Reviews

Outer-sphere interactions between anions

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The properties of anion associates are reviewed. Experimental electronic absorption spectra of anion-anion and anion-cation pairs were analyzed and compared with calculated data. Stability constants of ion pairs were determined in the framework of the theory of outer-sphere association of ions. Anion association was shown to be a specific case of typical cation-anion association, in which associates of the $2Na^+,[Coedta]^-$ type play the role of a complex cation.

Key words: electrolyte solutions, outer-sphere interactions, ion pairs, anion pairs, electronic absorption spectra.

Introduction

Studies of coordination compounds are mostly focussed on transformations and reactions in the first coordination sphere of the metal atom. However, in addition to transformations in the nearest ligand environment of the metal atom, the properties of the system under study are strongly affected by interactions in the second coordination sphere of the metal atom, which are mostly of the Coulomb type. Outer-sphere interaction between oppositely charged ions in solution results in the formation of ion pairs, which in some instances is accompanied by changes in the electronic absorption spectra (EAS) of systems under study. Additional light absorption by ion pairs is associated with phototransfer of the charge from a donor ion (nucleophile) to an acceptor ion (electrophile). Information on the electron transfer between the ions is obtained by analyzing the positions of maxima and the shape and intensity of outer-sphere charge transfer bands. From the dependence of additional absorption on the concentration of the compound in solution it is possible to determine the concentration, thermodynamic stability constants, and the extinction coefficients of light-absorbing associates formed by ion pairs.[1–5] Using such a procedure, one can characterize, in particular, "reactive associates" that are formed as intermediates in the redox reactions between ions. Outer-sphere charge transfer bands can be observed if the following basic conditions are met:

1. One of the ions is a weak oxidizing agent, whereas the other ion is a weak reducing agent (in this case no appreciable changes in EAS occur due to dark redox reactions and substitution reactions).

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2. Both ions exhibit weak absorption in that region of EAS where the appearance of additional absorption bands is expected.

3. Both ions are rather inert species and interact with each other electrostatically.

The ion pairs whose formation is accompanied by covalent bonding of ions (*e.g.*, at the formation of Prussian blue[6] from Fe^{3+} and $[Fe(CN)_6]^{4-}$, nitrososulfite complex[7,8] from $[RuNO(NH_3)_5]^{3+}$ and SO_3^{2-}, *etc.*) are called inner-sphere ion pairs.[2] Differences between the properties of inner-sphere ion pairs and anion ion pairs considered in this review are discussed below. Complex ions containing transition-metal atoms with the d^6 electron configuration seem to be the most convenient for studying the properties of ion pairs. In fact, most studies are carried out using inert octahedral low-spin complexes of cobalt and iron because they are well studied by other methods, readily available, cheap, and their properties can be varied with ease by replacing the ligands.

Charge transfer in the $[Co(NH_3)_6]^{3+},Cl^-$ ion pairs was first reported in 1944.[9] Observation of additional bands in EAS due to outer-sphere association of like ions was first reported in 1986.[10,11] By now, about twenty publications concerned with the phenomenon of outer-sphere anion association have been reported. Various terms are used for the associates consisting of two different anions and characterized by additional (associated with outer-sphere charge transfer) absorption in EAS.[12–14] Along with the concepts of the "ion pair"[12] and "reactive associates,"[13] we use the term "anion pair,"[14] thus focussing attention on the composition of unusual associates. Conditionality of the above terms is discussed below.

In this review we attempted to systematize the available data and to compare the properties of anion associates and ordinary ion pairs. Composition and stability of anion associates including the possibility of the presence of cations therein, as well as optical properties of these associates, are considered first.

Theory of electrostatic interaction between ions

Outer-sphere electrostatic interaction between spherical charged particles in a structureless solvent is described by the Fuoss equation[15]:

$$K_{IP} = 4\pi N d^3 \exp[-U(d)/(kT)]/3000, \qquad (1)$$

where $U(d)$ is the electrostatic potential,

$$U(d) = z_1 z_2 e^2/[D_s d(1 + Kd)],$$

$$K = [8\pi N e^2 I/(1000 D_s kT)]^{1/2},$$

K_{IP} is the formation constant of the ion pair, N is the Avogadro constant, d is the interreactant separation (the distance between the centers of the ions), z_1 and z_2 are the charges of the corresponding ions, e is the electron charge, D_s is the static dielectric constant, I is the ionic strength of the solution, T is absolute temperature, and k is the Boltzmann constant (dimensionality of all quantities corresponds to the CGS system of units).

