

Simulation of ion association in hexacyanoferrate solutions

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The spectral manifestations of ion association in hexacyanoferrate solutions can be described based on calculations of various ionic forms by the Fuoss equation.

The concentration dependence of absorption at the maxima of outer-sphere charge transfer (OSCT) bands is widely used to assess the stability constants and extinction coefficients of ion pairs. In such cases, the solution ionic strength (I) is maintained by supporting electrolytes (KCl, KNO₃ etc.). Since the inactivity of these electrolytes is quite arbitrary (the ions they contain are themselves involved in ion–ion interactions), the observed stability constants and extinction coefficients strongly depend on experimental conditions. For example, the extinction coefficients obtained for the MV²⁺, [Fe(CN)₆]^{4–} ion pair (where MV²⁺ is methyl viologen or the *N,N'*-dimethyl-4,4'-bipyridine cation) differ considerably (73,¹ 150–200,² 47³ and 690⁴ dm³ mol^{–1} cm^{–1}). We suggest an approach to describe the spectral manifestation of ion association in hexacyanoferrate solutions without mandatory addition of supporting electrolytes.

First, the interionic distance in ion associates is estimated from structural or spectral data. Further, the stability constants of ion pairs and more complex ion associates are computed using the Fuoss equation.⁵ After that, the concentrations of all ionic forms are computed. Finally, the optical densities at absorption maxima are found using extinction coefficients evaluated independently. In this case, the stability constants and concentrations of ionic forms are computed in iterations *via* intermediate computation of I based on estimated concentrations for ions and ion pairs present in the system. The applicability of this method was demonstrated by a comparison of experimental and computed values for the Dq²⁺, [Fe(CN)₆]^{4–} system (where Dq²⁺ is diquat or the *N,N'*-ethylene-2,2'-bipyridine cation). Dq₂[Fe(CN)₆].6H₂O contains only two different ions; it was characterised by cyclic voltammetry, X-ray diffraction⁶ and electronic absorption spectroscopy.⁷

To answer the question of whether it is correct to use estimates of concentrations of various ionic forms using the Fuoss equation⁵ for interactions of non-spherical ions, we computed the dependence of redox potential (E) on I for the [Fe(CN)₆]^{3–/4–} pair and compared it with experimental data.^{8,9} The calculations were carried out by the Nernst equation:

$$E = E^0 + RT/nF \ln \{ a([\text{Fe}(\text{CN})_6]^{3-}) / a([\text{Fe}(\text{CN})_6]^{4-}) \},$$

taking $E^0 = 0.355$ V for the [Fe(CN)₆]^{3–/4–} pair.⁸ The activities a of free hexacyanoferrate ions were calculated as products of concentrations of these ions by activity factors f . The activity factors for hexacyanoferrate ions were calculated using the classical equation $\log f = -0.509 z^2 I^{1/2} / (1 + I^{1/2})$. When calculating the concentrations of ions and ion associates, it was assumed

that I is created by a totally dissociated potassium salt with a one-charged anion. The Fe–K distances in K⁺, [Fe(CN)₆]^{4–} and K⁺, [Fe(CN)₆]^{3–} ion pairs were taken equal to 4.07 Å based on the crystallographic interatomic distance in crystalline ethyl viologen–potassium hexacyanoferrate.¹⁰ The resulting logarithms of thermodynamic stability constants for K⁺, [Fe(CN)₆]^{4–} and K⁺, [Fe(CN)₆]^{3–} ion pairs calculated by the Fuoss equation were found to be 2.28 and 1.51, respectively. The experimental values¹¹ are 2.35 and 1.46, respectively. For associates that are more complex than ion pairs (for example, for describing the interaction between an ion pair and a potassium ion), it was assumed that the Fe–K distances were constant and the Fuoss equation was acceptable for calculating the concentrations of all ionic forms. The results of calculating the distribution of ionic forms and the calculated potentials of the [Fe(CN)₆]^{3–/4–} pair can be found in Online Supplementary Materials. The dependence of the redox potential on the solution ionic strength obtained for the [Fe(CN)₆]^{3–/4–} pair is presented in Figure 1; it agrees well with experimental data.

For ion pairs similar to Dq²⁺, [Fe(CN)₆]^{4–}, it is impossible to estimate unambiguously the distance between ions from structural data due to the low symmetry of the cation. Therefore, it was evaluated by analysing spectral data based on the positions of OSCT bands. By a comparison of these values with electrochemical data, we estimated the solvent reorganization energies (χ_0):

$$E_{lv} = \Delta E + \chi, \quad \chi = \chi_i + F_{\chi} + \chi_0$$

and found distances between ions from these values. We used sucrose as the cosolvent, which allowed us to work with

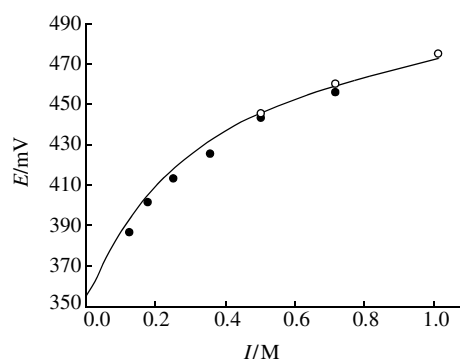


Figure 1 Dependence of the formal redox potential of the [Fe(CN)₆]^{3–/4–} pair on the solution ionic strength. The solid line shows the calculated results. Solid and hollow dots correspond to experimental data from refs. 8 and 9, respectively.

