Thermochimica Acta, 52 (1982) 201–209
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMODYNAMICS OF FERROUS-2,2′-DIPYRIDYL IN *TERT*-BUTANOL–WATER AND GLYCEROL–WATER MIXTURES AT 25°C

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(Received 26 June 1981)

ABSTRACT

The enthalpies of formation of 2,2′-dipyridyl–iron(II) complex in *t*-BuOH–water and glycerol–water mixtures at 25°C have been determined by calorimetry. The dissociation constants of the complex in the mixed solvents have been determined spectrophotometrically. The entropy changes have been calculated combining the enthalpy values with the corresponding free energy changes calculated from p*K* values. The influence of solvents on the thermodynamic parameters is discussed.

INTRODUCTION

The influence of solvents on the thermodynamic parameters of ligands and their complexes has received much attention in recent years. Such studies are helpful in understanding the various factors associated with solute–solvent interactions. Only a few reports are known on the thermodynamics of the ligand 2,2′-dipyridyl and its complex in mixed solvents though these have been widely known for their analytical applications [1]. The thermodynamics of 2,2′-dipyridinium ions in methanol–, ethanol–, *t*-butanol– and glycerol–water systems and its ferrous complex in methanol– and ethanol–water systems have been reported earlier [2–6].

In this communication we report the enthalpies of formation of $Fe(dipy)_3^{2+}$ in different *t*-butanol– and glycerol–water mixtures at 25°C determined by calorimetry, the dissociation constants by spectrophotometry and ΔG^0 and ΔS^0 values calculated from these experimental results.

EXPERIMENTAL

Ferrous ammonium sulphate (G.R.-E. Merck) was dissolved in a known quantity of $HClO_4$. The purity was checked by estimating the iron content analytically with standard $K_2Cr_2O_7$ solution in the usual way. The solution was utilized within several hours. A fresh solution was used for each run. Dipyridyl solution was prepared as

0040-6031/82/0000–0000/$02.75

reported previously [4]. Purification of solvents has been described in an earlier communication [7].

Measurement of the enthalpy change was carried out using a calorimeter fabricated in this laboratory [8,9]. For each run, 5 ml of freshly prepared solution of ferrous ammonium sulphate (concentration range 3–1 × 10^{-2} M) in $HClO_4$ was taken in a Pyrex glass bulb and 250 ml of dipyridyl (concentration range 2–1 × 10^{-2} M) was taken in the Dewar flask. Both the solutions were in the mixed solvent of the same composition. Three different concentrations of $HClO_4$ (5 × 10^{-2} M, 1 × 10^{-2} M, 5 × 10^{-3} M) were used for the Mohr salt solution. In each case, the heat changes due to the formation of dipyridinium ion were taken into account. For this purpose, a blank experiment with no Mohr salt (5 ml of solution containing $HClO_4$ and 250 ml of dipy) was carried out. The concentration of dipyridyl was always more than 30 times the concentration of Fe^{2+} ion. The dissociation constants of $Fe(dipy)_3^{2+}$ at 25°C in mixed solvents have been determined spectrophotometrically as reported in detail previously [3].

RESULTS

From the measured heat liberated, the enthalpy change per mole for the reaction

$$Fe^{2+} + 3\ dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$$

was calculated using the relation $\Delta H = -Q/X$, where Q represents the heat liberated in Joules for X moles of $Fe(dipy)_3^{2+}$ formed. The ionic strengths of the solutions in which the reactions were carried out were ~ 10^{-2} M. The reaction is iso-electric in nature. As such, the effect of ionic strength would be small. The measured ΔH values over the range of ionic strength of the solutions used was constant, so this has been taken as ΔH^0. The dissociation constants and the ΔH^0 values for $Fe(dipy)_3^{2+}$

TABLE 1

Thermodynamics of

$Fe(dipy)_3^{2+} \rightleftharpoons Fe^{2+} + 3\ dipy$

in glycerol- and *t*-BuOH–water media at 25°C

Wt % of solvent	p*K* diss	
	Glycerol–water	*t*-BuOH–water
0	17.54 (±1.44) [a]	17.54 (±1.44)
10	16.60	16.76
20	15.90	16.13
30	15.25	15.50
40	15.65 (±0.51)	15.50
50		15.79 (±0.57)

