Notes

Studies on the Solubility of 2,2′-Bipyridyl, 1,10-Phenanthroline, and Their Tris Iron(II) Perchlorates in Methanol–Water Mixtures, and the Determination of the 'Medium Effect' of Ions

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The solubilities of 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and their complexes $[FeL_3]^{2+}$ as perchlorates have been determined in water and methanol–water mixtures (up to 87 wt. % organic solvent) at 295 K. The changes in free energies of transfer, $\Delta G^{\ominus}_{t}$, thus obtained have been coupled with the free energies of transfer for the reactions (i) and (ii) to determine the $\Delta G^{\ominus}_{t}$ values of the ions

$$\text{Hbipy}^{+}\ (\text{or Hphen}^{+}) \rightleftharpoons \text{bipy (or phen)} + H^{+} \qquad \text{(i)}$$

$$[Fe(bipy)_3]^{2+}\ \{\text{or } [Fe(phen)_3]^{2+}\} \rightleftharpoons Fe^{2+} + 3\ \text{bipy (or phen)} \qquad \text{(ii)}$$

H^{+}, Hbipy^{+}, Hphen^{+}, and Fe^{2+}. The $\Delta G^{\ominus}_{t(H^{+})}$ values in methanol–water reported are qualitatively in good agreement with literature values, although quantitative disagreement exists. Values of $\Delta G^{\ominus}_{t(Fe^{2+})}$ from water to methanol–water mixtures have also been calculated.

The importance of the 'medium effect' of ions has been widely stressed and a large number of theoretical and experimental approaches have been outlined to determine the free energies of transfer or 'medium effects' of ions. However, the values so obtained are very divergent.[1–5]

In spite of certain limitations, the free energy of transfer of an ion can be regarded as composed of a 'neutral' part and an 'electrostatic' part [1–5] [equation (1)]. This has now been

$$\Delta G^{\ominus}_{t(i)} = \Delta G^{\ominus}_{t(el)} + \Delta G^{\ominus}_{t(neut)} \qquad (1)$$

utilized by us to calculate the 'medium effects' of ions like H^{+}, Fe^{2+}, Hbipy^{+} (bipy = 2,2′-bipyridyl), and Hphen^{+} (phen = 1,10-phenanthroline) from water to methanol-water mixtures based on the free-energy changes[6–8] for the reactions (2) and (3) and the solubility values of L and $[FeL_3][ClO_4]_2$ (L = bipy or phen).

$$HL^{+} \rightleftharpoons L + H^{+} \qquad (2)$$

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

The utility of the method lies in the fact that we can work in very dilute solutions so that 'salt effects' can be eliminated and the solutions are in their respective standard states, a condition essential for the determination of 'medium effects' of ions.

Experimental

The complexes $[Fe(bipy)_3][ClO_4]_2$ and $[Fe(phen)_3][ClO_4]_2$ were prepared and purified as described by Dwyer and McKanzie.[9] The solutions of the ligands and their complexes were allowed to equilibrate at 295 K for 24 h in Campbell solubility apparatus [10] and the solutions were filtered by inversion of the apparatus at the same temperature. The solubility values as determined spectrophotometrically using a Beckman DU-2 spectrophotometer are recorded in Table 1. Other experimental details are similar to those described earlier.[6, 8]

Results and Discussion

The free energies of transfer from water to mixed solvents are given by equation (4) where *c* represents a molar concentration. For reaction (2) we can write expressions (5) or (6). The

$$\Delta G^{\ominus}_{t} = -2.303\, RT \log (c_s/c_w) \qquad (4)$$

$$\Delta\Delta G^{\ominus}_{t(2)} = \Delta G^{\ominus}_{t(L)} + \Delta G^{\ominus}_{t(H^{+})} - \Delta G^{\ominus}_{t(HL^{+})} \approx \Delta G^{\ominus}_{t(L)} + \Delta G^{\ominus}_{t(H^{+})} - [\Delta G^{\ominus}_{t(L)} + \Delta G^{\ominus}_{t(el)(HL^{+})}] \qquad (5)$$

$$\Delta G^{\ominus}_{t(H^{+})} = \Delta\Delta G^{\ominus}_{t(2)} + \Delta G^{\ominus}_{t(el)(HL^{+})} \qquad (6)$$

$\Delta G^{\ominus}_{t(el)(HL^{+})}$ values were calculated using the Born equation [11] with $\gamma_{\text{Hphen}^{+}}$ or $\gamma_{\text{Hbipy}^{+}} = 3.70$ Å from standard bond-distance values (one would not expect the radii of these large ions to be affected by solvation). Similarly, we can write equations (7) [from (3)] and (8) [from (2)].

