Determination of extinction coefficients of ion pairs formed by multicharged ions

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The reasons for discrepancies between reported values of extinction coefficients of ion pairs formed by multicharged ions are analysed and approaches to a correct description of such systems are suggested.

The concentration dependences of absorption at the maxima of bands corresponding to outer-sphere charge transfer are widely used to assess the stability constants (K_{IP}) and molar absorption coefficient (ε) of light-absorbing ion pairs. The Benesi–Hildebrand equation[1]

$$C_0 l/A = (1 + K_{IP}C)/(K_{IP}C\varepsilon) \text{ or } C_0 l/A = \frac{1}{K_{IP}\varepsilon}\frac{1}{C} + \frac{1}{\varepsilon}, \qquad (1)$$

where C_0 is the constant concentration of the deficient reagent; C is the variable concentration of the reagent which is present in excess (the condition $C_0 \ll C$ is used to derive the equation), l is the optical path length and A is the absorption at the band maximum, allows one to obtain reliable results in studies of systems where there are practically no other interactions. To avoid calculations of activity factors, experiments are carried out at a constant solution ionic strength. This allows concentration stability constants to be determined. The ionic strength (I) of the solution is maintained by supporting electrolytes (KCl, KNO_3, *etc.*). The inactivity of such electrolytes is quite tentative since their constituent ions are involved in competitive ion–ion interactions. Let us designate the stability constant of an ion pair that does not absorb light and is composed of ion of the supporting electrolyte and of the ion of the deficient reagent as K'_{IP}. Taking into account the competitive process, the modified Benesi–Hildebrand equation takes the form

$$C_0 l/A = (1 + K_{IP}C + K'_{IP}C')/(K_{IP}C\varepsilon), \qquad (2)$$

where C' is the concentration of the supporting electrolyte ions.

The concentrations C and C' at constant I calculated by the classical equation

$$I = 0.5\sum c_i z_i^2 \qquad (3)$$

are related by an expression that depends on the charges of the supporting electrolytes and reagent ions. In a study of the reaction of a double-charged methyl viologen cation (*N*,*N*′-dimethyl-4,4′-bipyridine, MV^{2+}) and four-charged hexacyanoferrate anion

$$MV^{2+} + [Fe(CN)_6]^{4-} = MV^{2+}, [Fe(CN)_6]^{4-} \qquad (4)$$
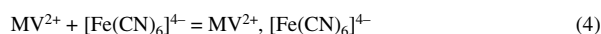
with an alkali metal chloride as the supporting electrolyte

$$MV^{2+} + Cl^- = MV^{2+}, Cl^- \qquad (5)$$

we can write

$$0.5[(-4)^2\times 1 + 1^2\times 4]C + 0.5[(-1)^2\times 1+1^2\times 1]C' = 10C + C' = I.$$

The first term of this equation is connected with alkali metal hexacyanoferrate concentration. The second one is the contribu-

tion from alkali metal chloride. The viologen concentration is very low, and it can be neglected. Then,

$$C_0 l/A = (1 + K'_{IP}I)/(K_{IP}\varepsilon C) + (1 - 10K'_{IP}/K_{IP})/\varepsilon. \qquad (6)$$

Analysis of equation (2) shows that the dependence of the optical density in the maximum of the absorption band on the concentration of the reagent, which is present in excess, is described by a straight line in inverse coordinates. The same is true for equation (1). However, the free term in the linear equation that allows one to determine ε depends on the K'_{IP}/K_{IP} ratio. Since K'_{IP} and, especially, K_{IP} depend on I, it is believed that changes in I will affect K_{IP} and ε calculated by equation (1). It is known that published ε values[2–5] for the MV^{2+},$[Fe(CN)_6]^{4-}$ ion pair vary from 47 to 690 $dm^3 mol^{-1} cm^{-1}$. Is it possible that neglecting the relatively weak interaction of the MV^{2+} cation with anions of the supporting electrolyte leads to such a dramatic result? To answer this question, we used the Fuoss equation[6] to calculate the stability constants for the MV^{2+},$[Fe(CN)_6]^{4-}$ and MV^{2+},Cl^- ion pairs (for simplicity, both interionic distances in the ion pairs were assumed to be 6.2 Å) and found the corresponding values of $1 - 10K'_{IP}/K_{IP}$. As follows from the computations (Figure 1), the values of ε determined by equation (1) considerably depend on I and can become negative for certain values. Replacement of the classical equation for I computation by the empirical equation[7]

