

CHAPTER - III

Solubility and the Dissociation Constants of Benzoic Acid in ME - Water and DME - Water Mixtures and Free Energies of Transfer of Benzoate Ion.

Accurate solubility data have diverse applications in different branches of science and technology<sup>1,2</sup>. This prompted us to determine the accurate solubility of benzoic acid, an antifungal preservative widely used in lotions and ointments, in pure and mixed solvents. In this chapter an attempt has been made to determine the solubilities and thermodynamic dissociation constants of benzoic acid in ME-water and DME-water mixed solvents over the entire range of their solvent compositions from pH - metric and spectrophotometric measurements. An attempt has also been taken to determine the dissociation constants of benzoic acid in these mixed solvents from conductance measurements. The study is likely to enable us to determine the effect of solvents on the dissociation constants of benzoic acid and free energies of transfer of benzoic acid and benzoate ion in these solvent mixtures<sup>3</sup>.

Experimental

Benzoic acid (G.R.E. Merck) was recrystallised from alcohol and dried. 2-methoxy ethanol (G.R.E. Merck) was distilled twice and the middle fraction was utilised. 1,2-dimethoxyethane (Fluka) was shaken well with  $\text{FeSO}_4$  (A.R., BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and distilled

over metallic sodium. Other chemicals were of analytical grade. For the determination of the solubility of benzoic acid at 25 °C in mixed solvents, saturated solutions of benzoic acid were prepared in the appropriate solvents at about 30 °C and filtered. The solution was taken in the Campbell solubility apparatus<sup>4</sup> fitted with a sintered disc and a fine tube. The solutions were then allowed to equilibrate in a thermostatic bath maintained at 25 °C ( $\pm$  0.01) for 24 h. After equilibrium, the solutions were filtered by inverting the apparatus keeping it in the thermostat. The benzoic acid content of the filtered solution was determined by titration against standard NaOH solution. The process was repeated several times for each set of measurements. However, it is to be noted that the phase separation of two layers containing water and ME or DME takes place in the region 70 to 90 wt% of mixed solvents. The phase separation may form the basis of separation of ME or DME from ME or DME-water mixture. We, therefore, tried to obtain the maximum concentrations of benzoic acid present in homogeneous mixtures of water and ME or DME. To determine the solubility of benzoic acid in this region, we took a definite amount of the mixed solvent and the benzoic acid was added in small amounts until turbidity just begins (which disappears with the addition of one or two drops of the solvent mixture). Repeated trials make the process reproducible. The errors involved in the solubility measurements are in the range 0.1-0.3%. The solubility was also determined spectrophotometrically by measuring the o.d.

values at 272 nm, the wave length for the absorption maximum of benzoic acid (Fig. 3). The band at 272 nm has been assumed as the B-band<sup>5</sup> of  $C_6H_5-COOH$ . The solubility values determined by the above two methods are within the limit of  $\pm 0.2\%$ . The average values have been reported in column 3 of Tables 1 and 2.

For the determination of the dissociation constant of benzoic acid, the hydrogen ion concentrations of the saturated solutions of benzoic acid in mixed solvents were measured pH-metrically using combined glass and calomel electrodes. The glass electrode have been found to function satisfactorily in aqueous binary mixtures of ME and DME. The calibration of the glass electrode and 'correction factors' in different percentages of the mixed solvents have been determined in the way suggested by Van Uitert and Haas<sup>6</sup>, Irving and Manhot<sup>7</sup> and also described by us previously<sup>8</sup>. The correction factor have been found to depend slightly on the nature of solvents, aging and asymmetry potential of the glass electrode. However, consistent and reproducible results are obtained if the 'correction factors' are determined before each set of measurements. The error range for pH-measurements are usually  $\pm 0.02$  at low percentages of ME-water or DME-water mixtures and  $\pm 0.03$  at higher percentages of the mixed solvents.

For conductometric determination of the dissociation constants of benzoic acid, conductances of benzoic acid solutions at different concentrations ( $10^{-4}$  -  $10^{-3}$  M) were measured. The values of benzoic acid in water was determined by applying

Kohlrausch law from the  $\Lambda_0$  values of  $\text{HClO}_4$ ,  $\text{KClO}_4$  and  $\text{C}_6\text{H}_5\text{COOK}$ ; the conductances of the solutions of these salts at different concentrations ( $6 \times 10^{-4}$  to  $3 \times 10^{-2}$  M) were measured in water. However, it has been observed that the method cannot be used in ME-water and DME-water mixtures as the value of conductance at infinite dilution obtained by the above way has a rather large uncertainty. So, in mixed solvent  $\Lambda_0$  was estimated by employing Walden's rule. Conductance measurements were made by a Pye-Unicam PW 9509 conductivity meter at a frequency of 2 kHz using a dip-type cell of cell constant  $0.73 \text{ cm}^{-1}$ . The value of the cell constant was repeatedly checked during the course of the experiment. Measurements were done at  $25 \pm 0.01^\circ \text{C}$ . Conductance measurements were made using dilute solutions, and corrections for the activity coefficients of ions were taken into consideration. The method is particularly suitable for the determination of the dissociation constants of weak acids in mixed solvents, as the method is free from assumptions.

The dielectric constants and viscosity of the solvent mixtures were taken from the literature<sup>9-11</sup>.