$$\Delta G^{\ominus}_{t(Fe^{2+})} = \Delta\Delta G^{\ominus}_{t(3)} - 3\Delta G^{\ominus}_{t(L)} - \Delta G^{\ominus}_{t(FeL_3^{2+})} \qquad (7)$$

$$\Delta G^{\ominus}_{t(HL^{+})} = \Delta G^{\ominus}_{t(L)} + \Delta G^{\ominus}_{t(H^{+})} - \Delta\Delta G^{\ominus}_{t(2)} \qquad (8)$$

Since perchlorate ion would occur on both sides of equations (6)—(8), the $\Delta G^{\ominus}_{t(ClO_4^{-})}$ values cancel. The $\Delta G^{\ominus}_{t(FeL_3^{2+})}$ values were calculated from equation (4) assuming the solubility [3] of large $[FeL_3]^{2+}$ to be independent of the anion present. However, in case of the electrolyte $[FeL_3][ClO_4]_2$ the *c* values should be replaced by the solubility product, *K* [equation (9)].

$$K = 4S^3 f_{FeL_3^{2+}} f^2_{ClO_4^{-}} \qquad (9)$$

The activity coefficients, *f*, of the ions were calculated from the Debye–Hückel equation with appropriate values of the constant *A* therein for water and mixed solvents. The *K* values are recorded in Table 1. Free energies of transfer of different compounds and ions are given in Tables 2 and 3.

It is to be noted that 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. In the determination of $\Delta G^{\ominus}_{t}$ of $[FeL_3][ClO_4]_2$ complexes it has been assumed that the composition in aqueous and mixed solvents is the same as that in

Table 1. Molar absorption coefficients and solubilities of 2,2′-bipyridyl, 1,10-phenanthroline, their tris iron(II) complexes, and solubility products in methanol–water mixtures at 295 K

Methanol	ε/dm^3 mol^{-1} cm^{-1}		Solubilities (mol dm^{-3})				Solubility product ($\times 10^9$ mol^2 dm^{-6})	
(wt. %)	bipy at 280 nm	phen at 264 nm	bipy ($\times 10^2$)	phen ($\times 10^2$)	$[Fe(bipy)_3]$-$[ClO_4]_2$ ($\times 10^3$)	$[Fe(phen)_3]$-$[ClO_4]_2$ ($\times 10^3$)	$[Fe(bipy)_3]$-$[ClO_4]_2$	$[Fe(phen)_3]$-$[ClO_4]_2$
0	12 400	27 400	3.49	1.69	1.75	0.45	12.71	0.29
8	11 450	26 500	5.88	2.69	2.86	1.20	52.20	4.64
16.4	12 500	27 450	10.56	5.91	4.19	1.68	146.40	12.19
25.2	13 175	28 400	22.73	14.96	4.65	2.81	2 007.95	54.08
34.4	13 350	28 500	54.53	44.91	12.20	6.58	2 719.42	557.90
44.1	13 550	28 450	123.98	114.12	13.26	8.87	3 726.62	1 702.78
54.2	13 525	28 600	269.13	250.72	15.23	10.48	6 010.43	2 290.79
64.7	13 650	28 200	536.85	510.28	13.22	10.12	4 603.80	2 247.23
75.9	13 950	29 000	1 146.06	105.28	7.44	9.71	1 046.67	2 239.06

the solid phase. This implies the transfer of six molecules of water from water to mixed solvents, the free-energy change of which can be calculated from the excess free energy of mixing of methanol–water mixtures. However, in view of the low solubility of the complexes, the corrections would be small.

Slight errors in the results may also arise since $\Delta\Delta G^\ominus_{t(2)}$ and $\Delta\Delta G^\ominus_{t(3)}$ values are at 298 K but $\Delta G^\ominus_{t(L)}$ and $\Delta G^\ominus_{t[FeL_3][ClO_4]_2}$ have been determined experimentally at 295 K.

The solubilities of bipy are greater than those of phen in water and in methanol–water mixtures but less than those in ethanol–water mixtures.[12] The values are in good agreement with those reported by Burgess and Haines.[13,14] The solubilities of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ increase with increasing content of organic solvent, reach a maximum at about 54 wt. % methanol, and then decrease. Although it is not possible to correlate the data with behaviour exhibited by the mixed solvents, it is to be noted that $-\Delta H^E$ (excess enthalpy of mixing) of methanol–water is a maximum when the mole fraction of organic solvent is *ca.* 0.3.[15]

The $\Delta G^\ominus_{t(H^+)}$ values calculated using bipy and phen are in good agreement, qualitatively and almost quantitatively, considering the limitations of such measurements. Errors of the order of 0.2—0.4 kJ can be expected in view of the error of 0.02—0.04 p*K* units in the determination of p*K* values in mixed solvents.

