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Mendeleev Commun., 2016, **26**, 154–156
Mendeleev Communications

Unusual stability of anionic associates in mixed solvents

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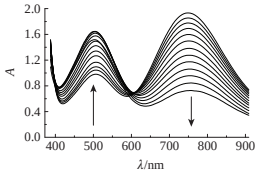
DOI: 10.1016/j.mencom.2016.03.025

The ion associates $[Fe(CN)_6]^{4-}$, M^+, $[Cu\ edta]^{2-}$, which are observed in the UV-VIS spectra of $K_4[Fe(CN)_6] + Na_2[Cu\ edta]$ solutions as an absorption band at 500 nm, contain alkali metal cations, and they are more stable in water-organic solutions than in aqueous solutions.



Complex ions, like other charged particles, are sensitive to their environment, and they can interact with other ionic forms in solution.[1] A reason for this interaction is the formation of an ionic environment, which is described by the Debye–Hückel theory for dilute solutions. The Brønsted–Bjerrum–Christiansen equation was suggested to describe the dependence of the rate of reaction between ions in solutions with various ionic strengths. For a bimolecular reaction, it is as follows.

$$\ln k = \ln k_0 + (2Az_1z_2\sqrt{\mu})/(1 + B\sqrt{\mu}), \quad (1)$$

where k is the reaction rate constant; k_0 is the reaction rate constant in infinitely dilute solution; z_1 and z_2 are the charges of the two reacting ions; μ is the ionic strength of the solution; A and B are values dependent on the dielectric constant of the medium (D) and the absolute temperature (T), that shows that ions interact through the formation of an intermediate complex (ion pair). For dilute solutions, the constant of ion pair formation (K^0_{ip}) is described by the Fuoss equation[2]

$$K^0_{ip} = (4\pi Nd^3/3000)\exp[(-z_1z_2e^2/(DkTd)], \quad (2)$$

where N is the Avogadro constant, e is the electron charge, k is the Boltzmann constant, and d is the contact distance between the ions.

The possibility of ion pair formation from similarly charged ions was shown by Hemmes.[3] Using equation (2), he showed that contact interaction between two similarly charged particles can occur in solutions. Ideal conditions for the formation of an outer-sphere complex consisting of similarly charged ions include small charges and large radii of ions and high ionic strength of the solution. According to equation (2), a decrease in solvent polarity should reduce the rate of reactions between two anions in dilute solutions, which was observed experimentally.[4]

Subsequently, outer-sphere complexes containing two anions were detected in aqueous solutions with $\mu > 1$ mol dm^{-3} based on the fact that outer-sphere charge transfer bands appeared in the electronic absorption spectrum.[5,6] Furthermore, anion–anion interaction was observed not only for ions that had small charges but also for multicharged anions,[7] *e.g.*, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. Expression (1) satisfactorily describes the interaction of ions in dilute solutions, however, it is no longer valid above a certain concentration. Cationic catalysis was observed in reactions between anions in concentrated solutions (a linear plot of reaction rate *versus* the concentration of inert electrolyte added and a difference between the reaction rates for two anions depending on the cation nature).[8] An explanation of this fact was suggested[9] on the basis of the assumption that, in concentrated solutions, the anionic associate containing two multicharged anions also contains two cations. However, if this is the case, the solvent polarity should be decreased rather than increased in order to stabilize such outer-sphere complexes, in contrast to ion pairs consisting of two anions. This work was aimed at a study of whether it is possible to stabilize anionic associates in water–organic solutions. Interaction of multi-charged anions $[Cu\ edta]^{2-}$ and $[Fe(CN)_6]^{4-}$ was tested.

A potassium hexacyanoferrate solution is pale yellow, whereas a sodium ethylenediaminetetraacetatocuprate solution is blue. Upon mixing aqueous $K_4[Fe(CN)_6]$ and $Na_2[Cu\ edta]$ solutions, the solution turns reddish brown. The appearance of an additional absorption band at 500 nm in electronic absorption spectra[†] (Figure 1) is due to the formation of outer-sphere complexes containing both types of anions in the solution. The composition of the resulting 1:1 complex was determined by Job's method in aqueous solution (μ = 0.8 mol dm^{-3}, KBr):

$$[Fe(CN)_6]^{4-} + [Cu\ edta]^{2-} + nM^+ = [Fe(CN)_6]^{4-}, nM^+, [Cu\ edta]^{2-}.$$

