

## Interaction of *p*-Nitrophenol & Ethylenediamine in Acetone-Water Medium: Effect of Solvent Composition on Proton Donor-Acceptor Equilibrium

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The proton transfer complex formation involving *p*-nitrophenol and ethylenediamine in acetone-water mixtures has been investigated spectrophotometrically. From the evaluated thermodynamic parameters of the process, it is observed that while  $\Delta H^\circ$  and  $\Delta S^\circ$  vary,  $\Delta G^\circ$  remains fairly constant in all the solvent compositions. Specific solvation of the complex as well as solvent structural effects are considered to be the vital factors as compared with the minimal contribution of dielectric constant of the medium.

COMPLEX formation between a phenol and an amine in aquo-organic solvents involving proton-transfer may serve well as a model for the hydrogen-bonded interactions commonly occurring in biological systems having aqueous-nonaqueous surroundings<sup>1</sup>. Though the investigations in this area are growing in number, a few very recent works have become critical in approach<sup>1-7</sup>. In these, the general features of mixed solvents in controlling the complex formation for systems involving *p*-nitrophenol and ethylenediamine as well as *p*-nitrosalicylic acid and ethylenediamine have been presented in detail. Specific solvation and solvent structural effects have been considered to play a dominant role in the hydrogen-bonded ion pairs or proton transfer complexes<sup>4-7</sup>. The present paper mainly deals with this particular aspect of *p*-nitrophenol (PNP) and ethylenediamine (en) interaction in acetone-water mixtures of varying composition. The choice of PNP was favoured by its appreciable interaction with the diamine in wide proportions of the mixed solvent. The dipolar aprotic nature of acetone is expected to help in understanding the specific role of the hydroxylic cosolvent, water. The thermodynamic parameters of the PNP-en interaction have been evaluated.

### Materials and Methods

The details of the materials used and the experimental methods followed were similar to those reported in our earlier papers<sup>4-7</sup>.

### Results and Discussion

**Solvent effects** — The solvent dependent complex formation is shown in Fig. 1, where a comparison of the effects of acetone, 1,4-dioxane and *n*-propanol reveals an initial increase in absorbance for a small addition of each of the solvents. The observed absorbance decrease past the maximum is rather sharp for acetone and 1,4-dioxane. However, the

effect of the hydroxylic solvent, *n*-propanol is much less pronounced. If these solvents are compared at iso-mole fractions in the light of dielectrics of the media, the log *A* against  $D^{-1}$  plots are observed to be excellently linear giving three separate lines corresponding to the three nonaqueous solvents (Fig. 2). This is expected in view of our recent findings<sup>7</sup> that the hydroxylic solvents when compared in a similar manner fall on one line from which the nonhydroxylic solvents sharply deviate. The specific solvent effects, similar to those observed in the case of *p*-nitrosalicylic acid-en system, are thus envisaged. It is quite likely that a significant part of this specific effect depends on how the nonaqueous molecules interact with aqueous ones. In the present study acetone has been chosen as a probe solvent, which, besides being nonhydroxylic, can impart appreciable dielectrics to the mixed media.

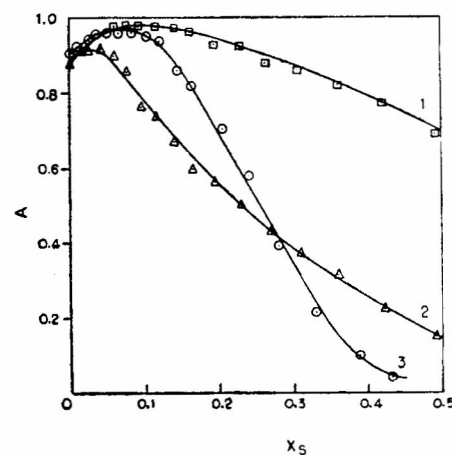


Fig. 1 — Plots of absorbance of the complex at 405 nm against the mole fraction ( $X_s$ ) of added cosolvents (1, *n*-Propanol, 2, acetone, 3, dioxane). For curves 1 and 2:  $[PNP] = 4.92 \times 10^{-5}M$  and  $[en] = 3.60 \times 10^{-4}M$ ; for curve 3:  $[PNP] = 4.92 \times 10^{-5}M$  and  $[en] = 7.7 \times 10^{-3}M$

