

CHAPTER - IV

Solubilities and Free Energies of Transfer for p-Nitro, p-Chloro and p-Bromo-benzoic Acids in Aqueous Mixtures of 2-Methoxyethanol and 1,2-Dimethoxyethane.

Solubilities and dissociation of substituted benzoic acids were reported earlier^{1,2} in aqueous mixtures of methanol and ethanol. In this chapter we report our studies on solubilities and dissociation constants of p-nitro, p-bromo and p-chloro benzoic acids in a series of aqueous mixtures of 2-methoxy ethanol (ME) and 1,2-dimethoxyethane (DME). Since the solvent effect involves $\Delta G_t^{\circ}(\text{H}^+)$ and $\Delta G_t^{\circ}(\text{H}^+)$ values have been found to be different between alcohols and studied solvent systems, it would be interesting to study the proton transfer processes in these particular class of solvents media. Thus 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.

Experimental

ME (G.R., E. Merck) was distilled twice and the middle fraction was utilised. DME (Fluka, Purum) was first shaken with FeSO_4 (A.R., B.D.H.) for 1-2 h, decanted and then distilled. The distillate was then successfully refluxed for 12 h and distilled over metallic sodium. Other chemicals were of analytical grade. Double distilled water from all glass distilling sets was used for preparing the solutions.

p-chloro benzoic acid (Puriss, Fluka), p-bromo benzoic acid (Puriss, Fluka) and p-nitro benzoic acid (G.R., E. Merck) were all crystallised from ethanol-water mixtures. The purity of the samples was tested by melting point determination.

The solubilities of these acids were determined with the help of a Campbell solubility apparatus³. The solutions were taken in stoppered bottles, which were shaken in a mechanical shaker for 12 h at room temperature (27-35 °C). The bottles were then thermostated at 25 ± 0.01 °C for 24 h with occasional shaking and then filtered by inversion of the apparatus at the same temperature. The concentrations of the saturated solutions from each bottle were determined by titration with a standardised (0.1-0.01 N) caustic soda solution with phenolphthalein as indicator. The operations were repeated until successive results were in agreement. Four sets of experiments were performed for each percentage of the solvent mixture. The solubilities of p-chloro, p-bromo and p-nitro benzoic acids in molarity are recorded in Tables 1-5. The solubilities in water are found to be 0.0008, 0.0005 and 0.0025 mol dm⁻³ respectively which agree fairly well with the literature values^{2,4}.

The pH of the saturated solutions of the acids for each percentage of the mixed solvents were measured using an ECIL pH-meter having an accuracy of ± 0.01 pH unit. Proper calibration of the glass Calomel electrode and appropriate corrections⁵ for

the change of the solvent compositions were made. The measurements were made at $25 \pm 0.01^\circ \text{C}$. The dielectric constants of the solvent mixtures were taken from the literature^{6,7}.

Results and Discussion

The thermodynamic dissociation constant for the reaction



(A^- = substituted benzoate ion)

can be written as

$$K_T = \frac{C_{\text{H}^+} \times C_{\text{A}^-}}{C_{\text{HA}}} \times \frac{f_{\pm}^2}{f_{\text{HA}}} = \frac{C_{\text{H}^+}^2}{[\text{C}]_T - C_{\text{H}^+}} \times f_{\pm}^2 \quad \dots (2)$$

where $[\text{C}]_T$ = Total benzoic acid concentration; C_{H^+} = concentration of $[\text{H}^+]$ in the saturated experimental solutions determined pH - metrically. The mean molar activity coefficient of the ions at different concentrations in aqueous and mixed solvents have been determined using the Debye-Huckel limiting law,

$$-\log f_{\pm} = A\sqrt{\mu} \quad \dots (3)$$

with appropriate A-values in mixed solvents calculated from the dielectric constant values in the literature. The activity coefficients of neutral benzoic acid have been assumed to be

unity in the saturated solutions of benzoic acid in the respective solvents. The ionic strengths of the solutions have been determined from C_H^+ values based on equation (1). The dissociation constant values of the acids determined by the solubility measurements in aqueous mixtures of ME and DME have been recorded in Tables 1-5.

The free energies of transfer for the dissociation of substituted benzoic acids have been calculated using equation (4)

$$\begin{aligned} \Delta G_t^\circ(1) &= \Delta G_s^\circ - \Delta G_w^\circ \\ &= -2.303 RT [\log K_{T(s)} - \log K_{T(w)}] \quad \dots (4) \end{aligned}$$

The standard free energies of transfer from water to mixed solvents were calculated using the relation

$$\begin{aligned} \Delta G_t^\circ(\text{HA}) &= \Delta G_s^\circ(\text{HA}) - \Delta G_w^\circ(\text{HA}) \\ &= -2.303 RT \log \frac{C_s}{C_w} \times \frac{f_s(\text{HA})}{f_w(\text{HA})} \quad \dots (5) \end{aligned}$$

where C_s and C_w are solubilities of the acid in water and respective solvents in molar scale. However, the validity of this relation depends on the assumption that the ratio of the activity coefficients of the neutral acid in the saturated solutions in the mixed solvent and in water is unity⁸.

The free energy change accompanying the transfer of benzoate ion from the standard state in water to that in mixed solvent has been calculated using equation (7).

$$\Delta G_t^\circ(1) = \Delta G_t^\circ(H^+) + \Delta G_t^\circ(A^-) - \Delta G_t^\circ(HA) \quad \dots (6)$$

$$\Delta G_t^\circ(A^-) = \Delta G_t^\circ(1) - \Delta G_t^\circ(H^+) + \Delta G_t^\circ(HA) \quad \dots (7)$$

$\Delta G_t^\circ(H^+)$ in equation (7) stands for the free energy change for the transfer of H^+ from the standard state in water to that in the solvent and may be taken as a measure of the basicity of the solvents with respect to that of water. The $\Delta G_t^\circ(H^+)$ values were taken from our earlier works as described in Chapter II. The values of $\Delta G_t^\circ(HA)$, $\Delta G_t^\circ(H^+)$, $\Delta G_t^\circ(1)$ and $\Delta G_t^\circ(A^-)$ have been recorded in tables 6-10.