[a] Values in parentheses indicate maximum errors

TABLE 2

Thermodynamics of

$Fe(dipy)_3^{2+} \rightleftharpoons Fe^{2+} + 3$ dipy

in different solvent media at 25°C

Wt % of solvent	ΔG^0 (kJ mole^{-1})				ΔH^0 (kJ mole^{-1})				$T\Delta S^0$ (kJ mole^{-1})			
	Glycerol	*t*-BuOH	EtOH	MeOH	Glycerol	*t*-BuOH	EtOH	MeOH	Glycerol	*t*-BuOH	EtOH	MeOH
0	99 74	99.74	99 73	100 05	117 15	117 15	117 15	117 15	17 41	17.41	17 40	17.14
10	94 39	95 27	96 38	101 67	129 79 (±0.08)	132 17 (±0.21)	153 97	133 68	35.39	36 90	57 59	32 01
20	90 41	91 71	93 53	101 46	144 89	148 20	184 10	162 34	54 48	56 49	90 57	60 88
30	86 69	88 11	90 97	99 99	140 79	155.52	191 71	158.57	54 10	67 41	100 74	58 58
40	88 99	88 11	88 42	96 86	136 61	150 71	176 27	138 95	47 61	52.60	87 85	42 09
50		70.79	85 86	93 51	132 47 (±0 13)	147 19 (±0 25)	159 87	131 80		56 40	74 01	38 29

Values of ΔG^0 at 15% and 25% for glycerol–water medium are 92 09 and 88.12 kJ mole^{-1}, and for *t*-BuOH–water medium are 93 18 and 90 42 kJ mole^{-1}, respectively Values of ΔH^0 at 2 5% and 5% for glycerol–water media are 119 83 (±0 13) and 123 05 (±0 08) kJ mole^{-1}, and for *t*-BuOH–water media are 121 17 (±0 13) and 124 73 (±0 17) kJ mole^{-1}, respectively

$\rightleftharpoons Fe^{2-} + 3$ dipy in glycerol–water and *t*-BuOH–water are given in Tables 1 and 2, respectively.

DISCUSSION

The thermodynamic parameters (ΔG^0, ΔH^0 and $T\Delta S^0$) for the above-mentioned reaction in glycerol- and *t*-butanol–water are given in columns 2, 3, 6, 7, 10 and 11 of Table 2 along with the same in EtOH–, and MeOH–water (reported earlier [3,6]) in columns 4, 5, 8, 9, 12 and 13 of the same table. Figures 1–3 indicate the nature of the plots of ΔH^0, ΔG^0 and $T\Delta S^0$ against wt.% and mole fraction of organic solvent and the reciprocal of the dielectric constant ($1/D$) of aquo-organic solvents. From extrapolation of the ΔH^0 and ΔG^0 values in the region of lower percentages of organic constituents in water, the same parameters have been determined in water. The thermodynamics of the tris-dipyridyl-ferrous complex in aqueous medium reported in the literature along with those determined in this work are given in Table 3.

Our values are in good agreement with those reported by Davies and Dunning [11]. Anderegg's [10] value seems a little too high.

From Figs. 1–3 it is seen that ΔG^0 changes linearly up to 30% of *t*-BuOH (which corresponds to 0.09 mole fraction) and 20% of glycerol (corresponding to a mole fraction of 0.04), and deviates at higher percentages, whereas ΔH^0 and $T\Delta S^0$ first increase with increasing solvent and pass through a maximum at about 30% in the case of *t*-BuOH and 20% in the case of glycerol in the respective solvent mixtures. Similar behaviour has been observed by us in the case of dipy H^- in *t*-BuOH- and

