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DETERMINATION OF THE FREE ENERGY OF SOLVATION OF FERROUS ION IN WATER AND FREE ENERGIES OF TRANSFER OF FERROUS ION FROM WATER TO ETHANOL–WATER MIXTURES

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ABSTRACT

The free energy of solvation of ferrous ion in water and the free energies of transfer of ferrous ion from water to ethanol + water mixtures have been determined without extrathermodynamic assumptions Some comments are made regarding the utility of the method

In our previous communication [1], we reported the free energies of transfer of Fe^{2+} ion, $\Delta G_t^{\ominus}(Fe^{2+})$ from water to ethanol + water mixtures To calculate $\Delta G_t^{\ominus}(Fe^{2+})$, we have used the $\Delta G_t^{\ominus}(1)$ values for the isoelectric reactions

$$FeL_3(ClO_4)_2 \rightleftharpoons Fe(ClO_4)_2 + 3L \tag{1}$$

which is usually written as

$$FeL_3^{2+} \rightleftharpoons Fe^{2+} + 3L \tag{2}$$

(where L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)) and the $\Delta G_t^{\ominus} Fe(ClO_4)_2$ and $\Delta G_t^{\ominus}(L)$ values determined from solubility measurements in water and water + ethanol mixtures

Both Fe^{2+} and FeL_3^{2+} are present as perchlorates so that the contributions due to $\Delta G_t^{\ominus}(ClO_4^-)$ ions automatically cancel each other and need not be determined Moreover, both $FeL_3(ClO_4)_2$ and $Fe(ClO_4)_2$ are associated with six molecules of water of crystallisation and thus the free energy changes associated with the transfer of water molecules from water to mixed solvents also cancel out The utility of the method lies in the fact that the method gives the $\Delta G_t^{\ominus}(Fe^{2+})$, i e free energy of transfer of single ion, directly from the experimental values without any extrathermodynamic assumptions

However, we have used the solubility values of $FeL_3(ClO_4)_2$ to calculate $\Delta G_t^{\ominus} FeL_3(ClO_4)_2$ However it is well-known that the solubility of a salt

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TABLE 1

Activity solubility products of perchlorates of tris-complexes (nmol dm^{-3})

EtOH (wt %)	Ferrodin	Ferroin	Ferrodin	Ferroin
0 0	1 747	0 453	12 818	0 287
8 0	2 688	0 840	39 022	1 613
16 4	3 057	1 248	50 782	4 631
25 3	4 698	2 463	132 880	26 213
34 4	7 452	6 484	323 052	237 258
44 0	10 634	9 092	488 314	362 631
54 1	9 835	6 117	258 623	109 842
64 7	8 336	5 031	121 882	51 686
76 0	5 940	2 567	35 988	8 541

depends much on the solvation of cations and anions and it is desirable to use the activity solubility product K_s of the electrolyte $FeL_3(ClO_4)_2$ to obtain the accurate values of $\Delta G_t^{\ominus}(Fe^{2+})$, the free energy of transfer of Fe^{2+} ion [2,3] The activity solubility product K_s for the reaction

$$FeL_3(ClO_4)_2 \rightleftharpoons FeL_3^{2+} + 2ClO_4^- \qquad (3)$$

has been calculated using the relation

$$K_s = 4S^3 f_{FeL_3^{2+}} f_{ClO_4^-}^2 = 4S^3 f_{\pm}^3 \qquad (4)$$

where S is the solubility of $FeL_3(ClO_4)_2$ in the respective solvents

TABLE 2

(a) Values for the free energies of transfer of Fe^{2+} (from bipy and phen complexes) from water to ethanol + water in mixtures

From bipy complex

EtOH (wt %)	$\Delta G_t^{\ominus}(L)$	$\Delta G_t^{\ominus}(1)$	$\Delta G_t^{\ominus}(FeL_3^{2+})$	$\Delta G_t^{\ominus}(Fe^{2+})$
8 0	2 49	3 36	2 7	−1 4
16 4	4 70	4 91	3 4	−5 8
25 3	7 50	5 13	5 7	−11 6
34 4	9 01	8 73	7 9	−10 4
44 0	11 33	12 15	8 9	−12 9
54 1	12 73	15 06	7 4	−15 8
64 7	14 21	17 63	5 5	−19 5
76 0	15 74	14 72	2 5	−30 0

