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THERMODYNAMICS OF 1,10-PHENANTHROLINIUM ION AND FERROUS-1,10 PHENANTHROLINE COMPLEX IN DIOXANE–WATER AND ETHANOL–WATER AT 25°C

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ABSTRACT

Enthalpies of formation of 1,10-phenanthrolinium ion and ferrous-1,10-phenanthroline (tris) complex in dioxane–water and ethanol–water media at 25°C have been determined by calorimetry. Results are discussed in the light of ion–solvent and solvent–solvent interactions.

INTRODUCTION

The complexes of 1,10-phenanthroline are well-known. The dissociation constants of this ligand and its ferrous complexes have been determined[1–4] using different techniques. From the dissociation constants at different temperatures, ΔH and ΔS were determined by Nasanen and Uusitalo[5]. Recently, Anderegg[6] determined ΔH of the ferrous-1,10-phenanthroline complex by calorimetry. All these works were carried out in aqueous medium. In this work, we report the determination of $\Delta H°$ of 1,10-phenanthrolinium ion and ferrous-1,10-phenanthroline complex by calorimetry in mixed solvents. The values of $\Delta S°$ have been calculated using the $\Delta H°$ in the present work and the corresponding $\Delta G°$ from earlier work in this laboratory and in the literature.

EXPERIMENTAL

The stock phenanthroline solution was prepared by directly weighing 1,10-phenanthroline (G. R. E. Merck) and dissolving it in ethanol or in dioxane, purified by the standard procedure as in our earlier work[7,8].

Ferrous solution was prepared by dissolving ferrous-ammonium sulphate (E. Merck, G. R.) in double-distilled water containing sufficient perchloric acid to prevent hydrolysis. The iron content was checked with standard dichromate. For each set of measurements a freshly prepared ferrous-ammonium sulphate solution was used.

Perchloric acid and caustic soda used, were of E. Merck reagent grade. The stock acid and alkali solutions were stadardised in the usual way. Any dilution of the solutions for the experiment was made with the organic solvent and water to have the desired solvent composition.

For the determination of $\Delta H°$, the enthalpy change of formation of the 1,10-phenanthrolinium ion and the ferrous complex, 1,10-phenanthroline solution was taken in the reaction vessel and the temperature of the solution was raised to 25°C by an auxiliary heater. The perchloric acid solution for the study of the 1,10-phenanthrolinium system and ferrous solution for the ferroin system, were taken in the burette or in the bulb maintained or equilibrated to attain the temperature of the solution in the dewar. The reactants were mixed by releasing the solution from the burette or by breaking the bulb. The heat liberated was followed by noting the change in the resistance box in the bridge of the calorimeter as used by O'Hara et al.[9] and Armstrong[10]. Veco thermistors 31A6 and 32A1 were used as temperature sensors. The calibration heater was similar to the one used by Stern and Hansen[11].

In the case of the 1,10 phenanthrolinium ion system, excess acid was added to the solution of 1,10-phenanthroline, so that the pH of the medium was around 2.5. The pK value for the 1,10-phenanthrolinium ion as presented by the equilibrium, $o\text{-PhH}^+ \rightleftharpoons o\text{-Ph} + \text{H}^+$ (1) is 5.05 at 25°C in water and in the aqueo–organic media, is about 4. So around pH of 2.5, for all practical purposes, the total phenanthroline in solution after the addition of acid, has been taken to be present as PhH^+. The enthalpy change per mole may be calculated from the heat change using the equation.

$$Q = -\Delta H_{o\text{-PhH}^+} \times C_{o\text{-Ph}}$$

where Q is the total heat evolved during the formation of o-PhH$^+$, $\Delta H_{o\text{-PhH}^+}$ is the enthalpy change per mole for the formation of phenanthrolinium ion and $C_{o\text{-Ph}}$ is the concentration of 1,10-phenanthroline.

Kolthoff et al.[2] observed that at a pH of less than 3, 1,10-phenanthroline is present only as o-PhH$^+$ and the equilibrium for the formation of ferroin may be represented as,

$$\text{Fe}^{2+} + 3(o\text{-PhH}^+) \rightleftharpoons \text{Fe}(o\text{-Ph})_3^{2+} + 3\text{H}^+ \qquad (2)$$

The stability constant of the $\text{Fe}(o\text{-Ph})_3^{2+}$ complex[12–15] indicates that in the presence of 10-fold excess of 1,10-phenanthroline added to react with the Fe^{2+} ion in a medium with a pH of about 2.5, all the ferrous iron is present as $\text{Fe}(o\text{-Ph})^{2+}$. So for the determination of the enthalpy change of reaction (2), we have Fe^{2+} solution to 1,10-phenanthroline solution having pH ≈ 2.5 and that phenanthroline is ten-fold excess. Under these experimental conditions one does not have to take into consideration the presence of other complex species. The enthalpy change may be calculated using the equation

$$Q = -\Delta H_{\text{Fe}(o\text{-Ph})_3^{2+}} \times C_{\text{Fe}^{2+}}$$

where the terms have their usual significance.

