

CHAPTER -- VI

Electrolytic Conductance and Dissociation Constant
of Picric Acid in ME-Water and DME-Water Mixtures.

2-Methoxy ethanol (ME) and 1,2-Dimethoxy ethane (DME) are potential solvents now-a-days for using non-aqueous batteries and their applications in organic synthesis^{1,2} and electro-chemical³ studies have been widely stressed. As they are mono-methyl and dimethyl ether of ethylene glycol, it is very likely to show their physico-chemical characteristics lying intermediate between protic and dipolar aprotic solvents. Hence, it becomes of very much interest to study the behaviour of electrolytes in such solvent media. The conductometric method is well known to give valuable information regarding ion-solvent interactions. Although a number of studies have been made in ME^{4,5} dealing with picric acid but literature provides no information regarding the conductometric behaviour in pure DME as well as in ME-water and DME-water mixtures.

In this chapter conductance measurements are reported for picric acid in pure ME and DME and also in binary aqueous mixtures of ME and DME (20, 40, 60 and 80 wt% of ME or DME) at 25 °C.

The conductance data have been analysed by the Shedlovsky⁶ and the Fuoss^{7,8} conductance equations and the limiting equivalent conductance (Λ_0) and the dissociation constants of picric acid

have been determined. In addition, in view of the importance of the solvents employed in the study, dipolar and amphiprotic in nature, it would also have been desirable to have more data on the relative values of the standard Gibbs energies of transfer of picric acid $\left[\Delta G_t^{\circ}(1) \right]$ in the two solvent systems. The thermodynamic data can contribute to an understanding of solute-solvent interactions as well as problems specifically involved in acidity in solvents or solvent mixtures other than water.

Experimental

Purifications of 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME) have been described in Chapter II. Triply distilled water (specific conductance $< 1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$) from all glass distilling set was used. Freshly distilled solvents were always utilized for solution preparation. Properties of solvent mixtures are given in Table 1 and are found to be in good agreement with literature values.

Picric acid (2,4,6-trinitro phenol) (Glaxo, Special quality) was purified from ethanol-water mixtures as described in the literature⁹.

The solvent mixtures were prepared by weight. A stock solution for each salt ($\sim 0.01M$) in the appropriate solvent mixture was prepared by weight and the working solutions were obtained by weight dilution. The concentration varied between 10^{-3} - $10^{-4}M$. Dielectric constants of the solvent mixtures were taken from the literature^{10,11}.

A Pye-Unicam conductometric bridge (PW 9509) was used for measuring the conductances of the solutions at the frequency of 2 KHZ with a dip-type cell of cell constant 0.73 cm^{-1} and having an accuracy of $\pm 0.1\%$. The measurements were carried out in a thermostatic bath maintained at $25 \pm 0.01^\circ \text{C}$.

Results

The measured equivalent conductances and the corresponding molar concentrations at different percentages of ME + H₂O and DME + H₂O mixtures at 25°C are given in Tables 2 and 3. Picric acid has been assumed to be associated in ME + H₂O and DME + H₂O mixtures. We have first analysed our data using Shedlovsky's method using the set of equations as given below:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda S f_{\pm}^2}{K\Lambda_0^2} \quad \dots (1)$$

$$S = \left[\frac{\beta\sqrt{C\Lambda}}{2\Lambda_0^{3/2}} + \sqrt{\left(1 + \frac{\beta C\Lambda}{4\Lambda_0}\right)} \right]^2 \quad \dots (2)$$

$$\beta = \frac{8.204 \times 10^5 \Lambda_0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta(\epsilon T)^{1/2}} \quad \dots (3)$$

$$\log f_{\pm} = - \frac{1.8246 \times 10^6 (C\alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.29 \times 10^8 R(C\alpha)^{1/2} / (\epsilon T)^{1/2}} \quad \dots (4)$$

$$\alpha = \frac{S\Lambda}{\Lambda_0} \quad \dots (5)$$

The terms in the equations have their usual significance. The Bjerrum critical distance $q = \frac{e^2}{2\epsilon kT}$ has been put equal to R in equation (4) to calculate the mean ionic activity coefficients. The dissociation constants, K, and the limiting equivalent conductance (Λ_0) have been iteratively calculated. A Wipro Z-650 Computer was used for the purpose.

The Λ_0 and μK values thus obtained are recorded in Tables 4-6. The low values of the dissociation constants upto 80 wt% of ME or DME suggest that the electrolytes are present as free ions in those solvent mixtures.

In order to improve our results, we have applied the recent method of computation suggested by Fuoss. For a set of conductance data ($C_j, \Lambda_j, j = 1 \dots n$), the three adjustable parameters Λ_0, K_A and R can be obtained by solving the following set of equations (eqns. 6-11) :

$$\Lambda = \rho[\Lambda_0(1 + RX) + EL] \quad \dots (6)$$

$$\rho = [1 - \alpha(1 - \gamma)] \quad \dots (7)$$

$$\gamma = 1 - K_A C \gamma^2 f^2 \quad \dots (8)$$

$$-\ln f = \beta k / 2(1 + kR) \quad \dots (9)$$

$$\beta = \frac{e^2}{\epsilon kT} \quad \dots (10)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_B) \quad \dots (11)$$

where RX and EL are relaxation and hydrodynamic terms respectively as derived by Fuoss and other terms have their usual significance. The parameters Λ_0 , K_A and R are obtained by solving the above equations. The calculations were performed from a Wipro Z-650 Computer using the program furnished by Prof. R.M. Fuoss. Initial Λ_0 value for the iteration procedure were obtained from Shedlovsky extrapolations of the data (Table 4). The calculations were made by finding the values of Λ_0 and α which minimize

$$\sigma^2 = \sum_j [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n-2) \quad \dots (12)$$

for a sequence of R-values and from the plotting of $\sigma\% = 100\sigma/\Lambda_0$ against R, the best fit R corresponds to the minimum in the $\sigma\%$ vs. R curve.

