

## THERMODYNAMICS OF 2,2'-DIPYRIDINIUM ION AND ITS IRON(II) COMPLEX IN METHANOL-WATER MIXTURE AT 25°C

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### ABSTRACT

The enthalpies of formation of the 2,2'-dipyridinium ion and the 2,2'-dipyridyl-iron(II) complex in methanol-water media at 25°C have been determined by calorimetry. The entropy-changes have been calculated combining the enthalpy values with the corresponding free-energy changes previously reported. The role of solvents on the thermodynamic parameters has been discussed.

### INTRODUCTION

The ligand 2,2'-dipyridyl and the tris-dipyridyl ferrous complex have been widely known for their analytical applications<sup>1</sup>. No systematic studies have, however, been made in mixed solvents.

The role of solvents on the dissociation constants of ligands and their complexes are receiving much attention in recent years. These studies are helpful in understanding the various factors associated with solute-solvent interactions. Recently, Hazra and Lahiri<sup>2</sup> determined the free energy change for the "iso-electric reactions" of the type:



However, it is well known that an insight into the structural modifications and ionic solvations cannot be had from free-energy measurements only. A knowledge of the enthalpy change is needed to have a better understanding of the role of solvents on the "isoelectric reactions" mentioned above.

With the above objects in view, we determined the enthalpy values for the reactions (1), (2) and (3) by calorimetry which is described in this communication.

## EXPERIMENTAL

The calorimeter (fabricated in our laboratory) as reported earlier<sup>3</sup> consists of a dewar flask with temperature sensing unit made of thermistors in opposite arms of a Wheatstone bridge as used by O'Hara et al.<sup>4</sup> and Armstrong<sup>5</sup>. Veco thermistors 31A6 and 32A1 were used. The calibration heater was of the type used by Stern and Hansen<sup>6</sup> with modification.

Methanol (G.R., E. Merck) was distilled and the middle fraction was utilized within forty-eight hours. The slight trace of water, if any, in the organic solvents was neglected.

Ferrous-ammonium sulphate (G.R.-E.M.) was dissolved in a known quantity of HClO<sub>4</sub> (G.R.-E.M.). The purity of ferrous-ammonium sulphate was checked by estimation of the iron-content analytically with standard K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the usual way. The solution was utilized within several hours. For each set of measurements a freshly prepared solution was used.

2,2'-Dipyridyl solution was prepared by directly weighing dipyridyl (G.R.-E. Merck) and dissolving it in the appropriate solvent.

Perchloric acid, caustic soda were E. Merck's reagent grade and were estimated in the usual way. Other chemicals were also of reagent grade. All the solutions were made with double-distilled water.

For the enthalpy-change-measurements of 2,2'-dipyridinium ion in mixed solvents, 250 ml of HClO<sub>4</sub> solution in the mixed solvent (final concentration 0.2N) was taken in the reaction flask. This was done to ensure complete conversion of dipyridyl into dipyridinium ion whose pK values ranged from 4.5 to 3.2<sup>2</sup>. Different concentrations of the ligand in the appropriate solvents (5 ml) to avoid any heat change due to mixing of the solvents were taken in glass bulbs.

For the enthalpy-change measurements of the complex, a large excess of 2,2'-dipyridyl (concentrations ranging between 2-6 × 10<sup>-3</sup> M) in 250 ml of appropriate solvents was taken in the dewar flask. 5 ml of Mohr salt (~10<sup>-3</sup> M) in dilute acid (5 × 10<sup>-3</sup> M HClO<sub>4</sub>) were taken in the glass bulb. The concentration of dipyridyl was always more than 20 times the concentration of the Fe<sup>2+</sup> ion and therefore, complete complexation of iron(II) could be safely assumed.

The weight percentages of the organic solvents in the mixture were determined in the same way as described before<sup>2</sup>.

