CHAPTER-I

Section I

In recent years there has been increasing interest in the study of the behaviour of electrolytes in mixed solvents. The effect of solvent structure and solute-solvent interactions on equilibrium constants and rate constants of chemical reactions in mixed solvents is not well-understood. Addition of organic solvent in water brings about a radical change in the properties of the medium. Theories[1] of the structure of water, an extensively used and studied solvent, are inadequate and this is further complicated by the addition of organic components. It is now agreed that the thermodynamics of solute-solvent interactions will help in throwing more light on the nature of ionic solutes. Attempts are being made to identify the factors determining specific solvation of ions. Inadequate models for the structure of solvents and an incomplete understanding of the forces in the immediate vicinity of the surface of the ions make the theoretical treatment[2,3] of the problem of solvation difficult.

Acid-base equilibria are particularly suited for such studies. The effect of solute-solvent interactions on chemical equilibria have been investigated both by alteration of the solvent composition and by variation of solute-structure and charge type.

The determination of dissociation constants of the ligands in different mixed solvents and non-aqueous solvents provides an important step in this direction. Such studies in mixed solvents may throw light on the structure of the liquid molecules, the effect of the dielectric constant and the acid-base properties of the organic solvents on the dissociation constants of the ligands and ion-solvent, solvent-solvent interactions etc.

The addition of an organic solvent to water makes the situation much more engrossing and anomalous than water. The mixed solvents show a wide range of dielectric constants. Extensive studies on the physical properties of different solvent systems have been made. A lamentable gap still exists. Several classifications of organic solvent systems based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding[4], have been proposed as a result the properties of different mixed solvent systems would show a wide divergence of properties which would naturally be reflected on the thermodynamic properties of ligands and their complexes. The determination of the thermodynamic properties of the ligands and their complexes in different solvent systems are very limited, though a considerable amount of work has been done in methanol-water, ethanol-water mixtures. This inspired us to undertake the studies of acid-base equilibria in mixed solvents. The classical researches of Harned and co-workers[5- 10], Bates, Robinsons and co-workers[11-23], Ligny and co-workers[24-33], Shedlovsky[34], Grunwold[35-37], Feakins and others[38-48], Lahiri and others[49-72], Strehlow[73], Das, Kundu and co-workers[74-85], and others[86-127] led to further investigations in this direction.

A brief survey of the investigations in mixed solvent systems, and the problems associated with such studies is presented to highlight the importance of such studies.

Dissociation constants of ligands in mixed solvents :-

Stability constants of chelate compounds and the dissociation constants of chelating agents have often been measured in mixed solvents because of the insolubility of one or more of the reactants in water. However, since these constants vary with the solvent compositions, the comparison and correlation of these constants are very difficult owing to the wide range of experimental conditions. In addition, the thermodynamic quantities for these reactions calculated from these data are limited to specific solvent systems. Consequently, studies have been made to determine the effect of the solvent on the dissociation constants.

The quantitative approach correlating the dissociation constants of a series of acid with that for a reference acid and the dielectric constant was made by Wynne - Jones.[128] If we consider the equilibrium constant K of the reaction between two acid - base systems, viz.,

$$HA + A_o^- \rightleftharpoons A^- + HA_o \qquad \ldots \quad (1)$$

we find

$$K = \frac{a_{A^-} \times a_{HA_o}}{a_{A_o^-} \times a_{HA}} = \frac{K_a}{K_o} \qquad \ldots \quad (2)$$

(K_a and K_o are the dissociation constants of the acids HA and the corresponding reference acid HA_o in the same solvent.)

The standard free energy change of the process is given by

$$\Delta G^{o} = -RT \ln K = \Delta G^{o}el + \Delta G^{o} non\text{-}el \qquad \ldots \quad (3)$$

or,
$$- \log K = \frac{\Delta G \ non\text{-}el}{2.303\ RT} + \frac{a}{\varepsilon} \qquad \ldots \quad (4)$$

where
$$a = \frac{Ne^{2}}{2 \times 2.303\ RT} \left(\frac{1}{r_{A^-}} - \frac{1}{r_{A^-_o}} \right)$$

(according to Born[129] equation).

[assuming the effective radii of the ions to remain approximately constant in a series of solvents].

The plots of - log K against $\frac{1}{\varepsilon}$ should thus be a straight line which have been found to be true in several cases when ε is $\geq$ 30. The intercept for $\frac{1}{\varepsilon} = 0$, i.e., for infinite dielectric constant, should give a measure of the dissociation constant free from electrostatic effetcts. The slope of the line, however, varies with the nature of the acid, so that an acid which is stronger than another in one solvent may be weaker in a second solvent[130-133]. The comparison of the dissociation constants of a series of acids in a given solvent may consequently be misleading, since a different order of strengths would be contained in another solvent. It has suggested, therefore, that when comparing the dissociation constants of acids, the values employed should be extrapolated to infinite dielectric constant; in this way the electrostatic effect, at least, of the solvent should be eliminated.

However, Elliot and Kilpatrik[134] and Harned[135] find that the relationship ($-\log K$ vs $\frac{1}{\varepsilon}$) fails in dioxane-water.

Other theoretical approaches using the dielectric constant as a parameter in describing any solvent system may be found in the Bjerrum - Fuoss[136,137] ion-pair model and Denison and Ramsey's[138] model. Though the variation of log K with $\frac{1}{\varepsilon}$ has theoretical bearing, some authors[139-145] have favoured of the plot of log K against mole - fraction of the organic solvents because the constants exhibit linearity with the latter over a wide range, even though it has no theoretical basis.

The thermodynamic formulation for the dissociation constant of the acid-base equilibrium $A \rightleftharpoons B + H^+$ on the molal scale is given by

$$K = \frac{m_{H^+} \times m_B}{m_A} \times \frac{\gamma_{H^+} \times \gamma_B}{\gamma_A} \qquad \ldots (5)$$

The numerical value is fixed by the choice of a standard state in which the activity co-efficients are assigned values of unity. In aqueous solutions, the customary standard state is so chosen that γ_i approaches unity as m approaches zero.

When the compositions of the solvent media and the solute concentrations change (and ionic strength), it is convenient to seperate each activity co-efficient γ_i into factors $\gamma_i = {}_m\gamma_i \cdot \times {}_s\gamma_i$[14,23,146]. γ_i is measured relative to the standard state in pure water and becomes unity only in infinitely dilute aqueous solution. On the contrary, the activity co-efficient ${}_s\gamma_i$ in equation above becomes unity when $m = o$ in the solvent s, where ${}_m\gamma_i$ has a value different from unity whenever the solvent differs from pure water.

The 'salt effect' ${}_s\gamma_i$ varies with the solute concentration. To determine the thermodynamic dissociation constant in mixed solvents, ${}_s\gamma_i$ is to be determined. Simple Debye-Hüchel equation with appropriate allowance for the effect of altering the dielectric constant of the medium s, can be used to estimate ${}_s\gamma_i$ when ionic species are involved. The thermodynamic dissociation constant can also be determined in very dilute solution when ${}_s\gamma_i \rightarrow o$ and this is the best method for the determination of the thermodynamic dissociation constant as it involves no error in estimating ${}_s\gamma_i$.

The 'medium effect' ${}_m\gamma_i$ is a function of the free energy of the species 'i' in the two standard states,

$$\Delta G_i = {}_s\mathcal{G}_i - {}_w\mathcal{G}_i = RT \ln {}_m\gamma_i \qquad \ldots \quad (6)$$

In spite of the limitations of Born's equation due to the complexity of medium effect, considering only the electrostatic contribution to the free energy using Born's equation, we have

$$\ln {}_m\gamma_i = \frac{N\, Z_i^2\, e^2}{2\,RTr}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right) \qquad \ldots \quad (7)$$

The mass law equation for equilibrium yields

$${}_sK = {}_wK \times \frac{m\gamma_A}{m\gamma_A \,.\, m\gamma_B} \;,$$

where ${}_wK$ and ${}_sK$ are the dissociation constants referred to the standard states in water and in solvent respectively. Combining equations above, we obtain

$$p({}_sK) - p({}_wK) = \frac{Ne^2}{4.6052\ RT}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\left(\frac{z_B^2}{r_B} - \frac{z_A^2}{r_A} + \frac{1}{r_{H^+}}\right) \ldots \quad (8)$$

(Charges on r_A etc omitted).

with the dissociation equilibrium of the charge-type A^oB^- (for example, A^o = uncharged acetic acid, B^- = acetate anion, $z_A = 0$) equation predicts that p $({}_sK)$ will be greater than p $({}_wK)$ if the dielectric constant ε_s is lower than that of water (as it is in methanol - water and ethanol - water solvents and in pure methanol and ethanol). Actually the pK for acids of this charge type has been found to vary from 3 to 5 units higher in methanol and ethanol than in water[23,34,147]. The observations are also true in other alcohols and dioxane.

If the equilibrium is of the charge type A^+B^o (for example, A^+ = anilinium cation, B^o = uncharged aniline, $z_B = 0$) and γ_{H^+} is about equal to γ_A, however, the electrostatic treatment alone would lead one to expect pK to be almost unaffected by changes in the dielectric constant of the solvent. It is unlikely γ_A will often be less than γ_{H^+} and therefore, an increase in pK would be more easily explained on electrostatic grounds than a decrease would be.

Selective Solvation and Ion-Solvent Interaction:

The question of specific solvation is of great importance in solution chemistry[106,148-159]. The solvation and preferential or selective solvation of ions in different solvents were used in interpreting data on conductivity, transference, solubility, u.v. visible spectra and other results[106,149-159].

The importance of anion solvation in determining the relative strengths have been stressed by Grunwald and Price[160-162] and Parker and co-workers[163].

The relative strengths of picric, acetic and trichloroacetic acids in different solvent environments have been ascribed to strong London-dispersion interactions of the solute molecules with the surrounding medium.

The results of the investigations of clare et.al.[163]

(on the relative strengths of a series of acids HA and HB in dimethylformamide and methanol) confirm the belief that acid-base equilibria and medium effects are very sensitive to a change from a dipolar aprotic solvent to a polar protic solvent presumably because of hydrogen bonding interactions between anions and the molecules of the protic solvent.

For each of the species participating in reaction, the free-energy change on the transfer from dimethylformamide to methanol is given by (according to Parker and co-workers)

$$\Delta G_t^o = RT\ (\ln 10)\ \log\ {}_m\gamma_i = RT\ (\ln 10)\ \log\ \gamma_i^H\ \gamma_i^*$$

The co-efficient γ_i^H embodies the changes in chemical potential of i due to hydrogen-bonding by methanol on transfer from dimethylformamide, Whereas other changes in the transfer energy are included in γ_i^*.

The ratio of the rate constant for the reaction

$$A^- + CH_3I \rightleftharpoons [ACH_3I]^- \rightarrow ACH_3 + I^-$$

in methanol to that in dimethylformamide has been taken to be a measure of $\gamma_{A^-}^H$. The excellent correlation between the hydrogen-bonding coefficient and to changes of the equilibrium constant of reaction on transfer from dimethylformamide to methanol emphasizes the importance of solvent anion interaction.

In view of the solvation properties, the free-energies of transfer in different solvents can be written as

$$\Delta G_t^o = \Delta G_{t(el)}^o + \Delta G_{t(solv)}^o$$

$\Delta G_{t(solv)}^o$ includes the contribution of solvation and other specific ion-solvent interactions[164].

Solvation and free-energy of transfer of single ions :

The applications and implications of the studies of reactions in non-aqueous and mixed solvents[165] and ion-solvent interactions have been described in details[1-4,23,45,73,99,166-171]. But the most important but elusive aspect of the solution chemistry in the determination of 'single ion' thermodynamics or more precisely the 'medium effects' of ions in mixed or non-aqueous solvents.

The experimental methods, however, yield the transfer thermodynamic changes of neutral combinations but offer no means of separating them into single-ion characteristics. According to Strehlow[73] "single ion thermodynamics is a legitimate branch of physical chemistry. This division of thermodynamic functions of electrolytes into single ion values may reveal correlation between measurable but from a thermodynamic point of view unrelated quantities".

Various theoretical and semiemperical[172-177] extra thermodynamic attempts have been made to obtain single ion thermodynamics with moderate success. However, the free-energy of transfer or 'medium effect' of ion in different solvents is yet to be determined in an unambiguous way. This aspect is a matter of continuous review[73,99,166,178-181], the most recent being the extensive review made by Lahiri and Aditya[182].

The free-energy changes associated with the transfer of a chemical entity (HX) from solvent (1, say water) to solvent (2, say S) is known as "total medium effect"[183] (ΔG_t^o) which is splitted into primary medium effect or medium effect and secondary medium effect or salt effect as exemplified from the consideration of the cell of the type

$$(pt)\ H_2 \left| \ HX(m)\ \text{solvent} \ \right| \ AgX - Ag$$

The measurement of e.m.f. of cells of the type in two different solvents namely water(W) and solvent(S) gives the total medium effect of any electroneutral combination HX

$$\Delta G_t^o = \Delta G_t^o + 2RT \ \ln \ {}^s\gamma_\pm / {}^w\gamma_\pm$$

$$= \Delta G_t^o + 2RT \ \ln {}^m\gamma_\pm$$

$\Delta G_t^o = - ZF ({}^SE^o - {}^WE^o)$ is the primary medium effect and measures ion-solvent interactions whereas the logarithmic term is known as secondary medium effect denoting ion-ion interactions and solvation.

The 'medium effect' log ${}_m\gamma_i$ of an ion is the reversible work of transfer of 1 mole of ion i from the standard state in solvent 1 (water) to the standard state in solvent 2(s) by the expression

$$\log {}_m\gamma_i = \frac{{}^s\mu^o_i - {}^w\mu^o_i}{RT} \qquad \ldots \quad (11)$$

obviously, the primary medium effect is independent of molality but the exact value of 'medium effect' could only be determined in absence of appreciable concentrations of electrolytes which changes not only the structure of the solvent molecules but also the solvent concentration due to solvation of ions. The secondary medium effect (salt effect) is a function of solute-concentration and can be determined with the help of theoretical equations like Debye-Huckel or Davies equations with appropriate values of A and B arising from the changed values of dielectric constants of the solvents. The equations fail at higher concentrations. Thus, it is desirable to work in dilute solutions so that ${}^s\gamma_{\pm} \longrightarrow 0$ and the measurements account for the 'Primary medium effect' only.

Real free-energy of solvation

The 'medium effect' of an ion in actually related to the real free-energy of solvation[170].

The real free-energy of solvation α_i [184-187] is defined as the change in ion-energy upon transfer from the gas phase into the solution. It is expressed by the relationship

$$\alpha_i = \mu_i + z_i \; F = \mu_i + RT \ln a_i + z_i F\chi$$

$$= \alpha_i^{\circ} + RT \ln a_i$$

where α_i is the standard real free-energy of solvation of ion.

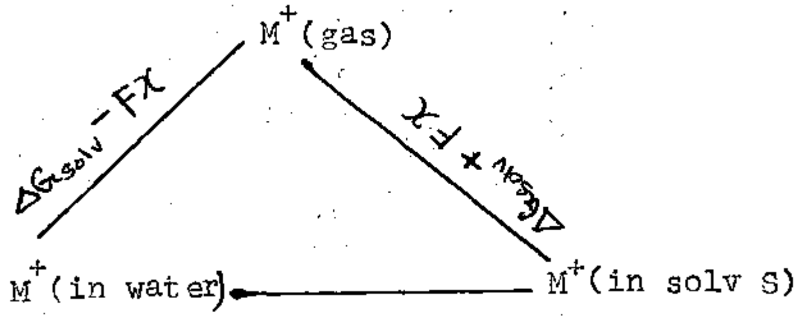
μ_i (or μ_i°) represents the free-energy of ion-solvent interaction or chemical solvation. χ represents the surface potential of solvent and the term $z_i F\chi$ is the electrostatic work owing to the passage of the ion through the surface potential at the vacuum solvent interface. The surface potential cannot be measured directly or calculated.

The real free-energy of transfer of an ion from water to a second solvent have been determined from the volta potential measurements as done by Case and Parsons[185,186].

$$\Delta\alpha_i = \alpha_i^{s} - \alpha_i^{w}$$

From $\Delta\alpha_i$ and Randle's values[184] of α_i^{w}, α_i^{s} can be determined.

The medium effect of an ion M^+ and the real free-energy of transfer can be correlated from the consideration of Born-Haber Cycle as follows :



Born-Haber Cycle

$$\Delta\alpha_t = \Delta\alpha^{(M^+)S}_{solv} - \Delta\alpha^{(M^+)W}_{solv}$$
$$= \Delta G^{(M^+)S}_{solv} + ZF\chi_s - \Delta G^{(M^+)W}_{solv} - ZF\chi_w$$
$$= \Delta G^{(M^+)}_t + ZF(\chi_s - \chi_w) \quad \ldots \quad (13)$$

If both the solvents have the same ionic concentrations, then the "total medium effect" $\Delta\alpha_t$ can be represented as

$$\Delta\alpha_t = \Delta\alpha^o_t + RT \ln(\gamma^s_\pm / \gamma^w_\pm)$$

$$= \Delta G^o_{t(ion)} + ZF(\chi_s - \chi_w) + RT \ln(\gamma^s_\pm / \gamma^w_\pm) \quad \ldots \quad (14)$$

$\Delta\alpha^o_t$ is the primary medium effect and log term represents the "secondary medium effect" having a negligible contributions ($\sim$ 0.1 K.Cal or less) under ordinary conditions and is neglected compared to $\Delta\alpha^o_t$. ($\chi_s - \chi_w$) values are generally of the order of $\sim$ 0.1V so that F ($\chi_s - \chi_w$) $\sim$ 2 K.Cal/mole which is of the same order of magnitude as $\Delta G^o_{t(ion)}$ values.

ΔG^o_t values cannot be experimentally determined but $\Delta\alpha^o_t$ (ions) are experimentally measurable inspite of limitations. However, it is to be noted that for electroneutral combinations

$$Z_{M^+} + Z_{X^-} = 0 \text{ so that } \Delta\alpha^o_t\,(MX) = \Delta G^o_t\,(MX)$$

Determination of the medium effect

Thermodynamic properties of single ions in aqueous and non-aqueous solvents and thermodynamics of transfer have been presented by a number of workers[188-201]. It is apparent that the 'medium effect' of individual ions can only be obtained from the measured "medium effect" of electroneutral combinations using various extrathermodynamic assumptions.

The determination of "medium effect" of H^+ ions ($\log {}_m\gamma_H$) evoked considerable interest as it determines directly the relative basicities of two solvents and can be obtained from the direct measurement of the cell

$$H_2(Pt) \;\Big|\; a_{H^+} = 1 \;\Big\vdots\; a_{H^+} = 1 \;\Big|\; H_2(Pt)$$

where $E = -\frac{RT}{F} \ln {}_m\gamma_H + E_{LJ}$

In view of limitations of having liquid-junction potential of uncertain magnitude, the "medium effect" of proton was first determined by Bjerrum and Larsson[202] from e.m.f. measurement of Cells composed of hydrogen electrode in a non-aqueous medium and aqueous calomel reference electrode connected with a bridge of aqueous 3.5 N KCl on the assumption of negligible liquid junction potential.

The values are of academic interest. The systematic efforts to determine the "medium effect" are given as what follows.

Models based on modification of Born Equation :-

The medium effect of an ion can be obtained from the simple Born equation

$$\log {}_m\gamma_i = \frac{NZi^2\ e^2}{2\ RT\ {}_i} \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \qquad \ldots (15)$$

It is to be noted that solvent molecules become inhomogeneous due to strong influence of solute molecules near the solvent molecules. Two extreme cases are dielectric saturation in the vicinity of ions[203] and formation of a Clathorate[204] by water molecule in the vicinity of a non-polar solute due to hydrophobic bonding effects.