First approximate runs over a fairly wide range of R-values were made to locate the minimum and then a fine scan around the minimum was made. Finally, the minimizing value of R was read into the computer and the corresponding values of Λ_0 and α were calculated.

As the dielectric constant of solvent mixtures were very low, a wide range of R-values reproduced the data equally well in most of the cases except for 60 wt% of ME and 20 and 40 wt% of DME where a fairly well defined minimum in the $\sigma\%$ vs. R

curve were obtained. This insensitivity of goodness of fit to the parameter R was also observed by Fuoss⁷.

In order to treat the data for which σ % vs. R curves did not show a sharp minimum R was arbitrarily preset⁷ at the centre-to-centre distance of the solvent separated pair

$$R = a + d \quad \text{as} \quad a + d > \beta / 2$$

where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d = (M/N\rho)^{1/3} = [1.183(M/\rho)^{1/3} \text{A}^\circ] \quad \dots (13)$$

where M is the molecular weight of solvent and ρ is its density. For mixed solvents, M is replaced by the mole-fraction average molecular weight

$$M_{AV} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad \dots (14)$$

where W_1 is the weight fraction of the first component of Molecular weight M_1 . Though this is an over simplification which ignores possible selective solvation but it at least provides a self-consistent way to obtain an acceptable value for the parameter when a broad range of R-values fit the data.

The values of Λ_0 , K_A and R obtained by this procedure are recorded in Tables 5 and 6. From K_A values dissociation constants of picric acid have been calculated.

Discussion

The Λ_0 values obtained using Shedlovsky's method and the Fuoss method are in reasonably good agreement with each other with marginal variations. The variations of Λ_0 values of picric acid with solvent composition are shown in Fig. 2. It is found that the Λ_0 values decrease as the organic solvent component in the mixed solvent increases. The Λ_0 values decrease with the increase/decrease in viscosity (η) of solvent mixtures but the Walden product is different. The results indicate that the difference in solvation of ions is responsible for the change in mobility of the ions and hence Λ_0 .

The assumption that the dielectric constant is not involved in affecting the Λ_0 values since the ionization would be complete at infinite dilution, is untenable as the change in Λ_0 -values is not due to any change in the number of ions. The difference in the mobility of the ions is actually responsible for the change in λ_+^0 or λ_-^0 of ions. The cations and anions are moving in the opposite directions, the attractive forces of the opposite ions decrease with increasing dielectric constant of the solvent medium, and the mobility of the ions is inversely proportional to the dielectric constant of the medium.

Among other factors, the equivalent conductance Λ_0 of an electrolyte at infinite dilution is likely to depend on:

i) solvation of ions.

ii) flow of ions through the holes under the influence of electric field. The flow is likely to be determined by the energy required to occupy the volume of the hole into which the ion jumps plus that required by the ion to break the bonds with other molecules.

iii) the dielectric constant of the solvent which determines the ionizing capability of the solvent.

It is to be expected that the hydrodynamic entity around the picrate ions is likely to be greater in water than in ME or DME but the increased values of Λ_0 in water may be due to greater freedom of ions to move through the polar hydrogen bonded solvent system having high dielectric constant. The three dimensional water structure has 'holes' through which the transference of ions can occur rather easily and making or breaking of solvated chains are quick enough for a rapid transfer of ions through water. The transfer process is obviously difficult in ME + H₂O or DME + H₂O mixtures as the 'holes' may be blocked by ME/DME or ME-H₂O/DME-H₂O complex and the structure making or breaking would be a slow process.

From Tables 5 and 6 we find that association constants, K_A , are very low for picric acid at 20, 40 and 60 wt% of ME-water and DME-water mixtures. This indicates that the picric acid is not associated i.e. almost completely dissociated in these solvent

mixtures having high dielectric constants. However, at higher wt% of ME or DME (>60 wt%) K_A is comparatively high and increases continuously. A plot of pK vs. wt% of co-solvent has been shown in Fig. 4. The value for pK (4.33) in pure ME of picric acid (Table 5) is quite in good agreement with the results obtained by Tosi et al⁴ ($pK = 4.62$). However, we observed that the pK values reported by Simon et al⁵ in ME and ME-water mixtures are not in conformity with the present values. Similar discrepancy in the acid dissociation constants of this substance in other solvents has also been observed^{12, 13}.

Variation of Walden product with solvent composition is shown in Fig. 3. The $\Delta_0\eta$ values of picric acid (Tables 5 and 6) pass through a maximum at 20 wt% of ME or DME. The corresponding Δ_0 values in water taken from literature¹⁴ and are also included for comparison.

From Fig. 1 it is observed that the viscosity (η) of solvent mixtures increases rapidly to reach a maximum at about 60 wt% of ME and 40 wt% of DME, where η is about three times the viscosity of water and η decreases afterwards. This indicates that the three dimensional structure of water is increased with the addition of organic co-solvent due to hydrophobic interactions of methoxy groups in ME or DME with water. The addition of ME or DME to water first enhances the three dimensional structure of water; breakdown of the structure of water with further addition of ME or DME is, however, associated with the formation of ME - H₂O or DME - H₂O complexes. The maximum structuredness seems to

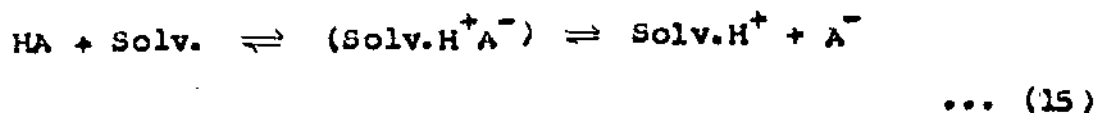
occur at 60 and 40 wt% of ME and DME respectively, due to the formation of ME-H₂O¹⁵ and DME-H₂O¹⁶ complexation and thereafter cleavage of the complexes take place. The sharply downward trends are of course the reflection of the usual structure breaking effect due to packing imbalances at higher compositions of the co-solvents.

