α , $(1 - \alpha)$, A , B , a_0 , and I have the same significance as in eq 2. $\text{p}_s K_{\text{B}_1\text{H}^+}$ is the dissociation constant of Tris H⁺, m_{B_1} and $m_{\text{B}_1\text{H}^+}$ are the molalities of Tris and Tris H⁺ in solution. The ionic strength I is equal to $m_{\text{B}_1\text{H}^+\text{Cl}^-}$ (molality of Tris hydrochloride). The concentrations of HA⁻ and A²⁻ being extremely small with respect to $m_{\text{B}_1\text{H}^+\text{Cl}^-}$, their contribution to ionic strength can be neglected. The values of $\alpha / (1 - \alpha) = D - D_1 / D_2 - D$ in all the three cases were obtained from the absorbances D_1 , D_2 , and D of the completely acid form, completely base form, and the mixture of the two forms respectively, measured at an identical total concentration of the indicator in the same cell.

In each instance, $\text{p}_s K'$ is a linear function of ionic strength (I) and thermodynamic dissociation constants $\text{p}_s K$ of the three acids were determined from the respective $\text{p}_s K'$ vs. I plots extrapolated to $I = 0$. Plots of $\text{p}_s K'_{\text{H}_2\text{A}}$ and $\text{p}_s K'_{\text{HA}^-}$ against I for different values of a_0 ($a_0 = 0, 1, 2, 3, 4$) are found to result in straight lines with different slopes and give same value of $\text{p}_s K$.

Values of m_{HCl} , D , and $\text{p}_s K'$ for BH⁺ and H₂A are given in Tables II and III, respectively. Table IV lists the values of I , $\text{p}_s K_{\text{B}_1\text{H}^+}$, $m_{\text{B}_1} / m_{\text{B}_1\text{H}^+}$, D , and $\text{p}_s K'_{\text{HA}^-}$. The values of $\text{p}_s K_{\text{B}_1\text{H}^+}$

Table II. Data for Spectrophotometric Determination of $p_s(K)_{BH^+}$ of *m*-Nitroanilinium Ion at 25 °C in Glycerol-Water Mixtures

m_{HCl}	D	$p_s(K)_{BH^+}$
10 wt % GL; ^a [Indicator] = 3.72×10^{-4} M		
completely basic	0.498	
0.001464	0.390	2.354
0.001837	0.370	2.355
0.003666	0.295	2.363
0.005458	0.255	2.340
0.007391	0.218	2.352
0.009160	0.193	2.360
0.01094	0.174	2.368
0.01268	0.160	2.372
0.01824	0.132	2.364
completely acidic	0.044	
30 wt % GL; ^b [Indicator] = 3.57×10^{-4} M		
completely basic	0.483	
0.001119	0.398	2.324
0.001677	0.367	2.328
0.002255	0.341	2.322
0.004554	0.264	2.334
0.006929	0.220	2.325
0.009302	0.192	2.315
0.01153	0.171	2.318
0.01348	0.153	2.340
0.01865	0.129	2.334
completely acidic	0.041	
50 wt % GL; ^c [Indicator] = 3.49×10^{-4} M		
completely basic	0.458	
0.001138	0.374	2.369
0.001748	0.341	2.370
0.003012	0.286	2.386
0.004024	0.261	2.361
0.006031	0.216	2.371
0.007054	0.198	2.380
0.01016	0.165	2.373
0.01403	0.136	2.385
completely acidic	0.040	
70 wt % GL; ^d [Indicator] = 3.60×10^{-4} M		
completely basic	0.481	
0.001079	0.372	2.520
0.001617	0.334	2.526
0.002588	0.283	2.531
0.003803	0.240	2.530
0.004414	0.221	2.542
0.005092	0.210	2.526
0.005690	0.196	2.536
0.006415	0.183	2.542
completely acidic	0.045	

^a $p_s(K)_{BH^+} = 2.35$. ^b $p_s(K)_{BH^+} = 2.32$. ^c $p_s(K)_{BH^+} = 2.37$. ^d $p_s(K)_{BH^+} = 2.52$.