**Equilibrium constant of the complex** — The formation constant ( $K$ ) of the complex in various acetone-water mixtures has been evaluated following the procedure described earlier<sup>4-7</sup>. The absorbance data at 405 nm obtained with increasing addition of the amine to PNP have been processed to give the  $K$  values. The absorbance of PNP alone in the medium has been subtracted from the values in the presence of amine to obviate the effect of solvent-induced proton transfer<sup>5,6</sup> on the equilibrium between the donor phenol and the acceptor amine. The significant increase in absorbance by the addition of amine indicates only minimal proton donation to the solvent in presence of the base<sup>2,6</sup>.

The complex formation process may be represented by Eq. (1)



where  $a$ ,  $b$  and  $x$  are the concentrations of the donor, acceptor and the complex, respectively (the donor being non-absorbing at  $\lambda_{\text{max}}$  of the complex having extinction coefficient,  $\epsilon_c$ ).

When  $b \gg a$ , it can be shown<sup>7</sup> in a manner analogous to the treatment of the modified Benesi-Hildebrand equation<sup>8</sup> that

$$a/A = 1/\epsilon_c + 1/\epsilon_c K b \quad \dots(2)$$

where  $A$  is the absorbance of the complex.

The plots of  $a/A$  versus  $1/b$ , from which the values of  $K$  and  $\epsilon_c$  can be evaluated, are linear at different temperatures as demanded by Eq. (2). The values of  $K$  and  $\epsilon_c$  thus evaluated are given along with their appropriate standard deviations in Table 1.

**Effect of temperature** — The absorbances have been measured at four different temperatures and the  $K$  values have been computed for various compositions of the solvent. The  $\Delta H^\circ$  values have been evaluated from the least square plots of  $\log K$  versus  $T^{-1}$ , and the  $\Delta G^\circ$  and  $\Delta S^\circ$  calculated using the well known thermodynamic relationship of Gibbs. The standard states of the reactants have been considered to be the hypothetical states of ideal solution of unit molarity. The thermodynamic parameters at 25° for various acetone-water mixtures are given in Table 2. The variation of  $K$  with temperature may as well be considered to be partly due to the electrostatic effect inherent in the medium, keeping in view the temperature dependence of dielectric constant of a medium. The dielectric constants of various solvent mixtures at different temperatures are given in Table 3. The marked dependence of  $\log K$  versus  $D^{-1}$  relationship on the solvent composition (Fig. 3) is thus corroborated by our earlier findings<sup>7</sup>.

**Comparison of thermodynamic parameters** — The nature of the plots of  $\Delta H^\circ$  and  $\Delta S^\circ$  versus the mole fraction of acetone (Fig. 4) are similar to the absorbance versus mole fraction plots in Fig. 1.