In the electronic absorption spectrum of an aqueous solution containing 0.02 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.02 mol dm^{-3} $Na_2[Cu\ edta]$, the intensity ratio of bands at 500 and 740 nm is about 1:2. The dilution of solution with water quickly decreases absorption at 500 nm and the solution acquires the blue color of the $[Cu\ edta]^{2-}$ complex ion [Figure 1(*a*)]. On dilution of the starting solution with acetone, the absorption band intensity at 740 nm also linearly decreased with diminishing the concentration of $[Cu\ edta]^{2-}$ ions in accordance with the Bouguer–Lambert–

[†] Electronic absorption spectra were recorded using a Specord 50PC spectrophotometer with 1 cm thick cells in a range of 350–900 nm immediately after mixing the solutions. The characteristics of the absorption bands were obtained from the absorption spectra by treatment using the MATLAB software package. Each spectrum was approximated by three or four Gaussian shaped absorption bands.

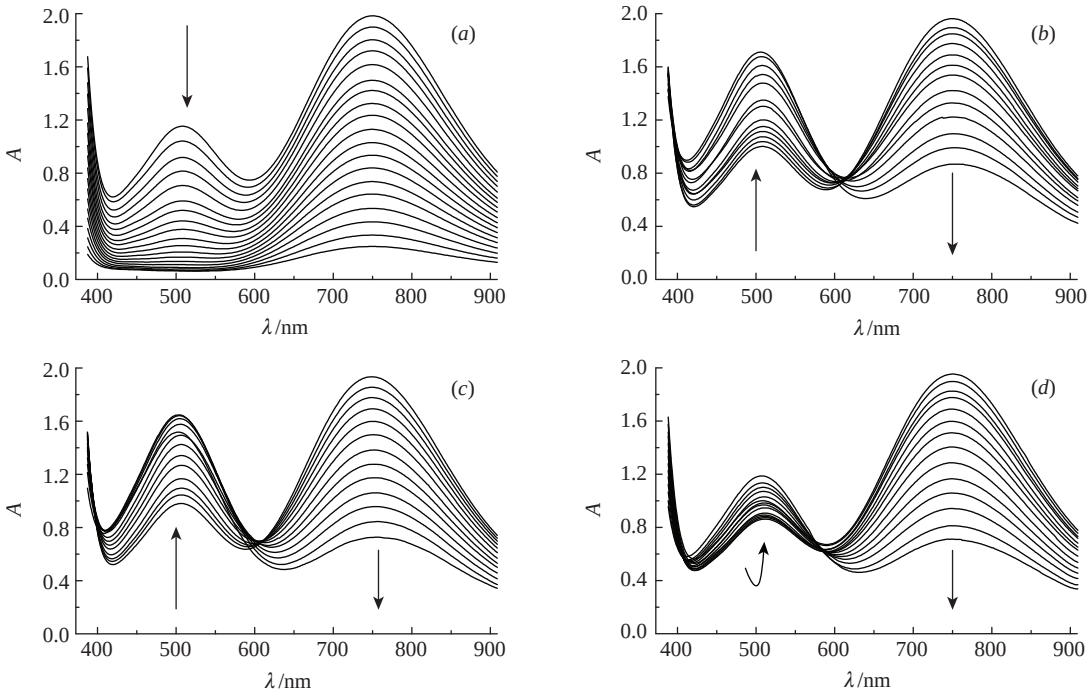


Figure 1 Electronic absorption spectra of the solution containing 0.02 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.02 mol dm^{-3} Na_2[Cu edta] in water (upper curve) and solutions obtained by its dilution with (*a*) water, (*b*) acetone, (*c*) isopropanol or (*d*) acetonitrile. Dilution step 5%.

Beer law. However, this is accompanied by an increase in the absorption band intensity at 500 nm [Figure 1(*b*)]. In the solution containing 60 vol% acetone, the intensity ratio of the bands at 500 and 740 nm is 2:1, and the solution changes its colour to bright red. The subsequent dilution of the solution with acetone resulted in opacification due to the liberation of complex compounds. The position of the [Cu edta]$^{2-}$ anion absorption band at 740 nm does not change with associate formation. This fact means that the chromophore group CuN_2O_4 does not change and the outer-sphere complex is formed (this group should transform into CuN_3O_3 if a binuclear complex is formed in this system). The Bouguer–Lambert–Beer law suggests the formation of an outer-sphere complex. The position of the absorption band of the ion associate does not change upon acetone addition, indicating that there is almost no resolvation of the anionic associate in the course of charge transfer. The increase in absorption in the system upon the addition of an organic solvent allows us to refrain from considering an excluded volume hypothesis[10] in the description of ion association in mixed solvents.

