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STUDIES ON HEXACYANOFERRATE(II) COMPLEXES. FORMATION CONSTANTS FOR ALKALI METAL, AMMONIUM AND CALCIUM(II) COMPLEXES AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS IN AQUEOUS SOLUTION

SANTI CAPONE, ALESSANDRO DE ROBERTIS and SILVIO SAMMARTANO

Istituto di Chimica Analitica dell'Università, via dei Verdi, 98100 Messina (Italy)

CARMELO RIGANO

Dipartimento di Matematica dell'Università, viale A. Doria 6, 95125 Catania (Italy)

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ABSTRACT

The formation constants of H^+, Li^+, Na^+, K^+, NH_4^+ and Ca^{2+} hexacyanoferrate(II) complexes in aqueous solution have been obtained by pH-metric measurements at 10, 25 and 35°C and $0.05 \leqslant I \leqslant 1$ mol l^{-1}. The species [ML], [M_2L] and [MLH] have been found for all cations. The dependence of formation constants on ionic strength has been obtained by a simple Debye–Hückel type equation. From the dependence on temperature, estimates of ΔH^0 and ΔS^0 for the formation of all complexes have been calculated. Some linear relationships have been found for the formation constants. Comparisons with literature data are reported.

INTRODUCTION

Though the protonation and complexation with alkali metal and alkaline earth metal ions of hexacyanoferrate(II) have been studied by several authors [1–6,39–51], the quantitative information at $I > 0.1$ mol l^{-1} and $t \neq 25$°C has so far been insufficient. Moreover, the existence of poynuclear species [M_nL] has been proposed to justify some experimental data [3,4], but no stability constants have been reported for alkali metal ions (except in one case [2]). Polynuclear species have been reported for alkaline earth metal ions, but the formation constants seem heavily dependent on the choice of activity coefficients at various ionic strengths [5,6]. The complexes of ammonium ion, that are likely to behave like alkali metal ions, have been completely neglected.

This lack can be attributed to the following factors. (a) Generally, weak complexes are difficult to study, due to the uncertainties in activity coefficients, in particular when polynuclear and/or protonated species are formed.

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(b) In order to keep the ionic strength constant, a background must be used: in the present case it is very difficult to choose the appropriate salt because almost all cations (also tetraalkylammonium cations [6]) form significant complexes with $Fe(CN)_6^{4-}$. (c) The first dissociation constant ($pK_1 < 2$) is difficult to calculate with a high degree of accuracy. Moreover the difference $pK_2 - pK_1 < 2$ does not allow one to neglect the first dissociation when calculating the second. (d) The complexation scheme is quite complicated: in addition to [ML] simple species, both protonated and polynuclear species are formed. Furthermore, in mixed alkali metal solutions ternary species $[MM'(Fe(CN)_6)]^{2-}$ are formed [7].

Some recent papers on the ionic strength dependence of formation constants [8–16] and on the formation of weak complexes [17–34] showed that a general model for the dependence of activity coefficients on ionic strength, together with some computer calculation methods [30–34], may overcome the above difficulties.

In this paper we report a potentiometric determination of formation constants of H^+, Li^+, Na^+, K^+, NH_4^+ and Ca^{2+} complexes with $Fe(CN)_6^{4-}$ in the ionic strength range $0.05 \leqslant I \leqslant 1$ mol l^{-1}, at 10, 25 and 35°C, in aqueous solution.

EXPERIMENTAL

Chemicals

Potassium hexacyanoferrate(II) (Fluka, purity > 99.5%) was used without further purification. The working solution was prepared daily, in order to avoid decomposition. Alkali metal chlorides and ammonium chloride (C. Erba, purity > 99.5%) were dried in an oven at 110°C or in vacuum. Calcium chloride solution was prepared from C. Erba solid salt and titrated with EDTA [35]. HCl stock solution was prepared by diluting concentrated C. Erba ampoules. Grade A glassware and twice-distilled water were employed for all solutions.

