CHAPTER - II

Thermodynamic Acid Dissociation Constants of the Protonated Form of 2,2'-Bipyridine and 1,10-Phenanthroline in Aqueous Binary Mixtures of 2-Methoxyethanol and 1,2-Dimethoxyethane at 25°C

As part of our comprehensive studies[1-4] on dissociation equilibria in different aquo-organic mixtures, we report in this chapter the results of our measurements of the dissociation constants of protonated forms of 2,2'-bipyridine and 1,10-Phenanthroline in 2-methoxyethanol (ME) + water and 1,2-dimethoxyethane (DME) + water mixtures at 298K. Such studies give important reflections regarding the role of solvent on the dissociation equilibria and ion-solvent interactions and also on the acid base properties of these solvents as well as on their structural features.

Both ME and DME (monomethyl and dimethyl ethylene glycols) are well known for their various industrial uses[5-7]. ME is quasi-aprotic in nature and DME is a wholly aprotic solvent. It will be very interesting to study the behaviour of these two closely related co-solvents in aqueous mixtures from dissociation equilibria and other thermodynamic parameters. With this end in view we have undertaken the present work and the results are described in this chapter.

Experimental

2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) (G.R., E. Merck) were used as such. 2-methoxy ethanol (G.R., E.

Merck) was distilled twice before use. The b.p. (124°C) and density (0.96092 gm/c.c. at 25°C) compare well with literature values[8]. 1,2-dimethoxyethane (Fluka)was shaken well with $FeSO_4$ (A.R., BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and distilled over metallic sodium (b.p. = 83.5°C, density = 0.8626 gm/c.c.).

All other reagents were of analytical grade. The solutions were prepared using triply distilled water.

The ME - H_2O and DME - H_2O mixtures employed in the study were prepared by appropriate mixing of the solvents by weight.

The solubility of 2,2'-bipyridine and 1,10-phenanthroline in ME + H_2O and DME + H_2O mixtures at 298K were determined in the way reported before[9,10]. Saturated solutions of the ligands were allowed to equilibrate at 298K for 24 hours in Campbell Solubility apparatus[11] and the solutions were filtered by inversion of the apparatus at the same temperature. Concentrations in the saturated solutions were computed using the molar absorptivities determined on known concentrations of each of the compounds in several solvent-water mixtures. The solubility values have been determined spectrophotometrically at 282 nm and 262 nm for 2,2'-bipyridine and 1,10-phenanthroline respectively.

The pK values of the ligands were determined pH - metrically and spectrophotometrically as described in our previous communications[1-4]. Molar absorption measurements were taken at 280, 295 and 300 nms for 2,2'-bipyridine and at 260, 270 and 275 nms for

1,10-phenanthroline. The absorption maxima varied only slightly with solvent composition indicating little solute-solvent interaction (Fig. 3). Shimadzu UV - 240 spectrophotometer maintained at 298 K was used for spectrophotometric measurements. The pH was measured with a ECIL pH meter having an accuracy of $\pm$ 0.01.

The dielectric constant values of ME - H_2O mixtures and DME - H_2O mixtures were taken from the works of Sadek et al[12] and Justice[13] respectively.

Calibration of Glass electrode:

The determination of the dissociation constants of the acids requires accurate values of H^+ ion concentration. The glass-calomel electrode combination has been employed successfully for the determination of H^+ ion concentrations in different mixed and non-aqueous solvents. Glass electrode is reported to function satisfactorily in different dipolar aprotic solvents though the response is not always found to be Nernstian particularly in pure solvents[14].

However, the glass electrode has been found to work reversibly in ME + H_2O and DME + H_2O mixtures and the reproducible results of the H^+ ion concentrations have been obtained.

The calibration of the glass electrode and 'correction factors' in the different percentages of the mixed solvents have been determined in the way suggested by Van Uitert and Haas[15],

Bates[16], Irving and Manhot[17], Lahiri, Aditya and co-workers[18-20].

The pH meter was first standarized with potassium-hydrogen-phthalate ($\frac{M}{20}$) buffer and then with 10^{-4} mol dm^{-3} $HClO_4$ acid solution. The glass electrode was then kept immersed in the appropriate solvent medium for equilibration and the meter readings of 10^{-4} mol dm^{-3} $HClO_4$ in the particular solvent medium was taken. The method gives reproducible results. The correction factors log U_H in the particular medium were calculated by the relationship $-\log \left[H^+ \right]$ = B + log $\left[U_H \right]$ where $\left[H^+ \right]$ is the stoichiometric hydrogen ion concentration assuming 100% dissociation of the acid in the aqueous and in mixed solvents.

The 'correction factors' 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 correction factors, log U_H, in different percentages of ME + H_2O and DME + H_2O mixtures are presented in Tables 1 and 2.

Results

The thermodynamic dissociation constants for the reaction

$$LH^+ \rightleftharpoons L + H^+ \qquad \cdots (1)$$

(where L = 2,2'-bipyridine or 1,10-phenanthroline) is written as

$$K_T = \frac{C_L \times C_{H^+}}{C_{LH^+}} \times \frac{f_L \times f_{H^+}}{f_{LH^+}} \qquad \cdots (2)$$

In the determination of the dissociation constants, the use of inert electrolytes is avoided[9,10,21] and the concentrations of electrolytes are kept very low so that their effects on the solvent structure are minimum, a condition essential for the determination of 'medium effects' of ions.

The activity coefficients of f_{LH^+} and f_{H^+} have been assumed to be the same in dilute solutions though a slight variation in f_{H^+} and f_{LH^+} values is expected in view of the difference in the solvational characteristics and ion-size parameters of H^+ and LH^+ ions. Thus, the variations of $\frac{f_{H^+} \times f_L}{f_{LH^+}}$ will be definitely small and will not exceed experimental error limits at low ionic strengths ($3 - 7 \times 10^{-4}$ M) in pH-metric method and even less in spectrophotometric method. Under this condition equation (2) can be represented as

$$K_T = \frac{C_L \times C_{H^+}}{C_{LH^+}} \qquad \cdots (3)$$

Thus

$$pK_T = pC_{H^+} + \log \frac{C_{LH^+}}{C_L} \qquad \cdots (4)$$

$$= B + \log U_H + \log \frac{C_{LH^+}}{C_L} \qquad \cdots (5)$$

$$= B + \log U_H + \log \frac{d - d_M}{d_I - d} \qquad \cdots (6)$$

(B = meter reading of the solution)

where d_M, d_I and d are the optical densities of either 2,2'-bipyridine or 1,10-phenanthroline at pH's corresponding to the molecular and ionic form and mixtures of molecular and ionic forms respectively.

Further

$$\left[H^+\right]_{Total} = \left[H^+\right]_{free} + \left[LH^+\right] \qquad \cdots (7)$$

$$\left[L\right]_T = \left[L\right] + \left[LH^+\right] \qquad \cdots (8)$$

Thus, from the known concentrations of $\left[L\right]_T$, $\left[H^+\right]_T$ and $\left[H^+\right]_{free}$ (determined experimentally) values, pK_T can be calculated using (5), whereas equation (6) can be utilized when d_M, d_I, d and $\left[H^+\right]_{free}$ are available. Few representative calculations in ME - water and DME - water have been given in Tables 3-10.

The pK_T values have been calculated in the way described in our previous communications[1-4,9,10].

The free energy of transfer of the ligands from water to mixed solvents have been calculated using the relation

$$\Delta G_t^o(L) = -2.303 \, RT \, \log \frac{C_s}{C_w} \qquad \cdots (9)$$

where C_s and C_w represent the molar concentrations of L in aquo-organic solvents and water respectively.

The free energies of transfer for the ionisation of LH^+ have been calculated from equation (10)

$$\Delta G_t^o(1) = 2.303 \, RT \left[pK_s(1) - pK_w(1) \right] \qquad \cdots (10)$$

Discussion

The average values of pK_T for 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) determined pH-metrically and spectrophotometrically (recorded in Tables 1 and 2) give excellent consistency.

The pK_T values of the ligands have been found to decrease with the addition of organic solvent in ME + H_2O and DME + H_2O mixtures. The minima are found at ~80 wt% and 70 wt% of ME and DME respectively (Fig. 1). Similar behaviour has been observed in other solvents.

The pK_T values when plotted against mole-fraction of organic solvents show linearity at best upto 70 wt% beyond which considerable deviations occur (Fig. 2).

The Tables 1 and 2 show that the solvent effects on the dissociation equilibrium of LH^+ type acids (isoelectronic in nature) are more or less similar in aqueous ME or DME solutions. The $\Delta G_t^O(l)$ values in both solvent systems pass through minima with addition of non-aqueous component, the variation being more marked in DME than in ME. The appearance of such minima can be attributed to:

1) increased solubility leading to greater dissociation of LH^+

2) changed solvational properties of ligands and their conjugate acids

3) enhanced basicity of the solvent mixtures upto 70-80% of organic solvents and subsequent decrease in basicity.

No useful conclusion can be derived from the analysis of $\underline{/}\ \Delta G_t^O(LH^+)\ -\ \Delta G_t^O(L)\ \underline{/}$ values as it implies increasingly positive values of $\Delta G_{t(el)(LH^+)}^O$, an inherent limitation arising from the assumption, $\Delta G_{t(LH^+)}^O = \Delta G_{t(L)}^O + \Delta G_{t(el)(LH^+)}^O$.