### Results and Discussion

The thermodynamic dissociation constant for the reaction



can be written as

$$K_T = \frac{C_{H^+} \times C_{Bz^-}}{C_{HBz}} \times \frac{\gamma_{\pm}^2}{\gamma_{HBz}}$$

$$= \frac{C_{H^+}^2}{[C]_T - C_{H^+}} \times \frac{\gamma_{\pm}^2}{\gamma_{HBz}} \quad \dots (2)$$

where  $[C]_T$  = total benzoic acid concentration and  $C_{H^+}$  = concentration of  $H^+$  in the saturated experimental solutions determined pH-metrically. The activity co-efficient of the ions at different concentrations have been determined using Davies equation<sup>12</sup>

$$-\log \gamma_{\pm} = AZ_+ Z_- \sqrt{\mu} / (1 + \sqrt{\mu}) - 0.2 \mu \quad \dots (3)$$

with appropriate A-values in each solvent taking into account the changed dielectric constants of the mixed solvents. The activity co-efficients using Debye-Huckel limiting law have also been attempted but the  $\gamma_{\pm}$  values by the two methods differ only in the third place.

The dissociation constants of benzoic acid in the mixed solvents were also determined spectrophotometrically in the way suggested by Robinson and Biggs<sup>13</sup>. For this method a number of buffer solutions of known pH were employed. According to Robinson and Stokes<sup>14</sup> the value of the pH of the buffer solution should be equal to the pK of the organic acid. In this investigation the range of possible pK values at 25°C is 4.2-8.6. We have used the acetic acid-sodium acetate buffer for the pH range 4.2-4.7 and phosphate buffer solution e.g. 0.06 M potassium dihydrogen phosphate

and 0.06M disodium hydrogen phosphate for measurements outside this range. The experimental pH of the buffer solution used was closed to the value of the pK of the acid in each percentage of mixed solvent. The pH values were measured with an ECIL pH-meter having an accuracy of  $\pm 0.01$  pH unit. The spectrophotometric measurements were recorded with a Shimadzu UV-240 spectrophotometer maintained at 25°C. The analytical wave length for spectrophotometric measurement was 240 nm and concentration of the acid was  $(5-9) \times 10^{-5}$  (M). The thermodynamic dissociation constants ( $pK_T$ ) of benzoic acid calculated from solubility data and determined by spectrophotometric methods in aqueous binary mixtures of ME and DME have been recorded in columns 7 and 8 of Tables 1 and 2 respectively.

In order to calculate dissociation constants from conductance measurements, the equivalent conductances,  $\Lambda$ , of benzoic acid were measured at the corresponding concentrations (Tables 4 and 5) and the data were analysed by the Shedlovsky<sup>15</sup> equation which can be expressed as,

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} + \frac{C \Lambda S f^2}{K \Lambda_0^2} \quad \dots (4)$$

where the symbols have their significance as given below:

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

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

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

$$\alpha = \frac{S\Lambda}{R}$$

$$R = e^2 / 2\epsilon RT$$

If  $\frac{1}{S\Lambda}$  is plotted vs  $C\Lambda Sf^2$ , the intercept  $\frac{1}{\Lambda_0}$  and the slope is  $\frac{1}{K\Lambda_0^2}$ . In practice an initial value of  $\Lambda_0$  was estimated from Walden's rule and then an iterative procedure allows us to calculate  $K$  and  $\Lambda_0$ . The calculations were performed on a WIPRO Z-650 computer using the program devised by us.

The free energies of transfer for the dissociation of benzoic acid have been calculated using equation (5).

$$\delta(\Delta G_t^\circ) = \Delta G_s^\circ - \Delta G_w^\circ$$

$$= -2.303 RT \left[ \log K_{T(s)} - \log K_{T(w)} \right] \dots (5)$$

The free energy of transfer of neutral benzoic acid is given by

$$\Delta G_t^\circ(\text{HBz}) = \Delta G_s^\circ(\text{HBz}) - \Delta G_w^\circ(\text{HBz})$$

$$= -2.303 RT \log \frac{C_s}{C_w} \times \frac{f_s(\text{HBz})}{f_w(\text{HBz})} \dots (6)$$

where  $C_s$  and  $C_w$  are the molar concentrations of undissociated benzoic acid in the solvent (s) and water (w) respectively in

saturated solution. These are equal to the total acid in saturated solutions minus the concentration of the dissociated acid. Since the benzoic acid is present in its saturated state in respective solvents, the ratio of activity coefficient of neutral benzoic acid in the mixed solvent and in water has been assumed as unity <sup>16</sup>.

The free energy changes accompanying the transfer of benzoate ion from the standard state in water to that in the solvents have been calculated from the following relations <sup>17</sup>.

$$\delta(\Delta G_t^\circ) = \Delta G_t^\circ(\text{H}^+) + \Delta G_t^\circ(\text{Bz}^-) - \Delta G_t^\circ(\text{HBz}) \quad \dots (7)$$

$$\text{or } \Delta G_t^\circ(\text{Bz}^-) = \delta(\Delta G_t^\circ) - \Delta G_t^\circ(\text{H}^+) + \Delta G_t^\circ(\text{HBz}) \quad \dots (8)$$