Apparatus

Measurements of the free hydrogen ion concentration were carried out by means of a potentiometer (Metrohm model E 605), coupled with glass and saturated-calomel electrodes, supplied by the same firm. The titrant was delivered from an Amel dispenser, minimum reading 0.001 cm^3. The measurement cell (50 cm^3) was thermostated at $t \pm 0.2$°C. Magnetic stirring was employed. Purified N_2 was bubbled through all the solutions under study.

Procedure

The solution under study (25 cm^3) ($C_{\mathrm{Ligand}} = 4–6$ mmol l^{-1}, $C_{\mathrm{Metal}} = 0.01–0.95$ mol l^{-1}) was titrated with HCl (0.4000 mol l^{-1}) down to pH ~ 1.5. An excess of HCl was necessary in order to complete the protonation of the hexacyanoferrate(II) ion and to calculate the internal E^0, E^0_{int}. By means of separate titrations we also calculated E^0_{ext} in the same conditions as the considered solution, but in the absence of the ligand; if $|E^0_{\mathrm{int}} - E^0_{\mathrm{ext}}|$ was > 1.0 mV, the titration was repeated. The pH reproducibility for the system was ± 0.02 units, in the range $1.5 \leqslant \mathrm{pH} \leqslant 2$ and ± 0.005 in the range $2 \leqslant \mathrm{pH} \leqslant 4.5$.

Calculations

The potentiometric data were elaborated by the computer programs ACBA and/or ESAB [36,37] by assuming no complex formation. In this manner we obtained the "conditional" protonation constants, log β'_{oqr} *, as reported in Table 1. Then the formation constants of Li^+, Na^+, K^+, NH_4^+ and Ca^{2+} complexes were calculated by the nonlinear least-squares computer program ES2WC [34,38]. For the dependence of formation constants on ionic strength the Debye–Hückel type equation was used [8–16]:

$$\log \beta_{pqr}(I) = \log \beta_{pqr}(I') - z^*_{pqr}\left(\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}}\right) + C_{pqr}(I - I') + D_{pqr}(I^{3/2} - I'^{3/2}) \qquad (1)$$

where C_{pqr} and D_{pqr} are empirical parameters; I' is the reference ionic strength; and $z^*_{pqr} = pz^2 + 16q + r - (pz - 4q + r)^2$.

RESULTS

As mentioned above, some authors have hypothesized the formation of polynuclear complexes [3,4], in addition to the simple $[M(Fe(CN)_6)]$ species in solutions containing $C_M > 0.01$ mol l^{-1}. Cohen and Plane [39] observed that, with an excess of potassium chloride ($C_{K^+} > 16$ mmol l^{-1}, $C_L < 1$ mmol l^{-1}), the optical density of potassium hexacyanoferrate(II) was significantly lower than the extrapolated value for complete association; this was attributed to the formation of the binuclear species $[K_2(Fe(CN)_6)]^{2-}$. Eaton et al. [40] found, from K^+-glass selective electrode measurements, that for

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* In general the formation constants are defined as β_{pqr} according to the reaction $pM^z + q(Fe(CN)_6^{4-}) + rH^+ \rightleftarrows [M_p(Fe(CN)_6)_qH_r]^{(pz+r-4q)}$, and are expressed in the molar scale.

TABLE 1

Conditional protonation constants of hexacyanoferrate(II) in different backgrounds

