

A STUDY OF THE EFFECT OF SOLVENT COMPOSITION ON THE ACIDITY FUNCTION H_o

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ABSTRACT

A spectrophotometric method was used to determine the dissociation constant of *p*-nitronaphthylamine indicator in acetamide-water, and propionamide-water mixtures at 25°C. The pK_a values, calculated by a stepwise comparison method, were found to decrease with increasing the organic solvent: water ratio. The addition of the organic solvent component increases the basicity of water due to the progressive breakdown of the tetrahedral structure of water [1]. Thus, instead of having only the structure $H^+(H_2O)_4$, one may also have the structure $H^+(H_2O)_2$, since the affinity in the open structure is less than in the compact structure in which the proton becomes more firmly bound. The free energies of transfer $\Delta G_i^{\circ}(H^+)$ were calculated for the transfer of the solvated proton from water to aqueous acetamide (Ac) or aqueous propionamide (Pr). In this system, the acidity function of hydrochloric acid solutions was found to increase with increasing the organic solvent component. The partition of the proton between H_2O and the organic solvent was calculated in both water-rich and solvent-rich mixtures.

In water-rich solvent mixtures, the equilibrium $A: H_3O^+ + S \xrightleftharpoons[k_2]{k_1} HS^+ + H_2O$ is shifted to the right, and applies successfully up to 30 wt % solvent. Plots of $H_o + \log [HCl]$ against the solvent composition ratio $[S]/[H_2O]$ are straight lines in all cases with slopes equal to $K'_1/2.3$. The values of the equilibrium constant K'_1 amount to 14.95 and 19.55 for the H_2O -Ac and H_2O -pr solvent systems, respectively. In the organic solvent rich system (>40 wt % solvent), the equilibrium A is shifted to the left. The value of the equilibrium constant K'_2 amounts to 0.207 for Ac- H_2O . With known values of K'_1 and K'_2 , it is possible to calculate $[H_3O^+]$ and $[HS^+]$ in any solvent system. Such calculations show that, at a fixed acid concentration, $[H_3O^+]$ decreases with progressive addition of solvent, while the $[HS^+]$ values show an increase.

Keywords: Dissociation constant, acidity function; *p*-nitronaphthylamine; free energies of transfer, solvent effect.

INTRODUCTION

The study of the protonation of weak organic bases in strong acidic aqueous media led to the definition of some acidity function scales valid for each acidic medium [2]. These functions are based on Hammett's hypothesis [3] (equation 1)

$$H_o = -\log(a_H \cdot f_A / f_{AH^+}) \quad (1)$$

where f_A and f_{AH^+} are the activity coefficients of the non protonated, and protonated forms, respectively, of a given indicator taken as a reference.

The dissociation constant can be estimated as shown in equation (4) (2),

$$pK_{AH^+} = \log \frac{C_{AH^+}}{C_A C_H^+} + \log \frac{f_{AH^+}}{f_A f_H^+} \quad (2)$$

In infinitely dilute solutions equation (2) can be converted into equation (4) (3)

$$pK_{AH^+} = \lim_{c_a \rightarrow 0} \left[\log \frac{C_{AH^+}}{C_A} - \log C_{H^+} \right] \quad (3)$$

where C_a is the molar concentration of a strong acid in water.

However, for very weak bases the direct determination of pK_{AH^+} is not feasible, and the stepwise comparison method [5] is preferred. Consequently, the pK_a^{i+1} of a base can be calculated compared to the dissociation constant of the known reference indicator pK_a^i (equation 4)

$$pK_a^i - pK_a^{i+1} = \log I^i - \log I^{i+1} \quad (4)$$

This equation requires a linear relationship between $\log I$ and $\log C_{H^+}$

$$\text{where } I = \frac{C_{AH^+}}{C_A}$$

Another way of determining the pK_a values of indicators by the direct stepwise comparison method is that proposed by Pytela et al [6]. equation (5)

$$pK_a^i - pK_a^{i+1} = \frac{\int_{c_1^{i+1}}^{c_2^{i+1}} \log I^i - \int_{c_1^{i+1}}^{c_2^{i+1}} \log I^{i+1}}{c_2^{i+1} - c_1^{i+1}} \quad (5)$$

where C_1^{i+1} and C_2^{i+1} are the acid concentrations limiting the concentration range used simultaneously for two indicators.