The use of the Born equation, which is applicable strictly to ions having spherical radii, for flat molecules like $Hphen^+$ or $Hbipy^+$ is likely to introduce some error. However, the limitations of this equation or of modified Born equations with arbitrarily adjusted radii or dielectric constant values are well known.[1-5] Ions in solutions are likely to lose sphericity due to ion–dipole interactions. Moreover, even the crystallographic radii of simple spherical ions like Na^+, K^+, Cl^-, Br^-, *etc.* have been found to be different by different workers.[5]

The ions $Hphen^+$ and $Hbipy^+$ are fairly large and relatively non-polarizable and their solute–solvent interactions have been found to be small from spectral measurements.[16]

In spite of the limitations, the $\Delta G^\ominus_{t(H^+)}$ values reported here are in good agreement with those reported by Wells,[17] Kalidas *et al.*[18] (except at 20 wt. %), Tomkins,[19] and Alfenaar and Deligny,[3] qualitatively and to some extent quantitatively at low percentages of alcohol if we consider the wide variations in results in the literature.

The total free energy of transfer for the proton $[\Delta G^\ominus_{t(H^+)}]$, as calculated by Wells,[17] in different aqueous-organic solvents, involves the use of equation (10) ($R = CH_3$) where $\Delta G^\ominus_{t(H^+)_e}$

$$\Delta G^\ominus_{t(H^+)} = \Delta G^\ominus_{t(H^+)_e} + \Delta G^\ominus_{t(ROH_2^+)} \qquad (10)$$

is the free energy change deriving from the transfer of the charge from pure water of dielectric constant D_w to a mixed solvent of dielectric constant D_s and is given by equation (11)

$$\Delta G^\ominus_{t(H^+)_e} = (Ne^2/6r_{H_2O})(D_s^{-1} - D_w^{-1}) \qquad (11)$$

(N = Avagadro's, e = electronic charge, and r_{H_2O} = radius of the water molecule) by the application of the Born equation to the transfer of a sphere containing the tetrahedral structure $H_3O^+(H_2O)_4$. This equation, however, takes no account of the possible changes in radius in mixed solvents. The major contribution is from $\Delta G^\ominus_{t(ROH_2^+)}$ which covers all subsequent structural changes induced by the presence of the tetrahedral $H_3O^+(H_2O)_4$ in mixed solvents. The use of *p*-nitroaniline (*cf.* Wells [17]) in determining $\Delta G^\ominus_{t(ROH_2^+)}$ is likely to be vitiated by solute–solvent interactions of varied nature, and the use of data obtained at high ionic strengths involving structural changes in solvent molecules is hardly justifiable for the determination of ' medium effects.'

In the ferrocinium–ferrocene model [3,18] for determination of $\Delta G^\ominus_{t(H^+)}$, assumptions are made about the elimination of the liquid-junction potential by salt bridges and that $\Delta G^\ominus_{t(neut)(ferrocinium)} = \Delta G^\ominus_{t(ferrocene)}$. However, the presence of a large amount of ' indifferent ' electrolyte (*e.g.* KCl) in the determination of the standard electrode potential from the polarographic half-wave potential in this method may change the solvent structure and thus the ' medium effects.' In addition ferrocene may have a residual electrostatic component of the ion arising from the ferrocene-ferrocinium couple, and specific interactions of redox couples with water and other solvents are known.[20]

No values of $\Delta G^\ominus_{t(H^+)}$ are available for methanol–water mixtures based on the use of $[NBu(CH_2CH_2CHMe_2)_3]BPh_4$ or $AsPh_4BPh_4$ as ' reference electrolytes ' except at 100% methanol.[21] However, the method also has its limitations. It is not clear why the $\Delta G^\ominus_t$ of $[NBu(CH_2CH_2CHMe_2)_3]^+$ or $AsPh_4^+$ and BPh_4^- are of the same sign when the $\Delta G^\ominus_t$ values (from water to methanol–water, *etc.*) are generally negative for cations and positive for anions. Moreover, the ' reference ions ' must be large and relatively non-polarizable, having a small charge density. This precludes the formation of ionic compounds. Association between the ions at low dielectric constants cannot be ruled out.

In spite of the inherent limitations of the different methods, the use of such methods is necessary to arrive at reasonably consistent values of $\Delta G^\ominus_{t(H^+)}$. Our values of $\Delta G^\ominus_{t(H^+)}$ in ethanol–water mixtures [12] are in very good agreement quantitatively with the values reported by Popovych and Dill [21] based on the