It is to be noted that the relative affinities of water or the non-aqueous component towards the base (L) or its conjugated acid (LH^+) may be expected to arise from the relative bonding

capacities of solvent dipoles exerted largely through hydrogen bond formation. However, their contributions to $\Delta G_t^o(l)$ values cannot be calculated.

$\Delta G_{t(L)}^o$ values can be obtained from the solubility values of the ligands at 298 K (Tables 12 and 13). The accuracy of the solubility values are within 0.5 - 1.0%. The solubility values increase with the increase in hydrophobic character of the solvent mixtures. The solubility values of bipy and phen in water have been determined to be 0.0347 moles dm^{-3} and 0.0136 moles dm^{-3} at 298 K respectively. However, the solubility value of bipy is agreement with the values reported earlier[9,10] but some discrepancy is observed in case of phen[9,10]. $\Delta G_t^o(L)$ values are found to be increasingly negative with increasing wt% of ME or DME because of stabilization of large organic molecules containing benzene rings, primarily through dispersion forces as in the case of uncharged bases like nitroanilines[22].

In order to understand the structural complexities, ion-solvent interactions and the basicities of the solvent mixtures, attempts have been made to determine $\Delta G_{t(H^+)}^o$ values in aquo-organic mixtures using the method suggested by Lahiri and co-workers[9,10]. $\Delta G_{t(H^+)}^o$ gives the quantitative measure of the free energy of transfer or 'medium effects' when H$^+$ is transferred from water to mixed solvents and is regarded to be the best measure of solvent basicity compared to that of water.

Thus we have the equation (12) for the reaction (1)

$$\Delta G^o_{t(1)} = \Delta G^o_{t(L)} + \Delta G^o_{t(H^+)} - \Delta G^o_{t(LH^+)} \qquad \cdots (11)$$

$$\text{or} \quad \Delta G^o_{t(H^+)} = \Delta G^o_{t(1)} + \Delta G^o_{t(el)(LH^+)} \qquad \cdots (12)$$

$$\underline{\diagdown}\ \text{Since}\ \Delta G^o_{t(LH^+)} = \Delta G^o_{t(L)} + \Delta G^o_{t(el)(LH^+)}\ \underline{\diagup}$$

In absence of any suitable and reliable equation in calculating $\Delta G^o_{t(el)}$ unambiguously, we are forced to use the Born equation[23] inspite of its limitations in calculating $\Delta G^o_{t(el)}$ in going from water of relative permitivity ϵ_w to a solvent of relative permittivity ϵ_s

$$\Delta G^o_{t(el)(Born)} = \frac{Nz^2 e^2}{2 r_{LH^+}} \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \qquad \cdots (13)$$

where r_{LH^+} has been taken to be $3.70\ \overset{o}{A}$ [9,10]. It is expected that considerable uncertainties in $\Delta G^o_{t(el)}$ values will arise from Born equation in case of unsymmetrical ions like Phen$\bigcirc$H$^+$ as even in case of spherical ions like Na$^+$, K$^+$, Cl$^-$ etc, the results are found to be defective. Moreover, it is expected that the ions will lose their sphericity in solutions. Therefore, the use of Born equation assuming spherical orientation of Phen$\bigcirc$H$^+$ with the solvent molecules can be taken to be in order.

However, in calculating $\Delta G^o_{t(el)}$, we consider the energy of interactions arising not only from Born charging (BC) but also energy of interactions like ion-dipole (i-d), ion-induced-dipole (i-i-d), ion-quadrupole (i-q)[24-26] etc. The charge-transfer and other weak interactions are usually neglected.

Thus,

$$\Delta G^o_{t(el)} = \Delta G^o_{t(el)(BC)} + \Delta G^o_{t(i-d)} + \Delta G^o_{t(i-i-d)} + \Delta G^o_{t(i-q)}$$

Due to lack of knowledge of the accurate values of quadrupole moments of the solvents, $\Delta G^o_{t(i-q)}$ term is also neglected.

The expressions for the energy terms are

$$\Delta G^o_{t(i-d)} = -\frac{n \cdot N \cdot z_i e \mu}{(r_i + r_s)^2} \qquad \cdots (14)$$

and

$$\Delta G^o_{t(i-i-d)} = -\frac{n N \propto (z_i e)^2}{2(r_i + r_s)^4} \qquad \cdots (15)$$

where n, μ, $\propto$ and r_s are solvation number, dipole moment, polarizability and radius of the solvent respectively.

The polarizability $\propto$ of ME and DME values have been calculated using the relation

$$\propto = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \cdot \frac{3}{4 \pi N} \qquad \cdots (16)$$

The n_D values for ME and DME have been taken from the literature[27]. The radius of the solvent mixtures have been calculated from their molar volumes. The $\Delta G^o_{(i-d)}$ and $\Delta G^o_{(i-i-d)}$ in water, ME and DME have been calculated using the following parameters

$\mu_w = 1.86 \times 10^{-18}$ esu, $\alpha_w = 1.47 \times 10^{-24}$ cm^3, $r_w = 1.38 \times 10^{-8}$ cm

$\mu_{ME} = 2.18 \times 10^{-18}$ esu, $\alpha_{ME} = 7.62 \times 10^{-24}$ cm^3, $r_{ME} = 3.14 \times 10^{-8}$ cm

$\mu_{DME} = 1.71 \times 10^{-18}$ esu, $\alpha_{DME} = 9.57 \times 10^{-24}$ cm^3, $r_{DME} = 3.45 \times 10^{-8}$ cm

The values $\Delta G^o_{t(i-d)}$ and $\Delta G^o_{t(i-i-d)}$ in aquo-organic mixtures have been calculated assuming the solute to be distributed in the binary mixtures in the ratio of their mole-fractions X_1 and X_2. Thus

$$\Delta G^o_{t(i-d)} = \left[X_1 \, \Delta G^o_{i-d(w)} + X_2 \, \Delta G^o_{i-d \,(org.solv.)} \right] - \Delta G^o_{i-d(w)} \text{ etc.} \qquad \cdots (17)$$

The values of $\Delta G^o_{t(el)(BC)}$, $\Delta G^o_{t(el)} \left[BC+i-d+i-i-d \right]$ assuming mono-solvation of the LH^+ ions have been recorded in columns I and II of Table 11. The column III contains the $\Delta G^o_{t(el)}$ values based on 'one-layer solvation model'[28].

$$\Delta G^o_{t(el)} = \frac{Nz^2e^2}{2} \left[\frac{1}{\epsilon_1} - 1 \right] \left(\frac{1}{r_{LH^+}} - \frac{1}{b} \right) + \frac{Nz^2e^2}{2} \left(\frac{1}{\epsilon_0} - 1 \right) \left(\frac{1}{b} \right)$$

$$\cdots (18)$$

where $b = r_{LH^+} + r_s$, r_s is the radius of the solvent molecules, $\epsilon_1 = 2$ and $\epsilon_o =$ bulk dielectric constant. The mean molar mass of the assorted solvent is determined from the relation

$$M_s = 100 \left\{ \frac{W}{M} + \frac{100 - W}{18.02} \right\}^{-1} \qquad \cdots (19)$$

where M = Molecular weight for ME or DME respectively. The density values have been experimentally determined.

It is seen that the contributions due to ion-dipole and ion-induced dipole interactions are high. It is noted that $\Delta G^o_{t(el)}$ $\underline{/}$ BC $+$i-d+i-i-d $\underline{/}$ and $\Delta G^o_{t(el)(one-layer)}$ differ considerably in most cases. The nature of uncertainties in $\Delta G^o_{t(el)}$ values from different equations can be ascertained from the results.

$\Delta G^o_{t(H^+)}$ values in ME + H_2O and DME + H_2O mixtures using bipyridine, phenanthroline and their averages are recorded in Tables 12 and 13. The conversion factor to get $\Delta G^o_{t(H^+)_N}$ values (in mole-fraction scale) are obtained from the relationship

$$\Delta G^o_{t(H^+)_N} = \Delta G^o_{t(H^+)_C} + 5.7 \log \frac{M_W \times d_s}{d_W \times M_s} \qquad \cdots (20)$$

$\Delta G^o_{t(H^+)}$ values using bipy and phen show excellent consistency both qualitatively as well as quantitatively at low percentages but vary considerably at higher percentages. However, an error to the extent of 0.5 kJ mole^{-1} can be assumed due to errors in the determination of pK-values in mixed solvents and other

extraneous factors. It is particularly assuring when we consider
that an error to the extent of 8 - 12 kJ gion^{-1} is usually asso-
ciated with single ion free energies[29].

It is apparent that the different equations give different
results and slight fluctuations in $\Delta G^o_{t(H^+)}$ are expected in view
of inherent limitations involved in any method of calculation
of single ion values involving extra thermodynamic assumptions.
The agreement between $-\Delta G^o_{t(H^+)}$ values (mole fraction scale)
determined in the present work with those reported by Kundu
et al[30,31] using TATB method (Table below) are very good (except
at 50 wt% DME) inspite of widely divergent methods used.

Wt% of ME or DME	ME		DME	
	Present Work	Kundu[30] et al	Present work	Kundu[31] et al
10	1.3(1.2)	0.2	1.9(1.6)	2.0
30	3.0(2.3)	2.3	4.0(3.0)	5.9
50	4.2(2.6)	4.4	5.8(3.8)	10.5
70	5.0(2.1)	5.3		

$\sqrt{}$ Values in parenthesis are based on $\Delta G^o_{t(el)(Total)}$ $\underline{7}$

$\Delta G^o_{t(H^+)}$ value becomes increasingly negative in going
from water to ME + H_2O mixtures or DME + H_2O mixtures indicating
that the binary mixtures are more basic than water. The basicity
becomes maximum at 80 wt% of ME (ME : $H_2O \approx 1:1$) and at 70 wt%
DME (DME : $H_2O \approx 1:2$), thereafter basicity decreases and ultimately

becomes less basic than water at about 90 wt% of organic solvents.