We observed a similar behavior of the system upon the dilution of an aqueous solution containing 0.02 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.02 mol dm^{-3} Na_2[Cu edta] with isopropanol [Figure 1(*c*)]. An increase in the absorption band intensity corresponding to an outer-sphere complex was also detected in the electronic absorption spectrum upon dilution. Opacification that did not disappear on stirring also occurred at 65 vol% of the organic solvent.

The dilution of the above aqueous solution with acetonitrile [Figure 1(*d*)] initially resulted in a small decrease in the absorption of the associate (up to 20 vol% acetonitrile) and then in a growth of the peak corresponding to the absorption of the outer-sphere complex. In the solution containing 65 vol% acetonitrile, the intensity ratio of the bands at 500 and 740 nm approaches 2:1. In the solution containing 70 vol% acetonitrile, separation into two liquid phases occurs. The water–acetonitrile system was chosen for further quantitative studies of the $[Fe(CN)_6]^{4-}$, nM^+, [Cu edta]$^{2-}$ ion associates because of the unusual behavior of this system.

In order to determine the stability constants of anionic associates and the extinction coefficients at charge-transfer band maxima, water–acetonitrile solutions containing 0.01 mol dm^{-3} $K_4[Fe(CN)_6]$, 0.01 mol dm^{-3} Na_2[Cu edta] and 0.74 mol dm^{-3} KBr (μ = 0.8 mol dm^{-3}) were prepared. They were diluted using water–acetonitrile solutions containing 0.8 mol dm^{-3} KBr. Processing of the concentration dependences of optical density at the maximum of the absorption band of the ion associate in order to determine the stability constants of the ion associate at the selected solution ionic strength (K_{ia}) and the extinction coefficient (ε_{max}) was carried out according to a published procedure.[11] The plots of the calculated stability constants and extinction coefficients of ion associates $[Fe(CN)_6]^{4-}$, nM^+, [Cu edta]$^{2-}$ in water–acetonitrile solutions *versus* the volume fraction of acetonitrile are presented in Figure 2.

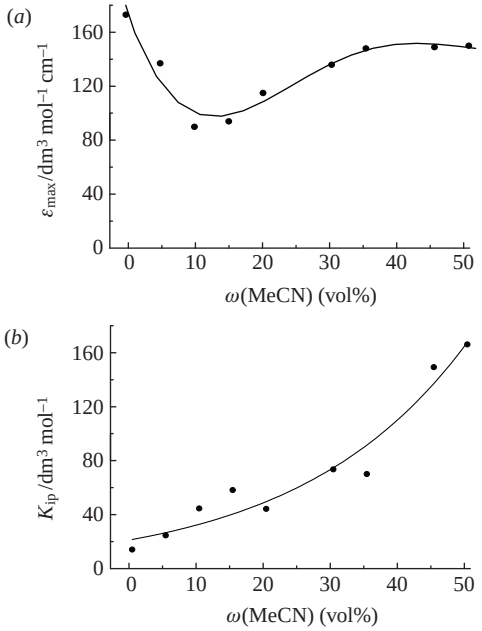


Figure 2 Plots of (*a*) the extinction coefficient of the anionic associate and (*b*) its stability constant *versus* the volume fraction of acetonitrile in solution. The starting solutions contained 0.01 mol dm^{-3} $K_4[Fe(CN)_6]$ and 0.01 mol dm^{-3} Na_2[Cu edta]. μ = 0.8 mol dm^{-3}, KBr.

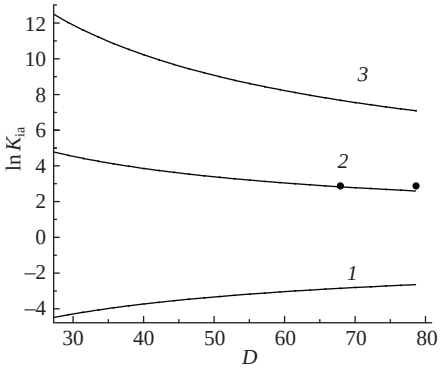


Figure 3 Plots of stability constant logarithms *versus* dielectric constant of the medium calculated within the models: (*1*) an ion pair consisting of two anions (by the Fuoss equation), (*2*) an ion associate including also one cation, and (*3*) an ion associate including also two cations. The points show experimental values at D = 78.5 and 69 (see the text). μ = 0.8 mol dm^{-3}.

