

CHAPTER - V

Solubilities and Dissociation Constants of o- and m- Substituted Benzoic Acids in Different Mixed Solvents at 25°C

Despite extensive studies¹⁻⁷ the solvent effect on the dissociation of weak acids and bases⁸ can hardly be considered completely understood. Previously solvent effect was believed to be chiefly guided by the change of dielectric constant of the solvents. But recent observation that the extent of proton transfer processes differs in different isodielectric solvent systems⁸ leads to recognize that the dielectric constant can not be the sole factor but the chemical nature of the cosolvents also plays an important role in dictating the overall solvent effects. In this connection the importance and varied applications of solubility measurements^{9,10} have been widely recognized.

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In the course of our studies on ion-solvent interactions, it has been observed that the determinations of the free energies of transfer of solutes from one solvent to other and the determination of ionic free energies of transfer provide the quantitative measure of solute-solvent and ion-solvent interactions. However, the determinations of the free energy of transfer of an ion requires the value of the free energy of transfer of the corresponding uncharged species.

These considerations led us to determine the solubilities and the thermodynamic dissociation constants of o- and m-substituted benzoic acids in 2-methoxyethanol + water (0-100%) and 1,2-dimethoxyethane + water (0-100%) mixtures. The results are reported in this chapter.

Experimental

Methods of purification of 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME) and the preparation of weight percentages of aquo-organic solvents have been described before (Chapter II & III), o-chloro-benzoic acid (G.R.E. Merck), o-nitro-benzoic acid (Riedel, Germany), m-chloro-benzoic acid (Purum, Fluka) and m-bromo-benzoic acid (Puriss, Koch Light) were all crystallised from alcohol. The purity of the samples was tested by melting point determination.

The solubilities of the acids in different aquo-organic solvents were determined in the way described earlier (Chapter II). The concentrations of the acid solutions were estimated by titration against standardised caustic soda solution using phenolphthalein as indicator. Usually four sets of experiments were performed for each percentage of the solvent mixture. The average values of the solubilities are recorded in Tables 1 and 2. The errors involved in the solubility measurements are within 0.2 to 0.4%.

For the determination of dissociation constants of these acids, the hydrogen ion concentrations of the saturated solutions of the acids were measured with an Orion pH-meter (Model EA 920) having an accuracy of ± 0.01 pH unit. Necessary corrections were made in the way described earlier (Chapter II). The uncertainties in the pK_T values are ca. ± 0.01 unit for lower percentages and ± 0.03 for higher percentages of aquo-organic solvents.

Results and Discussion

The thermodynamic constant (K_T) for the reaction,



can be written as

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

(Since $C_{H^+} = C_{A^-}$)

(A^- = Substituted benzoate ion)

where $[C]_T$ = total concentration of the acids; C_{H^+} = concentration of H^+ ion in the saturated experimental solutions determined pH-metrically. In mixed solvents the H^+ ion concentration was obtained from the pH-meter readings using the necessary corrections^{16,17}.

However, in water the hydrogen ion concentration has been determined from the relation,

$$C_{H^+} = \frac{a_{H^+}}{f_{\pm}} \quad \dots (3)$$

The mean activity coefficients of the ions at different concentrations in aqueous and mixed solvents have been determined using Debye-Huckel limiting law,

$$-\log f_{\pm} = AZ_1^2 \sqrt{\mu} \quad \dots (4)$$

as well as using Davies equation¹⁸,

$$-\log f_{\pm} = \frac{AZ_1^2 \sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2 \mu \quad \dots (5)$$

The appropriate A -values in mixed solvents have been calculated taking the dielectric constant values from the literature^{19,20}. The pK_T values obtained using Davies equation have been reported in Tables 3 and 4. However, these values do not differ much if the calculations are being performed with the help of eqn. (4). The free energies of transfer of *o*- and *m*- substituted benzoic acids can be written as,

$$\begin{aligned} \Delta G_t^{\circ}(\text{HA}) &= -2.303 RT \log \frac{C_S}{C_W} \times \frac{f_S(\text{HA})}{f_W(\text{HA})} \\ &\approx -2.303 RT \log \frac{C_S}{C_W} \quad \dots (6) \end{aligned}$$

where C_s and C_w refer to the molar concentrations of the saturated solutions of *o*- and *m*- substituted benzoic acids in the solvent mixtures (s) and water (w) respectively. Appropriate corrections were made for the possible dissociation of the acids in the different solvents. Moreover, the activity coefficients of neutral acids in their saturated solutions have been considered to be unity where the activity coefficient refers to the standard states in the respective solvents.