(Table IV) were taken from literature (9). $p_s(K)_{H_2A}$ and $p_s(K)_{HA^-}$ values reported in Tables III and IV are for $a_0 = 0$. The values of $p_s(K)$ in molal scale are given at the end of each section of the Tables II-IV. pK of H_2A in water, i.e., $p_s(K)_{H_2A}$ reported recently (5) agreed fully with the literature value (10). Literature value of $p(K)_{HA^-}$ in water is 9.20 which compares favorably with our experimental value of 9.19. The uncertainty in the pK value is about ± 0.01 .

The solubilities of *m*-nitroaniline (B) in different solvent mixtures at 25 °C are presented in Table V. Standard free energies of transfer at 25 °C of B from water to aqueous mixtures of GL on the mole fraction scale were calculated (7, 3) by eq 5, where wX_B and sX_B are the solubilities of B in water and

$$\Delta G^\circ_i(B) = 2.303RT \log (wX_B/sX_B) \quad (5)$$

respective solvents (SH) on the mole fraction scale.

Discussion

The solvent effect on the dissociation of the acid, $\delta(\Delta G^\circ)$, in the mole fraction scale, has been calculated by using the

Table III. Data for Spectrophotometric Determination of $p_s(K)_{H_2A}$ of Thymolsulfonephthalein in Glycerol-Water Mixtures at 25 °C

m_{HCl}	D	$p_s(K)_{H_2A}$
10 wt % GL; ^a [Indicator] = 0.70×10^{-5} M		
completely basic	0.006	
0.005159	0.044	1.662
0.01034	0.068	1.662
0.01557	0.088	1.688
0.02073	0.105	1.717
0.02575	0.115	1.718
0.03116	0.126	1.736
0.03590	0.131	1.727
0.04100	0.140	1.752
0.04627	0.146	1.761
completely acidic	0.236	
30 wt % GL; ^b [Indicator] = 0.91×10^{-5} M		
completely basic	0.009	
0.004528	0.061	1.766
0.009048	0.094	1.778
0.01350	0.116	1.780
0.01897	0.142	1.819
0.02257	0.150	1.807
0.02703	0.163	1.825
0.03155	0.175	1.846
0.03644	0.182	1.843
0.04056	0.187	1.841
completely acidic	0.300	
50 wt % GL; ^c [Indicator] = 3.23×10^{-6} M		
completely basic	0.002	
0.003715	0.024	1.937
0.007439	0.037	1.947
0.01116	0.045	1.941
0.01468	0.051	1.945
0.01873	0.058	1.977
0.02246	0.061	1.967
0.02584	0.065	1.990
0.02951	0.068	1.999
0.03337	0.071	2.016
completely acidic	0.108	
70 wt % GL; ^b [Indicator] = 6.17×10^{-6} M		
completely basic	0.003	
0.002879	0.076	2.300
0.005762	0.095	2.299
0.01517	0.134	2.307
0.01732	0.142	2.342
0.02304	0.151	2.349
0.02870	0.156	2.342
0.03453	0.160	2.340
0.04027	0.166	2.377
0.04534	0.168	2.376
completely acidic	0.206	

^a $p_s(K)_{H_2A} = 1.65$. ^b $p_s(K)_{H_2A} = 1.77$. ^c $p_s(K)_{H_2A} = 1.91$. ^d $p_s(K)_{H_2A} = 2.29$.

relation (1, 5, 10), $\delta(\Delta G^\circ) = 2.303RT [p_s(K)^N - p_w(K)^N]$. Values of $p_s(K)^N$ and $\delta(\Delta G^\circ)$ are recorded in Table VI. Figure 1 shows the widely different nature of variation of $\delta(\Delta G^\circ)$ with mole percent GL for different acids. $\delta(\Delta G^\circ)$ is determined by the interactions of H^+ , acid, and its conjugate base with the mixed solvent relative to that of water and can be expressed (11, 12) by eq 6, where $\Delta G^\circ_i(i)$ is the Gibbs energy change

$$\delta(\Delta G^\circ) = \Delta G^\circ_i(H^+) + \Delta G^\circ_i(\text{conjugate base}) - \Delta G^\circ_i(\text{acid}) \quad (6)$$

accompanying the transfer of 1 mol of species *i* from the standard state in water to that in the mixed solvent.