The results suggest that ME and DME are probably less basic than water. It is also apparent that DME + H_2O mixtures are comparatively more basic than ME + H_2O mixtures.

The results can be well understood from the structural considerations.

ME, with one methoxy group is quasiprotic in character and is less acidic than water due to restricted availability of the hydrogen bonded acidic H-atom. Since the acidity of the co-solvent is likely to be relayed through co-operative structure of H-bonding between the co-solvent and water molecules in the aquoues solutions[30,32,33], the possible H-bonded co-solvent water complex should make ME + H_2O less acidic than water. This explains the increase in basicity and consequent decrease in pK-values with increase in ME content. The dipolar aprotic DME having no acidic hydrogen atom is highly hydrophilic and more basic than ME due to the presence of two flexible electron rich etheral-O-atoms. The changes in basicity are reflected in the free energy of transfer of H^+ ion :

$$\angle \ \Delta G^o_t(H^+)_{ME} > \Delta G^o_t(H^+)_{DME} \ \diagup \ \text{and} \ \ pK\text{-values of the ligands}$$

$$(pK_{ME + H_2O} > pK_{DME + H_2O}).$$

The addition of organic solvent to water usually enhances the 3D-structure of water molecules. However, due to the presence of -OCH$_3$ groups, the addition of ME or DME induces the initial

break down of 3D-structure of water followed by possible structure

promoting effect of H-bonded ME + H_2O and DME + H_2O complexation

which goes upto 80 wt% ME and 70 wt% DME. However, the basicity

of ME is considerably reduced due to intramolecular hydrogen

bonding (CH$_2$-OMe

    |

    CH$_2$-OH $\longrightarrow$

CH$_2$-O-Me

    | $\searrow$ H

    CH$_2$-O $\nearrow$)
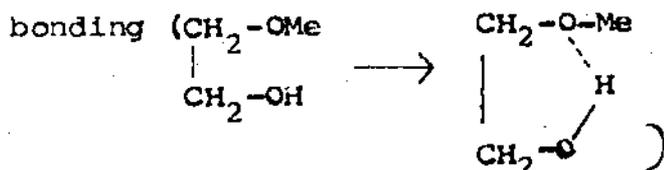
In case of DME, a transition takes place in the region 70-82 wt%

where DME, $2H_2O$ is converted to DME, H_2O complex. Possible inter-

molecular hydrogen bonding may take place in this region leading

to the decrease in basicity.

CH$_2$-OMe

|

CH$_2$-OMe   + H_2O $\longrightarrow$ CH$_2$ —— O----H

                        (CH$_3$ / ... \ O)

                  |

                  CH$_2$ —— O----H

                             CH$_3$
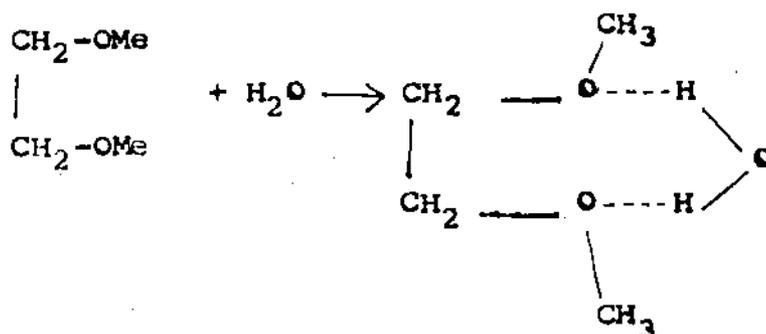
The changes in pK-values and the decrease in basicity

at higher compositions can be attributed to structure breaking

of the solvent complexes and consequent formation of pure solvent

structure. Pure ME and DME appear to be less basic than water

contrary to the facts based on their structures. It is to be

noted that the basicity of a solvent in the gaseous state is a microscopic property being determined by the intrinsic properties of individual molecules related to their structures. But the basicity of the solvent in the liquid state is a macroscopic property being determined by hydrogen bonding, molecular associations, polarisibility, dipole moment and a host of other factors. Thus for solvents in the liquid state the acidity and basic properties belong to the entire phase[34] and have less localised meaning.

Therefore, the order in the basicity in the gaseous state[34] ButOH $>$ EtOH $>$ MeOH $>$ H$_2$O can be explained with the increase in the electron density on the O-atom due to inductive effect of alkyl group. The order reverses in the liquid state due to structural complexities though MeOH + H$_2$O, EtOH + H$_2$O mixtures are more basic than H$_2$O resulting from the structural breakdown of water molecules.

Thus, ME and DME may be more basic than water in the gaseous phase but the order of basicity probably changes in liquid state. It is to be noted that the basicity of the solvent molecules usually arises from the attachment of H$^+$ ions to the oxygen or nitrogen atoms (with lone pair of electrons) of these solvent molecules.

The basicity, being a macroscopic property, should change from solvent to solvent as there are $\sim$55.5 moles of water, $\sim$31 moles of CH$_3$OH, $\sim$22 moles of C$_2$H$_5$OH, $\sim$16 moles of ethylene

glycol (EG), ~13 moles in ME, ~11 moles of DME in 1000 gms of solvents. The number of O-atoms (which is responsible for cation-O-centre interacting capacities) and other bulk properties change drastically in the liquid state. Thus, water is more basic than ME and DME in liquid state but diprotic DME with two electron rich O-atom should be more basic than ME molecules. This is corroborated from the trends in $\Delta G^o_{t(H^+)}$ values in ME + H_2O and DME + H_2O determined by us.

We now examine the values of $\Delta G^o_t(1)$ of equation (10). The values together with the corresponding values of H^+ ion, $\Delta G^o_{t(H^+)}$ are shown in Table 12 and 13. Despite the uncertainities in the free energy values for the individual ions, it is noteworthy that, like $\Delta G^o_{t(M^+)}$ values for all the cations, $\Delta G^o_t(1)$ values are also found to be negative. The relative affinities of water or the non-aqueous component towards the base (L) or its conjugate acid (LH^+) may be expected to arise from the relative bonding capacities of solvent dipoles exerted largely through hydrogen bond formation. The strength of hydrogen bonding should be largely guided by the relative charge densities on the oxygen and hydrogen charge centres of the isolated dipoles. Owing to the inductive effect of the methyl group in ME or DME, the negative charge density on the oxygen atom is presumably somewhat greater than the corresponding quantity in water, so that the protonic character of the hydrogen atom of the hydroxyl group in ME is weaker than in water. The 'electrostatic' contribution to

$\Delta G^o_{t(LH^+)}$ should obviously be positive because water has a higher dielectric than any of the mixed solvents, but the overall negative values of $\Delta G^o_t(1)$ indicate the primary solvation of the LH$^+$ ions arising from ion-dipole interactions, outweigh the electrostatic or "secondary solvation" effect[22,32,35].

Both phenanthrolinium and bipyridinium ions are likely to be solvated in ME and DME through their partially protonated hydrogen atoms attached to the nitrogen atoms and the negatively charged oxygen centre of the solvent dipoles. Since the negative charge density on oxygen atom in ME or DME is greater than that in water, the $\Delta G^o_{t(LH^+)}$ (Table 12 & 13) values should be increasingly negative, as has been observed in both the solvent systems. However, the $\Delta G^o_{t(LH^+)}$ values for bipyridinium ions in both solvents are found to be less negative than those of the phenanthrolinium ions. The benze ring being hydrophobic, 1,10-phenanthroline should have a greater affinity toward the organic solvents. This presumably suggest that the hydrophobism of the benzene ring as well as its solvophilism toward either of the organic components in mixed media exerts a stronger influence on the $\Delta G^o_{t(LH^+)}$ values for phenanthrolinium ion, leading to the larger negative values.

In conclusion it may be said that the overall dissociation of 2,2'-bipyridine and 1,10-phenanthroline in these two solvent systems is dictated by specific solute-solvent interactions besides the effect of relative solvent basicities.