The solubility values of *o*-chloro benzoic acid, *m*-chloro benzoic acid and *m*-bromo benzoic acid in water have been found to be in good agreement with the values reported in the literature²¹ (Table 1). Table 1 also shows that the solubility values of *o*-chloro, *o*-nitro, *m*-chloro and *m*-bromo benzoic acids increase gradually with increase in proportion of ME in the solvent. In case of DME, the solubility values also increase with wt% of DME, the maximum being observed at 90 wt% of DME (*o*-nitro benzoic acid shows maximum at 80% of DME) and then the values decreases in pure DME in all cases. Again, like benzoic acid and *p*-substituted benzoic acids¹¹ as studied before, the solubility values of these salts are also greater in binary mixtures of DME than ME. However, in case of pure solvent solubility is found to be greater in ME than DME contrary to the values obtained with benzoic acid and *p*-substituted benzoic acids.

It is particularly interesting in view of the greater hydrophobic character of DME compare to ME. In the present study the solubility values in water and binary aqueous mixtures of ME and DME are in the order:

α -nitro > o -chloro > m -chloro > m -bromo benzoic acid.

The pK -values (Tables 3 and 4) can be regarded to be thermodynamic values as the ionic strengths of the solutions are low and proper corrections have been made. The pK -values of o -chloro (2.93), o -nitro (2.18) and m -chloro (3.83), m -bromo (3.80) benzoic acids in water agree well with the literature²² values of 2.90, 2.17, 3.84 and 3.81 respectively. The pK -values of these acids increase continuously with the increase in the percentage of organic solvent and show a linear relationship when plotted against $\frac{1}{\epsilon}$ at low percentages but deviations occur at higher percentages (Fig. 1). It is also observed that pK -values are higher in DME + H₂O mixtures than those in ME + H₂O mixtures, the values being greater for m -chloro or m -bromo benzoic acids than o -nitro benzoic acid, contrary to the solubility values of these acids in the solvent mixtures.

Instead of analysing our data in terms of the equation, $\Delta pK_T = \Delta pK_t(\text{el}) + \Delta pK_t(\text{non-el})$, as done by Bates and Robinson²³, we have tried to determine the free energies of transfer of substituted benzoate ions from water to mixed solvents in the present study. It would give more insight into the nature of ion-solvent interactions which are the controlling

forces in dilute solutions where ion-ion interactions are absent. One of the advantages of determining pK-values of weak acids like the present acids by the solubility method is that the solutions are dilute and ions are in their standard states in the respective solvents, an essential condition for the determination of medium effects of ions.

In spite of limitations, the free energy of transfer of a single ion can be determined using the relation²⁴,

$$\Delta G_t^\circ(\text{ion}) = \Delta G_t^\circ(\text{neut})(\text{ion}) + \Delta G_t^\circ(\text{el})(\text{ion}) \quad \dots (7)$$

where $\Delta G_t^\circ(\text{neut})(\text{ion})$ has been assumed to be equal to that of its uncharged analogue. $\Delta G_t^\circ(\text{el})$ is the electrical free energy change in charging neutral molecule from 0 to charge ze in solution. $\Delta G_t^\circ(\text{neut})(\text{ion})$ values have been experimentally determined. But in view of the limitations of the Born equation²⁵ or the modified equation²⁶ and particularly due to the uncertainty regarding the radius of unsymmetrical benzoate ions, the calculated $\Delta G_t^\circ(\text{el})$ values may be considerably in error. We, therefore, preferred to calculate $\Delta G_t^\circ(\text{ion})$ in the following way instead of using equation (7),

$$\begin{aligned} \Delta G_t^\circ(1) &= \Delta G_s^\circ(1) - \Delta G_w^\circ(1) \\ &= \Delta G_t^\circ(\text{H}^+) + \Delta G_t^\circ(\text{A}^-) - \Delta G_t^\circ(\text{HA}) \end{aligned}$$

$$\text{or } \Delta G_t^\circ(\text{A}^-) = \Delta G_t^\circ(1) - \Delta G_t^\circ(\text{H}^+) + \Delta G_t^\circ(\text{HA})$$

The values of $\Delta G_t^{\circ}(\text{HA})$ have been determined from solubility measurements. Corrections for the dissociation of the acids in different solvents have been made. $\Delta G_t^{\circ}(\text{A}^-)$ values in different solvents have been calculated using $\Delta G_t^{\circ}(\text{l})$, $\Delta G_t^{\circ}(\text{HA})$ values from this experiment and $\Delta G_t^{\circ}(\text{H}^+)$ values previously reported in Chapter II. The values are presented in Tables 5 and 6.

The $\Delta G_t^{\circ}(\text{A}^-)$ values are predominantly positive. This is in agreement with the fact that ΔG_t° of anions are usually positive^{27,28}. Moreover, $\Delta G_t^{\circ}(\text{A}^-)$ values show that transfer of A^- is non-spontaneous from water to organic solvents (Fig. 2).