$\Delta G_t^\circ(\text{H}^+)$  in equation (8) stands for the free energy change for the transfer of one mole of  $\text{H}^+$  ion from the standard state in water to the standard state in the solvent concerned and may be taken as a measure of the basicity <sup>18, 19</sup> of the solvent with respect to that of water.  $\Delta G_t^\circ(\text{H}^+)$  values are limited to few percentages (mostly at low percentages) of ME +  $\text{H}_2\text{O}$  and DME +  $\text{H}_2\text{O}$  mixtures in the literature. We prefer to use the  $\Delta G_t^\circ(\text{H}^+)$  values determined by us based on the experimental measurements of transfer of  $\text{BH}^+$  (B = 2,2'-bipyridine or 1,10-phenanthroline) and related data <sup>20</sup>. It is to be noted that  $\Delta G_t^\circ(\text{H}^+)$  values are always determined

using extra thermodynamic assumptions with their inherent limitations. But  $\Delta G_t^{\circ}(\text{H}^+)$  values determined by us are consistent and in good agreement both qualitatively and almost quantitatively at low percentages of ME and DME with the available literature values<sup>21,22</sup> (based on TATB assumption).

Tables 1 and 2 show that the solubility values and  $\text{pK}_T$  values of benzoic acid increase progressively with increase in the percentage of ME or DME in the solvent. The comparison with other mixed solvents show that the solubility values in ME-H<sub>2</sub>O are less but in DME-H<sub>2</sub>O are greater than the corresponding values in alcohol-water mixtures<sup>23,24</sup>. The  $\Delta G_t^{\circ}(\text{H}^+)$  values becomes increasingly negative in going from water to ME + H<sub>2</sub>O and DME + H<sub>2</sub>O mixtures indicating that the binary mixtures are more basic than water. The basicity becomes maximum at 80 wt% of ME (ME : H<sub>2</sub>O  $\approx$  1:1) and at 70 wt% DME (DME : H<sub>2</sub>O  $\approx$  1:2), thereby basicity decreases and ultimately becomes less basic than water at about 90 wt% of organic solvents (Fig. 2). The results also coincides with the fact that DME-H<sub>2</sub>O is more basic than ME-H<sub>2</sub>O mixtures<sup>21</sup>. The changes of the basicity of solvent mixtures are reflected in the  $\text{pK}_T$  values of benzoic acid. Thus the  $\text{pK}_T$  values of benzoic acid in ME-H<sub>2</sub>O mixtures are less than those in DME-H<sub>2</sub>O mixtures. The two solvent also differ on their dielectric constant values and solvating capabilities. The dielectric constants of ME-water mixtures are greater than those of DME-water mixtures of similar mol% non-aqueous component, electrostatic interactions thus impart

less positive contribution to  $\Delta G_t^{\circ}(\text{Bz}^-)$  in ME + H<sub>2</sub>O than in DME + H<sub>2</sub>O resulting in more ionization in the former than in the latter solvent system (Table 3).

The measurement of the electrical conductance of a non-aqueous electrolyte solution provide several important parameters. Determination of the equivalent conductance,  $\Lambda$ , as a function of concentration of the electrolyte, followed by analysis using an appropriate equation gives rise to a value for the dissociation constant. In order to calculate dissociation constants of benzoic acid in mixed solvent from conductance measurements, we have used the Shedlovsky equation and the values have been reported in Tables 4 and 5. An excellent agreement can be found for the dissociation constant of benzoic acid obtained from conductance studies with those of solubility and spectrophotometric data within the limits of our experimental accuracy. However, as noted previously in the present <sup>study,</sup> the conductometric method cannot be used in the range above 60 wt% of ME-water or DME-water mixtures, where due to strong association the value of the conductance has a rather large uncertainty<sup>25</sup>.

The solvent effect on the dissociation equilibrium of HBz can also be seen from equation (8). The values of  $\delta[\Delta G^{\circ}(\text{HBz}-\text{Bz}^-)]$  increase with increase in mol% of ME or DME, the rate of increase being larger at higher percentage of organic co-solvents. Since the dissociation of benzoic acid produces extra charges, it

is expected that  $\delta \Delta G^\circ (\text{HBz}-\text{Bz}^-)$  value should necessarily increase with increase in wt% of ME or DME (Fig. 2).

Table 3 shows the increasingly negative magnitudes of  $\Delta G_t^\circ (\text{HBz})$  with increase in mol% of ME or DME, the values are less negative in ME than DME (Fig. 1). This indicates the stabilization of benzoic acid in these mixed solvents, primarily through dispersion forces<sup>26</sup>. The number of  $-\text{CH}_3$  group relative to that of hydrophilic  $-\text{OH}$  group being greater in DME, a greater dispersion effect is expected in  $\text{DME}-\text{H}_2\text{O}$  and this may be largely responsible for the greater stability of HBz (more negative  $\Delta G_t^\circ (\text{HBz})$ ) in  $\text{DME}-\text{H}_2\text{O}$  as observed. The  $\Delta G_t^\circ (\text{Bz}^-)$  values are predominantly positive, is in agreement with the fact that  $\Delta G_t^\circ$  of anions are usually positive<sup>27,28</sup>. The result indicates that the transfer of  $\Delta G_t^\circ (\text{Bz}^-)$  is non-spontaneous from water to organic solvents.