From Eq. (1) it follows that the optimum conditions for the formation of ion pairs between oppositely charged ions are the interaction of ions carrying large charges in nonpolar solvents and a low ionic strength of the solution. And that is the case. According to the Fuoss equation, one can expect that association of like ions will be maximum in the case of interaction between large ions carrying small charges in polar solvents and a high ionic strength of the solution. It should be emphasized that the increase in the distance between interacting anions leads to a decrease in the calculated Gibbs energy due to both probability (entropy) and electrostatic (enthalpy) components:

$$\Delta S = R\ln(4\pi N d^3/3000), \qquad (2)$$

$$\Delta H = z_1 z_2 e^2 N/[D_s d(1 + Kd)], \qquad (3)$$

where R is the universal gas constant.

Thus, on the basis of the theory of electrostatic interaction between the ions, it should be expected that the outer-sphere interaction between anions will first of all manifest itself in the spectra recorded in concentrated aqueous solutions of electrolytes.

Manifestation of outer-sphere interaction between anions in EAS

If complex anions satisfying the above conditions for observation of outer-sphere charge transfer bands and nucleophilic anions I^-, SCN^-, or $S_2O_3^{2-}$ (at high concentrations) are simultaneously present in an aqueous solution, additional absorption is observed in the UV region (at $\nu > 30000$ cm^{-1}) of EAS of the solutions (Table 1).[11,12,14,16]

Table 1. Spectral characteristics[a] of the absorption bands of anion pairs

Anion pair[b]	ν_{max}[c]	$\nu_{1/2}$[d]
	cm^{-1}	
$[FeNO(CN)_5]^{2-},I^-$	31000	7500
$[FeNO(CN)_5]^{2-},SCN^-$	33100	8000
$[Coedta]^-,I^-$	33100	6700
$[Coedta]^-,SCN^-$	34500	7200
$[Cocydta]^-,S_2O_3^{2-}$	31700	8000
$[Cohmta]^-,S_2O_3^{2-}$	32100	8100
$[Coedta]^-,S_2O_3^{2-}$	32400	7500
cis-$[Coida_2]^-,S_2O_3^{2-}$	33000	8600

[a] Obtained from differential absorption spectra.[14,18]

[b] H_4cydta, H_4hmta, H_4edta, and H_2ida is *trans*-1,2-diaminocyclohexanetetraacetic, hexamethylenediaminotetraacetic, ethylenediaminotetraacetic, and iminodiacetic acid, respectively.

[c] Position of the band maximum.

[d] The bandwidth at half-height.

To obtain the characteristics of additional absorption bands, the overall spectra are most often resolved into Gaussian components. Spectra of associates containing I^- ions are processed taking into account two spin-orbit excited states of the $I^{\cdot}$ radicals.[17] In some instances it is possible to detect new bands in EAS without interference by varying the concentrations of interacting ions. It was shown that if cobalt(III) aminocarboxylate complexes and thiosulfate ions are simultaneously present in solution, additional absorption bands in EAS have a Gaussian shape.

At a small degree of ion association the optical density in the systems studied depends linearly on the concentration of both complex ions and nucleophilic anions. Replacement of potassium cations present in the system as counterions by cations of other alkali metals has no effect on the absorption intensity in EAS within the limits of experimental error.

The fact that the absorption intensity is dependent on the concentration of complex anions and nucleophilic anions and independent of the nature of counterions, as well as the absence of changes in the self-absorption of complex ions in the visible region of EAS, suggests that the appearance of additional absorption bands is due to the formation of anion pairs:

$$[\mathrm{Coedta}]^- + \mathrm{SCN}^- = [\mathrm{Coedta}]^-,\mathrm{SCN}^-; \qquad (4)$$

$$[\mathrm{Coedta}]^-,\mathrm{SCN}^- \xrightarrow{h\nu} [\mathrm{Coedta}]^{2-},\mathrm{SCN}^{\cdot}.$$

The energies corresponding to the maxima of the absorption bands of anion pairs depend on the size of the complex ion and decrease as the number of additional CH_2 groups in the ion increases. Analogous behavior is also characteristic of ion pairs formed by cobalt(III) cationic complexes.[1] The hypsochromic shift of the absorption band observed with increasing size of the complex anion[18] is in agreement with the results of quantum-chemical calculations of ion pairs.[19]

The $K_3[Fe(CN)_6]$—$K_4[Fe(CN)_6]$ system is the most studied system whose EAS contains additional absorption bands caused by outer-sphere interaction between the anions.[10,13,20–24] Broad weak absorption bands of anion pairs in this system and in similar systems are observed in the visible and near IR spectral regions (Table 2).