The equation consists of two disposable parameters like radius and dielectric constant. Refinements are based on

a) Increase in crystallographic radii due to solvation[205-210]. The model is due to Voet and successfully applied by Latimer et.al. Strehlow and co-workers and Coetzee et.al. in non-aqueous solvents where ionic radii are adjusted to account for the differences between the free-energies of transfer of pairs of alkali metal ions.

$$\begin{aligned} \Delta G_t^o &= ({}_sG_t - {}_wG_t) \\ &= \frac{NZ^2\ e^2}{2} \left[\frac{1 - \frac{1}{\varepsilon_s}}{r_+ + R_+(S)} - \frac{1 - \frac{1}{\varepsilon_W}}{r_+ + R_+(W)} \right] \qquad \ldots (16) \end{aligned}$$

However, the equation lacks theoretical significance and is restricted to differences between very similar cations and similar solvents.

b) Dielectric solvation in the vicinity of the ion reducing the effective dielectric constant of the solvent[211-217]. Noyes[203] found that for cations having the electronic structure of an inert gas, the effective dielectric constant is given by

$$\varepsilon_{eff} = 1.000 + 1.376 \; (\gamma - 0.054)$$

and the local dielectric constant is given by

$$\varepsilon_{loc} = 78.30 \text{ for } \; r > 2.86 \text{ Å}$$

$$= \frac{1}{0.6009 + 0.1163/r} \quad \text{for } \; r < 2.86 \text{ Å}$$

Graham's relations[210] for differential dielectric ($\varepsilon_d = \frac{d\varepsilon}{dE}$) constant is $\varepsilon_d = n^2 + \frac{\varepsilon_o - n^2}{1 + b E^2}$ where E is the field strength at a distance r, n is the refractive index and b is a parameter independent of ε. It has been found that ε_d becomes equal to ε_o, above a certain initial value of r and ε_{sat} below a certain critical value of $r = r_o$. The radii for dielectric saturation of water and a number of alcohols are known.

Hepler[213] expressed ε as a function of r and took Hasted et.al.'s[214] value $\varepsilon_{sat} = 5$ for $r < 1.5$ Å, $\varepsilon_o = 78.30$ for $r > 4.0$ Å and expressed $\varepsilon = (\varepsilon_o - \varepsilon_{sat/2.5}) (r - 1.5) + \varepsilon_{sat}$ in the range of 1.5 Å $< r <$ 4.0 Å.

The free-energy change due to hydration of an ion is given by

$$\Delta G_{el} = \frac{Ne^2}{2} \left[\int_{r}^{1.5} dr/\varepsilon_{sat} \cdot r^2 + \int_{1.5}^{4} \frac{dr}{(Xr - Y) r^2} + \int_{0}^{\propto} \frac{dr}{\varepsilon_o r^2} \right] \qquad \text{... (17)}$$

$$X = \frac{\varepsilon_o - \varepsilon_{sat}}{2.5} \text{ and } Y = 1.5\,X - \varepsilon_{sat}$$

The corresponding Stoke's[215] equation is

$$\mu^{el}_{aq} = \frac{NZ^2 e^2}{2} \left[\frac{2nr_w}{r_e(r_e + 2nr_w)\,\varepsilon_{eff}} + \frac{1}{\varepsilon\,(r_e + 2nr_w)} \right] \quad ...(18)$$

where $2nr_w$ is the thickness of n layers of water molecules around the ion, r_e is the crystal radius, ε = bulk dielectric constant $\varepsilon_{eff} = \frac{1}{2}\left(\frac{1}{5} + \frac{1}{78}\right)$.

It is likely that partial or complete solvation of ions by other non-aqueous solvents may occur leading to changed values of r, ε_{sat} or ε_{eff} and ΔG^o_t. The equation should, therefore, be restricted to water-rich solvents. The equations were utilized by Bates and co-workers[14,15,18,217] to calculate ΔG^o_{el} values and the basicities of different methanol + water mixtures.

All the treatments consider the interactions of the ions with solvents to be predominantly electrostatic and neglects specific solute-solvent interactions and non-specific "neutral" component of the solvation energies of ions. Complete understanding require the knowledge of ion-dipole, ion (induced) dipole, ion-quadrupole, dipole-dipole and London dispersion forces which are functions of r^{-2}, r^{-4}, r^{-3}, r^{-3} and r^{-6} in that order where r is the corresponding interaction distance which contain the ionic radius term but not always equal to it[218]. An actual calculation of solvation energies thus requires knowledge of radii of ions and solvents. The various interaction distances, the polarizabilities and multipole moments of the solvent molecules and the ions, the co-ordination numbers for the primary solvation shell and various geometric factors. The reliable quantitative calculation of hydrational and solvational energies are thus very difficult.

The other methods of calculation of hydrational energies but not ΔG_t^0 (in most cases) are due to Noyes[203], Goldman and Bates[219], Padova[220,221], Beveridge and Schnulle[222,223]. A number of mathematically complex molecular orbital and statistical mechanical methods[224-234] have also been suggested but they are relatively little used due to complexity of the models.

<u>Methods based on measurement of oxidation-reduction potential and the E.M.F. of different cells</u> :-

The search a suitable reference electrode having the same e.m.f. value in all solvents thus appears imperative. Pleskov[234] proposed that the potential of Rb/Rb^+ couple, because of low polarizability and large radius of Rb^+ ion, should be equal in all solvents. However, both electrostatic considerations and experimental free-energy transfer values of halides (having larger radii), Rb^+ and Cs^+ in different solvent point the inherent limitations of the assumption. Strehlow and co-workers[73,206,235] made appropriate allowances for the changed dielectric constants in different solvents and for the residual electrostatic free-energy terms and developed a modified Rb - scale which was utilized by Coetzee et.al.[236] for measurements of polarographic half-wave potentials of a series of cations present as perchlorates in seven solvents.

Koepp, Wendt and Strehlow[73,208,235] (also studied by Kuwana et.al.[237]) selected the redox - systems of large symmetrical complexes Ferricinium | Ferrocene and Cobalticinium | Cobaltocene, having very little residual charges on the surface, so that the standard e.m.f. of the Fic | Foc or Cic | Coc [i.e. $\Delta G^o_t(\mathrm{Foc}) - \Delta G^o_t(\mathrm{Fic})$] can be regarded to be solvent - independent. Thus the measurement of standard oxidation potentials in water and solvents gives the value of $\Delta G^o_{t(H^+)} - \Delta G^o_{t(\mathrm{Fic})} + \Delta G^o_{t(\mathrm{Foc})}$

According to Strehlow,

$$\Delta G^o_{t(\mathrm{Fic})} - \Delta G^o_{t(\mathrm{Foc})} = \frac{NZ^2 . e^2}{2} \left[\left(\frac{1 - \frac{1}{\varepsilon_1}}{r + a_1} \right) - \frac{1 - \frac{1}{\varepsilon_2}}{r + a_2} \right] \qquad \ldots (19)$$

where a_1 and a_2 are constants, specific for the solvents in question Strehlow used $a_1 = 0.85$; $0.72 \leq a_2 \leq 0.90$ based on data of alkali ions. In addition to the inherent limitations due to liquid-junction potentials, the contributions due to surface potentials in measuring the real free-energies of transfer have been neglected[238].

Inspite of the limitations, the method seems to be one of the most useful method for the determination of the 'medium effect' of single ions and widely used by de Ligny and co-workers[28-32,238-240]. They used the cells of the type

$$\mathrm{Pt(H_2)} \left| \begin{array}{c} \mathrm{HClO_4}(m_1) \text{ in water or} \\ \text{solvents, respectively} \end{array} \right| \mathrm{KCl(Satd.)\ in\ H_2O} \left| \mathrm{Hg_2Cl_2{-}Hg} \right. \qquad (C)$$

and

$$(\mathrm{Pt}) \left| \begin{array}{l} \mathrm{Ferrocene}(m_2),\mathrm{Ferricinium} \\ \mathrm{perchlorate}(m_3) \text{ in } H_2O \text{ and} \\ \mathrm{S, respectively} \end{array} \right\vdots \; \mathrm{KCl(Satd.)in}\ H_2O \; \Big| \; Hg_2Cl_2\text{-}Hg \qquad (\mathrm{D})$$

to get

$$E^o_s(\mathrm{Fic}) - E^o_w(\mathrm{Fic}) = \frac{1}{F} \left[\Delta G^o_t(H) - \Delta G^o_{t(\mathrm{Fic})} + \Delta G^o_{t(\mathrm{Foc})} \right]$$

However, due to low solubility of ferrocene and instability of ferricinium in water, the determination of E is generally supplemented by the polaragraphic half-wave potentials, $\mathrm{Foc} \rightleftharpoons \mathrm{Fic}^+ + e$ have been proved to be diffusion controlled and the ratio of diffusion constants of ferrocene and the ferricinium ion appeared to be independent of solvent composition. The method has been used to determine the ΔG^o_t of H^+ and the other ions in different solvents. The method has been recently used by Kalidas et.al.[241] to measure $\Delta G^o_{t(H^+)}$ in different methanol - water, propylene glycol - water and methanol - propylene glycol mixtures.

However, the presence of considerable amount of indifferent electrolyte should change the solvent structure, E^o- values and thus the medium effects. The diffusion constant of ferrocene and ferricinium ions may be unequal. It has been shown by Alfenaar et.al.[240] that the contribution of the solvent molecules to the diffusion potential cannot be neglected and is a function of solvent composition and the nature of electrolyte. The primary medium effect is the most important contribution to the diffusion potential. The diffusion potential of electrolyte solutions in methanol - water mixtures cannot be suppressed by salt - bridge.

Ferrocene may have residual electrostatic component of the ion[167] and the specific interactions of the redox couple with water and other solvents are also known[210]. There may be uncertainties in the crystal radii of ferrocene[238] (3.8 Å) and ferricinium[32] (3.3 Å) ions.

Other redox couples studied are ferrocene /ferricinium picrate; ferroin/ ferriin couple[243], (4,7-dimethylferroin/(4,7-dimethyl) ferriin couple[244], bisdiphenyl chromium (0,1) couple[245, 246] with relative little success.

Parker and co-workers[168,188,191] feel that the ferrocene assumption is not valid when water is one of the solvents. Parker & Alexander recommended the cells of the type

$$\text{Ag(s)}\;\left|\;\begin{array}{l}\text{AgNO}_3\\ \text{(0.01 M)}\\ \text{in}\\ \text{CH}_3\text{OH}\end{array}\right\|\;\begin{array}{l}\text{Satd.}\\ \text{NEt}_4\text{ Pic}\end{array}\;\left\|\;\begin{array}{l}\text{AgNO}_3\text{(0.01M)}\\ \text{in solvents}\end{array}\right|\;\text{Ag(E)}$$

or

$$\text{Ag(s)}\;\left|\;\begin{array}{l}\text{AgClO}_4\\ \text{(0.01 M)Solvent, S}\end{array}\right|\;\begin{array}{l}\text{0.1M NEt}_4\text{Pic}\\ \text{in solvent, S or O}\end{array}\;\left|\;\begin{array}{l}\text{AgClO}_4\\ \text{(0.01M)}\\ \text{solvent O}\end{array}\right|\;\text{Ag(F)}$$

to determine medium effects. The bridge electrolyte contains tetraethyl ammonium picrate having large and comparable anion and and cation size with no specific interactions with the solvents as apparent from roughly equal molar conductances in all solvents studied. Thus there is a negligible liquid-junction potential E_j.

Parker and co-workers[168,169] also measured the potential of fic/foc couple against the Ag^+/Ag electrode in fifteen solvents using the cell

$$\text{Ag}\left|\begin{array}{l}0.01\text{ M AgClO}_4\\ \text{NEt}_4\text{ ClO}_4\\ \text{Solvents}\end{array}\right|\begin{array}{l}\text{NEt}_4\text{ ClO}_4\\ 0.1\text{ M}\\ \text{Solvent}\end{array}\left|\begin{array}{l}0.002\text{ M Fic/Foc}\\ 0.02\text{ M NEt}_4\text{ ClO}_4\\ \text{in Solvent, S}\end{array}\right|\text{Pt(G)}$$

Thus the values based on the ferrocene assumption can be readily converted to the negligible E_j assumption.

However, the suppression of E_j by means of a salt-bridge is impossible as the liquid-junction potential E_j at an interface of two different media is itself primarily a function of the medium effects for the single ions transported across it[242].

Extrapolation Method : The extrapolation method has its origin in the works of Izmaylov[104,246,247] who assumed G^o of an infinitely large ion to be zero and all significant components of the solvation energy G^o of an ion are functions of $\frac{1}{r^n}$ (r = crystallographic radii, n = 1 - 4 or 6). He plotted thermodynamically allowed combinations like $(G_M^o - G_H^o)$ vs $\frac{1}{r_M}$ and $-(G_H^o + G_X^o)$ vs $\frac{1}{r_X}$ (M = alkalimetal ions, X = halide ions) and used extrapolations to get $-G_M^o$ at $(\frac{1}{r}) = 0$. The plot of $[-G_H^o + (\frac{G_M^o - G_X^o}{2})$ vs $\frac{1}{r_{av}} = \frac{1}{2}(\frac{1}{r_M} + \frac{1}{r_X})]$ improve the value of G_H^o. Izmaylov[104,247] also considered solvation of ions as complex formation between solvent molecules (donors) and ions with vacant orbitals as acceptors.

He determined the solvation energies of anions and cations from the plots of $(G_M^o + G_X^o)$ vs $\frac{1}{r^2}$, $(G_M^o - G_H^o)$ vs $\frac{1}{r^2}$ and

$\left[-G_i^o + \frac{G_M^o - G_X^o}{2} \right.$ vs $\frac{1}{n^2}$ (n = 3,4,5 etc.)] for different isoelectronic pairs like ($Na^+ F^-$), (K^+Cl^-), (Rb^+Br^-) and (Cs^+I^-) where n is the principal quantum numbers of the lowest vacant orbital of the ion. He considered the second method to be more reliable. However, Izmaylov's assumption that $\Delta G^o_{(neut)}$ account for 1 - 2% of the total solvation energy was found to be erroneous from the estimates of $\Delta G^o_{(neut)}$ via inert gas assumption or experimental determination of $\Delta G^o_{(neut)}$. Moreover, the calculations of Izmaylov[104,246,247] were dependent on the large errors involved in the determination of the dissociation energies of molecular hydrogen, the sublimation energies of the metal and of atomic hydrogen in the gas phase and crystal lattice energies of silver halides. The extrapolations are non-linear and generally based on three points. Therefore, large errors in the determination of ΔG_t^o or 'medium effect' are but expected.

Feakins and Watson and their associates[39-46,248,249] used the e.m.f. methods to determine the ΔG_t^o(free-energies of transfer from water to different solvents) values of HCl, HBr and HI on one hand and LiCl, NaCl and KCl on the other and utilized the extrapolations

$$\Delta G_t^o(HX) = \Delta G_t^o(H^+) + a\, r_X^{-1} \qquad (21)$$

and

$$\Delta G_t^o(MCl) = \Delta G_t^o(Cl^-) + b\, r_M^{-1} \qquad (22)$$

to get $\Delta G_t^o(H)$ at $\frac{1}{r_X} = 0$ and $\Delta G_t^o(Cl)$ at $\frac{1}{r_M} = 0$

Cations are found to be in lower free-energy states in the mixed solvents compared to water, while the anions show the reverse trend. However, linearity is poor in most cases due to incomplete compensation of ΔH_t and $T \Delta S_t$ terms which are complex functions of radius and estimations based on the dependence of $\frac{1}{r}$ appear to be oversimplification. The major contributions to free-energy of solvation arises from ion dipole interaction term $Ze\mu / r^2$ in addition to Born charging energy beyond the solvation shell[25]. In consistent values of ΔG_t^o of individual ions result from the plots of $\Delta G^o_{t(M\,Cl)}$ vs $\frac{1}{r_M}$ and $\Delta G_t^o(HX)$ vs $\frac{1}{r_X}$. Other inconsistencies are also noted[238]. However, it has been now recognized that the solvation energy of an ion is composed of an electrostatic part ΔG^o_{el} and neutral part ΔG^o_{neut}, ie.,

$$\Delta G_t^o = \Delta G^o_{neut} + \Delta G^o_{el}$$

The assumption was originally put forward by Bjerrum and Larson[202] and applied by Haugen and Friedman[251] and most of the workers now a days. The neutral component was equated to the 'medium effect' of the uncharged species of similar size and structure as the ion (known as inert gas assumption). For benzoate ion, benzoic acid is the neutral analogue while for ions like Li^+, Na^+, K^+, Rb^+, Cs^+ the isoelectric inert gases are the corresponding neutral analogues[167].

The method has been elegantly put forward by Alfenaar and de Ligny[31,238] and more recently by Kim[252], Abraham and Liszi[199].

In view of the difficulty of calculation ΔG^o_{neut}, it has been determined experimentally. Alfenaar and de Ligny[31,238] took ΔG^{o}_{neut} of very large ions to be equal to ΔG^{o}_{neut} of the corresponding uncharged particle of equal radius but for small ions, a difference arises from the changed solvent structure around the ions of the solvent molecules.

The free-energy of transfer of ions between two solvents including ion-ion, ion-dipole, ion-quadrupole interactions etc. are given by

$$\Delta Gi(ion) = \Delta G^{o}_{neut} + \frac{a}{\gamma} + \frac{b}{\gamma^2} + \frac{c}{\gamma^3} + \cdots \qquad \ldots (24)$$

The free-energy of transfer of electroneutral combinations of ions have been divided by Alfenaar and de Ligny into the contributions of the individual ions M and A as follows :

$$\Delta G^{o}_{M} + \Delta G^{o}_{A} - \Delta G^{o}_{neut}, A = \Delta G^{o}_{H} + \frac{a}{\gamma_A} + \frac{b}{\gamma_A^2} + \frac{c}{\gamma_A^3} \cdots \qquad \ldots (25)$$

$$\Delta G^{o}_{H} - \Delta G^{o}_{M} - \Delta G^{o}_{neut}, M = \Delta G^{o}_{H} - \frac{a}{r_M} + \frac{d}{r_M 2} + \frac{e}{\gamma_M 3} + \ldots (26)$$

The values of the left hand sides can be determined experimentally. a_{Born} is calculated using the Born equation from the slope at $\frac{1}{\gamma} = 0$, and $\Delta G^{o}_{t}(H)$, b, c etc can be estimated by the method of least square. When the left hand side of the two equations (25) and (26) are plotted against $\frac{1}{\gamma}$, two curves will have a common intercept ΔG^{o}_{H}, the larger the ions, the greater the accuracy of the results.

The extrapolations, however, are non-linear. The contributions of $\Delta G^o_{t(neut)}$ appear to be considerable and the reliability of the determination of $\Delta G^o_{t(neut)}$ via 'inert gas assumption' have not been proved.

de Ligny and co-workers[28-32,238-240] later slightly modified the method by incorporating ideas of Buckingham[253], Halliwell and Nyburg[254], Muirhead-Gould and Laidler[255].

Salomon[180,196,257] determined the individual free-energies of solvation from plot of differences in conventional free-energies vs $\frac{1}{\gamma_i}$, where γ_i is the gas-phase radius of Gouray and Adrion. $\Delta G^o_{solv}(H^+)$ is obtained from

$$\left[\Delta G^o_{conv}(M^+) - \Delta G^o_{conv}(X^-) \right] = \frac{\text{constant}}{\gamma_i} - 2\,\Delta G^o_{solv}(H^+) \qquad \ldots (29)$$

$$\left[\Delta G^o_{conv}(M^+) = \Delta G^o_{solv}(M^+) - \Delta G^o_{solv}(H^+) \right.$$

$$\left. \Delta G^o_{conv}(X^-) = \Delta G^o_{solv}(X^-) + \Delta G^o_{solv}(H^+) \right]$$

M^+ and X^- are ions of equal charge and radius.

It is known that the enthalpy and entropy terms are complex functions of r, but due to compensation of the enthalpy and entropy solvation, the free-energy term is relatively independent of terms higher than r^{-1}. $\Delta G^o_{solv}(H^+)$ is found to be -235.0 K cal/mole.