Table 1 : The pK values of 2,2'-Bipyridine and 1,10-phenanthroline in the ME - water mixtures (Temp = 298K)

Wt% of ME	Mole fraction of ME	$\frac{1}{\epsilon} \times 10^2$	Correction factor	pK_T of Bipyridine			pK_T of Phenanthroline		
				pH-metric a	Spectro-photometric b	Average of a & b	pH-metric a	Spectro-photometric b	Average of a & b
00	00	1.27	± 0.00	4.49±0.01	4.47±0.01	4.48	5.07±0.01	5.05±0.01	5.06
10	0.0255	1.34	+ 0.11	4.32±0.01	4.28±0.01	4.30	4.83±0.01	4.81±0.02	4.82
20	0.0558	1.43	+ 0.15	4.14±0.01	4.13±0.01	4.14	4.66±0.01	4.61±0.01	4.64
30	0.0921	1.56	+ 0.19	3.99±0.01	3.94±0.01	3.97	4.55±0.01	4.52±0.02	4.54
40	0.1363	1.74	+ 0.27	3.92±0.01	3.88±0.01	3.90	4.49±0.01	4.46±0.01	4.48
50	0.1914	1.99	+ 0.31	3.69±0.02	3.66±0.02	3.68	4.34±0.01	4.33±0.02	4.34
60	0.2620	2.37	+ 0.35	3.59±0.01	3.58±0.02	3.59	4.21±0.02	4.19±0.01	4.20
70	0.3559	2.92	+ 0.38	3.41±0.01	3.37±0.01	3.39	4.02±0.01	4.03±0.02	4.03
80	0.4864	3.77	+ 0.48	3.23±0.01	3.18±0.01	3.21	3.89±0.01	3.91±0.02	3.90
90	0.6806	5.26	+ 1.07	3.37±0.01	3.33±0.01	3.35	4.16±0.01	4.20±0.02	4.18
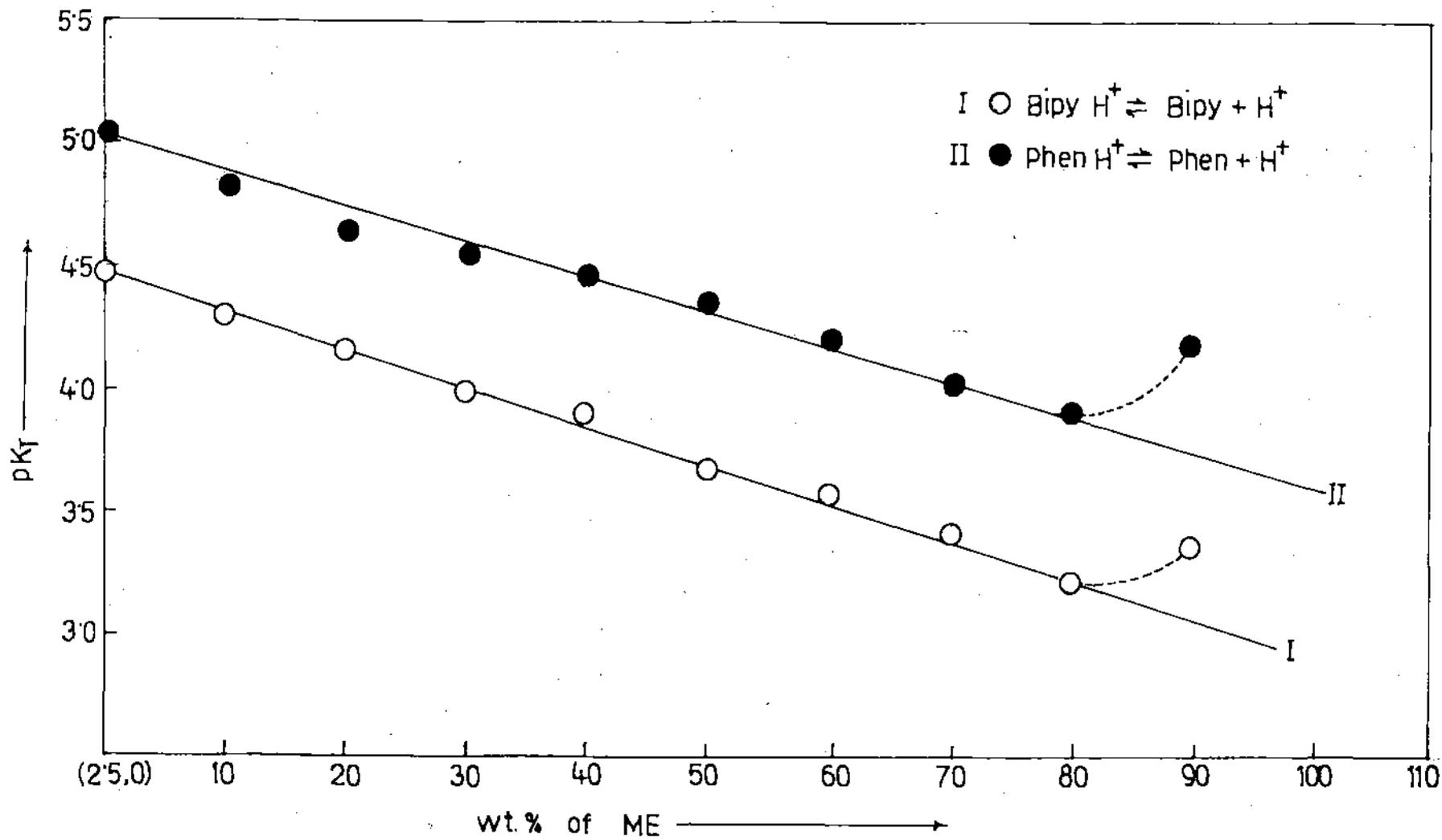
Fig - 1(a)
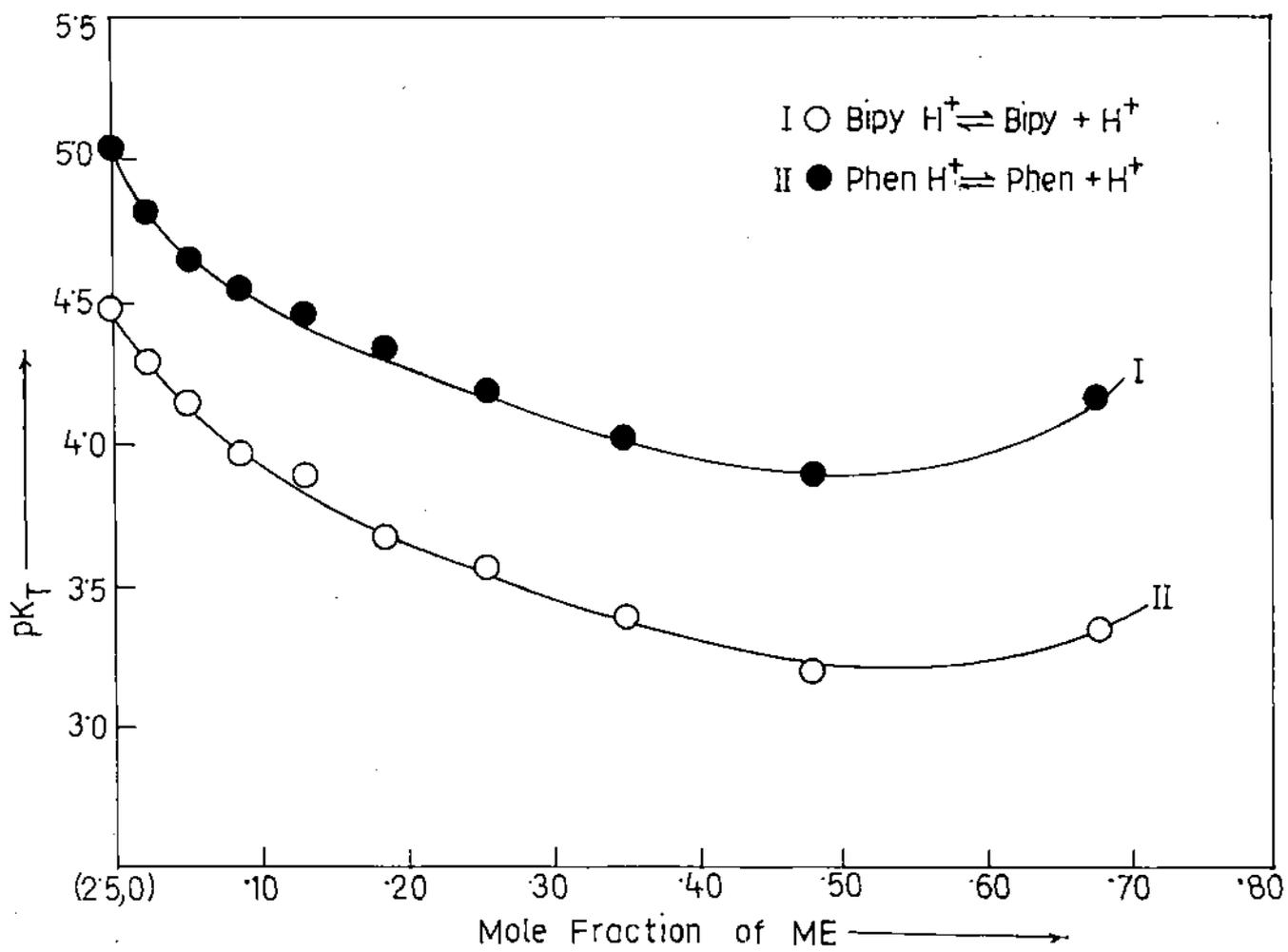
Fig. – 2 (a)

Table 2 : The pK values of 2,2'-Bipyridine and 1,10-Phenanthroline in DME - Water mixtures (Temp=298K)

Wt% of DME	Mole fraction of DME	Correction factor	$\frac{1}{\varepsilon} \times 10^2$	pK_T of Bipyridine			pK_T of Phenanthroline		
				pH-metric a	Spectro-photometric b	Average of a&b	pH-metric a	Spectro-photometric b	Average of a & b
10	0.0217	- 0.04	1.40	4.18±0.01	4.17±0.02	4.18	4.69±0.01	4.68±0.02	4.69
20	0.0475	- 0.03	1.56	3.92±0.02	3.90±0.01	3.91	4.54±0.01	4.53±0.01	4.54
30	0.0788	- 0.02	1.75	3.73±0.01	3.71±0.01	3.72	4.37±0.02	4.35±0.01	4.36
40	0.1175	- 0.01	2.01	3.50±0.02	3.47±0.01	3.48	4.19±0.01	4.16±0.02	4.18
50	0.1666	± 0.00	2.35	3.29±0.01	3.25±0.02	3.27	4.02±0.01	4.01±0.01	4.01
60	0.2308	+ 0.02	2.79	3.15±0.01	3.12±0.01	3.14	3.82±0.01	3.78±0.01	3.80
70	0.3182	+ 0.11	3.58	3.03±0.02	3.01±0.01	3.02	3.56±0.02	3.54±0.01	3.55
80	0.4445	+ 0.52	4.79	3.14±0.02	3.10±0.01	3.12	3.63±0.01	3.59±0.02	3.61
90	0.6428	+ 1.48	7.42	3.38±0.02	3.34±0.01	3.36	4.06±0.02	4.03±0.01	4.05

I ○ Bipy $H^+ \rightleftharpoons$ Bipy + H^+

II ● Phen $H^+ \rightleftharpoons$ Phen + H^+

wt.% of DME ⟶

Fig. −1 (b)

Fig – 2 (b).