I	t	$\log \beta'_{01}$	$\log \beta'_{02}$	$\log \beta'_{01}$	$\log \beta'_{02}$	$\log \beta'_{01}$	$\log \beta'_{02}$	$\log \beta'_{01}$	$\log \beta'_{02}$	$\log \beta'_{01}$	$\log \beta'_{02}$
		Li^+		Na^+		K^+		NH_4^+		Ca^{2+}	
0.05	10	3.51	5.37	3.32	5.07	3.18	5.01	3.24	5.02	2.93	4.59
	25	3.47	5.34	3.33	5.14	3.23	5.03	3.25	5.07	2.94	4.60
	35	3.44	5.32	3.34	5.18	3.27	5.03	3.26	5.10	2.95	4.61
0.10	10	3.31	5.05	3.13	4.71	2.96	4.65	3.03	4.66	2.80	4.30
	25	3.27	5.00	3.13	4.77	3.02	4.65	3.04	4.70	2.82	4.32
	35	3.24	4.96	3.13	4.81	3.06	4.63	3.05	4.72	2.83	4.33
0.20	10	3.12	4.72	2.96	4.36	2.76	4.30	2.85	4.30	2.67	4.00
	25	3.08	4.65	2.95	4.41	2.82	4.26	2.84	4.32	2.70	4.02
	35	3.05	4.60	2.94	4.44	2.86	4.23	2.84	4.34	2.71	4.03
0.40	10	2.90	4.36	2.81	4.01	2.60	3.96	2.68	3.95	2.53	3.63
	25	2.89	4.30	2.79	4.05	2.65	3.88	2.67	3.96	2.57	3.67
	35	2.88	4.26	2.77	4.08	2.68	3.81	2.66	3.96	2.59	3.69
0.70	10	2.71	4.03	2.70	3.70	2.48	3.68	2.56	3.64	2.39	3.23
	25	2.73	3.99	2.67	3.75	2.51	3.56	2.53	3.64	2.45	3.28
	35	2.74	3.96	2.65	3.79	2.52	3.46	2.52	3.65	2.48	3.31
1.00	10	2.57	3.78	2.60	3.47	2.39	3.47	2.46	3.41	2.28	2.91
	25	2.62	3.77	2.58	3.53	2.40	3.32	2.43	3.42	2.34	2.96
	35	2.65	3.75	2.56	3.57	2.41	3.21	2.42	3.42	2.38	3.00

TABLE 2

Protonation constants, and Li^+, Na^+, K^+, NH_4^+ and Ca^{2+} complex formation constants of hexacyanoferrate(II) in aqueous solution

I [a]	t [a]	$\log \beta_{011}$ [b]	$\log \beta_{012}$	M = Li^+			M = Na^+		
				$\log \beta_{110}$	$\log \beta_{210}$	$\log \beta_{111}$	$\log \beta_{110}$	$\log \beta_{210}$	$\log \beta_{111}$
0.05	10	3.74(4) [c]	5.69(7)	1.28(7)	1.82(10)	4.42(10)	1.76(8)	2.08(13)	4.79(11)
	25	3.79(4)	5.77(6)	1.48(6)	1.88 (8)	4.57 (8)	1.78(6)	2.09(10)	4.78(10)
	35	3.82(4)	5.83(7)	1.61(7)	1.93(10)	4.68(10)	1.79(8)	2.10(12)	4.78(12)
0.10	10	3.64(4)	5.52(6)	1.18(6)	1.64 (8)	4.24 (8)	1.65(7)	1.91(10)	4.62(10)
	25	3.68(3)	5.58(5)	1.37(6)	1.69 (7)	4.38 (6)	1.67(6)	1.90(10)	4.59 (9)
	35	3.70(4)	5.63(6)	1.49(7)	1.73 (8)	4.48 (8)	1.68(7)	1.90(11)	4.58(10)
0.20	10	3.58(3)	5.42(6)	1.13(6)	1.54 (9)	4.14 (7)	1.59(6)	1.81(10)	4.52(10)
	25	3.61(2)	5.46(5)	1.30(5)	1.57 (7)	4.26 (6)	1.60(5)	1.78 (9)	4.47 (9)
	35	3.63(3)	5.50(6)	1.42(6)	1.60 (8)	4.35 (7)	1.60(6)	1.77(11)	4.44(10)
0.40	10	3.62(3)	5.49(6)	1.16(7)	1.61 (8)	4.21 (7)	1.63(6)	1.88(10)	4.59 (9)
	25	3.63(2)	5.51(5)	1.32(5)	1.62 (7)	4.31 (6)	1.62(5)	1.83 (9)	4.52 (9)
	35	3.64(3)	5.52(6)	1.43(6)	1.62 (8)	4.37 (8)	1.61(6)	1.79(10)	4.47 (9)
0.70	10	3.74(4)	5.71(6)	1.28(7)	1.83 (8)	4.43 (8)	1.76(6)	2.10 (9)	4.81 (9)
	25	3.75(3)	5.72(5)	1.44(5)	1.84 (7)	4.52 (7)	1.74(5)	2.04(10)	4.73 (9)
	35	3.75(4)	5.73(6)	1.54(7)	1.84 (9)	4.58 (9)	1.73(6)	2.00(10)	4.68(11)
1.00	10	3.85(4)	5.91(7)	1.39(6)	2.03 (9)	4.63 (9)	1.86(7)	2.30(12)	5.01(10)
	25	3.87(4)	5.94(6)	1.56(6)	2.05 (8)	4.74 (9)	1.85(6)	2.26(10)	4.95 (9)
	35	3.89(5)	5.97(8)	1.67(7)	2.07 (9)	4.82(10)	1.85(7)	2.24(12)	4.92(12)