The solubility values (Tables 1-5) of the acids increase with the increase in the organic solvent content of the mixed solvents and show linear relationship when plotted against (i) mole-fraction and (ii) $1/\epsilon$ well upto ~ 70 wt% beyond which deviation occurs (Fig. 1 and 2). It is observed that the solubility increases with decreasing dielectric constant of the medium with the exception of p-bromo benzoic acid in pure DME. This increase might be due to the solute-solvent interactions and the preferential solvation of the solute molecules by the organic solvent at the higher percentages of the mixed solvents may cause this deviation. However, it is interesting to note that the

solubility of the respective acid is greater in DME or DME + H₂O mixtures compared to that in ME or ME + H₂O mixtures, the values are approximately in the order p-nitrobenzoic acid > p-chlorobenzoic acid > p-bromobenzoic acid. The number of -CH₃ groups relative to that of hydrophilic -OH groups being greater in DME, a greater dispersion effect is expected in DME - H₂O and this may be largely responsible for the greater stability of the acids (more negative $\Delta G_t^{\circ}(\text{HA})$) in DME - H₂O compared to ME - H₂O as observed. Again, the difference in the behaviour of the solubilities of these substituted acids in the solvent systems can be qualitatively explained on the basis of solute-solvent dipole interactions and the relative solvent basicities. The $\Delta G_t^{\circ}(\text{H}^+)$ values are found to be increasingly negative both in ME + H₂O and DME + H₂O indicating increased stabilization of H⁺ in the mixed solvents upto 80 wt% of organic co-solvents. The $\Delta G_t^{\circ}(\text{H}^+)$ values indicate that the solvent mixtures become increasingly basic in character compare to water as the organic solvent component increases. The changes of the basicity of the solvent mixtures are reflected in the free energy of transfer of H⁺ ion and the solubility values of the acids. Presence of nitro group than the chloride or the bromide group in the para position of the benzene ring increases the polarity of that solute molecule to a large extent and the basicity is much greater in DME than in ME leading to an increase in solubility with increase in DME content of the solvent medium, the rate of

increase being larger at higher percentage of the mixed solvents.

It can be seen from the tables that the pK_T values increase continuously with the increase in the percentage of organic solvent and show a linear relationship when plotted against $1/\epsilon$ at low percentages but deviations occur at higher percentages (Fig. 3). It is also observed that the pK_T values are in the order, $\text{DME} - \text{H}_2\text{O} > \text{ME} - \text{H}_2\text{O}$ mixtures, the values are generally greater for *p*-bromobenzoic acid and *p*-chlorobenzoic acid has higher pK_T values than *p*-nitrobenzoic acid, contrary to the solubility values of these acids in these solvent mixtures. The two solvents differ on their dielectric constant values and solvating capabilities. The dielectric constant of $\text{ME} - \text{H}_2\text{O}$ is greater than $\text{DME} - \text{H}_2\text{O}$ of similar mol% non-aqueous component, electrostatic interactions thus impart less positive contribution to $\Delta G_t^\circ(\text{A}^-)$ in $\text{ME} + \text{H}_2\text{O}$ than in $\text{DME} + \text{H}_2\text{O}$ resulting in more ionization in the former than in the latter solvent system. However, the behaviour as reflected in the relative pK_T values of *p*-chloro, *p*-bromo and *p*-nitro benzoic acids may be attributed to relative destabilization of anions in these solvent systems and the results indicate that their order are being $\text{Br}^- > \text{Cl}^- > \text{NO}_2^-$. The destabilization of the anions are the results of decreased acidity of aquo-cosolvent mixture.

Table 6-10 show the increasingly negative magnitudes of $\Delta G_t^\circ(\text{HA})$ with increase in mol% of ME or DME, the values are less negative in ME than DME (Fig. 4). This indicates the

stabilization of these acids in these mixed solvents, primarily through dispersion forces¹⁰ and the basicity of the solvents are reflected on the ΔG_t° values, DME - H₂O is less acidic than ME - H₂O. The $\Delta G_t^\circ(A^-)$ values are predominantly positive is in agreement with the fact that ΔG_t° of anions are usually positive¹¹. The results indicate that the transfer of $\Delta G_t^\circ(A^-)$ is non-spontaneous from water to mixed solvents.

In conclusion it may be said that the overall dissociation behaviour in these two solvent systems is dictated by specific solute-solvent interactions besides the effects of relative solvent basicities.

Table 1 : Solubility and pK-Values of p-Nitrobenzoic Acid in ME-Water Mixtures at 25 °C

Wt% of ME	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol dm ⁻³)	-2 log f _±	Corrected pH	pK	pK _T
00	1.27	0.509	0.0025 (0.002516)*	0.02	3.12	3.48	3.50
10	1.34	0.549	0.0028	0.03	3.13	3.57	3.60
20	1.43	0.606	0.0039	0.03	3.12	3.73	3.76
30	1.56	0.691	0.0119	0.04	3.06	4.16	4.20
40	1.74	0.813	0.0146	0.04	3.14	4.42	4.46
50	1.99	0.995	0.0259	0.05	3.24	4.88	4.93
60	2.37	1.293	0.0518	0.06	3.23	5.17	5.23
70	2.92	1.768	0.0930	0.08	3.33	5.63	5.71
80	3.77	2.593	0.1984	0.10	3.43	6.15	6.25
90	5.26	4.278	0.3739	0.12	3.72	7.01	7.13
100	5.91	5.087	0.4884	-	-	-	-

* Ref. 2.

Table 2 : Solubility and pK-Values of p-Nitrobenzoic Acid in DME-Water Mixtures at 25 °C

Wt% of DME	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol dm ⁻³)	$-2 \log f_{\pm}$	Corrected pH	pK	pK _T
10	1.40	0.587	0.0031	0.03	3.15	3.68	3.71
20	1.56	0.691	0.0042	0.04	3.15	3.84	3.88
30	1.76	0.827	0.0123	0.05	3.12	4.30	4.35
40	2.01	1.009	0.0294	0.05	3.07	4.59	4.64
50	2.35	1.277	0.0379	0.06	3.19	4.95	5.01
60	2.79	1.652	0.1821	0.09	3.09	5.44	5.53
70	3.58	2.401	0.3300	0.12	3.15	5.82	5.94
80	4.79	3.714	0.6534	0.15	3.37	6.56	6.71
90	7.42	7.160	0.7509	0.19	3.75	7.38	7.57
100	14.12	18.811	0.8324	-	-	-	-

Table 3 : Solubility and pK-Values of p-Chlorobenzoic Acid in ME-Water Mixtures at 25 °C

Wt% of Solvent	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol dm ⁻³)	-2 log f _±	Corrected pH	pK	pK _T
00	1.27	0.509	0.0008(0.000797)*	0.01	3.62	3.99	4.00
10	1.34	0.549	0.0013	0.01	3.78	4.61	4.62
20	1.43	0.606	0.0026	0.02	3.70	4.78	4.80
30	1.56	0.691	0.0056	0.02	3.67	5.07	5.09
40	1.74	0.813	0.0112	0.03	3.62	5.28	5.31
50	1.99	0.995	0.0162	0.03	3.75	5.71	5.74
60	2.37	1.293	0.0334	0.03	3.85	6.22	6.25
70	2.92	1.768	0.0535	0.04	3.87	6.47	6.51
80	3.77	2.593	0.1268	0.06	3.92	6.94	7.00
90	5.26	4.278	0.2589	0.07	4.13	7.67	7.74
100	5.91	5.087	0.4031	-	-	-	-

* Ref. 4.