It is desirable to analyse the results in the way suggested by Treiner<sup>29,30</sup>,

$$\Delta G_t^\circ (\text{Bz}^-) = \Delta G_t^\circ (\text{Cav})_1 + \Delta G_t^\circ (\text{specific})_1 + \Delta G_t^\circ (\text{structural})_1 + \Delta G_t^\circ (\text{el})_1$$

$\Delta G_t^\circ (\text{Cav})_1$ , representing the free energy change due to cavity formation, is usually calculated by using the scaled particle theory as deduced by Pierotti<sup>31</sup> and used by others<sup>32,33</sup>. However, in view of the limitations in the calculation of  $\Delta G_t^\circ (\text{el})_1$ , we do not consider that the method would give more information

regarding the (specific + structural) effects. (The actual value of  $\Delta G_t^{\circ}(el)$  should include terms like,  $\Delta G_t^{\circ}(el)$  (Born) +  $\Delta G_t^{\circ}$  (ion-dipole) +  $\Delta G_t^{\circ}$  (ion-induced-dipole) +  $\Delta G_t^{\circ}$  (ion-quadrupole). Thus, the actual value of  $\Delta G_t^{\circ}(el)$  should be more complicated than is usually assumed). In the case of  $\Delta G_t^{\circ}(HBz)$ , we have

$$\Delta G_t^{\circ}(HBz) = \Delta G_t^{\circ}(Cav)_2 + \Delta G_t^{\circ}(\text{Structural})_2 + \Delta G_t^{\circ}(\text{specific})_2$$

Though we can assume  $\Delta G_t^{\circ}(Cav)_1$  and  $\Delta G_t^{\circ}(Cav)_2$  to be equal, the structural and specific terms would be different for  $\Delta G_t^{\circ}(Bz^-)$  and  $\Delta G_t^{\circ}(HBz)$ .  $\Delta G_t^{\circ}(el)$  would predominate in case of  $\Delta G_t^{\circ}(Bz^-)$  but the dipole-dipole and dispersion interactions would be the main factors for  $\Delta G_t^{\circ}(HBz)$ . It is known that the calculation of  $\Delta G_t^{\circ}(Cav)$  involves an element of uncertainty and the calculation of  $\Delta G_t^{\circ}(Bz^-)$  is based on extra-thermodynamic assumptions with their inherent limitations. Thus, instead of attempting to find out the specific and structural effects, it is advisable to calculate the  $\Delta G_t^{\circ}(\text{ion})$  using different extra-thermodynamic assumptions to have consistent set of values. It is also desirable to attempt a correlation of the experimental values of  $\Delta G_t^{\circ}(\text{ion})$  with the different models of ion-solvent interactions. Obviously, more data of the 'medium effect' of ions are required to obtain a clear picture regarding the ion-solvent interactions.

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

Table 1 : Solubility and  $pK_T$  values of Benzoic Acid in ME-Water Mixtures at 25 °C

Wt% of ME	$\frac{1}{\epsilon} \times 10^2$	Total Benzoic Acid Concentration $[C_T]$ (mol dm <sup>-3</sup> )	Corrected pH of saturated solution	A	$-2 \log Y_{\pm}$	$pK_T$ (from solubility data)	$pK_T$ (Spectro-photometric)	Average $pK_T$
00	1.27	0.0285	2.90	.509	.03	4.23	4.21	4.22
10	1.34	0.0444	2.97	.549	.03	4.60	4.57	4.59
20	1.43	0.0782	2.90	.606	.04	4.73	4.69	4.71
30	1.56	0.1422	2.87	.691	.05	4.94	4.90	4.92
40	1.74	0.3973	2.84	.813	.06	5.34	5.31	5.33
50	1.99	0.5314	2.91	.995	.07	5.61	5.58	5.60
60	2.37	1.2555	2.85	1.293	.09	5.89	5.87	5.88
70	2.92	1.4429	2.99	1.768	.11	6.25	6.24	6.25
80	3.77	1.5965	3.30	2.593	.11	6.91	6.88	6.90
90	5.26	2.2988	3.52	4.278	.14	7.54	7.55	7.55
100	5.91	3.0535	-	5.087	-	-	-	-

The uncertainty in the  $pK_T$  value is  $\pm 0.02$  unit.

Table 2 : Solubility and  $pK_T$  values of Benzoic Acid in DME-Water Mixtures at 25 °C

Wt% of DME	$\frac{1}{\epsilon} \times 10^2$	Total Benzoic Acid Concentration $[C_T]$ (mol dm <sup>-3</sup> )	Corrected pH of saturated solution	A	$-2 \log \delta_t$	$pK_T$ (from solubility data)	$pK_T$ (Spectro-photometric)	Average $pK_T$
10	1.40	0.0486	2.93	.587	.04	4.57	4.54	4.56
20	1.56	0.1292	2.87	.691	.05	4.90	4.89	4.90
30	1.76	0.5093	2.90	.827	.06	5.57	5.57	5.57
40	2.01	1.2322	2.85	1.009	.07	5.86	5.83	5.85
50	2.35	2.1032	2.82	1.277	.10	6.06	6.03	6.05
60	2.79	2.7123	2.94	1.652	.11	6.42	6.41	6.42
70	3.58	2.8909	3.05	2.401	.14	6.70	6.67	6.69
80	4.79	3.5260	3.38	3.714	.15	7.46	7.43	7.45
90	7.42	4.4288	3.90	7.160	.16	8.61	8.62	8.62
100	14.12	3.2025	-	18.811	-	-	-	-

The uncertainty in the  $pK_T$  value is  $\pm 0.03$  unit.

