Thermochimica Acta, 185 (1991) 183–203
Elsevier Science Publishers B.V., Amsterdam

Ionic solvation in water + co-solvent mixtures. Part 22. Free energies of transfer of complex ions from water into water + methanol mixtures

Cecil F. Wells

School of Chemistry, University of Birmingham, Edgbaston, P.O. Box 363, Birmingham B15 2TT (UK)

(Received 16 November 1990)

Abstract

The solubility data of a large number of complex cations and anions in water + methanol have been examined using the solvent sorting method to separate free energies of transfer for salts from water into water + methanol, $\Delta G_t^\ominus$(salt), into free energies of transfer for individual ions, $\Delta G_t^\ominus$(i), to compare with $\Delta G_t^\ominus$(i) determined earlier for simple cations and anions. Broadly, the spread of values of $\Delta G_t^\ominus$(i) for varying i is similar to that found earlier for the simple ions in water + methanol: $\Delta G_t^\ominus(\text{cation}) \approx 0$ or < 0, and $\Delta G_t^\ominus(\text{anion}) > 0$, with $\Delta G_t^\ominus$(cation) becoming more negative as more hydrophobic organic groups are present in the surface of the ion and $\Delta G_t^\ominus$(anion) becoming negative when such hydrophobic organic groups are present. In general, $\Delta G_t^\ominus(X^{n-})$ increases as n increases and $-\Delta G_t^\ominus(M^{m+})$ increases as m increases with similar ligands attached. The data for $\Delta G_t^\ominus(Fe^{2+})$ are re-examined, and it is concluded that, although large errors result from the only method currently available, $\Delta G_t^\ominus(Fe^{2+}) < 0$.

INTRODUCTION

The spectrophotometric solvent sorting method for determining free energies of transfer of single ions, $\Delta G_t^\ominus$(i), from water into mixtures of water with co-solvents was first applied to simple ions in mixtures of water with methanol [1]. Following this, the method was applied to ions in mixtures of water with a wide range of other components [2–4]. This method [2,3] derives $\Delta G_t^\ominus(H^+)$ by considering the transfer in two steps. Firstly, the standard state of the solvated proton $P = H^+(H_2O)_5$ with activity coefficient $y = 1$ for $[P] = 1.00$ mol dm^{-3} with $y \to 1$ as $[P] \to 0$ is transferred as a charged sphere of radius three times the radius of the water molecule from water (w) into the mixture(s) as in eqn. (1)

$$\Delta G(\text{Born}) = \mu_s^\ominus(P) - \mu_w^\ominus(P) = 167.6\left(D_s^{-1} - D_w^{-1}\right) \text{ kJ mol}^{-1} \qquad (1)$$

where D is the dielectric constant. Secondly, the free energy ΔG_2 of the rearrangement of the solvent molecules around the proton for the new

0040-6031/91/$03.50

standard state in the mixture is determined experimentally by investigating spectrophotometrically the competition of the two protonated forms, $P = H^+(H_2O)_x$ and $SH^+ = H^+(H_2O)_{x-1}S$ for $x \geqslant 5$ for an added trace concentration of 4-nitroaniline (S is a co-solvent molecule). From this, $K_c = [SH^+]/[P][S]$ is determined and ΔG_2 is given by

$$\Delta G_2 = -[SH^+]RT \ln K_c[H_2O]F_c \tag{2}$$

It is found that the symmetrical $F_c = y(SH^+)y''(H_2O)/y(P)y''(S) = 1.0$, where y is defined as above in the particular solvent mixture and for the bulk components $y'' \rightarrow 1.0$ as Σ[dissolved species] $\rightarrow 0$ in the mixture. $\Delta G_t^{\ominus}(H^+)$ on the mole fraction scale is then given by

$$\Delta G_t^{\ominus}(H^+) = \Delta G(\text{Born}) + \Delta G_2 + RT \ln \frac{d_s M_w}{d_w M_s'} \tag{3}$$

where d is density and M is molecular weight, with $M_s' = 100/\{(\text{wt\% } S/M_s) + (\text{wt\% } H_2O/M_w)\}$. Free energies for simple anions X^- can then be derived from

$$\Delta G_t^{\ominus}(X^-) = \Delta G_t^{\ominus}(HX) - \Delta G_t^{\ominus}(H^+) \tag{4}$$

where $\Delta G_t^{\ominus}(HX)$ is usually determined from $E^{\ominus}$ measurements. Free energies of transfer for cations M^{m+} can now be determined from

$$\Delta G_t^{\ominus}(M^{m+}) = \Delta G_t^{\ominus}(MX_m) - m\,\Delta G_t^{\ominus}(X^-) \tag{5}$$

where $\Delta G_t^{\ominus}(MX_m)$ can be determined from $E^{\ominus}$ or solubility measurements.

Since this initial investigation for water + methanol mixtures [1,2], the solubilities of salts M_nX_m containing a wide variety of complex cations and anions have been determined [5,6]. We wish to compare the free energies of transfer of these complex cations and anions on the solvent sorting scale with those for the original simple ions [1,2] and with those for the complex cations $Co(Rpy)_4Cl_2^+$ [7,8] on the same scale.

Free energies of transfer have been determined for these single complex ions derived from the new data [5,6] on the TPTB scale, which is based on

$$\Delta G_t^{\ominus}(Ph_4P^+) = \Delta G_t^{\ominus}(BPh_4^-) = \tfrac{1}{2}\,\Delta G_t^{\ominus}(Ph_4P^+ \cdot BPh_4^-) \tag{6}$$

where $\Delta G_t^{\ominus}(Ph_4P^+)$ is nearly equal to $\Delta G_t^{\ominus}(Ph_4As^+)$. Thus the solubility of the salt $Ph_4P^+ \cdot BPh_4^-$ is determined in water and in the mixtures of water with the co-solvent. Values for $\Delta G_t^{\ominus}(i)'$ on the TPTB scale differ from those on the solvent sorting scale $\Delta G_t^{\ominus}(i)$, and the validity under all conditions of assumptions (7) and (8)

$$\Delta G_t^{\ominus}(Ph_4P^+)_n \gg \Delta G_t^{\ominus}(PhP^+)_e \tag{7}$$

$$\Delta G_t^{\ominus}(BPh_4^-)_n \gg \Delta G_t^{\ominus}(BPh_4^-)_e \tag{8}$$

has been questioned [9]: subscript n indicates the component arising from the electrically neutral bulk and subscript e indicates the component arising from the charge on the ionic species. Such $\Delta G_t^{\ominus}(\mathrm{i})'_c$ from the TPTB method are presented on the molar scale [5,6] and, if these are first converted to the mole fraction scale via

$$\Delta G_t^{\ominus}(\mathrm{i})' = \Delta G_t^{\ominus}(\mathrm{i})'_c + RT\ \ln\frac{M_w d_s}{M'_s d_w} \tag{9}$$

they can then be converted to the solvent sorting scale (method A) using eqn. (10) for $\mathrm{i} = \mathrm{X}^{n-}$

$$\Delta G_t^{\ominus}(\mathrm{X}^{n-}) = \Delta G_t^{\ominus}(\mathrm{X}^{n-})' - n\ \Delta G_t^{\ominus}(\mathrm{Ph_4P^+}) + \frac{n}{2}\Delta G_t^{\ominus}(\mathrm{Ph_4^+}\cdot\mathrm{BPh_4^-}) \tag{10}$$

or eqn. (11) for $\mathrm{i} = \mathrm{M}^{m+}$

$$\Delta G_t^{\ominus}(\mathrm{M}^{m+}) = \Delta G_t^{\ominus}(\mathrm{M}^{m+})' - m\ \Delta G_t^{\ominus}(\mathrm{BPh_4^-}) + \frac{m}{2}\Delta G_t^{\ominus}(\mathrm{Ph_4P^+}\cdot\mathrm{BPh_4^-}) \tag{11}$$

Alternatively, $\Delta G_t^{\ominus}(\mathrm{M}_n\mathrm{X}_m)$ can be determined from the solubilities C on the molar scale, and converted to the mole fraction scale via

$$\Delta G_t^{\ominus}(\mathrm{M}_n\mathrm{X}_m) = (m+n)RT\left\{\ln\frac{C_w}{C_s} + \ln\frac{M_w d_s}{M_s d_w}\right\} \tag{12}$$

Values for $\Delta G_t^{\ominus}(\mathrm{X}^{n-})$ and $\Delta G_t^{\ominus}(\mathrm{M}^{m+})$ can then be calculated (method B) directly on the solvent sorting scale using eqns. (13) and (14) and known values for $\Delta G_t^{\ominus}(\mathrm{i})$.

$$\Delta G_t^{\ominus}(\mathrm{X}^{n-}) = \frac{\Delta G_t^{\ominus}(\mathrm{M}_n\mathrm{X}_m) - n\ \Delta G_t^{\ominus}(\mathrm{M}^{m+})}{m} \tag{13}$$

$$\Delta G_t^{\ominus}(\mathrm{M}^{m+}) = \frac{\Delta G_t^{\ominus}(\mathrm{M}_n\mathrm{X}_m) - m\ \Delta G_t^{\ominus}(\mathrm{X}^{n-})}{n} \tag{14}$$

Although both methods A and B have been applied to the wide range of data available for salts of complex ions, method B has invariably been used where the actual solubilities have been published.