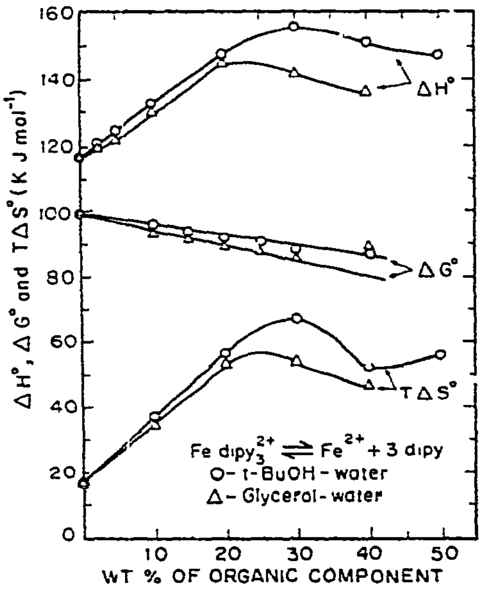

Fig 1. Plots of ΔG^0, ΔH^0 and $T\Delta S^0$ vs. wt % of organic components

glycerol–water mixtures [4] and also by Pointud et al. [13] for the transfer enthalpies of HCl and LiCl in the *t*-BuOH–water system. The same type of maximum structuring was also reported by Mishchenko and Poltoratskii [14] and Krestov and Klopov [15].

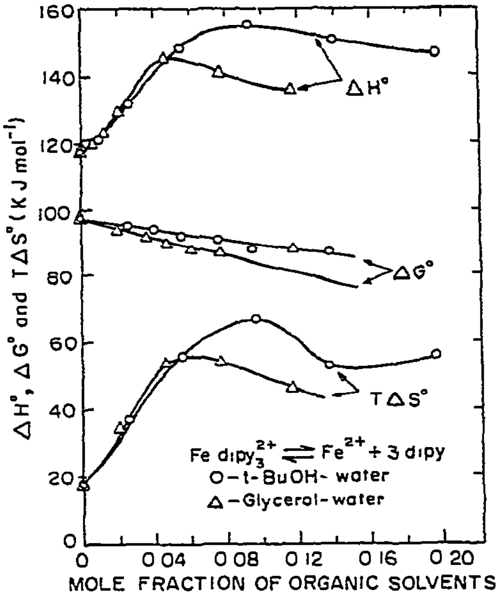

Fig 2 Plots of ΔG^0, ΔH^0 and $T\Delta S^0$ vs mole fraction of organic solvents.

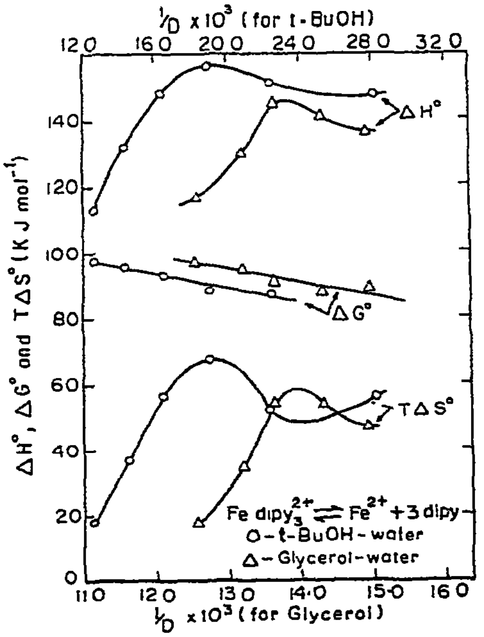

Fig. 3. Plots of ΔG^0, ΔH^0 and $T\Delta S^0$ vs. $1/D$ of solvent mixture.

TABLE 3

Thermodynamic functions of the tris-dipyridyl-ferrous complex in aqueous medium

Reaction	ΔG^0 (kJ mole^{-1})	ΔH^0 (kJ mole^{-1})	$T\Delta S^0$ (kJ mole^{-1})
$Fe(dipy)_3^{2+} \rightleftharpoons Fe^{2+} + 3\,dipy$	97.91	131.80	33.89 [a]
	99.58	117.15	17.57 [b]
	100.42	100.42	0.00 [c]
	99.74	117.15	17.41 [d]

[a] Calorimetric value, $\mu=0.1$ $NaNO_3$ [10]

[b] Calorimetric value, $\mu=1.0$ KNO_3 [11]

[c] Spectrophotometric value from temperature coefficient measurement (25–35°C), $\mu=0.025$ [12]

[d] Our values extrapolated from lower percentages of *t*-butanol and glycerol

Interpretation of the thermodynamic data in mixed solvents is extremely difficult as it involves knowledge of the structure of the liquid mixture and structure modification of the media when an ionic system is introduced in the media in addition to ionic solvation effects. However, attempts will be made to examine the free energy, enthalphy and entropy changes semi-quantitatively.