Table 3 : Free Energies of Transfer of Benzoate Ion,  $\Delta G_t^\circ(\text{Bz}^-)$  in Solvent-Water Mixtures at 25 °C  
(values are in  $\text{kJ mol}^{-1}$ )

Wt% of Solvent	$\Delta G_t^\circ(\text{HBz})$		$\delta(\Delta G_t^\circ)$		$\Delta G_t^\circ(\text{H}^+)$		$\Delta G_t^\circ(\text{Bz}^-)$	
	ME	DME	ME	DME	ME	DME	ME	DME
10	-1.15	-1.38	2.11	1.94	-1.07	-1.67	2.03	2.23
20	-2.58	-3.84	2.79	3.88	-1.88	-2.57	2.09	2.61
30	-4.08	-7.26	3.99	7.70	-2.40	-3.26	2.31	3.70
40	-6.64	-9.45	6.33	9.30	-2.43	-3.99	2.12	3.84
50	-7.36	-10.77	7.87	10.44	-2.99	-4.43	3.50	4.10
60	-9.49	-11.40	9.47	12.55	-2.93	-4.57	2.91	5.72
70	-9.84	-11.56	11.58	14.09	-2.96	-4.15	4.70	6.68
80	-10.09	-12.06	15.29	18.43	-2.25	-1.42	7.45	7.79
90	-10.99	-12.62	19.00	25.11	1.75	5.46	6.26	7.03
100	-11.69	-11.82	-	-	-	-	-	-

Uncertainties in  $\Delta G_t^\circ$  values are of the order  $\pm 0.17 \text{ kJ mol}^{-1}$

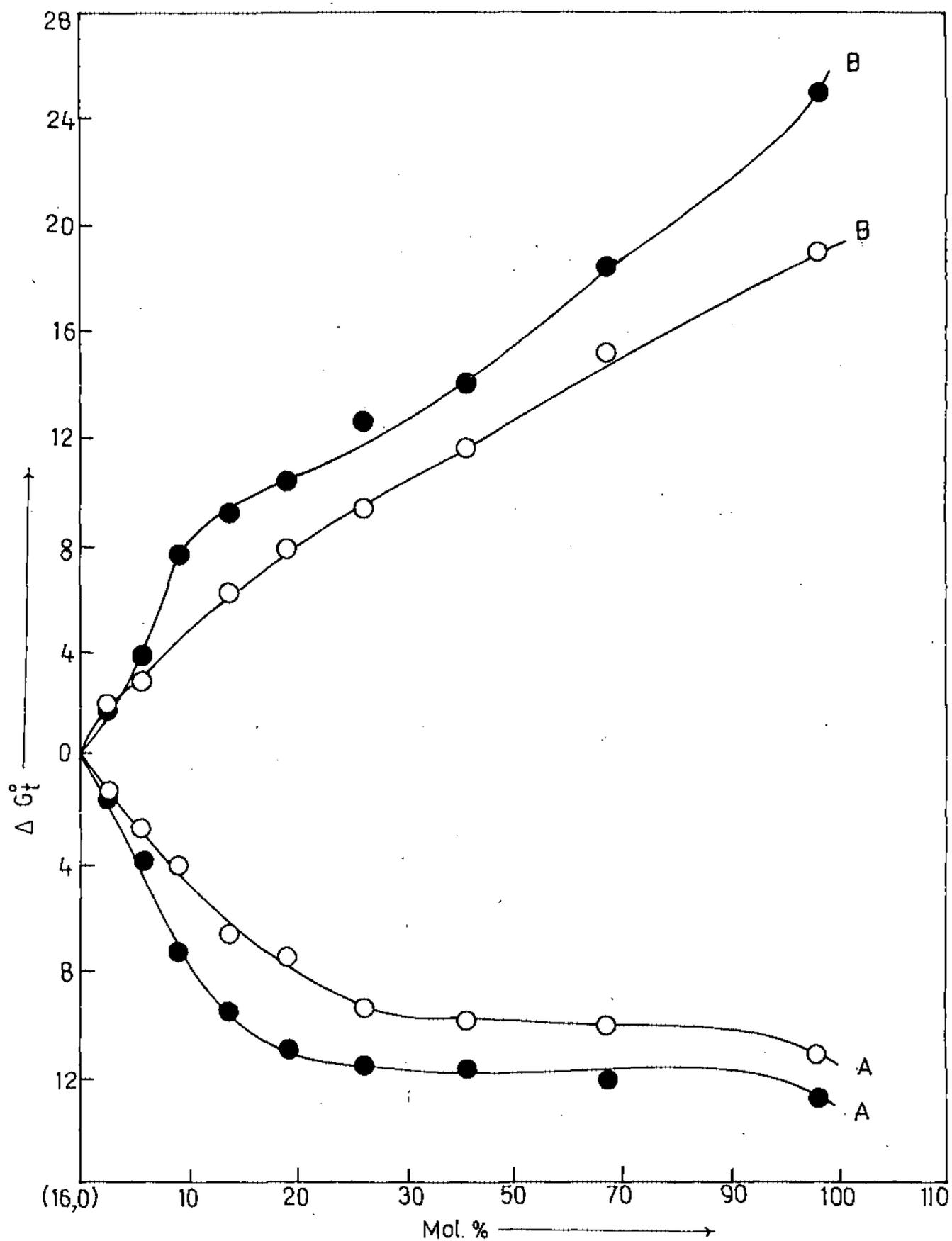


Fig. 1 Variation of (A)  $\Delta G^\ddagger(\text{HB}_z)$  and (B)  $\delta(\Delta G^\ddagger)$  in ME+H<sub>2</sub>O (O) and DME+H<sub>2</sub>O (●).