$\Delta G^{\ominus}(Fe^{2+})$ (in water) $= \Delta G^{\ominus}(1) + \Delta G^{\ominus}(FeL_3^{2+}) - 3\Delta G^{\ominus}(L)$ Solubility values of bipy and phen at 298 K are $4\ 15 \times 10^{-2}$ and $8\ 85 \times 10^{-2}$ M respectively $\Delta G^{\ominus}(1)$ values are 100 00 and 117 00 kJ of Fe^+ bipy and phen complexes at 298 K, and $\Delta G^{\ominus}$ values calculated from the

Since the solubility values (mol dm^{-3}) of $FeL_3(ClO_4)_2$ are very small, the Debye–Huckel limiting equation

$$-\log f_{\pm} = AZ_{+}Z_{-}\sqrt{\mu} \tag{5}$$

was used for the calculation of the activity coefficients of ions The values of the constant A in different solvents were calculated using dielectric constant values of the mixed solvents from the literature [1] The K_s values are reported in Table 1 The $\Delta G_t^{\ominus}(Fe^{2+})$ values from water to different ethanol + water mixtures using bipy and phen are given in Tables 2(a) and 2(b) respectively

The use of $\Delta G_t^{\ominus}(1)$ and $\Delta G_t^{\ominus}(FeL_3(ClO_4)_2)$ values at 295 K introduce error in our values of $\Delta G_t^{\ominus}(Fe^{2+})$

It should also be noted that the errors in the experimental determination of $\Delta G_t^{\ominus}(1)$, $\Delta G_t^{\ominus}(L)$ and $\Delta G_t^{\ominus}(FeL_3(ClO_4)_2)$ introduce considerable error in the values of $\Delta G_t^{\ominus}(Fe^{2+})$ In spite of the limitations, the method is useful as it gives the free energy change or free energies of transfer of Fe^{2+} directly without any extrathermodynamic assumption or without use of the Born equation or other improved equations which are open to question [4,5] We have also used the method to calculate the free energy change of Fe^{2+} ion in water simply from the relation

$$\Delta G^{\ominus}(Fe^{2+}) = \Delta G^{\ominus}(1) - 3\Delta G^{\ominus}(L) + \Delta G^{\ominus}(FeL_3(ClO_4)_2)$$

by using the solubility values of bipy and phen determined by Bandyopadhyay et al [6] and other values from the literature [1,7,8] The results for $\Delta G^{\ominus}(Fe^{2+})$ in water using bipy and phen differ by about 8–9 kJ Similarly, the $\Delta G_t^{\ominus}(Fe^{2+})$ values in ethanol + water mixtures using bipy and phen show variations

(b) Values for the free energy transfer of Fe^{2+} (from phen complex) from water to ethanol + water mixtures

From phen complex				
EtOH (wt %)	$\Delta G_t^{\ominus}(L)$	$\Delta G_t^{\ominus}(1)$	$\Delta G_t^{\ominus}(FeL_3^{2+}(ClO_4)_2)$	$\Delta G_t^{\ominus}(Fe^{2+})$
8 0	2 33	4 42	4 2	1 7
16 4	4 45	7 30	6 8	0 8
25 3	7 42	10 89	11 1	−0 3
34 4	10 03	12 26	16 5	−1 3
44 0	12 01	18 25	17 6	−0 3
54 1	13 38	21 68	14 6	−3 9
64 7	14 71	20 42	12 7	−11 0
76 0	16 22	22 59	8 3	−17 7

solubility products of $Fe(bipy)_3(ClO_4)_2$ and $Fe(phen)_3(ClO_4)_2$ at 295 K are 50 2 and 53 9 kJ respectively $\Delta G^{\ominus}(Fe^{2+})$ (in water) = 126 5 (bipy) and 135 8 kJ using phen (average = 131 2 kJ) $\Delta G^{\ominus}(Fe^{3+}) = 205$ 3 kJ