Bunnett-Olsen [7], Cox et al [8] and Marziano et al [9] developed a relationship (equation 6) between the activity coefficients of a given indicator and those of another reference indicator, to interpret its behaviour as a function of the medium acidity.

$$\log f_A f_H / f_{AH^+} = m \cdot \log f_A \cdot f_H / f_A \cdot H^+ \quad (6)$$

Previously, the dissociation constants of the indicators β -benzoyl-naphthalene [4], p-naphtholbenzein [4] and N,N dimethyl-2-4-dinitro-1-naphthylamine [10] were determined.

In this investigation, the dissociation constant of p-nitronaphthylamine and the acidity function H_0 were determined at 25°C in Ac-H₂O and Pr - H₂O

mixtures. In the light of this study, the partition was calculated of the proton at different solvent compositions.

EXPERIMENTAL

Reagents:

Acetamide (Ac) was of the best grade available from B.D.H and propionamide (pr) was a Merk product. P-nitronaphthyl-amine was prepared [11] and purified by recrystallization from alcohol m.p 191°C.

Acetamide-water solutions contained 10-50 wt%Ac, and propionamide-water solutions contained 10-30 wt%Pr, because this is the limit of their solubilities in water.

A p-nitronaphthylamine stock solution (1×10^{-3} M in 50%(v/v) alcohol solution) was added to the respective mixed solvent systems containing the acids, and their final concentrations was 1×10^{-4} M. The Hydrochloric acid stock solution was obtained from the middle fractions of the twice-distilled constant boiling HCl solution.

EQUIPMENT

A Pye Unicam SP8-400 ultraviolet spectrophotometer was used. This makes use of a double beam and is equipped with a thermostated cell. The temperature was kept constant at $25 \pm 0.01^\circ\text{C}$.

The absorbance of the protonated form of the indicator AH^+ , non protonated form A_A and the absorbance in which the indicator is partly ionized A were measured at 443 nm.

The ionization ratios (or indicator ratios) were calculated as $I = (A - A_A) / (A_{AH^+} - A)$.

RESULTS AND DISCUSSION

The experimental U.V spectra of hydrochloric acid solutions containing p-nitronaphthylamine indicator in Ac-H₂O and Pr-H₂O mixtures shows an isobestic point at 362 nm which is characteristic of the presence of an equilibrium between the basic and protonated form A and AH^+ respectively.

The relationship between $\log I$ and $\log C_{H^+}$ gives good parallel straight lines if compared with p-nitroaniline as a reference indicator (Figure (1)). This indicates the accuracy of applying equation(4).