$\Delta G^\circ_i(H^+)$ values for this solvent system based on the widely used reference electrolyte (RE) (RE = Ph_4AsBPh_4 where Ph = phenyl) assumption, $\Delta G^\circ_i(Ph_4As^+) = \Delta G^\circ_i(Ph_4B^-) = 1/2 \Delta G^\circ_i(Ph_4AsBPh_4)$, are available in the literature (13). This permits the computation of the combined terms, viz., $\Delta G^\circ_i(HA^-) - \Delta G^\circ_i(H_2A)$, $\Delta G^\circ_i(A^{2-}) - \Delta G^\circ_i(HA^-)$, and $\Delta G^\circ_i(BH^+)$

Table IV. Necessary Quantities for the Determination of $p_s(K)_{HA^-}$ of Thymolsulfonephthalein in Glycerol-Water Mixtures at 25 °C

<i>I</i>	<i>D</i>	$p_s(K)_{HA^-}$
Water; ^a [Indicator] = 1.93×10^{-5} M $p_s(K)_{B_1H^+} = 8.07$; $m_{B_1}/m_{B_1H^+} = 7.473$		
completely basic	0.461	
0.004043	0.198	9.196
0.01221	0.218	9.216
0.02042	0.228	9.244
0.02879	0.237	9.265
0.03728	0.247	9.275
0.04589	0.257	9.281
completely acidic	0.0	
10 wt % GL; ^b [Indicator] = 1.30×10^{-5} M $p_s(K)_{B_1H^+} = 7.95$; $m_{B_1}/m_{B_1H^+} = 11.45$		
completely basic	0.307	
0.004712	0.133	9.274
0.009455	0.140	9.294
0.01417	0.145	9.313
0.02400	0.154	9.339
0.03382	0.155	9.397
0.04386	0.158	9.435
0.05368	0.160	9.470
completely acidic	0.0	
30 wt % GL; ^c [Indicator] = 1.61×10^{-5} M $p_s(K)_{B_1H^+} = 8.20$; $m_{B_1}/m_{B_1H^+} = 10.96$		
completely basic	0.387	
0.006244	0.178	9.501
0.01251	0.186	9.545
0.01685	0.193	9.556
0.02715	0.204	9.592
0.03495	0.208	9.627
0.04018	0.212	9.642
0.04802	0.217	9.659
completely acidic	0.0	
50 wt % GL; ^d [Indicator] = 1.40×10^{-5} M $p_s(K)_{B_1H^+} = 8.31$; $m_{B_1}/m_{B_1H^+} = 16.83$		
completely basic	0.338	
0.003970	0.147	9.824
0.008023	0.155	9.856
0.01220	0.164	9.868
0.02085	0.167	9.946
0.03448	0.173	10.029
0.05120	0.183	10.090
completely acidic	0.0	
70 wt % GL; ^e [Indicator] = 1.46×10^{-5} M $p_s(K)_{B_1H^+} = 8.55$; $m_{B_1}/m_{B_1H^+} = 25.96$		
completely basic	0.347	
0.004074	0.138	10.362
0.008233	0.150	10.392
0.01241	0.160	10.413
0.02141	0.168	10.491
0.03070	0.175	10.556
0.04051	0.178	10.630
0.04868	0.183	10.665
completely acidic	0.0	

^a $p_s(K)_{HA^-} = 9.19$. ^b $p_s(K)_{HA^-} = 9.25$. ^c $p_s(K)_{HA^-} = 9.48$. ^d $p_s(K)_{HA^-} = 9.80$. ^e $p_s(K)_{HA^-} = 10.33$.