For the direct evaluation of the enthalpy change corresponding to the reaction, $Fe^{2+} + 3o\text{-Ph} \rightleftharpoons Fe(o\text{-Ph})_3^{2+}$, Fe^{2+} solution was added to an excess of 1,10-phenanthroline in neutral aqueo–organic medium. The enthalpy change was calculated with equation

$$Q = -\Delta H_{Fe(o\text{-Ph})_3^{2+}} \times C_{Fe^{2+}}.$$

To avoid the extrapolation of the ΔH values to zero ionic strength to get the thermodynamic values, ΔH°, we have carried out measurements in solutions with ionic strength of the order of 10^{-3} M, where it is reasonable to assume that

$$f_{Fe^{2+}} = f_{Fe(o\text{-Ph})_3^{2+}} \qquad \text{and} \qquad f_{o\text{-PhH}^+} = f_{H^+}$$

where f is the activity coefficient. Under these conditions, the K_c's of reactions (1) and (2) become equal to the thermodynamic equilibrium constants K_T's. As the ionic strength is low and the activity coefficients of the same valence-type ions may be taken to be equal, the ΔH's determined experimentally may be taken equal to the thermodynamic enthalpy change, ΔH°.

RESULTS

The enthalpy changes are given in Table 1. Columns 2 and 3 give the mole-fraction of ethanol and dioxane in the media. Columns 4 and 5 give the ΔH° for the reaction corresponding to eqn (1) for the 1,10-phenanthrolinium ion and columns 6 and 7 give the ΔH° for reaction (2) in ethanol–water and dioxane–water, respectively. In columns 8 and 9 are reported the values of ΔH° for $Fe^{2+} + 3o\text{-Ph} \rightarrow Fe(o\text{-Ph})_3^{2+}$ in the two aqueous–organic media. The values in the parenthese are corresponding numbers calculated on the basis

$$\underset{\text{in neutral media}}{\Delta H^\circ_{Fe(o\text{-Ph})_3^{2+}}} \rightleftharpoons \underset{\text{in acidic media}}{\Delta H^\circ_{Fe(o\text{-Ph})_3^{2+}}} + 3\Delta H^\circ_{o\text{-PhH}^+}$$

DISCUSSION

In the present work, ΔH° of the formation of $o\text{-PhH}^+$ in 10, 20, 30, 45 and 60% by weight of dioxane in dioxane–water media and that of ethanol in ethanol–water media have been determined by extrapolation to zero percentage of organic component, the ΔH° of the formation in aqueous medium has been found. The extrapolated value in both cases, dioxane–water as well as ethanol–water media is -3.95 (± 0.05) kcal mol^{-1} at 25°C. The values of ΔH° in water determined calorimetrically, in literature are -4.6 (Kulba and Makashev[16]), -3.95 (Anderegg[6]), -3.5 (Perkampus and Kohler[17]), -3.6 (Eatough[18]) and -3.45 (Paoletti, Dei and Vacca[19]). The present value is the same as that by Anderegg and is in good agreement with the value -4.07 (± 0.25)[15] by spectrophotometry. The value of -3.4 for ΔH° obtained by potentiometric measurement[5] is a bit too low.

TABLE I

ENTHALPY OF FORMATION OF 1,10-PHENANTHROLINIUM ION AND FERROUS(II)-1,10 PHENANTHROLINE COMPLEX IN ETHANOL- AND DIOXANE-WATER MEDIA AT 25°C

Wt. % of organic solvent ethanol or dioxane	*Ethanol*	*Dioxane*	$-\Delta H°$ *of*					
			1,10-Phenanthrolinium ion		$Fe^{2+} + 3\,o\text{-}PhH^{+} \rightarrow Fe(o\text{-}Ph)_3^{2+} + 3H^{+}$		$Fe^{2+} + 3\,o\text{-}Ph \rightarrow Fe(o\text{-}Ph)_3^{2+}$	
			In ethanol	*In dioxane*	*In ethanol*	*In dioxane*	*In ethanol*	*In dioxane*
0	0	0	4.00[a] (4.07[b] ±0.25)	4.00[a] (4.07[b] ±0.25)	19.0[a]	19.0[a]	31.05[a] (31.31[b])	31.05[a] (31.31[b])
10	0.0417	0.0222	4.30	4.46	18.56	20.95	31.28 (31.40)	34.37 (34.23)
20	0.0897	0.04865	4.57	4.73	18.30	12.68	31.84 (32.01)	37.41 (36.87)
30	0.1436	0.0806	4.32	4.47	17.75	21.20	30.70 (30.71)	35.29 (34.61)
45	0.2425	0.1432	3.75	3.47	—	19.07	—	31.26 (29.48)
60	0.37	0.244	3.45	3.50	—	—	—	—

[a] Extrapolated value. [b] Spectrophotometric determination.

