Simulation of ion association in hexacyanoferrate solutions

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Experimental
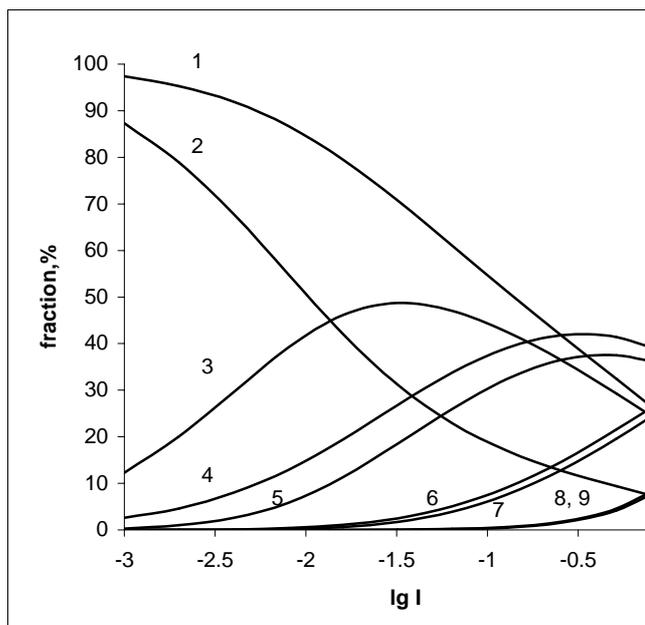

Fig. 1. Plots of calculated fractions of hexacyanoferrate ionic forms in solution *versus* logarithm of solution ionic strength. 1 - $[Fe(CN)_6]^{3-}$, 2 - $[Fe(CN)_6]^{4-}$, 3 - $K^+,[Fe(CN)_6]^{4-}$, 4 - $K^+,[Fe(CN)_6]^{3-}$, 5 - $2K^+,[Fe(CN)_6]^{4-}$, 6 - $2K^+,[Fe(CN)_6]^{3-}$, 7 - $3K^+,[Fe(CN)_6]^{4-}$, 8 - $3K^+,[Fe(CN)_6]^{3-}$, 9 - $4K^+,[Fe(CN)_6]^{4-}$
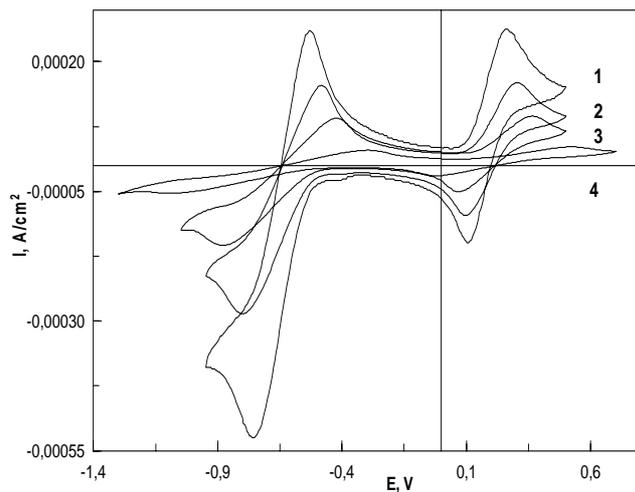
Fig. 2. Cyclic voltammograms of 0.1 mol dm^{-3} solutions of Dq$_2$[Fe(CN)$_6$]. 1-4 solution, containing 0, 400, 600 and 800 g sucrose per 1dm^3 of water. $V = 25$ mV/s.
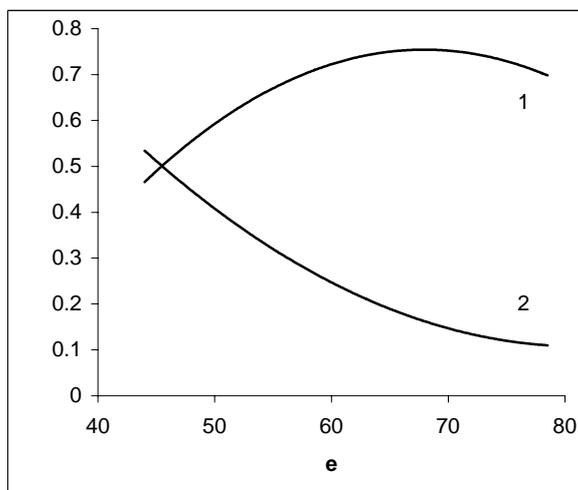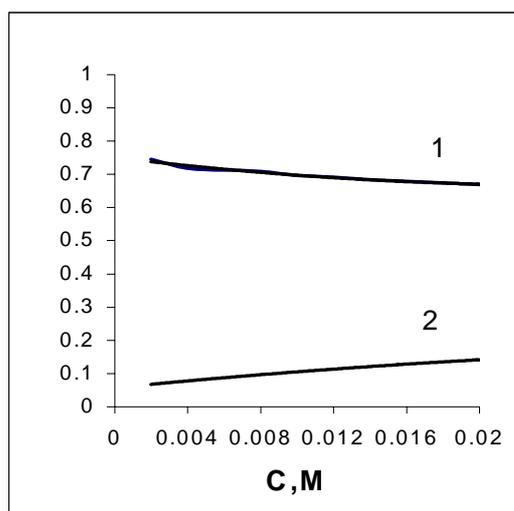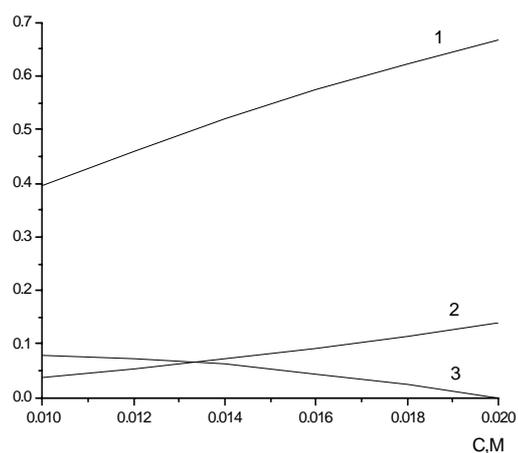