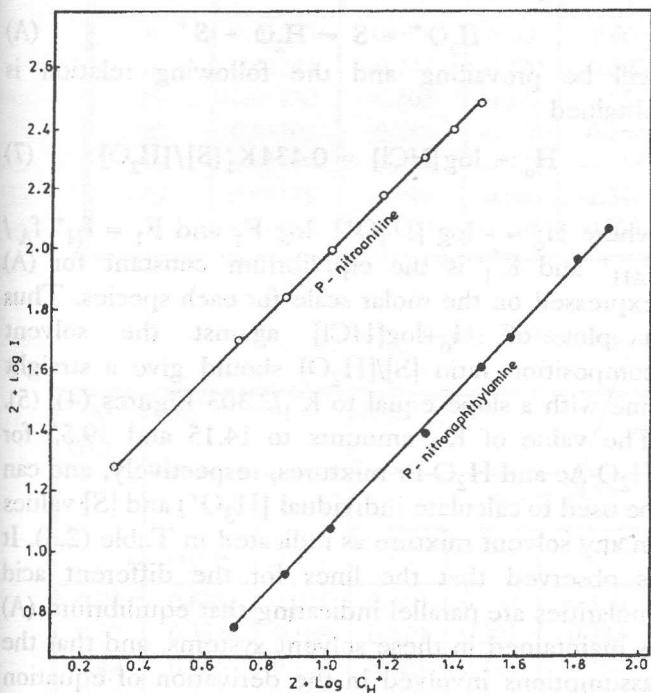


Figure 1. Variation of $\log I$ with $\log C_{H^+}$ in aqueous solution at 25°C.

THE ACIDITY FUNCTION H_0

Values of H_0 at several HCl concentrations in AC- H_2O and Pr- H_2O mixtures were calculated from the relation:

$$H_0 = (pK_a)_w - \log I,$$

where $(pK_a)_w$ is the dissociation constant of the indicator in the pure aqueous medium. The plots of $(\log I - \log C_{H^+})$ against C_{H^+} should give straight lines with intercept equal to pK_a in that solvent. Table (1) represents the values of pK_a . Figure (2) illustrates the trend of the acidity function change with acid concentration, at different weight percentage of the organic solvent. It is observed that H_0 decreases as the acid concentration increases. In the mean time, the H_0 values increase with increasing amount of the solvent for a definite molality of the acid Figure (3), which confirm the

view that the solvent basicity increases with the addition of AC or Pr, due to the formation of a large number of basic water molecules through a breakdown of the complex water structure [12]. The initial increase in H_0 with increasing organic solvent composition is due to the decrease in the activity coefficient of the molecular indicator. It has a salting - in effect [4].

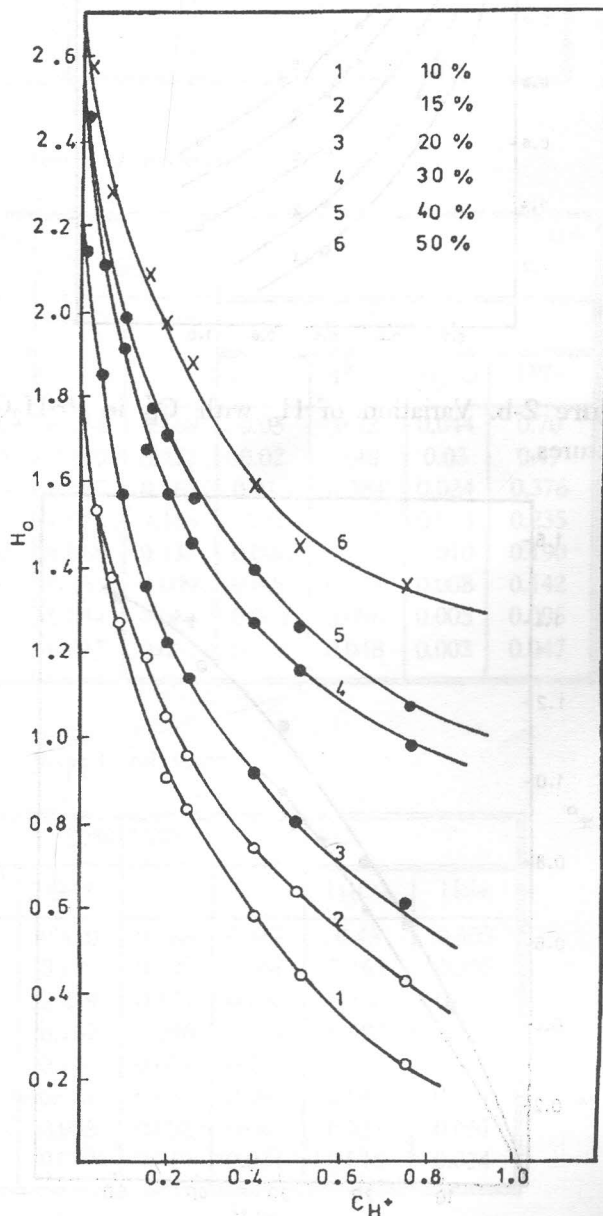
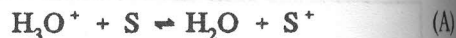


Figure 2-a. Variation of H_0 with C_{H^+} in AC- H_2O mixtures.