EVALUATION OF $\Delta G_t^{\ominus}(\mathrm{Ph_4P^+})$ AND $\Delta G_t^{\ominus}(\mathrm{BPh_4^-})$

To use method A, values for $\Delta G_t^{\ominus}(\mathrm{Ph_4P^+})$ and $\Delta G_t^{\ominus}(\mathrm{BPh_4^-})$ on the solvent sorting scale are required. The logarithm of the mean medium activity coefficient for saturated solutions of potassium picrate given by LaBrocca et al. [10] was converted to $\Delta G_t^{\ominus}(\mathrm{KPic})_c$, which was then converted to the mole fraction scale using

$$\Delta G_t^{\ominus}(\mathrm{KPic}) = \Delta G_t^{\ominus}(\mathrm{KPic})_c + 2RT\ \ln\frac{M_w d_s}{M'_s d_w} \tag{15}$$

with the densities of water + methanol mixtures interpolated from the data of Chu and Thompson [11]. Our data for $\Delta G_t^{\ominus}(K^+)$ [1,2] were then used in

$$\Delta G_t^{\ominus}(\mathrm{Pic}^-) = \Delta G_t^{\ominus}(\mathrm{KPic}) - \Delta G_t^{\ominus}(\mathrm{K}^+) \tag{16}$$

to produce $\Delta G_t^{\ominus}(\mathrm{Pic}^-)$. The log of the mean medium activity coefficient for the saturated solutions of $Ph_4P^+ \cdot Pic^-$ [10] was converted to $\Delta G_t^{\ominus}(Ph_4P^+ \cdot Pic^-)_c$ which was translated to $\Delta G_t^{\ominus}(PhP^+ \cdot Pic^-)$ using eqn. (15). Equation (5) was then used with the above $\Delta G_t^{\ominus}(Pic^-)$ to produce $\Delta G_t^{\ominus}(Ph_4P^+)$.

Likewise, the log of the mean medium activity coefficient for saturated solutions of $KBPh_4$ [10,12] was converted using equations analogous to (15) and (16) with $\Delta G_t^{\ominus}(K^+)$ [1,2] to produce $\Delta G_t^{\ominus}(BPh_4^-)$.

These values for $\Delta G_t^{\ominus}(Ph_4P^+)$, $\Delta G_t^{\ominus}(Pic^-)$ and $\Delta G_t^{\ominus}(BPh_4^-)$ are given in Table 1: both sets of values for $\Delta G_t^{\ominus}(BPh_4^-)$ are in good agreement.

TABLE 1

Free energy of transfer (kJ mol^{-1}) of complex anions Ph_4As^+ and Ph_4P^+ from water into water + methanol mixtures at 25 °C on the mole fraction scale

Ion	Ref. to data	Method and counter ion	Wt%				
			10	20	30	40	50
			Mole fraction				
			0.059	0.123	0.196	0.273	0.360
$Fe(CN)_6^{3-}$	5	A	-0.68	1.31	2.47	7.4	9.9
ReO_4^-	5	A	0.091	0.66	0.78	0.37	-
$IrCl_6^{2-}$	5	A	3.68	7.9	10.8	13.1	-
$IrCl_6^{3-}$	5	A	6.9	16.8	27.2	-	-
$ReCl_6^{2-}$	5	A	1.17	4.54	7.1	9.8	-
$ReBr_6^{2-}$	5	A	0.33	3.28	6.2	9.3	-
CN^-	5	A	-0.58	-0.27	-0.60	-0.59	0.74
$CoW_{12}O_{40}^{5-}$	5	A	-3.23	-3.02	-5.2	-	-
SCN^-	5	A	-0.035	0.78	0.99	4.43	-
BPh_4^-	12	B K^+	-1.77	-3.81	-	-7.4	-10.8 (60 wt%)
Ph_4As^+	12	B BPh_4^- [via (12)]	-2.76	-6.2	-	-13.6	-20.5 (60 wt%)
Ph_4As^+	12	B BPh_4^- [via (10)]	-2.82	-6.6	-	-12.5	-17.1 (60 wt%)
Picrate	10	B K^+	0.451	0.73	0.205	-0.34	-0.36
BPh_4^-	10	B K^+	-1.76	-3.19	-5.7	-8.6	-11.4
Ph_4P^+	10	B pic^-	-3.12	-7.2	-10.7	-14.6	-18.4
Anthraq.-2-SO_3^-	21	B Ca^{2+}	0.23 (6.50 wt%)	0.46	-0.32	-	-
Naphth.-2-SO_3^-	21	B K^+	0.029 (8.03 wt%)	-1.44	-3.05	-4.96	-5.6

Values for $\Delta G_t^{\ominus}(Ph_4P^+ \cdot BPh_4^-)$ used in eqns. (11) and (12) were taken from Abraham et al. [5] and converted to the mole fraction scale using an equation analogous to (15).

EVALUATION OF $\Delta G_t^{\ominus}$ FOR COMPLEX CATIONS AND ANIONS

The data for $\Delta G_t^{\ominus}(\text{anion})'$ of Abraham et al. [5] have been converted to the solvent sorting scale using eqn. (11) after first converting the value to the mole fraction scale with eqn. (9). These $\Delta G_t^{\ominus}(\text{anion})$ values on the solvent sorting scale are given in Table 1. This table also contains values for $\Delta G_t^{\ominus}(Ph_4As^+)$ derived using the mean medium activity coefficients for saturated solutions of the salt $Ph_4As^+ \cdot BPh_4^-$ [12] converted to the mole fraction scale using an equation analogous to (15), together with eqn. (5), and the values for $\Delta G_t^{\ominus}(BPh_4^-)$ derived from the data of LaBrocca et al. [10] and of Tissier [12]. Both sets of values for $\Delta G_t^{\ominus}(Ph_4As^+)$ are in good agreement. Method B has also been applied to the solubility data [13] of calcium anthraquinone-2-sulphonate and potassium naphthalene-2-sulphonate involving our values for $\Delta G_t^{\ominus}(Ca^{2+})$ and $\Delta G_t^{\ominus}(K^+)$ [1,2]. $\Delta G_t^{\ominus}(i)$ values for these ions are also included in Table 1.

Both methods A and B, but predominantly the latter, have been applied to the data of Blandamer, Burgess and co-workers [6,13–23] for complex cations and anions. The results of these calculations are collected in Table 2. As where method B is used for the data in Table 1, the counter ion involved in the calculation of $\Delta G_t^{\ominus}(i)$ is also indicated in Table 2. For $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$, the solubility data of Sengupta et al. [24] have been used, re-worked as described below. The more complex ligands attached to Fe^{2+} ions are classified as follows: N_2 is $MeN{=}C(R_1){-}C(R_2){=}NMe$, with Me and H being possibilities for R_1 and R_2 and for hexN_2 $R_1R_2 = -(CH_2)_4-$; N_2' is XPhN=C(Ph)(py) with py = pyridine and substituents X = 3,4-Me_2 or 3-MeO; N_3 = symmetrical 2,2′-di[RN=C(Me)]pyridine with R = H, Me or Ph; N_4 is MeCH=N–N=C(Me)–C(Me)=N–N=CHMe; N_5 is 2-py-CH=N–$(CH_2)_2NHCH_2$–N=CH–2-py; N_6 is the symmetrical 2-py–C(R)=N$[(CH_2)_2NH]_2CH_2$–N=C(R)–2-py with R = H or Ph; N_6' = 2-quinoline–CH=N$[(CH_2)_2NH]_2$–CH_2N=CH–2-quinoline; N_6'' = HON=C(Me)–C(R)=N–$[(CH_2)_2NH]_2CH_2$–N=C(R)–C(Me)=NOH with R = H or Ph; and N_2'' = R′N=C(R)(2-py) with R′ and R being H or Me. The cages are described in detail in the references marked in Table 2, but all are complexed through N atoms with Me_2cage having methyl groups on the outer surface and cxcage having cyclohexyl groups on this surface; Bcage has a boron substituent, with BcageOBu having butoxyl groups at the edge substituted for the boron atoms and, likewise, BcageF has F atoms at the edge. Some of the perchlorates of the complex ions of Fe^{2+} had their solubilities determined in the presence of a constant added concentration of perchlorate ions of 0.40 mol

TABLE 2

Free energy of transfer (kJ mol^{-1}) of ions and complexes from water into water + methanol mixtures at 25 °C on the mole fraction scale