The Λ_0 values decrease with the increase in viscosity of solvent mixtures but the Walden product ($\Lambda_0 \eta$) are found to be different. As the Walden product of an ion is inversely proportional to the effective radius of the ion in a solvent, the initial variation in the Walden products in the mixed solvents can be explained in terms of selective solvation of ions (Pic⁻ and H⁺) by ME, DME and water molecules respectively. The decrease in Walden product after 20 wt% of ME or DME indicates the preferential solvation of ions by ME or DME in their aquo-organic mixtures. From the results it can be suggested that these ions (H⁺ and Pic⁻) are solvated to different extent in these solvent mixtures.

It is thus apparent that the selective solvation of ions, the viscosity of the medium, the exchange of ions with neighbouring solvent molecules, and the movement of ions through the holes in hydrogen bonded solvent systems are of importance to determine the variation of the Walden product with solvent composition.

More extensive studies, however, are required to arrive at reasonable conclusions about the conductance behaviour in different aquo-organic mixtures and the nature of ion-solvent interactions.

Continuing our conductometric studies, the dissociation constants of picric acid in water and mixed solvents have been used to evaluate certain thermodynamic parameters and the data obtained are discussed. The reaction under study in the two solvents is



In order to have a better understanding of the solvent effect, the changes of standard free energy accompanying the ionization of the acid HA in any solvent, $\Delta G_t^\circ(s)$, relative to that in water, $\Delta G_t^\circ(w)$, have been computed at 25°C on the molar scale using equation (16).

$$\begin{aligned} \text{Solvent effect} &= \Delta G_t^\circ(l) = \Delta G_t^\circ(s) - \Delta G_t^\circ(w) \\ &= 2.303 RT [\text{p}K_B - \text{p}K_W] \quad \dots (16) \end{aligned}$$

Fig. 5 illustrates the variation of $\Delta G_t^\circ(l)$ with mol% of ME and DME. The dissociation constant of picric acid in water ($\text{p}K = 0.42$) was taken from literature¹⁷. In ME-water and DME-water systems, $\Delta G_t^\circ(l)$ decreases with increase in mol% of ME or DME, the effect being greater in DME + H₂O (Table 7).

Solvent effect is determined by the interactions of H⁺, HA and A⁻ with the solvent molecules and is better understood in terms of $\Delta G_t^\circ(i)$ values in equation (17) of all the three species involved in the dissociation equilibrium^{18, 19}.

$$\Delta G_t^{\circ}(i) = \Delta G_t^{\circ}(H^+) + \Delta G_t^{\circ}(A^-) - \Delta G_t^{\circ}(HA) \quad \dots (17)$$

where $\Delta G_t^{\circ}(i)$ 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 molar scale.

$\Delta G_t^{\circ}(H^+)$ values for the studied solvent systems have been given in Chapter II of the present thesis. The values of $\Delta G_t^{\circ}(H^+)$ facilitates the evaluation of the combined term $\Delta G_t^{\circ}(A^-) - \Delta G_t^{\circ}(HA)$ from equation (17).

Variations of $\Delta G_t^{\circ}(A^-) - \Delta G_t^{\circ}(HA)$ with mol% organic co-solvent has been shown in Fig. 5. It can be observed that the value of $\Delta G_t^{\circ}(A^-) - \Delta G_t^{\circ}(HA)$ in ME + H₂O and DME + H₂O continuously decreases with increasing mol% of organic co-solvent.

The dispersion interaction contribution to the combined term is expected to be cancelled to a large extent. The solvents, however, differ in their dielectric constant (ϵ) values and solvating capabilities. Again, ϵ value of ME-water being greater than that of DME-water of similar mol% non-aqueous component, electrostatic interactions should impart less positive contribution to $\Delta G_t^{\circ}(A^-)$ in ME-water than in DME-water. Approximately similar behaviour has been reflected in the relative positions of $\Delta G_t^{\circ}(A^-) - \Delta G_t^{\circ}(HA)$ curves (Fig. 5) upto 60 wt% of mixed solvents. Contrary behaviour at higher mol% of organic co-solvent may be attributed to stronger anion desolvating capability of DME compared to ME.

Increased number of $-CH_3$ groups in DME makes positive end of the dipole less available to anion than in ME and this is probably responsible for the observed relative behaviour of $\Delta G_t^\circ(A^-) - \Delta G_t^\circ(HA)$ in ME-water and DME-water at higher percentage of mixed solvent. The hydrogen bond formed by A^- are expected to be stronger with ME or DME than with water, causing greater stabilization of A^- and more negative ΔG_t° values with increasing proportion of ME or DME in the solvent.

The interaction of H^+ is reflected in $\Delta G_t^\circ(H^+)$ values which may be considered as a measure of relative solvent basicities. In conclusion it may be said that the overall dissociation behaviour of the acid in the two solvent system is primarily dictated by the specific chemical nature of the solute-solvent interaction besides the effect of relative solvent basicities.