Before discussing the transfer thermodynamic parameters, it is in order to examine the nature of the mixed solvents used. Alcohol–water mixtures are known to present interesting behaviour because of the polar and apolar groups in the alcohols: the apolar hydrocarbon group in monohydric alcohols, because of its hydrophobic character, produces structure promotion when present in small amounts till the structure collapses and the hydrophilic –OH group takes part in H-bonding with water when the alcohol content increases. The hydrocarbon group in *t*-BuOH is the largest among MeOH, EtOH, *i*-PrOH and *t*-BuOH. As R′ (hydrocarbon group) decreases in size, the maximum in ΔS^E shifts to a higher mole fraction; it becomes shorter and broader at the same time. In the case of *t*-BuOH the maximum is at 0.22 while for EtOH it is 0.32 mole fraction. The monohydric alcohols containing a larger number of hydrophobic groups cause a more rapid and more extensive structure promotion [16] followed by a complete collapse due to packing imbalance at which ΔS^E occurs.

The temperature of maximum density for alcohol–water mixtures shows that normal alcohols, MeOH, EtOH, *n*-PrOH and *n*-BuOH, have decreasing structural contribution [17] to change in temperature of maximum density, $\Delta\theta_{str}(=\Delta\theta_{obs}-\Delta\theta_{id})$ with maximum shifting to lower x_2. Partial molar volume [18] $(\bar{V}_2 - V_2^0)$ also shows a minimum shifting to lower x_2 with EtOH, *i*-PrOH and *t*-BuOH.

In the case of the glycerol–water mixture the structure promoting propensities of the hydrophobic $-CH_3$ group in isopropyl alcohol is reduced by the $-CH_2OH$ group in glycerol, the –OH sites of the $-CH_2OH$ might tend to hydrogen-bonding with water, thus reducing structure promotion. No report of ΔS^E measurement is available. Variation of viscosity and partial molal volume suggests gradual breakdown of the 3D structure of water on addition of glycerol, though variation of the

β-parameter of the Jones-Dole equation for HCl and HBr in glycerol–water medium shows a maximum, and transport number measurements indicate structuring on addition of a very small amount of glycerol [19]. Basumallic and Kundu [20] in their estimate of transfer entropy report a broad maximum for $T\,\Delta S_t^0$ similar to that observed in the case of the MeOH–water system.

For the free energy change for the reaction

$Fe(dipy)_3^{2+} \rightleftharpoons Fe^{2+} + 3$ dipy

ΔG^0 values are found to decrease in all cases, indicating that the free energy change of transfer from water to the mixed solvent decreases (or is becoming more negative) with the increase in concentration of the organic component. ΔG_t^0, the transfer free energy, consists of an electrostatic part and a non-electrostatic part, the former depending on the dielectric constant of the medium and the latter indicating ion–solvent, solvent–solvent and other interactions. In the present case, since the reaction is iso-electric, the contribution of $\Delta G_{t\,el}^0$ will be negligible due to the small difference in the ionic ratio of $Fe(dipy)_3^{2+}$ and $Fe(H_2O)_x^{2+}$ which is always solvated. ΔG_t^0 will be mainly due to ion–solvent and solvent–solvent interactions. In view of this we would ascribe the ΔG_t^0 to the following. ΔG_t^0 indicates that the reaction is favoured in mixed solvents possibly because of (1) the higher solubility of "dipy" in the mixed solvent, (2) the difference in the solvation properties of $Fe(H_2O)_x^{2+}$ and $Fe(dipy)_3^{2+}$ in the media, and (3) the solvent–solvent interaction.

It may be interesting to examine the transfer parameters in light of the models based on those of Frank and Wen [21], later modified by Parker and co-workers [22,23] and Kundu and Bose [24] and others. The transfer of any species from water to a mixed solvent may be considered as taking place in four successive steps:

(1) dismantling of the hydration zone to give the bare species and infinitely dilute gas of water molecules;

(2) condensation of the gas to give structural liquid water;

(3) evaporation of the solvent molecules for forming a cavity to dissolve the solute;

(4) solvation of the solute and introduction into the cavity.