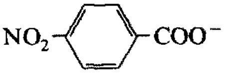
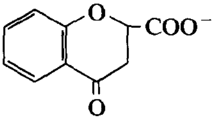
Ion or molecule [a]	Ref. to data	Method and counter ion	Wt%					
			8.03	16.00	24.50	33.59	43.00	52.33
			Mole fraction					
			0.047	0.097	0.154	0.221	0.298	0.382
NO_3^-	18	B $Co(NH_3)_6^{3+}$	–	1.37	–	3.35	–	6.1
NCS^-	18	B $Coen_2ox^+$	–	1.24	–	2.82	–	7.1
SO_4^{2-}	18	B $Cr(urea)_6^{3+}$	5.0	10.6	–	20.2	–	–
$S_2O_3^{2-}$	18	B $Cr(urea)_6^{3+}$	6.6	13.7	–	24.3	–	32.8
$S_2O_3^{2-}$	18	B $Coen_2ox^+$	–	7.1	–	16.2	–	25.9
$S_2O_6^{2-}$	18	B $Cr(urea)_6^{3+}$	4.51	9.5	–	17.4	–	–
$S_2O_6^{2-}$	18	B $Copy_4Cl_2^+$	–	5.9	–	11.7	–	–
$S_2O_8^{2-}$	18	B $Cr(urea)_6^{3+}$	4.47	8.8	–	15.7	–	22.5
$S_2O_8^{2-}$	18	B $Coen_2ox^+$	–	3.5	–	9.1	–	21.3
IO_3^-	21	B K^+	2.25	4.11	7.2	9.7	11.9	–
IO_3^-	21	B Tl^+	–	3.64	–	7.3	–	13.5
IO_3^-	21	B $Co(NH_3)_6^+$	–	3.43	–	6.0	–	10.7
BrO_3^-	21	B Ag^+	1.44	2.91	4.48	6.0	7.6	–
CrO_4^{2-}	21	B Sr^{2+}	–	5.6	–	13.1	–	–
CrO_4^{2-}	21	B Tl^+	–	6.3	–	8.3	–	–
$Cr_2O_7^{2-}$	21	B Rb^+	–	3.11	–	6.6	–	11.2
$Cr_2O_7^{2-}$	21	B $Coen_2Cl_2^+$	–	1.30	–	4.29	–	8.2
	21	A	0.53	2.79	5.2	8.1	10.0	11.7
BPh_4^-	14	B Cs^+	−3.29	−4.24	−6.6	−7.3	–	–
BPh_3CN^-	16	B Cs^+	−1.36	−2.36	−4.06	−6.4	–	–
cis-$[Crox_2(OH)_2]^-$	17	B K^+	–	1.26	–	0.99	–	3.73
$Fe(CN)_5NO^-$	21	B $Fephen_3^{2+}$	–	4.12	–	12.1	–	21.8
$Sb_2(tartrate)_2^{2-}$	18	B $Fephen_3^{2+}$	–	6.8	–	7.0	–	–
Tl^+	16	B BPh_3CN^-	−0.60	−1.06	−0.91	−0.86	–	–
Tl^+	21	B pic^-	–	−0.48	−0.39	–	–	−1.64
La^{3+}	21	A	−0.18	−1.10	−1.83	–	–	–
Ca^{2+}	21	A	–	−2.08	–	−4.14	–	–
Pb^{2+}	21	B NO_3^-	–	1.13	–	−0.11	–	−2.48
Hg^{2+}	14	B BPh_4^-	6.1	6.8	10.0	10.9	–	–
Cu^{2+}	21	B IO_3^-	–	−3.17	–	−3.19	–	–
$Cophen_3^{3+}$	21	A	–	–	−12.7	–	−22.6	–
$Co(NH_3)_6^{3+}$	20	B Br^-	–	0.99	–	0.37	–	−1.21
$Coen_2ox^+$	17	B ClO_4^-	–	0.78	–	−0.28	–	−1.91
$Cren_2ox^+$	17	B Cl^-	–	0.48	–	0.93	–	–
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	17	B ClO_4^-	–	3.27	–	4.55	–	3.35
$Co(NH_3)_4CO_3^+$	17	B ClO_4^-	–	1.67	–	2.38	–	3.84
$Cophen_2CO_3^+$	17	B ClO_4^-	–	−3.84	–	−7.4	–	−10.5
$Cr(urea)_6^{3+}$	17	B ClO_4^-	–	−12.7	–	−23.5	–	−33.5
$Co(NO_2)_6^{3-}$	17	A	–	5.4	–	12.6	–	–
trans-$Coen_2Cl_2^+$	18	B NO_3^-	–	−0.31	–	−1.42	–	−3.00
$Co(sepulchrate)^{3+}$	21	B Cl^-	–	−2.90	–	−5.2	–	−6.8

TABLE 2 (continued)

Ion or molecule [a]	Ref. to data	Method and counter ion	Wt%					
			8.03	16.00	24.50	33.59	43.00	52.33
			Mole fraction					
			0.047	0.097	0.154	0.221	0.298	0.382
Fephen$_3^{2+}$	18	B NCS^-	–	−9.2	–	−23.1	–	−39.9
Fephen$_3^{2+}$	14	B $ReCl_6^-$	−3.97	−8.2	−14.0	−19.0	–	–
Fephen$_3^{2+}$	30	B ClO_4^-	−8.5	−12.4	−17.4	−24.4	−27.6	−29.8
Fephen$_3^{2+}$	21	B NCS^-	–	−9.4	–	−21.0	–	−36.2
Febipy$_3^{2+}$	30	B ClO_4^-	−4.81	−8.7	−10.7	−18.1	−19.8	−21.5
Febipy$_3^{2+}$	21	B ClO_4^-	–	−7.1	–	−15.0	–	−22.2
$Fe(N_2)^{2+}$	21	B ClO_4^-	−2.28	−3.89	−6.0	−8.2	–	−9.9
$Fe(N_2)^{2+}$ (0.4M ClO_4^-)	21	B ClO_4^-	–	−4.17	–	−8.2	–	−10.6
$Fe(MeHN_2)^{2+}$ (0.4M ClO_4^-)	21	B ClO_4^-	−2.12	−4.37	–	−8.7	–	−12.8
$Fe(Me_2N_2)^{2+}$ (0.4M ClO_4^-)	21	B ClO_4	–	−5.5	–	−10.9	–	−15.9
$Fe(Me_2N_2)^{2+}$	19	B ClO_4^-	–	−4.05	–	−9.9	–	–
$Fe(hexN_2)^{2+}$ (0.4M ClO_4^-)	21	B ClO_4^-	−3.27	−6.7	−10.6	−14.6	–	−20.4
$Fe(N_3)^{2+}$	21	B ClO_4^-	−4.46	−7.4	−10.9	−14.4	–	−22.0
$Fe(N_3)^{2+}$	21	B NCS^-	–	−8.6	–	−15.2	–	−27.1
$Fe(Me_2N_3)^{2+}$	21	B ClO_4^-	−3.76	−6.4	−9.9	−13.5	–	−19.5
$Fe(Me_2N_3)^{2+}$	19	B ClO_4^-	–	−4.05	–	−9.9	–	–
$Fe(Ph_2N_3)^{2+}$	21	B ClO_4^-	–	−10.8	–	−23.3	–	−34.8
$Fe(4MePh_2N_3)^{2+}$	21	B ClO_4^-	–	−8.1	–	−17.1	–	−27.7
$Fe(3MeOPh_2N_3)^{2+}$	21	B ClO_4^-	–	−9.6	–	−17.5	–	−27.1
$Fe(3MeOPh_2N_3)^{2+}$	21	B NCS^-	–	−9.8	–	−19.9	–	−34.3
$Fe(3{,}4Me_2Ph_2N_3)^{2+}$	21	B ClO_4^-	–	−13.2	–	−24.1	–	−33.9
$Fe(N_4)^{2+}$	21	B ClO_4^-	−1.19	−5.5	–	−4.62	–	−7.6
$Fe(N_5)^{2+}$	19	B NCS^-	–	−4.58	–	−9.7	–	−21.6
$Fe(N_6)^{2+}$	21	B NCS^-	–	−4.39	–	−9.2	–	–
$Fe(Ph_2N_6)^{2+}$	21	B NCS^-	–	−8.7	–	−19.3	–	−36.2
$Fe(N_6')^{2+}$	21	B ClO_4^-	−2.30	−5.6	−9.0	−12.8	–	−18.4
$Fe(N_7)^{2+}$	21	B ClO_4^-	–	−14.8	–	−19.6	–	–
$Fe(Ph_2N_7)^{2+}$	19	A	–	−7.9	–	−14.8	–	–
$Fe(Me_2cage)^{2+}$	21	B ClO_4^-	–	−4.86	–	−11.7	–	−15.7
$Fe(cxcage)^{2+}$	23	A	–	−9.8	–	−15.7	–	−21.1
Fe(BcageOBu)	23	A	–	−5.8	–	−11.4	–	−15.8
Fe(BcageF)	26	A	–	−4.26	–	–	−12.9	−16.8
$Fe(Me_2N_2')^{2+}$	6	A	–	−18.0	–	−30.8	–	−41.3
$Fe(MeON_2')^{2+}$	19	B ClO_4^-	−5.4	−12.8	−20.3	−28.4	−32.3	−40.6
$Fe(MeHN_2'')(CN)_2$	22	A	–	−1.05	–	−2.73	–	−4.35
$Fe(Me_2N_2'')(CN)_2$	22	A	–	−2.11	–	−3.95	–	−5.8
Fephen$_2$(CN)$_2$	22		–	−3.04	–	−7.2	–	−9.7
Fephen$_2$(CN)$_2^+$	22	A	–	−5.8	–	−11.0	–	−15.0
$Fe(CN)_4bipy^{2-}$	22	A	–	3.85	–	8.4	–	11.6

TABLE 2 (continued)