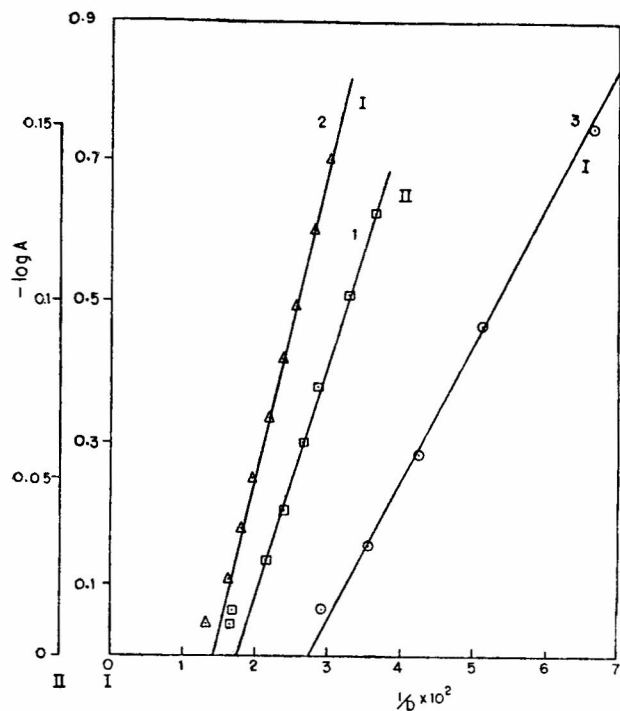


Fig. 2 — Plots of  $\log A$  versus  $D^{-1}$  (1, *n*-Propanol; 2, acetone; 3, dioxane). For curves 1 and 2:  $[\text{PNP}] = 4.92 \times 10^{-5} M$  and  $[\text{en}] = 3.60 \times 10^{-4} M$ ; for curve 3:  $[\text{PNP}] = 4.92 \times 10^{-5} M$  and  $[\text{en}] = 7.7 \times 10^{-3} M$

TABLE 1 — MOLAR EXTINCTION AND EQUILIBRIUM CONSTANT OF THE COMPLEX IN ACETONE-WATER MIXTURES

Acetone wt % (mole fraction)	$\epsilon_c \times 10^{-4}$ litre mole <sup>-1</sup> cm <sup>-1</sup> ( $K \times 10^{-3}$ litre mole <sup>-1</sup> ) at			
	25°	30°	35°	45°
0.0	2.95 ± 0.24	2.67 ± 0.15	2.22 ± 0.07	1.80 ± 0.09
(0.0)	(7.70 ± 0.03)	(8.57 ± 0.02)	(11.30 ± 0.01)	(19.50 ± 0.03)
16.37	3.46 ± 0.14	3.04 ± 0.18	2.58 ± 0.09	2.11 ± 0.06
(0.058)	(5.03 ± 0.01)	(6.17 ± 0.02)	(8.53 ± 0.01)	(15.00 ± 0.01)
34.32	3.53 ± 0.62	3.15 ± 0.28	3.01 ± 0.26	2.53 ± 0.14
(0.140)	(4.85 ± 0.37)	(5.97 ± 0.19)	(6.72 ± 0.17)	(10.45 ± 0.09)
43.92	3.10 ± 0.09	2.69 ± 0.05	2.48 ± 0.05	2.21 ± 0.03
(0.195)	(4.47 ± 0.03)	(5.60 ± 0.02)	(6.30 ± 0.03)	(9.20 ± 0.07)
48.92	2.56 ± 0.05	2.34 ± 0.05	2.08 ± 0.06	2.15 ± 0.07
(0.229)	(5.63 ± 0.04)	(6.35 ± 0.10)	(7.07 ± 0.17)	(7.65 ± 0.28)
54.04	2.31 ± 0.05	2.24 ± 0.02	2.16 ± 0.04	2.18 ± 0.05
(0.268)	(8.21 ± 0.25)	(7.41 ± 0.10)	(7.11 ± 0.16)	(8.81 ± 0.17)
59.23	2.32 ± 0.04	2.23 ± 0.09	2.16 ± 0.06	2.04 ± 0.07
(0.310)	(4.65 ± 0.04)	(4.23 ± 0.08)	(4.11 ± 0.03)	(3.99 ± 0.03)
64.62	2.36 ± 0.03	2.39 ± 0.05	2.49 ± 0.10	2.51 ± 0.10
(0.362)	(3.37 ± 0.06)	(2.72 ± 0.02)	(2.14 ± 0.01)	(1.99 ± 0.01)