Table 1 : Solvent Properties of Aqueous Binary Mixtures at 25°C

<u>ME-Water</u>				
wt% ME	ϵ	$10^2 \eta/\rho$	$\rho/\text{g cm}^{-3}$	Specific conduc- tance $\times 10^6$ ($\text{ohm}^{-1}\text{cm}^{-1}$)
0	78.54	0.8903	0.99707	<1.05
20	69.73	1.51647	1.0024	37.30
40	57.41	2.36545	1.0069	20.00
60	42.11	2.88490	1.00233	7.22
80	26.53	2.5708	0.985715	3.84
100	16.93	1.5414	0.96002	1.01
<u>DME-Water</u>				
20	64.10	1.6230	0.98789	28.20
40	49.75	2.1250	0.96349	19.10
60	35.84	1.6320	0.93921	4.20
80	20.87	0.9240	0.90987	0.90
100	7.075	0.4100	0.8613	0.81

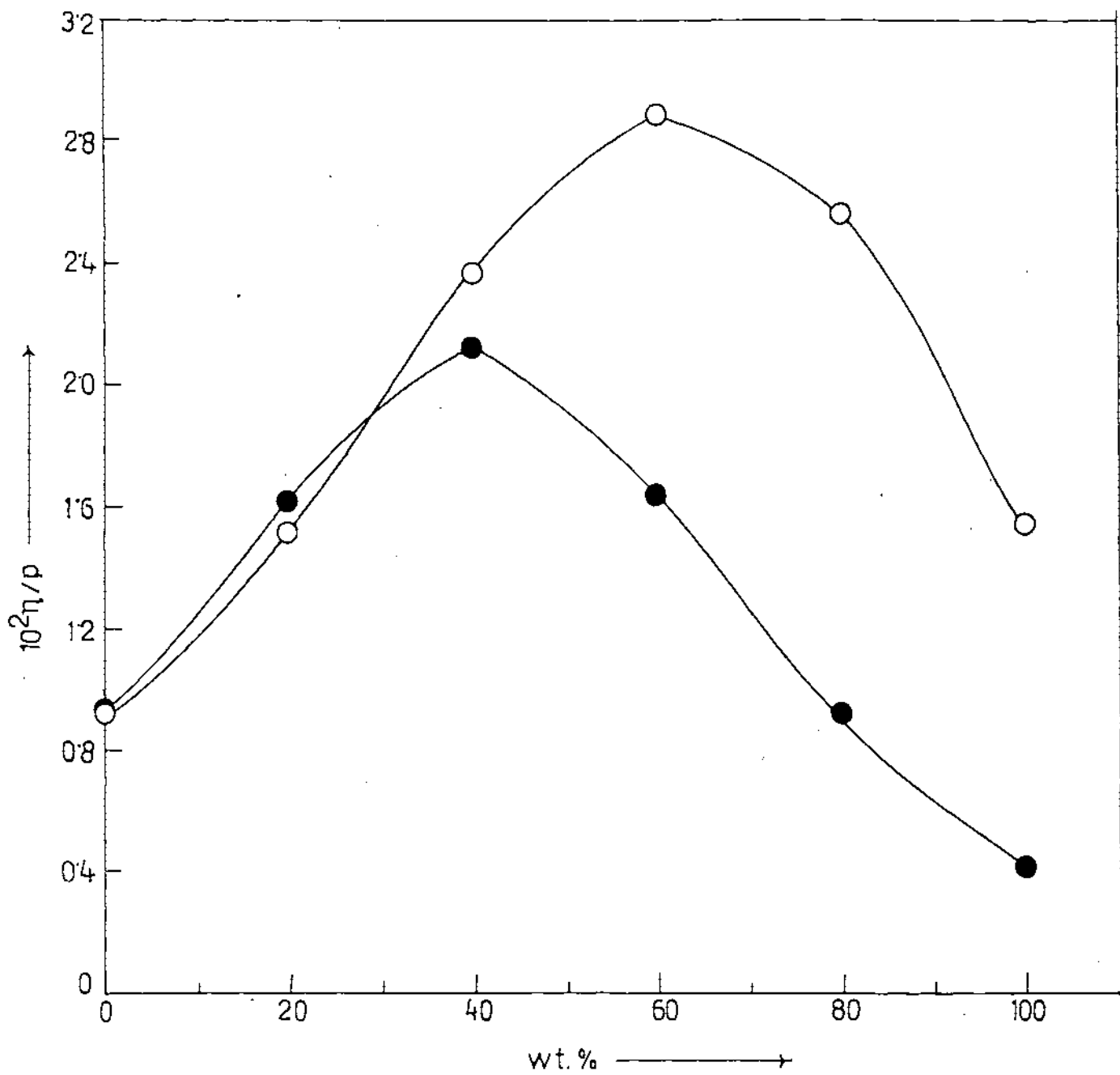


Fig. 1.- Viscosity of the mixtures vs wt% of the organic components. ME-H₂O,(O); DME-H₂O,(●).

Table 2 , Equivalent Conductance (\wedge) of Picric Acid in Aqueous Binary Mixtures of ME at 25°C

20 Wt% ME		40 Wt% ME		60 Wt% ME	
$10^4 C$ (mol dm ⁻³)	\wedge ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	$10^4 C$ (mol dm ⁻³)	\wedge ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	$10^4 C$ (mol dm ⁻³)	\wedge ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
2.4704	236.95	2.7760	144.40	2.5926	82.45
6.1761	235.75	5.5519	143.80	3.6297	82.10
11.1169	234.78	9.7159	143.07	6.4816	81.46
18.5282	233.40	16.6557	142.29	11.6668	80.70
29.6451	232.08	27.7596	141.21	18.1484	79.85
43.2325	230.38	44.4153	139.82	25.9264	79.07
80 Wt% ME		100 Wt% ME			
1.5308	47.95	1.0563	17.70		
3.0616	47.36	2.6407	15.68		
8.1643	46.42	5.2813	11.63		
12.6025	45.75	7.9219	9.49		
20.9210	44.79	10.5630	8.38		
27.5625	44.15	26.4070	5.57		

Table 3 : Equivalent Conductance (\wedge) of Picric Acid in Aqueous Binary Mixtures of DME at 25 °C