Ion or molecule [a]	Ref. to data	Method and counter ion	Wt%					
			8.03	16.00	24.50	33.59	43.00	52.33
			Mole fraction					
			0.047	0.097	0.154	0.221	0.298	0.382
$Fe(CN)_2bipy_2^+$	22	A	–	−2.58	–	−7.7	–	−11.4
$Fe(CN)_2bipy_2$	22		–	−1.95	–	−6.7	–	−10.1
$Fe(oxime)^{2+}$	21	B ClO_4^-	–	−4.3	–	−9.8	–	−17.2
$Fe(Ph_2oxime)^{2+}$	21	B ClO_4^-	−2.62	−5.7	−9.7	−13.6	–	−22.8
	20	A	–	−1.31	–	−2.01	–	−2.58
BF_4^-	23	A	–	−0.13	–	0.44	–	2.37
PF_6^-	23	A	–	1.53	–	1.35	–	1.81
$Co[(OH)_2Co(NH_3)_4]_3^{6+}$	17	B SO_4^{2-}	–	−7.4	–	−21.2	–	−42.4
$PtCl_4^{2-}$	15	B K^+	–	3.70	–	7.3	–	–
$Pd(Et_4dien)Cl^+$	15	B Cl^-	–	−4.18	–	−8.0	–	−13.4
$Pt(4CNpy)_2Cl_2$	13		–	–	−0.84 (21.02 wt%)	–	−3.51 (44.40 wt%)	–

[a] See text for abbreviations.

dm^{-3} [21]. In these cases, $\Delta G_t^{\ominus}$(salt) values on the mole fraction scale were calculated from the solubilities of the salts using

$$\Delta G_t^{\ominus}(\text{salt}) = RT\left\{\ln\frac{C_w}{C_s} + 2\ln\frac{(0.4+2C_w)}{(0.4+2C_s)} + 3\ln\frac{M_w d_s}{M_s' d_w}\right\} \tag{17}$$

Some of the problems encountered in deriving values for $\Delta G_t^{\ominus}(Fe^{2+})$ have been discussed earlier [25]. Essentially, the solubility of a salt $Fe(phen)_3X_2$ or $Fe(bipy)_3X_2$ is measured and $\Delta G_t^{\ominus}(Fephen_3^{2+})$ or $\Delta G_t^{\ominus}$ $(Febipy_3^{2+})$ calculated from the procedures outlined above. For $Fe(phen)_3^{2+}$, the equilibrium constant for

$$Fe^{2+} + 3\ \text{phen} \rightleftharpoons Fe(phen)_3^{2+} \tag{18}$$

is measured, from which $\Delta G_F^{\ominus}$ for (18) can be determined. $\Delta G_t^{\ominus}(Fe^{2+})$ is then calculated [25] using

$$\Delta G_t^{\ominus}(Fe^{2+}) = \Delta G_t^{\ominus}(Fephen_3) - 3\,\Delta G_t^{\ominus}(\text{phen}) - \Delta\Delta G_F^{\ominus} \tag{19}$$

where $\Delta\Delta G_F^{\ominus}$ is the change in $\Delta G_F^{\ominus}$ in transferring equilibrium (18) from water into the mixture and $\Delta G_t^{\ominus}$(phen) can be determined from the solubility of 1,10-phenanthroline in water and in the mixture. Unfortunately, Blandamer and Burgess [26] in eqn. (19) used $+\Delta G_F^{\ominus}$ derived from the data of Biswas et al. [27] for equilibrium (18) together with their own values for

$\Delta G_t^{\ominus}$(phen) [28]; they have subsequently [29] also used $+\Delta G_F^{\ominus}$ in an analysis of the equilibrium (18) with values for $\Delta G_t^{\ominus}$(phen) of Sengupta et al. [24]. Using eqn. (19) with the solubility data for $Fe(phen)_3ReCl_6$ and $Fe(phen)_3(ClO_4)_2$ of Blandamer and Burgess [29] and the solubility data for $Fe(phen)_3(ClO_4)_2$ of Sengupta et al. [24], together with Burgess and Haines' values for $\Delta G_t^{\ominus}$(phen) [28], we obtained relatively high negative values [25] for $\Delta G_t^{\ominus}(Fe^{2+})$. Blandamer and Burgess also used $+\Delta G_F^{\ominus}$ for equilibrium (18) for the formation of $Fe(bipy)_3^{2+}$ in the analogous equation to (19) in their analysis [26] of the data of Sengupta et al. [24].

We have now re-examined the analysis of the equilibrium and solubility data of Sengupta et al. [24] for both $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ along the lines suggested by Sengupta et al. [30] with the following modifications. Firstly, in calculating the ionic product K_{ip} for the perchlorates, Davies' equation [31] has been applied to the calculation of the activity coefficient $y_{\pm}$ on the molar scale. In water + methanol mixtures, this becomes [5]

$$-\log y_{\pm} = \left(\frac{D_w}{D_s}\right)^{3/2} \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.30I\right) \tag{20}$$

for a 1 : 2 salt, where I is ionic strength. Values for D were interpolated from the data of Åkerlöf [32]. Values for K_{ip} were then calculated from the product of the solubility product obtained without activity coefficients [29] and $(y_{\pm})^3$. $\Delta G_t^{\ominus}[Fephen_3(ClO_4)_2]$ and $\Delta G_t^{\ominus}[Febipy_3(ClO_4)_2]$ on the mole fraction scale were obtained using

$$\Delta G_t^{\ominus}(\text{salt}) = RT\left\{\ln\frac{(K_{ip})_w}{(K_{ip})_s} + 3\ln\frac{M_w d_s}{M_s d_w}\right\} \tag{21}$$

and by using eqn. (5) with our values for $\Delta G_t^{\ominus}(ClO_4^-)$ [1,2], the values for $\Delta G_t^{\ominus}(Fephen_3^{2+})$ given in Table 2 were obtained. A similar procedure was

TABLE 3

Derivation of the free energy of transfer (kJ mol^{-1}) at 25 °C of Fe^{2+} ions from water into water + methanol mixtures using $\Delta G_t^{\ominus}(Fephen_3^{2+})$; subscript c indicates the molar scale and subscript x the mole fraction scale

[Methanol]		$\Delta G_t^{\ominus}$-$(Fephen_3^{2+})_c$	$-3\Delta G_t^{\ominus}$-$(phen)_c$	$-\Delta\Delta G_F^{\ominus}$	$\Delta G_t^{\ominus}$-$(Fe^{2+})_c$	$\Delta G_t^{\ominus}$-$(Fe^{2+})_x$
Wt%	Mole fraction					
8.03	0.047	−8.4	3.46	−2.3	−7.2	−7.4
16.00	0.097	−12.1	9.3	−3.9	−6.7	−6.9
24.50	0.154	−17.0	16.2	−5.3	−6.1	−6.4
33.59	0.221	−23.8	24.4	−8.3	−7.7	−8.3
43.00	0.298	−26.9	31.3	−11.3	−6.9	−7.6
52.33	0.382	−28.9	37.2	−16.3	−8.0	−8.9

TABLE 4

Derivation of the free energy of transfer (kJ mol^{-1}) at 25 °C of Fe^{2+} ions from water into water + methanol mixtures using $\Delta G_t^{\ominus}(\mathrm{Febipy}_3^{2+})$; subscript c indicates the molar scale and subscript x the mole fraction scale

[Methanol]		$\Delta G_t^{\ominus}$-$(\mathrm{Febipy}_3^{2+})_c$	$-3\Delta G_t^{\ominus}$-$(\mathrm{bipy})_c$	$-\Delta\Delta G_F^{\ominus}$	$\Delta G_t^{\ominus}$-$(\mathrm{Fe}^{2+})_c$	$\Delta G_t^{\ominus}$-$(\mathrm{Fe}^{2+})_x$
Wt%	Mole fraction					
8.03	0.047	−4.81	3.88	0.34	−0.59	−0.71
16.00	0.097	−8.7	8.2	1.09	0.59	0.35
24.50	0.154	−10.7	13.9	0.06	3.26	2.88
33.59	0.221	−18.1	20.5	−3.37	−0.97	1.51
43.00	0.298	−19.8	26.6	−5.4	1.40	0.70
52.33	0.382	−21.5	32.3	−9.2	1.60	0.72

used to produce the $\Delta G_t^{\ominus}(\mathrm{Febipy}_3^{2+})$ values in Table 2 from the data for $\mathrm{Fe(bipy)_3(ClO_4)_2}$ [24,29,30].

$\Delta G_t^{\ominus}(\mathrm{Fephen}^2_{3+})$ was then converted to the molar scale using eqn. (9) and $\Delta G_t^{\ominus}(\mathrm{phen})$ calculated from the solubility data of Sengupta et al. [24]. The values for $\Delta G_t^{\ominus}(\mathrm{Fe}^{2+})$ calculated using these data in eqn. (19) with those of $\Delta G_F^{\ominus}$ of Biswas et al. [27] are given in Table 3 after being converted to the mole fraction scale using eqn. (5).

A similar procedure applied to $\Delta G_t^{\ominus}(\mathrm{Febipy}_3^{2+})$ and $\Delta G_t^{\ominus}(\mathrm{bipy})$ calculated from the solubility of 2,2′-bipyridine in water + methanol [24] and $\Delta G_F^{\ominus}$ calculated [29] from the data of Hazra and Lahiri [33] results in another set of values for $\Delta G_t^{\ominus}(\mathrm{Fe}^{2+})$ (see Table 4).

The values for $\Delta G_t^{\ominus}(\mathrm{Fe}^{2+})$ from both sources will be compared later.

