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STUDIES ON THE SOLUBILITY AND THE STABILITY CONSTANTS OF FERROUS-TRIS-BIPYRIDINE AND PHENANTHROLINE COMPLEXES AND THE DETERMINATION OF FREE ENERGY OF TRANSFER OF FERROUS ION FROM WATER TO 2-PROPANOL–WATER MIXTURES

BISHNU PADA DEY, DIPAK SENGUPTA and SUJIT CHANDRA LAHIRI

Department of Chemistry, Kalyani University, Kalyani 741235, West Bengal (India)

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ABSTRACT

The equilibrium constants for the reactions

$$[\mathrm{Fe(bipy)_3}]^{2+}\,\{\text{or }[\mathrm{Fe(Phen)_3}]^{2+}\} + 3\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{2+} + 3\,\text{bipy H}^+ \;(\text{or } 3 \text{ Phen H}^+)$$

and

$$[\mathrm{Fe(bipy)_3}]^{2+}\,\{\text{or }[\mathrm{Fe(Phen)_3}]^{2+}\} \rightleftharpoons \mathrm{Fe}^{2+} + 3\,\text{bipy (or 3 Phen)}$$

were determined spectrophotometrically in 2-propanol–water mixtures (up to 75.8 wt% of 2-propanol) at 298 K. The results were coupled with the solubility values of $[\mathrm{Fe(bipy)_3}]^{2+}$ or $[\mathrm{Fe(Phen)_3}]^{2+}$ as perchlorates and bipy (or Phen) to obtain values for the free energy of transfer of ferrous ion from water to 2-propanol–water mixtures.

INTRODUCTION

The variation of medium, i.e. change in solvent, is known to exert profound influence on the properties of solute, the rate and the equilibrium constants of chemical reactions. The studies have found varied applications in chemistry [1]. These considerations have led us to study the equilibrium constants of the well-known "isoelectric reactions" of the type

$$[\mathrm{FeL_3}] + 3\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{2+} + 3\mathrm{HL}^+ \qquad (1)$$

and

$$[\mathrm{FeL_3}]^{2+} \rightleftharpoons \mathrm{Fe}^{2+} + 3\mathrm{L} \qquad (2)$$

and the solubility values of $[\mathrm{FeL_3(ClO_4)_2}]$ (L = bipy or Phen) in different 2-propanol + water mixtures.

The value of such studies lies in the fact that the free energies of Fe^{2+} ion can easily be calculated from them without any extrathermodynamic assumptions [2,3]. The method, if properly used, may form the basis for the

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determination of the "medium effects" of other ions without any assumption.

EXPERIMENTAL

2-Propanol (AR, BDH) was distilled and the middle fraction collected for preparing the solutions. Freshly distilled 2-propanol was always used. All other chemicals were of guaranteed reagent (Merck) grade. Ferrous ammonium sulphate solution was prepared by dissolving a weighed amount of the salt in a known quantity of perchloric acid. Stock solutions of the ligands (2,2′-dipyridyl and 1,10-phenanthroline (GR, Merck)) in the appropriate solvents were prepared by direct weighing.

The determination of the equilibrium constants at 298 K for the reactions (1) and (2) in 2-propanol + H_2O mixtures are similar to those previously reported [4,5]. The wavelengths of absorption maxima of tris-bipyridine iron(II) (524 nm) and tris-phenanthroline iron (II) (510 nm) complexes are independent of pH but the absorptivities are at a maximum at around pH 5.

The molar absorption coefficients of the tris-complexes at different wavelengths were determined from absorption measurements of solutions containing 12- to 20-fold concentrations of the ligands in different concentrations of ferrous ion, thus ensuring complete complexation of the ferrous ions as was apparent from the constancy in optical density readings.

For determination of the stability constants, the absorbances of solutions of strength $8\text{–}20 \times 10^{-5}$ M were measured at the appropriate wavelengths after equilibration at 298 K.