Table - 3

Dissociation Constants of 2,2'-bipyridine at 20% by wt% of ME

(pH-metric)

Temp: 298K   Conc. $= 5 \times 10^{-3}$ mole dm^{-3}

Fraction of the ligand neutralised (10^{-3} mol. dm^{-3})	Meter Reading	pH-after correction	pK	Average pK
1.5	4.34	4.49	4.13	
2.0	4.16	4.31	4.14	
2.5	3.99	4.14	4.14	4.14 ± 0.01
3.0	3.84	3.99	4.16	
3.5	3.64	3.79	4.15	

(Spectrophotometrically)

Analytical wave length = 300 nm   cell length = 1 cm

Optical density of the molecular form (d_M) = 0.080

Optical density of the ionic form (d_I) = 0.716

Obs.o.d. (d)	$d_I - d$	$d - d_M$	$\log \dfrac{d-d_M}{d_I - d}$	Meter Reading	pH-after correction	pK
.274	.442	.194	−0.35	4.33	4.48	4.13
.351	.365	.271	−0.12	4.10	4.25	4.13
.400	.316	.320	+0.01	3.96	4.11	4.12
.449	.267	.369	+0.14	3.85	4.00	4.14
.478	.238	.398	+0.22	3.76	3.91	4.13
.502	.214	.422	+0.29	3.69	3.84	4.13

Average pK value from o.d.'s at 300nm
$= 4.13 \pm 0.01$
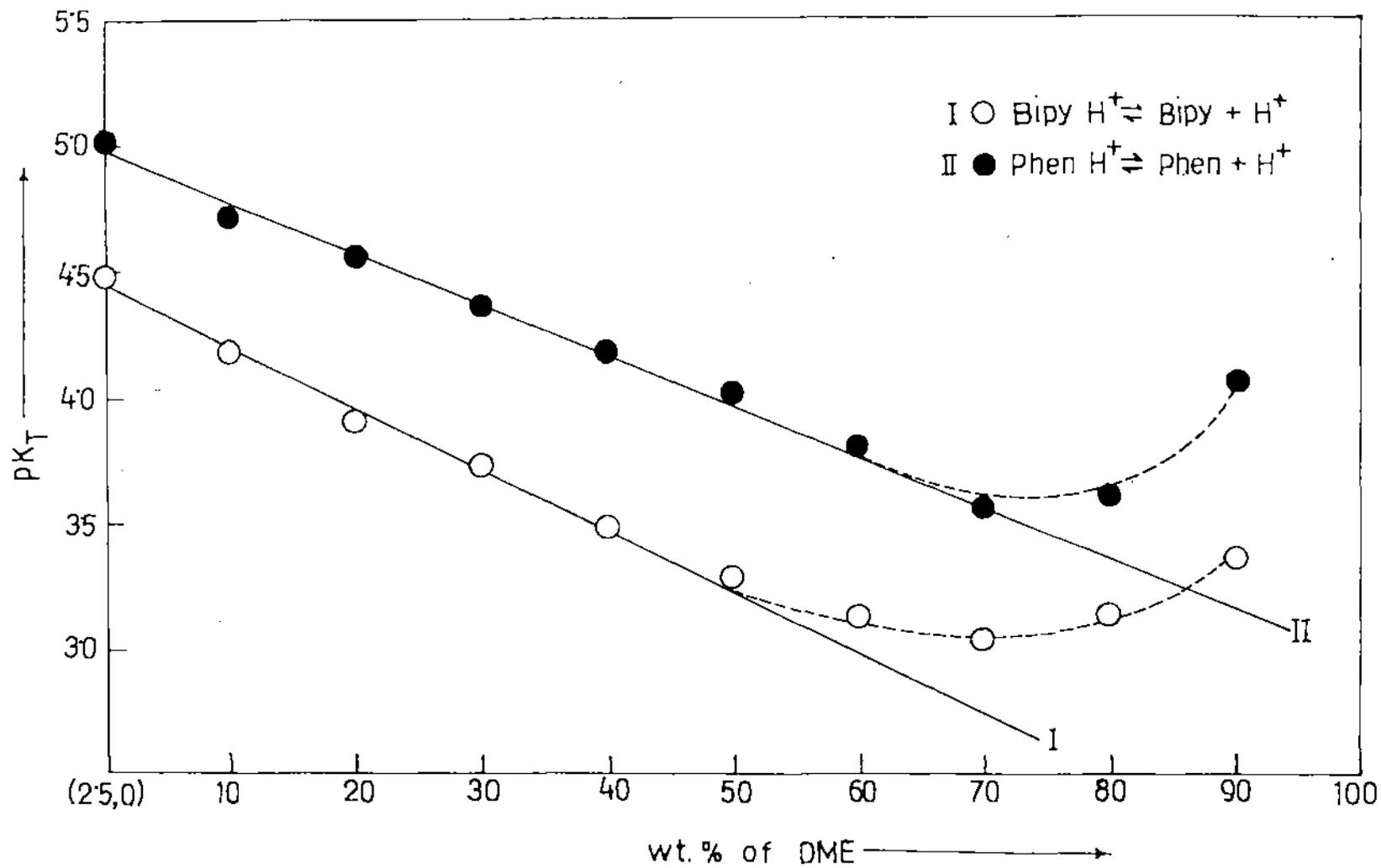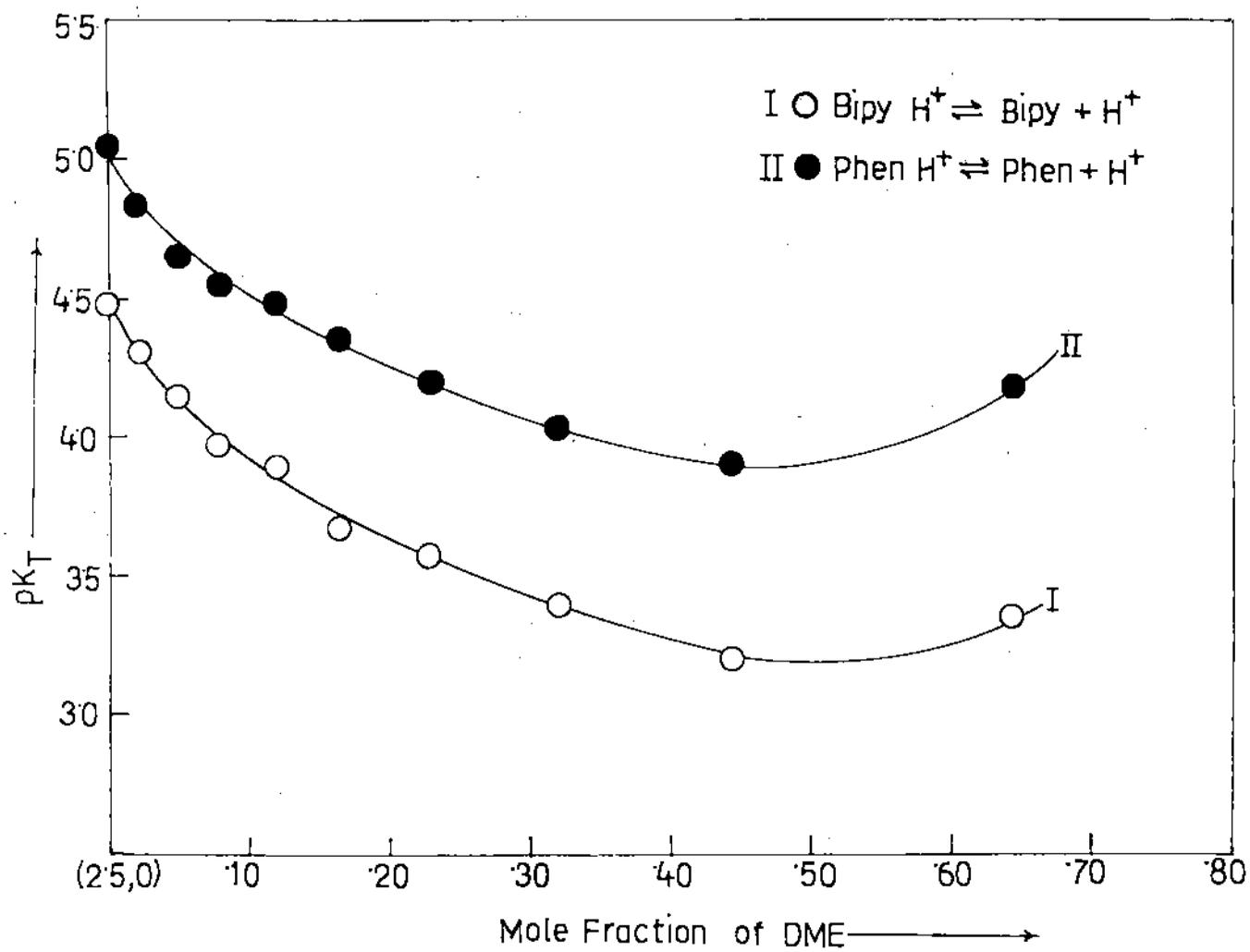
Table - 4