Since ΔG^{o}_{neut} is dependent of ionic radius, the choice of crystal radii as determined by different workers are noted. Criss and Salomon[180] considered it desirable to take differences in $\Delta G^{o}_{t,conv}$(ion) which automatically cancells $\Delta G^{o}_{t,neut}$, for anions and cations of equal charge and radius. The choice of crystal radius thus becomes less important.

Abraham and Liszi[199] determined the free-energy (and other thermodynamic properties) of solvation of gaseous univalent ions using a one-layer and two layercontinum model for $\Delta G^{o}_{t,el}$ utilizing the equation $\Delta G^{o}_{t} = \Delta G^{o}_{t,el} + \Delta G^{o}_{t(neut)}$, $\Delta G^{o}_{t(neut)}$ is the free-energy of solvation of a non-polar gaseous solute of the same size as the ions in question.

Wells[257] calculated the free-energies of transfer of H^+ ions from water to water + co - solvent mixtures (like MeOH, Pr^iOH, t - BuOH, ethylene - glycol, glycerol, acetone, dioxane, dmso) assuming that $\Delta G^{o}_{t}(H^+)$ consists of two parts

$$\Delta G^{o}_{t}(H^+) = \Delta G^{o}_{t}(H^+)_e + \Delta G^{\circ}\ (RO^+H_2)$$

$\Delta G^{o}_{t}(H^+)_e$ is the free-energy change of the transfer of a sphere containing the tetrahedral structure $H_3O^+(H_2O)$ (having $r = 3\,r_{H_2O}$) from ε_w to ε_s (dielectric constant of the mixture) using Born equation

$$\Delta G^{o}_{t}(H^+)_e = \frac{e^2}{6\,r_{H_2O}} \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right).$$

$\Delta G^{o}\ (RO\overset{+}{H})_2$ covers all subsequent structural changes induced by the presence of the tetrahedral $H_3O^+ (H_2O)_4$ in the mixed solvent.

However, the method is applicable only in water-rich media. The limitations of the method are discussed elsewhere.

Method based on 'Reference Electrolyte'

The most widely advocated and promising approach to the estimation of 'medium effects' for single ions (and also for the estimation of partial molar volume, the solvation enthalpies and other thermodynamic properties of single ions) are those based on 'reference electrolytes'. The reference electrolyte[167,258-262] should be composed of large symmetrical counter ions of equal size and solvation properties, so that the 'medium effect' should be equally divided between the cations and the anions. The central atom and the charge of such counter ions should be shielded by large organic residues to minimize both the charge density and specific interactions with the solvent.

Tetraphenyl phosphonium tetraphenyl borate ($Ph_4 P B Ph_4$) was first used by Grunwald and co-workers[151] to estimate the 'medium effects' of single ions. If $\frac{dG_t^o}{dZ_1}$ for the reference electrolyte is denoted G_t^o, the equation separating the transfer energy into the individual contributions of positive and negative ions becomes

$$G_t^o(+) = G_t^o(-) = \Delta G^o_{t(neut)} - \frac{Ne^2}{2r\varepsilon} \cdot \frac{d \ln \varepsilon}{dZ} \qquad \ldots(32)$$

The Ph_4C was chosen as neutral analogue.

The experimental values chosen from the 'reference electrolyte' method agreed well with the values predicted by the equation. Slight positive G_t^o values for alkali metal cations and negative G_t^o values for inorganic anions indicate preferential solvation of ions. Popovych[259] proposed tri-isoanyl-n-butylammonium tetraphenyl borate (TABB Ph_4) as 'reference electrolyte' based on the equality of the Stoke's radii of ions in water, methanol + acetonitrile, Tetraphenyl arsonium tetraphenyl borate ($Ph_4As\ B\ Ph_4$) has been proposed by Parker and co-workers[188,191].

Because of their low solubility in different solvents, the reference electrolytes are suitable for determining free-energies of solvation without uncertain activity corrections.

The limitations of the method can be summarized as follows :

1) The results are based on solubility data and errors may arise from the possible[167,181]

    a) formation of crystal solvents
    b) micelle formation
    c) formation of complex ions
    d) ion-pair formation

2) Insufficient evidence or no direct experimental evidence for the equality of radii of counter ions.

3) Approximate equality of Stoke's radii or calculated radii from models are not real indices of ion-sizes or imply a direct correlation between transport or thermodynamic properties[261-264]. Dielectric relaxation, size of secondary solvation effects must be taken into account to determine free energies of solvation[180].

4) The method should not be applied to dipolar aprotic solvent, which differentiates strongly between the relative solvation of anions and cations[210].

Inspite of the defects, the results obtained with $TABBPh_4$ of Popovych and co-workers and with $Ph_4AsB\ Ph_4$ assumption of Alexander and Parker are in good agreement, Discripancies between two methods arise from Parker's use of formal solubility product rather than thermodynamic ion activity product used by Popovych[166].

Berne and Popovych[265] studied the medium effects of tetraphenyl germane (Ph_4Ge), tetraphenyl methane (Ph_4C) and tetraphenyl silane $(Ph_4\ Si)$ which are excellent neutral analogues of tetraphenyl borate $(B\ Ph_4^-)$, tetraphenyl arsonium $(Ph_4\ As^+)$ and tetraphenyl phosphonium ions $(Ph_4\ P^+)$, the 'reference ions' widely used in the estimation of 'medium effects' of single ions and whose ion-sizes roughly fall in the range of 4.0 - 5.5 Å. Thus, for ions with radii 4 - 5 Å

$$\Delta G_t^o = \Delta G_{t(neut)}^o + \Delta G_{t(Born)}^o$$

(experimental)

the interactions expressed by higher order terms in r^{-1} appear to be unimportant.

Medium effects of Ph_4 Ge, Ph_4C and Ph_4Si referred to standard states in ethanol were calculated from solubilities in acetonitrile methanol, ethanol-water solvents containing 60 - 100 wt% ethanol, when the 'medium effects' of tetraphenyl compounds are added to the corresponding estimates of $\log_m \gamma$ (Born) for an ion with r = 4-5 Å, the results are in fair agreement with the observed values of $\frac{1}{2}$ log m γ for the Ph_4As B Ph_4, Ph_4P B Ph_4 and TABB Ph_4 in ethanol-water solvents, methanol but not in acetonitrile.

Recently, Kim[252] after a critical and extensive study strongly recommends Ph_4 As B Ph_4 as 'reference electrolyte' to calculate single ion thermodynamics. The electrostatic free energy of transfer [ΔG_+ (Born)] are calculated by the Buckingham theory, $\Delta G_{t(neut)}^o$ are replaced by the experimental values of $\Delta G_t^o(Ph_4Ge)$ and $\Delta G_t^o(Ph_4C)$. Ph_4Ge and Ph_4C have proved to be by their size and structure [as determined from the determination of molar volume V, packing density(d) and volume co-efficients

$$f = \frac{V\ (Ph_4Ge)}{V\ (Ph_4C)} \quad \text{and} \quad f = \frac{V\ (Ph_4As^+)}{V\ (Ph_4B^-)}$$] the ideal

neutral analogues of Ph_4As^+ and Ph_4B^- respectively. Good agreement have been reported between ΔG_t^o (= ΔG_{el}^o + ΔG_{neut}^o) values calculated and experimental values of ΔG_t^o (Ph_4 As B Ph_4) in various organic solvents.

The partition of the values for the reference cation and anion has shown slight and marginal difference in standard free energies of transfer, in most cases slightly greater for the cations than for the anion.

Miscellaneous Methods

A number of methods of minor importance have been suggested to obtain 'medium effect' of which the method based on linear free energy relationships suggested by Grunwald and co-worker is of importance.

For the ionization of acids HA (aliphatic acids, benzoic acids) and BH^+ (anilinium ion, toluidinium ions etc.) in alcohol + water mixtures and water, we have,

$$(pk_s - pk_w)HA = \log \gamma_{H^+} + \log \frac{\gamma_{A^-}}{\gamma_{HA}} = \log \gamma_{H^+} + m_A Y^- \quad ...(33$$

and $(pk_s - pk_w)BH^+ = \log \gamma_{H^+} + \log m_B Y_o$, m_A and m_B are substituent constants independent of the nature of the solvent; Y- and Y_o are the solvent parameters dependent on the solvent only where

$$\gamma_{-} = (1 - w^2) \qquad \ldots (34)$$

and $$\gamma_{o} = -(1 - w)^2 \qquad \ldots (35)$$

w = weight fraction of water in the solvent.

Now, $(pk_s - pk_w)_{HA} - (pk_s - pk_w)_{BH^+} = m_A \gamma^{-} - m_B \gamma_o \quad \ldots(36)$ m_A and m_B were determined by multiple-regression method which enables one to calculate log γ_{H^+} .

The method, however, is of little value due to the inherent limitations regarding the assumptions of m_A, γ as pointed out by Wyne-Jones[266] and Popovych[166,260] and more recently by Maity and Lahiri[267-269].

Basicity of the mixed solvents :

The complexity of ion-solvent interactions is well-illustrated by the conflicting evidence concerning the relative "basicities" of water and alcohols in the mixed solvents about which there is no general agreement. The investigation of transfer of free energies by Feakins and co-workers[38-45,248] brings one to the conclusion that the anions are in a higher free-energy state in methanol-water mixtures than in water, whereas cations are in a lower free energy state indicating methanol to be more basic than water. Considering the charge distribution in the solvent molecules, Feakins suggests that due to the inductive effect of the methyl group, methanol is more basic than water and methanol will confer "greater basicity" on water to which it is hydrogen bonded. This idea is in line with the views of Frank and Wen[268]. Similar conclusions have been drawn by Wells[269] from the behaviour of p-nitroaniline in solutions of strong acids in methanol and in isopropanol. The medium effect for the proton, $\log {}_m\gamma_H$ estimated by Popovych and co-workers[166,258-261,265] is negative in ethanol-water mixtures containing from 10 to 98 wt% ethanol and passes through a minimum at 60% by wt. Negative values of $\log {}_m\gamma_H$ between 10 and 98 wt% ethanol indicate that ethanol-water mixtures in that range are more basic than either of the pure liquids, with maximum basicity occuring at 60 wt%. Braude and Stern[270] observed a similar variation in solvent basicity from the behaviour of the acidity function, Ho in mixtures of ethanol, dioxane and acetone with water. In all three cases,-Ho passes through a minimum (maximum solvent basicity) at approximately equimolar solvent composition and then rises sharply in the region of the pure organic solvents. Calculations by Paabo, Bates and Robinson[15] point to the existence of a basicity maximum also in methanol - water mixtures, as do the estimates of $\log {}_m\gamma_H$ by Alfenaar and deligny[238]. The conclusion of Braude and Stern[270] was that water is more basic in mixtures with other solvents than in the pure liquid state, whereas its proton affinity is lowered by strong intermolecular hydrogen bonding. Addition of organic solvent to water is believed to bring about a gradual destruction of the water structure, thus liberating polymerised, condensed system having a considerable degree of structure, 2) the thermodynamic significance of K is doubtful[148]. These apparently conflicting views have led Frank and Ives[148] to suggest that in a hydrogen bonded liquid system, it is not possible or even meaningful to assign relative instrinsic basic or acidic strengths to molecular species which exist so strongly under each others influence.

According to Feakins[45], dioxane molecule is more basic than water and also enhances the basicity of water molecules to which it is bonded.

Feakins[45] also suggests that pK possibly measures basicity but only over part of the solvent-composition range and the basicity of the solvent may well change depending on their environment and therefore, change over the range of methanol-water concentration. Thus, it is apparent that pK can give some idea regarding basicity provided the full nature of the environment is known.

Muirhead, Gould and Laidler[2] have given the different types of forces which are present in solutions. In addition to an increasing number of basic sites on the water molecules for bonding with the protons. The effective proton affinity of the solvent reaches its maximum when the higher aqueous solvent $H^+(H_2O)_n$ are replaced by H_3O^+ ions. This condition corresponds to the minima in the plots of $-H_o$ or log ${}_m\gamma_H$ vs solvent composition. Beyond the minima, the H_3O^+ ions are gradually replaced by the organic oxonium ions, which the case of $C_2H_5OH_2^+$ are more acidic than H_3O^+ (positive log ${}_m\gamma_H$). The conductance of HCl[271] in alcohol-water mixtures however appears to indicate that protons are bound more tightly to water molecule than to methanol. Calculation of the equilibrium constants for the simple proton transfer reaction $ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+$ have given results (e.g. $K \sim 100$ for MeOH, ~ 250 for EtOH) supported by indicator[272], e.m.f. [273] and catalytic studies[274] taken to mean that water is a much stronger base than alcohols. But 1) k-calculated for the hypothetical proton-transfer reaction is a gross oversimplification of something more complex happening in the ion-ion forces, ion-dipole forces, ion-induced dipole forces, ion-quadrupole forces (may be termed ion-solvent interactions in a broader sence), dipole-dipole forces, dispersion forces, and charge-transfer forces exist in solution. Parker[178] also suggested that there are four kinds of strong solute-solvent interaction : ion-dipole, dipole-dipole, π-complex forming and hydrogen bonding. Full and proper knowledge of these factors are necessary before we can say definitely about the basicity of the solvents.

In view of the complexities of the problem, Pal and Lahiri[53] determined the dissociation constants of salicyclic andsulphosalicyclic acids in a number of equidielectric mixtures of different solvent compositions to get the relative magnitude of the basicities of the different solvent mixtures.

In view of the uncertainties of the radii values of anions (specially in case of unsymmetrical electrolytes) and lack of exact knowledge of solvation[53], the basicity of the solvent mixtures could not be ascertained but only the relative idea regarding the non-electrostatic contributions could be made. Since "non-electrostatic terms" (termed 'basicity' by Paabo et.al.) is predominantly negative for methanol-water mixtures, Pal and Lahiri[53] observed ΔG^{o}_{el} term (- ve) is in the order dioxane $\rangle$ isopropanol $\rangle$ ethanol $\rangle$ methanol. But equidielectric mixtures invariably make the mole-fraction of different solvents to differ considerably. Though there is constancy in ΔG^{o}_{el} parts (assuming r to be same in equidielectric mixtures), only the difference in ΔG^{o}_{nonel} parts of different percentages of mixed solvents could be obtained. But ΔG^{o}_{nonel} changes with solvent-composition as the free-energy of mixing and solvent basicity change with solvent composition. Thus, the idea of even the relative basicity of the solvents could not be made from these measurements. They stressed the importance of determining the ion-solvent interactions to determine the basicity of mixed solvents.

Inspite of the progress that has been made in understanding ion-solvent interactions and their role in medium effects, there is yet no means of evaluating in a reliable way the proton affinity of one medium with respect to that of another. For this reason, a single pH-scale applicable more than one medium can not yet be considered a practical possibility.

A satisfactory treatment of the theoretical basis of complex formation in various solvents and mixed solvent does not yet seen possible. Complex formation occurs in a way analogous to corresponding reactions in water. A consideration of electrostatic effects involved will complicate the treatment appreciably. No systematic investigations have been done as to the effect of dielectric constant and change in acid-base character of the solvents on the complexes. However, change in the stability constants of the complexes with solvent compositions are noted but the values are not simple functions of the dielectric constants[53-55,67,141,275].

Dioxane-water mixtures have been widely used for the determination of stability constant of complexes slightly soluble in water. Irving and Rossotti[276] compared log K_{HL} and log K_{ML} in mistures water + dioxane & in some other solvents. The thermodynamic significance of the difference between these constants was discussed. In aqueous dioxane and aqueous alcohols, the stability constant of the complexes containing an O-M linkage increases with increasing organic solvents whereas the stabilities of complexes containing N - M linkage decrease. But Irving and Rossotti found no simple relationship between stability and solvent composition for complexes of ammonia, ethylenediamine and pyridine, although the silver ethylenediamine complex is more stable in pure ethanol and isopropanol than water.

Complex formation in non-aqueous or mixed solvents and their systematic correlations offer possibilities for future research. The free energies of transfer of metal complexes and ligands may be of great help to determine the free-energies of transfer of metal ions and metal complexes.

In recent years, free-energies of transfer of metal complexes (particularly alkaline metal complexes) of macrocyclic ligands like cryptands and crown ethers have been made[277]. A positive value of the transfer activity co-efficients $^{S_1}\gamma^{S_2}_{LM^+}$

[L = cryptands or crown ether, M^+ = alkali metal ion] denotes that $[LM^+]$ is more strongly solvated in S_1 than in S_2.

However, attempts for qualitative and quantitative correlations are still very few.

From the disscussions, it is apparent that inspite of the extensive studies, the role of solvents on the dissociation constants of the ligands, the exact nature of ion-solvent, solvent-solvent interactions, and solvent basicities are yet provoed to be elusive as a result nothing specific an be said about the 'medium effects' a quantity of fundamental interest.

Systematic and extensive studies are needed for the proper understanding of the solution chemistry in aqueous and mixed solvents. Studies on the dissociation constants of ligands and their complexes in mixed solvents may give us some idea regarding ion-solvent interactions, solvent-basicity and medium effects.

With the above objects in view, we have determined the dissociation constants of 2,2'-bipyridine, 1,10-phenanthroline in dmso + water, dmf + water and formamide + water mixtures and ferrous-tris-2,2'-bipyridine complex in dmso + water and formamide + water mixtures.

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Section - II

Studies on the dissociation constants of ligands in different non-aqueous and the binary mixtures give us insight regarding the role of solvents on the dissociation equilibria and ion-solvent interactions.

Most of the studies are in protic solvents like methanol, ethanol, t-butanol etc. and their aqueous binary mixtures. Studies in dipolar-aprotic solvents and their binary mixtures may be of some help to understand the nature of the solute-solvent interactions and other solvent properties.

The peculiar properties and the various uses of dipolar-aprotic solvent dmso have led us to study the acid-base properties of ligands in dmso + H_2O mixtures. We report in this section the results of our study on the dissociation equilibria for the "isoelectric" reactions of the type

$$AH^+ \rightleftharpoons A + H^+ \qquad (1)$$

where A is either 2,2'-bipyridine (bipy) or 1,10-phenanthroline (Phen) in dmso + H_2O mixtures pH-metrically and spectrophotometrically. The evaluation of free-energies of transfer of H^+ ion in mixed-solvents have been attempted.

Experimental :

2,2'-bipyridine and 1,10-phenanthroline (G.R.E. Merck) were used without further treatment. Dimethylsulphoxide (Backer Analyzed Reagent) was dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. The distilled solvent was used within 24 hours. $HClO_4$, caustic soda and other chemicals used were of analar grade. Doubly distilled water was used to prepare the solutions.

The ligands are known to absorb strongly in the u.v. region. The absorption maxima were slightly changed indicating little solute-solvent interactions.

The pK-values of the ligands were determined PH-metrically and spectrophotometrically in the same way as described by Lahiri, Aditya and co-workers[1-4]. Since the ligands absorbs strongly in the u.v. regions, their optical density measurements were taken at 300 and 305 nms (for 2,2'-bipyridine) and 310 and 315 nms for 1,10-phenanthroline.

The weight percentages of the organic solvent at 298K were calculated from the known amounts of the two solvents by volume and the densities of the solvents.

The dielectric constant and density values of dmso + H_2O mixtures were interpolated from the data compiled by Covington and Dickinson[5].

Determination of H^+ ion in dmso + H_2O mixtures :

The glass electrode has been reported to function satisfactorily in demethylsulphoxide up to a pH of 28. Ritchie[6] Calibrated the glass electrode with solutions of p-toluene-sulphonic acid. Kolthoff et. al.[7] used buffer mixtures of 4-Chloro - 2, 6-dinitrophenol and 2,6-dinitrophenol (pK values determined conductometrically and spectrophotometrically) and their tetraethylammonium salts. But such studies in dmso + H_2O mixtures are not known. Since glass-electrodes work satisfactorily in dmso, therefore, the method suggested by Van Uitert et.al.[8] could be well utilised. The method has been extensively studied by Lahiri, Aditya and co-workers[9-10]. The instrument was first standarized with potassium-hydrogen-phthalate 0.05 mol dm^{-3} 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 $-\log[H^+] = B + \log[U_H]$ were $[H^+]$ is the stoichiometric hydrogen ion concentration assuming 100% dissociation of the acid in the aqueous and in mixed solvents.