It is well known that the ab initio calculation of electrostatic solvation energy of ions requires knowledge of the radii, dipole, quadrupole moments and the polarizabilities of the solvent and the ions Moreover, the number and the geometric arrangement of the solvent molecules in the primary solvation shell and the energetics of any structural effects on the solvent and other effects must be known [9]

It has been pointed out by Popovych [9] that even in the most widely studied solvent (water), the accuracy of the hydration energy calculations is no better than 2–3 kcal (g ion)$^{-1}$ i e about 8–12 kJ (g ion)$^{-1}$, and the accuracy of the $\Delta G^\ominus$ values in non-aqueous solvents would be expected to be of the same order of magnitude

Considering the limitations, the $\Delta G^\ominus(Fe^{2+})$ or $\Delta G_t^\ominus(Fe^{2+})$ values using bipy and phen in the present determination can be regarded as being in good agreement It is true that the anomaly in the $\Delta G^\ominus$ values may also be due to the error involved in measuring solubilities and determining the stability constants for such extremely stable complexes as $FeL_3(ClO_4)_2$ involving three ligands

We prefer the value of $\Delta G^\ominus(Fe^{2+})$ based on phen because [10] (1) bipy is present in the *cis* form in neutral solution but in the complex $Fe(bipy)_3^{2+}$ or in acid solution *trans*-bipy is converted to *cis*-bipy which involves energy changes of uncertain magnitude The error may be considerable as three molecules of bipy are involved, (2) the greater stability of phen and ferroin due to the fixed coplanarity of heterocyclic rings and greater resonance stabilization compared with bipy and $Fe(bipy)_3^{2+}$

Once the value of $\Delta G^\ominus(Fe^{2+})$ is known, we can calculate the value of $\Delta G^\ominus(Fe^{3+})$ using the value of $E^\ominus$ for the reaction $Fe^{3+} + e^{-1} \rightleftharpoons Fe^{2+}$ [11] The values of $\Delta G^\ominus(Fe^{2+})$ and $\Delta G^\ominus(Fe^{3+})$ in water are recorded in Table 2(b) $\Delta G^\ominus(Fe^{2+})$ becomes increasingly spontaneous except at 44 0 wt%, although full interpretation of the results requires more information

There are divergent views on the use of 'isoelectric' reactions to calculate the free energy of transfer of single ions Blandamer et al [12] erroneously consider that the method suggested by Lahiri et al [1,2] is based on the extrathermodynamic assumption that $\Delta(aq \rightarrow X_2)$ $\mu^\star(ClO_4^-, \text{soln}, T)$ or rather $\Delta(aq \rightarrow X_2)$ $\mu^\star(X^-, \text{soln}, T)$ is zero (where X^- is any monovalent anion)

In the determination of free energy of transfer of H^+ ion from the reaction $LH^+ \rightleftharpoons L + H^+$ (L = phen or dipy) Lahiri et al [1,2] calculated $\Delta G_{t(el)}^\ominus$ of LH^+ using the extrathermodynamic assumption but $\phi\Delta G_t^\ominus(ClO_4^-)$ for the system (including reactants and products) is zero

It should be noted that $\Delta G_t^\ominus(FeL_3^{2+})$ is always the same but the experimental values of $\Delta G_t^\ominus(FeL_3X_2)$ will differ depending on the nature of the anions Since there is no possibility of the existence of free cations in solutions or solids, the anions are important, though neglected The reaction scheme can be written as

$$\begin{array}{ccccc} \mathrm{FeL_3X_2} & \rightleftharpoons & \mathrm{FeX_2} & + & \mathrm{3L} \\ \text{(solid)} & & \text{(solid)} & & \text{(solid)} \\ \downharpoonleft\upharpoonright & & \downharpoonleft\upharpoonright & & \downharpoonleft\upharpoonright \\ \mathrm{FeL_3X_2} & \rightleftharpoons & \mathrm{FeX_2} & + & \mathrm{3L} \\ \text{(solution)} & & \text{(solution)} & & \text{(solution)} \end{array}$$