Dissociation Constants of 2,2'-bipyridine at 70% by wt% of ME

(pH-metric)

Temp: 298K   Conc. $= 5 \times 10^{-3}$ mole dm^{-3}

Fraction of the ligand neutralised (10^{-3} mole dm^{-3})	Meter-Reading	pH-after correction	pK	Average pK
1.5	3.37	3.75	3.41	
2.0	3.19	3.57	3.40	
2.5	3.05	3.43	3.43	3.41 ±0.01
3.0	2.85	3.23	3.40	
3.5	2.69	3.07	3.43	

(Spectrophotometric)

Cell length = 1 cm

Analytical wave length = 300 nm

Optical density of the molecular form (d_M) = 0.134

Optical density of the ionic form (d_I) = 0.652

Obs.o.d. (d)	d_I-d	$d-d_M$	$\log \frac{d-d_M}{d_I-d}$	Meter Reading	pH-after correction	pK
0.175	.477	.041	-1.07	4.05	4.43	3.36
0.185	.467	.051	-0.96	3.95	4.33	3.37
0.199	.453	.065	-0.84	3.81	4.19	3.35
0.219	.433	.085	-0.70	3.69	4.07	3.37
0.238	.414	.104	-0.59	3.59	3.97	3.38
0.246	.406	.112	-0.55	3.54	3.92	3.37

Average pK from o.d.'s at 300 nm = 3.37 ± 0.01

Table - 5

Dissociation Constants of 1,10-Phenanthroline at 50% by Wt% of ME
(pH - metrically)

Temp: 298K   Conc. 5×10^{-3} mol.dm^{-3}

Fraction of the ligand neutralised (10^{-3} mol.dm^{-3})	Meter-reading	pH after correction	pK	Average pK
1.5	4.37	4.68	4.32	
2.0	4.19	4.50	4.33	
2.5	4.02	4.33	4.33	4.34 ±0.01
3.0	3.86	4.17	4.34	
3.5	3.69	4.00	4.36	

(Spectrophotometrically)

Cell length = 1 cm

Analytical wave length = 275 nm
Optical density of the molecular form (d_M) = 0.372
Optical density of the ionic form (d_I) = 0.681

Obs.o.d. (d)	$d_I - d$	$d - d_M$	$\log \dfrac{d - d_M}{d_I - d}$	Meter-reading	pH after correction	pK
0.457	.224	.085	−0.42	4.42	4.73	4.31
0.507	.174	.135	−0.11	4.10	4.41	4.30
0.542	.139	.170	0.08	3.96	4.27	4.35
0.562	.119	.190	0.20	3.81	4.12	4.32
0.578	.103	.206	0.30	3.72	4.03	4.33
0.593	.088	.221	0.39	3.64	3.95	4.34

Average pK value from o.d.'s at 275 nm

= 4.33 ± 0.02.

Table - 6

Dissociation Constants of 1,10-Phenanthroline at 80% by wt% of ME
(pH-metrically)

Tem: 298K   Conc. 5×10^{-3} mol. dm^{-3}

Fraction of the ligand neutralised (10^{-3}mol.dm^{-3})	Meter-reading	pH after correction	pK	Average pK
1.5	3.75	4.23	3.87	
2.0	3.57	4.05	3.88	
2.5	3.41	3.89	3.89	3.89 ± 0.02
3.0	3.26	3.74	3.91	
3.5	3.08	3.56	3.92	

(Spectrophotometrically)   Cell length = 1 cm

Analytical wave length = 275 nm
Optical density of the molecular form (d_M) = 0.355
Optical density of the ionic form (d_I) = 0.618

Obs.o-d (d)	$d_I - d$	$d - d_M$	$\log \dfrac{d - d_M}{d_I - d}$	Meter-reading	pH after correction	pK
0.395	.223	.040	-0.75	4.18	4.66	3.91
0.431	.187	.076	-0.39	3.79	4.27	3.88
0.440	.178	.085	-0.32	3.73	4.21	3.89
0.471	.147	.116	-0.10	3.54	4.02	3.92
0.488	.130	.133	0.009	3.45	3.93	3.93
0.507	.111	.152	0.13	3.32	3.80	3.93

Average pK value from o.d.'s at 275 nm

$= 3.91 \pm 0.02$

Table -7

Dissociation Constants of 2,2'-bipyridine at 30% by wt% of DME

(pH-metric)

Temp: 298K   Conc. 5×10^{-3} (M)

Fraction of the ligand neutralised (10^{-3} mole dm^{-3})	Meter Reading	pH after correction	pK	Average pK
1.5	4.11	4.09	3.73	
2.0	3.91	3.89	3.72	
2.5	3.76	3.74	3.74	3.73 ± 0.01
3.0	3.60	3.58	3.75	
3.5	3.39	3.37	3.73	

(Spectrophotometrically)

Cell length = 1 cm

Analytical wave length = 300 nm
Optical density of the molecular form (d_M) = 0.112
Optical density of the ionic form (d_I) = 0.701

Obs.o.d. (d)	$d_I - d$	$d - d_M$	$\log \dfrac{d - d_M}{d_I - d}$	Meter reading	pH after correction	pK
.228	.473	.116	-0.61	4.34	4.32	3.71
.243	.458	.131	-0.54	4.27	4.25	3.71
.270	.431	.158	-0.43	4.15	4.13	3.70
.293	.408	.181	-0.35	4.08	4.06	3.71
.330	.371	.218	-0.23	3.96	3.94	3.71
.397	.304	.285	-0.02	3.77	3.75	3.73

Average pK = 3.71 ± 0.01

Table -8

Dissociation Constants of 2,2'-bipyridine at 60% by wt% of DME

(pH-metric)

Temp: 298K   Conc. 5 x 10^{-3} (M)

Fraction of the ligand neutralised (10^{-3} mole dm^{-3})	Meter Reading	pH-after correction	pK	Average pK
1.5	3.48	3.50	3.14	
2.0	3.30	3.32	3.15	
2.5	3.12	3.14	3.14	3.15 ± 0.01
3.0	2.96	2.98	3.15	
3.5	2.78	2.80	3.16	

(Spectrophotometrically)

Analytical wave length = 300 nm   Cell length = 1 cm

Optical density of the molecular form $(d_M) = 0.139$

Optical density of the ionic form $(d_I) = 0.691$

Obs.o.d. (d)	d_I-d	$d-d_M$	$\log \dfrac{d-d_M}{d_I-d}$	Meter Reading	pH after correction	pK
.188	.503	.049	-1.01	4.11	4.13	3.12
.203	.488	.064	-0.88	3.99	4.01	3.13
.224	.467	.085	-0.74	3.84	3.86	3.12
.234	.457	.095	-0.68	3.78	3.80	3.12
.245	.446	.106	-0.62	3.72	3.74	3.12
.254	.437	.115	-0.58	3.68	3.70	3.12

Average pK = 3.12 ± 0.01

Table - 9

Dissociation Constants of 1,10-Phenanthroline at 40% by wt% of DME.

(pH-metrically)

Temp = 298K   Conc. 5×10^{-3} (M)

Fraction of the ligand neutralised (10^{-3} mole dm^{-3})	Meter Reading	pH after correction	pK	Average pK
1.5	4.65	4.64	4.28	
2.0	4.47	4.46	4.29	
2.5	4.30	4.29	4.29	4.29 ± 0.01
3.0	4.14	4.13	4.30	
3.5	3.94	3.93	4.29	

(Spectrophotometrically)

Cell length = 1 cm

Analytical wave length = 275 nm
Optical density of the molecular form (d_M) = 0.325
Optical density of the ionic form (d_I) = 0.426

Obs.o.d. (d)	d_I-d	$d-d_M$	$\log \frac{d-d_M}{d_I-d}$	Meter reading	pH after correction	pK
.374	.052	.049	-0.03	4.33	4.32	4.29
.382	.044	.057	+0.11	4.18	4.17	4.28
.391	.035	.066	0.28	3.99	3.98	4.26
.395	.031	.070	0.35	3.91	3.90	4.25
.399	.027	.074	0.44	3.81	3.80	4.24
.408	.018	.093	0.66	3.61	3.60	4.26

Average pK = 4.26 ± 0.02

Table - 10

Dissociation Constants of 1,10-Phenanthroline at 90% by wt% of DME

(pH-metrically)

Temp = 298K   Conc. 5×10^{-3} mole dm^{-3}

Fraction of the ligand neutralised (10^{-3} mole dm^{-3})	Meter Reading	pH after correction	pK	Average pK
1.5	2.92	4.40	4.04	
2.0	2.75	4.23	4.06	
2.5	2.59	4.07	4.07	4.06 ± 0.02
3.0	2.41	3.89	4.06	
3.5	2.25	3.73	4.09	

(Spectrophotometrically)