The transfer free energy for the reaction $Fe(dipy)_3^{2+} \rightleftharpoons Fe^{2+} + 3$ dipy is given by

$$\Delta G_t^0 = 3\mu_{t(dipy)} + \mu_{t(Fe^{2+})} - \mu_t[Fe(dipy)_3]^{2+}$$

To gain some idea about the μ_t of the different species one may use the Frank–Wen model for the Fe^{2+} ion, taking into account the behaviour of the alcohol–water mixture for the mixed solvent, and for the μ_t values of dipy and $[Fe(dipy)_3]^{2+}$ one could use a model utilizing the hydrophobic properties of the molecules (hydrophobic effects based on the suggestion of Parker and co-workers [22,23], which assumes the formation of a highly ordered solvent 'skin', initially of water and subsequently in mixed solvent (with bulk property different from bulk water), the property of the 'skin' being modified due to the presence of the organic component).

For the first transfer term (i.e. for dipy), the free energy of transfer has been found to be favourable for both glycerol–water as well as *t*-BuOH–water systems

[4]. For Fe^{2+} ion one would expect μ_t to be negatively favourable if the aquo-organic medium is more basic than water. The *t*-BuOH–water system is decidedly more basic than water. Although glycerol–water is reported to be less basic than water, recent results of Basumallick and Kundu [20] and also our work [7] indicate it to be more basic. In any case its magnitude will be small. As for $\mu_{t[Fe(dipy)_3]^{2+}}$, because of the large size, the contribution will be small. As expected, the transfer free energy for the reaction follows the same trend as the transfer free energy of dipy in glycerol–water and *t*-BuOH–water mixtures.

One may examine $T\Delta S^0$ and ΔH^0 in light of the above model. Since the reaction is iso-electric, one may assume both the transfer entropy and transfer enthalpy changes due to the non-electrostatic part as being the result of mainly ion–solvent and solvent–solvent interactions, so we have for the entropy change

$$T\Delta S_t^0 = T\Delta S_{t(Fe^{2+})} + 3T\Delta S_{t(dipy)} - T\Delta S_{t[Fe(dipy)_3]^{2+}}$$

Assuming that the ionic species are mainly solvated by water, $T\Delta S_{t(Fe^{2+})}$ will depend on the difference in entropy of the solvent media and the entropy transfer will pass through a maximum. Franks and Reid [25] found the ionic entropies in mixed MeOH–water systems to reach a maximum in the vicinity of 40 mole% methanol and explained it in terms of the solvent having the highest degree of structuring at this composition.

For "dipy", similar to the observations of Kundu and Bose [24] who found that the transfer entropy of nitroaniline passes through a maxima, one would expect the same trend. As for $[Fe(dipy)_3]^{2+}$, the change, because of its large size, is expected to be small. This accounts for the maximum in $T\Delta S^0$ as found experimentally. Thus the variation in ΔH^0 will also pass through a maximum, depending on the degree of structuring of the mixed solvent with composition.

It may be interesting to examine the position of the maximum with the nature of the solvent which, as pointed out earlier, has hydrophobic hydrocarbon and hydrophilic –OH groups. Of the monohydric alcohols the position of the maxima in structuring shifts to lower x_2 as one passes from CH_3OH to *t*-BuOH. In glycerol–water medium it is still smaller. A similar trend in the position of maximum in ΔH^0 and $T\Delta S^0$ is found although, because of a different contributing factor, the position is not exactly at that corresponding to only solvent mixtures The same type of difference in position of the maxima [20] has been found for $T\Delta S^0$ in the case of HI. The position of maxima in the present system does not agree with the HX system in glycerol–water. The present maximum in the case of the glycerol–water system supports the maximum in the case of the β-parameter as reported by Khoo [19]. The height of the maximum follows the sequence EtOH > MeOH > *t*-BuOH > glycerol.

It may be concluded that the behaviour of the system is possibly more complicated than depicted in the simple model. More experimental work is required with iso-electric and non-iso-electric systems in mono- and poly-ols.

ACKNOWLEDGEMENT

One of the authors (S.B.) thanks the C.S.I.R., New Delhi, for the award of a Senior Research Fellowship during the course of the work.

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