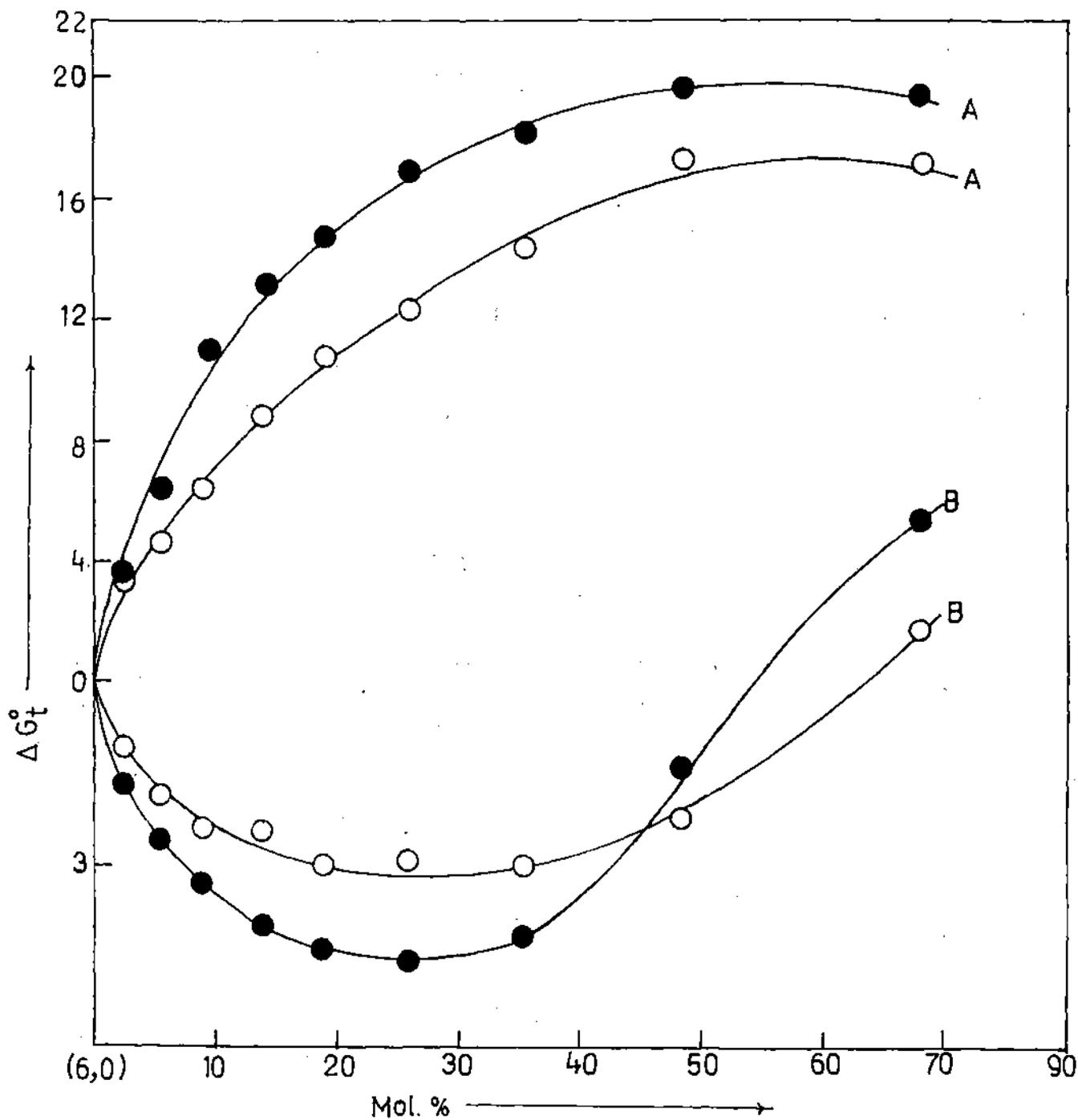


Fig. 2 & Variation of (A)  $\Delta G^\circ(B_2^-) - \Delta G^\circ(HB_2)$  & (B)  $\Delta G^\circ(H^+)$  in Aqueous mixtures of ME (○) and DME (●).

Table - 4

Equivalent Conductances and Dissociation Constants  
of Benzoic Acid in ME-Water Mixtures at 25°C

Water

Concentration x 10 <sup>4</sup> (mol dm <sup>-3</sup> )	$\Lambda$ ( $\Omega$ cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_0$	$\Lambda_0 \eta_0$	pK
8.989	85.39			
6.758	96.61			
5.288	107.14	375.5	3.356	4.23
2.889	136.73			
1.438	176.71			

20 Wt% ME

Concentration x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	$\Lambda$ ( $\Omega$ cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_0$	$\Lambda_0 \eta_0$	pK
6.762	11.58			
5.761	12.52			
4.843	13.62	219.0	3.321	4.72
4.091	14.77			
2.892	17.46			
2.451	18.89			

Contd..

Table - 4 (Contd..)