Table V. Solubilities and $\Delta G^\circ_i(B)$ of *m*-Nitroaniline in Glycerol-Water Solvents at 25 °C (ΔG° in kJ mol^{-1} (Mole Fraction Scale))

wt % GL	$10^3 m_B^a$	$10^4 X_B^b$	$\Delta G^\circ_i(B)$
0	6.839 ^c	1.231 ^c	0
10	8.478	1.659	-0.739
30	11.750	2.787	-2.025
50	17.490	5.263	-3.601
70	23.500	9.679	-5.111

^a m_B = solubility in mol/kg of GL + H₂O solvent. ^b X_B = mole fraction of the base in the saturated solution. ^c Reference 1.

- $\Delta G^\circ_i(B)$ from eq 6. Variations of $\Delta G^\circ_i(H^+)$ and of the combined terms (Table VII) with mole percent GL are shown

Table VI. Values of $p_s(K)^N$ and $\delta(\Delta G^\circ)$ for First and Second Dissociation of Thymolsulfonephthalein and *m*-Nitroanilinium Ion in Glycerol-Water Mixtures at 25 °C ($\delta(\Delta G^\circ)$ Values Are in Mole Fraction Scale)

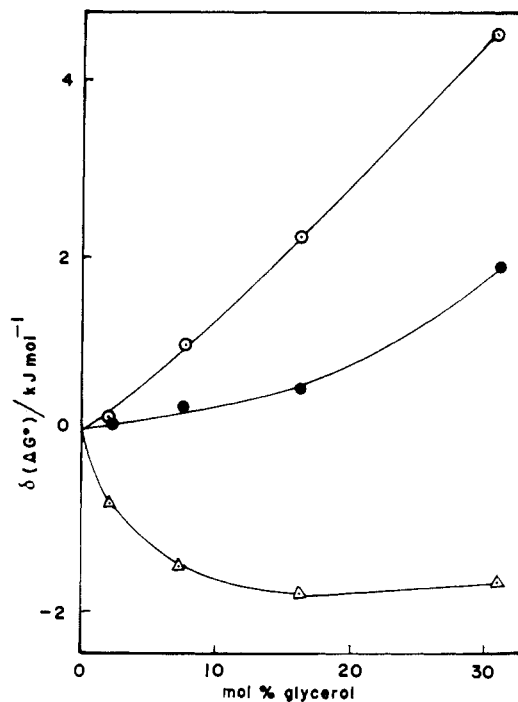
wt % GL	$p_s(K)_{H_2A}^N$ ^c	$p_s(K)_{HA^-}^N$	$p_s(K)_{BH^+}^N$	$\delta(\Delta G^\circ)/(\text{kJ mol}^{-1})$		
				H ₂ A	HA ⁻	BH ⁺
0	3.344 ^a	10.934	4.204 ^b	0	0	0
10	3.358	10.958	4.058	0.080	0.137	-0.833
30	3.395	11.105	3.945	0.291	0.976	-1.478
50	3.431	11.321	3.891	0.496	2.209	-1.786
70	3.675	11.715	3.905	1.889	4.457	-1.706

^a Reference 5. ^b Reference 15. ^c Mole fraction scale; $p_s(K)^N$ values were obtained by the relation $p_s(K)^N = p_s(K)_{\text{molal}} + \log(1000/M_s)$ where M_s is the mean molecular weight of the mixed solvent.