Table 2. Characteristics[13] of anion pairs[a] containing $[Fe(CN)_6]^{3-}$ ions

Anion pair	ν_{max}[b]	$\nu_{1/2}$[c]	$\varepsilon_{\nu_{max}}$[d]
	cm^{-1}		/L mol^{-1} cm^{-1}
$[Fe(CN)_6]^{3-}$,$[Fe(CN)_6]^{4-}$	12200	7900	28
$[Fe(CN)_6]^{3-}$,$[Os(CN)_6]^{4-}$	16400	10100	45
$[Fe(CN)_6]^{3-}$,$[Mo(CN)_8]^{4-}$	13900	6500	13
$[Fe(CN)_6]^{3-}$,$[W(CN)_8]^{4-}$	11900	7200	24

[a] The formation constant of the anion pair (at C_{K^+} = 2.5 mol L^{-1}) K_{AP} = 0.055 L mol^{-1}.

[b] Position of the band maximum.

[c] The bandwidth at half-height.

[d] The extinction coefficient at ν_{max}.

The position of the absorption band maximum of the $[Fe(CN)_6]^{3-}$,$[Fe(CN)_6]^{4-}$ anion pair is shifted by 460 cm^{-1} when using D_2O as solvent instead of water.[22] This indicates a strong solvent effect on the properties of the ions (including ionization potential and proton affinity) in solution. The shift of the maximum of the additional absorption band caused by the introduction of a supporting electrolyte into the system is of the same order of magnitude.[22] Replacement of potassium cations by those of other alkali metals has almost no effect on the positions of the absorption maxima of anion pairs in EAS.[22]

Positions of the maxima of absorption bands and the band half-widths of ion pairs

The energies (E_{opt}) corresponding to the maxima of the outer-sphere charge transfer bands in the spectra of ion pairs are determined[25] by two parameters, I_d and I_a, characteristic of the donor and acceptor, respectively (Table 3):

$$E_{opt} = I_d - I_a. \qquad (5)$$

This simple model makes it possible to predict the E_{opt} energies with good accuracy. For instance, the mean deviation of calculated E_{opt} values from the experimental values is ~0.06 eV for 99 ion pairs (including 8 anion pairs). The calculated I_d and I_a values can be (taking into account certain assumptions[25]) related to the vertical ionization potentials of donor ions ($IP_{v,d}$) and the electron affinities of acceptor ions ($EA_{v,a}$) in aqueous solution.[25] The error introduced is likely small (about 0.2 eV) and the $IP_{v,d}$ values of donor ions found using this model are in good agreement with experimental[26] data. Knowing the standard reduction potentials of the donor (E_d) and acceptor (E_a), one can determine the reorganization energies of donor (χ_d) and acceptor (χ_a) ions in aqueous solution from the calculated $IP_{v,d}$ and $EA_{v,a}$ values[25]:

$$\chi_d = IP_{v,d} - E_d - 4.5, \qquad (6)$$

$$\chi_a = E_a - EA_{v,a} + 4.5. \qquad (7)$$

Table 3. Parameters of donor (I_d) and acceptor (I_a) ions[25] in aqueous solutions at 298 K

Donor ion	$I_d \cdot 10^{-3}$/cm^{-1}	Acceptor ion	$I_a \cdot 10^{-3}$/cm^{-1}
$[W(CN)_8]^{4-}$	45.5±0.1	$[Fe(CN)_6]^{3-}$	33.5±0.1
$[Fe(CN)_6]^{4-}$	45.9±0.5	$[Ru(NH_3)_6]^{3+}$	32.4±0.3
$[Mo(CN)_8]^{4-}$	47.3±0.4	$[Ru(NH_3)_5Cl]^{2+}$	30.6±0.4
$[Os(CN)_6]^{4-}$	49.8±0.2	$[Fe(CN)_5NO]^{2-}$	26.7±0.3
$S_2O_3^{2-}$	57.0±0.5	$[Ru(NH_3)_5NO]^{3+}$	25.7±0.8
I^-	58.1±0.5	$[Coedta]^-$	24.1±0.2
SCN^-	59.3±0.4	$[Os(NH_3)_5Cl]^{2+}$	23.7±0.4
Br^-	63.0±1.4	$[Co(NH_3)_6]^{3+}$	21.5±0.7