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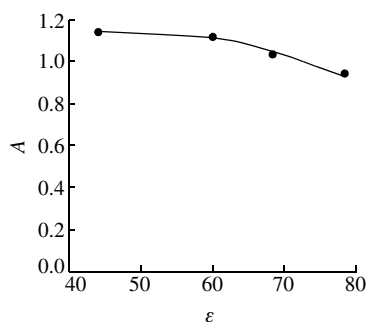


Figure 2 Dependence of the optical density at the maxima of OSCT bands on the solution dielectric constant. The dielectric constant was varied by additions of sucrose. The solid line shows the calculated results. The dots represent experimental data. $C(\text{Dq}_2[\text{Fe}(\text{CN})_6]) = 0.01 \text{ mol dm}^{-3}$.

supersaturated solutions of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$. The frequencies at the maxima of OSCT[‡] bands for 0.01 mol dm^{−3} solutions of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$ in water, in 1 mol dm^{−3} KCl, and in sucrose solutions (400, 600 and 800 g dm^{−3}) are 17300, 17800, 17030, 16900 and 16780 cm^{−1}, respectively. The corresponding energies of electron transitions (E_{hv}) are 2.145, 2.207, 2.111, 2.095 and 2.080 eV. According to cyclic voltammetry data,[§] the differences in the half-wave potentials of quasi-reversible redox processes (ΔE) for diquat and hexacyanoferrate ions in these solutions are 0.826, 0.862, 0.844, 0.872 and 0.943 V. This allowed us to find the energies of reorganization (χ) due to electron transition (1.318, 1.345, 1.267, 1.223 and 1.137 eV); in turn, these energies consist of the inner spheric constituent (χ_i), the ionic atmosphere reorganization energy (F_χ) and the solvent reorganization energy (χ_0). The estimated value of χ_i is 0.06 eV.¹² The value of F_χ was calculated according to ref. 13. It equals 0.004–0.005 eV for aqueous and aqueous-sucrose solutions and 0.026 eV for a solution of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$ in 1 mol dm^{−3} KCl. The values of χ_0 obtained for the test systems, viz., 1.255, 1.259, 1.202, 1.158 and 1.072 eV, depend on the Pekar factor, which characterises solvent properties,¹⁴ formal ion radii (r_1 and r_2) and inter-ionic distance (d).¹⁵ Considering the similarity of Dq^{2+} and $[\text{Fe}(\text{CN})_6]^{4-}$ ions⁶ and using the transformation ($1/2r_1 + 1/2r_2 - 1/d \approx 1/d$), the formal inter-ionic distance in

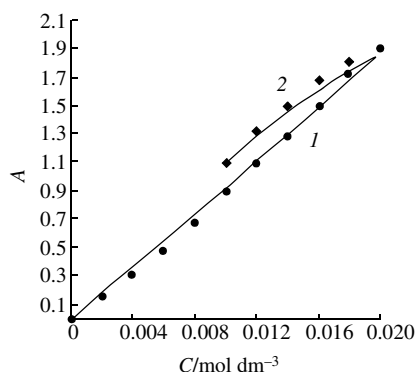


Figure 3 Dependence of the optical density at the maximum of the OSCT band on the concentration of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$. The solid lines show the calculated results. The dots and squares represent experimental data. (1) aqueous solutions of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$. (2) aqueous solutions of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ at 0.02 mol dm^{−3} total concentration of hexacyanoferrate ions.

[‡] Electronic absorption spectra in the range 400–700 nm were recorded with a Specord 50PC spectrophotometer in quartz cells 1 cm thick.

[§] Cyclic voltammograms were recorded using an EG&G PARC 273A potentiostat–galvanostat controlled by a PC. The measurements were carried out in a three-electrode glass cell using a saturated calomel electrode (SCE) as the reference connected with a cell via a Luggin capillary with a saturated KCl salt bridge and a Pt plate as the auxiliary electrode. A gold wire was used as the working electrode.

the $\text{Dq}^{2+}, [\text{Fe}(\text{CN})_6]^{4-}$ ion pair was evaluated as 6.21, 6.34, 6.03, 6.01 and 6.16 Å. The value of 6.2 Å was used for subsequent calculations.

The extinction coefficient was estimated under conditions of complete ion association (in solutions containing 800 g of sucrose per 1 dm³). It was assumed that the ion pair and the $2\text{Dq}^{2+}, [\text{Fe}(\text{CN})_6]^{4-}$ ion triplet have the same extinction coefficients. The value of $115 \pm 1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ was found for 0.008–0.012 mol dm^{−3} solutions of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$; it was used for subsequent calculations. Note that the value obtained is slightly smaller than that found using the Beneshi-Hildebrand method, i.e., $130 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.⁷

The iteration method with the Fuoss equation was used to calculate the concentrations of ionic forms in solution and the optical densities at the maxima of OSCT bands. The results of calculating the fractional distribution of ionic forms can be found in the Online Supplementary Materials. The calculated dependences of optical density on the concentration of $\text{Dq}_2[\text{Fe}(\text{CN})_6]$ and the corresponding experimental data demonstrated in Figures 2 and 3 are in good agreement. Thus, the suggested algorithm using the Fuoss equation makes it possible to describe complex ion association processes in solutions in the following cases:

- (1) The formation of ion associates is accompanied by the appearance of OSCT bands in electronic absorption spectra.
- (2) The peaks of quasi-reversible one-electron processes of ions involved in the associate do not overlap in the voltammograms.
- (3) The associates consist of multicharged ions comparable in size.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2007.03.016.

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