PARTITION OF PROTON

The change of H_0 with solvent composition at constant molality has been treated [13,14] in two systems. For water rich system, the equilibrium



will be prevailing and the following relation is obtained

$$H_0 + \log[HCl] = 0.434 K_1 [S]/[H_2O] \quad (7)$$

where $H_0 = -\log [H_3O^+] - \log F_1$ and $F_1 = f_H^+ f_A / f_{AH^+}$ and K_1 is the equilibrium constant for (A) expressed on the molar scale for each species. Thus a plot of $H_0 + \log[HCl]$ against the solvent composition ratio $[S]/[H_2O]$ should give a straight line with a slope equal to $K_1/2.303$ Figures (4), (5). The value of K_1 amounts to 14.15 and 19.55 for H_2O -Ac and H_2O -Pr mixtures, respectively, and can be used to calculate individual $[H_3O^+]$ and $[S]$ values in any solvent mixture as indicated in Table (2,3). It is observed that the lines for the different acid molarities are parallel indicating that equilibrium (A) is maintained in these solvent systems, and that the assumptions involved in the derivation of equation (7) are substantially correct. In organic solvent rich system, the proton is considered [15] to be mainly solvated by the organic solvent component as HS^+ . Addition of water will shift equilibrium (A) to the left [15]. Therefore, plots of $H_0 + \log [HCl]$ vs. solvent ratio $[H_2O]/[S]$ should give straight lines with a slope of $K_2/2.303$. The estimated value of K_2 amounts to 0.207 for Ac- H_2O mixtures Figure (4) which is used to calculate the individual $[H_3O^+]$ and $[SH^+]$ values, Table (2). It should be noted that K_2 differs markedly from $1/K_1$ due to the operation of the electrostatic effect and the changing dielectric constant of the solvent medium. The equilibrium constant K_1 indicates that the basicity of the solvent increase in the order $Ac < Pr$.

MEDIUM EFFECT

The medium effect is related to Gibbs free energy change of transfer ΔG_t° and to the ΔpK_a by the relation [16,17]

$$2.303RT \Delta pK_a = \sum \Delta G_t^\circ = \Delta G_t^\circ(H^+) - [\Delta G_t^\circ(AH^+) - \Delta G_t^\circ(A)]$$

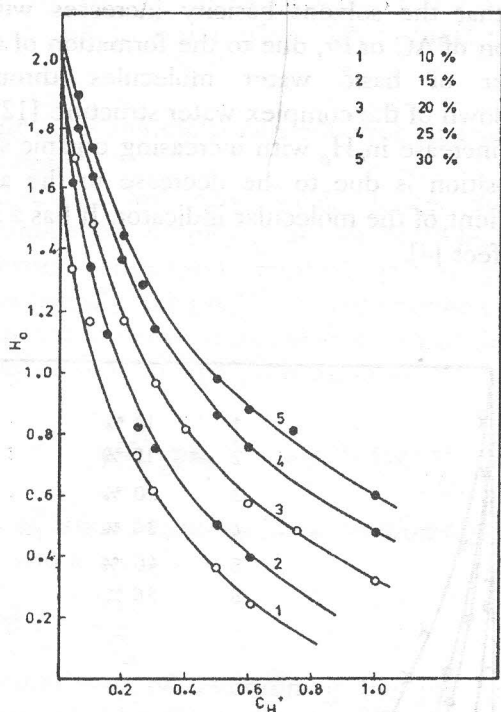


Figure 2-b. Variation of H_0 with C_H^+ in Pr- H_2O mixtures.