20 Wt% DME		40 Wt% DME		60 Wt% DME	
$10^4 C$ (mol dm ⁻³)	$(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	$10^4 C$ (mol dm ⁻³)	$(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	$10^4 C$ (mol dm ⁻³)	$(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$
5.4501	238.01	4.4890	145.50	3.0946	97.27
16.3502	235.02	10.2400	143.75	7.7365	95.65
27.2600	233.50	17.2225	142.25	12.3783	94.60
38.1601	232.00	24.0100	141.00	17.0202	93.70
49.0602	231.01	34.8101	139.50	21.6620	92.79
59.9600	229.50	44.8900	138.25	30.9458	91.40
80 Wt% DME		100 Wt% DME			
3.4132	72.40	0.1225	12.50		
8.5330	70.43	0.4225	11.00		
13.6528	68.63	0.9864	8.50		
20.4792	67.04	1.6901	6.02		
30.7188	65.11	2.1025	4.70		
37.8225	63.80	2.4661	3.30		

Table 4 , Limiting Conductances (Λ_0) of Picric Acid in ME-Water and DME-Water Mixtures at 25°C

Wt%	Λ_0	
	ME	DME
00	380.24 ^a	—
20	238.61	240.59
40	145.78	147.82
60	83.68	99.59
80	49.09	76.89
100	41.09	21.18

^a Ref. 14

Table 5 : Conductance Parameters and Dissociation Constants (pK) of Picric Acid in ME-Water Mixtures at 25 °C from 1978 Fuoss Equation

Wt%	Λ_0 ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	K_A ($\text{dm}^3\text{mol}^{-1}$)	$\Lambda_0\eta$	R (Å)	σ %	pK
00	—	—	3.3853 ^a	—	—	0.42 ^b
20	238.66(± 0.06)	3.43(±0.13)	3.6191	9.00	0.03518	0.54(±0.016)
40	145.76(±0.03)	5.40(±0.09)	3.4479	17.00	0.02564	0.73(±0.007)
60	83.75(±0.04)	10.97(±0.39)	2.4160	9.70	0.05518	1.04(±0.015)
80	49.09(±0.03)	33.01(±0.69)	1.2622	22.00	0.08260	1.52(±0.018)
100 ^c	41.09	21338.69	0.6334	—	—	4.33

^aRef. 14

^bRef. 17

^cRef. From Shedlovsky's method

Table 6 : Conductance Parameters and Dissociation Constants (pK) of Picric Acid in DME-Water Mixtures at 25 °C from 1978 Fuoss Equation.

Wt%	Λ_0 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	K_A ($\text{dm}^3 \text{mol}^{-1}$)	$\Lambda_0 \eta$	$\frac{R}{\Omega}$ (A)	σ %	pK
20	240.69(± 0.22)	4.35(± 0.31)	3.9064	9.50	0.10115	0.64(± 0.030)
40	147.94(± 0.11)	10.46(± 0.37)	3.1437	9.60	0.08203	1.02(± 0.015)
60	99.69(± 0.04)	19.62(± 0.36)	1.6269	14.00	0.04733	1.29(± 0.008)
80	76.78(± 0.11)	55.28(± 1.44)	0.7094	23.00	0.14479	1.74(± 0.022)
100 ^d	21.18	73561.38	0.0868	—	—	4.87