Apart from the outer-sphere charge transfer energy, another important characteristic of the optical band is its half-width $\nu_{1/2}$. Usually, the band half-widths for ion pairs and associates are rather large (4000—10000 cm^{-1}), which indicates an appreciable rearrangement of the system upon electronic transition. Theoretical estimates of $\nu_{1/2}$/cm^{-1} values can be obtained using the Marcus—Hush theory[27–29]:

$$\nu_{1/2} = 2.78(\chi T)^{1/2}, \tag{8}$$

where χ/cm^{-1} $= \chi_d + \chi_a = E_{opt} - \Delta E$ is the reorganization energy of the system.

Additional factors determining the increase in the $\nu_{1/2}$ values and, in some instances, the appearance of new absorption bands are the follows. A donor or acceptor ion can possess several allowed excited states with close-lying energies in the optical region. In addition, an anion associate can consist of more than two anions. The former fact can be due to the splitting of degenerate electronic states because of the low proper symmetry of ions (*e.g.*, on going from octahedral symmetry to a lower one) and to the spin-orbit interaction, which is of particular importance for the ions of heavy elements.[4] For instance, the $\nu_{1/2}$ value for $[\text{Coedta}]^-,S_2O_3^{2-}$ coincides with that calculated in accordance with the simplest concepts of the Marcus—Hush theory,[25] while broadening of the bands of other anion pairs with participation of thiosulfate ions (see Table 1) compared with calculated $\nu_{1/2}$ values is in agreement with that of the self-absorption bands of cobalt aminocarboxylate complexes.[18] Much larger $\nu_{1/2}$ values for the anion pairs containing the $[\text{Os(CN)}_6]^{4-}$ ion compared to those of the pairs with the $[\text{Fe(CN)}_6]^{4-}$ ion (see Table 2) can be explained[13] by strong spin-orbit interaction for osmium complexes.

Photochemical behavior of anion pairs

The fact that no changes are observed in the region of outer-sphere charge transfer bands in the spectra of the systems simultaneously containing $[\text{FeNO(CN)}_5]^{2-}$ ions and nucleophilic anions upon their irradiation indicates that these bands are photochemically inactive.[11] This is explained by the fast recombination reaction of primary radical products of the photoreduction of nitroso complex with nucleophilic reagent. At the same time, irradiation of $[\text{Coedta}]^-,I^-$ ion pairs by light at a wavelength of 313 nm leads to photoreduction of complex ions[12]:

$$2\ \{[\text{Coedta}]^-,I^-\} + I^- \xrightarrow{h\nu} 2\ [\text{Coedta}]^{2-} + I_3^-. \tag{9}$$

The quantum yield with respect to the complex product is 0.16 mol Einstein^{-1}. In this case the efficiency of irradiation of the anion pair is due to close values of the standard reduction potentials of the pairs for the products of photoreaction $[\text{Coedta}]^-/[\text{Coedta}]^{2-}$ and $I_3^-/I_2^- + I^-$ (see Ref. 12) and to the low rate of dark reverse reaction.[30] It should be noted that anion pairs are similar in their photochemical behavior to the conventional ion pairs formed by complex cations whose properties are close to those of the anions studied.[2,31]

Stability and molar extinction coefficients of anion pairs

The relationship between the optical density (*D*) in differential absorption spectra and the concentration of the nucleophilic anion (*C*) for solutions with constant ionic strength (at a constant overall concentration of complex ions $C_0 \ll C$) can be written[3] as follows:

$$D = \varepsilon C_0 K_{AP} C l/(1 + K_{AP} C), \tag{10}$$

where K_{AP} is the formation constant of the anion pair, ε is the molar extinction coefficient, and l is the optical path length.

In the form of the Benesi—Hildebrand equation[32] this expression describes a straight line in the $C_0 l/D$—$1/C$ coordinates. Indeed, analogous experimental dependences are linear.[13,14,33] The K_{AP} and ε values of corresponding absorption bands calculated using the Benesi—Hildebrand equation are listed in Tables 2 and 4.