## RESULTS

From the measured heat liberated, the enthalpy changes were calculated. Since the pH of the solutions for the measurement of enthalpy changes for reaction (1) was kept below 0.1, it is reasonable to assume that all the ligand had been converted to dipyH<sup>+</sup>. The enthalpy change per mole was thus calculated using the relation

$$\Delta H_1 = - \frac{Q_1}{C_{\text{DipyH}^+}} \text{ cal}$$

TABLE I  
THERMODYNAMICS OF 2,2'-DIPYRIDYL AND ITS Fe(II) COMPLEXES IN METHANOL-WATER AT 25°C

Wt. % of MeOH	Reaction		$dipyH^+ \rightarrow dipy + H^+$ <sup>a</sup>			$Fedipy_3^{2+} + 3H^+ \rightarrow Fe^{2+} + 3dipyH^+$			$Fedipy_3^{2+} \rightarrow Fe^{2+} + 3dipy$ <sup>b</sup>		
	$\Delta G$ (kcal mol <sup>-1</sup> )	$\Delta H$ (kcal mol <sup>-1</sup> )	$\Delta S$ (e.u.)	$\Delta G$ (kcal)	$\Delta H$ (kcal)	$\Delta S$ (e.u.)	$\Delta G$ (kcal)	$\Delta H$ (kcal)	$\Delta S$ (e.u.)	$\Delta G$ (kcal)	$\Delta H$ (kcal)
0	6.09	2.40	-12.40	5.94	17.80	39.8	24.25	25.00	2.5		
8.0	6.00	3.69	-7.75	6.37	18.06	39.00	24.35	29.13	15.70		
16.4	5.79	4.36	-4.80	7.01	22.11	50.70	24.39	35.19	36.24		
25.2	5.66	6.33	2.25	7.26	21.06	47.30	24.24	40.05	53.07		
34.4	5.45	5.56	0.36	7.16	19.64	42.04	23.47	36.32	43.12		
44.1	5.22	4.86	-1.21	7.31	18.26	36.80	22.97	32.84	33.12		
54.2	4.91	3.95	-3.22	7.32	19.80	43.00	22.04	31.65	32.25		
64.7	4.53	3.38	-3.86	7.58	20.71	44.20	21.13	30.85	32.62		

<sup>a</sup>  $\mu = 0.2M$ , <sup>b</sup>  $\mu = \sim 10^{-3}M$ .

when  $Q$  = amount of heat evolved for the conversion of  $C$  g mol of dipyridyl to dipyridinium ion.

It is well known that under the conditions of the experiment  $\text{Fedipy}^{2+}$  and  $\text{Fedipy}_2^{2+}$  are not present in detectable amounts. Hazra and Lahiri also observed that in aqueous solutions and aqueous methanolic solutions, about six-fold concentrations of the ligand were sufficient to bring about the complete complexation. Since in our experiments, the concentrations of the ligand were more than 20 times the iron(II) concentration, all the iron was present as  $\text{Fe(dipy)}_3^{2+}$ , the enthalpy change could be calculated from the relationship.

$$\Delta H_3 = - \frac{Q_3}{C_{\text{Fe}^{2+}}} \text{ cal}$$

where  $Q_3$  is the amount of heat evolved for the formation of  $C$  g mol of the iron(II) complex. The uncertainties in the values of  $\Delta H$  in water is  $\pm 0.10$  kcal mol<sup>-1</sup> and in methanol-rich media  $\pm 0.20$  kcal mol<sup>-1</sup>. In the present report the reactions studied are of iso-electric nature which are in general less affected by the ionic strength. For this reason and also in consideration of the limits of uncertainty the measured enthalpies may be taken as  $\Delta H^\circ$ . The  $\Delta H$  values for the reaction  $\text{Fedipy}_3^{2+} + 3\text{H}^+ \rightarrow \text{Fe}^{2+} + 3\text{dipyH}^+$  have been calculated from the relationship

$$\Delta H_2 = \Delta H_3 - 3\Delta H_1$$

Hazra and Lahiri<sup>2</sup> have determined the thermodynamic dissociation constants for reactions (1), (2) and (3) in methanol-water mixtures. Using the values of  $\Delta G$  from Hazra and Lahiri's work and the  $\Delta H$  values from the present work,  $\Delta S$  values for the reactions have been calculated. The results are given in Table 1.