TABLE 2 (*continued*)

		$M = K^+$			$M = NH_4^+$			$M = Ca^{2+}$		
		$\log \beta_{110}$	$\log \beta_{210}$	$\log \beta_{111}$	$\log \beta_{110}$	$\log \beta_{210}$	$\log \beta_{111}$	$\log \beta_{110}$	$\log \beta_{210}$	$\log \beta_{111}$
0.05	10	1.85(8)	2.04(11)	4.56(12)	1.82(10)	2.14(11)	4.70(12)	2.81(6)	3.57 (9)	5.51(8)
	25	1.91(6)	2.33 (8)	4.82(10)	1.86 (8)	2.22(10)	4.75(10)	2.89(4)	3.61 (8)	5.62(7)
	35	1.94(7)	2.53(10)	5.00(11)	1.88(10)	2.28(11)	4.79(12)	2.94(5)	3.64 (9)	5.69(8)
0.10	10	1.75(6)	1.86 (9)	4.38(10)	1.72 (8)	1.96(10)	4.53(10)	2.60(5)	3.26 (9)	5.25(8)
	25	1.80(5)	2.14 (6)	4.63 (8)	1.75 (7)	2.03 (9)	4.56 (9)	2.66(4)	3.28 (8)	5.34(6)
	35	1.83(6)	2.33 (8)	4.80 (9)	1.77 (8)	2.08(10)	4.59(10)	2.70(5)	3.29(10)	5.40(7)
0.20	10	1.69(5)	1.77 (8)	4.29 (8)	1.66 (7)	1.87 (9)	4.43 (9)	2.48(5)	3.08(10)	5.11(7)
	25	1.73(4)	2.02 (6)	4.51 (6)	1.68 (6)	1.91 (9)	4.44 (8)	2.51(4)	3.06 (8)	5.17(6)
	35	1.75(5)	2.20 (8)	4.67 (9)	1.69 (7)	1.95(10)	4.46 (9)	2.54(5)	3.05 (9)	5.21(6)
0.40	10	1.73(5)	1.83 (7)	4.35 (8)	1.69 (7)	1.93 (9)	4.50 (9)	2.53(5)	3.17 (9)	5.19(7)
	25	1.75(4)	2.07 (6)	4.56 (7)	1.70 (6)	1.96 (8)	4.49 (8)	2.54(3)	3.11 (8)	5.21(6)
	35	1.76(5)	2.22 (7)	4.69 (8)	1.70 (7)	1.97(10)	4.48 (9)	2.54(5)	3.07 (9)	5.22(7)
0.70	10	1.85(6)	2.05 (8)	4.57 (8)	1.82 (8)	2.15 (9)	4.72(10)	2.74(5)	3.51 (9)	5.48(7)
	25	1.87(5)	2.28 (7)	4.77 (7)	1.82 (6)	2.17 (9)	4.70 (8)	2.74(5)	3.43 (8)	5.49(7)
	35	1.88(6)	2.43 (8)	4.90 (8)	1.83 (8)	2.18 (9)	4.69(10)	2.75(5)	3.38 (9)	5.50(7)
1.00	10	1.96(7)	2.25(10)	4.77(11)	1.93 (9)	2.35(11)	4.92(11)	2.93(6)	3.80(10)	5.73(8)
	25	1.99(6)	2.50 (8)	4.99 (9)	1.94 (7)	2.39 (9)	4.92 (9)	2.96(5)	3.77 (9)	5.78(8)
	35	2.01(8)	2.67(10)	5.14(11)	1.95(10)	2.42(11)	4.93(12)	2.98(6)	3.75(11)	5.81(9)

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[a] Ionic strength in mol l^{-1} temperature in degrees centigrade.