TABLE 1

Molar absorption coefficients of the complexes, equilibrium constants (in terms of pK), solubilities and solubility products of [Fe(bipy)$_3$(ClO$_4$)$_2$] and [Fe(Phen)$_3$(ClO$_4$)$_2$] in 2-propanol–water mixtures at 295 K

2-Propanol (wt%)	Molar absorption coefficients of the complexes (dm^3 mol^{-1} cm^{-1})				pK for reaction (1)	
	bipy		phen		bipy	phen
	520 nm	530 nm	510 nm	520 nm		
0	8416	8250	11342	10765	4.36	5.35
8.0	8160	7060	10666	10300	3.69	4.90
16.3	8927	7807	10733	10333	3.04	4.73
25.1	9127	8127	10500	10000	3.32	4.71
34.3	9067	8327	10166	9666	3.73	4.56
43.9	8413	7800	10000	9333	4.93	5.23
54.0	8660	7993	10333	9700	5.87	5.88
64.6	8560	7833	9666	9058	6.19	6.05
75.8	7500	6807	9933	9116	6.05	6.57

It was observed that the yellow 1 : 1 complex having a broad absorption maximum around 450 nm is formed only in the presence of excess of iron(II) in acidic solutions. The complex was rapidly converted into tris-complex, but under the experimental conditions used in this study FeL^{2+} and FeL_2^{2+} complexes were not formed. Similar observations were made by Kolthoff et al. [6].

The concentrations of the complex FeL_3^{2+}, calculated from the optical density values and the molar extinction coefficients of the complexes at each wavelength, were found to be the same (within 0.2%) and the average value was used in the calculations of the constant for reaction (1).

The complexes $FeL_3(ClO_4)_2$ were prepared and purified as described by Dwyer and McKanzie [7]. The solubilities of the complexes at 295 K were determined as reported previously [2,3].

The extinction coefficients, solubilities of the complexes and the equilibrium constant values were determined spectrophotometrically using a Beckman DU-2 spectrophotometer and are recorded in Table 1.

RESULTS AND DISCUSSION

The equilibrium constant K_a for reaction (1) is

$$K_a = \left(\frac{C_{Fe^{2+}} C^3_{HL}}{C_{FeL_3^{2+}} C^3_{H^+}} \right) \left(\frac{f_{Fe^{2+}} f^3_{HL^+}}{f_{FeL_3^{2+}} f^3_{H^+}} \right) \approx \left(\frac{C_{Fe^{2+}} C^3_{HL^+}}{C_{FeL_3^{2+}} C^3_{H^+}} \right) \tag{3}$$

and since the ionic strengths of the solutions ranged between 2.4×10^{-4} and

pK for reaction (2)		Solubility of tris complexes (mol dm^{-3})		Activity solubility product of tris complexes (mol^2 dm^{-6})($\times 10^9$)	
bipy	phen	bipy ($\times 10^3$)	phen ($\times 10^3$)	bipy	phen
17.77	20.50	1.75	0.45	12.82	0.28
16.37	19.38	2.71	0.79	39.34	1.36
15.04	18.66	3.24	1.68	56.13	10.05
14.44	17.59	5.34	3.41	163.70	55.96
14.08	16.94	5.67	6.73	144.37	206.98
14.62	16.84	5.55	5.65	95.96	97.24
15.04	16.86	4.83	3.44	42.64	22.29
15.06	16.31	2.55	2.90	6.39	8.08
14.68	16.12	2.43	1.31	2.38	0.87

1.4×10^{-3} mol dm^{-3}, it is reasonable to assume that $f_{\mathrm{Fe}^{2+}} = f_{\mathrm{FeL}_3^{2+}}$ and $f_{\mathrm{HL}^+} = f_{\mathrm{H}^+}$. The use of "inert electrolytes" to maintain ionic strengths was carefully avoided as it was likely that the "solute–solvent" interactions of unknown magnitude could mask the "medium effects" on the equilibrium constants [8].

The H^+ ion concentrations were calculated theoretically. Other relevant values were obtained as follows

$$[\mathrm{Fe}^{2+}]_{\mathrm{free}} = [\mathrm{Fe}^{2+}]_{\mathrm{Total}} - [\mathrm{FeL}_3^{2+}] \tag{4}$$

and

$$[\mathrm{LH}^+] + [\mathrm{L}]_{\mathrm{free}} = [\mathrm{L}]_{\mathrm{Total}} - 3[\mathrm{FeL}_3^{2+}]_{\mathrm{free}} \tag{5}$$

and

$$\mathrm{p}K_T = \mathrm{p}C_{H^+} + \log \frac{[\mathrm{LH}^+]}{[\mathrm{L}]} \tag{6}$$

The $\mathrm{p}K_T$ values for the reaction

$$\mathrm{HL}^+ \rightleftharpoons \mathrm{H}^+ + \mathrm{L} \tag{7}$$

were taken from results obtained in our laboratory [9]. The equilibrium constants for reaction (2) are given by

$$K = K_{\mathrm{a}} \times K_T^3 \tag{8}$$

The results are recorded in Table 1.