The results further indicate that $\Delta G_t^{\circ}(\text{A}^-)$ is maximum at 80% of ME and DME i.e., in this region the free energy of mixing of solvents is maximum²⁹. It is to be noted that the addition of organic solvent first strengthens the three dimensional (3D) water structure. However, due to the presence of $-\text{OCH}_3$ group, the addition of ME or DME induces the initial breakdown of 3D-structure of water followed by possible structure promoting effect of H-bonded $\text{ME-H}_2\text{O}$ and $\text{DME-H}_2\text{O}$ complexation which goes upto 48.64 mol% of ME and 44.45 mol% of DME. Above this mol%, the destabilization of solvent-water bond takes places leading to the gradual formation of solvent structure. H^+ ion leads to the stabilization of solvent structures due to its capability of H-bond formation and $\Delta G_t^{\circ}(\text{H}^+)$ becomes negative whereas anion destabilises the solvent structures leading to positive free energy changes.

Tables 3 and 4 also show the increasingly negative magnitudes of $\Delta G_t^{\circ}(\text{HA})$ with increase in non aqueous component in the solvent mixture. Results indicate the stabilization of benzene ring primarily through dispersion forces as in the case of uncharged bases like nitroanilines³⁰. Solvation will also occur through hydrogen bond formation in which the substituent groups will be involved, and these factors should make their independent contributions to the overall values of $\Delta G_t^{\circ}(\text{HA})$. But the hydrophobism of the benzene ring is presumably the largest single factor causing an increased affinity of these weak acids towards the organic component rich solvent.

Conclusion

Substituent groups can change the electron density on an acidic group by polar interactions³¹. Many workers have attempted to divide polar interactions into inductive effects, displacements of electrons along the molecular chain or ring, and direct or electrostatic field effects which occur, at least in part, through the solvent³²⁻³⁷. The distinction is a fruitless one because there is no way to estimate one type of interaction independently of the other. It has often been assumed that the Kirkwood-Westheimer³⁸ theory can be used to calculate the direct effect, but this view cannot be maintained³⁹. The model is a highly artificial one which

makes some allowance for induction by its choice of an internal dielectric constant.

In aromatic acids the electron density on the acidic group is changed not only by induction but also by resonance, and separation of the two effects is difficult. For acids containing a benzene ring the inductive effect should be largest at the ortho position and smallest at the para position. Ortho derivatives exhibits various peculiarities associated with the proximity of the substituent to the ionizing group; there is probably no acid in which the interaction from the ortho position is purely inductive. The difference in inductive effects at the more remote meta and para positions is so small that it is often ignored. Most substituents enter into resonance with the aromatic ring. Such conjugation is largest at the ortho and para positions. Groups may be classed according to whether they withdraw electron density from the ring ($-\text{NO}_2$, $-\text{CN}$) or supply it from their lone pair electrons ($-\text{F}$, $-\text{Cl}$, $-\text{Br}$). Groups in the first class will strengthen acids by resonance because withdrawal of electron density from the ring is accompanied by shift in electron density from the acid group to the ring. Groups in the second class increase the electron density on the acidic group by conjugation through the aromatic ring; resonance has an acid-weakening effect. Meta derivatives cannot conjugate directly with the acidic group. Their resonance interaction with the aromatic

ring produces changes with the electron density at the ortho and para positions and these affect acid strengths by induction.

Let us examine the acidity constants of some substituted benzoic acids in the light of these arguments. All these acids are stronger than benzoic acid itself (Table 7) because of the inductive effect. In the nitro benzoic acids resonance has a further acid strengthening effect and the ortho derivatives are stronger acids than the para or meta derivative. For the chloro-, and bromo benzoic acids induction and resonance oppose each other. Chlorine is expected to conjugate with the ring to a larger extent than bromine, for the p-orbitals of its lone pair electrons are smaller and overlap more with the π -orbitals of the ring. Thus p-chloro benzoic acid is weaker than p-bromo benzoic acid. The meta acids are stronger than the para acids (except for p-nitrobenzoic acid in few percentages of mixed solvents) because there is less opposition by resonance to the inductive effect. Meta chloro benzoic acid is perhaps weaker than m-bromobenzoic acid because of the resonance-stimulated inductive effect. Still, the difference in acid strength is very small (in water and in ME-Water mixed solvents) judgement should be reserved until these acids have been studied at other temperatures and in other solvents.

Steric effects and intramolecular hydrogen bonding may also play an important role in the dissociation process but the effects are often small and hard to disentangle from other influences with the result that there are considerable

differences in interpretation^{40,41}. Bulky substituents next to an acidic group may affect the loss of a proton in several ways. The steric effect on the proton itself is negligible because of its very small size. The substituent by its bulk may prevent solvent molecules from solvating and stabilizing a cation acid or an anion base. Bulky groups interposed between a polar substituent and the ionizing group increase electrostatic interaction by confining it to a Cavity⁴² of low dielectric constant. Bulky substituents in an ortho position may interfere with resonance by causing the carboxyl group to twist out of alignment with the π electron system of the ring. For this reason ortho substituted benzoic acids are stronger than expected, as may be seen from the data in Table 7. Internal hydrogen bonding will be an effect superimposed on inductive, resonance and other steric effects and hard to separate from them. Moreover, the intramolecular hydrogen bond must be strong if it is to persist in competition with intermolecular hydrogen bonds between the acid and the solvent. Formation of such a bond in a base lowers its potential energy relative to that of the conjugate acid and enhances acid strength. Hydrogen bonding in ortho nitrobenzoic acid may occur in the unionized acid and this may be one of the reasons which makes it considerably stronger than p-nitrobenzoic acid.