^d From Shedlovsky's method

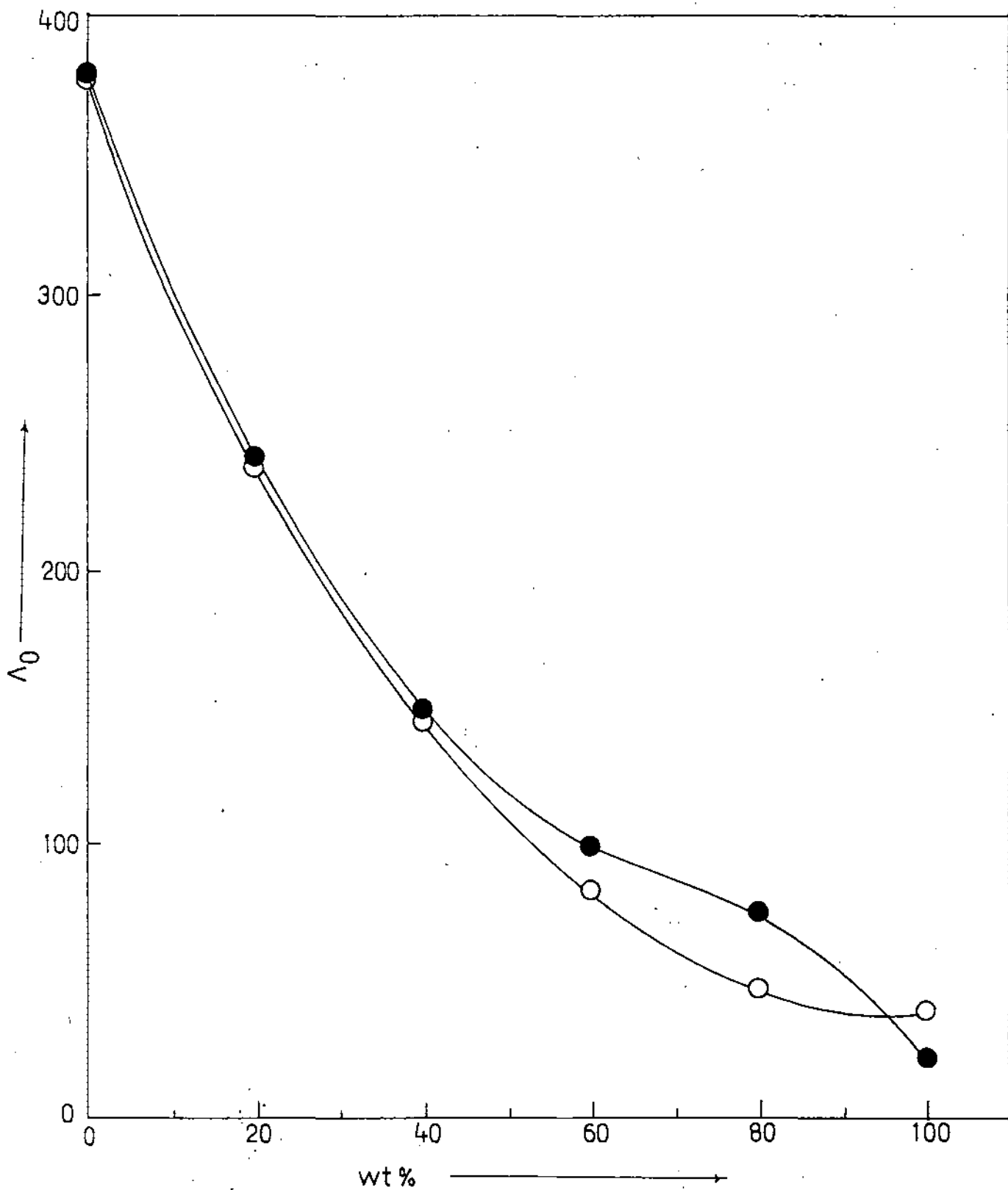


Fig. 2. - Variation of limiting equivalent conductance of Picric acid (Λ_0) with composition of the solvent mixture.

(O) ME-H₂O; (●) DME-H₂O.

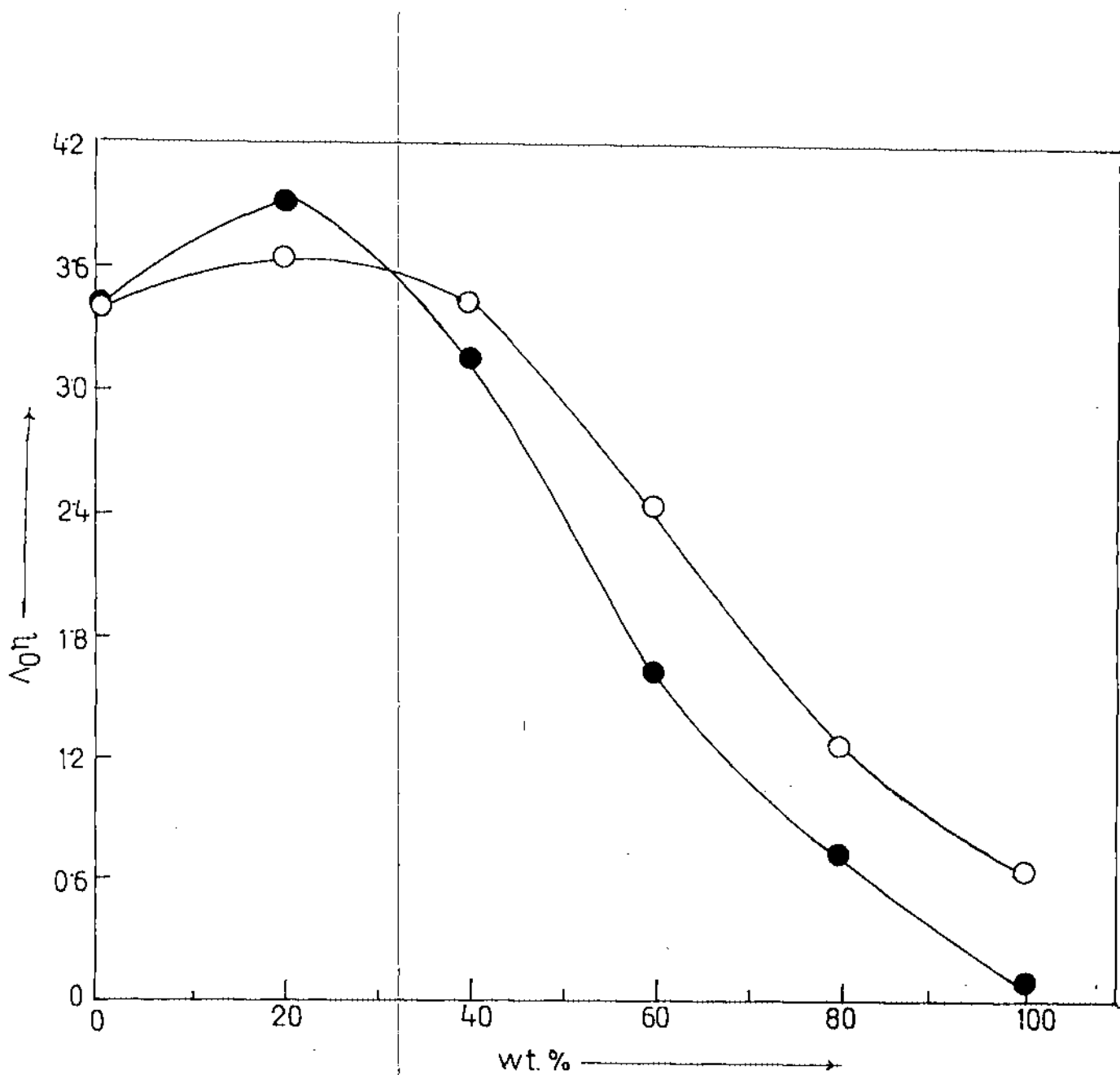


Fig. 3.- Variation of Walden product ($\Lambda_0\eta$) of Picric acid with composition of the solvent mixture.