40 wt% ME

Concentration x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	$\hat{\Lambda}$ ( $\Omega \text{ cm}^2 \text{ mol}^{-1}$ )	$\Lambda_0$	$\Lambda_0 \eta_0$	$\rho K$
9.734	3.09			
9.003	3.21			
7.394	3.54	141.0	3.335	5.34
6.251	3.85			
5.282	4.18			
4.004	4.79			

60 wt% ME

Concentration x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	$\hat{\Lambda}$ ( $\Omega \text{ cm}^2 \text{ mol}^{-1}$ )	$\Lambda_0$	$\Lambda_0 \eta_0$	$\rho K$
5.569	1.76			
4.841	1.88			
3.764	2.13	115.0	3.318	5.89
3.240	2.29			
2.538	2.59			

Table - 5

Equivalent Conductances and Dissociation Constants  
of Benzoic Acid in DME-Water at 25°C

20 wt% DME

Concentration x 10 <sup>4</sup> (mol dm <sup>-3</sup> )	$\Lambda^{\circ}$ ( $\Omega \text{ cm}^2 \text{ mol}^{-1}$ )	$\Lambda_0$	$\Lambda_0 \gamma_0$	pK
5.288	29.43			
4.409	31.99			
2.891	38.71	205.9	3.342	4.91
1.003	61.24			
0.487	81.32			

40 wt% DME

Concentration x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	$\Lambda^{\circ}$ ( $\Omega \text{ cm}^2 \text{ mol}^{-1}$ )	$\Lambda_0$	$\Lambda_0 \gamma_0$	pK
3.601	3.12			
2.489	3.74			
1.848	4.34	157.26	3.475	5.85
1.296	5.16			
0.961	5.98			
0.625	7.38			

Cont d..

Table - 5 (Contd..)

60 wt% DME				
Concentration x 10 <sup>4</sup> (mol dm <sup>-3</sup> )	$\Lambda^{\circ}$ ( $\Omega \text{ cm}^2 \text{ mol}^{-1}$ )	$\Lambda_0$	$\Lambda_0 \eta_0$	pK
3.386	6.75			
2.558	7.74			
1.959	8.82	204.77	3.563	6.43
1.002	12.24			
0.774	13.85			
0.129	32.19			