The correction factors log U_H in different percentages of dmso + H_2O mixtures are presented in Table (1).

The optical density readings were recorded with a

Backman DU2 spectrophotometer maintained at 298K. The pH-meter readings were noted with a ECIL digital pH-meter having an accuracy of ± 0.01.

Results :

The thermodynamic dissociation constants for the reaction(1) is represented by

$$K_T = \frac{a_A \times a_{H^+}}{a_{AH^+}} = \frac{C_A \times C_{H^+}}{C_{AH^+}} \times \frac{f_A \times f_{H^+}}{f_{AH^+}} = \frac{C_A \times C_{H^+}}{C_{AH^+}} \qquad (2)$$

(in very dilute solutions)

$$\text{Thus } pK_T = pH + \log \frac{C_{AH^+}}{C_A} \qquad (3)$$

$$= B + \log U_H + \log \frac{C_{AH^+}}{C_A} \qquad (4)$$

$$= B + \log U_H + \log \frac{d - d_M}{d_I - d} \qquad (5)$$

(B = meter readings of the solutions)

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

$$\text{Further } [H^+]_{Total} = [H^+]_{free} + [AH^+] \qquad (6)$$

$$[A]_T = [A] + [AH^+] \qquad (7)$$

Thus, from the known concentrations of $[A]_T$, $[H^+]_T$ and $[H^+]_{free}$ [determined experimentally] values, pK_T can be calculated using (4), whereas equation (5) has to be utilized where d_M, d_I, d and $[H^+]$ ion concentrations are available. Tables 2 - 4 give the result of dissociation constants in mixed solvents. The average pK-values of 2,2'bipyridine or 1,10-phenanthroline at different dmso + H_2O mixtures are given in the Table 5.

Discussions :

In view of ion-pairing and homoconjugation of acids, it is desirable to work with very low concentrations in dmso. But we always prefer to determine the dissociation constants of acids at very low ionic strengths and in absence of neutral electrolytes so that the thermodynamic dissociation constants could be determined..

In mixed solvents, the activity co-efficients of the ith species can be written as

$$\gamma_i = {}_{m}\gamma_i \cdot {}_{s}\gamma_i$$ [11]

However, in very dilute solutions ${}_{s}\gamma_i \longrightarrow 1$ so that only the "medium effects" which could be properly assessed so that we get the role of solvents and the nature of the solute-solvent interactions.

The results in the table (5) show that the pK-values of 2,2'-bipyridine and 1,10-phenanthroline decrease as the percentage of organic solvents increase but the change is quite appreciable particularly at the begining. The change is quite large when we compare ΔpK-change in comparable methanol-water mixtures[2,3] where the dielectric constants are considerably lower. The greater solubility of the ligands in organic solvents is one of the factors for change in pK-values. The pK of 1,10-phenanthroline decreases, reaches a minimum at about 80 wt% of organic solvent and then increases whereas no such minimum is observed in case of 2,2'-bipyridine.

The pK-values show linear relationship when plotted against weight percentage (Fig - 1). But the plots of pK vs 1/D or mole-fractions are linear at best up to 60 wt% beyond which considerable deviations arise (Fig 2,3). It is apparent that specific solute-solvent interactions are important to account for the variation of pK-values.

In order to have some understanding regarding the contributions of non-electrostatic parts, it is desirable to calculate ΔG_t^o (non-el). ΔG_t^o(el) has been calculated using the simple Born[12] equation inspite of its limitations and uncertainty regarding the radii of ions.

$$\Delta G^o_{t(el)} = 166 \times 4.184 \left(\frac{1}{D} - 0.0127 \right) \left(\frac{1}{r_{H^+}} - \frac{1}{r_{AH^+}} \right)$$

r_{H^+} has been taken equal to 0.86 Å [13,14], $r_{phen\ H^+}$ or $r_{bipy\ H^+}$ has been calculated to be 3.70 Å. The change in pK-values in going from water to dmso + H_2O mixtures have been usually ascribed to solute-solvent interactions. The effects due to dielectric constants in case of 'isoelectronic reactions' being negligible. However, in view of the differences of radii of H^+ and AH^+ ions, the effects of the dielectric constants are quite appreciable.

In view of the limitations of Born equations, we have also utilised the 'one layer' solvation model as suggested by Abraham and Lisze[15]

$$\Delta G^o_{t(el)} = \frac{NZ^2}{2}\left(\frac{1}{\varepsilon_1} - 1\right)\left(\frac{1}{a} - \frac{1}{b}\right) + \frac{NZ^2}{2}\left(\frac{1}{\varepsilon_o} - 1\right)\left(\frac{1}{b}\right)$$

a = radius of the ion.

$b = a + r_s$ (r_s = radius of the solvent molecule)

$\varepsilon_1 = 2$ and ε_o = bulk-dielectric constant.

r_{dmso} and r_{H_2O} have been taken from the literature[15].

$r_{dmso + H_2O}$ has been assumed to vary with solvent compositions.

As expected, the differences between $\Delta G^o_{t(el)}$ values calculated using Born equation and Abraham's[15] equation are quite large. The use of Born equation or other modified equations, which are appreciable to ions having spherical radii, in case of flat molecular ions like phenH^+ or bipyH^+ is likely to introduce some error. However, the limitations of the Born equation or other equations with adjusted radii or dielectric constant values are well-known[16]. However, there are also uncertainties in the radii values of simple spherical ions. The ion-dipole interactions may also be quite appreciable.

But whatever may be the method of calculating the $\Delta G^o_{t(el)}$ values, $\Delta G^o_{t(non\ el)}$ have been found to increasingly negative (Table 6) indicating the inceased basicity of the solvent mixtures compared to H_2O. It is known that dmso is basic in nature and the dmso + H_2O mixtures are likely to be more basic than H_2O. But the correction factor ($-\log U_H$) increases as the percentage of organic solvent increases reaches a maximum at about 80 wt% of dmso and then decreases again. This means that the basicity is maximum at about 80 wt% of dmso.

Since the $\Delta G^o_{t(H^+)}$ of transfer or 'medium effect' from water to dmso + H_2O mixtures would enable us to have better insight regarding the solvent basicity and ion-solvent interactions, attempts have been made to determine the $\Delta G^o_{t(H^+)}$ values utilizing the free-energies of transfer for the reaction (1). Since the work has been carried out in very dilute solutions, the solutions may be regarded to be their standard states.

Thus,

$$\Delta\Delta G^o_{t(1)} = \Delta G^o_{s(1)} - \Delta G^o_{w(1)}$$

$$= \Delta G^o_{t(A)} + \Delta G^o_{t(H^+)} - \Delta G^o_{t(AH^+)}$$

$$= \Delta G^o_{t(H^+)} - \Delta G^o_{t(el)(AH^+)}$$

$$\left[\text{as } \Delta G^o_{t(AH^+)} = \Delta G^o_{t(A)} + \Delta G^o_{t(el)(AH)^+} \right]$$

Thus,

$$\Delta G^o_{t(H^+)} = \Delta\Delta G^o_{t(1)} + \Delta G^o_{t(el)(AH^+)}$$

$\Delta G^{o}_{t(H^{+})}$ values from H_2O to dmso + H_2O mixtures have been presented in table 6 using the dissociation constant values of 2,2'-bipyridine and 1,10-phenanthrolene and $\Delta G^{o}_{t(el)(AH^{+})}$ values calculated from Born equation and one layer solvation model as described before. The limitations of determining the free-energies of transfer of ions are well known[16]. We have particularly chosen bipyridine and phenanthroline for the measurement of $\Delta G^{o}_{t(H^{+})}$ as the solute-solvent interactions of the ligands are known to be very small from spectral measurements[17].

Inspite of the limitations of calculating $\Delta G^{o}_{t(el)(AH^{+})}$ (we prefer Born equation than the one layer solvation model), $\Delta G^{o}_{t(H^{+})}$ values calculated using bipy or phen are in good agreement qualitatively and almost quantitatively if one considers the limitations of such measurements. Assuming an error of ± 0.02 (at low percentages of organic solvent) - ± 0.04 (at high percentages) in pK-values, an error to the extent of ± (0.20 to 0.40)KJ are expected. In view of lack of data, it is difficult to compare our $\Delta G^{o}_{t(H^{+})}$ values with those in the literature. However, the values can be compared with the values reported by Wells[18]. The values are qualitatively in agreement but not quantitatively. For better comparison, the $\Delta G^{o}_{t(H^{+})(molar)}$ values have been converted into mole-fraction scale and the values come closer. Still the differences are appreciable about -1.0 KJ at 10.89 wt% - 4.67 KJ at 42 wt% and about -3.8 KJ at about 72 wt% (Table 7). No values are available at higher percentages. The results thus can be regarded to be in good agreement.

In view of the inherent limitations of the various extra thermodynamic models of calculating 'medium effects' of ions arising from simplified generalisation, the method suggested by us is simple and reliable. The $\Delta G^{o}_{t(H^{+})}$ values calculated by Wells[18] in dmso + H_2O mixtures involve the use

$$\Delta G^{o}_{t(H^{+})} = \Delta G^{o}_{t(H^{+})e} + \Delta G^{o}(R\overset{+}{O}H_2)$$

where $\Delta G^{o}_{t(H^{+})e}$ has been calculated by the application of Born equation to the transfer of a sphere containing the tetrahedral structure, $H_3O^{+}(H_2O)_4$ using

$$\Delta G^{o}_{t(H^{+})e} = \frac{Ne^2}{6\, r_{H_2O}} (D_s^{-1} - D_w^{-1})$$

r_{H_2O} is the radius of water ions. The reactions as suggested by Wells implies a change in radius values in mixed solvents. The generalisations and the use of data obtained at high ionic strengths are hardly justifiable for the determination of 'medium effects'. The $\Delta G^{o}_{t(H^{+})}$ values are increasingly negative indicating the spontaneity for the transfer of H^{+} ions in mixed solvents. Thus the mixed solvents appear to be more basic compared to water. However, $\Delta G^{o}_{t(H^{+})}$ increases above 80 wt% of dmso indicating that 'the basicity' decreases beyond this region which is in good accord with the observed 'Correction factor' values.

Though it is hardly possible to throwlight on the solvent structures from the limited data, but attempts can be made.

It is expected that dmso would first enhance the three-dimensional polymeric structure of water but unlike the alcohol + water mixtures, the maximum structure formation has been reported to be in the region of $X_{dmso} \approx 0.35$ or higher[19,20]. The changes of other physico-chemical properties are also in the region $X_{dmso} \approx$ 0.35 to 0.50[19-22].

It is likely that after initial structure formation breakdown of water-structure and dissociation of dmso and disruption of water structure take place with concommittant formation of hydrogen-bonded dmso + H_2O system upto about 80 wt% of dmso. Beyond this region, disruption of dmso + H_2O occurs. That is why the changes in physico-chemical properties occur in this region. The $- \Delta G^o_{t(H^+)}$ or 'correction factor' ($- \log U_H$) is also maximum indicating the maximum solvent basicity in this region.

Table - 1

Correction factor of dmso + H_2O mixtures

Wt% of dmso	Mole-fraction	$\frac{1}{D} \times 10^2$	Correction factors
1	2	3	4
10.87	0.027	1.28	- 0.02
21.53	0.060	1.30	- 0.07
32.02	0.098	1.31	- 0.14
42.28	0.144	1.32	- 0.28
52.35	0.202	1.35	- 0.46
62.24	0.280	1.39	- 0.66
71.94	0.371	1.45	- 0.89
81.46	0.503	1.55	- 1.14
90.81	0.692	1.72	- 1.03

Table - 2

Dissociation Constants of 2,2'-bipyridine at 32.02% by wt% of dmso

(pH-metric)

Concentration of 2,2'-bipyridine soln. = 5 X 10^{-3} mol dm^{-3}

(Temp = 298 K)

Fraction of the ligand neutralised (10^{-3}mol dm^{-3})	Meter readings	pH-after Correction	pK	Average pK
1	2	3	4	5
1.5	4.35	4.21	3.84	
2.0	4.17	4.03	3.85	
2.5	3.99	3.85	3.85	3.85
3.0	3.82	3.68	3.86	
3.5	3.63	3.49	3.86	

Table - 3

Dissociation Constants of 2,2'-bipyridine at 32.02% by wt of dmso
(Spectrophotometric)

Temp = 298 K Cell length = 1 cm.

Analytical wave length = 300 nm

Optical density of the molecular form (d_M) = 0.062

Optical density of the ionic form (d_I) = 0.418

Meter reading	pH after correction	Observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.21	4.07	0.191	0.129	0.227	- 0.24	3.83
4.03	3.89	0.234	0.172	0.184	- 0.03	3.86
3.91	3.77	0.255	0.187	0.163	0.06	3.83
3.80	3.66	0.275	0.213	0.143	0.17	3.83
3.75	3.61	0.287	0.225	0.131	0.25	3.85
3.66	3.52	0.300	0.238	0.118	0.30	3.82

Average pK = 3.83 ± 0.01

Average pK value from O.d.'s at 300 nm = 3.83 ± 0.01.

Table - 4

Dissociation Constants of 1,10-phenanthroline at 32.02% by wt of dmso

(spectrophotometrically)

Temp = 298 K

Analytical wave length = 310 nm

Optical density of the molecular form (d_M) = 0.235

Optical density of the ionic form (d_I) = 1.17

Meter reading	pH after correction	Observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.49	4.35	0.730	0.495	0.440	0.05	4.40
4.38	4.24	0.780	0.545	0.390	0.14	4.38
4.25	4.11	0.832	0.597	0.338	0.25	4.36
4.16	4.02	0.885	0.650	0.285	0.36	4.38
4.11	3.97	0.900	0.665	0.270	0.39	4.36
4.06	3.92	0.940	0.705	0.230	0.49	4.41

Average pK = 4.38 ± 0.01

Average pK value from O.d.'s at 315 nm = 4·38 ± 0·01

Table - 5

Dissociation constants of 2,2'-bipyridine and 1,10-phenanthroline in dmso + water mixtures

Temp = 298K

	2,2'-bipyridine			1,10-phenanthroline		
Wt%	pK(pH-metric)	pK(Spectro-photometric)	Average	pK(pH-metric)	pK(Spectro-photometric)	Average
10.87	4.17	4.21	4.19	4.69	4.68	4.69
21.53	4.00	4.02	4.01	4.55	4.53	4.54
32.02	3.85	3.83	3.84	4.42	4.38	4.40
42.28	3.70	3.72	3.71	4.28	4.20	4.24
52.35	3.44	3.40	3.42	3.99	3.93	3.96
62.24	3.17	3.11	3.14	3.73	3.68	3.71
71.94	2.72	2.66	2.69	3.46	3.42	3.44
81.46	2.30	2.24	2.27	3.14	3.18	3.16
90.81	2.23	2.15	2.19	3.35	3.41	3.38

Table - 6

Free-energy of transfer of Protons and related properties in dmso + H_2O mixtures.

Temp = 298K.

Wt% of dmso	ΔG^o_{t}(K Joules)		$\Delta G^o_{t(el)}$(KJoules)				$\Delta G^o_{t(H^+)}$ (KJoules)					
	Bipy	Phen	A		B		A			B		
			r = 0.86	r = 3.70	r = 0.86	r = 3.70	Bipy	Phen	Average	Bipy	Phen	Average
10.87	- 1.60	-2.05	0.08	0.02	5.39	1.17	- 1.58	-2.03	- 1.81	-0.43	-0.88	-0.66
21.53	- 2.62	-2.91	0.24	0.06	10.09	2.29	- 2.56	-2.85	- 2.71	-0.33	-0.62	-0.48
32.02	- 3.59	-3.71	0.32	0.08	14.50	3.30	- 3.51	-3.63	- 3.55	-0.29	-0.41	-0.35
42.28	- 4.34	-4.62	0.40	0.09	18.62	4.27	- 4.25	-4.53	- 4.39	-0.07	-0.35	-0.21
52.35	- 5.99	-6.22	0.65	0.15	23.29	5.19	- 5.84	-6.07	- 5.96	-0.80	-1.03	-0.92
62.24	- 7.59	-7.65	0.97	0.23	26.35	6.40	- 7.36	-7.42	- 7.39	-1.19	-1.25	-1.22
71.94	-10.15	-9.19	1.45	0.34	29.74	7.24	- 9.81	-8.85	- 9.33	-2.91	-1.95	-2.43
81.16	-12.55	-10.78	2.26	0.53	32.94	8.07	-12.02	-10.25	-11.14	-4.48	-2.71	-3.60
90.81	-13.00	- 9.53	3.63	0.84	36.28	9.28	- 12.16	-8.69	-10.43	-3.52	-0.25	-1.89

A = Calculated using Born Equation

B = Calculated using one layer continum model.

Table - 7

$-\Delta G^{o}_{t(H^{+})}$ (KJoules) (mol-fraction scale)

Wt% of dmso	Wells	Our work
10.89	3.01	2.00
21.53	5.60	3.09
32.02	7.90	4.14
42.28	9.90	5.23
52.35	11.70	7.06
62.24	13.70	8.80
71.94	14.90	11.10
81.46	-	13.35
90.81	-	13.17