COMPARISON OF $\Delta G_t^{\ominus}$(i) FOR SINGLE IONS IN WATER + METHANOL

For the more hydrophobic co-solvents, like propan-2-ol, *t*-butyl alcohol and acetone, which modify the physical properties of water, a clear separation of $\Delta G_t^{\ominus}$(i) into positive values for anions and negative values for cations occurs at low mole fractions of co-solvent [2,4]. For more hydrophilic co-solvents, like ethane-1,2-diol and glycerol, this separation is less clear [2,4], with the differences in $\Delta G_t^{\ominus}(\text{anion}) - \Delta G_t^{\ominus}(\text{cation})$ in general being much smaller than those found for the hydrophilic co-solvents [2,4]. With methanol as co-solvent, a situation is found for simple ions that is rather like that for the hydrophilic co-solvents [1,2]. For the latter, the electron availability at the basic oxygen site is greater than the electron availability at the basic site in the glycols, owing to the presence of the multiple electron attracting OH groups, or in methanol, with its single electron-repelling methyl group. Accordingly, methanol should show less ability than the more hydrophobic alcohols in attaching itself to a cation in its solvation shell and, as a result, some positively charged ions like K^+, Na^+ and Rb^+ have positive values for $\Delta G_t^{\ominus}(i)$ at low mole fractions of methanol [1,2]. Correspondingly, ion NMR measurements in water + methanol show [34] that Na^+ and Rb^+ have a preference for water molecules over methanol molecules in their coordination shells. Hence, we might well expect $\Delta G_t^{\ominus}$(cations) in water + methanol to overlap the zero line, some with negative values and others with small positive values like those found for some simple ions.

The variation of $\Delta G_t^{\ominus}(i)$ for aqua-cations calculated here is similar (Fig. 1) to that found earlier for other aqua-cations [1,2]: Pb^{2+} has very low positive values for mole fraction of methanol $x_2 < 0.2$, becoming negative for $x_2 > 0.2$. However, the negative or positive deviations of $\Delta G_t^{\ominus}(Pb^{2+})$

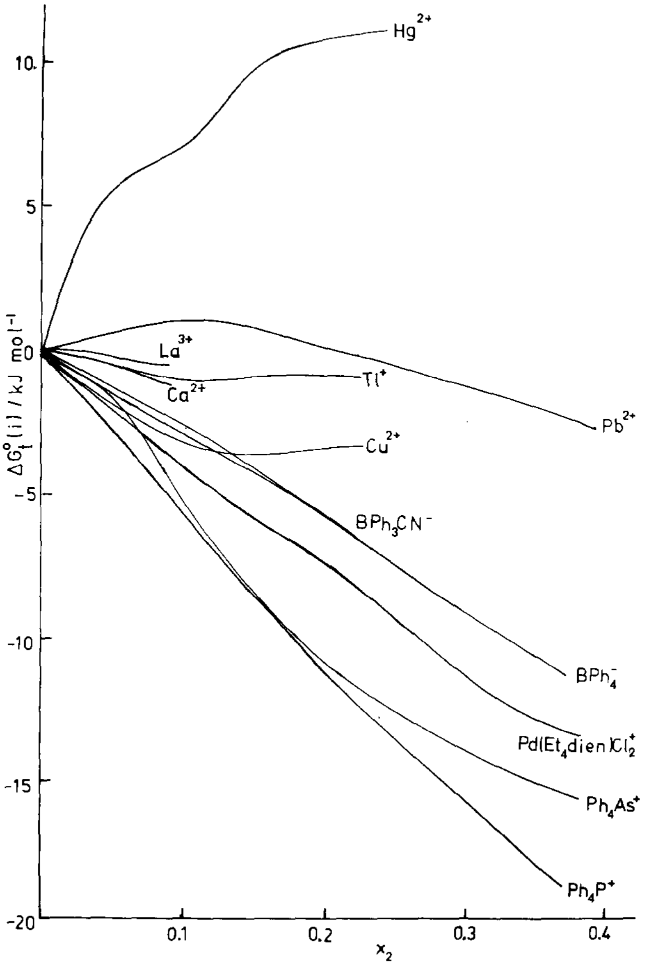


Fig. 1. Gibbs free energy of transfer of simple and complex ions from water into water + methanol mixtures with varying mole fraction of methanol.

from zero are such that we conclude that $\Delta G_t^{\ominus}(Pb^{2+})$ approximates to zero, like indeed also $\Delta G_t^{\ominus}(i)$ for $i = La^{3+}$, Ca^{2+} and Tl^+; this matches very closely the earlier observations [1,2] with non-transitional metal ions. $\Delta G_t^{\ominus}(Cu^{2+})$ is a little more negative, and indeed more negative than $\Delta G_t^{\ominus}(i)$ for $i = Zn^{2+}$ and Cd^{2+} [1,2], suggesting that Cu^{2+} has a definite preference for methanol over water. The large positive values for $\Delta G_t^{\ominus}(Hg^{2+})$ are unique for simple cations, perhaps suggesting that $Hg(BPh_4)_2$, from which this result is derived, is not fully dissociated in water + methanol, leading to a spurious result for $\Delta G_t^{\ominus}(Hg^{2+})$. The presence of hydrophobic groups, like phenyl groups, in cations, as in Ph_4As^+ and Ph_4P^+, produces large negative values in water + methanol, as found for other water + co-solvent systems [2,4]. This is in accord with the observation for water + alcohol mixtures that $\Delta G_t^{\ominus}$ for neutral organic molecules becomes increasingly negative as the size of the organic molecule increases [35]. It should be noted also that, although (as found for other water + co-solvent systems [24]) the hydrophobic phenyl groups make $\Delta G_t^{\ominus}(BPh_4^-)$ also negative for water + methanol, as in the other systems [2,4], $\Delta G_t^{\ominus}(BPh_4^-)$ is less negative than either $\Delta G_t^{\ominus}(Ph_4As^+)$ or $\Delta G_t^{\ominus}(Ph_4P^+)$. It has been argued elsewhere [9] that the assumption described above on which the TPTB method (and the corresponding ones for the TATB method) separates $\Delta G_t^{\ominus}(\text{salt})$ into values of $\Delta G_t^{\ominus}$ for its constituent ions is unlikely to hold for all conditions, as demonstrated here and elsewhere [2,4] by the values for $\Delta G_t^{\ominus}(Ph_4As^+)$, $\Delta G_t^{\ominus}(Ph_4P^+)$ and $\Delta G_t^{\ominus}(BPh_4^-)$. Now, we have additional evidence of this in Fig. 1. It is argued in the TPTB method that $\Delta G_t^{\ominus}(Ph_4P^+)$ should be equal to $\Delta G_t^{\ominus}(BPh_4^-)$, because each large species presents the same surface to the solution; yet Fig. 1 shows that the replacement of a phenyl group in BPh_4^- by CN^- to produce BPh_3CN^- with no alteration in charge gives $\Delta G_t^{\ominus}(BPh_3CN^-) = \Delta G_t^{\ominus}(BPh_4^-)$, which it should not do if the values of $\Delta G_t^{\ominus}(BPh_4^-)$ [and of $\Delta G_t^{\ominus}(Ph_4P^+)$ and $\Delta G_t^{\ominus}(Ph_4As^+)$] are determined only by the hydrophobicity of the ionic surface. Presumably, also, the large negative values for $\Delta G_t^{\ominus}(PdEt_4dienCl_2^+)$ arise largely from the hydrophobicity of the organic ligand.

Figures 2 and 3 show a comparison of $\Delta G_t^{\ominus}(i)$ values for i = anions with the metal atom complexed with halide ions and for i = oxyanions. In general, these show the same trend found for simple anions; in the main, $\Delta G_t^{\ominus}(\text{anion})$ is positive. The one exception in Fig. 3 is CN^-, but $\Delta G_t^{\ominus}(CN^-) \approx 0$. The exceptions in Fig. 2 are oxyanions with large hydrophobic organic groups attached, which are expected [35] to produce a negative contribution to the free energy of transfer; but, even here, $\Delta G_t^{\ominus}(i) \approx 0$ for i = picrate or anthraquinone-2-sulphonate anions. The main exception in Fig. 2 is the very large inorganic anion $CoW_{12}O_{40}^{5-}$. We must conclude here that, although the size of the negative charge may appear large in comparison with the other anions, it is small relative to the size of the anion, and is so effectively diluted by the spread over such a large