As should be expected, the optical density in the systems studied changes in parallel with the ionic strength of the solution. Using the Fuoss equation (see Eq. (1)), it has been found[14] that thermodynamic stability constants of anion pairs determined for solutions of constant and variable ionic strength (see Table 4) are in best agreement with those calculated by Eq. (1) at interionic distances of about 5.0 Å. In this case the thermodynamic constants themselves are equal to 0.011 and 0.076 L mol^{-1} for $[\text{FeNO(CN)}_5]^{2-},I^-$ and $[\text{Coedta}]^-,I^-$, respectively.[14]

It should be emphasized that the Fuoss equation derived for dilute solutions and neglecting different non-Coulomb interactions between the ions makes it possible to obtain consistent results also for solutions with high concentrations of nucleophilic anions when using potassium chloride as the supporting electrolyte.[14]

Table 4. Formation constants (K_{AP}) and molar extinction coefficients ($\varepsilon_{\nu_{max}}$) of the anion pairs[14,33]

Anion pair	K_{AP}/L mol^{-1}		$\varepsilon_{\nu_{max}}$ /L mol^{-1} cm^{-1}
	$I = 3$ (KI + KCl)	$I \neq$ const (KI)*	
$[\text{FeNO(CN)}_5]^{2-},I^-$	0.10	0.11	1500
$[\text{Cocydta}]^-,I^-$	0.19	—	900
$[\text{Coedta}]^-,I^-$	0.20	0.21	2000
cis-$[\text{Coida}_2]^-,I^-$	0.28	0.30	2500
trans-$[\text{Coida}_2]^-,I^-$	—	0.26	1500

* The values listed correspond to $I = 3$.

Effect of the nature of anions of supporting electrolytes on the absorption of anion pairs

Replacement of potassium chloride by other supporting electrolytes changes the type of the dependence of absorption of the anion pairs on the ionic strength of the solution. The absorption of anion pairs increases in the case of potassium fluoride and decreases in the case of bromides and perchlorates of alkali metals.[34] Similar behavior of the systems is also characteristic of competing processes of ion pair formation between anions and complex cations.[35] Processing of experimental data in the coordinates of the Benesi—Hildebrand equation made it possible to draw the following conclusions.

First, the closest values of the parameters of the Benesi—Hildebrand equation correspond to the systems containing no additional supporting electrolyte and to the systems in which potassium chloride is used as supporting electrolyte. Therefore, the classical Fuoss equation is applicable to the description of anion pairs of electrolytes in systems close in composition to those under study only when using alkali-metal chlorides as supporting electrolytes.

Second, the series $F^- < H_2O, Cl^- < Br^- < I^- < ClO_4^-$, in which the secondary salt effect observed upon competing formation of "complex anion—nucleophilic anion" anion pairs increases, is analogous to the series, in which the partial molar volumes of these anions are changed.

Effect of complex anion geometry on stability constants and molar extinction coefficients of anion pairs

The intensity of light absorption in ion associates upon electronic transition from the ground state (ψ_i) to an excited state (ψ_f) is determined by the value of the matrix element of the dipole moment operator M[36]:

$$f = \mathrm{const}\cdot E_{\mathrm{opt}}\langle\psi_i|\mathbf{M}|\psi_f\rangle^2, \qquad (11)$$

where f is the oscillator strength.

Since mixing of donor and acceptor orbitals in ion associates is insignificant, in the case of outer-sphere electron transfer the dependence of the intensity on the donor—acceptor distance will asymptotically approach an inverse exponential one. Transition intensities in the electronic spectra of anion associates containing only complex ions (see Table 2) are rather low (ε = 10 to 50 L mol^{-1} cm^{-1}) because of the long distance between the donor and acceptor ions. The low intensity of transitions is also characteristic of associates containing oppositely charged ions with analogous electron configuration.[13] For anion associates containing one complex ion, the intensity of outer-sphere electronic transition is one to two orders of magnitude higher. This fact can be explained by shorter donor—acceptor distances and a stronger orbital overlap. The latter is particularly characteristic of associates containing complex anions with d^6 electron configuration (see Table 4), since the e_g acceptor orbital is an antibonding orbital.

Table 5. Charges (q) on the atoms and atomic groups in cobalt aminooxalate complexes calculated by the ZINDO/S method[37]

Complex	q/au		
	Co	C_2O_4	NH_3
$[Co(NH_3)_6]^{3+}$	+0.06	—	+0.49
$[Co(NH_3)_4C_2O_4]^+$	+0.10	−0.84	+0.45/+0.42
cis-$[Co(NH_3)_2(C_2O_4)_2]^-$	+0.16	−0.98	+0.40
$[Co(C_2O_4)_3]^{3-}$	+0.24	−1.08	—

As has been shown in studies of the properties of anion pairs formed by isomeric *cis*- and *trans*-bis(iminodiacetate)cobalt complexes,[33] these associates are almost equally stable (see Table 4). This suggested that the formation of anion pairs is affected by the nonuniform charge distribution in complex ions rather than by the dipole structure of the complex ions. In this case the change in the structure of positively charged fragments of the complex ion must have an appreciable effect on the absorption of anion pairs. ZINDO/S calculations[37] showed that the positive charge in aminocarboxylate complexes is mainly localized on the amino ligands (Table 5).