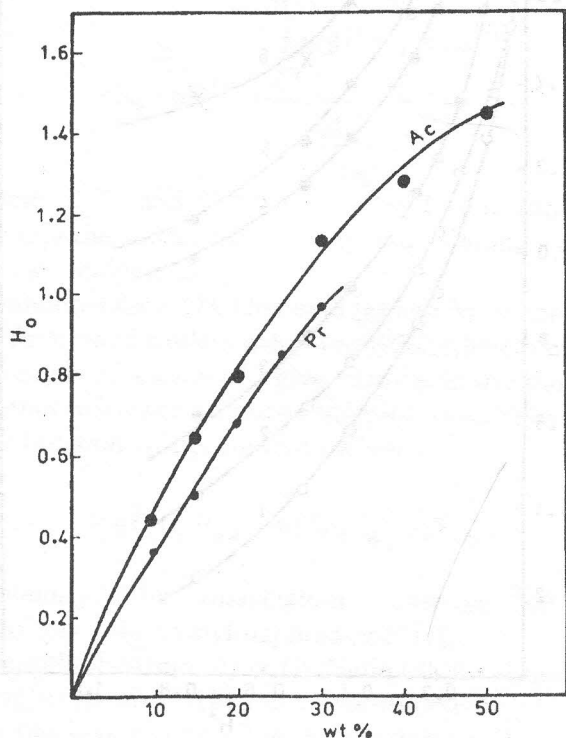


Figure 3. Variation of H_0 for 0.5 N HCl with solvent composition.

Table 1. The dissociation constant of p-nitronaphthylamine (in Ac-H₂O and Pr-H₂O mixtures) and the standard Gibbs energy of transfer in k cal/mole at 25°C.

Acetamide					Propionamide				
wt%	I/D	pK _a	ΔpK _a	ΔG _t ^o	wt%	I/D	pK _a	ΔpK _a	ΔG _t ^o
0	0.01275	0.073	0.00	0.00	10	0.01269	-0.132	-0.205	-0.281
10	0.01244	-0.147	-0.220	-0.300	15	0.01267	-0.287	-0.360	-0.494
15	0.01230	-0.302	-0.375	-0.541	20	0.01264	-0.430	-0.503	-0.690
20	0.01206	-0.485	-0.558	-0.762	25	0.01263	-0.571	-0.644	-0.884
30	0.01175	-0.698	-0.771	-1.058	30	0.01261	-0.665	-0.738	-1.013
40	0.01149	-0.910	-0.983	-1.342					
50	0.01117	-1.220	-1.293	-1765					

Table 2. Proton partition in Ac-H₂O mixtures.

M HCl	10%		15%				20%		30%		40%		50%	
	H ₃ O+	HS+	K' ₁ = 14.95				H ₃ O+	HS+	K' ₂ = .207					
			H ₃ O+	HS+	H ₃ O+	HS+			H ₃ O+	HS+	H ₃ O	HS+		
0.75	0.673	0.077	0.418	0.332	0.350	0.400	0.254	0.469	0.03	0.72	0.044	0.70		
0.50	0.332	0.168	0.279	0.221	0.233	0.267	0.169	0.331	0.02	0.48	0.03	0.47		
0.40	0.266	0.134	0.223	0.117	0.187	0.213	0.135	0.265	0.016	0.384	0.024	0.376		
0.25	0.166	0.084	0.139	0.111	0.117	0.133	0.085	0.165	0.01	0.24	0.015	0.235		
0.20	0.132	0.068	0.112	0.088	0.093	0.107	0.068	0.132	0.008	0.192	0.010	0.190		
0.15	0.100	0.050	0.084	0.066	0.070	0.08	0.051	0.009	0.006	0.144	0.008	0.142		
0.10	0.066	0.034	0.056	0.044	0.047	0.053	0.034	0.066	0.004	0.096	0.005	0.095		
0.05	0.003	0.017	0.027	0.023	0.023	0.027	0.017	0.033	0.002	0.048	0.003	0.047		

Table 3. Proton partition in Pr-H₂O mixtures.