Table 1 : Solubility (molar) of *o*- and *m*-substituted Benzoic Acids in ME and in their Aqueous Binary Mixtures at 25°C

Wt% of ME	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol dm ⁻³)			
			<i>o</i> -Chlorobenzoic	<i>o</i> -Nitrobenzoic	<i>m</i> -Chlorobenzoic	<i>m</i> -Bromobenzoic
00	1.27	0.509	0.0136	0.0454	0.0026	0.0021
20	1.43	0.606	0.0409	0.0987	0.0075	0.0071
40	1.74	0.813	0.2047	0.5719	0.0404	0.0367
60	2.37	1.293	1.0716	1.8421	0.3664	0.1579
80	3.77	2.593	2.1198	2.6019	1.0468	0.2173
90	5.26	4.278	2.5034	2.9443	1.6236	0.3077
100	5.91	5.087	2.5336	3.1090	1.8768	0.3278

Table 2 : Solubilities of o- and m-Substituted Benzoic Acids in DME and in their Aqueous Binary Mixtures at 25°C

Wt% of DME	$\frac{1}{\epsilon} \times 10^2$	A	Solubility (mol dm ⁻³)			
			o-Chlorobenzoic	o-Nitrobenzoic	m-Chlorobenzoic	m-Bromobenzoic
20	1.56	0.691	0.1131	0.2493	0.0137	0.0099
40	2.01	1.009	0.4795	0.8509	0.2519	0.0940
60	2.79	1.652	1.8879	2.2449	0.7928	0.2971
80	4.79	3.714	2.8827	3.4469	1.6626	0.3021
90	7.42	7.160	2.9821	3.1135	2.2154	0.3543
100	14.12	18.811	2.5224	3.0133	1.7549	0.3349

Table 3 : pK_T values of *o*- and *m*- Substituted Benzoic Acids in ME-Water Mixtures at 25 °C

Wt% of ME	<u><i>o</i>-Chlorobenzoic Acid</u>		<u><i>o</i>-Nitrobenzoic Acid</u>		<u><i>m</i>-Chlorobenzoic Acid</u>		<u><i>m</i>-Bromobenzoic Acid</u>	
	Corrected pH	pK_T	Corrected pH	pK_T	Corrected pH	pK_T	Corrected pH	pK_T
00	2.49	2.98	1.90	2.24	3.27	3.85	3.30	3.82
20	2.63	3.91	1.99	3.04	3.25	4.37	3.29	4.43
40	2.66	4.70	1.97	3.83	3.20	5.03	3.21	5.02
60	2.71	5.56	2.02	4.53	3.04	5.72	3.23	5.72
80	2.93	6.36	2.29	5.34	3.12	6.40	3.45	6.33
90	3.10	6.82	2.37	5.73	3.14	6.72	3.50	6.49