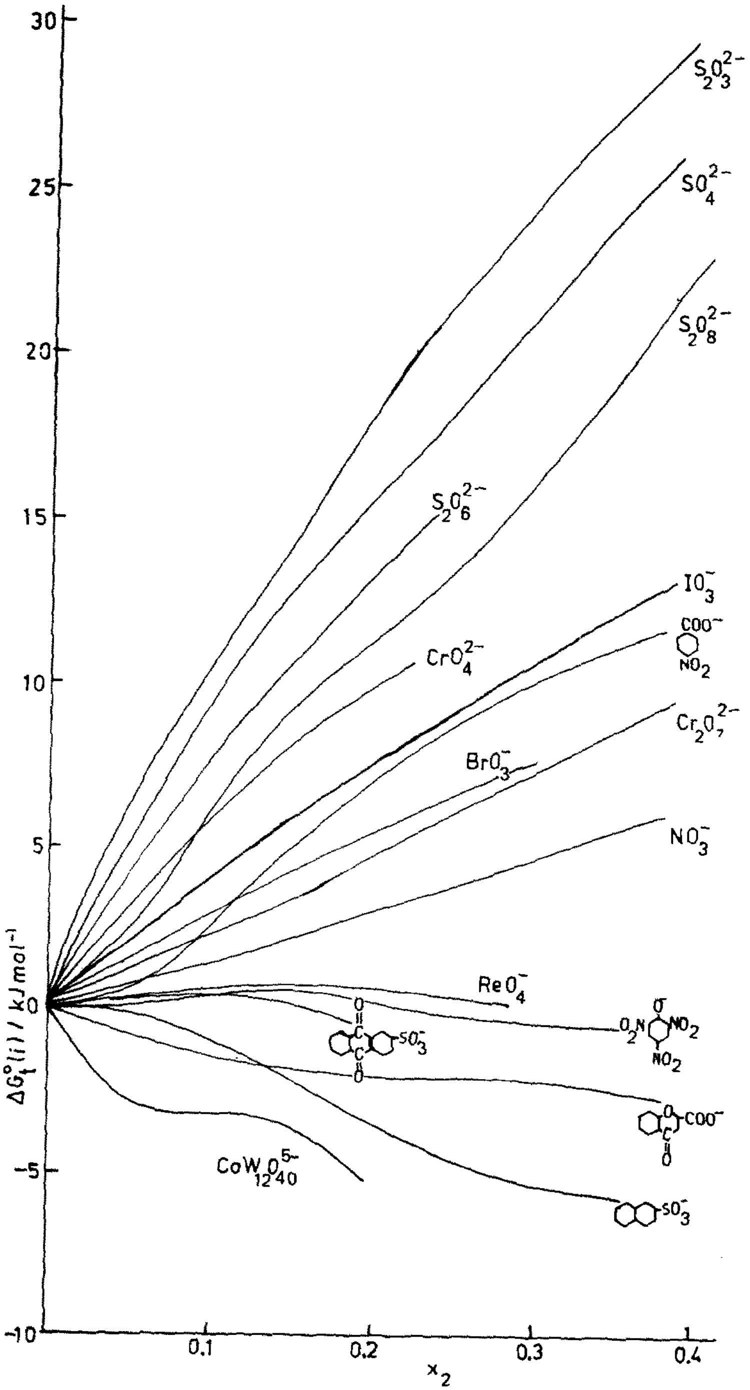


Fig. 2. Gibbs free energy of transfer of oxyanions from water into water + methanol mixtures with varying mole fraction of methanol.

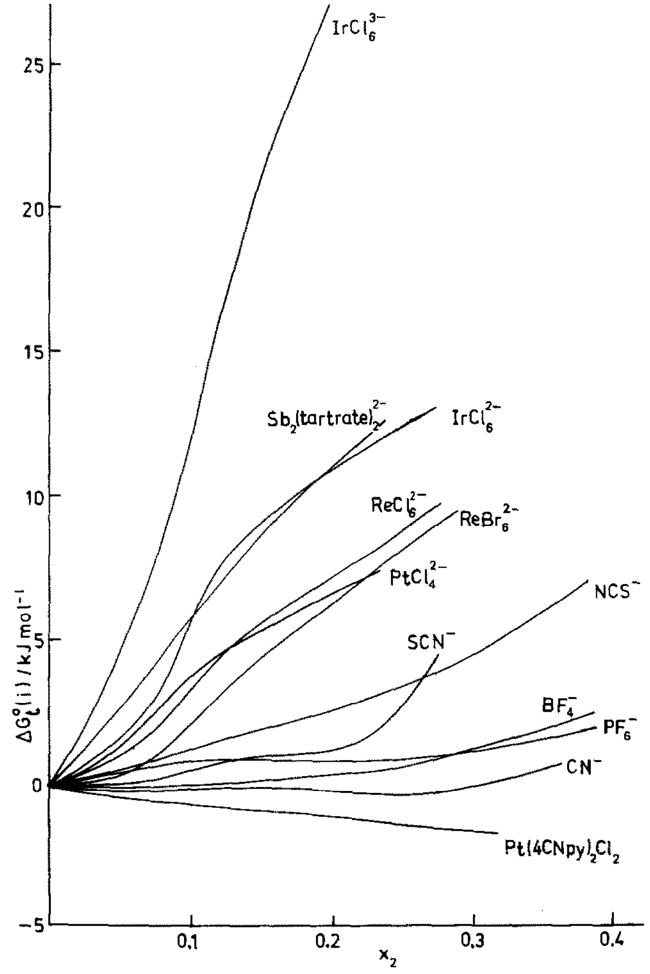


Fig. 3. Gibbs free energy of transfer of halo-anions, cyano-anions and other complexes from water into water + methanol mixtures with varying mole fraction of methanol.

surface in contact with the solution that the small negative $\Delta G_t^{\ominus}$(i) arises in the same way as the small negative values found for neutral inorganic species in water + alcohol mixtures [35]. In support of this, among the oxy di-sulphur anions, $\Delta G_t^{\ominus}$(i) becomes less positive for increasing size for a constant charge, and $\Delta G_t^{\ominus}(Cr_2O_7^{2-}) < \Delta G_t^{\ominus}(CrO_4^{2-})$. Otherwise, there is a tendency for $\Delta G_t^{\ominus}(\text{anion}^{n-})$ to increase with the size of n for ions of approximately the same size. The value for the electrically neutral $Pt(4CNpy)_2Cl_2$ is negative, as found for other electrically neutral molecules in water + alcohol mixtures [35].

A similar variation to those discussed above for Figs. 1–3 and for the simple ions [1,2] is found in Fig. 4 for complex cations and anions based on Co^{3+}. Those with moderate overall positive charges remain with $\Delta G_t^{\ominus}$(cat-

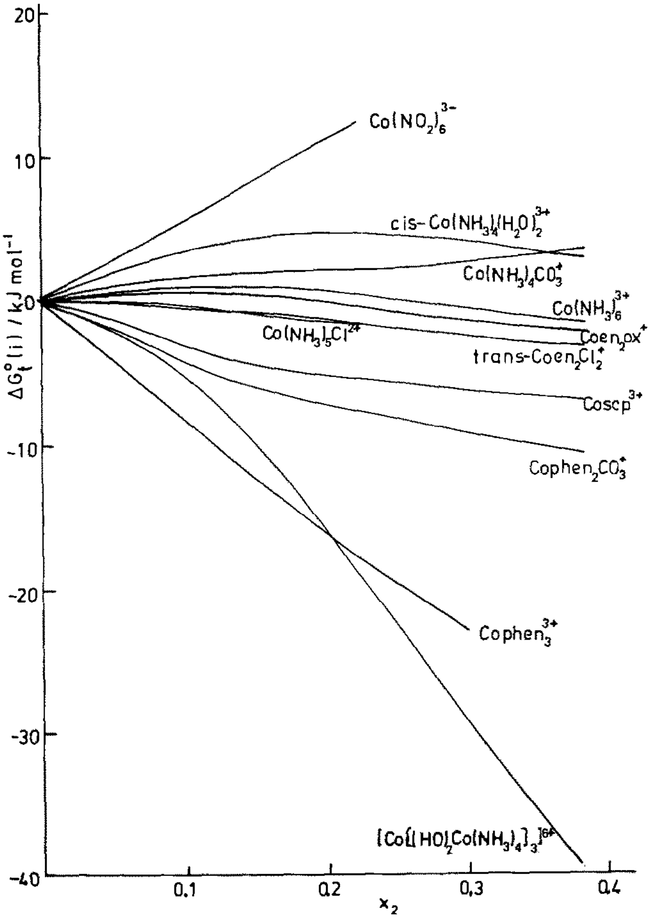


Fig. 4. Gibbs free energy of transfer of complexes of Co^{III} from water into water + methanol mixtures with varying mole fraction of methanol.

ion) ≈ 0, with a tendency for the hydrophobic organic ligands to make negative contributions to the free energy of transfer. $\Delta G_t^\ominus[Co(NO_3)_6^{3-}]$ is firmly positive and $\Delta G_t^\ominus(i)$ for the cation with an overall charge of 6 + has large negative values. $\Delta G_t^\ominus[Coox_2(H_2O)_2^-]$ in Fig. 5 is positive, as expected [1,2].

The complex cations of Cr^{3+} show a similar variation in Fig. 5 to those of Co^{3+} in Fig. 4. For those with overall charges of 1 + or 2 +, $\Delta G_t^\ominus$(cation) ≈ 0, whereas, for a charge of 3 +, $\Delta G_t^\ominus$(cation) becomes definitely negative.