M HCl	10%		15%		20%		25%		30%	
			H ₃ O+	HS+	H ₃ O+	HS+			H ₃ O+	HS+
0.75	0.488	0.262	0.406	0.344	0.340	0.410	0.288	0.462	0.45	0.505
0.50	0.326	0.174	0.270	0.230	0.227	0.273	0.192	0.308	0.163	0.337
0.40	0.260	0.140	0.216	0.184	0.181	0.219	0.154	0.246	0.130	0.270
0.25	0.163	0.087	0.135	0.115	0.133	0.137	0.096	0.154	0.082	0.168
0.20	0.130	0.070	0.108	0.092	0.091	0.109	0.077	0.123	0.065	0.135
0.15	0.098	0.052	0.081	0.069	0.068	0.082	0.058	0.092	0.049	0.101
0.10	0.065	0.035	0.054	0.046	0.045	0.055	0.038	0.062	0.033	0.067
0.05	0.032	0.018	0.027	0.023	0.023	0.027	0.019	0.031	0.016	0.034

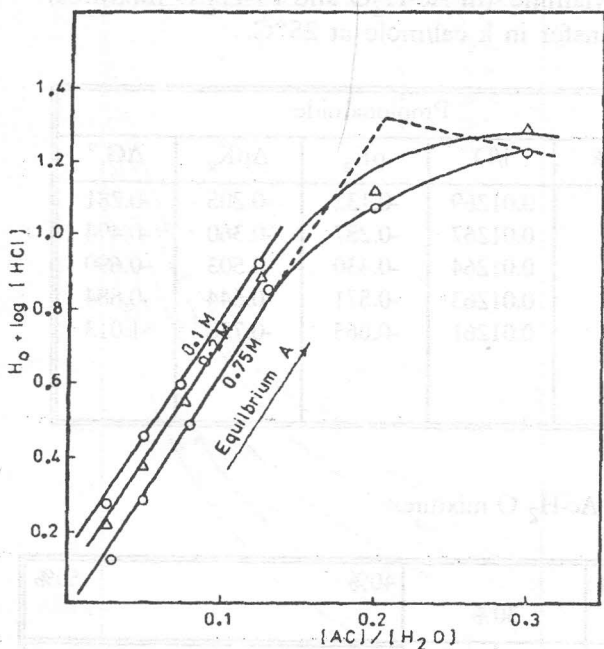


Figure 4. Variation of $H_0 + \log [HCl]$ with solvent composition.

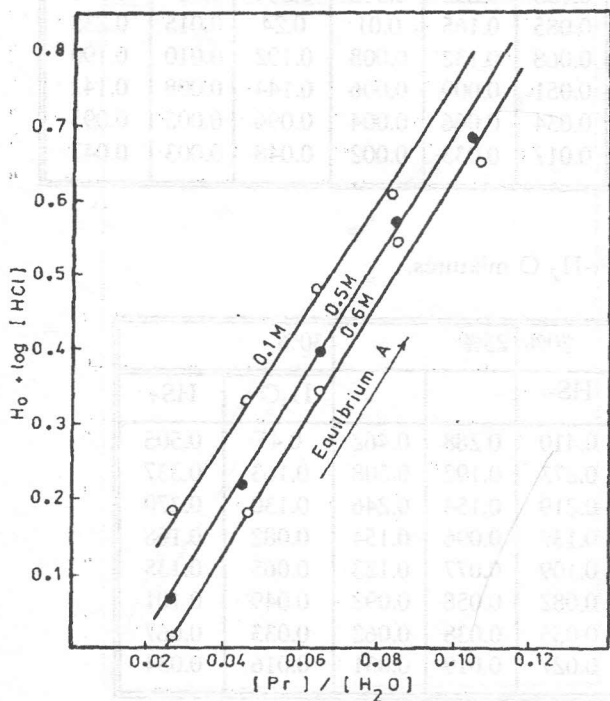


Figure 5. Variation of $H_0 + \log [HCl]$ with solvent composition.