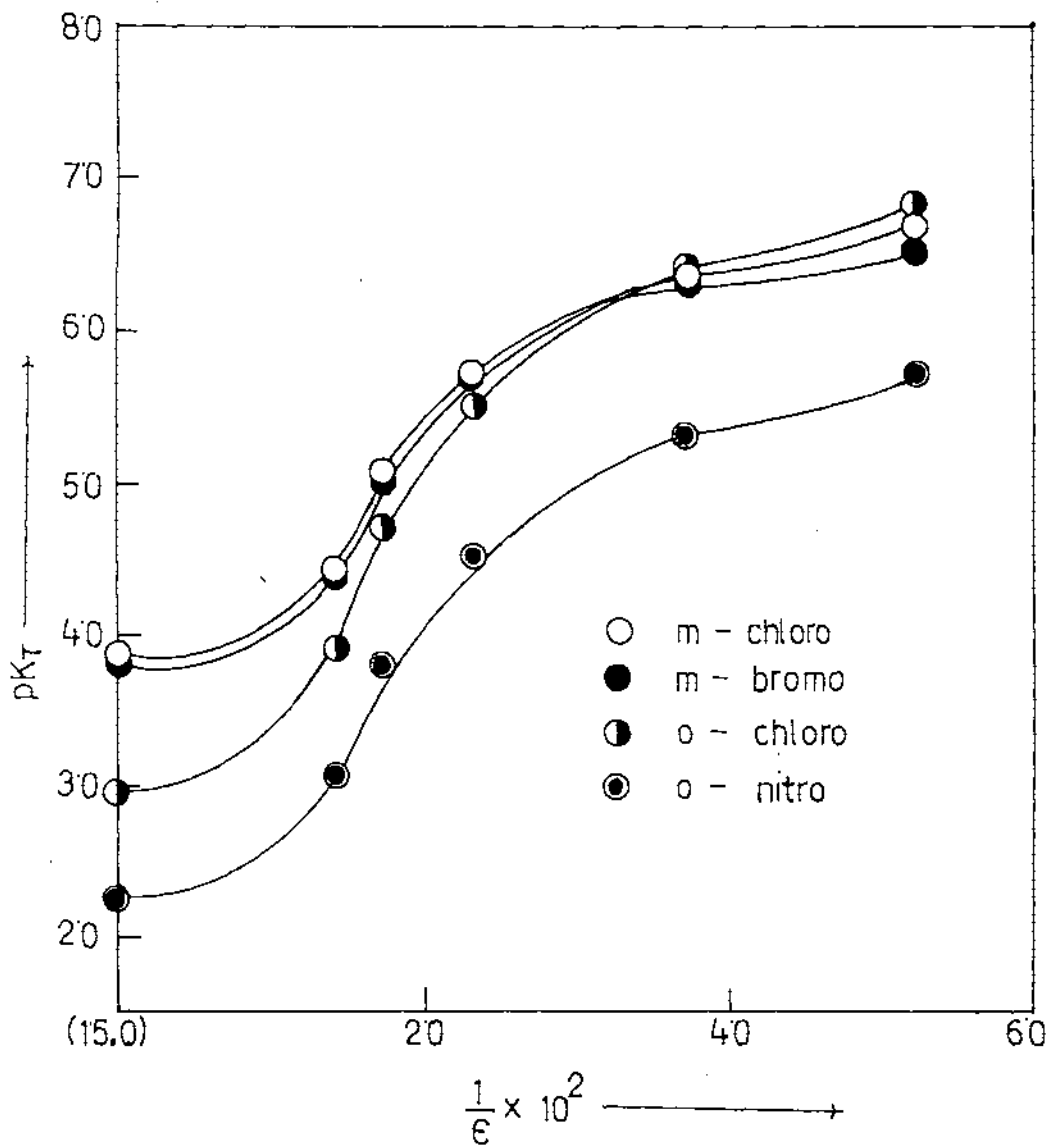


Fig.1(a) variation of pK_T with ϵ in ME+H₂O mixture.

Table 4 . pK_T values of *o*- and *m*- Substituted Benzoic Acids in DME-Water Mixtures at 25 °C

Wt% of DME	<u><i>o</i>-Chlorobenzoic Acid</u>		<u><i>o</i>-Nitrobenzoic Acid</u>		<u><i>m</i>-Chlorobenzoic Acid</u>		<u><i>m</i>-Bromobenzoic Acid</u>	
	Corrected pH	pK_T	Corrected pH	pK_T	Corrected pH	pK_T	Corrected pH	pK_T
20	2.41	3.94	1.85	3.21	3.27	4.69	3.28	4.56
40	2.60	4.97	2.02	4.14	3.05	5.56	3.11	5.24
60	2.74	5.89	2.22	5.03	3.20	6.38	3.18	5.91
80	3.07	6.81	2.55	6.02	3.37	7.11	3.46	6.54
90	3.34	7.45	2.73	6.54	3.57	7.72	3.55	6.89