Table 4 : Solubility and pK-Values of p-Chlorobenzoic Acid in DME-Water Mixtures at 25°C

Wt% of DME	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol.dm ⁻³)	-2 log f _±	Corrected pH	pK	pK _T
10	1.40	0.587	0.0015	0.01	3.82	4.77	4.78
20	1.56	0.691	0.0030	0.02	3.83	5.12	5.14
30	1.76	0.827	0.0071	0.02	3.72	5.28	5.30
40	2.01	1.009	0.0202	0.03	3.67	5.64	5.67
50	2.35	1.277	0.0484	0.04	3.65	5.98	6.02
60	2.79	1.652	0.0946	0.05	3.71	6.39	6.44
70	3.58	2.401	0.2631	0.06	3.74	6.90	6.96
80	4.79	3.714	0.5107	0.07	4.09	7.88	7.95
90	7.42	7.160	0.6318	0.09	4.37	8.54	8.63
100	14.12	18.811	1.0369	-	-	-	-

Table 5 : Solubility and pK-Values of p-Bromobenzoic Acid in ME-Water and DME-Water Mixtures at 25 °C

Wt%	Solubility (mol dm ⁻³)		-2 log f _±		Corrected pH		pK _T	
	ME	DME	ME	DME	ME	DME	ME	DME
00	0.0005	-	0.01	-	3.73	-	3.98	-
10	0.0009	0.0034	0.01	0.02	3.75	3.51	4.41	4.53
20	0.0012	0.0079	0.01	0.02	3.85	3.55	4.72	5.00
30	0.0023	0.0124	0.02	0.02	3.83	3.66	5.01	5.43
40	0.0035	0.0181	0.02	0.03	3.92	3.77	5.39	5.82
50	0.0090	0.0283	0.02	0.03	3.90	3.91	5.77	6.30
60	0.0127	0.0498	0.03	0.03	4.01	4.04	6.15	6.81
70	0.0206	0.2400	0.03	0.05	4.11	3.98	6.56	7.39
80	0.0521	0.3698	0.05	0.06	4.09	4.13	6.94	7.89
90	0.0637	0.5958	0.07	0.11	4.20	4.19	7.27	8.27
100	0.2895	0.4575	-	-	-	-	-	-

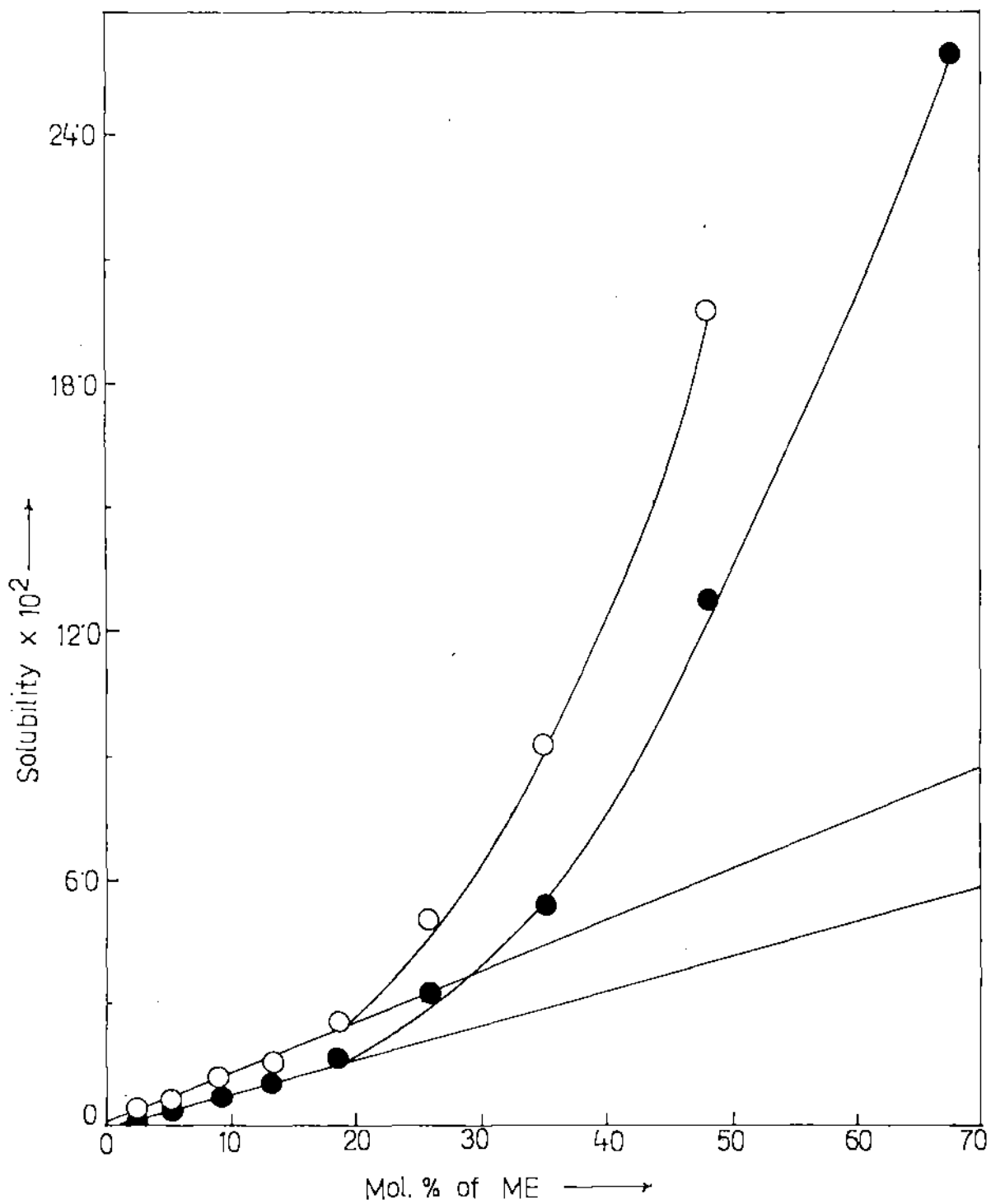


Fig. 1(a) - Variation of solubility of (●), p-Chlorobenzoic acid and (○), p-Nitrobenzoic acid with solvent composition.