In water–acetonitrile solutions, the plot of extinction coefficient *versus* organic solvent concentration is non-linear and has a minimum at 10–15% acetonitrile [Figure 2(*a*)]. This minimum explains the previously observed decrease in absorption at 500 nm followed by its increase as the solutions were diluted with acetonitrile. The negative synergism of the molar absorption coefficients observed in the system was previously noted in a study of methylpyrazinium iodide association in an acetone–chloroform system.[12] However, in the system studied previously, it was accompanied by positive synergism of the energy of the charge transfer band maximum. The energy of the charge transfer band maximum does not change in the system described here. The plot of stability constants of outer-sphere complexes *versus* organic solvent concentration is non-linear [Figure 2(*b*)]. However, the stability constants of associates increase with raising the volume fraction of acetonitrile in solution.

The magnitude of the stability constant of the ion associate in aqueous solution, K_{ia} = 13.8 dm^3 mol^{-1}, cannot be explained by the Fuoss equation that describes the contact interaction of two charged particles. The K_{ip} constant calculated by the Fuoss equation using a contact distance of 7.3 Å (this value is close to the half-sum of the shortest distances between iron atoms in a $K_3[Fe(CN)_6]$ crystal[13] and between copper atoms in K_2[Cu edta] $3H_2O$[14]) is K_{ip} = = 0.083 dm^3 mol^{-1} at D = 78.5 (for the solvent) [or 0.067 dm^3 mol^{-1} at D = 69 (for the 0.8 mol dm^{-3} KBr solution[15])]. These values are about two orders of magnitude smaller than the experimental ones (Figure 3). Similarly, the anion–anion associate could not be described by the model with two anions and two alkali metal cations arranged in rhombus vertices. Based on published data,[16] it was assumed in calculations that the angle formed by two anions and a cation was 30°, the distance between the anions was 7.3 Å, and the distance between an alkali metal cation and a complex anion was 4.08 Å. This distance corresponds to the sum of radii of a hexacyanoferrate ion and a potassium ion located on a third-order axis of the complex anion.[17] The entropy component of energy was neglected in calculations of the stability constants of the associates formed. The enthalpy of anionic associate formation was calculated as the sum of the enthalpies of ion interaction ($z_1z_2Ne^2/Dd$) in the associate. The calculated stability constants of ionic quadrupoles (K_{ia} = 453 dm^3 mol^{-1} at D = 78.5 or K_{ia} = 842 dm^3 mol^{-1} at D = 69) are considerably larger than the experimental value.

At the same time, the model with the participation of only one alkali metal cation in the ion associate (ionic triplet $[Fe(CN)_6]^{4-}$, M^+, [Cu edta]$^{2-}$ with the angle formed by two anions and the cation being 30°, the distance between the anions being 7.3 Å, and the distance between the alkali metal cation and the complex anion being 4.08 Å) gives K_{ia} = 9.84 dm^3 mol^{-1} at D = 78.5 or K_{ia} = 12.6 dm^3 mol^{-1} at D = 69, which is nearly equal to the experimental values. This allows us to conclude that one alkali metal cation is involved in the light absorbing associate in an aqueous KBr solution (μ = 0.8 mol dm^{-3}). We believe that the dipole structure of the [Cu edta]$^{2-}$ ion is a possible reason why only one alkali metal ion provides the stabilization of anion–anion associates.

In the calculations, we assumed that the contribution of non-electrostatic interactions to the stability of associates was insignificant, and it could be neglected. It followed from the small values of stability constants and the similarity of the plot of stability constants of ion associates *versus D* to that expected for purely electrostatic interaction of ions in the system. Furthermore, the observed lack of solvatochromic effect in the test systems, the insignificant variation of extinction coefficients of ion associates and the preferential solvation of alkali metal cations with water in water–acetonitrile mixtures[18] allowed us to conclude that the contact distance between ions upon addition of the organic solvent varies insignificantly and can be considered as a constant in the calculations. In solutions with high acetonitrile content, based on higher stability constants of associates in comparison with those expected for electrostatic interaction of ions in the ionic triplet $[Fe(CN)_6]^{4-}$, M^+, [Cu edta]^2, the involvement of a second alkali metal ion or acetonitrile molecules in the associate can be assumed.

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Received: 9th October 2015; Com. 15/4745