Simulation of anion associates

Vitalii Yu. Kotov

Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation. Fax: +7 095 200 4204

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According to the proposed model of anion associates, two singly charged cations would suffice to retain two multiply charged anions in close contact.

The formation of ion pairs cannot be neglected even in dilute electrolyte solutions. Thus, at 298 K, 46% anions in a 4×10^{-3} M $K_4[Fe(CN)_6]$ solution are associated.[1] In more concentrated solutions, associates that contain two or more potassium ions per hexacyanoferrate ion are formed. In concentrated solutions with salt concentrations higher than 0.3 mol dm^{-3}, anion associates in which two complex anions occur at a contact distance can be formed.[2–4] In this work, anion associates were simulated in order to obtain information on a minimum number of cations required for their occurrence and on optimum distances between likely charged ions in such associates.

In the absence of cations from an associate, negatively charged ions undergo Coulomb repulsion, and the interaction is unfavourable in terms of energy. In the general case, the addition of a singly charged cation also does not result in a stable system. The presence of the second singly charged cation (this situation corresponds to the interaction between two ion pairs) can stabilise the system as a rhombus. Likely charged ions are arranged at the opposite vertexes of the rhombus (Figure 1). The distances and angles between the centres of charged particles in this associate significantly depend on ionic charges. Let us consider the case when the charges of spherical multiply charged anions are equal ($z_1 = z_2$). The resultant of forces acting on each of the negatively charged particles, which is aligned with the centre-line between anions, can be written as the difference

$$F_1 = Az_1^2/d^2 - 8Az_1 \cos^3 \alpha/d^2,$$

where A is a constant for a given solvent, d is the distance between the centres of anions, and α is the angle between the centres of two negatively charged particles and a positively charged particle (anion–anion–cation). The resultant force for either of the positively charged particles is

$$F_2 = A \cot^2 \alpha/d^2 - 8Az_1 \cos \alpha^2 \sin \alpha/d^2.$$

The positive or negative sign of F reflects the fact that ions repel each other or have an attraction for each other, respectively. Both singly charged anions and singly charged cations have an attraction for each other in the angle range from 30 to 60° [Figure 2(*a*)]. With an increase in the negative charge of the anion, this range is shifted towards small angles, and it is 18–37° for a system containing two four-charged anions [Figure 2(*d*)]. In the latter case, the angle at which the attracting forces of anions and cations are equal ($F_1 = F_2$) is 26°. To find an optimum distance between the anions in this system, the distance between oppositely charged ions should be known. According to structure data,[5] the shortest distance between the hexacyanoferrate ions and potassium ions in ion pairs is equal to 4.07 Å. Then, the optimum distance between the anions in a four-ion associate is 4.07·2·cos 26° = 7.3 Å. For triply charged ions ($F_1 = F_2$ at $\alpha = 31°$) at the same distance between oppositely charged ions, the distance between the anions in an associate is 7.0 Å. Thus, two singly charged can retain two multiply charged anions in contact at a distance close to 7 Å by the cooperative interaction of ions. The conclusion drawn for the associate that consists of spherical ions can be extended to real structures. Figure 3 illustrates the results of optimising the geometry of the $2NH_4^+$, $2[RhCl_6]^{3-}$ system containing two octahedral anions and two tetrahedral cations by the ZINDO/1 method.[6] Complex anions in this system are arranged along the twofold axes of symmetry of each other. The N–Rh–Rh angle is 28°, which is close to the values obtained from the equality of F_1 and F_2. The introduction of additional ammonium cations to the simulated system does not significantly change the arrangement of ions in the $2NH_4^+$, $2[RhCl_6]^{3-}$ unit. This fact suggests that two cations will suffice for binding two anions. Note that values close to 7.0 Å were obtained previously[7] by evaluating the distances between anions in anion associates containing hexacyanometallate ions from the rate constant of electron transfer between anions, the dependence of the rate of electron transfer on the ionic strength of solution and the stability constant of the anion associate. The conclusion that the cooperative interactions of ions in solution results in contact of likely charged ions is supported by the fact that the calculated distances between anions in four-ion associates are close to the shortest distances between anions in crystals, where anions are in contact because of the cooperative interactions of ions. Thus, $d = 7.05$ Å for $K_4[Fe(CN)_6]\cdot3H_2O$, and $d = 6.98$ Å for $(NH_4)_2[IrCl_6]$. The mutual arrangement of ions in these crystals is similar to that shown in Figure 3.

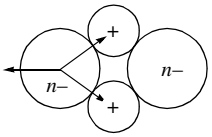

Figure 1 Ion associate model.

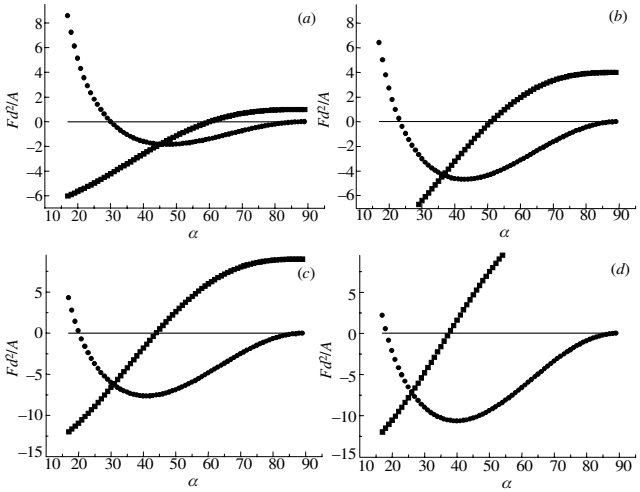

Figure 2 Relative resultant force acting on each of the likely charged particles in a system of four ions (squares and circles indicate multiply charged anions and singly charged cations, respectively) as a function of the angle between the centres of two negatively charged particles and a positively charged particle: (*a*) $z = -1$, (*b*) $z = -2$, (*c*) $z = -3$, and (*d*) $z = -4$.

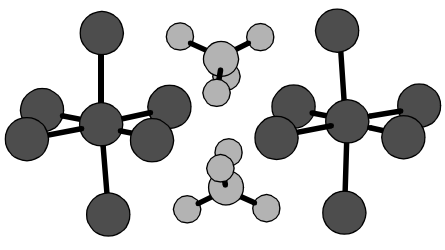

Figure 3 Result of optimising the geometry of the $2NH_4^+$, $2[RhCl_6]^{3-}$ system by the ZINDO/1 method.

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