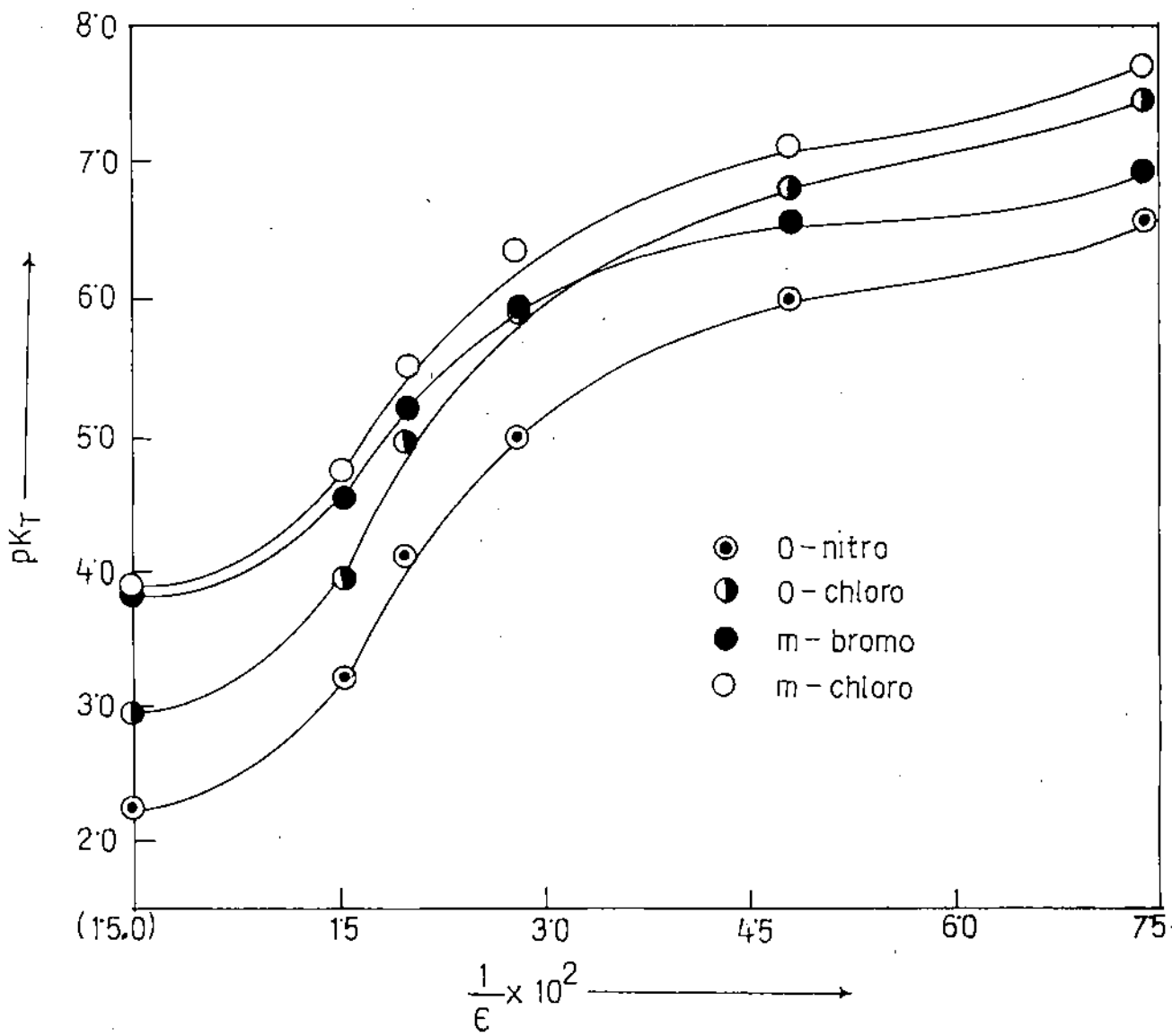


Fig.1(b) - Variation of pK_T with ϵ in DME + H₂O mixture.

Table 5(a) : Free Energy of Transfer of Anion, $\Delta G_t^\circ(A^-)$ of Substituted Benzoic Acids (in kJ) in ME-Water Mixtures at 25 °C

Wt% of ME	O-Chlorobenzoic Acid			O-Nitrobenzoic Acid		
	$\Delta G_t^\circ(l)$	$\Delta G_t^\circ(HA)$	$\Delta G_t^\circ(A^-)$	$\Delta G_t^\circ(l)$	$\Delta G_t^\circ(HA)$	$\Delta G_t^\circ(A^-)$
20	5.31	-3.26	3.93	3.94	-2.46	3.36
40	9.81	-7.37	4.87	9.07	-7.04	4.46
60	14.72	-11.49	6.16	13.07	-9.97	6.03
80	19.29	-13.18	8.36	17.69	-10.83	9.11
90	21.91	-13.59	6.57	19.91	-11.14	7.02
100	-	-13.63	-	-	-11.28	-

Table 5(b) Free Energy of Transfer of Anion, $\Delta G_t^{\circ}(A^-)$ of Substituted Benzoic Acids (in kJ) in ME-Water Mixtures at 25°C

Wt% of ME	m-Chlorobenzoic Acid			m-Bromobenzoic Acid		
	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$
20	2.97	-2.99	1.86	3.48	-3.51	1.85
40	6.73	-7.31	1.85	6.85	-7.72	1.56
60	10.67	-12.81	0.79	10.84	-11.37	2.40
80	14.55	-15.41	1.39	14.33	-12.17	4.41
90	19.38	-16.50	1.13	16.09	-13.03	1.31
100	-	-16.86	-	-	-13.19	-

Table 6(a) : Free Energy of Transfer of Anion, $\Delta G_t^{\circ}(A^-)$ of Substituted Benzoic Acid (in kJ) in DME-Water Mixtures at 25°C

Wt% of DME	o-Chlorobenzoic Acid			o-Nitrobenzoic Acid		
	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$
20	5.48	-5.84	2.21	5.53	-4.88	3.22
40	11.36	-9.49	5.86	10.84	-8.04	6.79
60	16.60	-12.89	8.28	15.92	-10.46	10.03
80	21.85	-13.95	9.32	21.57	-11.53	11.46
90	25.51	-14.03	6.02	24.54	-11.28	7.80
100	-	-13.62	-	-	-11.20	-

Table 6(b) : Free Energy of Transfer of Anion, $\Delta G_t^{\circ}(A^-)$ of Substituted Benzoic Acid (in kJ) in DME-Water Mixtures at 25°C