(O) ME-H₂O ; (●) DME-H₂O

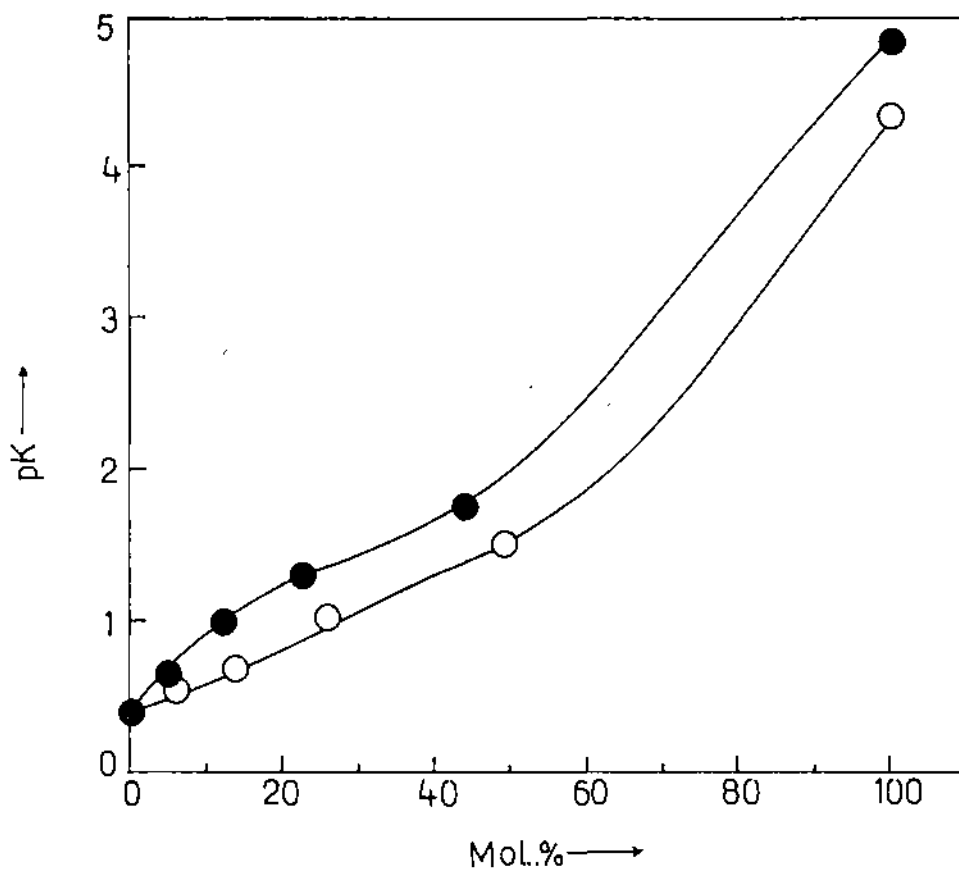


Fig. 4(a) - Variation of pK with mol.% of the solvent. (●), DME - H₂O ; (○), ME - H₂O.

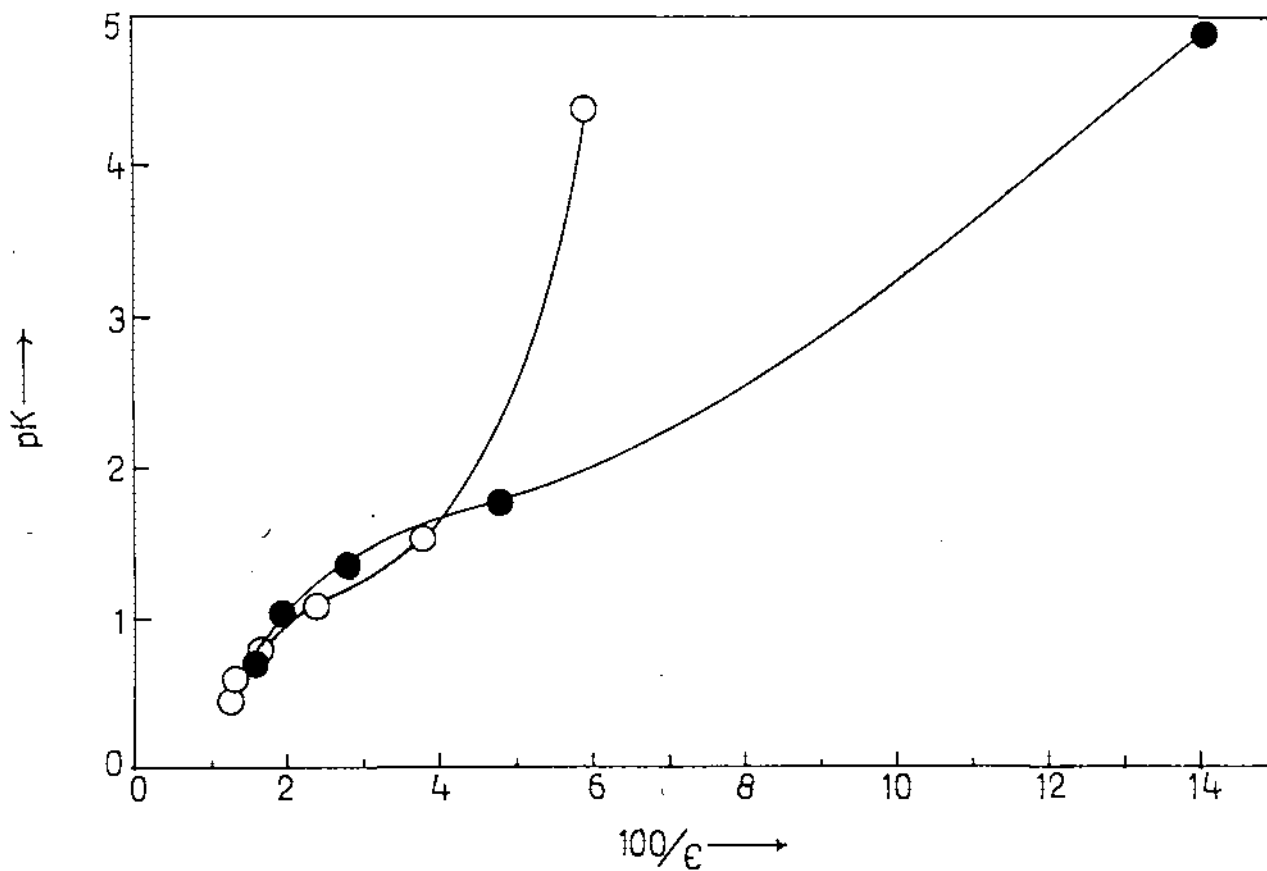


Fig 4(b) - Variation of pK with Dielectric constant (ϵ) of the solvent mixture. (●), DME-H₂O ; (○), ME-H₂O.