#### DISCUSSIONS

The thermodynamics of 2,2'-dipyridyl and tris-dipyridyl ferrous complex (referred to as ferrodin) in aqueous solutions have been reported by a number of workers. The results are tabulated below:

	$\Delta G$ (kcal mol <sup>-1</sup> )	$\Delta H$ (kcal mol <sup>-1</sup> )	$\Delta S$ (e.u.)
Reaction (1)	6.4	4.0	-8.0 a
	6.0	3.66	-8.2 b
	6.09	2.0	-13.0 c
		2.4	e
Reaction (3)	23.40	31.50	27.00 b
	23.80	28.00	13.8 d
	24.00	24.00	0.0 c
		25.00	e

(a) = Calorimetrically determined from neutralization of 2,2'-dipyridyl in (M)  $\text{NaNO}_3$  with 0.5M  $\text{HNO}_3$ <sup>7</sup>; (b) = calorimetric value  $\mu = 0.1$   $\text{NaNO}_3$ <sup>8</sup>; (c) = Spectrophotometric value from temperature-coefficient measurement (25-35°C)  $\mu = 0.025$ <sup>9</sup>; (d) = calorimetric value  $\mu = 1.0$  at 30.3°C<sup>10</sup>; (e) = our value extrapolated from low percentages of alcohol.

Our values are close to the values reported by George and Baxendale<sup>9</sup> in case of reaction (1) but slightly different in case of reaction (3). Appreciable changes have been noted in the  $\Delta H$  values for reactions (1), (2) and (3) in mixed solvents. The explanation is obviously difficult in view of the lack of data in mixed solvents. A change to the extent of  $-4.0$  to  $+5$  kcal in  $\Delta H$  values has been reported by Rodante, Rallo and Fiordiponti<sup>11,12</sup> in the calorimetric and potentiometric measurements of the water ionization enthalpy in dimethyl sulphoxide–water mixtures at  $25^\circ\text{C}$ . The results have been explained in terms of ion-solvation and structural aspects. The solvent system as well as the reaction are, needless to mention, completely different from the reactions and solvent systems under the present study.

The interpretation of thermodynamic data is extremely complex in view of our lack of knowledge of the structure of the liquid mixtures and the extent of ion-solvation effects which have marked contributions towards  $\Delta H$  and  $\Delta S$  (not on  $\Delta G$  due to compensating effects of  $\Delta H$  and  $T\Delta S$ ), the evaluation and proper interpretations of these parameters ( $\Delta H$  and  $\Delta S$ ) are intriguing. In mixed solvents, modifications of the solvent molecules and addition of new species with different acid–base properties further complicate the situation. It is to be noted that for methanol–water mixtures, the excess free energy of mixing is positive and is comprised of a negative and unsymmetrical enthalpy (which passes through a minimum at  $x_2 = 0.3$ ) and a positive entropy of mixing<sup>13</sup>. These factors must be given due consideration in interpreting the thermodynamic parameters of ligands and complexes in mixed solvents.

The plot of  $\Delta G$ ,  $\Delta H$  and  $T\Delta S$  against mole fractions of organic solvents are given in the Figs. 1, 2, and 3.