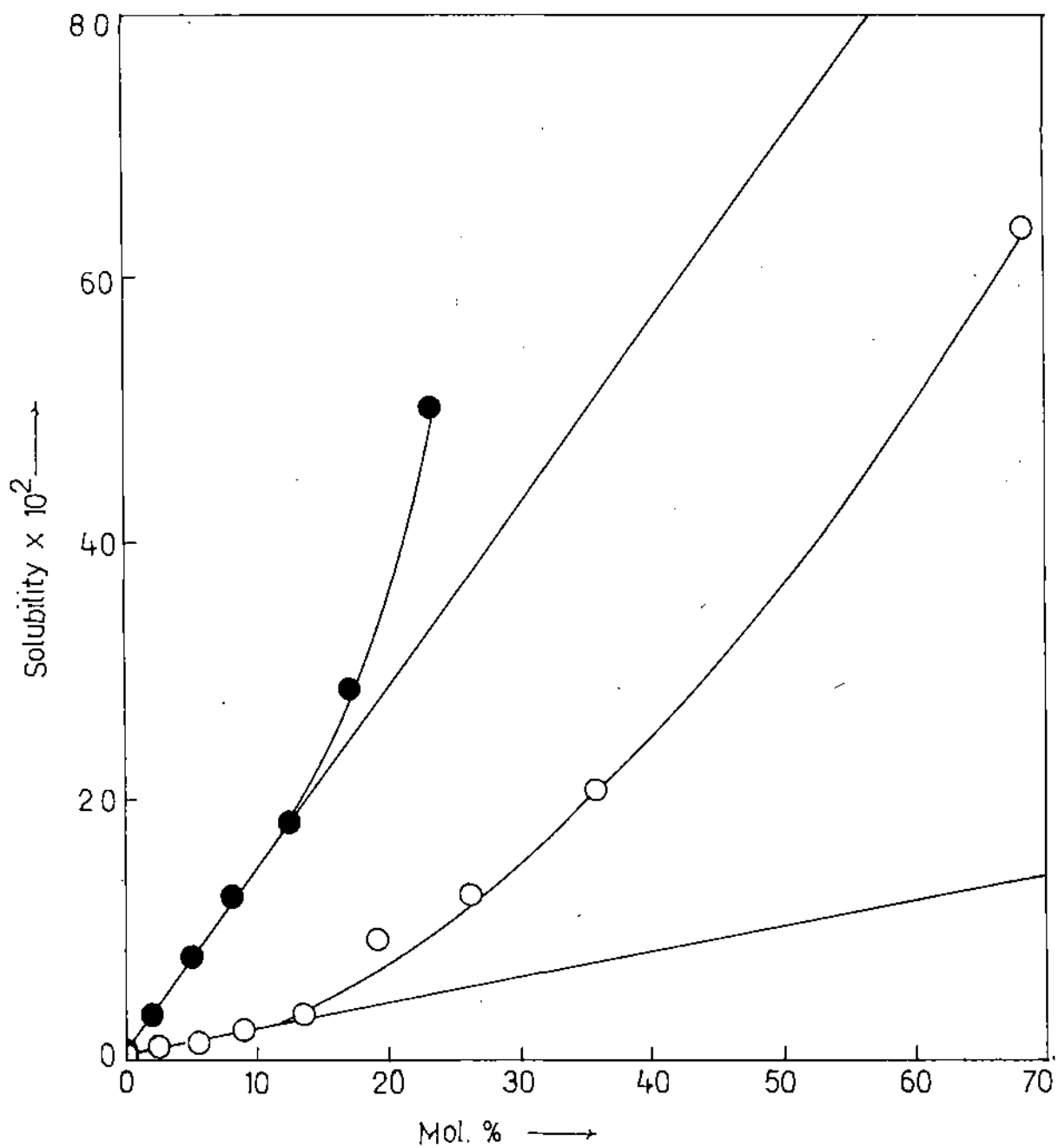


Fig.1 (b) - Variation of solubility with Mol % of (●) DME-H₂O and (○) ME-H₂O of p-Bromobenzoic acid.