Free energies of transfer of iron complexes with cyano, phenanthroline and bipyridine ligands are compared in Figs. 5 and 6. All such complexes with overall negative charges have $\Delta G_t^\ominus$(anion) positive, in conformity with the general findings above and elsewhere [1–4] for water + alcohol mixtures. The two electrically neutral species, $Fephen_2(CN)_2$ and $Fe(bipy)_2(CN)_2$, have negative free energies of transfer, in agreement with the previous

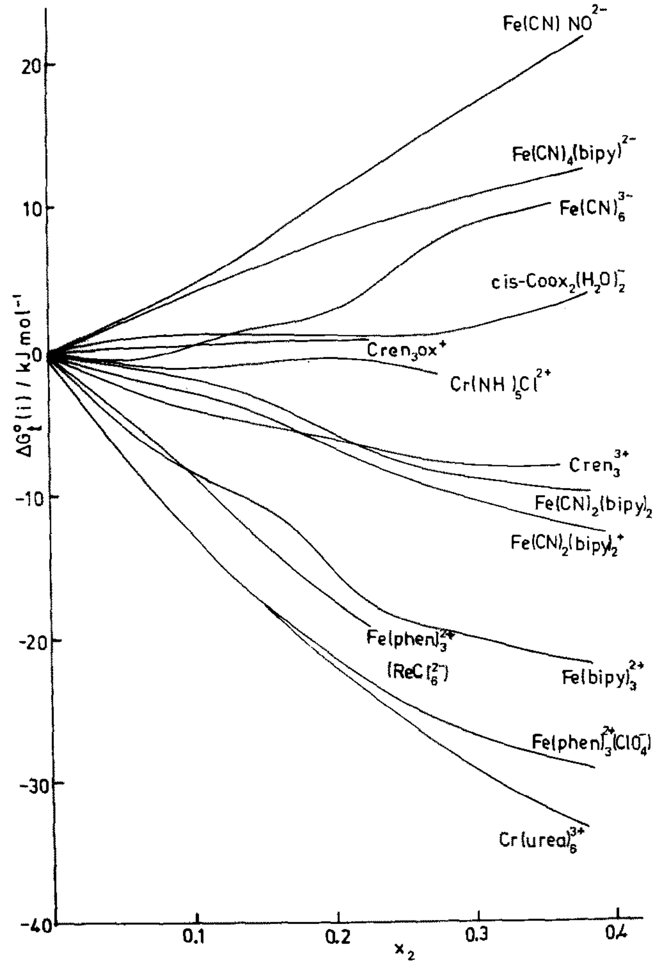


Fig. 5. Gibbs free energy of transfer of complexes of Co^{III}, Cr^{III} and Fe^{II} from water into water + methanol mixtures with varying mole fraction of methanol.

findings for such inorganic and organic species in water + alcohols [35]. Adding a single positive charge to these two molecules makes $\Delta G_t^{\ominus}$(i) slightly more negative, suggesting that the hydrophobicity of the phen and bipy ligands make the more important contribution. Replacement of all the cyano groups by phen or bipy, makes $\Delta G_t^{\ominus}$(cation) more negative still, but here the positive charge also increases.

Figures 7 and 8 show the variation of $\Delta G_t^{\ominus}$(i) for Fe^{2+} complexed with large ligands attached with nitrogen atoms. These are classified according to the number of complexing nitrogen atoms in the ligand and the number and type of organic groups attached. All have negative $\Delta G_t^{\ominus}$(i), as expected for cations, but it is clear that the size of the ligand as represented by the number of complexing nitrogen atoms has little, if any, effect in controlling

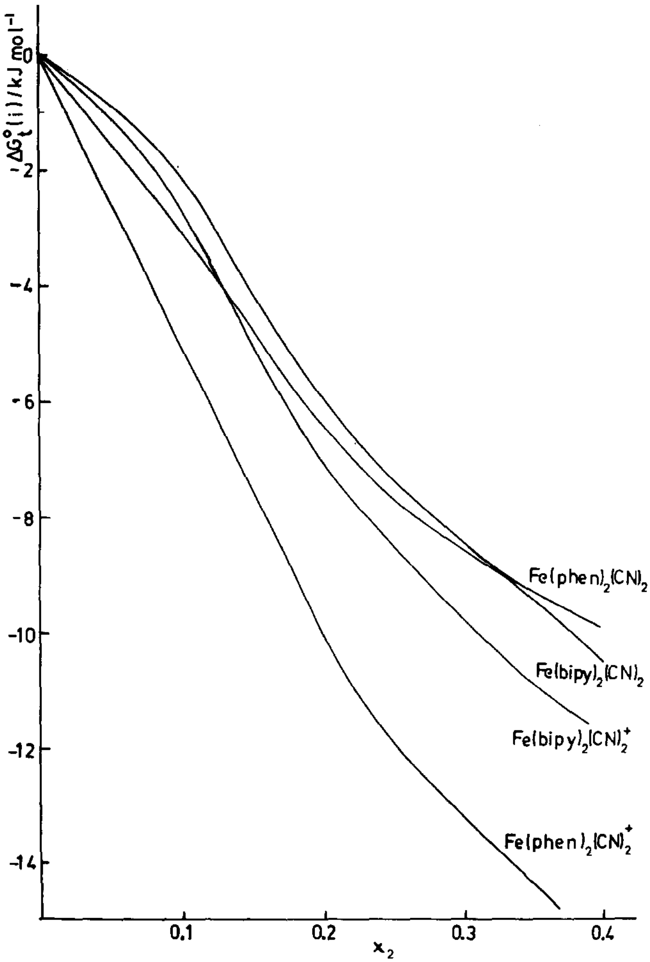


Fig. 6. Gibbs free energy of transfer of cyano(2,2′-bipyridine)iron complexes and of cyano(1,10-phenanthroline)iron complexes from water into water + methanol mixtures with varying mole fraction of methanol.

$\Delta G_t^{\ominus}(i)$. However, as found above and as expected from $\Delta G_t^{\ominus}(i)$ for neutral molecules in water + alcohol mixtures [35], $\Delta G_t^{\ominus}(\text{cation})$ becomes increasingly negative for the linear ligands as the degree of hydrophobicity increases: examples exist for the ligands N_2, N_3, N_6 and N_6'' in Figs. 7 and 8. Again, for the cages complexed with Fe^{2+}, that with the cyclohexyl groups on the surface has a more negative free energy than that with only methyl groups in contact with the solution. $\Delta G_t^{\ominus}(i)$ for the two neutral mixed cyano complexes in Fig. 8 are negative, as expected for neutral molecules [35], but the small increase in hydrophobicity in going from $MeHN_2''(CN)_2$ to $Me_2N_2''(CN)_2$ makes $\Delta G_t^{\ominus}(i)$ more negative.

The one question remaining is, how do these $\Delta G_t^{\ominus}(\text{cation})$ values for complexed Fe^{2+} ions in Figs. 5–8 compare with $\Delta G_t^{\ominus}(Fe^{2+})$? The earlier

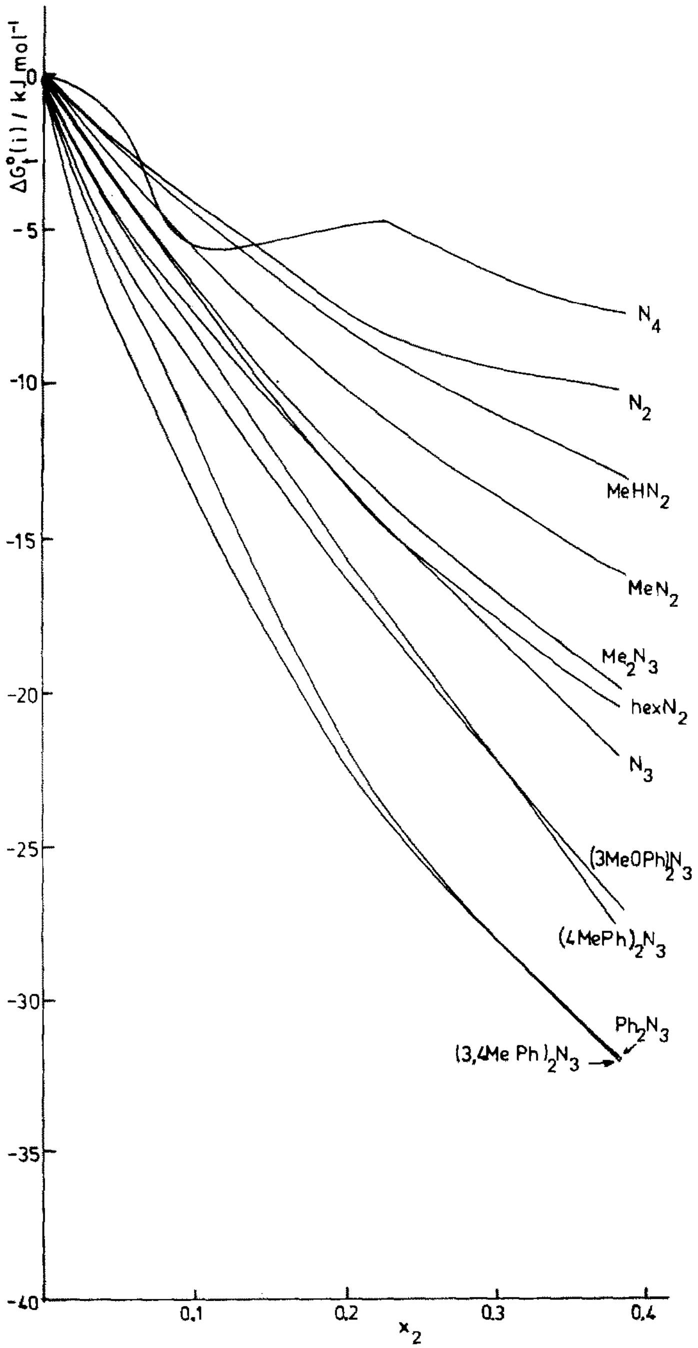


Fig. 7. Gibbs free energy of transfer of complexes of Fe^{II} from water into water + methanol mixtures with varying mole fraction of methanol.