Wt% of DME	m-Chlorobenzoic Acid			m-Bromobenzoic Acid		
	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(HA)$	$\Delta G_t^{\circ}(A^-)$
20	4.79	-4.57	2.79	4.22	-4.38	2.41
40	9.76	-11.88	1.87	8.10	-10.08	2.01
60	14.44	-14.73	4.28	11.93	-12.94	3.56
80	18.60	-16.56	4.46	15.52	-12.99	3.95
90	23.08	-17.27	0.35	19.52	-13.38	0.68
100	-	-16.69	-	-	-13.24	-

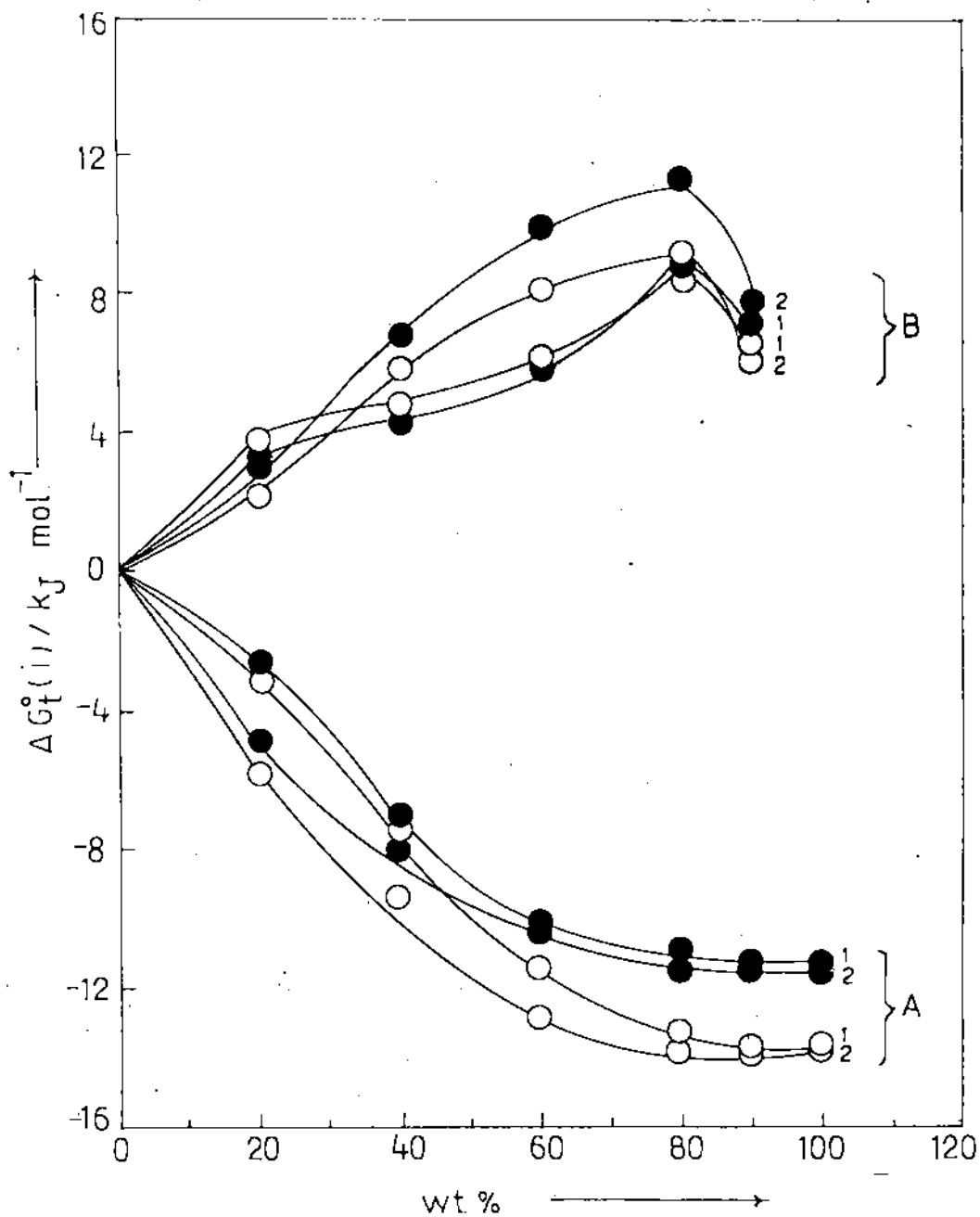


Fig 2 (a) - Variation of (A) $\Delta G_f^0(\text{HA})$ and (B) $\Delta G_f^0(\text{A}^-)$ in (1) ME+H₂O (2) DME+H₂O mixtures.

(O), o-Chlorobenzoic acid; (●), o-Nitrobenzoic acid.