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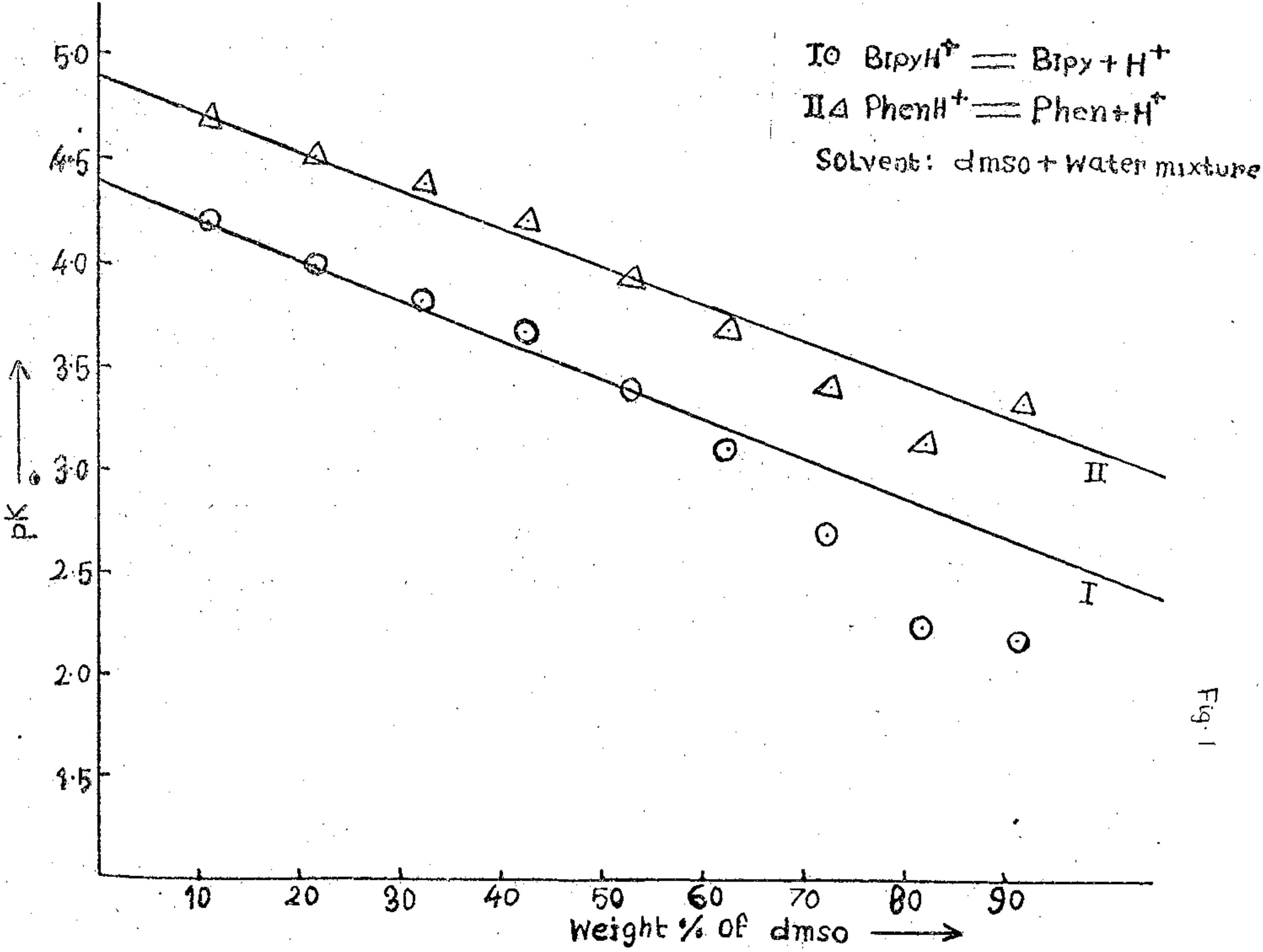
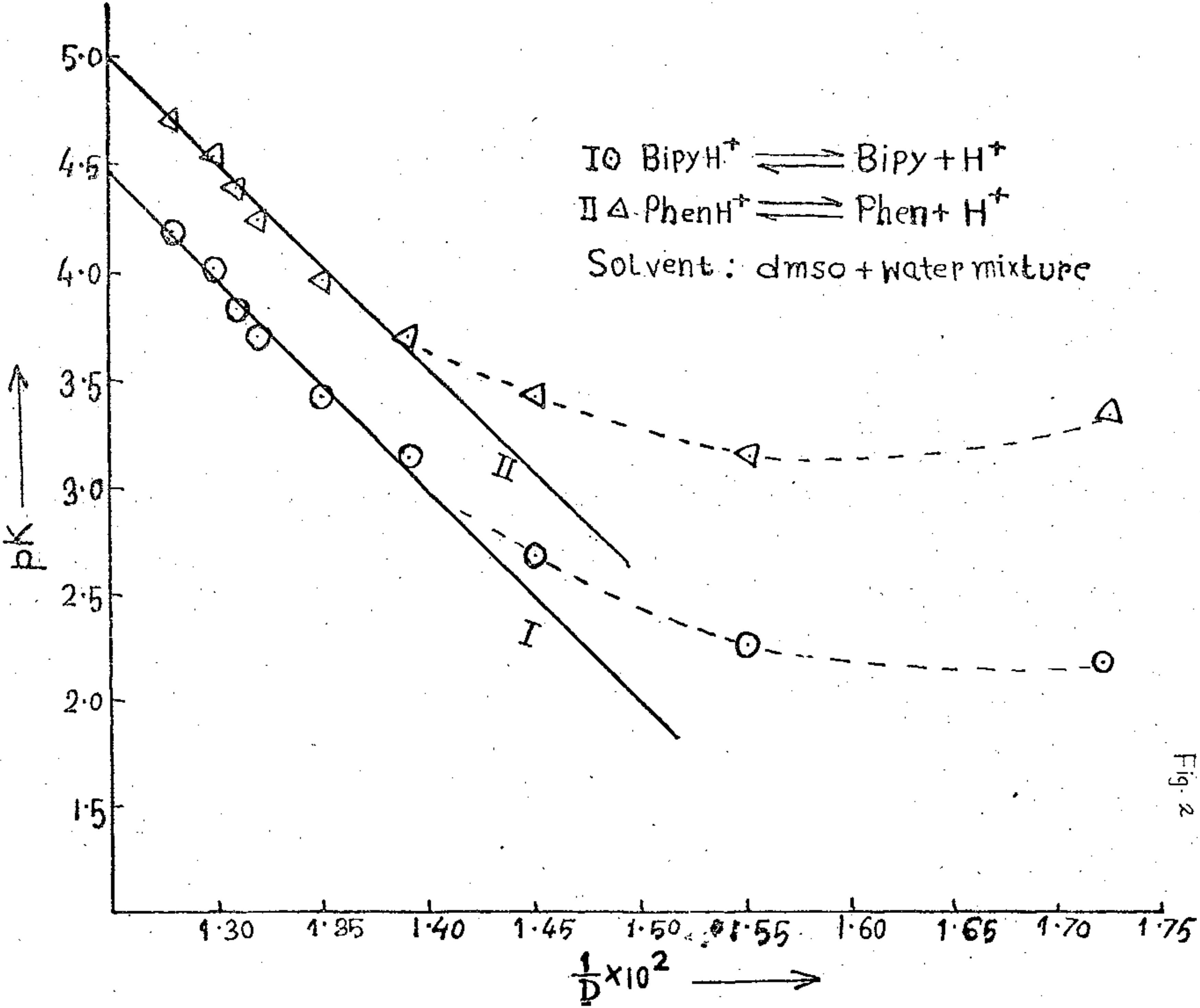

I ○ BipyH$^+$ ⇌ Bipy + H$^+$
II △ PhenH$^+$ ⇌ Phen + H$^+$
Solvent: dmso + water mixture
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
pK
10
20
30
40
50
60
70
80
90
Weight % of dmso
II
I

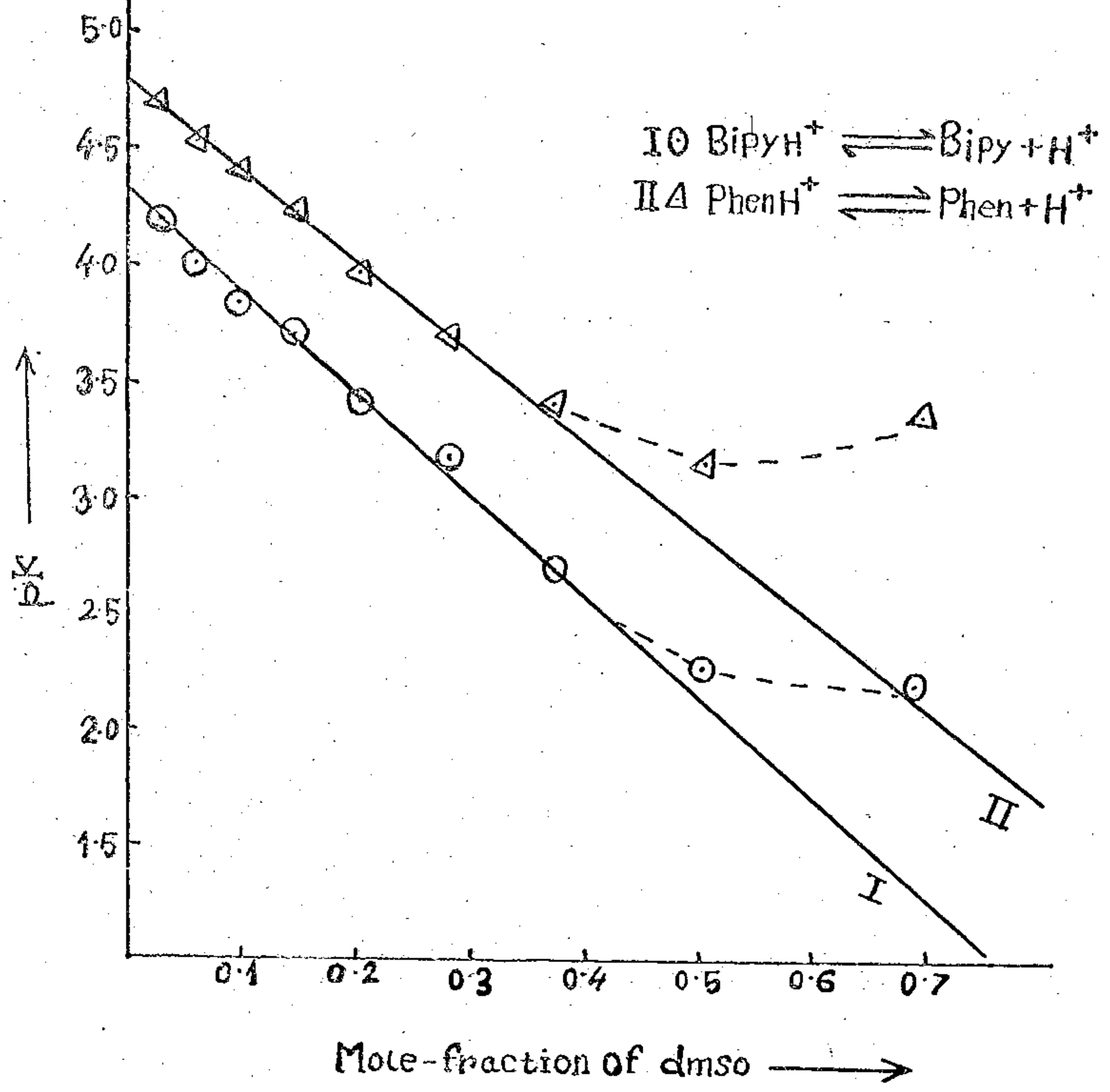
Fig. 1



I ⊙ BipyH$^+$ ⇌ Bipy + H$^+$
II △ PhenH$^+$ ⇌ Phen + H$^+$
Solvent : dmso + water mixture
pK
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·30
1·35
1·40
1·45
1·50
1·55
1·60
1·65
1·70
1·75
$\frac{1}{D} \times 10^2$
II
I

Fig. 2

Fig. 3


I ⊙ $BipyH^+ \rightleftharpoons Bipy + H^+$
II △ $PhenH^+ \rightleftharpoons Phen + H^+$
pK
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
0·1
0·2
0·3
0·4
0·5
0·6
0·7
I
II
Mole-fraction of dmso

Section - III

The effects of solvent structure and solute-solvent interactions on equilibrium constants and rate constants of chemical reactions in non-aqueous and mixed solvents are not well-understood. The effects could be investigated both by the alteration of the solvent composition and by variation of solute structure and charge type. Studies on the acid-base equilibria in different non-aqueous and their binary mixtures are particularly suited to study the role of the solvents and their solute-solvent interactions. The dissociation constants of ligands in different non-aqueous (mostly protic) solvents and their binary mixtures have been widely studied and attempts have been made to determine the free-energies of transfer of single ions. However, such studies in dipolar aprotic solvents like dmf and hydrogen-bonding amide solvent like formamide and their binary aqueous mixtures are relatively few.

This prompted us to study the dissociation equilibria for the "isoelectric" reactions of the type

$$AH^+ \rightleftharpoons A + H^+$$

where A = 2,2'-bipyridine (bipy), 1,10-phenanthroline in dmf + water and formamide + water mixtures pH-metrically and spectrophotometrically.

Attempts have been made to explore the role of the solvents and evaluate the values of the free-energies of transfer of H^+ ions from water to dmf + water and formamide + water mixtures.

The results are reported in the present section.

Experimental

2,2'-bipyridine and 1,10-phenanthroline (G.R.E. Merck) were used as such, Formamide (G.R.E. Merck) were dried over freshly ignited quicklime for several hours and then distilled under reduced pressure. N,N'-dimethylformamide i.e. dmf (E. Merck) was purified by fractional distillation under reduced pressure after drying the solvent over freshly ignited quicklime for several hours. The distilled solvents were used within 24 hours.

$HClO_4$, Caustic soda and other chemicals were of analar grade. Doubly distilled water from all glass distilling set was used to prepare the solutions.

All the ligands absorb strongly in the U.V. region and the absorption maxima of the ligands are 280 (molecular) nm and 301 (ionic) nm for 2,2'-bipyridine and 264 (molecular and 272(ionic) nms for 1,10-phenanthroline. The solvents also absorbed strongly in the U.V. region and optical density measurements are possible only at longer wave lengths. We have selected 300 and 305 nms for 2,2'-bipyridine and 310 and 315 nms for 1,10-phenanthroline.

The pK-values of the ligands were determined pH-metrically and spectrophotometrically in the same way as described in the previous sections.[1-3]

In formamide solutions, the optical density corresponding to ionic forms of the ligands could not be determined as a white precipitate was observed with the addition of considerable amount of $HClO_4$ to formamide. Therefore, pK-values in formamide solutions were determined only pH-metrically.

The weight percentages of organic solvents at 298K were calculated from the volumes of the solvents and their density values[4].

The dielectric constants for dmf + water mixtures and formamide + water mixtures were taken from the literature[5,6]. The optical density readings were recorded with a Beckman DU-2 spectrophotometer maintained at 298K. The pH-meter readings were noted with a ECIL expanded scale pH-meter (having an accuracy of ± 0.01) and used the glass and the calomel electrode.

Determination of H^+ ion in dmf + water and formamide + water mixtures

For the determination of H^+ ion concentrations in mixed solvents, the glass and the Calomel electrodes should be properly calibrated in the solvent in question and the appropriate correction factors are to be determined. Due to moderately large dielectric constants homoconjugation and ion-pairing are extensive in dmf-medium which can be avoided only at very low concentrations of salts and acids. However, it is always preferable to determine the dissociation constants of acids and bases at very low ionic strengths and in absence of enert electrolytes so that the thermodynamic dissociation constants could be determined.

The glass electrode is known to function satisfactorily in dmf. Kolthoff and co-workers[7] used 4-chloro-2,6-dinitrophenol and

2,6-dinitrophenol as standard acids and used buffer mixtures of these acids and their tetramethylammonium salts for calibration of glass electrodes. However, there is almost no report of the used of glass electrodes in formamide solutions.

We, however, used the glass and the Calomel electrodes both in dmf + H_2O and formamide + H_2O mixtures. For calibration of electrodes, the same procedure suggested by Van Uitert[8] and extensively used by Lahiri, Aditya and co-workers[9,10] was followed. The instrument was first standardized with potassium-hydrogen phthalate (0.05 mol dm^{-3}) 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 the meter readings of 10^{-4} mol dm^{-3} $HClO_4$ and other solutions with unknown H^+ ion concentrations were taken. The process was repeated to examine the reproducibility of the results. The calibration is to be performed in each solvent composition and for each set of measurement.

After the measurement, the glass electrode was dipped in 1N HCl for ten minutes and then kept in distilled water. The correction factors (log U_H) determined in the way described previously, are given in the Table 1.

Results :

The thermodynamic dissociation constants for the reaction(1) is represented by

$$K_T = \frac{a_A \times a_{H^+}}{a_{AH^+}} = \frac{c_A \times c_{H^+}}{c_{AB^+}} \times \frac{f_A \times f_{H^+}}{f_{AH^+}} \approx \underset{\text{(in very dilute solutions)}}{\frac{c_A \times c_{H}{}^{+}}{c_{AH^+}}} \quad \ldots (2)$$

$$\text{Thus, } pK_T = pH + \log \frac{[AH^+]}{[A]} \qquad \ldots \quad (3)$$

$$= B + \log U_H + \log \frac{[AH^+]}{[A]} \qquad \ldots \quad (4)$$

$$= B + \log U_H \pm \log \frac{d - d_M}{d_1 - d} \qquad \ldots \quad (5)$$

the terms have the usual significance as described previously[2,3]

$$\text{Moreover, } [H^+]_{Total} = [H^+] + [AH^+] \qquad \ldots \quad (6)$$

$$\text{and } [A]_{Total} = [A] + [AH^+] \qquad \ldots \quad (7)$$

Thus, with the use of the appropriate values, pK-values could be determined. Tables 2 - 6 gives the result of dissociation constants in the mixed solvents. The average of pK-values are recorded in Table 7.

The ionic strength of the solutions range between 1.5 - 3.5 x 10^{-3} mol dm^{-3}.

Discussions :

Since the pK-values are determined at low concentrations of acid and ionic strengths, these are regarded to be thermodynamic values. Furthermore, since the solutions are dilute, the "medium effect" could be easily determined as ${}_s\gamma_i \rightarrow 1$ and $\gamma_i = {}_m\gamma_i \cdot {}_s\gamma_i \approx {}_m\gamma_i$ This is particularly important to elucidate the role of the solvents.

The results (Table 7) show that the pK-values of 2,2-bipyridine and 1,10-phenanthroline decrease with the addition of organic solvents but the change is appreciable in formamide + water mixtures at the begining but the subsequent changes are small.

It is obvious that the greater solubility of the ligands in organic solvents and the solvational properties of bipy H^+, Phen H^+ and H^+ ions are responsible for the changes in pK-values[2] but the solubility of bipy is probably much higher than phen at higher percentages of dmf + water mixtures. Moreover, the pK of 1,10-phenanthroline decreases, reaches a maximum at about 80 wt% of organic solvents and then decreases. No such behaviour is observed in case of 2,2'-bipyridine.

However, the pK-values decrease , reach minimum at about 40 wt% and then increase again in case of formamide + water mixture (Figs. 1,2).

The pK-values when plotted against mole-fraction or $\frac{1}{D}$ show linearity at best upto 50 wt% beyond which considerable deviations occur (Figs 3 - 6). This is particularly surprising in case of formamide + water mixtures when the dielectric constants are higher than 78.5. It is obvious that the specific solute-solvent interactions are of great importance in determining the pK-values.

The ligands are expected to be more basic in these basic solvents and basically should be greater in formamide + water mixtures which is not actually observed.

The changed behaviour of the ligands are due to differences in the characters of the solvents.

Formamide is highly basic hydrogen-bonding solvent (μ = 3.75D) with high dielectric constant (109.5) and whereas dmf is weakly basic dipolar aprotic solvent with low dielectric constant. Though the dielectric constant of dmf is comparable to that of methanol but the changes in pK-values are different in these two solvents due to differences in solute-solvent interactions. The bipy H^+ and phen H^+ are likely to be stabilised by hydrogen bonding in these solvents. The probability of hydrogen-bond formation by bipy or phen will diminish with increasing concentrations of dmf (but not in case of formamide). In both cases, however, solute-solvent interactions and dispersion forces would be high but dipole-dipole interactions are greater in cases of phen (μ = 4.11D)[11,12] than that of trans bipy (μ = 0.91D)[11,12]. Thus, the total effects of ion-dipole interactions and dipole-dipole interactions would determine the 'medium effects'[13].

In order to throw light on solvent basicity and ion-solvent interactions, it is necessary to dissect ΔG^o_t into $\Delta G^o_{t(el)}$ and $\Delta G^o_{t(nonel)}$. Inspite of the limitations, the simple Born equation[14] can be utilised to calculate the $\Delta G^o_{t(el)}$ for the reaction (1) using the relation

$$\Delta G^o_{t(el)} = 166 \times 4.184 \left(\frac{1}{D} - 0.0127 \right) \left(\frac{1}{r_{H^+}} - \frac{1}{r_{AH^+}} \right)$$

r_{H^+} has been taken equal to 0.86A°[15,16] and $r_{phen\,H^+}$ or r_{bipyH^+} has been calculated to be 3.70 Å. It is apparent that the electrostatic contributions are considerable even in case of isoelectric reaction(1) due to the differences in radii of ions.

In view of the limitations of Born equation, one layer solvation model was also utilised[17]

$$\Delta G^{o}_{t(el)} = \frac{NZ^2}{2} \left(\frac{1}{\varepsilon_1} - 1 \right) \left(\frac{1}{a} - \frac{1}{b} \right) + \frac{NZ^2}{2} \left(\frac{1}{\varepsilon_o} - 1 \right) \left(\frac{1}{b} \right)$$

$\varepsilon_1 = 2$; a = crystallographic radii of ions

b = a + solvent radius.

ε_o = bulk dielectric constant,

r_{H_2O}, r_{dmf} and $r_{formamide}$ have been taken from the literature. $r_{dmf + H_2O}$ and $r_{formamide + H_2O}$ have been assumed to vary with solvent composition.

The Born equation and one layer model, however, give widely divergent results and we prefer simple Born equation.

It has been suggested that greater negative values of $\Delta G^{o}_{t(nonel)}$ indicate increased basicity of the mixed solvents compared to water[18]. The $\Delta G^{o}_{t(nonel)} = [\Delta G^{o}_{t} - \Delta G^{o}_{t(el)}]$ values have been found to be increasingly negative in dmf + H_2O mixtures indicating that the basicity increases with increasing dmf content. But in case of formamide + H_2O mixtures, $-\Delta G^{o}_{t(nonel)}$ is maximum at about 40 wt%, and then decreases which means that the basicity is maximum at about 40 wt%. The values of $-\Delta G^{o}_{t(nonel)}$ is not consistent with the correction factors log U_H values. The log U_H values indicate that the basicity increases upto 80 wt% of dmf and then decreases in case of dmf + H_2O mixtures whereas the basicity continually increases in case of formamide + H_2O mixtures. The formamide + water mixtures are much more basic than those of the corresponding dmf + H_2O mixtures as well as alcohol + water mixtures.