A decrease was found in the formation constants and extinction coefficients of anion pairs containing iodide ions and cobalt complexes and differing in the structure of positively charged fragments, *viz.*, *cis*-$[Coida_2]^-$, $[Coedta]^-$, and $[Cocydta]^-$ (see Table 4). This made it possible, in particular, to conclude[33] that the overlap of the orbitals of nucleophilic anion and complex anion is the most favorable if the complex ion collides with a positively charged fragment of the nucleophilic anion.

^{59}Co NMR study of the state of ions in systems containing Na[Coedta]

The use of ^{59}Co NMR spectroscopy makes it possible to obtain quantitative characteristics of the formation of ion associates containing cobalt(III) complex ions from the dependence of the δ^{59}Co chemical shifts on the concentration of ions present in solution.[38] Based on the results of the ^{59}Co NMR study of the systems containing Na[Coedta],[39] the following model of interionic interaction in solution has been proposed. The first stage includes the formation of an ion pair:

$$Na^+ + [Coedta]^- = Na^+,[Coedta]^-. \qquad (12)$$

Na^+ ions are coordinated to the carboxylic fragments of the $[Coedta]^-$ anion and a specific interaction between them occurs. Previously,[40] such an "extra coordination" was observed, *e.g.*, in the solutions of several ethylenediaminetetraacetate complexes. In the second stage of ion association in the presence of a supporting electrolyte additionally introduced into the solution, species containing two alkali-metal ions are initially formed:

$$\mathrm{Na^+,[Coedta]^-} + \mathrm{Na^+} = \mathrm{2Na^+,[Coedta]^-}. \quad (13)$$

Differences in the chemical shifts at high concentrations of supporting electrolyte for the systems containing different anions indicate a further ion association, for instance:

$$\mathrm{2Na^+,[Coedta]^-} + \mathrm{Cl^-} = \mathrm{2Na^+,[Coedta]^-,Cl^-}. \quad (14)$$

The value of the constant of ion associate formation according to reaction (13), *viz.*, 0.87±0.09 L $\mathrm{mol^{-1}}$, is in agreement with the outer-sphere type of association.[15] This value is about 3 to 4 times larger than the formation constants of anion pairs[14] even if the ionic strength (*I*) of the solution is 3 L $\mathrm{mol^{-1}}$; for this reason, it is assumed that the ion associates of the $\mathrm{2Na^+,[Coedta]^-}$ type and the associates containing two anions (in this case, $\mathrm{2Na^+,[Coedta]^-,Cl^-}$ associates) are present in concentrated solutions.

Using the known values[39] of the formation constants of ion associates and the conclusion that the association constants are independent of the nature of the alkali metal and ionic strength of the solution, we calculated the fractional distribution of different species in the solutions containing Na[Coedta] and supporting electrolytes (Fig. 1). Comparison of the dependences shown with electronic spectroscopy data[14] clearly demonstrates that in the range of concentrations of supporting electrolytes at which outer-sphere interaction between nucleophilic anions and complex anions is observed in EAS, the latter exist mainly as associates with alkali metal cations. This shows the degree of conditionality of the concepts of the "ion pair" or "anion pair" as applied to the associates observed in the spectra. Thus, the anion association is a specific case of typical cation-anion association in which associates of the $\mathrm{2Na^+,[Coedta]^-}$ type play the role of a complex cation.