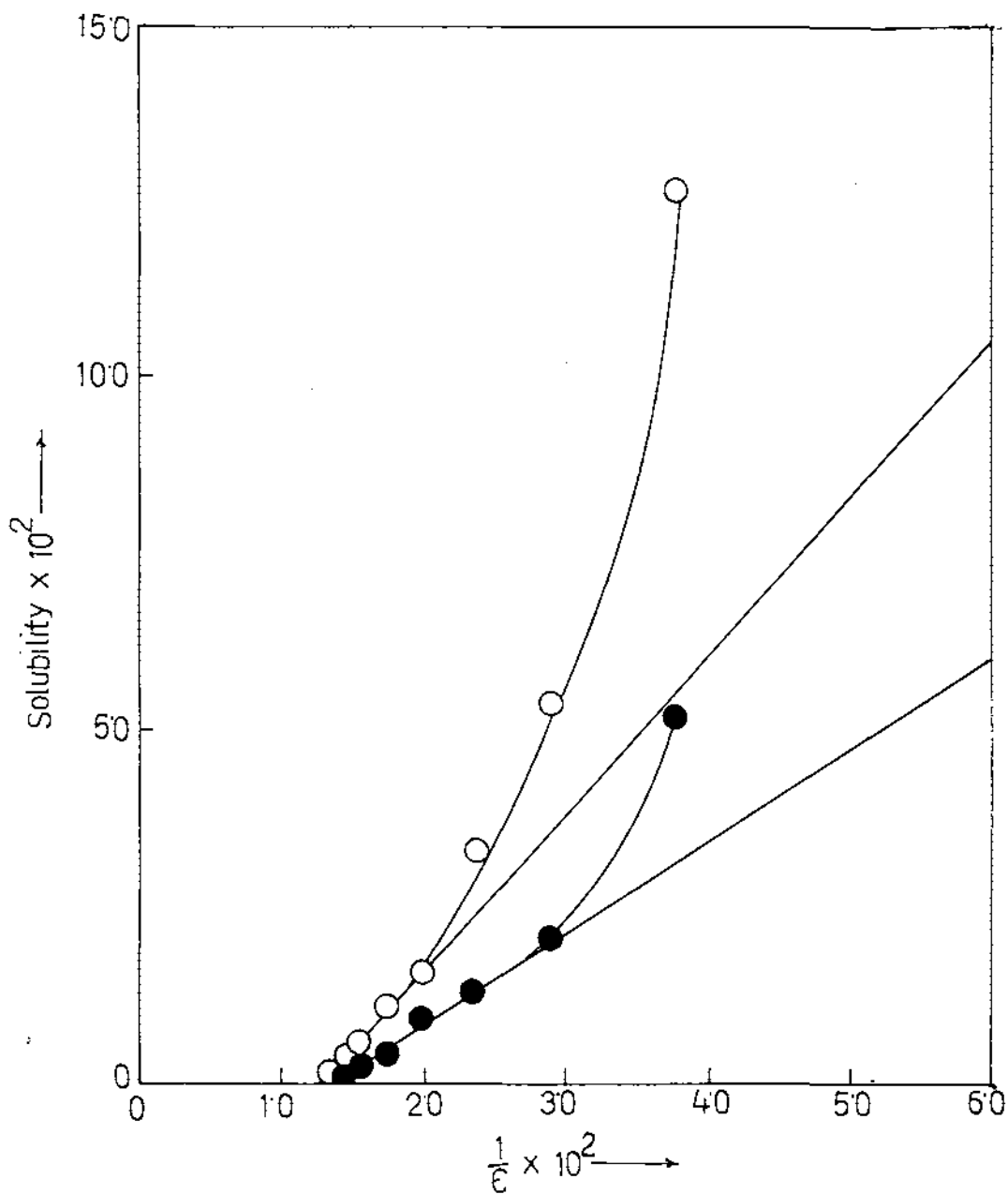


Fig 2(a) - Variation of solubility with ϵ of p-Chlorobenzoic acid (O) and p-Bromo-benzoic acid (●) in ME+H₂O.

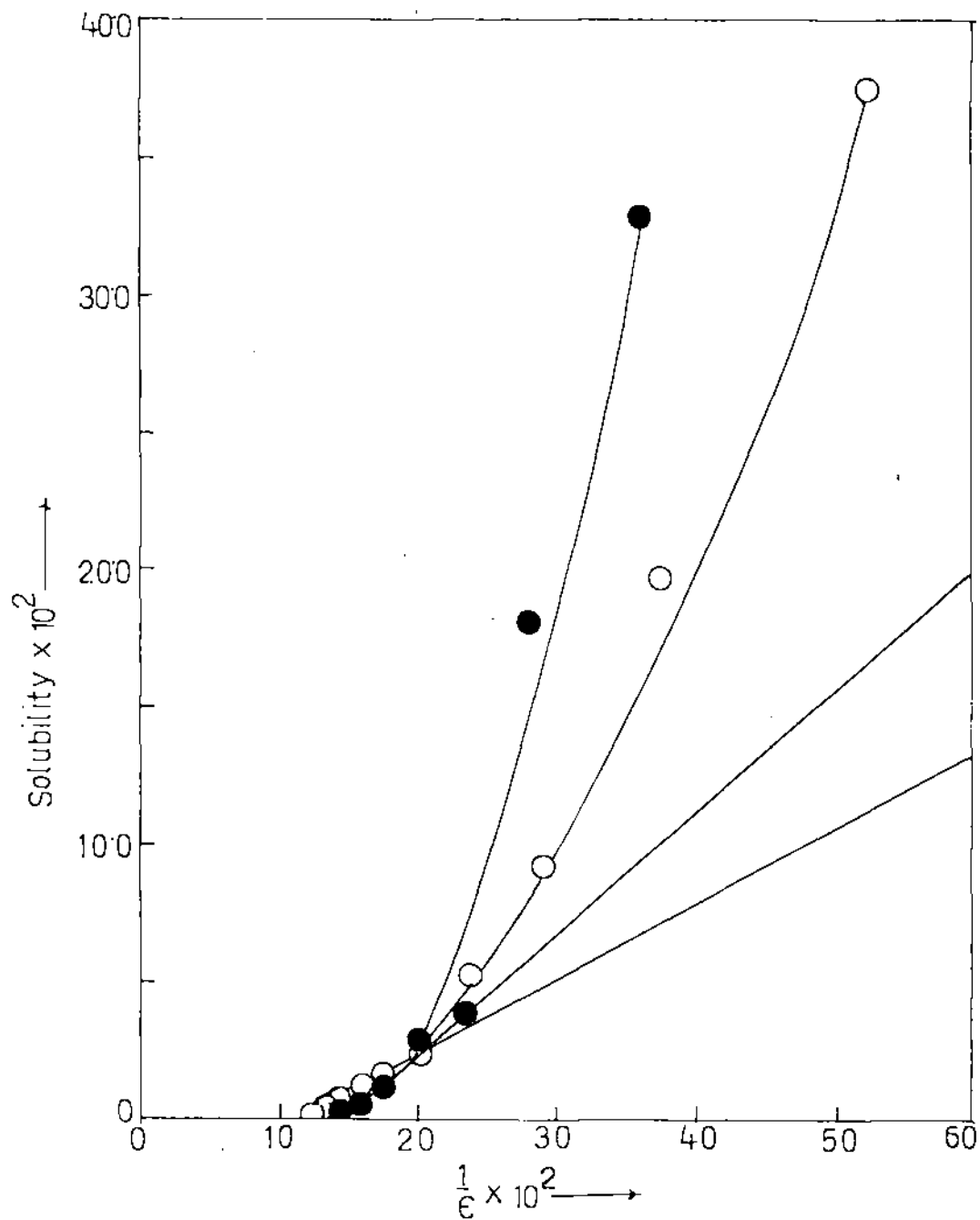


Fig 2(b) - Variation of solubility with ϵ of p-Nitrobenzoic acid in (●), DME-H₂O (○), ME-H₂O