[b] Indexes of formation constants refer to the reaction: $pM^z + q(Fe(CN)_6^{4-}) + rH^+ \leftrightarrows [M_p(Fe(CN)_6)_qH_r]^{(pz+r-4q)}$.

[c] 3σ in parentheses.

$C_{K^+} > 0.01$ mol l^{-1} a second K^+ binds to the hexacyanoferrate(II) ion; however, they affirmed that the uncertainties about assumptions concerning activity coefficients in these solutions precluded the formation constants of $[M_2(Fe(CN)_6)]$ species being determined. Binuclear Ca^{2+} complexes have been reported by James [5] and Lazarev et al. [6]. Although the formation of $[M(Fe(CN)_6)H]$ species has never been proposed, the appreciable lowering of the second protonation constants suggests that these protonated complexes are also present.

By analyzing the results of Table 1 with the computer program ES2WC [34,38], we were able to calculate the formation constants of the three species: $[M(Fe(CN)_6)]$, $[M_2(Fe(CN)_6)]$ and $[M(Fe(CN)_6)H]$. In Table 2 the values of the formation and protonation constants are reported at various temperatures and ionic strengths. From the dependence on temperature, estimates of ΔH^0 were calculated. In Table 3 ΔG^0, ΔH^0 and ΔS^0 values

TABLE 3

Thermodynamic parameters for the formation of H^+, Li^+, Na^+, K^+ and NH_4^+ hexacyanoferrate(II) complexes at 25°C and $I = 0$ mol l^{-1}

p	q	r [a]	M	$\log \beta_{pqr}$	$-\Delta G^0_{pqr}$ [b]	ΔH^0_{pqr} [b]	ΔS^0_{pqr} [b]
0	1	1	H^+	4.37 (5) [c]	5.96 [d]	1.6 [e]	25 [f]
0	1	2		6.79 (7)	9.27	2.7	40
1	1	0	Li^+	2.06 (7)	2.81	5.6	28
2	1	0		2.90 (9)	3.96	2.3	21
1	1	1		5.59 (9)	7.63	4.8	42
1	1	0	Na^+	2.36 (7)	3.22	0.9	14
2	1	0		3.11(11)	4.25	0.8	17
1	1	1		5.80(11)	7.92	0.2	27
1	1	0	K^+	2.49 (7)	3.40	1.8	17
2	1	0		3.35 (9)	4.57	8.5	44
1	1	1		5.84(11)	7.97	7.7	53
1	1	0	NH_4^+	2.44 (9)	3.33	1.3	16
2	1	0		3.24(11)	4.42	2.8	24
1	1	1		5.77(11)	7.88	1.9	33
1	1	0	Ca^{2+}	4.06 (6)	5.54	2.7	28
2	1	0		5.37(10)	7.32	2.1	32
1	1	1		7.08 (9)	9.66	3.8	45

[a] The indexes refer to the reaction: $pM^z + q(Fe(CN)_6^{4-}) + rH^+ \rightleftarrows [M_p(Fe(CN)_6)_q H_r]^{(pz+r-4q)}$.

[b] ΔG^0 and ΔH^0 in kcal mol^{-1}; ΔS^0 in cal mol^{-1} deg^{-1}; 1 cal = 4.184 Joules.

[c] 3σ in parentheses.

[d] $3\sigma(\Delta G^0) = 1.4 \times 3\sigma(\log \beta)$.