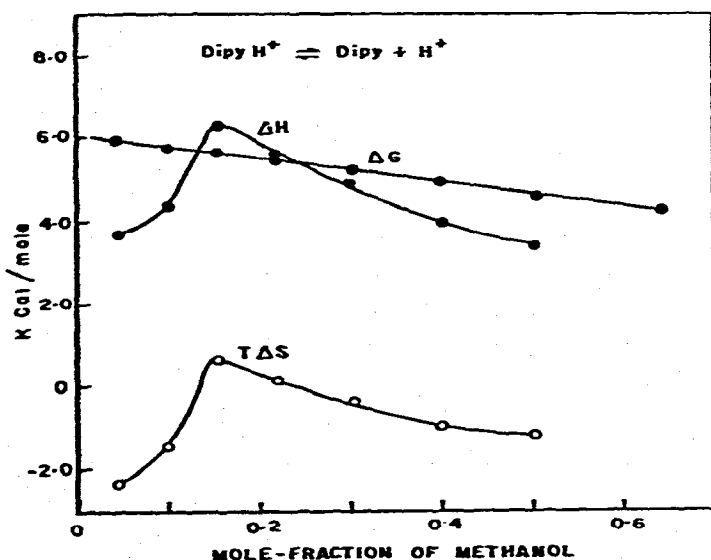


Fig. 1.  $\Delta G$ ,  $\Delta H$  and  $T\Delta S$  for the reaction  $\text{DipyH}^+ \rightleftharpoons \text{Dipy} + \text{H}^+$  vs. mole fraction of methanol in methanol–water at  $25^\circ\text{C}$ .

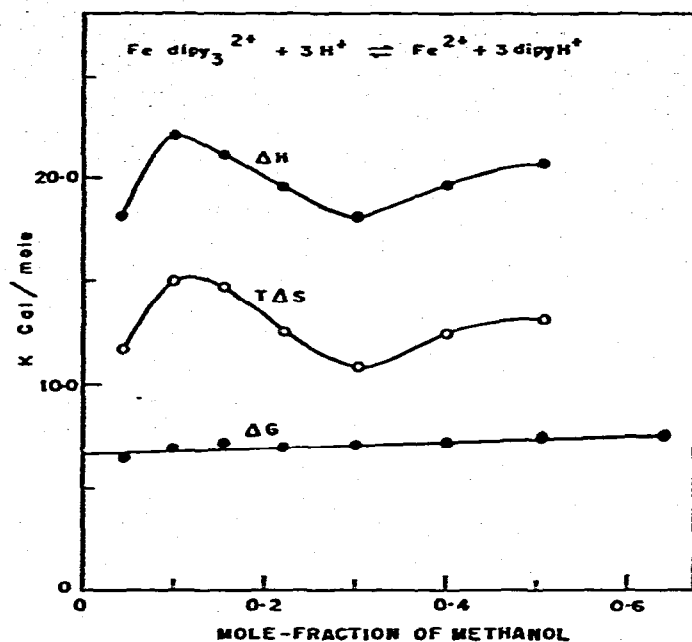


Fig. 2.  $\Delta G$ ,  $\Delta H$  and  $T\Delta S$  for the reaction  $\text{Fe(Dipy)}_3^{2+} + 3\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 3\text{DipyH}^+$  vs. mole fraction of methanol in methanol-water at 25°C.

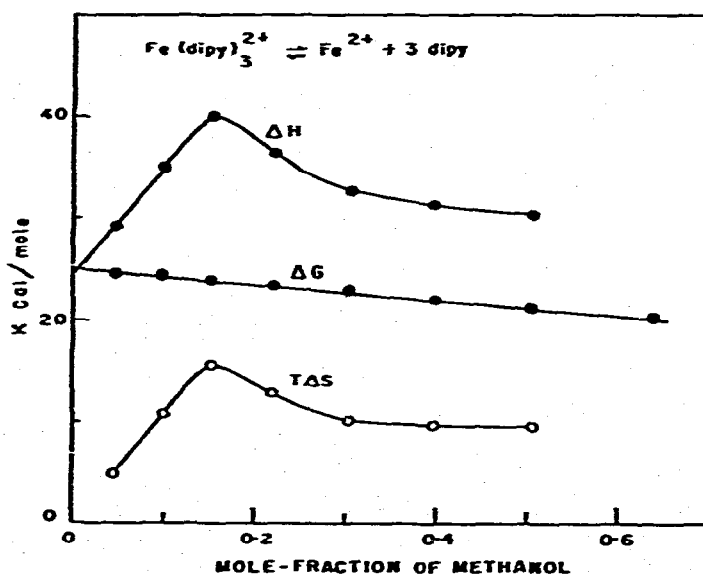


Fig. 3.  $\Delta G$ ,  $\Delta H$  and  $T\Delta S$  for the reaction  $\text{Fe(Dipy)}_3^{2+} \rightleftharpoons \text{Fe}^{2+} + 3\text{Dipy}$  vs. mole fraction of methanol in methanol-water at 25°C.