where $X^- = Cl^-$, ClO_4^-, CNS^-, etc
and $X^{2-} = SO_4^{2-}$ etc

Obviously, the free energy of formation and free energy of solvation of FeL_3X_2 and FeX_2 would be different depending on X^- The advantage of the "isoelectric" reactions is that the reaction

$$FeL_3X_2 \rightleftharpoons FeX_2 + 3L \tag{3}$$

can be written as

$$FeL_3^{2+} \rightleftharpoons Fe^{2+} + 3L \tag{2}$$

only if X^- cancels automatically from both sides There should be no artificial elimination of X^- from one of the components such as FeL_3X_2 as carried out by Blandamer et al [13] This would not satisfy reaction (1) as in solution, like FeL_3X_2, Fe^{2+} is present also as FeX_2 This means that $\phi\Delta G_t^{\ominus}(X^-)$ for the system (for the reactants and the products) is zero irrespective of the nature of the anions but not that $\Delta G_t^{\ominus}(X^-) = 0$ It is apparent that reaction (3) would be better represented by reaction (4) rather than reaction (2)

$$FeL_3^{2+} + 2X^- \rightleftharpoons Fe^{2+} + 2X^- + 3L \tag{4}$$

Similarly

$$HL^+ \rightleftharpoons H^+ + L \tag{5}$$

should be represented as

$$HL^+ + X^- \rightleftharpoons H^+ + X^- + L \tag{6}$$

Thus, the free energy changes due to the formation of HL^+ and FeL_3^{2+} i e $\Delta G^{\ominus}(HL^+)$ and $\Delta G^{\ominus}(FeL_3^{2+})$ are always the same but the experimental values for the equilibrium constants and the dissociation constants for reactions (4) and (6) may be different depending on the nature of the anion The anomaly in the equilibrium or dissociation constant values obtained by different workers may be due partly to the use of different anions

It should be noted that the specific rate constants for the dissociation reaction for ferroin or ferrodiin have been found to be dependent on the anions [14,15] The conversion of low spin FeL_3^{2+} to high spin FeL_2^{2+} ($FeL_3^{2+} \rightarrow FeL_2^{2+}$) has been universally accepted to be the rate determining step [14] However, for the formation of ferroin or ferrodiin, the rate dependence of the forward reaction on anions has not been studied extensively However the rate determining step suggested for the formation of ferroin or ferrodiin

$$\begin{array}{ccc} \mathrm{FeL_2^{2+}} & \rightarrow & \mathrm{FeL_3^{2+}} \\ \text{high-spin} & & \text{low spin} \\ \text{complex} & & \text{complex} \end{array}$$

cannot be tenable as the reaction is associated with orbital stabilisation and highly exothermic energy changes [16,17] The equilibrium constants or dissociation constants are thus expected to be dependent on anions

It should also be noted that though the free energy change due to the formation of $\mathrm{FeL_3^{2+}}$ i e $\Delta G^{\ominus}(\mathrm{FeL_3^{2+}})$ is always the same, the experimental values may be slightly different depending on the nature of the anions The formation of $\mathrm{FeL_3^{2+}X_2^{2-}}$ would obviously be dependent on the anion as no value of $\Delta G^{\ominus}(\mathrm{FeL_3^{2+}})$ is obtainable in their absence The slight variation in the results from different workers may arise from the use of different anions leading to changes in ionic environment, changes in solvation energy of the anions or heat of solution

We therefore feel that more work should be done in this direction to clarify ideas on the free energies of single ions. It is desirable to derive values of free energies of single ions using different extrathermodynamic assumptions in order to have a consistent set of single ion values It is also necessary to explore the possibility of deriving the free energies of single ions without extrathermodynamic assumptions

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