[e] $3\sigma(\Delta H^0) \simeq 8 \times 3\sigma(\log \beta)$.

[f] $3\sigma(\Delta S^0) \simeq 27 \times 3\sigma(\log \beta)$.

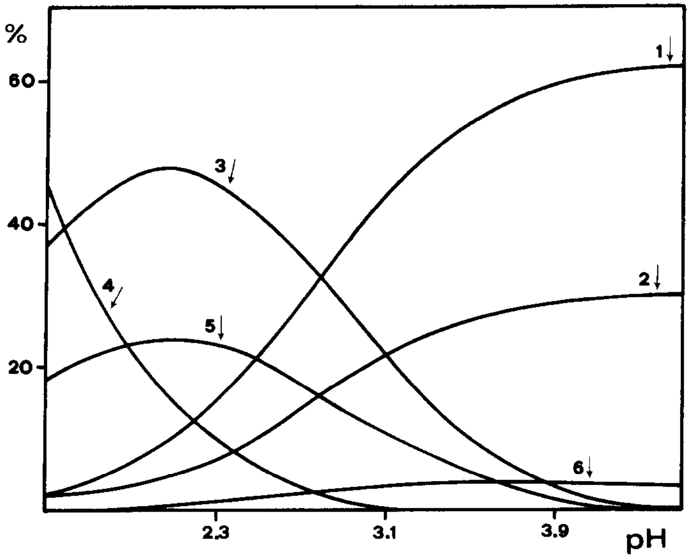

Fig. 1. Distribution of the species vs. pH, for the system K^+–$Fe(CN)_6^{4-}$, at $t = 25°C$. $C_{K^+} = 0.25$ mol l^{-1}; $C_L = 1$ mmol l^{-1}. The percentages are calculated with respect to the ligand. (1) $[K(Fe(CN)_6)]^{3-}$; (2) $[K_2(Fe(CN)_6)]^{2-}$; (3) $[K(Fe(CN)_6)H]^{2-}$; (4) $[(Fe(CN)_6)H_2]^{2-}$; (5) $[(Fe(CN)_6)H]^{3-}$; (6) free central ion.

are reported. In the calculations the dependence on ionic strength of the thermodynamic parameters was taken into account. We found that the variations of log β_{pqr} with I obey the simple model represented by eqn. (1), and that the values of empirical parameters can be expressed as:

$$\begin{aligned} C_{pqr} &= p^* c_0 + z^* c_1 \\ D_{pqr} &= z^* d \end{aligned} \qquad (2)$$

where $p^* = p + q + r - 1$ and c_0, c_1 and d are parameters valid for all reactions. The values of these parameters are:

$$\begin{aligned} & c_0 = 0.10 \\ & c_1 = 0.225 \quad \partial c_1/\partial T = -0.0021 \\ & d = -0.10 \quad \partial d/\partial T = 0.0018 \end{aligned} \qquad (3)$$

The formation percentages are highly significant for all the species reported in this work. In Fig. 1, as an example, the distribution diagram of the system K^+–$Fe(CN)_6^{4-}$ is reported.

DISCUSSION

In Tables 4 and 5 most of the representative literature data concerning the thermodynamic parameters for the protonation of hexacyanoferrate(II) and

TABLE 4

Literature thermodynamic data on $Fe(CN)_6^{4-}$ protonation together with some recommended values

t (°C)	I (mol l^{-1})	Medium	log β_{011} [a]	log β_{012}	Method	Ref.	Notes
25	0	–	4.25	–	quinhydrone electrode	1	–
25	0.01	KCl	3.85	6.00	(H^+) glass electrode	3	b
	0.02		3.74	5.26			
	0.1		3.17	4.39			
	0.5		2.72	–			
25	0	–	4.28	6.6	redox	40	–
25	0	–	$\Delta H^0_{011} = 0.5$ [c] $\Delta H^0_{012} = 1.5$ [c]		calorimetry	40	–
27	1	KCl	2.33	2.82	spectrophotometry	41	b
25	3	$LiClO_4$	4.72	7.46	(H^+) glass electrode	42	b
25	3		4.71	7.42	spectrophotometry	42	b
25	0	–	4.41	6.90	(H^+) glass electrode	2	–
25	1	KCl	2.37	2.93		2	b
25	0.1		3.07	4.72		2	b
25	0	–	4.33	6.8	–	1,2,40 [d]	e
25	0.1	(K^+)	3.07	–	–	3,40 [d]	b,e
25	1	(K^+)	2.37	–	–	40,41 [d]	b,e