The  $\Delta G$  for the reactions (1) becomes increasingly negative with increase in alcohol-content indicating the increase in case of ionization. The reverse trend is observed for reaction (2) indicating the increase in case for the reaction to go to the right. The  $\Delta G_i$  for (3) is a bit more complicated. The  $\Delta G_i$  is positive and increases upto 16.4 wt % but becomes increasingly negative as the percentage of organic solvent increases. It is interesting in this connection to note that  $\Delta G_i$  becomes increasingly positive with increase in alcohol-content in case of ionization processes like  $HA \rightarrow H^+ + A^-$ . From this, it could not be necessarily correlated with the change in water-structure, i.e., the structure of water is enhanced due to addition of alcohol or due to increase in the basicity of the solvents but the results could be explained in terms of ionic solvations and consequent change in entropy and enthalpy values. These also show that the dielectric constant is not the major factor affecting ionization, the main factor being solute-solvent interactions<sup>2,14,15</sup>. However, an increase in the solubility of dipyrindyl and differences in solvational properties of  $dipyH^+$ ,  $H^+$ ,  $Fe^{2+}$  and  $Fedipy_3^{2+}$  ( $H^+$  and  $Fe^{2+}$  are likely to be preferentially solvated by water rather than alcohol though the preferential solvation of ions in other solvents) cannot be ruled out. The enthalpy values and their complexes in mixed solvents have been only little studied. However, the nature of the curves of  $\Delta H$  and  $T\Delta S$  with solvent compositions shows a uniform trend.

The  $\Delta H$  and  $T\Delta S$  values for reactions (1) and (3) increase as the organic solvent increases, pass through a maximum around  $x_2 = 0.1-0.15$  ( $x_2 =$  mole fraction of organic solvent). The trend is slightly different for reaction (2). The observations are in agreement with reported enthalpies of transfer of HCl from water to aqueous alcohols (ethanol, methanol, propanol, etc.) by Stern and Hansen<sup>6</sup>. They interpreted the results in terms of significant structural and consequent entropy changes in the medium around 0.1 mole fraction and due to solvent ordering of ions on dissociation. The explanation is, however, not quite relevant for isoelectric reactions (1), (2) and (3).

Arnett<sup>16</sup> also holds the view that there is an enhancement of structure which is maximum around  $x_2 = 0.1$  of alcohol. Further addition of solvent cannot build structure without interfering with previous structure.

However, heats of solution of different electrolytes in methanol-water mixtures reported by Mischenko and Poltoratskii<sup>17</sup>, Krestov and Klopov<sup>18</sup> show that there is a maximum in the heat of solution at a solvent composition of approximately 20 mole-percent of methanol. Considering these facts our observations appear to be quite in order.

It will be interesting, however, to interpret the results in terms of solvational properties of the ligand and ions and ice-berg concept of Frank and Evans<sup>19</sup>. Due to large ion-size parameters,  $Fedipy_3^{2+}$  and  $dipyH^+$  ions will have less chance of being solvated compared to  $H^+$  and  $Fe^{2+}$  ions. This fact necessarily means a decrease in entropy value for reaction (1), even though there is an increase in the number of molecules due to dissociation. However, for reaction (3), increase in the solvent-ordering due to dissociation of  $Fedipy_3^{2+}$  to  $Fe^{2+}$  should lead to an entropy decrease

but at the same time, release of three molecules would result in an increase of entropy values. These are also the reasons for an entropy-increase for reaction (2).

It is thus apparent that the solvation of ions particularly of  $H^+$  and  $Fe^{2+}$  will play a major role leading to the changes in the values of thermodynamic quantities. For any definite explanation, extensive data in mixed solvents would be needed.

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