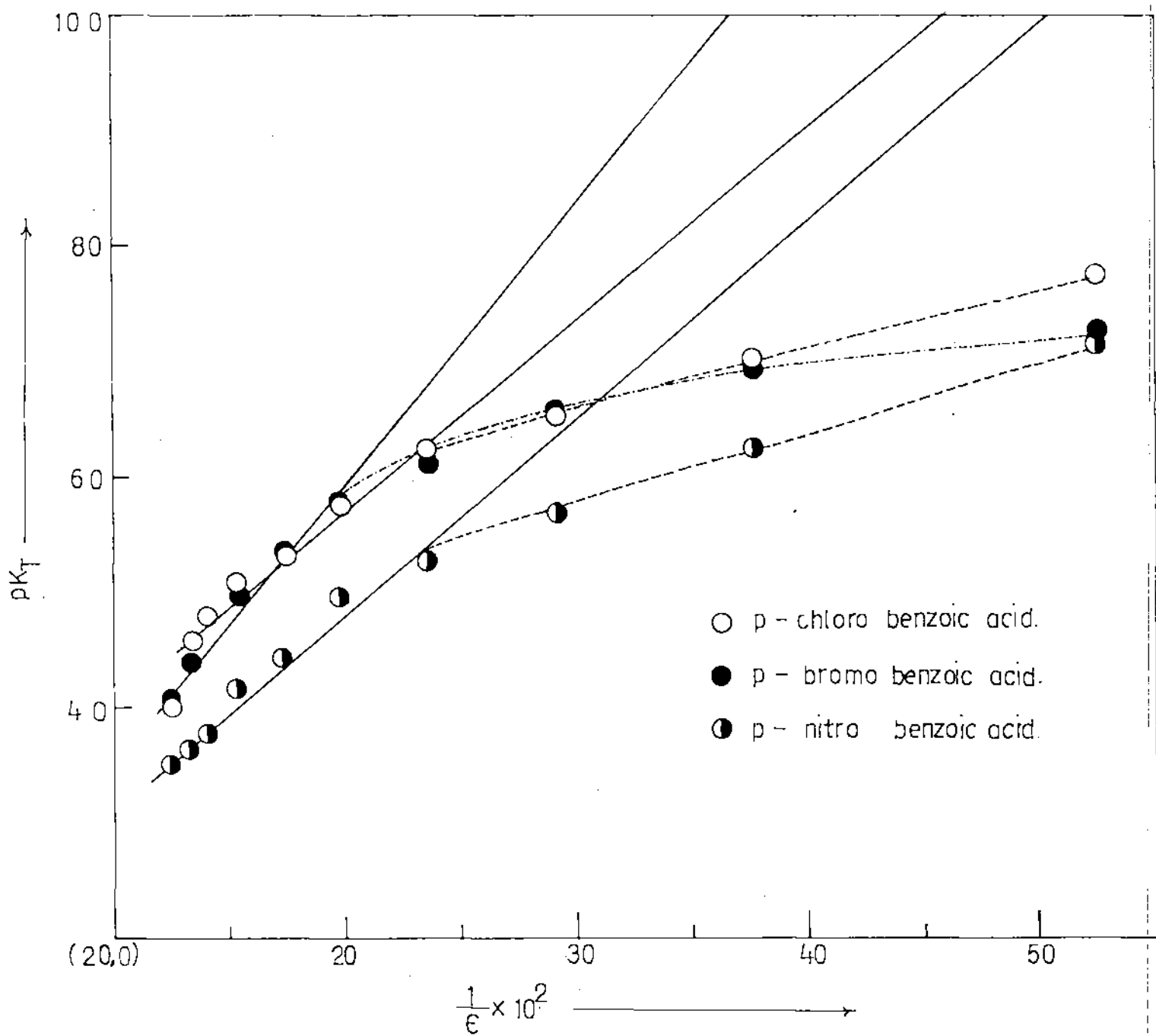


Fig. 3 (a) - Variation of pK_T with ϵ in ME + H₂O mixtures.

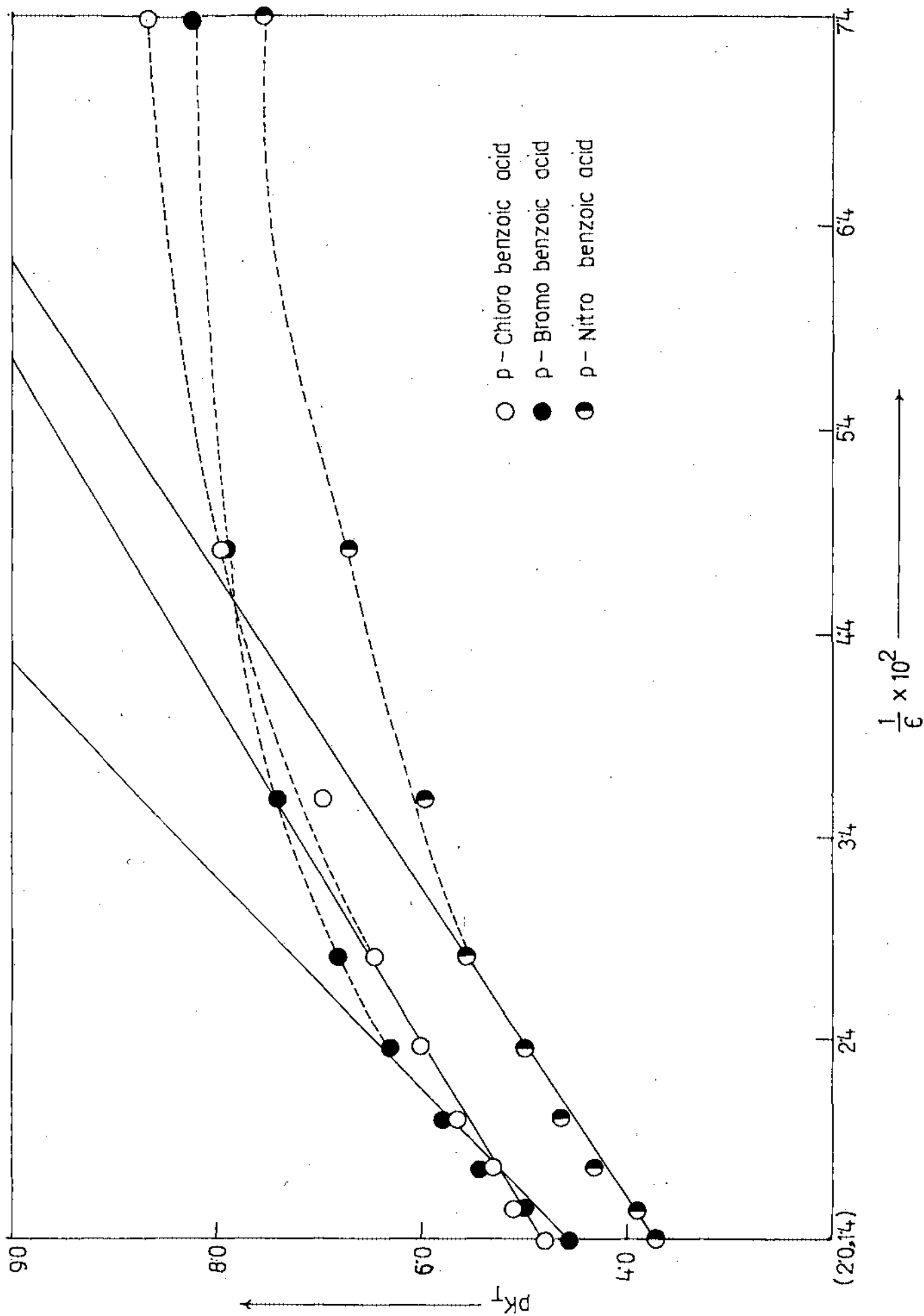


Fig.3(b) - Variation of pK_T with $\frac{1}{\epsilon}$ in DME + H₂O mixture.