[a] The indexes refer to the reaction: $pM^z + q(Fe(CN)_6^{4-}) + rH^+ \rightleftarrows [M_p(Fe(CN)_6)_qH_r]^{(pz+r-4q)}$.

[b] Values calculated without allowing for M^+ complexes.

[c] ΔH^0 in kcal mol^{-1}; 1 cal = 4.184 Joules.

[d] This work.

[e] Recommended values.

for the complexes of alkali metal ions and Ca^{2+} in aqueous solution are reported. With respect to the protonation constants, the agreement between the literature and our data is quite satisfactory and some recommended values are reported in Table 4. For the alkali metal formation constants, a fairly good agreement can be observed, in particular for 1 : 1 K^+ complexes; no comparisons can be made for protonated and polynuclear complexes. Reported values for $[Ca(Fe(CN)_6)]^{2-}$ formation constants are systematically lower than that found in this work. This fact can be attributed to some extent to the different treatment of the dependence of log β on ionic strength and to the different speciation of the system (several authors have neglected polynuclear species and no formation constants have been reported for protonated species). All the formation constants show the same dependence on ionic strength according to eqns. (1) and (2), and the values for the empirical parameters c_0, c_1 and d agree very well with those obtained in studies concerning other systems [8–16]. Furthermore, from the dependence of c_1 and d on temperature, the dependence on ionic strength of

TABLE 5

Literature thermodynamic data on alkali and alkaline earth metal $Fe(CN)_6^{4-}$ complexes

t (°C)	I (mol l^{-1})	Medium	M	log β_{110} [a]	Method	Ref.	Notes
25	0	–	K^+	2.3	conductimetry	43	–
24.65 39.3	0.1	Me_4NCl	K^+	1.50 1.61	K^+ selective electrode	44	Calculated without allowing for Me_4N^+ complexes; $\Delta H_{110} = 3.9$ [b]
25	0	–	K^+	2.37	spectrophotometry	39	–
	0.2	KCl		1.82			
25	0	–	Li^+ Na^+ K^+ Rb^+ Cs^+	1.78 2.18 (2.30) 2.50 2.86	electrical migration	45	The constants of alkali metal complexes are calculated by assuming log $\beta_{110}(K^+) = 2.30$ log $\beta_{110} = 4.1 - 2.8/r + 0.88/r^2$ (MD = 0.09)
25	dil	–	Li^+	1.95	redox	1,46	log $\beta_{110} = 4.04 - 2.94/r + 1.02/r^2$ (MD = 0.05)
			Na^+ K^+ Rb^+ Cs^+	2.13 2.28 2.51 2.72			
25	dil	–	K^+ Me_4N^+	2.2 1.95	conductimetry	47	
25	0	–	K^+	2.39 log $\beta_{210} = 3.20$	K^+ selective electrode	2	A very weak trinuclear complex species was found in ref. 2
	0.1	KCl	K^+	1.68 log $\beta_{210} = 1.96$			
9.9 15 25 40	0.009	–	K^+	1.95 1.97 2.00 2.01	K^+ selective electrode	40	$\Delta H^0_{110}(20°C) = 1.3$ (from temperature dependence of log β_{110}) $\Delta H^0_{110} = 1.0$ (from calorimetric measurements)