Cell length : 1 cm

Analytical wave length = 275 nms

Optical density of the molecular form (d_M) = 0.227
Optical density of the ionic form (d_I) = 0.393

Obs. o.d (d)	d_I-d	$d-d_M$	log $\dfrac{d-d_M}{d_I-d}$	Meter reading	pH after correction	pK
.260	.133	.033	-0.61	3.17	4.65	4.04
.279	.114	.052	-0.34	2.88	4.36	4.02
.287	.106	.060	-0.25	2.80	4.28	4.03
.299	.094	.072	-0.16	2.71	4.19	4.03
.308	.085	.081	-0.02	2.58	4.06	4.04
.322	.071	.095	+0.13	2.40	3.88	4.01

Average pK = 4.03 ± 0.01
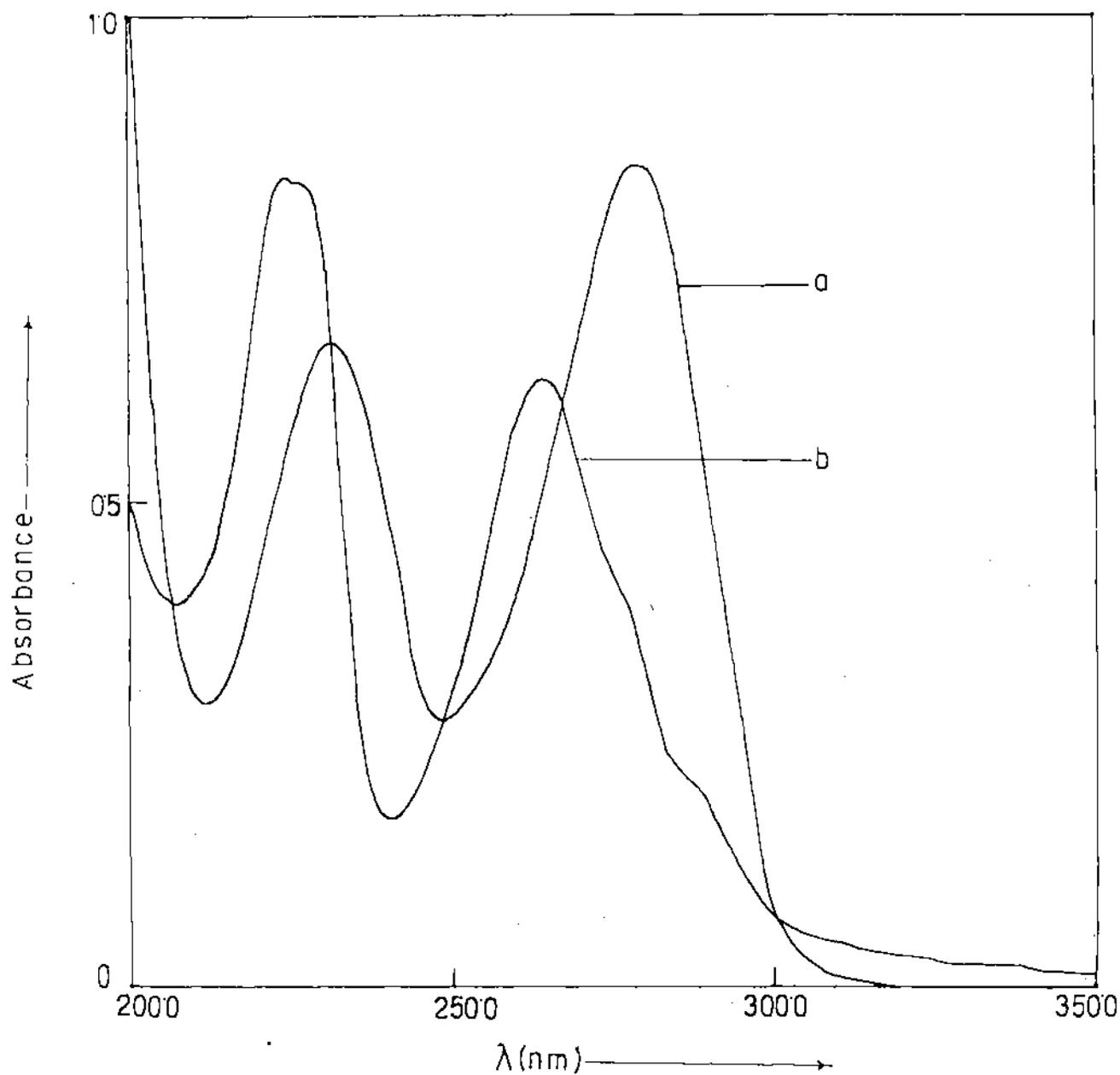
Fig. 3(i): Ultraviolet spectra of (a) Bipy [6.1464×10^{-5} mol. dm^{-3}] and (b) Phen [2.2094×10^{-5} mol. dm^{-3}] in H_2O.
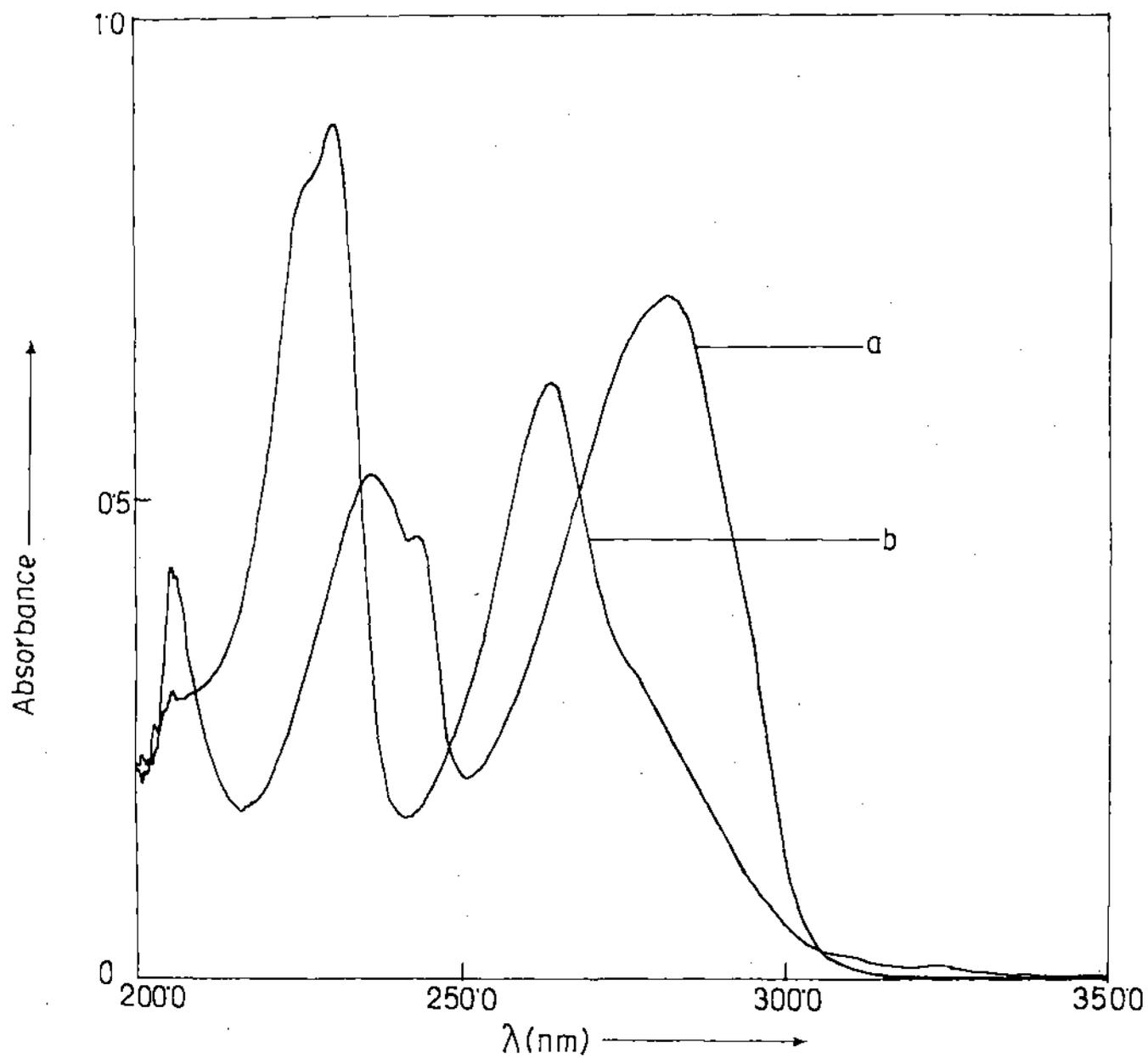
Fig. 3(ii) Ultraviolet spectra of (a) Bipy [4.6923×10^{-5} mol. dm^{-3}] and (b) Phen [1.6484×10^{-5} mol. dm^{-3}] . in ME.
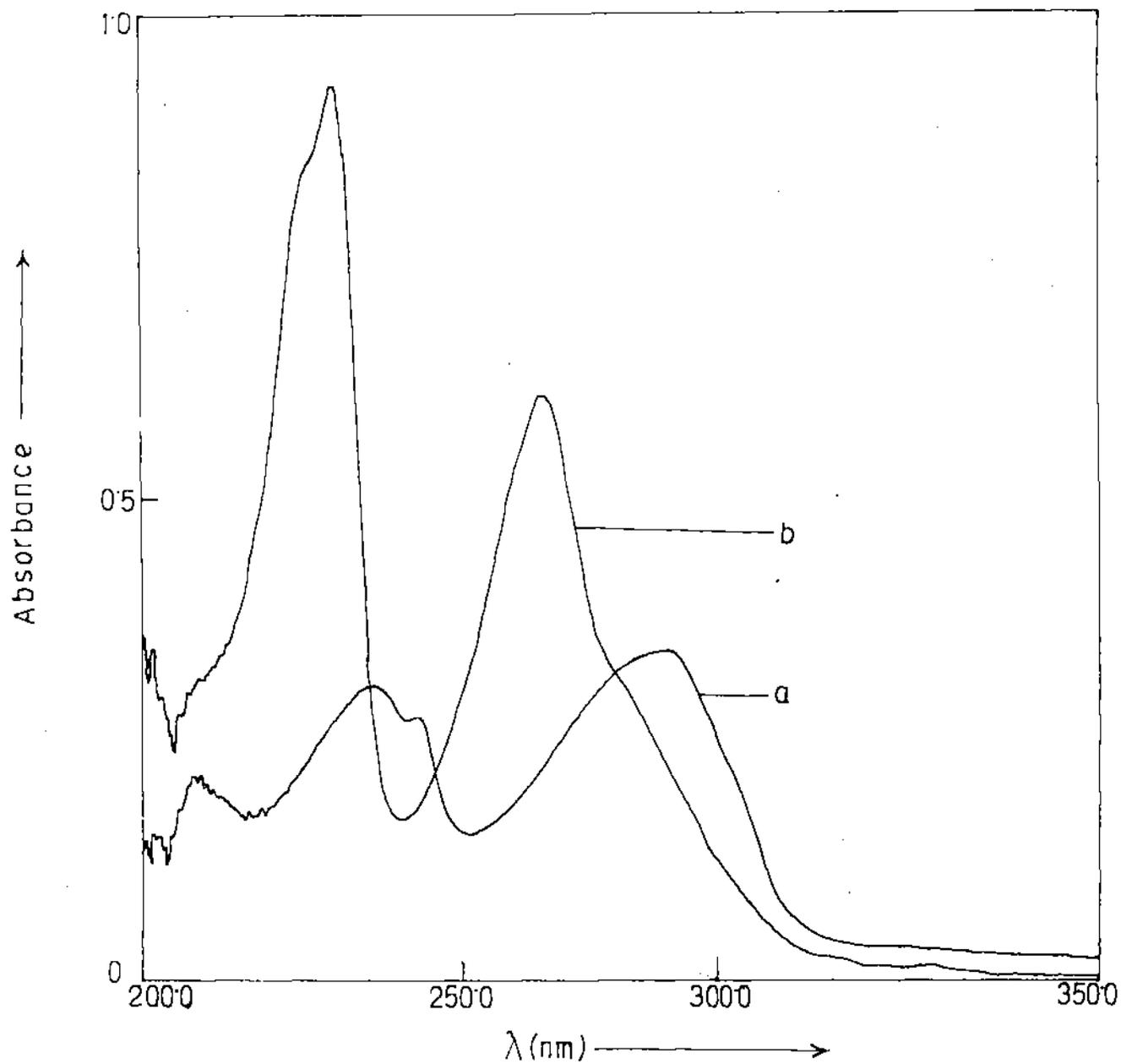
Fig.3(iii) – Ultraviolet spectra of (a) Bipy [3.0747×10^{-5} mol. dm.$^{-3}$] and (b) Phen [1.5335×10^{-5} mol. dm.$^{-3}$] in DME.