Table 6 : Free Energy of Transfer of Anion $\Delta G_t^{\circ}(A^-)$ of
p-Nitrobenzoic Acid (in kJ) in ME-H₂O Mixtures at 25 °C

Wt% of ME	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(I)$	$\Delta G_t^{\circ}(H^+)$	$\Delta G_t^{\circ}(A^-)$
10	-0.28	0.57	-1.07	1.36
20	-1.10	1.48	-1.88	2.26
30	-3.87	3.99	-2.40	2.52
40	-4.37	5.48	-2.43	3.54
50	-5.79	8.16	-2.99	5.36
60	-7.51	9.87	-2.93	5.29
70	-8.96	12.61	-2.96	6.61
80	-10.84	16.32	-2.25	7.73
90	-12.41	20.71	+1.75	6.55
100	-13.07	-	-	-

N.B. Due to previous error in computation, $\Delta G_t^{\circ}(H^+)$ values are little different from the reported values in the published paper (J. Ind. Chem. Soc.) which have been corrected now along with the $\Delta G_t^{\circ}(A^-)$ values.

Table 7 : Free Energy of Trans of Anion $\Delta G_t^\circ(A^-)$ of
 p-Nitrobenzoic acid (in kJ) in DME-H₂O mixtures
 at 25 °C

Wt% of DME	$\Delta G_t^\circ(HA)$	$\Delta G_t^\circ(l)$	$\Delta G_t^\circ(H^+)$	$\Delta G_t^\circ(A^-)$
10	-0.53	1.20	-1.67	2.34
20	-1.29	2.17	-2.57	3.45
30	-3.95	4.85	-3.26	4.16
40	-6.11	6.50	-3.99	4.38
50	-6.74	8.62	-4.43	6.31
60	-10.63	11.58	-4.57	5.52
70	-12.10	13.92	-4.15	5.97
80	-13.79	18.32	-1.42	5.95
90	-14.14	23.22	+5.46	3.62
100	-14.39	-	-	-

Table 8 : Free Energy of Transfer of Anion $\Delta G_t^{\circ}(A^-)$ of
 p-Chlorobenzoic Acid (in kJ) in ME-H₂O Mixtures
 at 25 °C

Wt% of ME	$\Delta G_t^{\circ}(\text{HA})$	$\Delta G_t^{\circ}(\text{l})$	$\Delta G_t^{\circ}(\text{H}^+)$	$\Delta G_t^{\circ}(\text{A}^-)$
10	-1.20	3.54	-1.07	3.41
20	-2.92	4.56	-1.88	3.52
30	-4.82	6.22	-2.40	3.80
40	-6.54	7.47	-2.43	3.36
50	-7.45	9.93	-2.99	5.47
60	-9.25	12.84	-2.93	6.52
70	-10.42	14.32	-2.96	6.86
80	-12.55	17.12	-2.25	6.82
90	-14.32	21.34	+1.75	5.27
100	-15.42	-	-	-

Table 9 : Free Energy of Transfer of Anion $\Delta G_t^\circ(A^-)$ of
 p-Chlorobenzoic Acid (in kJ) in DME-H₂O Mixtures
 at 25°C

Wt% of DME	$\Delta G_t^\circ(HA)$	$\Delta G_t^\circ(1)$	$\Delta G_t^\circ(H^+)$	$\Delta G_t^\circ(A^-)$
10	-1.56	4.45	-1.67	4.56
20	-3.28	6.50	-2.57	5.79
30	-5.41	7.42	-3.26	5.27
40	-8.00	9.53	-3.99	5.52
50	-10.17	11.53	-4.43	5.79
60	-11.83	13.92	-4.57	6.66
70	-14.36	16.89	-4.15	6.68
80	-16.00	22.54	-1.42	7.96
90	-16.53	26.42	+5.46	4.43
100	-17.76	-	-	-

Table 10 : Free Energy of Transfer of Anion $\Delta G_t^\circ(A^-)$ of p-Bromobenzoic Acid (in kJ) in ME-H₂O and DME-H₂O Mixtures at 25 °C

Wt%	$\Delta G_t^\circ(\text{HA})$		$\Delta G_t^\circ(l)$		$\Delta G_t^\circ(A^-)$	
	ME	DME	ME	DME	ME	DME
10	-1.62	-4.74	2.45	3.14	1.90	0.07
20	-2.08	-6.84	4.22	5.82	4.02	1.55
30	-3.79	-7.96	5.88	8.27	4.49	3.57
40	-4.80	-8.89	8.05	10.50	5.68	5.60
50	-7.16	-9.99	10.21	13.24	6.04	7.68
60	-8.02	-11.39	12.38	16.15	7.29	9.33
70	-9.21	-15.29	14.72	19.46	8.47	8.32
80	-11.51	-16.37	16.89	22.31	7.63	7.36
90	-12.01	-17.55	18.77	24.48	5.01	1.47
100	-15.76	-16.90	-	-	-	-