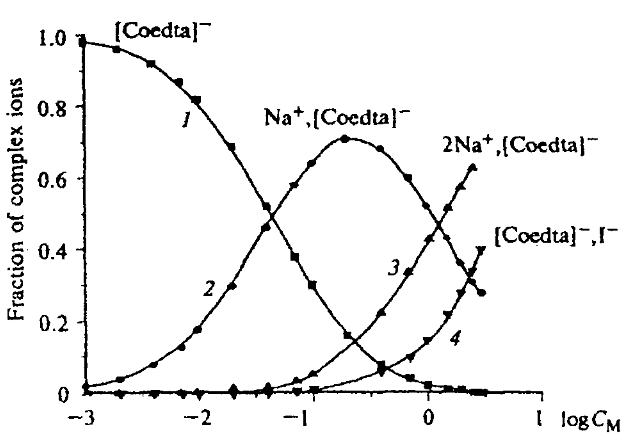

Fig. 1. Fractional distribution of complex species in the systems containing $\mathrm{Na^+}$—$\mathrm{[Coedta]^-}$ (*1—3*, according to NMR spectroscopy data[39]) and $\mathrm{[Coedta]^-}$—$\mathrm{I^-}$ (*4*, according to UV spectroscopy data[14]) anion pairs.

Simulation of electronic transitions in the cis-$[Co(NH_3)_2(C_2O_4)_2]^-$—$S_2O_3^{2-}$ system

The possibility of carrying out successful quantum-chemical simulation of electronic transitions in the anion pairs should be proved by performing preliminary trial calculations of ionic systems where the mutual arrangement of the atoms is *a priori* unknown. Calculations[19] of the simplest $\mathrm{[Co(NH_3)_6]^{3+}}$—$\mathrm{Cl^-}$ system chosen as an example have shown the following. To stabilize the singlet state of the $\mathrm{[Co(NH_3)_6]^{3+}}$ and $\mathrm{Cl^-}$ ions, one should perform calculations either taking into account a large number of solvent molecules or including several $\mathrm{Cl^-}$ anions as constituents of the associate (in such a way it is possible to simulate the electrostatic stabilization of ions, similar to that existing in crystals or in solution). For calculated electronic spectra of the $\mathrm{[Co(NH_3)_6]^{3+},4Cl^-}$ ion associates it was found that in the associates containing the $\mathrm{Cl^-}$ ions located on the two-fold and three-fold axes of the $\mathrm{[Co(NH_3)_6]^{3+}}$ octahedron the intensity of the $\mathrm{3p(Cl^-)} \rightarrow \mathrm{3d(e_g)([Co(NH_3)_6]^{3+})}$ electronic transition is two orders of magnitude lower than in the associates with $\mathrm{Cl^-}$ ions lying on the four-fold axes.

In addition to the symmetry-forbidden d → d transitions of the $\mathrm{[Co(NH_3)_6]^{3+}}$ ion, the calculated electronic spectra of the $\mathrm{[Co(NH_3)_6]^{3+},6Cl^-}$ ion associates[19] (the $\mathrm{Cl^-}$ ions are on the four-fold axes of the octahedron) contain an allowed transition from the t_{1u} HOMO to the e_g LUMO, which corresponds to the $\mathrm{Cl^-} \rightarrow \mathrm{[Co(NH_3)_6]^{3+}}$ charge transfer band. The energy of the charge transfer band and the oscillator strength of the transition decrease as the Co—Cl internuclear distance increases. The corresponding $(3p_z(\mathrm{Cl})|1s(\mathrm{H}))$ and $(3p_z(\mathrm{Cl})|2p_z(\mathrm{N}))$ overlap integrals also decrease. The overlap between the valent orbitals of cobalt and chlorine ions is virtually equal to zero.

In the diffuse reflection spectrum of the $\mathrm{[Co(NH_3)_6]Cl_3}$ crystal, the absorption in the visible region of EAS coincides with that of an aqueous solution of the system under study. A new band at 38400 $\mathrm{cm^{-1}}$,[42] which is absent in the spectrum of dilute aqueous solution, is observed in the UV spectral region. Comparison of the calculated energy of the $3p(\sigma)(\mathrm{Cl}) \rightarrow 3d(e_g)(\mathrm{Co^{III}})$ transition for a Co—Cl distance of 4.7 Å (corresponding to the average Co—Cl distance in the crystal[41]) and the energy of this band showed their good agreement.