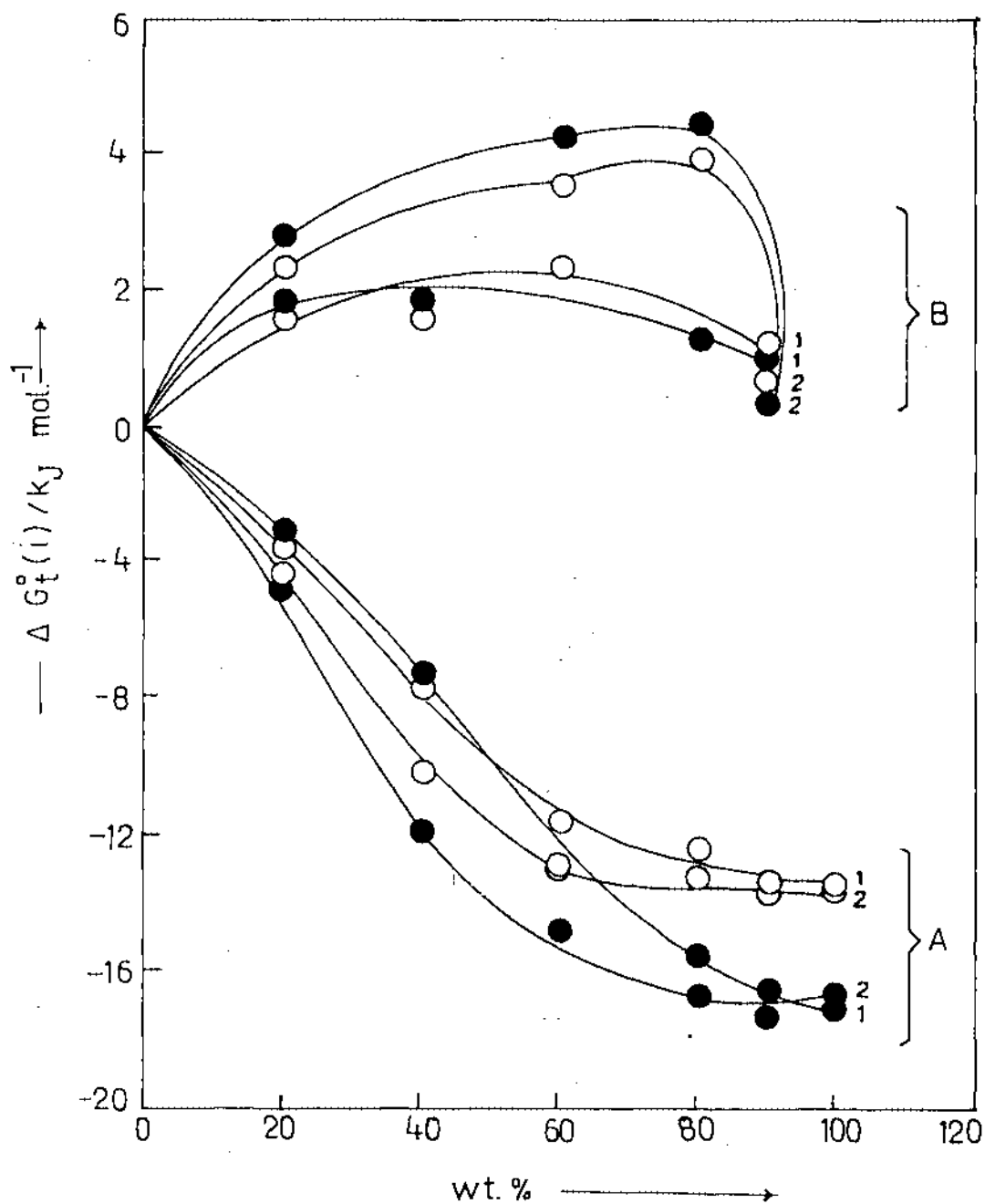


Fig 2 (b). - Variation of (A) $\Delta G_f^0(\text{HA})$ and (B) $\Delta G_f^0(\text{A}^-)$ in (1) ME+H₂O (2) DME+H₂O mixtures.

(●), m - Chlorobenzoic acid ; (○), m - Bromobenzoic acid.

Table 7: Acidity Constants of some Substituted Benzoic Acids in Water and Aqueous binary mixtures of 2-methoxyethanol and 1,2-dimethoxyethane at 25°C

Acid	PK _T		
	Water	90% ME	90% DME
Benzoic Acid	4.22	7.55	8.62
p-Chlorobenzoic Acid	4.00	7.74	8.63
p-Bromobenzoic Acid	3.98	7.27	8.27
m-Chlorobenzoic Acid	3.85	6.72	7.72
m-Bromobenzoic Acid	3.82	6.49	6.89
p-Nitrobenzoic Acid	3.50	7.13	7.57
o-Chlorobenzoic Acid	2.98	6.82	7.45
o-Nitrobenzoic Acid	2.24	5.73	6.54

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