Plots of $\Delta H°$ against mole fraction of the organic component in ethanol–water and dioxane–water for the formation of ferroin at 25°C for the reaction $Fe^{2+} + 3o\text{-}PhH^+ \rightarrow Fe(o\text{-}Ph)_3^{2+} + 3H^+$ as well as $Fe^{2+} + 3o\text{-}Ph \rightarrow Fe(o\text{-}Ph)_3^{2+}$ are shown in Fig. 1. In both cases the values in the region of low percentage of the organic component have been extrapolated to obtain the value of $\Delta H°$ in water. From the present measurement we have for the $\Delta H°$ for the reaction $Fe^{2+} + 3o\text{-}Ph \rightarrow Fe(o\text{-}Ph)_3^{2+}$ a value of −31.05 kcal mol^{-1} at 25°C. This is in good agreement with the value −31.31 kcal mole by spectrophotometry[15]. The value of −33.00 kcal mole at 20°C by direct calorimetry reported by Anderegg[6] appears to be a bit too high.

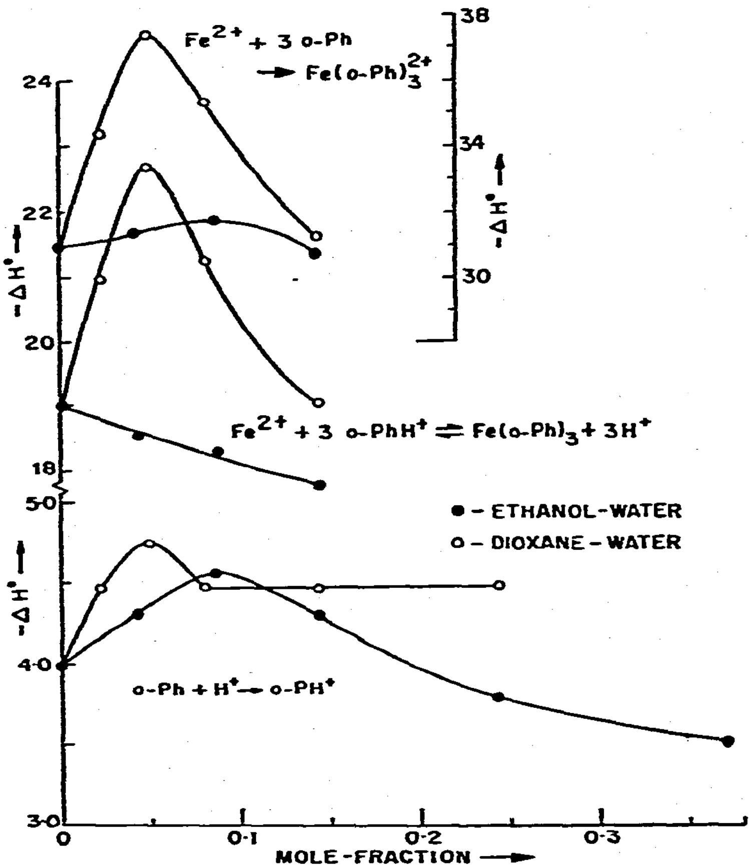

Fig. 1. Enthalpy of formation of 1,10-phenanthrolinium ion and Fe(II)-1,10-phenanthroline complex.

As seen from the figure, the values of $\Delta H°$ in media containing low mole fraction of the organic component is within experimental error linear in composition; for higher percentage, however, it passes through a maximum. The transfer enthalpy ($\Delta H°_{H_2O} - \Delta H_M$) except for reaction in ethanol–water media, increases linearly up to a mole fraction of ±0.1, and then decreases. The decrease is sharper in dioxane–water medium than in ethanol–water system.

Arnett[20] et al. suggested that there is a significant structural change in ethanol–water mixture at about 0.1 mole fraction of ethanol. The addition of ethanol up to a mole fraction of 0.1 there is an enhancement of structure in the solution and at that composition the maximum order is obtained. Additional ethanol can no longer build structure without interfering with the established order in the systems. Thus properties of the mixture such as partial molar volume, activity coefficient all show maximum at this composition. The nature of the ΔH° curve show similar trend. Frank and Evans[21] explained the entropy changes of complexes in light of structure making and structure breaking in the medium. Franks[22] recently reviewed the properties of mixed solvents in this light. In view of this it will be of interest to see how the ΔS° formation of ferroin as well as *o*-phenanthrolinium ion varies with solvent composition. Recently in our laboratory ΔG° for 1,10-phenanthrolinium ion in the ethanol–water system has been determined[8]. Combining these with ΔH°, ΔS°'s for the 1,10-phenanthrolinium ion in ethanol–water media have been calculated. Although ΔG° decreases continuously and ΔH° passes through a maximum the ΔS° values do not show any such trend. On addition of alcohol up to 20% a decrease is observed after which ΔS° remains practically the same. ΔG°'s for the complex in dioxane–water medium are not known and work is in progress for these determinations.

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