Application of Born equation shows a non-linear relation between ΔG_t^0 and $1/D$ (Figure (6)). This behaviour was observed for charged or neutral acids [18-22]. However, it is recognized that free energies of transfer of charged species from one solvent to another may be formally represented as the sum of the electrostatic and non electrostatic contributions [(23-25)]. In the same way, the observed change of pK_a , (ΔpK_a) has been regarded [22] as the sum of two terms (ΔpK) electrostatic and (ΔpK) nonelectrostatic. However, in the present investigation, the change in the non-electrostatic contribution has a great significance due to the change in the medium effect [22]. The proton transfer from water to the solvent, influences the medium effect as a result of the solvation factor. Therefore, the following equilibrium is established.

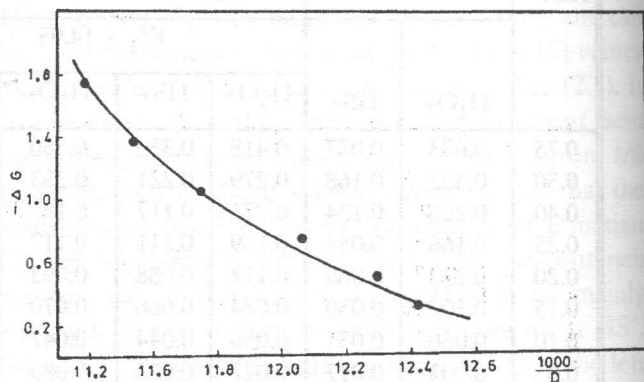


Figure 6-a. Variation of $-\Delta G_t^0$ with dielectric constant in AC- H_2O mixtures at $25^\circ C$.

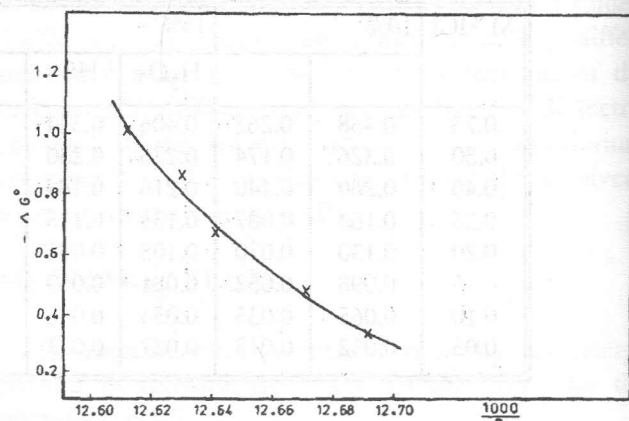


Figure 6-b. Variation of $-\Delta G_t^0$ with dielectric constant in Pr- H_2O mixtures at $25^\circ C$.

This equilibrium lies further to the left in aqueous mixtures of organic solvents than in pure water as indicated by values of K_a^s ($pK_a^s = -\log K_a^s$). By this criterion the solvent mixtures are more basic than water. In other words, the addition of the solvent increases the basicity of the water molecules. This result has been confirmed, since the quantity of ΔG_t^0 was found to be negative as shown in Table (1). This behaviour is similar to that obtained in different solvents for various indicators [22]. The Gibbs free energy and acidity function are different when using p-nitronaphthylamine than in the case of p-nitroaniline [26]. The structure of the indicator and its basicity are responsible for this variation [27].

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