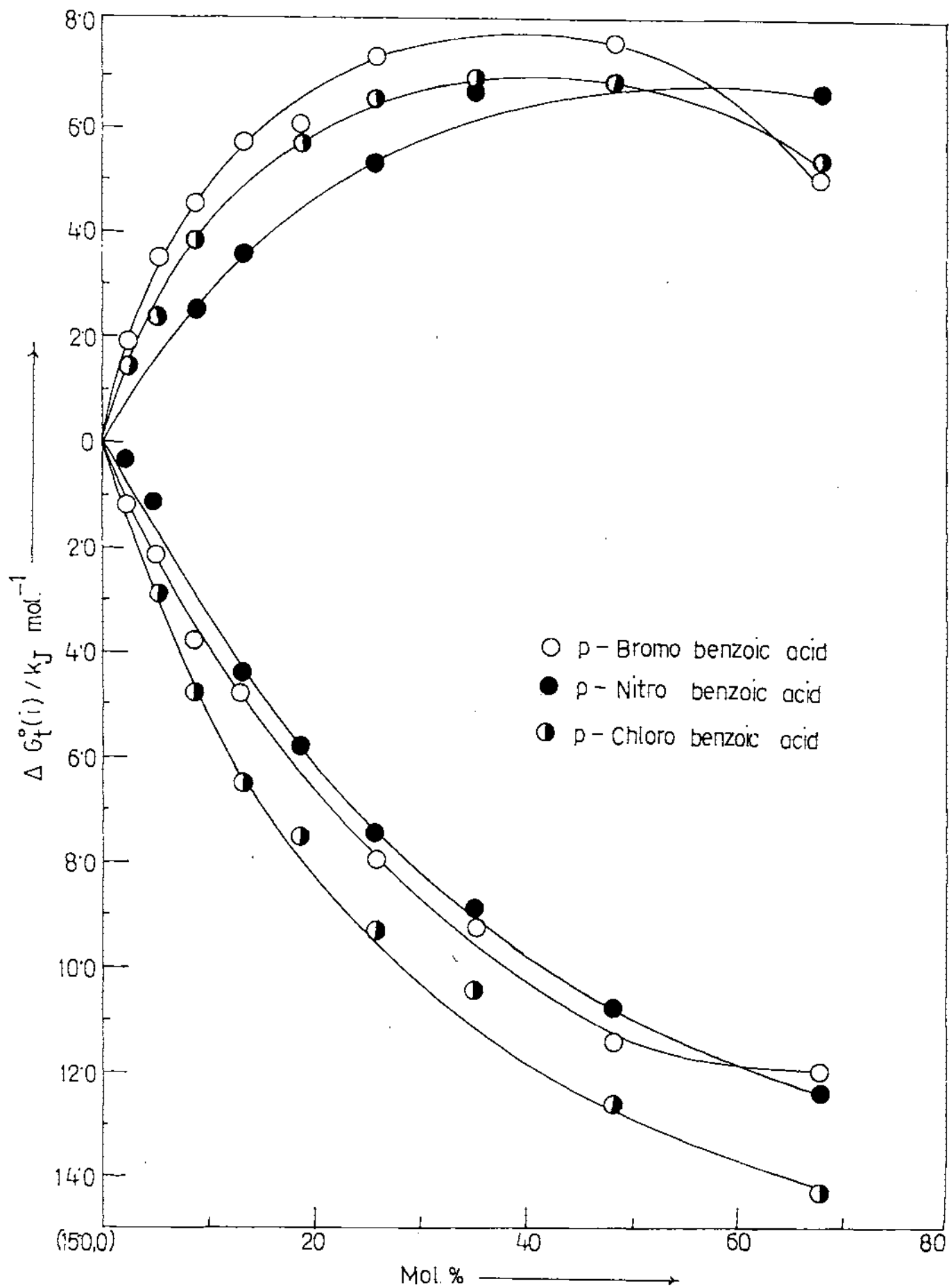


Fig.4 (a) - Variation of (A) $\Delta G_f^0(\text{A}^-)$ and (B) $\Delta G_f^0(\text{HA})$ in ME+ H_2O

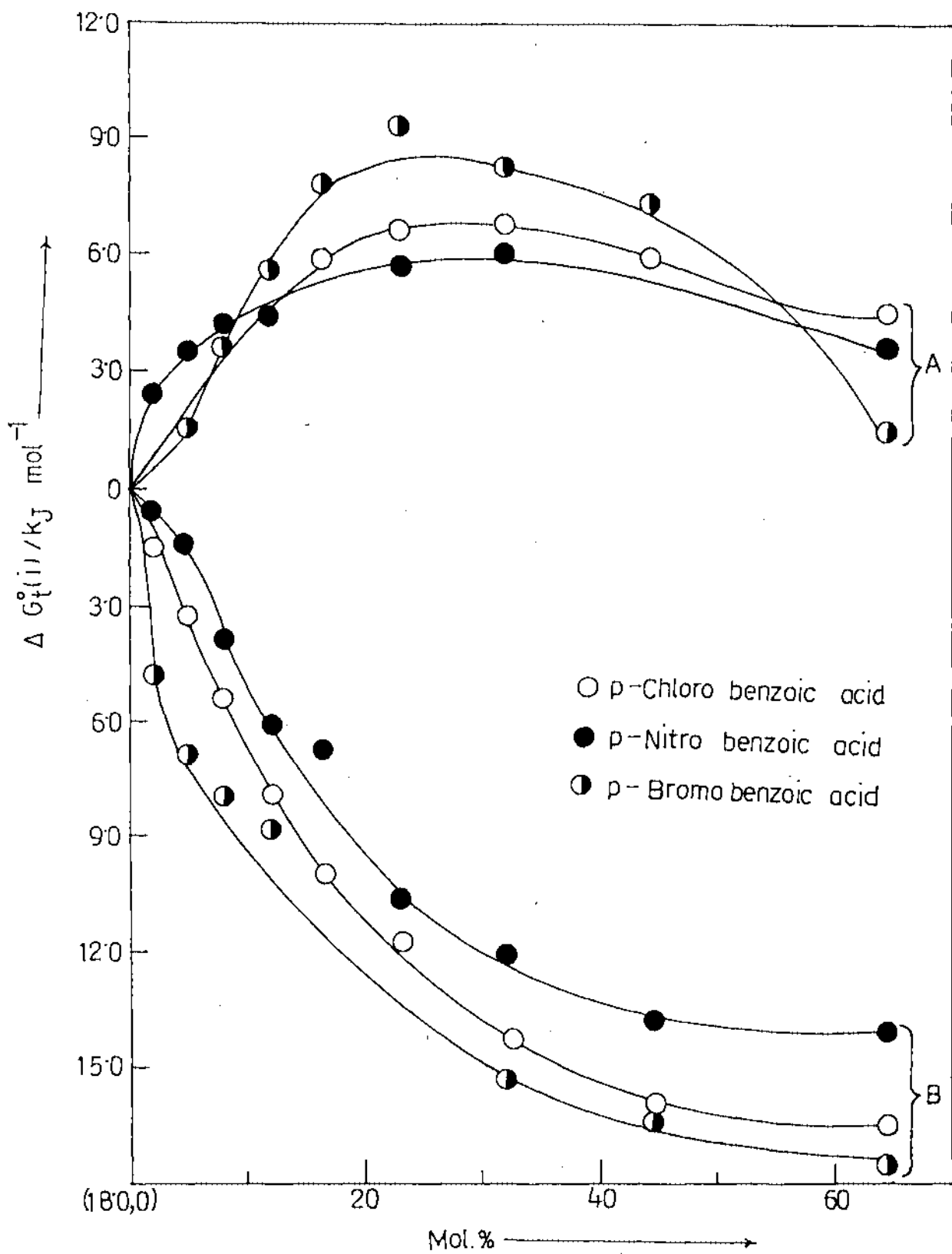


Fig.4 (b) - Variation of (A) $\Delta G_f^0(A^-)$ and (B) $\Delta G_f^0(HA)$ in DME+H₂O.

R E F E R E N C E S

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