Fig. 3. Plots of calculated fractions of hexacyanoferrate ionic forms in solution *versus* solution dielectric constant. Dq^{2+},[Fe(CN)$_6$]$^{4-}$ (1), 2Dq^{2+},[Fe(CN)$_6$]$^{4-}$ (2). C(Dq$_2$[Fe(CN)$_6$]) = 0.01 mol dm^{-3}.

a   b

Fig. 4. a) Calculated fractions of hexacyanoferrate ionic forms Dq^{2+},$[Fe(CN)_6]^{4-}$ (1) and $2Dq^{2+}$,$[Fe(CN)_6]^{4-}$ (2) in aqueous solutions of $Dq_2[Fe(CN)_6]$ *versus* solution concentration.

b) Calculated fractions of hexacyanoferrate ionic forms Dq^{2+},$[Fe(CN)_6]^{4-}$ (1), $2Dq^{2+}$,$[Fe(CN)_6]^{4-}$ (2) and Dq^{2+},K^+,$[Fe(CN)_6]^{4-}$ (3) in aqueous solutions of $Dq_2[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ *versus* $Dq_2[Fe(CN)_6]$ concentration; the total hexacyanoferrate concentration is 0.02 mol dm^{-3}.

Table 1. Computed redox potentials of the $[Fe(CN)_6]^{3-/4-}$ pair and contributions from the ratios of concentrations of free ions and the ratio of their activity factors to changes in the potential of the $[Fe(CN)_6]^{3-/4-}$ pair.

I, M	E, mV	$\Delta E\,(C)$, mV	$\Delta E\,(f)$, mV
0.001	364	2.8	6.3
0.002	369	4.8	8.8
0.004	375	7.8	12.1
0.008	383	11.7	16.6
0.016	394	16.3	22.3
0.032	406	21.0	29.6
0.064	419	25.1	38.6
0.128	432	28.3	48.9
0.256	446	30.4	60.5
0.512	459	31.8	72.6
1.024	473	33.2	84.5