It is observed that the plots of energy parameters against either the mole fraction ( $X_s$ ) or inverse of dielectric constant ( $D^{-1}$ ) hardly show any difference in the trend. The  $\Delta G^\circ$  values, however, remain fairly constant up to acetone composition as high as 65 wt per cent. The above observations clearly indicate the marked effect of acetone on  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the overall process in which the spontaneity of the complex formation remains practically unaffected. The mild increase in  $\Delta S^\circ$  and

$\Delta H^\circ$  for an initial small addition of acetone seems to be related to the breaking of water structure. An initial small addition of acetone breaks down the normal structure of water which is manifested by the increase of  $\Delta S^\circ$  and  $\Delta H^\circ$  for the overall process. Further addition of the nonaqueous

TABLE 2 — THERMODYNAMIC PARAMETERS OF THE COMPLEX FORMATION AT  $25^\circ \pm 0.1^\circ$  IN DIFFERENT ACETONE-WATER MIXTURES

Acetone wt % (mole fraction)	$\Delta G^\circ$ (kcal mole <sup>-1</sup> )	$\Delta H^\circ$ (kcal mole <sup>-1</sup> )	$\Delta S^\circ$ (cal deg <sup>-1</sup> mole <sup>-1</sup> )
0.0 (0.0)	$-5.30 \pm 0.03$	$+9.27 \pm 0.45$	$+48.87 \pm 1.61$
16.37 (0.058)	$-5.05 \pm 0.01$	$+10.19 \pm 0.21$	$+51.11 \pm 0.71$
34.32 (0.140)	$-5.03 \pm 0.05$	$+7.44 \pm 0.21$	$+41.81 \pm 0.84$
43.92 (0.195)	$-4.98 \pm 0.01$	$+6.41 \pm 0.25$	$+38.20 \pm 0.84$
48.92 (0.229)	$-5.12 \pm 0.01$	$+3.44 \pm 0.46$	$+28.71 \pm 1.56$
54.04 (0.268)	$-5.34 \pm 0.02$	$-1.60 \pm 0.30$	$+12.54 \pm 1.08$
59.23 (0.310)	$-5.00 \pm 0.01$	$-1.72 \pm 0.40$	$+11.00 \pm 1.36$
64.62 (0.362)	$-4.81 \pm 0.01$	$-9.53 \pm 0.15$	$-15.83 \pm 0.52$

TABLE 3 — TEMPERATURE INDUCED DIELECTRIC CONSTANTS OF THE SOLVENT MIXTURES

Acetone (mole fraction)	Dielectric constant at			
	25°	30°	35°	45°
0.000	78.5	76.7	74.9	71.5
0.058	69.0	67.5	66.0	63.0
0.140	58.0	56.5	55.0	52.5
0.195	51.5	50.5	49.5	47.0
0.229	48.5	47.5	46.5	44.0
0.268	45.5	44.5	43.5	41.0
0.310	42.0	41.0	40.0	38.0
0.362	39.0	38.0	37.0	35.0