Table 11 : Values of $\Delta G^o_{t(el)}$ (Born), $\Delta G^o_{t(el)} \underline{/} B+i-d+i-i-d \underline{/}$, $\Delta G^o_{t(el)}$ (one layer model), $\Delta G^o_{t(el)}$ from H_2O to ME + H_2O and DME + H_2O mixtures at 298K.

Wt% of ME	$\Delta G^o_{t(el)}$ (Born)	$\Delta G^o_{t(el)}$ (B+i-d+i-i-d)	$\Delta G^o_{t(el)}$ (total)	$\Delta G^o_{t(el)}$ (one layer model)	Wt% of DME	$\Delta G^o_{t(el)}$ (Born)	$\Delta G^o_{t(el)}$ (B+i-d+i-i-d)	$\Delta G^o_{t(Total)}$	$\Delta G^o_{t(one layer)}$
10	0.13	(0.19+0.02)	0.34	7.08	10	0.24	(0.24+0.01)	0.49	7.15
20	0.29	(0.40+0.05)	0.74	7.71	20	0.54	(0.52+0.05)	1.11	7.97
30	0.54	(0.65+0.08)	1.27	8.58	30	0.91	(0.90+0.08)	1.89	8.91
40	0.88	(1.0+0.12)	2.00	9.48	40	1.38	(1.10+0.12)	2.60	10.00
50	1.35	(1.4+0.17)	2.92	10.63	50	2.02	(1.80+0.17)	3.99	11.33
60	2.07	(1.9+0.23)	4.20	12.00	60	2.85	(2.50+0.23)	5.58	12.83
70	3.09	(2.53+0.32)	5.94	13.76	70	4.33	(3.50+0.32)	8.15	14.91
80	4.69	(3.5+0.43)	8.62	16.02	80	6.60	(4.90+0.45)	11.95	17.59
90	7.48	(4.8+0.61)	12.89	19.29	90	11.53	(7.00+0.65)	19.18	22.11

Table 12 : Free energies of transfer of $[H^+]$ and related ions (in k Joules mole^{-1}) in ME + H_2O mixture at 298K

Wt% of ME	$-\Delta G^o_t(1)$		$-\Delta G^o_{t(H^+)_C}$ based on*			Converion factor (-Ve) to be added to get $\Delta G^o_{t(H^+)_N}$ (mole fraction)	Solubility mole dm^{-3}		$-\Delta G^o_t$ (from eq. 11)	
	bipy	phen	bipy	phen	Average		bipy	phen	bipy⊃H$^+$	Phen⊃H$^+$
10	1.03	1.37	0.90 (0.69)	1.24 (1.03)	1.07 (0.86)	0.19	0.0812	0.0431	2.15 (1.94)	2.56 (2.35)
20	1.94	2.40	1.65 (1.20)	2.11 (1.66)	1.88 (1.43)	0.40				
30	2.91	2.97	2.37 (1.64)	2.43 (1.70)	2.40 (1.67)	0.60	0.2163	0.1478	4.02 (3.29)	5.34 (4.61)
40	3.31	3.31	2.43 (1.31)	2.43 (1.31)	2.43 (1.31)	0.88				
50	4.56	4.11	3.21 (1.64)	2.76 (1.19)	2.99 (1.42)	1.17	0.7326	0.2559	5.99 (4.42)	6.13 (4.56)
60	5.08	4.91	3.01 (0.88)	2.84 (0.71)	2.93 (0.80)	1.50				
70	6.22	5.88	3.13 (0.28)	2.79 (-0.06)	2.96 (0.11)	2.00	1.0998	0.8124	5.30 (2.45)	7.21 (4.36)
80	7.25	6.62	2.56 (-1.37)	1.93 (-2.00)	2.25 (-1.69)	2.34				
90	6.45	5.02	-1.03 (-6.44)	-2.46 (-7.87)	-1.75 (-7.16)	2.94				

$[$* Values in parenthesis are based on $\Delta G^o_{t(el)}$ (Total) $]$

Table 13 : Free energies of transfer of $\boxed{H^+}$ and related ions (in k Joule mole^{-1}) in DME + H_2O mixtures at 298K

Wt% of DME	$-\Delta G_t^O(1)$		$-\Delta G_t^O(H^+)_C$ based on [*]			Conversion factor(-Ve) to be added to get $\Delta G_t^O(H^+)_N$	Solubility (mole dm^{-3})		$-\Delta G_t^O$ (from eq. 11)	
	bipy	phen	bipy	phen	Average		bipy	phen	bipyH$^+$	PhenH$^+$
10	1.71	2.11	1.47 (1.22)	1.87 (1.62)	1.67 (1.42)	0.21	0.1077	0.0629	2.77 (2.52)	3.36 (3.11)
20	3.25	2.97	2.71 (2.14)	2.43 (1.86)	2.57 (2.00)	0.45				
30	4.34	3.99	3.43 (2.45)	3.08 (2.10)	3.26 (2.28)	0.71	0.3499	0.2206	4.65 (3.67)	6.17 (5.19)
40	5.71	5.02	4.33 (3.11)	3.64 (2.42)	3.99 (2.77)	1.01				
50	6.90	5.99	4.88 (2.91)	3.97 (2.00)	4.43 (2.46)	1.34	0.9256	0.3255	5.67 (3.48)	6.31 (4.12)
60	7.65	7.19	4.80 (2.07)	4.34 (1.61)	4.57 (1.84)	1.73				
70	8.33	8.62	4.00 (0.18)	4.29 (0.47)	4.15 (0.33)	2.20	1.4539	0.9028	5.08 (1.26)	5.93 (2.11)
80	7.76	8.27	1.16 (-4.19)	1.67 (-3.68)	1.42 (-3.94)	2.76				
90	6.39	5.76	-5.14 (-12.79)	-5.77 (-13.42)	-5.46 (-13.11)	3.44				

$\boxed{\text{* Values in parenthesis are based on } \Delta G_t^O{}_{(el)} \text{ (total)}}$

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