In order to have better insight regarding the basicity of the solvent mixtures and ion-solvent interactions, attempts have been made to determine the free energies of transfer of hydrogen ions $\Delta G^{o}_{t(H^+)}$.

For the reaction (1) we have,

$$\Delta\Delta G^{o}_{t}(1) = \Delta G^{o}_{s}(1) - \Delta G^{o}_{w}(1)$$

$$= \Delta G^{o}_{t(A)} + \Delta G^{o}_{t(H^+)} - \Delta G^{o}_{t(AH^+)}$$

$$= \Delta G^{o}_{t(H^+)} - \Delta G^{o}_{t(el)(AH^+)}$$

$$\left[\Delta G^{o}_{t(AH^+)} = \Delta G^{o}_{t(A)} + \Delta G^{o}_{t(el)(AH^+)} \right]$$

Thus, $\Delta G^{o}_{t(H^+)} = \Delta\Delta G^{o}_{t}(1) + \Delta G^{o}_{t(el)(AH^+)}$

From the experimental $\Delta\Delta G^{o}_{t}(1)$ and calculated $\Delta G^{o}_{t(el)(AH^+)}$ (Born) values, the $\Delta G^{o}_{t(H^+)}$ values in different solvents have been calculated. The results are recorded in tables 8 and 9. Since the ΔG^{o}_{t} value have been determined in very dilute solutions, the solutions may be regarded to be in their respective standard states.

The Born equation or other modified equations are strictly applicable to spherical ions. Thus, the use of Born equation in case of flat molecular ions like Phen H^+ or bipy H^+ may introduce some error. However, the limitations of Born equation or other equations with adjusted radii or dielectric constant values are well-known[19-21]. The uncertainties in the radii values of spherically symmetrical ions are also known.

Inspite of the limitations of calculating $\Delta G^{o}_{t(el)(AH^{+})}$, $\Delta G^{o}_{t(H^{+})}$ values calculated using bipy or phen are in good agreement qualitatively and almost quantitatively in formamide + water and dmf + H_2O mixtures.

It is to be noted that deviations arising from an error in pK-values (± 0.02 pK units at low percentages to ± 0.05 pK units at high percentages) would account for a change in about ± 0.5 KJ in $\Delta G^{o}_{t(H^{+})}$ values. The deviations are rather high in case of formamide + water mixtures and at higher percentages of dmf + water mixtures. The differences in $\Delta G^{o}_{t(H^{+})}$ values in these solvents may be due to differences in solute-solvent interactions.

The comparison of $\Delta G^{o}_{t(H^{+})}$ values however, are not possible due to lack of data.

The $\Delta G^{o}_{t(H^{+})}$ values are negative indicating the spontaneity of transfer of H^{+} ions from water to mixed solvents. This is reasonable in view of the known basicities of dmf and formamide. However, $-\Delta G^{o}_{t(H^{+})}$ increases with increase in dmf becomes maximum in the region 80 - 90 wt% but $-\Delta G^{o}_{t(H^{+})}$ is maximum at about 40 wt% of formamide indicating that the basicity is maximum in this region.

It is, however, difficult to correlate the "medium effects" with the solvent structure. In general, the addition of organic solvent to water first causes the enhancement of three-dimensional polymeric structure of water. Next, disruption of solvent structures (water, dmf etc.) and formation of H_2O-formamide or H_2O-dmf molecules take place and ultimately at higher percentages (above 70% by wt% of formamide and 80% by wt. of dmf) disruption of H_2O-organic solvent bond takes place. Thus the marked changes in the solvent structures take place at about 20 - 30 wt% and 75 - 90 wt% of organic solvents. Therefore, the solute-solvent interactions and basicity maximum would probably be observed in these regions.

Table - 1

Correction factors at various organic solvent

dmf				Formamide			
Wt%	Mole-Fraction	$\frac{1}{D} \times 10^2$	Correction factor	Wt%	Mole-Fraction	$\frac{1}{D} \times 10^2$	Correction factor
0	0	1.27	–	0	0	1.27	–
9.52	0.025	1.31	- 0.13	11.17	0.048	1.21	- 1.52
19.14	0.055	1.34	- 0.29	22.06	0.103	1.14	- 1.88
28.87	0.091	1.38	- 0.46	32.67	0.163	1.08	- 2.20
38.64	0.135	1.45	- 0.75	43.01	0.232	1.04	- 2.42
48.64	0.180	1.52	- 0.95	53.10	0.312	0.99	- 2.64
58.68	0.259	1.63	- 1.13	62.94	0.405	0.95	- 2.80
68.84	0.352	1.76	- 1.35	72.54	0.513	0.92	- 3.01
79.11	0.483	1.96	- 1.52	81.91	0.644	0.90	- 3.19
89.58	0.675	2.24	- 1.36	91.06	0.801	0.89	- 3.40

Table - 2

Dissociation constants of 2,2'-bipyridine at 48.64% by wt% of dmf

Concentration of 2,2'-bipyridine soln.=5 X 10^{-3} mol dm^{-3}

Temp = 298K

Fractions of the ligand neutralised (10^{-3} mol dm^{-3}) 1	Meter readings 2	pH after correction 3	pK 4	Average pK 5
1.5	3.96	3.01	2.64	
2.0	3.78	2.83	2.65	2.64
2.5	3.59	2.64	2.64	
3.0	3.40	2.45	2.63	
3.5	3.22	2.27	2.64	

Table - 3

Dissociation constants of 1,10-phenanthroline at 38.64% by wt% of dmf.

(pH-metric)

Concentration of 1,10-phenanthroline soln = 5 X 10^{-3} mol dm^{-3}

Fraction of the ligand neutralised (10^{-3} mol dm^{-3})	Meter readings	pH after correction	pK	Average pK
1.5	4.64	3.89	3.52	
2.0	4.46	3.71	3.53	3.53
2.5	4.29	3.54	3.54	
3.0	4.10	3.35	3.53	
3.5	3.89	3.14	3.51	

Table - 4

Dissociation constants of 2,2'-bipyridine at 53.10% by wt. of Formamide

Concentration of 2,2'-bipyridine soln = 5 X 10^{-3} mol dm^{-3}

Temp = 298K

Fraction of the ligand neutralised (10^{-3} mol dm^{-3}) 1	Meter readings 2	pH after correction 3	pK 4	Average pK 5
1.5	6.15	3.51	3.14	
2.0	5.97	3.33	3.15	
2.5	5.80	3.16	3.16	3.15
3.0	5.61	2.97	3.15	
3.5	5.43	2.79	3.16	

Table - 5

Dissociation constants of 1,10-phenanthroline at 53.10% by wt. of formamide

Concentration of 1,10-phenanthroline soln.= 5 X 10^{-3} mol dm^{-3}

Fraction of the liquid neutralised (10^{-3} mol dm^{-3})	Meter readings	pH after correction	pK	Average pK
1	2	3	4	5
1.5	6.33	3.69	3.32	3.32
2.0	6.14	3.50	3.32	
2.5	5.96	3.32	3.32	
3.0	5.78	3.14	3.32	
3.5	5.60	2.96	3.33	

Dissociation constants of 1,10-phenanthroline at 38.64% by wt% of dmf

(Spectrophotometrically)

Temp = 298K

Cell length = 1 cm.

Analytical wavelength = 310 nm.

O.d. of the molecular form (d_M) = 0.210

O.d. of the ionic form (d_I) = 1.17

Meter reading	pH after correction	observed d	$d - d_M$	$d_I - d$	$\log \frac{d - d_M}{d_I - d}$	pK
1	2	3	4	5	6	7
4.52	3.77	0.535	0.325	0.635	- 0.29	3.48
4.45	3.70	0.580	0.370	0.590	- 0.20	3.50
4.37	3.62	0.615	0.405	0.555	- 0.14	3.48
4.24	3.49	0.690	0.480	0.475	+ 0.01	3.50
4.19	3.44	0.716	0.506	0.454	+ 0.05	3.49
4.14	3.39	0.750	0.540	0.420	+ 0.11	3.50

Average pK value from O.d. reading = 3.49 ± 0.01

Table - 7

Wt% of dmf	pK_T of 2,2'-bipy			pK_T of 1,10-phen			Wt% of Formamide	pK_T of bipy (pH-metric)	pK_T of 1,10-phen (pH-metric)
	pH-metric	Spectrophotometric	Average	pH-metric	Spectrophotometric	Average			
0	4.47		4.47	5·05		5.05	0	4.47	5.05
9.52	4.07	4.03	4.05	4.48	4.45	4.47	11.17	3.23	3.69
19.14	3.75	3.71	3.73	4.17	4.14	4.16	22.06	3.13	3.50
28.87	3.42	3.36	3.39	3.91	3.87	3.89	32.67	3.09	3.31
38.64	2.98	2.92	2.95	3.53	3.49	3.51	43.01	3.08	3.26
48.64	2.64	2.60	2.62	3.30	3.25	3.28	53.10	3.15	3.32
58.68	2.34	2.27	2.31	3.03	2.97	3.00	62.94	3.25	3.41
68.84	1.82	1.74	1.78	2.81	2.75	2.78	72.54	3.32	3.44
79.11	1.46	1.38	1.42	2.50	2,42	2.46	81.91	3.43	3.49
89.58	1.28	1.18	1.23	2.66	2.58	2.62	91.06	3.49	3.54

Table - 8

Free-energy of transfer of Protons and related properties in dmf + H_2O mixture
Temp. = 298K

Wt% of dmf	ΔG_t^o (kJoules)		$\Delta G_{t(el)}^o$ (kJoules)				$\Delta G_{t(H^+)}^o$ (kjoules)					
			(A)		(B)		(A)			(B)		
	Bipy	Phen	r = 0.86	r = 3.70	r = 0.86	r = 3.70	Bipy	Phen	Average	Bipy	Phen	Averag
9.52	- 2.40	- 3.31	0.32	0.06	5.55	1.08	- 2.32	- 3.23	- 2.78	- 1.32	- 1.23	- 1.28
19.14	- 4.22	- 5.08	0.57	0.13	10.93	3.25	- 4.09	- 4.95	- 4.52	- 1.97	- 1.83	- 1.90
28.87	- 6.16	- 6.62	0.89	0.21	15.59	3.52	- 5.95	- 6.41	- 6.18	- 2.64	- 3.10	- 2.87
38.70	- 8.67	- 8.79	1.45	0.34	20.02	4.58	- 8.33	- 8.45	- 8.39	- 4.09	- 4.21	- 9.15
48.64	-10.56	-10.10	2.02	0.47	24.20	5.72	-10.09	- 9.63	- 9.86	- 4.84	- 4.38	- 4.61
58.68	-12.32	-11.70	2.91	0.67	28.28	6.86	-11.65	-11.03	-11.34	- 5.46	- 4.84	- 5.15
68.84	-15.35	-12.95	3.96	0.92	31.91	8.23	-14.43	-12.03	-13.23	- 7.12	- 4.72	- 5.92
79.11	-17.40	-14.78	5.57	1.29	35.94	9.26	-16.11	-13.49	-14.80	- 8.14	- 5.52	- 6.83
89.58	-18.49	-13.86	7.91	1.84	39.36	10.32	-16.65	-13.02	-14.83	- 8.17	- 3.54	- 5.86

A = Calculated using Born Equation.

B = Calculated using one layer continum model.

Table - 9

Free-energy of transfer of Protone and related properties in Formamide + H_2O mixtures

Temp. 298K

Wt% of Formamide	ΔG^o_t(Kjoules)		$\Delta G^o_{t(el)}$(kJoules)				$\Delta G^o_{t(H^+)}$(kJoules)					
			A		B		A			B		
	Bipy	Phen	r = 0.86	r = 3.70	r = 0.86	r = 3.70	Bipy	Phen	Average	Bipy	Phen	Average
11.17	-7.07	- 7.75	-0.48	-0.11	-6.31	-0.38	-7.18	-7.86	-7.52	-7.45	- 8.13	- 7.79
22.06	-7.65	- 8.84	-1.05	-0.24	-5.10	-1.09	-7.89	-9.08	-8.48	-8.75	- 9.93	- 9.34
32.67	-7.87	- 9.93	-1.53	-0.36	-7.53	-1.39	-8.23	-10.24	-9.26	-9.26	-11.32	-10.29
43.01	-7.93	-10.21	-1.86	-0.43	-9.52	-1.79	-8.36	-10.64	-9.50	-9.72	-12.00	-10.86
53.00	-7.53	- 9.87	-2.26	-0.52	-11.90	-2.46	-8.05	-10.39	-9.17	-9.99	-12.33	-11.16
62.94	-6.96	- 9.36	-2.58	-0.60	-13.98	-2.78	-7.56	- 9.96	-8.76	-9.74	-12.14	-10.94
72.54	-6.56	- 9.19	-2.82	-0.66	-16.20	-3.44	-7.22	- 9.85	-8.54	-9.90	-12.63	-11.27
91.91	-5.93	- 8.90	-2.98	-0.69	-18.29	-3.74	-6.62	- 9.59	-8.10	-9.67	-12.64	-11.16
91.06	-5.59	- 8.62	-3.06	-0.71	-20.28	-4.40	-6.30	- 9.33	-9.82	-9.99	-13.02	-11.51

A = Calculated using Born Equation

B = Calculated using one layer continum model.

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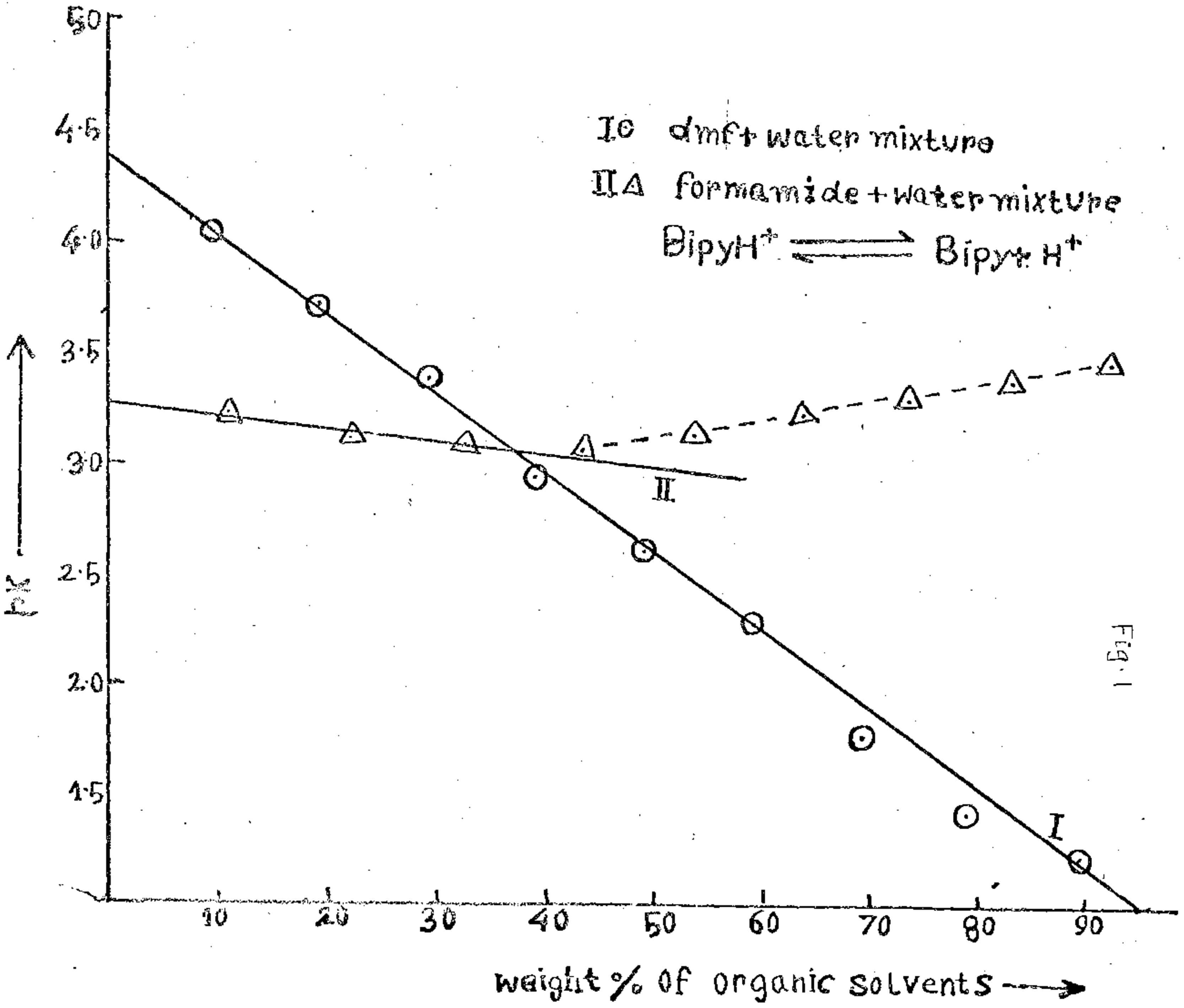


Fig. 1

I ⊙ dmf + water mixture
II △ formamide + water mixture
$BipyH^+ \rightleftharpoons Bipy + H^+$
pK
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
10
20
30
40
50
60
70
80
90
weight % of organic solvents
I
II