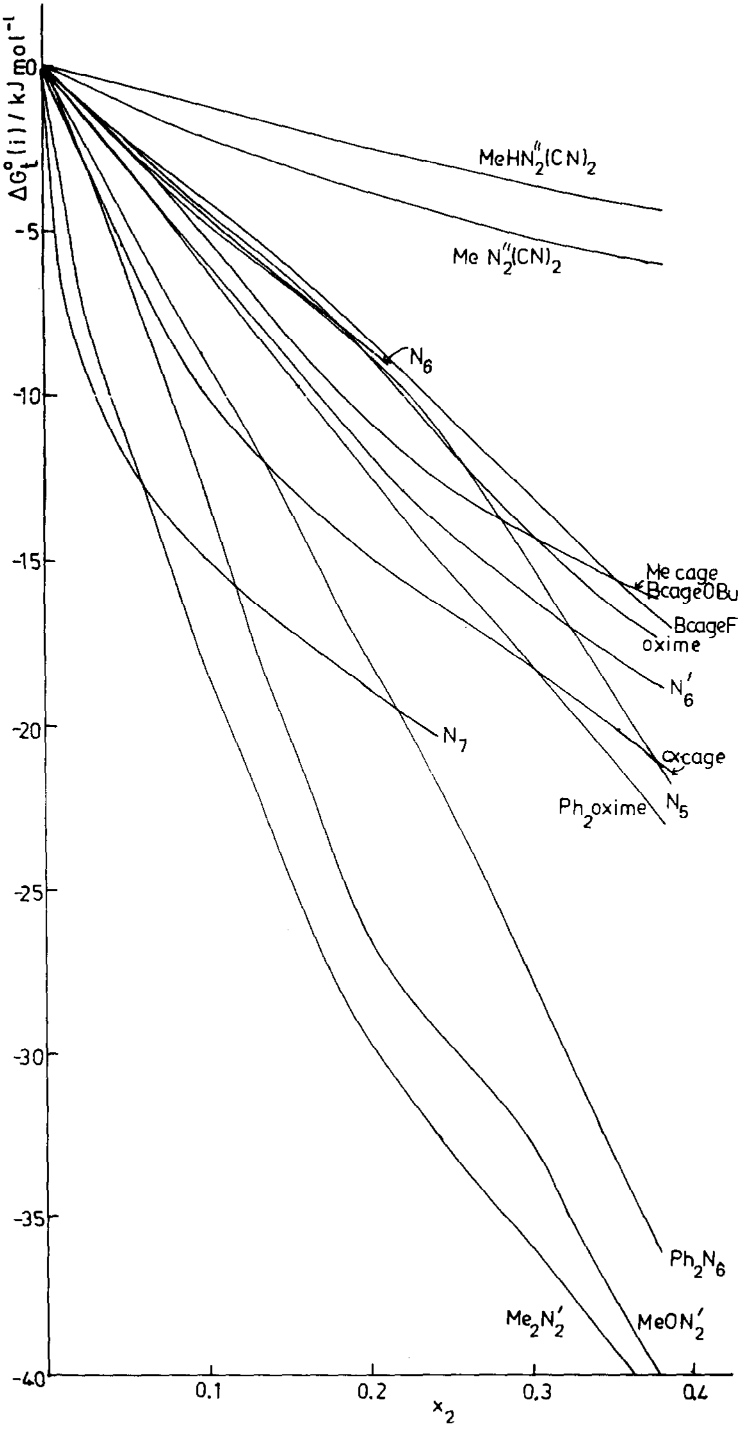


Fig. 8. Gibbs free energy of transfer of complexes of Fe^{II} from water into water + methanol mixtures with varying mole fraction of methanol.

calculations [25] of $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$ using eqn. (19) with $\Delta G_t^\ominus$(phen) derived from the solubilities of Burgess and Haines [28] showed that $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$ could have quite high negative values. Moreover, the calculations in Table 3 using $\Delta G_t^\ominus$(phen) derived from the solubilities of Sengupta et al. [24] and applying medium corrections to activity coefficients in the ionic products also show negative values for $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$. However, when an equation analogous to (19) is applied to $\mathrm{Fe(bipy)}_3^{2+}$ using the solubilities of Sengupta et al. [24], deriving $\Delta\Delta G_\mathrm{F}^\ominus$ from the pK data for (18), with bipy replacing phen of Hazra and Lahiri [33] and applying corrections to the activity coefficients, $\Delta G_t^\ominus(\mathrm{Fe}^{2+}) \approx 0$ (Table 4). The disparity between these two sets of data for $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$ probably arises from the operation of eqn. (19), where the right hand side opposes large positive and negative quantities, making the error on the final $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$ rather high. In the case of the bipyridine route, this may be accentuated by the very high errors which probably occur in $\Delta\Delta G_\mathrm{F}^\ominus$, owing to the relative invariance of the pK of eqn. (18) for bipyridine in water + methanol mixtures from the pK found in water alone. Nevertheless, it seems safe to conclude that $\Delta G_t^\ominus(\mathrm{Fe}^{2+})$ has small negative values and that the addition of organic ligands causes an increase in these negative values arising from the ligand hydrophobicity, as expected.

REFERENCES

1 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 69 (1973) 984.

2 C.F. Wells, Austral. J. Chem., 36 (1983) 1739.

3 I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 82 (1986) 2577.

4 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 70 (1974) 694; 71 (1975) 1868; 72 (1976) 601; 74 (1978) 1569; 77 (1981) 1515; Thermochim. Acta, 53 (1982) 67; J. Chem. Soc. Faraday Trans. 1, 80 (1984) 2445; G.S. Groves and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 81 (1985) 1985, 3091; I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 439; 84 (1988) 1153; G.S. Groves, K.H. Halawani and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 1281; K.H. Halawani and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 2185; J. Saxton and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 86 (1990) 1471.

5 M.H. Abraham, T. Hill, H.C. Ling, R.A. Schulz and R.A.C. Watt, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 275.

6 M.J. Blandamer and J. Burgess, Transition Met. Chem., 13 (1988) 1.

7 I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Dalton Trans., (1981) 2034; G.S. Groves and C.F. Wells, J. Solution Chem., 15 (1986) 211.

8 G.M.A. El-Subruiti, I.M. Sidahmed and C.F. Wells, J. Solution Chem., 20 (1991) 403.

9 C.F. Wells, Thermochim. Acta, 130 (1988) 127; K.H. Halawani and C.F. Wells, Thermochim. Acta, 155 (1989) 57.

10 P.J. LaBrocca, R. Phillips, S.S. Goldberg and O. Popovych, J. Chem. Eng. Data, 24 (1979) 215.

11 K.-Y. Chu and A.R. Thompson, J. Chem. Eng. Data, 7 (1962) 358.

12 C. Tissier, C.R. Acad. Sci., Ser. C, 286 (1978) 35.

13 M.J. Blandamer, J. Burgess and S.J. Hamshere, J. Chem. Soc. Dalton Trans., (1979) 1539.

14 M.J. Blandamer, J. Burgess and R.I. Haines, J. Chem. Soc. Dalton Trans., (1980) 607.
15 M.J. Blandamer, J. Burgess, P.P. Duce, A.J. Duffield and S.J. Hamshere, Transition Met. Chem., 6 (1981) 368.
16 M.J. Blandamer, J. Burgess and F.M. Mekhail, Inorg. Chim. Acta, 81 (1984) 121.
17 M.J. Blandamer, J. Burgess and E.-E.A. Abu-Gharib, Transition Met. Chem., 9 (1984) 193.
18 J. Burgess and E.-E.A. Abu-Gharib, Transition Met. Chem., 9 (1984) 234.
19 E.-E.A. Abu-Gharib, M.J. Blandamer, J. Burgess, N. Gosal, P. Guardado, F. Sanchez and C.D. Hubbard, Transition Met. Chem., 9 (1984) 306.
20 J. Burgess and E.-E.A. Abu-Gharib, J. Chem Res., Synop., (1984) 8; J. Chem. Res., Miniprint, (1984) 0275.
21 M.J. Blandamer, J. Burgess, B. Clark, P.P. Duce, A.W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C.D. Hubbard and E.-E.A. Abu-Gharib, J. Chem. Soc. Faraday Trans. 1, 82 (1986) 1471.
22 J. Burgess, S. Radulovic and F. Sanchez, Transition Met. Chem., 12 (1987) 529.
23 M.J. Blandamer, J. Burgess, J. Fawcett, S. Radulovic and D.R. Russell, Transition Met. Chem., 13 (1988) 120.
24 D. Sengupta, A. Pal and S.C. Lahiri, J. Chem. Soc. Dalton Trans., (1983) 2685.
25 A.E. Eid and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 81 (1985) 1401.
26 M.J. Blandamer and J. Burgess, Inorg. Chim. Acta, 64 (1982) L113.
27 G. Biswas, S. Aditya, A. Battacharyya and S.C. Lahiri, J. Indian Chem. Soc., 54 (1977) 1137.
28 J. Burgess and R.I. Haines, J. Chem. Eng. Data, 23 (1978) 196.
29 M.J. Blandamer and J. Burgess, J. Chem. Soc. Dalton Trans., (1985) 867.
30 D. Sengupta, A. Pal and S.C. Lahiri, J. Chem. Soc. Dalton Trans., (1985) 868.
31 C.W. Davies, Ion Association, Butterworth, London, 1962, Chap. 3.
32 G. Åkerlöf, J. Am. Chem. Soc., 54 (1932) 4125.
33 D.K. Hazra and S.C. Lahiri, Anal. Chim. Acta, 79 (1975) 335.
34 A.K. Covington and K.E. Newman, Adv. Chem. Ser., 155 (1976) 153.
35 C.F. Wells, Thermochim. Acta, 132 (1988) 141; 161 (1990) 223.