Table 7 : Values of $\Delta G_t^\circ(1)$, $\Delta G_t^\circ(H^+)$ and $\Delta G_t^\circ(A^-) - \Delta G_t^\circ(HA)$ for Picric acid in aqueous mixtures of ME and DME at 25°C [ΔG° values are in kJ mol⁻¹ (molar scale)]

Wt% Co-Solvent	Mol% Co-Solvent	$\Delta G_t^\circ(1)$	$\Delta G_t^\circ(H^+)$	$\Delta G_t^\circ(A^-) - \Delta G_t^\circ(HA)$
ME + Water mixtures				
20	5.58	-0.68	-1.88	1.19
40	13.63	-1.77	-2.43	0.66
60	26.20	-3.54	-2.93	-0.61
80	48.64	-6.28	-2.25	-3.35
100	---	-22.31	---	---
DME + Water mixtures				
20	4.75	-1.26	-2.57	1.31
40	11.75	-3.42	-3.99	0.57
60	23.08	-4.96	-4.57	-0.39
80	44.45	-7.53	-1.42	-6.11
100	---	-25.39	---	---

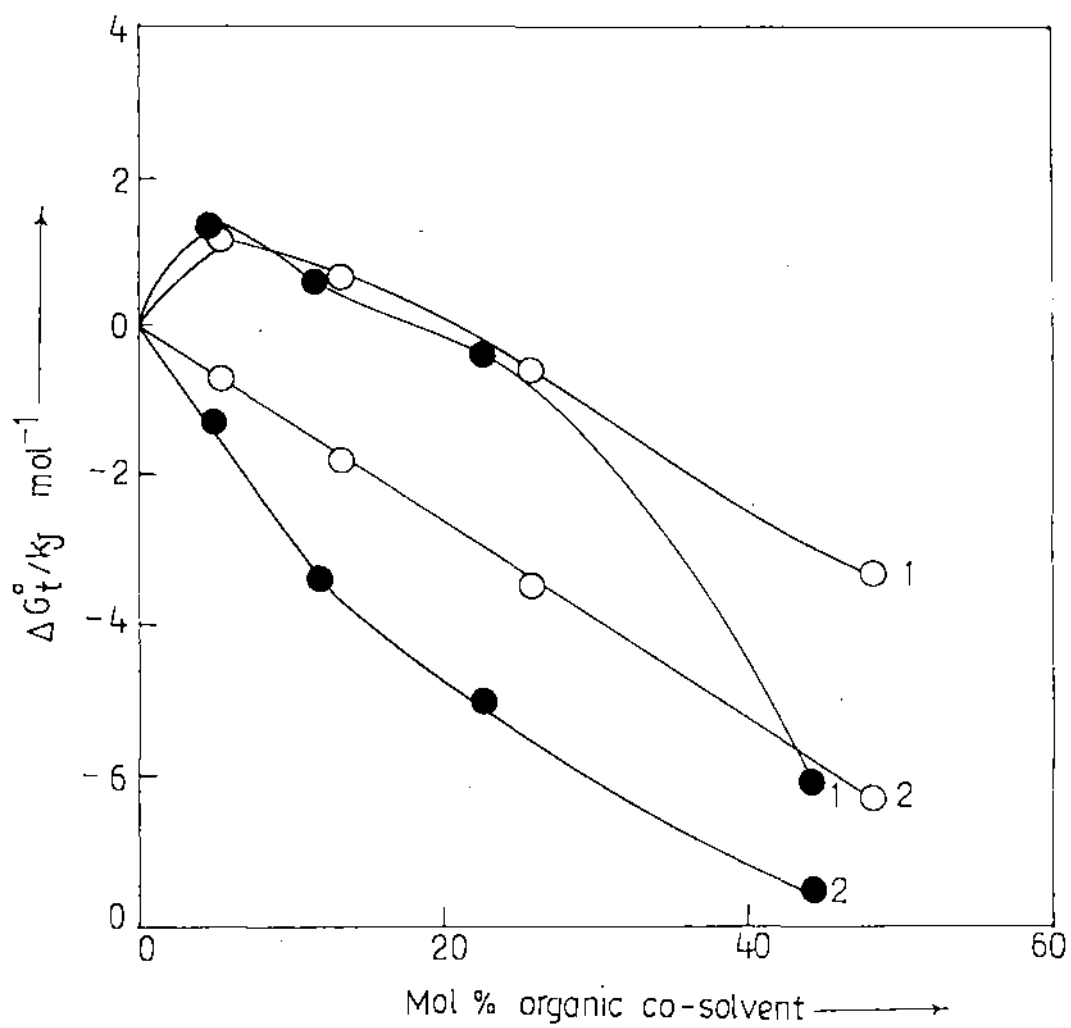


Fig. 5 - Variation of (1) $\Delta G^\circ(\text{A}^-) - \Delta G^\circ(\text{HA})$ and (2) ΔG° of Picric acid in aqueous mixtures of ME(O) and DME(●)

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