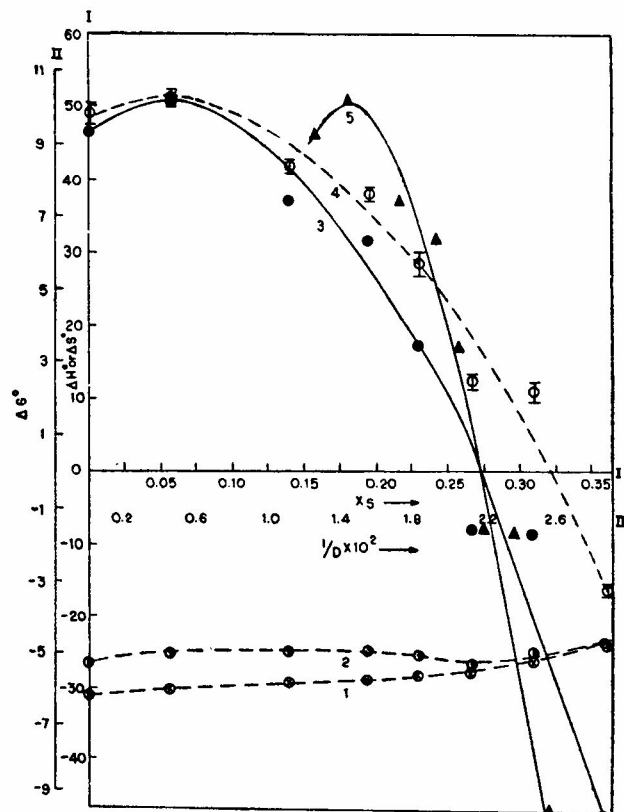


Fig. 4 — Acetone induced thermodynamic parameters for the complex formation process [1 and 2:  $\Delta G^\circ$  versus  $X_s$ ; 3:  $\Delta H^\circ$  versus  $X_s$ ; 4:  $\Delta S^\circ$  versus  $X_s$ ; 5:  $\Delta H^\circ$  versus  $D^{-1}$ ]

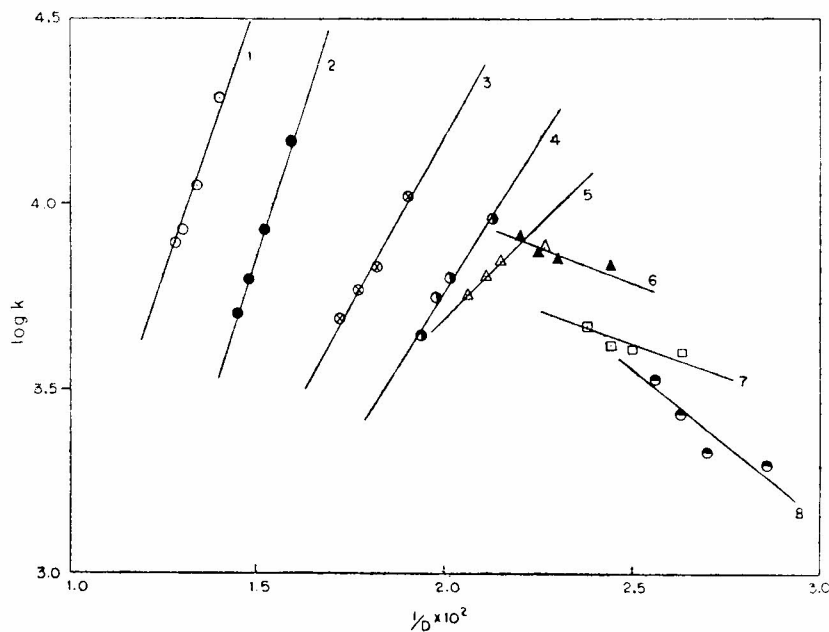


Fig. 3 — Temperature induced electrostatic effects on the equilibrium constant, plotted as  $\log K$  versus  $D^{-1}$  [Curves 1-8 represent 0, 0.058, 0.140, 0.195, 0.229, 0.268, 0.310 and 0.362 mole fraction of acetone, respectively]

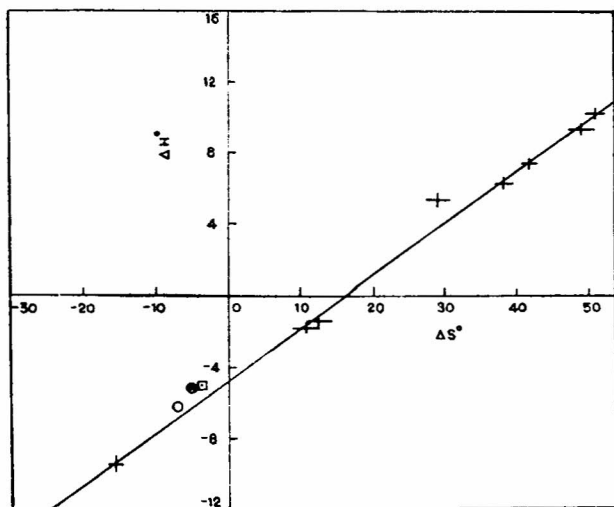


Fig. 5 — Linear enthalpy-entropy relationship at 25° for the complex formation process. Signs O, ● and □ represent the results on *p*-nitrosalicylic acid-en complex in water, 12.15 wt% ethanol, and 8.2 wt% *n*-propanol, respectively<sup>7</sup>

solvent subsequently leads to structure formation causing decrease in the overall entropy change.