The solubilities of $[\mathrm{Fe(bipy)_3(ClO_4)_2}]$ and $[\mathrm{Fe(Phen)_3(ClO_4)_2}]$ increase and pass through a maximum at about 34 wt% of 2-PrOH. It is hardly possible to correlate the solubility maximum with $-\Delta H^E$ (excess enthalpy of mixing) of mixed solvents but the results show that both $-\Delta H^E$ and the solubility maxima move towards lower mol fractions of organic solvent [10] from MeOH ($X_2 \sim 0.3$), EtOH ($X_2 \sim 0.2$) and 2-PrOH ($X_2 \sim 0.15$).

The presence of solubility maxima in alcohol + H_2O mixtures is probably due to opposing interactions of the complexes and the ligands with the solvent mixtures. The aromatic heterocyclic ligands undergo dispersion interactions with alkyl group of the alcohol molecules. The interactions increase with increasing percentage of alcohol as well as with the increasing hydrophobic character of the alkyl group of the alcohol leading to (i) increased stabilization of the ligands (which is in the order 2-PrOH > EtOH > MeOH for a given mol fraction of alcohol) and (ii) decreased stabililty of the complexes.

These opposing effects in the solvent mixtures explain why the solubilities of the complexes are higher at low percentages of 2-PrOH (where the 2-PrOH content is low) compared with those in MeOH + H_2O and EtOH + H_2O mixtures whereas the reverse is true at higher percentages.

It was observed that the molar extinction coefficients of the complexes showed no systematic variations and could not be correlated with other data obtained. Although the oscillator strengths of ferrodiin [11] were found to change in 2-PrOH + H_2O mixtures there is no study reported on the correlation of extinction coefficients and oscillator strengths.

The studies of the stability constant of the complex show that $\Delta G_t^0 (= 2.303RT\,\Delta pK_T)$ for reaction (2) is negative, i.e. the ΔG_t^0 values of the FeL_3^{2+} complexes are unstable in mixed solvents. However, ΔG_t^0 for reaction (1) is positive (except at the beginning). These results reflect the differences in the solvational properties of the different ions present in the solution. Since the free energies of transfer of ions generally provide better insight of ion–solvent interactions, attempts have been made to determine $\Delta G_t^0(Fe^{2+})$. For reaction (2), we can write eqn. (9)

$$\Delta G_t^0(Fe^{2+}) = \Delta G_t^0(2) - 3\,\Delta G_t^0(L) + \Delta G_t^0(FeL_3^{2+}) \tag{9}$$

Since perchlorate ions occur on both sides of eqns. (1) and (2) (though not shown), $\Delta G_t^0(ClO_4^-)$ cancels. Moreover, since both $Fe(ClO_4)_2$ and $[Fe(bipy)_3(ClO_4)_2]$ or $[Fe(Phen)_3(ClO_4)_2]$ are associated with six molecules of water of hydration, $\Delta G_t^0(H_2O)$ also cancels. Further it has been assumed that the composition of $[FeL_3(ClO_4)_2]$ complexes in aqueous and mixed solvents is the same as that in the solid phase.

The ΔG_t^0 (FeL_3^{2+}) values were calculated from eqn. (10)

$$\Delta G_t^0 = -2.303RT\,\log\left(\frac{C_s}{C_w}\right) \tag{10}$$

where C represents the molar concentration of $[FeL_3^{2+}]$ assuming the solubility of large $[FeL_3^{2+}]$ to be independent of the anion present.

However, it may be argued that the solubility of a salt depends very much on the solvation of cations and anions. Thus, in order to obtain accurate values, the values of solubility, C, for the electrolyte $[FeL_3(ClO_4)_2]$ should be replaced by values for the activity solubility product K_s (eqn. 11)

$$K_s = 4C^3\left(f_{FeL_3^{2+}}\right)\left(f^2_{ClO_4^-}\right) \tag{11}$$

Since the solubility (in mol dm^{-3}) of $FeL_3(ClO_4)_2$ is very small, the Debye–Huckel limiting law (eqn. 14)

$$-\log f_i = AZ_i^2\sqrt{\mu} \tag{12}$$

was used for calculation of the activity coefficient of ions. The values of the constant A were calculated using values for the dielectric constants of the mixed solvents from the literature [12]. The K_s values are recorded in Table 1.

From the experimental values of $\Delta G_t^0(L)$ [9] and $\Delta\Delta G_t^0$ (eqn. 2), $\Delta G_t^0(Fe^{2+})$ from water to 2-propanol + H_2O mixtures were calculated from eqn. (9) (Table 2).