Table VII. Values of $\Delta G^\circ_i(H^+)$, $\Delta G^\circ_i(HA^-) - \Delta G^\circ_i(H_2A)$, $\Delta G^\circ_i(A^{2-}) - \Delta G^\circ_i(HA^-)$, and $\Delta G^\circ_i(BH^+) - \Delta G^\circ_i(B)$ in the Glycerol-Water Solvent System at 25 °C (ΔG° in kJ mol^{-1} (Mole Fraction Scale))

wt % GL	$\Delta G^\circ_i(H^+)^a$	$\Delta G^\circ_i(HA^-) - \Delta G^\circ_i(H_2A)$		$\Delta G^\circ_i(BH^+) - \Delta G^\circ_i(B)$	
		$\Delta G^\circ_i(HA^-)$	$\Delta G^\circ_i(A^{2-}) - \Delta G^\circ_i(HA^-)$	$\Delta G^\circ_i(BH^+)$	$\Delta G^\circ_i(B)$
10	0.59	-0.510	-0.453	1.423	
30	1.34	-1.049	-0.364	2.818	
50	2.30	-1.804	-0.091	4.086	
70	3.93	-2.041	0.527	5.336	

^a Reference 13.

**Figure 1. Variation of $\delta(\Delta G^\circ)$ for different acids in glycerol-water mixtures at 298.15 K: ●, thymolsulfonephthalein (first dissociation); ○, thymolsulfonephthalein (second dissociation); △, *m*-nitroanilinium ion.**

in Figure 2. Contributions of the dispersion interaction and cavity formation interaction to the combined terms are likely to be very small. $\Delta G^\circ_i(H^+)$ values are increasingly positive (13) indicating decreased stabilization with an increased proportion of GL and results from the decreased basicity effect of these cosolvent mixtures. The BH⁺ cation is expected to be a higher free energy state compared to B in the mixed solvent and $\Delta G^\circ_i(BH^+) - \Delta G^\circ_i(B)$ should increase with increase in mole percent GL as observed. ΔG°_i values of some monovalent anions are found to be increasingly negative (13, 14) and specific solvation resulting from the effect of increased acidity of the solvent mixture exceeds the opposing Born-type elec-

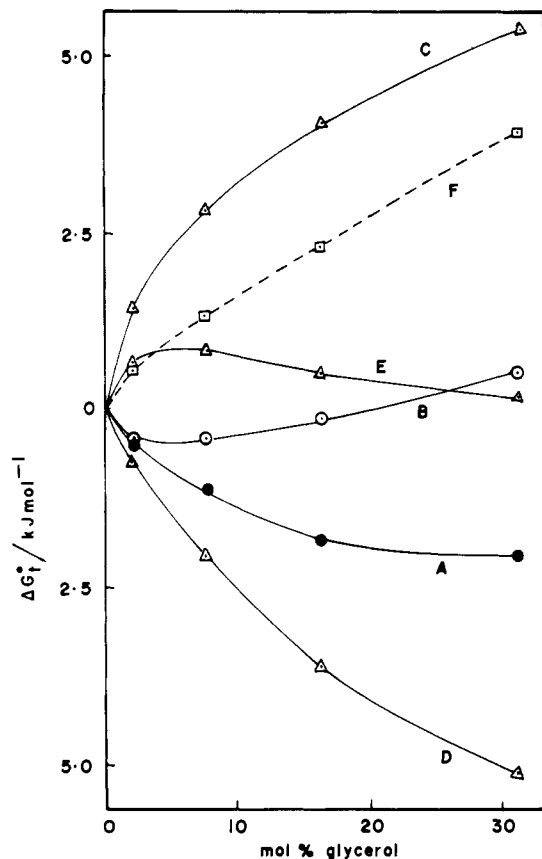


Figure 2. Variation of $\Delta G^\circ_f(\text{HA}^-) - \Delta G^\circ_f(\text{H}_2\text{A})$ and $\Delta G^\circ_f(\text{A}^{2-}) - \Delta G^\circ_f(\text{HA}^-)$ of thymosulfonephthalein; $\Delta G^\circ_f(\text{BH}^+) - \Delta G^\circ_f(\text{B})$, $\Delta G^\circ_f(\text{B})$, $\Delta G^\circ_f(\text{BH}^+)$ of *m*-nitroaniline and $\Delta G^\circ_f(\text{H}^+)$ in glycerol-water mixtures at 298.15 K: (A) $\Delta G^\circ_f(\text{HA}^-) - \Delta G^\circ_f(\text{H}_2\text{A})$; (B) $\Delta G^\circ_f(\text{A}^{2-}) - \Delta G^\circ_f(\text{HA}^-)$; (C) $\Delta G^\circ_f(\text{BH}^+) - \Delta G^\circ_f(\text{B})$; (D) $\Delta G^\circ_f(\text{B})$; (E) $\Delta G^\circ_f(\text{BH}^+)$; (F) $\Delta G^\circ_f(\text{H}^+)$.