The systematic variation of  $\Delta H^\circ$  and  $\Delta S^\circ$  at nearly constant  $\Delta G^\circ$  manifests energy utilization through solvent structure modification and consequently a case of enthalpy-entropy adjustment. Such a process must then reflect a linear relationship between  $\Delta H^\circ$  and  $\Delta S^\circ$  in an extra thermodynamic way<sup>9,10</sup>. This is strongly supported by the results of Fig. 5 where the linear enthalpy-entropy variation is almost exact. In this figure three pairs of data collected on *p*-nitrosalicylic acid-ethylenediamine system in water, 12 wt% methanol in water, and 8.2 wt% *n*-propanol in water, respectively have been shown to fit in  $\Delta H^\circ$  versus  $\Delta S^\circ$  plot. The extra thermodynamic relationship has thus the possibility of being a feature of the proton transfer processes reported herein. Such a relation is known to hold good for a given reaction involving substituted derivatives<sup>11</sup>, and we have seen that this relation also holds good under the changed environmental conditions. Fig. 5 shows that at 0.273 mole fraction of acetone the enthalpy change for the reaction is zero. It has been observed that the hydrogen-bonded dimerization of acetic acid in aq. medium ends up with a zero enthalpy change<sup>12</sup>.

Since the dielectric constants of acetone-water mixtures used are not low, stabilization of the complex by solvation<sup>2,5-7</sup> and the structure of the overall environment<sup>5</sup> are expected to play a vital role in the complex formation reaction. The two processes compete with each other, and destabilization of the complex by desolvation may eventually be offset by the stabilizing influence of the neighbouring surroundings. The two adjacent methyl groups in acetone may sterically hinder the approach of the whole molecule to the negative centre of the complex<sup>2</sup> to solvate it through the positive centre of acetone on its electron deficient carbon atom,  $[(\text{CH}_3)_2\text{C}^+\text{---O}^-]$ . But it can easily solvate at the positive centre of the complex via hydrogen bonding

through the negative oxygen centre. Such an impaired solvation is absent when the contributing molecules are all water. The crowding of acetone near the complex as well as PNP and the amine may, however, contribute a share to the observed entropy decrease with its increasing addition into the system.

It has been shown in Fig. 3 that for a constant solvent composition,  $\log K$  is a linear function of the reciprocal of temperature dependent dielectric constant of the medium and is displayed by the reversal of slopes. Taking into account that various phenomena may appear in the proton transfer process<sup>5-7</sup>, only a qualitative explanation can be offered. At a constant dielectric constant the formation of complex depends on  $pK$  of both the donor and acceptor<sup>3,7</sup>. Increasing the temperature affects the  $pK$  value, normally the dissociation constants are increased. This will favour the transfer of proton which at the same time will be disfavoured by the temperature effected decomposition of the complex. The decreasing dielectric constant of the medium with increasing temperature should also disfavour complex formation. The observed magnitude is, therefore, the resultant of all these effects. So long the mole fraction of acetone is  $>0.23$ , the complex formation decreases with decreasing dielectric constant which is a physical manifestation of the changing temperature. Below this mole fraction, the complex formation is favoured by the increase in temperature. Therefore, in this range the  $pK$ -controlled complex formation overrides the decomposition as well as dielectric induced restriction of the transfer process, which, in the other range, is just the reverse. Both solvation and solvent structural effects are considered to have little scope to obliterate this explanation since in Fig. 3 comparison of the results has been made at constant solvent compositions.

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