$$I = 0.5\sum c_i |z_i| \qquad (7)$$

$$C_0 l/A = (1 + K'_{IP}I)/(K_{IP}\varepsilon C) + (1 - 4K'_{IP}/K_{IP})/\varepsilon. \qquad (8)$$

provides more reasonable results (Figure 1). However, reliable values of ε^{-1} can only be found by extrapolation of these values to $I = 0$.
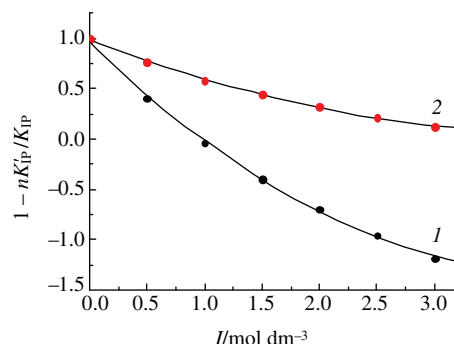
Figure 1 Plot of calculated parameter $1 - nK'_{IP}/K_{IP}$ *vs.* the solution ion strength. (*1*) $n = 10$ [according to equation (3)], (*2*) $n = 4$ (according to equation (7)].

Let us check our conclusions by studying the spectral properties of solutions of ethyl viologen hexacyanoferrate (EV^{2+}), ethyl viologen being the closest analogue of methyl viologen. The organic cation was replaced because it made possible to isolate crystalline ethyl viologen–potassium hexacyanoferrate[8] and determine the ε value of the ionic pair EV^{2+},$[Fe(CN)_6]^{4-}$ independently under conditions of nearly complete ion association (800 g dm^{-3} sucrose solution).[9] A study† of aqueous solutions of ethyl viologen–potassium hexacyanoferrate containing 0–800 g dm^{-3} sucrose gave $\varepsilon = 89\pm1$ dm^3 mol^{-1} cm^{-1} ($\varepsilon^{-1} = 0.011$ dm^{-3} mol cm).

The investigation of the EV^{2+}–$[Fe(CN)_6]^{4-}$ system using the Benesi–Hildebrand method was carried out with the starting experimental conditions described below. The ethyl viologen iodide concentration was 0.01 mol dm^{-3}. The concentration of potassium hexacyanoferrate (C) during the experiment was 10–20 times higher than that of EVI$_2$ (C_0). The I value was kept constant by adding KCl. In the subsequent experiments, the concentration of EVI$_2$ was decreased while the other conditions were kept unchanged. In this case, the I value changed in proportion to the ethyl viologen concentration. Figure 2 shows the plot of ε^{-1} *vs.* I for the EV^{2+},$[Fe(CN)_6]^{4-}$ ion pair obtained by the Benesi–Hildebrand method. Note that the behaviour of the experimental curves is similar to that shown in Figure 1. It is only for dilute solutions that the calculated ε^{-1} values are close to each other and to 0.011 dm^{-3} mol cm obtained previously under conditions of almost complete ion association.

Thus, the discrepancy between published data for the molar absorption coefficients of ion pairs formed by multicharged ions results from neglecting the interaction of these ions and ions from supporting electrolytes. Using empirical equation (7) for I calculations and extrapolation of results to $I = 0$ resulted in decreasing the error of ε calculations.

† Electronic absorption spectra were recorded in the range of 400–700 nm with a Specord 50PC spectrophotometer using 1 cm quartz cells.
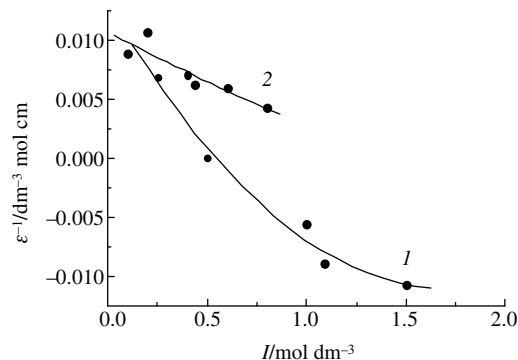
Figure 2 Plot of inverse extinction coefficient for the EV^{2+},$[Fe(CN)_6]^{4-}$ ion pair obtained by the Benesi–Hildebrand method *vs.* the solution ion strength. (1) I values calculated using equation (3), (2) I values calculated using equation (7).

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