45				2.01			
25	0		K^+	2.4 ± 0.1		2,39, 43 and this work	recommended value
25	0	–	Ca^{2+}	3.77 $\log \beta_{210} = 6.20$	conductimetry	5	–
25	0		Ca^{2+}	3.59	electrical migration	46	–
15			Ca^{2+}	3.57	Ca^{2+} selective electrode	48	$\Delta H^0_{110} = 2.0$ (from temperature dependence); $\Delta H^0_{110} = 2.1$ (from calorimetric measurements)
20				3.60			
25				3.63			
30				3.65			
35				3.67			
25	0.03	–	Ca^{2+}	$\Delta H^0_{110} = 2.82$	calorimetry	49	
	0.08			3.11			
25	3	$LiClO_4$	Mg^{2+}	3.40 $\log \beta_{210} = 4.50$	redox	6	
			Ca^{2+}	2.10 2.36			
			Sr^{2+}	1.18 –			
			Ba^{2+}	1.60 1.17			
25	0	–	Mg^{2+}	3.77	M^{2+} selective electrode	50	$\log \beta_{110} = 4.71 - 1.89/r + 0.83/r^2$
			Ca^{2+}	3.67			
			Sr^{2+}	3.66			
			Ba^{2+}	3.78			
15			Ca^{2+}	3.64	Ca^{2+} selective electrode	50	$\Delta H^0_{110} = 3.1$ (from temperature dependence of $\log \beta_{110}$)
35				3.79			

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[a] The indexes refer to the reaction: $pM^z + q(Fe(CN)_6^{4-}) + rH^+ \rightleftarrows [M_p(Fe(CN)_6)_qH_r]^{(pz+r-4q)}$.

[b] ΔH^0 in kcal mol^{-1}; 1 cal = 4.184 Joules.

ΔH can be obtained:

$$\Delta H(I) = \Delta H(0) + z^* RT^2 \ln 10 \left\{ I \frac{\partial c_1}{\partial T} + I^{3/2} \frac{\partial d}{\partial T} \right\} \tag{4}$$

or, at 25°C:

$$\Delta H(I) = \Delta H(0) + 0.407 z^* \{ -2.1 I + 1.8 I^{3/2} \} \mathrm{kcal\ mol^{-1}} \tag{5}$$

in agreement with previous findings [11,14,16,34].

The values of ΔH^0 reported in Table 3 were obtained from the dependence of formation constants on temperature. Values based on only three temperatures are obviously to be considered with care. Nevertheless the agreement with some literature findings (also obtained from direct calorimetric experiments) is acceptable if allowance is made for the large uncertainties. The ΔH values concerning the complexes $[M(Fe(CN)_6)]$ are about the same for Na^+, K^+ and NH_4^+ (slightly endothermic), whilst a significantly more endothermic value is observed for Li^+; for all complexes the stabilization is mainly entropic; this accounts for the ionic character of these complexes.

Some interesting linear relationships were found for $\log \beta$ of the complexes studied here. The stability of polynuclear complexes $[M_2(Fe(CN)_6)]$ for alkali metal and Ca^{2+} ions shows a linear dependence on the stability of $[M(Fe(CN)_6)]$ complexes according to the equation ($I = 0$, $t = 25$°C):

$$\log \beta_{210} = 0.18 + 1.27 \log \beta_{110} \ (\mathrm{MD} = 0.05) \tag{6}$$

where MD = mean deviation. This dependence indicates that stronger 1 : 1 complexes form weaker complexes with a second metal ion. The dependence of $\log \beta$ (for alkali metal ions) on $1/r$ (r = crystal radii) is fairly linear according to the equations ($I = 0$, $t = 25$°C).

$$\log \beta_{110} = 2.85 - 0.47/r \ (\mathrm{MD} = 0.01) \tag{7}$$

$$\log \beta_{111} = 6.07 - 0.28/r \ (\mathrm{MD} = 0.02) \tag{8}$$

$$\log \beta_{210} = 3.66 - 0.47/r \ (\mathrm{MD} = 0.04) \tag{9}$$

(In some cases it is better to use a quadratic equation of the type $\log \beta = a_0 + a_1/r + a_2/r^2$ but for the data reported in this work a simple linear equation is sufficient.) Equations (6)–(9) can be very useful in estimating formation constants in incomplete series of alkali metal (eqn. (6) also for alkaline earth metal) complexes.

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