Table 2. Free energies of transfer, $-\Delta G^\ominus_t$/kJ

Methanol (wt. %)	$-\Delta G^\ominus_t$						$\Delta G^\ominus_{t(el)}$ of $Hphen^+$ or $Hbipy^+$	$\Delta\Delta G^\ominus_t$ for the reaction $HL^+ \rightleftharpoons L + H^+$		$\Delta\Delta G^\ominus_t$ for the reaction $[FeL_3]^{2+} \rightleftharpoons Fe^{2+} + 3L$	
			$[Fe(bipy)_3][ClO_4]_2$		$[Fe(phen)_3][ClO_4]_2$						
	bipy	phen	*a*	*b*	*a*	*b*		bipy	phen	bipy	phen
8.0	1.27	1.14	1.21	3.50	2.39	9.21	−0.093	0.40	1.00	−0.57	2.34
16.0	2.71	3.06	2.16	6.02	3.22	12.86	−0.225	1.26	1.72	−0.69	3.89
25.2	4.59	5.34	2.40	6.88	4.49	18.59	−0.375	1.83	2.43	−0.06	5.35
34.4	6.74	8.04	4.77	13.18	6.57	21.32	−0.543	2.63	2.81	3.14	8.28
44.7	8.75	10.32	4.96	13.96	7.30	22.05	−0.768	3.65	4.23	5.25	11.34
54.2	10.65	12.26	5.31	15.13	7.71	22.00	−1.050	4.96	5.07	9.13	16.32
64.1	12.35	14.00	4.96	14.48	7.62	21.99	−1.369	6.56	6.03	12.34	23.76
75.9	14.21	15.77	3.55	10.84	7.52		−1.819	7.53	7.16	15.58	28.03
87.7							−2.419	8.16	6.81	15.46	29.79

[a] From simple solubility values. [b] From solubility product values.

Table 3. Free energies of transfer of ions, $-\Delta G^\ominus_t$/kJ

Methanol (wt. %)	H^+					Fe^{2+} [a]			Fe^{2+} [b]	
	Using bipy	Using phen	Average	$Hbipy^+$	$Hphen^+$	Using bipy	Using phen	Average	Using bipy [c]	Using phen
8.0	0.3	0.9	0.6	1.2	1.1	−3.2	+1.3	−0.9	1.7 (11.9)	4.2
16.0	1.0	1.5	1.3	2.5	2.8	−6.7	−2.1	−4.4	1.6 (13.8)	7.9
25.2	1.5	2.1	1.8	4.2	5.0	−11.4	−6.2	−8.8	1.3 (17.6)	10.8
34.4	2.1	2.3	2.1	6.2	7.5	−12.3	−9.3	−10.8	8.4 (20.6)	18.4
44.7	2.9	3.5	3.2	8.0	9.6	−16.0	−16.0	−14.2	8.4	20.0
54.2	3.9	4.0	4.0	9.6	11.2	−17.5	−17.5	−15.2	9.9	23.2
64.1	5.2	4.7	5.0	11.0	12.6	−19.3	−19.3	−15.0	7.6	27.7
75.9	5.7	5.3	5.5	12.4	14.0	−23.5	−23.5	−17.7	3.8	28.6
87.7	5.7	4.4	5.1							

[a] From simple solubility values. [b] From solubility product values. [c] Values in parentheses were obtained using $\Delta G^\ominus_{t[Fe(bipy)_3{}^{2+}]}$ from M. J. Blandamer, J. Burgess, and A. J. Duffield, *J. Chem. Soc., Dalton Trans.*, 1980, 1.

use of $[NBu(CH_2CH_2CHMe_2)_3]BPh_4$ but are lower compared to those measured by other methods.

The $\Delta G^\ominus_{t(H^+)}$ values in methanol–water mixtures are uniformly negative indicating that the transfer reaction is spontaneous. This means that the basicity is at a maximum near 75 wt. % methanol and then decreases, in agreement with the trend reported by Alfenaar and DeLigny[3] and others.[22–24] Moreover, the lower $-\Delta G^\ominus_{t(H^+)}$ values in methanol–water compared with ethanol–water mixtures indicate the greater basicity of the latter.[12]

The $\Delta G^\ominus_t$ values of $Hphen^+$ or $Hbipy^+$, calculated from equations (1) or (8), are increasingly negative with increasing content of organic solvent.

$\Delta G^\ominus_{t(Fe^{2+})}$ has been found to be negative but the two sets of values for bipy, $[Fe(bipy)_3][(ClO_4]_2$ and phen, $[Fe(phen)_3][ClO_4]_2$ differ considerably if we use the theoretical solubility products. The negative values indicate that Fe^{2+} prefers mixed solvents to water. However, if we use simple solubility values for $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$, $\Delta G^\ominus_{t(Fe^{2+})}$ becomes increasingly positive and the values from the two sets of data become similar if we consider the errors involved in the evaluation of $\Delta\Delta G^\ominus_t$, $\Delta G^\ominus_{t(L)}$, and $\Delta G^\ominus_{t(FeL_3{}^{2+})}$. However, it is difficult to say whether the transfer reactions of the iron(II) complexes are spontaneous or not. If we consider the transference of $[Fe(OH_2)_6]^{2+}$ from water to methanol–water, $\Delta G^\ominus_t$ for this ion is positive according to the Born equation.

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