The use of $\Delta G_t^0(L)$ and $\Delta G_t^0[FeL_3(ClO_4)_2]$ values at 295 K introduce error in our values of $\Delta G_t^0(Fe^{2+})$. However, the method involves no ex-

TABLE 2

Free energies of transfer ($-\Delta G_t^0$) in kJ

2-PrOH (wt%)	bipy	phen	$Fe(bipy)_3(ClO_4)_2$		$Fe(phen)_3(ClO_4)_2$		For the reaction $FeL_3^{2+} \rightleftharpoons Fe^{2+} + 3L$		(Fe^{2+})			
									(a)		(b)	
			(a)	(b)	(a)	(b)	bipy	phen	Using bipy	Using phen	Using bipy	Using phen
8.0	2.8	2.9	1.1	2.7	1.4	3.9	8.0	6.4	0.7	−0.9	1.0	1.4
16.3	5.3	4.9	1.5	3.6	3.2	8.8	15.6	10.5	1.2	−1.0	3.3	4.6
25.1	7.3	7.6	2.7	6.2	5.0	13.0	19.0	16.6	−0.2	−1.2	13.3	6.8
34.3	9.4	10.1	2.9	5.9	6.6	16.2	21.1	20.3	−4.2	−4.4	−1.2	6.2
43.9	11.9	12.2	2.8	4.9	6.2	14.3	18.0	20.9	−12.9	−9.5	−10.8	−1.4
54.0	13.1	13.9	2.5	3.0	5.0	10.7	15.6	20.8	−21.2	−15.9	−20.7	−10.2
64.6	14.9	15.5	0.9	−1.7	4.6	8.2	15.5	23.9	−28.3	−18.0	−30.9	−14.1
75.8	16.1	17.0	0.8	−4.1	2.6	2.8	17.6	25.0	−29.9	−23.4	−34.8	−23.2

(a) From simple solubility values; (b) from solubility product values.

trathermodynamic assumptions to separate ΔG_t^0 (electrolytes) into ionic ΔG_t^0 (i) values: neither does it use the Born equation or other improved equations, the limitations of which are well-known [13,14].

In spite of the anomalies observed in the value of $\Delta G_t^0(Fe^{2+})$, the values may be regarded as being in good agreement in view of the errors involved in the determination of ΔG_t^0 values for the ligands, their complexes and the stability constants of the complexes (eqn. 2). It is natural that the two sets of assumptions lead to considerable differences in $\Delta G_t^0(Fe^{2+})$ values. However, the results based on solubility product values should be preferred as they are theoretically acceptable.

It should be noted that considerable difficulties arise in measuring solubilities and determining the stability constants for such extremely stable complexes as $[FeL_3(ClO_4)_2]$ involving three ligands. The observed anomaly in transfer chemical potentials of Fe^{2+} (Table 2) may be ascribed to these factors. However, by suitable choice of systems involving monovalent ions and a smaller number of ligands, transfer chemical potentials of ions can be derived accurately without extrathermodynamic assumptions.

There are reports of wide divergence in ΔG_t^0 (monovalent ion) values (to the extent of 20–30 kcal mol^{-1}) [15]. Considering the values, our results can be regarded as being in good agreement. However, we consider the values based on Phen to be more acceptable due to the following reasons [11]: (i) greater stability of 1,10-phenanthroline and ferroin due to the presence of fixed coplanarity of heterocyclic rings and greater resonance stabilization compared to 2,2′-dipyridyl and ferrodiin; (ii) conversion of the *trans* form of 2,2′-dipyridyl to the *cis* form in acid solutions and complexes

$$Fedipy_3^{2+} \rightleftharpoons Fe^{2+} + 3\ dipy$$

The conversion of *trans* to the *cis* form involves energy changes which may vary with the solvents leading to an energy difference of uncertain magnitude particularly where three molecules of dipy are involved. Therefore, error in the $\Delta G_t^0(Fe^{2+})$ values may be high if we use ferrodiin complexes.

The results indicate that $\Delta G_t^0(Fe^{2+})$ is negative, i.e. spontaneous at the beginning but becoming increasingly positive indicating that the transfer process is increasingly non-spontaneous. The results are in conformity with the structural changes of water molecules with the addition of 2-propanol. It is apparent that the Fe^{2+} ion is preferentially solvated by water molecules. Addition of 2-propanol enhances the three dimensional structure of water molecules which may lead to firm attachment of water molecules to the Fe^{2+} ion. But after maximum structuration in solvent mixtures of strength about 25 wt% of 2-propanol, structural collapse takes place. This may lead to weakening of Fe^{2+}–H_2O bonds and replacement of H_2O molecules by isopropanol molecules at high percentages of the latter.

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