trostatic interaction. It follows that the HA^- ion will be more stabilized relative to neutral species, H_2A , in the mixed solvent leading to increasingly negative value of $\Delta G^\circ_f(\text{HA}^-) - \Delta G^\circ_f(\text{H}_2\text{A})$ as observed. Specific interaction of bivalent A^{2-} ion is expected to be larger than that of monovalent HA^- ion. Born-type electrostatic interaction being directly proportional to square of the valence of ion (15), $\Delta G^\circ_f(\text{A}^{2-})$ should be more positive compared to $\Delta G^\circ_f(\text{HA}^-)$ from electrostatic consideration. The minimum in $\Delta G^\circ_f(\text{A}^{2-}) - \Delta G^\circ_f(\text{HA}^-)$ curve (Figure 2) can be attributed to the decrease in the combined term due to specific interaction as the organic component is added and the simultaneous increase in the same due to electrostatic interaction.

Since $\Delta G^\circ_f(\text{B})$ is accessible by experimental means, the values of $\Delta G^\circ_f(\text{BH}^+)$ can be evaluated. Increasingly negative values of $\Delta G^\circ_f(\text{B})$ (Figure 2) with increase in mole percent GL may be primarily attributed to the dispersion interaction of the

benzene nucleus with cosolvent molecules, GL. The maximum in $\Delta G^\circ_f(\text{BH}^+)$ curve (Figure 2) results from the combined effect of opposing free energy-transfer values, viz., the positive contribution due to electrostatic interaction and the interaction of the three partially charged H atoms of $-\text{NH}_3^+$ group and negative contribution due to other reasons as for the neutral base B.

Finally, a comparison of the behavior of H_2A and HA^- acids in GL + H_2O under present study and ethylene glycol (EG) + H_2O (4, 16) and methanol (MeOH) + H_2O (5) reported earlier seems interesting. Values of $\Delta G^\circ_f(\text{HA}^-) - \Delta G^\circ_f(\text{H}_2\text{A})$ in MeOH + H_2O (5) as well as in EG + H_2O (4) and $\Delta G^\circ_f(\text{A}^{2-}) - \Delta G^\circ_f(\text{HA}^-)$ in EG + H_2O (16) are found to be increasingly positive with increase in mole percent nonaqueous component in the solvent, the magnitude of $\Delta G^\circ_f(\text{A}^{2-}) - \Delta G^\circ_f(\text{HA}^-)$ being greater at any mole percent of organic cosolvent. This contrasting behavior is the result of the anion destabilizing tendency of mixed EG + H_2O (4, 16, 17) and MeOH + H_2O (18) solvents in contrast to the anion stabilizing tendency of GL + H_2O (13, 14) solvents, relative to water. Similarly, with respect to BH^+ ion acid, it may briefly be mentioned that $\Delta G^\circ_f(\text{BH}^+)$ varies differently in GL + H_2O compared to the EG + H_2O (1) or MeOH + H_2O (15) systems and this difference can be understood in terms of contrasting nature of interaction of the three partially charged H atoms of $-\text{NH}_3^+$ group in BH^+ with the mixed solvents because it is known that interaction of proton (H^+) with GL + H_2O (13) mixed solvent is different in nature compared to those in EG + H_2O (16) or MeOH + H_2O (18) mixtures.

Registry No. Thymosulfonephthalein, 76-61-9; *m*-nitroanilinium, 18616-84-7; glycerol, 56-81-5; *m*-nitroaniline, 99-09-2.

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