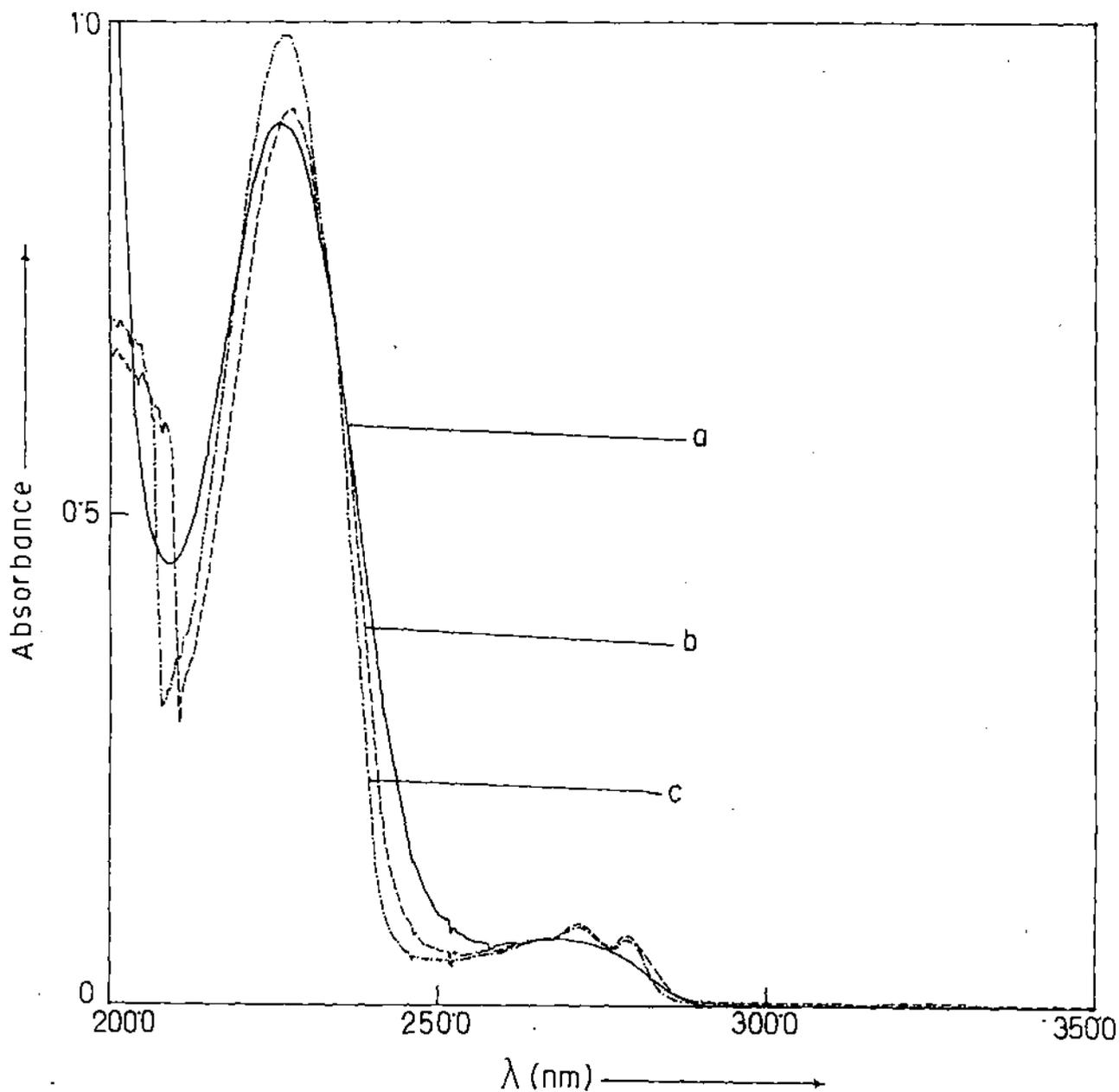


Fig3(i) - Ultraviolet spectra of Benzoic acid in H<sub>2</sub>O (—) ME (---) and DME (-·-·).

Concentration (a) =  $9.71175 \times 10^{-5}$  (M)

Concentration (b) =  $7.98597 \times 10^{-5}$  (M)

Concentration (c) =  $8.68408 \times 10^{-5}$  (M)

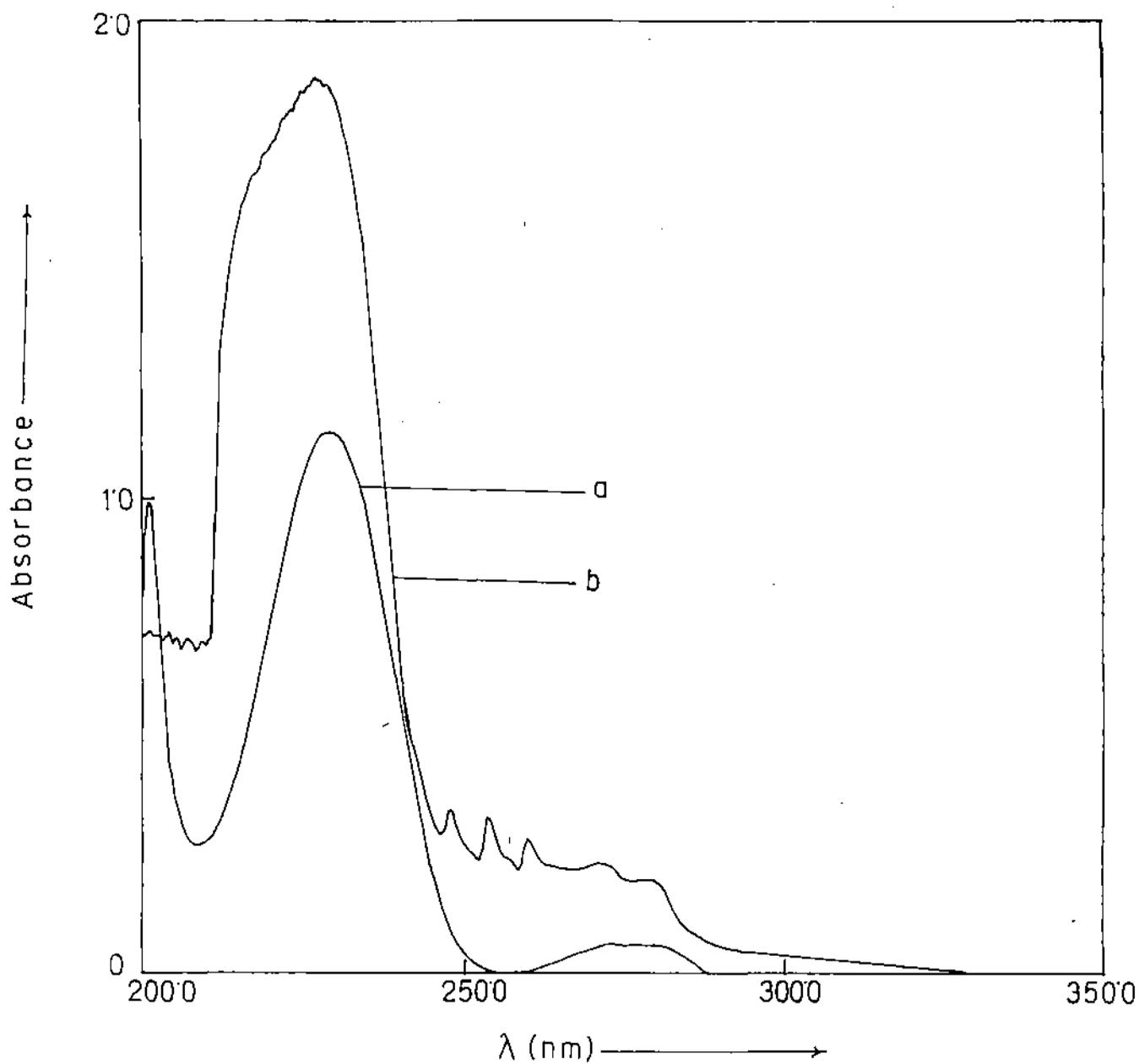


Fig. 3(ii) - Ultraviolet spectra of Benzoic acid in (a) 50% ME and (b) 80% DME.

Concentration (a) =  $7.7301 \times 10^{-5}$  (M)

Concentration (b) =  $1.2611 \times 10^{-4}$  (M)

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