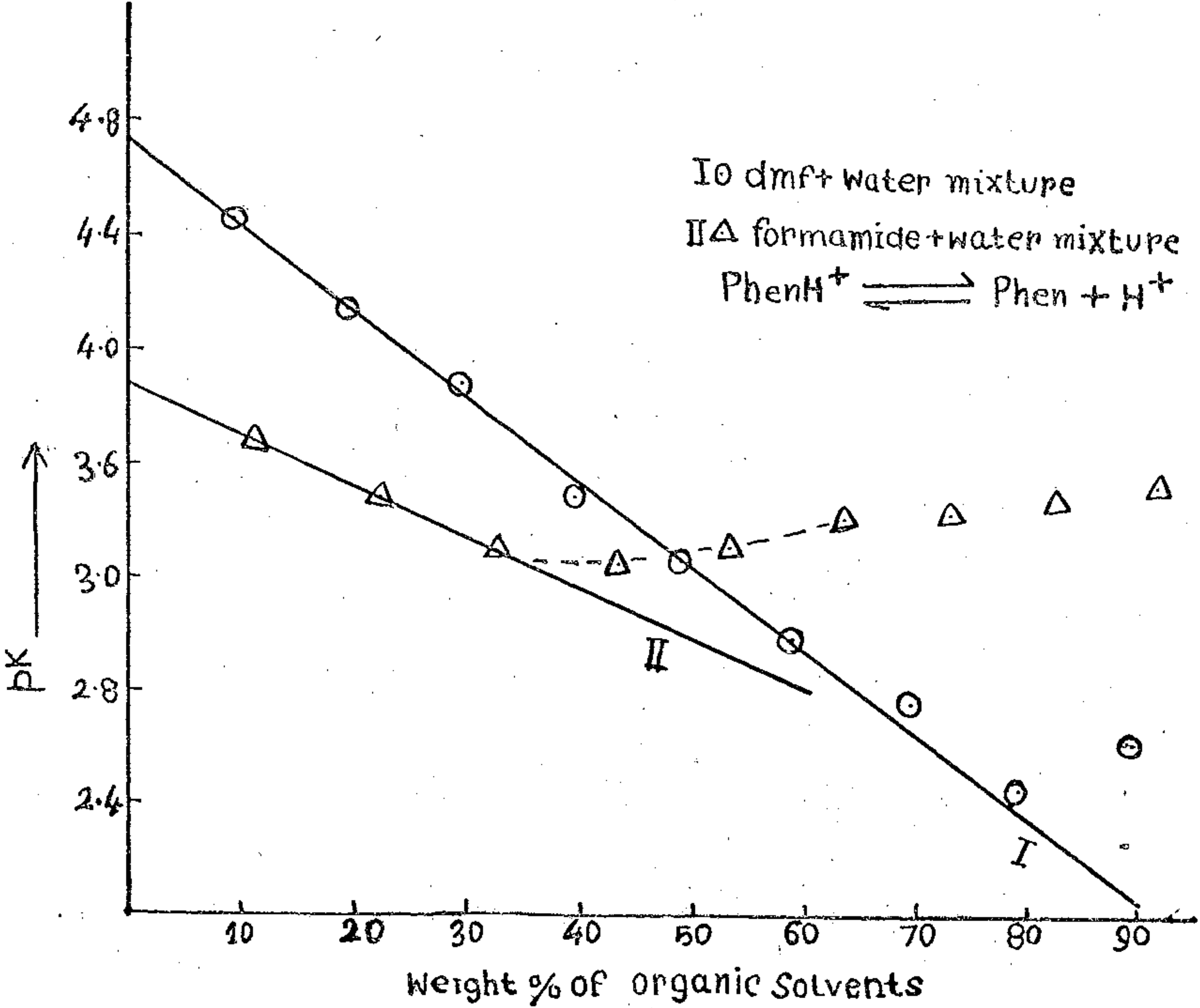
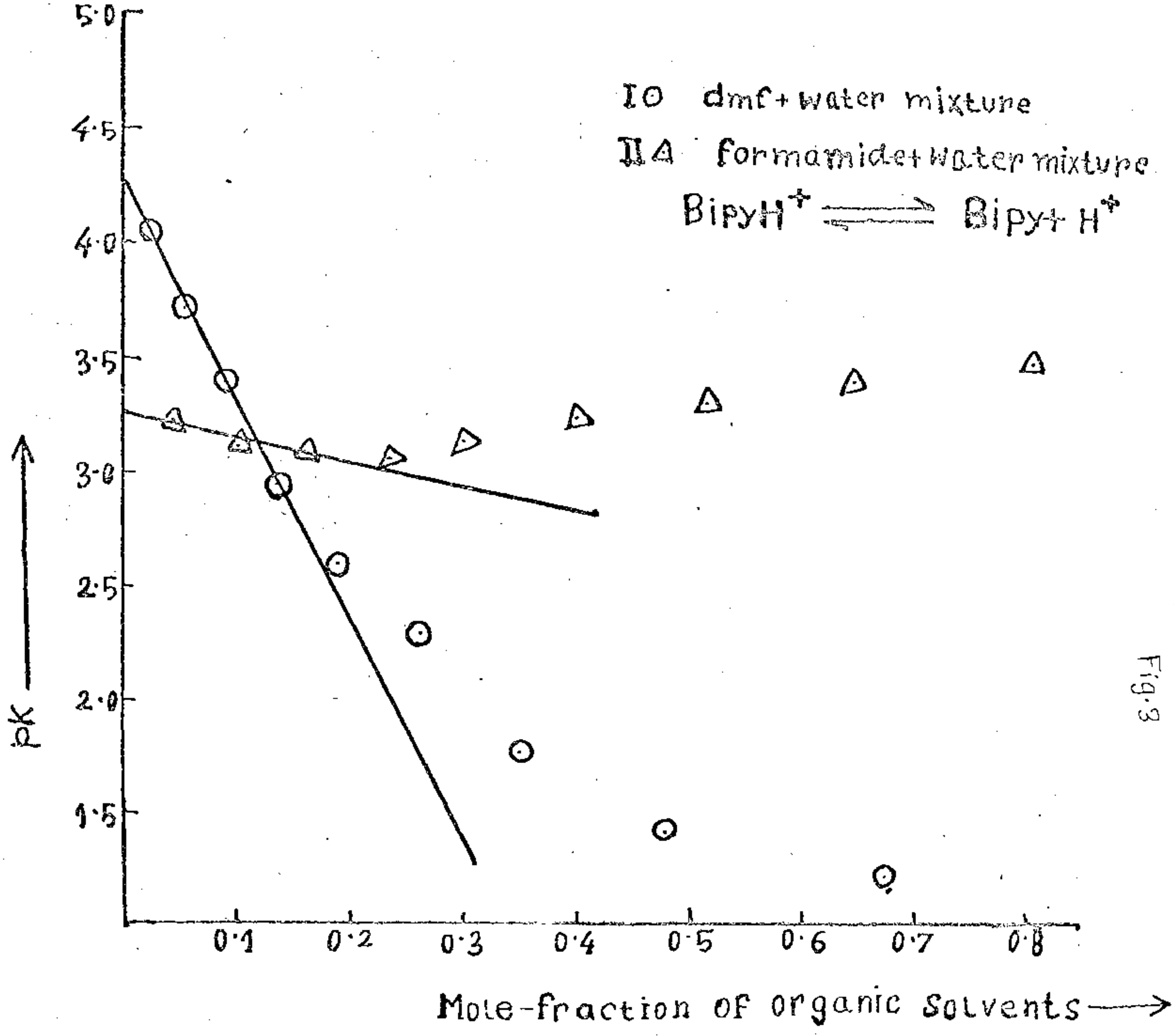

I ⊙ dmf+ water mixture
II △ formamide+water mixture
PhenH⁺ ⇌ Phen + H⁺
pK
4·8
4·4
4·0
3·6
3·0
2·8
2·4
10
20
30
40
50
60
70
80
90
Weight % of organic Solvents
I
II

Fig-2


I ○ dmf + water mixture
II △ formamide + water mixture
$\text{BipyH}^+ \rightleftharpoons \text{Bipy} + \text{H}^+$
pK
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
Mole-fraction of organic Solvents

Fig·3

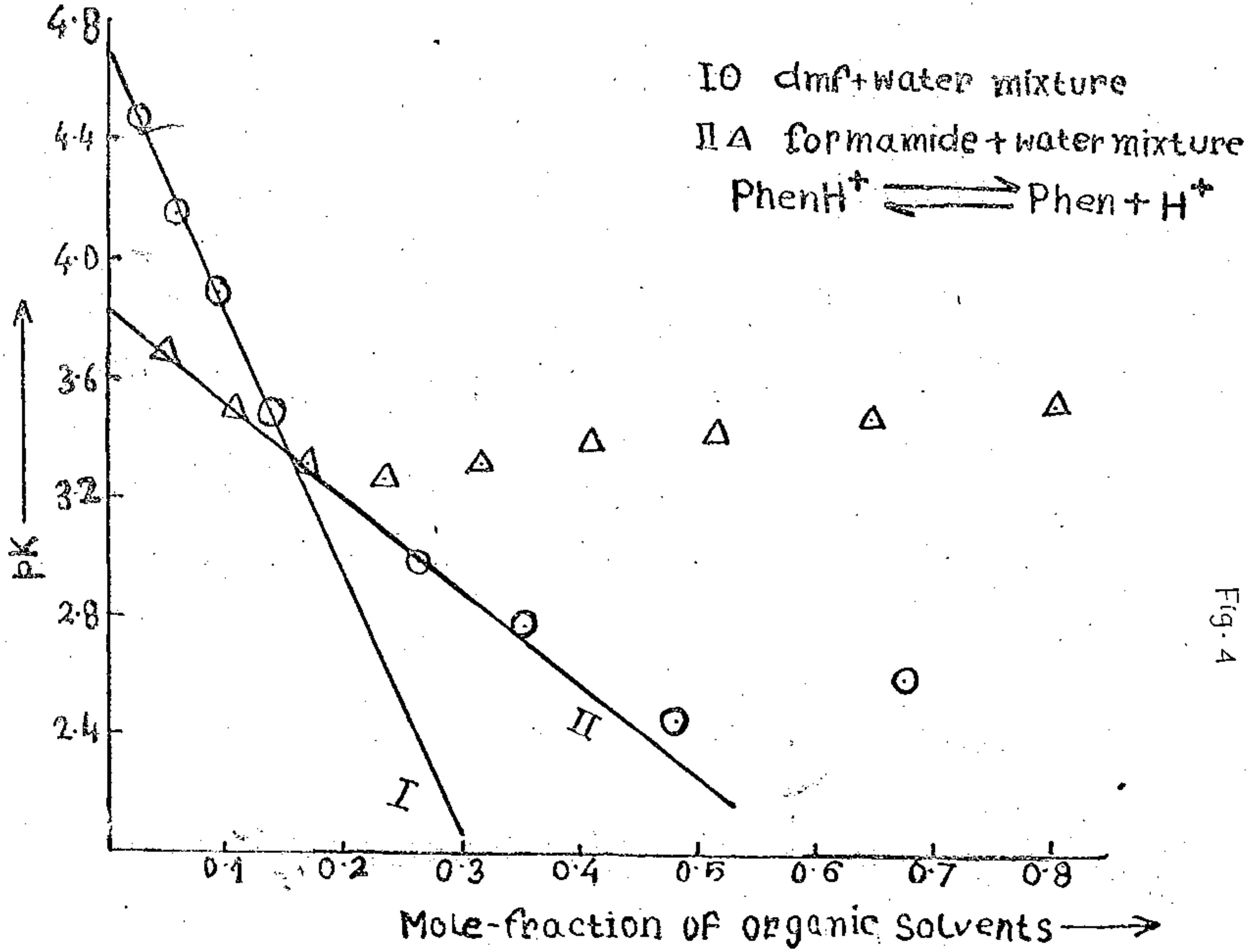

I ○ dmf+water mixture
II △ formamide+water mixture
$PhenH^+ \rightleftharpoons Phen + H^+$
pK
4·8
4·4
4·0
3·6
3·2
2·8
2·4
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
I
II
Mole-fraction of organic solvents

Fig. 4

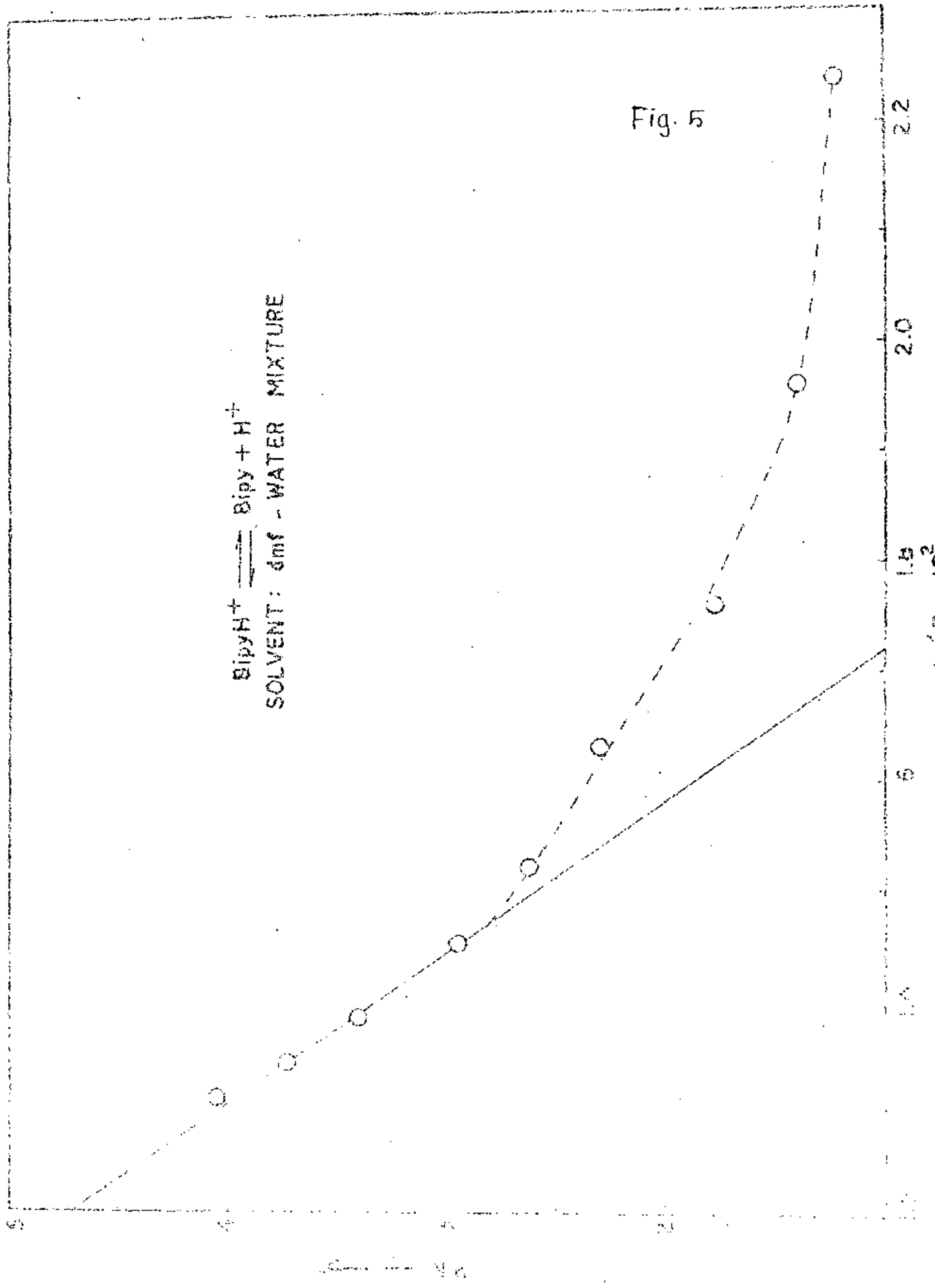


Fig. 5

$BipyH^+ \rightleftharpoons Bipy + H^+$
SOLVENT : dmf - WATER MIXTURE
$1/D \times 10^2$
1.4
1.6
1.8
2.0
2.2

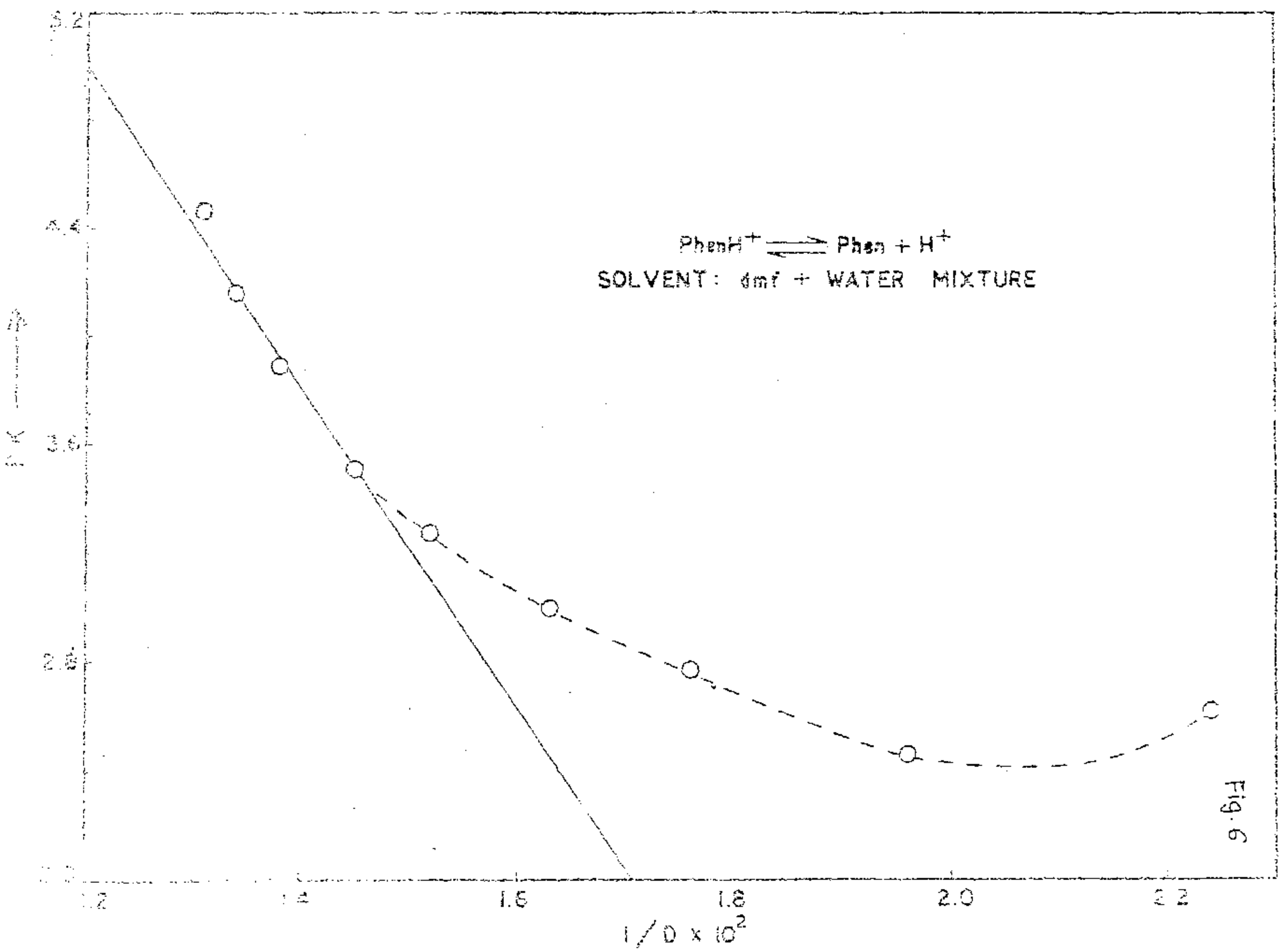

$PhenH^+ \rightleftharpoons Phen + H^+$
SOLVENT : dmf + WATER MIXTURE
pK ⟶
5.2
4.4
3.6
2.8
2.0
1.2
1.4
1.6
1.8
2.0
2.2
$1/D \times 10^2$

Fig. 6

Section - IV

The role of solvents on the dissociation constants of the weak acids are widely studied and relatively known, though clear picture is yet to come. But comparatively little is known about the effect of solvents on the dissociation constants of metal complexes. In order to explore the role of solvents on the dissociation constants of metal chelates, Pal and Lahiri[1] studied the equilibrium constants of ferric salicylate and ferric sulphosalicylate in a number of equidielectric mixtures of different solvent compositions. But owing to lack of fundamental data on dissociation constants of phenolic groups, the effect of solvents could not be predicted.

Hazra, Lahiri and others[2-5] studied the dissociation constants of ferrous-tris-bipyridine complex (ferrodiin) and ferroin in different mixed solvents so as to get informations and insight regarding the effect of solvents on the equilibrium constants of

$$\mathrm{BipyH^+} \rightleftharpoons \mathrm{Bipy + H^+} \qquad (1)$$

$$\mathrm{Febipy_3^{2+} + 3H^+} \rightleftharpoons \mathrm{Fe^{2+} + 3\ bipy\ H^+} \qquad (2)$$

$$\mathrm{Febipy_3^{2+}} \rightleftharpoons \mathrm{Fe^{2+} + 3\ bipy} \qquad (3)$$

Their works gave us the impetus to study the effect of other solvents on the reaction (1), (2) and (3) so that comparative study can be made regarding the behaviour of different solvents on the reaction (1) to (3).

In the present section, we describe the results of our studies on the dissociation constants for the reactions (1) to (3) in different dmso + water and formamide + water mixtures.

Experimental

Dimethylsulphoxide (Backer analyzed) and formamide (G.R.E. Merck) were purified in the same way as described in the previous sections. All the reagents were G.R.E. Merck grade. Ferrous ammonium sulphate (G.R.E. Merck) was dissolved in known quantity of $HClO_4$. The purity was checked by estimation of the iron-content analytically with standard potassium dichromate in the usual way. The solution was utilized within several hours. For each set of measurement freshly prepared solution was used. 2,2'-bipyridine solution was prepared by directly weighing bipyridine (G.R.E. Merck) and dissolving it in the appropriate solvent.

The addition of Fe^{2+} ion to bipyridine gives an intense red colouration with an absorption maximum at 524 nm (absorption maxima changes to 522 nm in mixed solvents having high percentages of organic solvents). The absorption maxima remained unchanged with change in pH, but the o.d. of the solution (same Fe^{2+} and ligand) was found to decrease with increasing H^+ ion concentrations. However, due to basicity of the solvent mixtures relatively high concentrations of acid are necessary to study the complexes. It has been assumed that under the experimental conditions used, $Febipy^{2+}$ and $Febipy_2^{2+}$ were not formed as suggested by Kolthoff et.al.[6], $Febipy_3^{2+}$ alone was formed in aqueous and mixed solvents. We have also observed that mono complex is formed only when Fe^{2+}

is present in large excess compared to bipy. The complex is rapidly converted to $Febipy_3^{2+}$ but no $Febipy_2^{2+}$ could be detected.

The extinction co-efficients (ϵ) of ferrodiin were determined from the measurements of O.d.'s of solutions containing 10 - 20 fold excess of ligand to different concentrations of Fe^{2+} ion at wave lengths 520 nm, 522 nm and 530 nm. Under the condition, the concentration of the complex could be taken equal to ferrous ion. This is confirmed by the fact that for the same concentration of ferrous ion and different concentration of bipyridine, the O.d. readings were same. The extinction co-efficients (ϵ) in different percentages of mixed solvents are given in tables 1 - 3.

For the determination of the stability constants, O.d.'s of solutions containing different concentrations of ferrous ion and bipyridine were measured (ferrous ion was added to bipyridine) at 520 nm, 522 nm and 530 nm. Measurements were made at 298K.

The concentrations of the complex were calculated from O.d. readings and extinction co-efficient values at these wave lengths. The concentrations of the complex came out to be almost equal at these wave lengths. For the calculation of equilibrium constant for the reaction (2), the average values of the complex obtained from measurements at three wavelengths were taken.

Optical density values were taken with a Beckman DU 2 spectrophotometer maintained at 298K. Other experimental details are the same as described in the previous section.

Results

Dissociation constant of ferrodiin

The equilibrium between ferrodiin and a strong acid may be represented as

$$Febipy_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3\ bipyH^+ \qquad (4)$$

Thus

$$k_a = \frac{c_{Fe^{2+}} \times c^3_{bipyH^+}}{c_{Febipy_3^{2+}} \times c^3_{H^+}} \times \frac{f_{Fe^{2+}} \times f_{bipyH^+}}{f_{Febipy_3^{2+}} \times f^3_{H^+}}$$

$$= k_c \times \frac{f_{Fe^{2+}} \times f_{bipyH^+}}{f_{Febipy_3^{2+}} \times f^3_{H^+}} \qquad (5)$$

if $f_{Fe^{2+}} = f_{Febipy_3^{2+}}$ and $f_{bipyH^+} = f_{H^+}$, k_c becomes equal to k_a. But since $bipyH^+$ is likely to have much larger size, it may that $f_{bipyH^+} \neq f_{H^+}$, which would need an accurate determination of f_{bipyH^+}.

Accurate determination of thermodynamic dissociation constants are possible only in dilute solutions where activity co-efficients are unity. In concentrated solutions the determination of activity co-efficients are difficult. Theoretical equations like Debye - Hückel equation or semi-emperical equations like Davies[7] equations are limited use and these equations are applicable only in dilute solutions. Deviations are appreciable in concentrated solutions. The complexity increases much more in mixed solvents. The orientation of solvent molecules around the ions are not known and it is difficult to know the extent of solute-solvent interactions in mixed solvents.

In mixed solvent it is convenient to seperate activity co-efficients of the i-th species into factors

$$\gamma_i = {}_m\gamma_i \;.\; {}_s\gamma_i \text{ [8]} \qquad (6)$$

The 'salt-effect' ${}_s\gamma_i$ varies with the solute concentration. Simple Debye-Hückel equation with appropriate allowances for the effect of altering the dielectric constant of the medium s can be used to estimate ${}_s\gamma_i$ when the ionic species are involved. The limitations which affect the actual determination of activity co-efficients in aqueous solutions would be much more in mixed or non-aqueous solutions. In dilute solutions ${}_s\gamma_i \rightarrow 1$ and thus only the 'medium effects' with which we are concerned in the study of dissociation constants will be involved.

In view of the above facts the present work has been carried out in solutions of μ of the order of 10^{-3} mol dm^{-3} (ionic strengths were of order 1.4×10^{-3} to 3.3×10^{-3} mol dm^{-3}) where it is reasonable to assume $f_{Fe^{2+}} = f_{Febipy_3^{2+}}$ and $f_{bipyH^+} = f_{H^+}$ (slight discrepancy, if any, may be neglected). Thus k_c becomes equal to thermodynamic equilibrium constant k_a.

Now

$$(\text{bipy H}^{+}) = (\text{bipy})_{\text{Total}} - 3(\text{Febipy}_{3}^{2+}) - (\text{bipy}) \qquad (7)$$

(bipyH^{+}) is calculated where necessary from previous section taking appropriate pK values.

The concentration Fe^{2+} is calculated from the relation

$$[\text{Fe}^{2+}]_{\text{free}} = [\text{Fe}^{2+}]_{\text{Total}} - [\text{Febipy}_{3}^{2+}] \qquad (8)$$

The measurement of the hydrogen ion concentrations of the solutions containing the complexes and bipyH^{+} are difficult. However, we have calculated H^{+} ion concentrations in the solutions from meter-readings after appropriate corrections.

The equilibrium constants for the reaction (2) in dmso + H_2O and in formamide + H_2O mixtures are given in table 4 - 5.

The equilibrium constants

$$k = \frac{[\text{Fe}^{2+}]\,[\text{bipy}]^{3}}{[\text{Fe bipy}_{3}^{2+}]} \qquad (9)$$

for the reaction

$$\text{Febipy}_{3}^{2+} \rightleftharpoons \text{Fe}^{2+} + 3\ \text{bipy} \qquad (10)$$

in different solvents are given by

$$K_{\text{dissn.}}\ \text{Febiy}_{3}^{2+} = k_a \text{ X } k_T^{3}$$

The results are given in Table - 6.

Discussions :-

It has been found that extinction coefficient of the complexes are higher in mixed solvents and the trend is quite regular in dmso + water mixtures. The extinction coefficient increases reaches a maximum at about 72 wt% but decreases from about 82% and onwards. The trend, however, is some what different in formamide + water mixtures where maxima are observed at about 63 wt% and 82 wt% (Table - 3). These results cannot be correlated with the solvent dielectric constant or other known solvent properties. However, since the extinction coefficients are related to the oscillator strengths, it is expected that oscillator strengths would change with change in solvent compositions obviously due to change in solute-solvent interactions.

The results show that pK-value for reaction(2) slightly decreases with the introduction of organic solvents but increases with increase in organic component. In case of dmso + water mixtures, pK-value reaches a minimum at about 30 wt% and then increases continuously but the pK-jump is very much conspicuous at about 82 wt% dmso. In case of formamide + water mixtures, the pK-value increases, reaches a maximum at about 53 wt% of formamide, then decreases but increases again at 82 wt% formamide. This is shown in Fig. 1. Thus, we find that ΔG_t^0 in most cases are positive i.e. the reaction is non-spontaneous in organic solvent mixtures. However, ΔG_t^0 values for the reaction (3) are increasingly negative in dmso + water mixtures indicating that the reaction (3) is spontaneous i.e. the dissociation of $Febipy_3^{2+}$ is favoured in mixed solvents. Similar conclusions may be derived in case of formamide + water mixtures. As in case of reaction (2), significant changes are also observed between 20 - 30 wt% of dmso and in the region 43 to 53 wt% and 82 wt% of formamide. The results indicate that $Febipy_3^{2+}$ is less stable in these organic solvent mixtures but the stability is less in formamide + water mixtures.

The reasons may be

1) Increase in basicity of the solvent mixtures and consequent removal of H^+ ions by the solvents.
2) Increase in solubility of bipyridine in the solvent mixtures.
3) The competition of the solvents to form complexes with Fe^{2+} and the consequent displacement of bipy by the solvents from $Febipy_3^{2+}$ particularly when the dmso or formamide concentrations are high.

All these reactions are isoelectric in character. Thus the decrease in dielectric constant should have slight effect on the dissociation constants, the change in pK-values must be due to solute-solvent interactions which is likely to be high in the solvent mixtures. The solvation of $Febipy_3^{2+}$ and $bipyH^+$ should be less compared to those of Fe^{2+} and H^+ ions.

It is seen that the pK values for reaction (2) is a linear function of $\frac{1}{D}$ at best upto 50 wt% beyond which considerable deviations arise.(Fig - 2). But it is impossible to get a clear idea of the solute-solvent interactions of the different ions in solutions.

These data however, could be utilised to have quantitative idea of $\Delta G^{o}_{t(Fe^{2+})}$ and $\Delta G^{o}_{t(Febipy_3^{2+})}$ provided we know the solubility values of $Fe(bipy)_3(ClO_4)_2$ and bipyridine and $\Delta G^{o}_{t(ClO_4)}$ in these solvent mixtures. For the reaction (3), we have

$$\Delta \Delta G^{o}_{t} (3) = \Delta G^{o}_{t(Fe^{2+})} + 3 \Delta G^{o}_{t(bipy)} - \Delta G^{o}_{t(Febipy)_3^{2+}}$$

$$\Delta G^{o}_{t(Febipy_3)^{2+}} = \Delta G^{o}_{t} [Fe (bipy)_3(ClO_4)_2] - 2 \Delta G^{o}_{t}(ClO_4^-)$$

and $\Delta G^{o}_{t}(Fe^{2+}) = \Delta \Delta G^{o}_{t}(3) - 3 \Delta G^{o}_{t} (bipy) + \Delta G^{o}_{t} (Febipy_3)^{2+}$.

It is thus apparent that the proper understanding of the role of the solvents on the dissociation constants and their successful utilization necessitate systematic investigations of the different aspects of the solution chemistry.

Table - 1

Media - 52.35% by weight of dmso

Temp. = 298K

Total Molar concentration of		pH	Optical density at 520nm	Extinction co-efficient at 520 nm	Optical density at 522nm	Extinction co-efficient at 522 nm	Optical density at 530nm	Extinction co-efficent at 530 nm
Fe^{++} X 10^5	2,2'-bipyridine X 10^5							
1	2	3	4	5	6	7	8	9
2.00	40.00	4.29	0.175	8750	0.177	8850	0.173	8650
3.00	60.00	4.18	0.267	8900	0.271	9030	0.262	8730
4.00	80.00	4.13	0.352	8800	0.355	8875	0.346	8650
5.00	100.00	4.09	0.442	8840	0.449	8980	0.435	8700
6.00	120.00	4.06	0.528	8800	0.532	8866	0.521	8683
7.00	140.00	4.03	0.612	8742	0.618	8820	0.608	8685
8.00	160.00	4.00	0.705	8812	0.705	8812	0.695	8687

Table - 2

Media - 43.01% by weight of formamide

Temp = 298K

Total Molar concentration of		Optical density at 520 nm	Extinction co-efficient at 520 nm	Optical density at 522nm	Extinction co-efficient at 522 nm	Optical density at 530nm	Extinction co-efficient at 530 nm
Fe^{++} X 10^5	2,2'-bipyridine X 10^5						
1	2	3	4	5	6	7	8
2.00	20.00	0.173	8650	0.175	8750	0.172	8600
3.00	30.00	0.261	8700	0.263	8766	0.258	8600
4.00	40.00	0.346	8650	0.348	8700	0.342	8550
5.00	50.00	0.430	8600	0.432	8640	0.427	8540
6.00	60.00	0.518	8633	0.520	8666	0.514	8566
7.00	70.00	0.604	8633	0 .607	8671	0.600	8571
8.00	80.00	0.695	8687	0.697	8712	0.691	8637

Table - 3

Extinction co-efficient of tris-(2,2'-bipyridine)-Fe(II) complex at different percentage of aqueous dimethylsulphoxide and formamide solution.

Percentage of dmso by wt	Extinction co-efficient at 520 nm	Extinction co-efficient at 522 nm	Extinction co-efficient at 530 nm	Percentage of formamide by wt	Extinction co-efficient at 520 nm	Extinction co-efficient at 522 nm	Extinction co-efficient at 530 nm
1	2	3	4	5	6	7	8
10.87	8490	8553	8401	11.17	8400	8456	8333
21.53	8563	8633	8513	22 .06	8490	8553	8401
32.02	8654	8671	8581	32.67	8560	8610	8513
42.28	8716	8800	8685	43.01	8650	8700	8581
52.35	8827	8862	8734	53.10	8733	8833	8633
62.24	8873	8933	8827	62.94	8800	8880	8671
71.94	8969	9018	8873	72.54	8563	8600	8490
81.46	8843	8911	8800	81.91	8843	9000	8827
90.81	8761	8830	8734	91.06	8761	8850	8761

Table - 4

Temp = 298K

Media - 42.28% by weight of dmso.

Total concentration of		pH after proper correction	Concentration of tris-(2,2'-bipyridine)-Fe(II)complex taking average from the three wavelengths. mol dm^{-3} X 10^{5}	Concentration of free F^{2+} mol dm^{-3} X 10^{5}	Concentration of bipyridine as Bipy H^{+} mol dm^{-3} X 10^{5}	$K_a \times 10^{5}$
Fe^{2+} X 10^{5}	2,2'-bipyridine X 10^{5}					
1	2	3	4	5	6	7
10.00	12.00	3.35	3.550	6.450	0.940	1.70
10.00	15.00	3.36	4.467	5.533	1.105	2.01
12.00	10.00	3.27	2.863	9.137	1.035	2.29
12.00	13.00	3.27	3.779	8.221	1.220	2.56
14.00	15.00	3.14	4.352	9.648	1.532	2.10
16.00	14.00	3.11	4.065	11.935	1.443	1.89
16.00	18.00	3.11	5.223	10.337	1.862	1.47
18.00	20.00	3.08	5.841	12.159	2.007	2.93

Average = 2.1

Table - 5

Dissociation constants of tris-(2,2'bipyridine)-Fe(II) complex in aqueous dimethylsulphoxide and Formamide solutions.

Wt% of dmso	K_a	pK	Wt% of Formamide	K_a	pK
1	2	3	4	5	6
0	7.56×10^{-5}		0	7.56×10^{-5}	
10.87	10.60×10^{-5}	3.97	11.17	9.34×10^{-6}	5.03
21.53	7.58×10^{-5}	4.12	22.06	8.96×10^{-6}	5.05
32.02	11.00×10^{-5}	3.93	32.67	7.63×10^{-6}	5.11
42.28	2.13×10^{-5}	4.67	43.01	5.01×10^{-6}	5.30
52.35	1.50×10^{-5}	4.82	53.10	2.75×10^{-6}	5.56
62.24	8.55×10^{-6}	5.07	62.94	5.67×10^{-6}	5.24
71.94	7.69×10^{-6}	6.11	72.54	1.42×10^{-5}	4.86
81.46	9.76×10^{-8}	7.01	81.91	1.21×10^{-5}	4.92
90.81	3.87×10^{-8}	7.41	91.06	2.53×10^{-5}	4.60

Table - 6

Values of $K_{dissn.}$ $Febipy_3^{2+}$ in aqueous dimethyl sulphoxide and formamide solutions

Wt% of dmso	k_a X k_T^3	Wt% of Formamide	k_a X k_T^3
0	2.94×10^{-18}	0	2.94×10^{-18}
10.87	2.85×10^{-17}	11.17	1.91×10^{-15}
21.53	7.07×10^{-17}	22.06	3.65×10^{-15}
32.02	3.52×10^{-16}	32.67	4.10×10^{-15}
42.28	1.58×10^{-16}	43.01	2.88×10^{-15}
52.35	8.24×10^{-16}	53.10	9.76×10^{-16}
62.24	3.52×10^{-15}	62.94	1.01×10^{-15}
71.94	6.54×10^{-15}	72.54	1.56×10^{-15}
81.46	1.51×10^{-14}	81.91	8.21×10^{-16}
90.81	1.04×10^{-14}	91.06	8.57×10^{-16}

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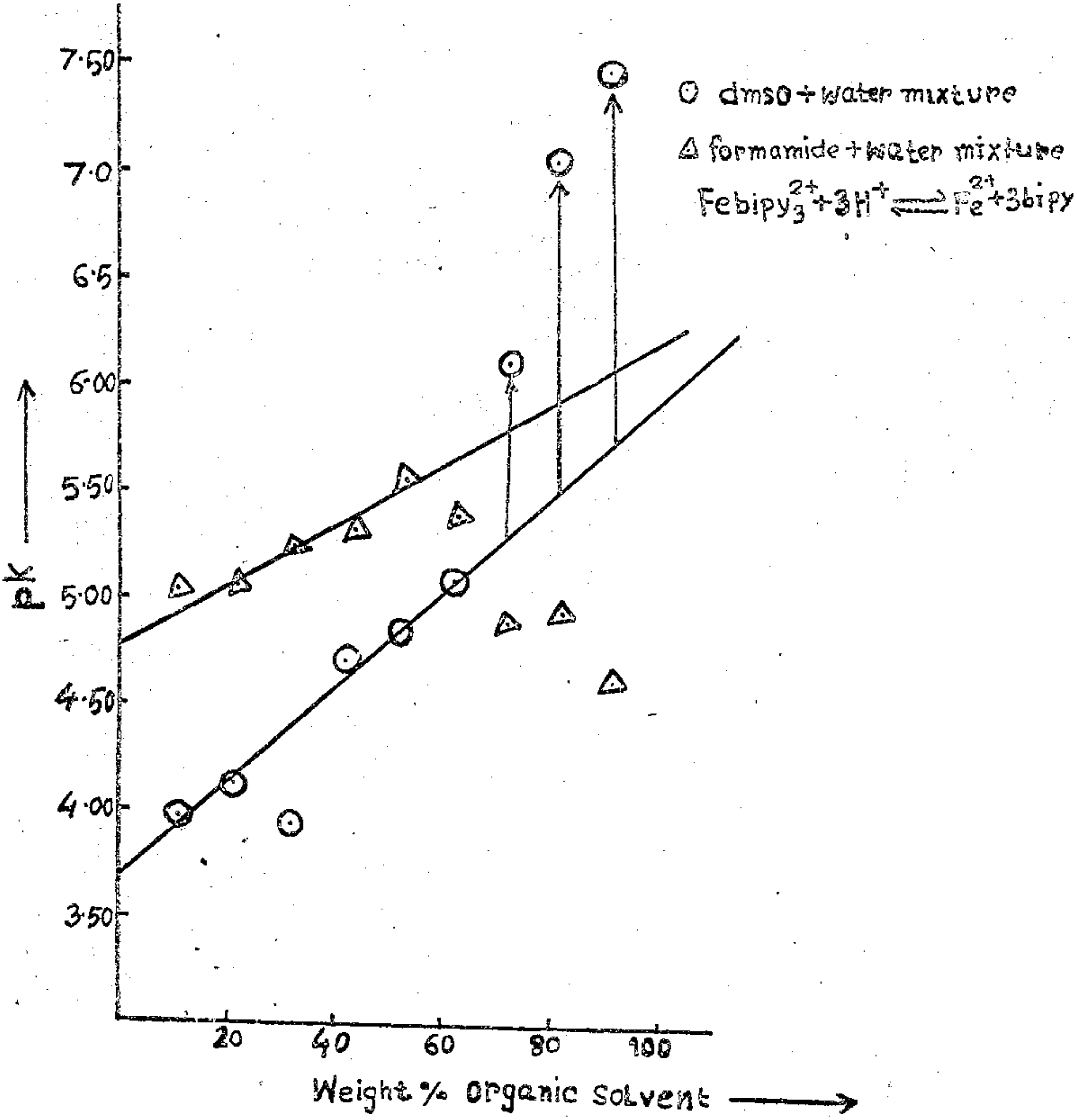
Fig. 1



⊙ dmso + water mixture
△ formamide + water mixture
$Febipy_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3bipy$
pK
7·50
7·0
6·5
6·00
5·50
5·00
4·50
4·00
3·50
20
40
60
80
100
Weight % organic solvent