To interpret the experimental spectrum of an anion associate observed in the *cis*-$\mathrm{[Co(NH_3)_2(C_2O_4)_2]^-}$—$\mathrm{S_2O_3^{2-}}$ system, the EAS of the following model complexes were calculated: *cis*-$\mathrm{[Co(NH_3)_2(C_2O_4)_2]^-}$, *cis*-$\mathrm{[Co(NH_3)_2(C_2O_4)_2]^-,Cl^-,F^-,4NH_4^+}$, and *cis*-$\mathrm{[Co(NH_3)_2(C_2O_4)_2]^-,S_2O_3^{2-},F^-,4NH_4^+}$.[37] Charge compensation in the anion associate was achieved by placing the cations near the coordinated oxalate ions. The results of calculations of the complexes are listed in Table 6. According to calculations, intense transitions in the region $\nu < 40000$ $\mathrm{cm^{-1}}$ are observed only for the

Table 6. Energies (E_{opt}) of electronic transitions[37] calculated by the ZINDO/S method

Electronic transition	$E_{opt} \cdot 10^{-3}$/cm^{-1}	f
	cis-$[Co(NH_3)_2(C_2O_4)_2]^-$	
d → d	18.8, 19.1, 19.1	0.0001
d → d	26.9, 27.1, 27.2	0.0000
$C_2O_4 \rightarrow C_2O_4$	22.6, 22.6, 27.3, 27.3	0.0008
	cis-$[Co(NH_3)_2(C_2O_4)_2]^-, S_2O_3^{2-}, F^-, 4NH_4^+$	
d → d	18.7, 18.8, 21.3	0.0002
d → d	25.6, 29.0, 29.0	0.0003
$C_2O_4 \rightarrow C_2O_4$	28.4, 28.6, 30.1, 30.2	0.0014
$S_2O_3 \rightarrow C_2O_4$	26.9, 28.8, 29.8, 29.9, 30.6, 31.2, 31.5	0.0000
S_2O_3(HOMO − 2) → → d(LUMO + 6)	31.0	0.0185
S_2O_3(HOMO − 2) → → d(LUMO + 7)	32.2	0.0822
	cis-$[Co(NH_3)_2(C_2O_4)_2]^-, Cl^-, F^-, 4NH_4^+$	
d → d	18.6, 18.9, 20.9	0.0002
d → d	25.7, 28.6, 29.0	0.0001
$C_2O_4 \rightarrow C_2O_4$	27.8, 27.8, 30.0, 30.1	0.0014
$Cl \rightarrow C_2O_4$	32.9, 36.1	0.0019
Cl(HOMO) → d(LUMO + 4)	37.1	0.0153
Cl(HOMO) → d(LUMO + 5)	39.6	0.2885

systems containing nucleophilic anions. These bands should be observed at 39600 (Cl^-) and 32200 cm^{-1} ($S_2O_3^{2-}$), the transition energy for the latter virtually coinciding with the experimental value of 33700 cm^{-1}. The difference in the transition energies for the systems containing Cl^- and $S_2O_3^{2-}$ anions, expressed in electron-volts (0.92 eV), is in good agreement with that of standard electrode potentials of nucleophilic anions (1.06 V).[43] The set of orbitals involved in the most intense transitions makes it possible to conclude[37] that a charge of about 0.90 to 0.95 e is transferred from the nucleophilic anions to the complex anion upon optical transitions and to unambiguously assign the absorption band at 33700 cm^{-1} observed in EAS of the *cis*-$[Co(NH_3)_2(C_2O_4)_2]^- - S_2O_3^{2-}$ system to outer-sphere charge transfer bands.

Differences in the properties of outer-sphere and inner-sphere anion pairs

Reaction of $K_4Fe(CN)_6$ with iron(III) salts results in the formation of insoluble Prussian blue ($K[Fe^{II}Fe^{III}(CN)_6]$), which absorbs at 14000 cm^{-1} (see Ref. 6). Replacement of Fe^{III} cations by Fe^{III} anionic complexonates results in stable true solutions. The maximum absorption of the $[FeedtaFe(CN)_6]^{5-}$ inner-sphere anion pair that formed is observed at 12500 cm^{-1} (see Ref. 44). From the analysis of concentration dependences of the absorption in the $[Feedta]^- - [Fe(CN)_6]^{4-}$ system it has been possible to reveal the distinctions in the properties of the outer-sphere and the inner-sphere anion pairs.

1. For the inner-sphere anion pairs, the contribution of the energy of the covalent bonding between complex-forming ions to the Gibbs free energy differs from zero. This leads to a substantial increase in the stability constants of inner-sphere ion pairs as compared to those of outer-sphere ion pairs.

2. The nature of the alkali metal used for maintenance of the ionic strength of the solution strongly affects the absorption of the complex.

3. Inner-sphere charge transfer bands are more narrow and observed at lower frequencies than analogous outer-sphere charge transfer bands.

Distinctions between outer-sphere and inner-sphere ion pairs observed at the formation of the $[FeN(O)SO_3(CN)_5]^{4-}$ nitrososulfite complex from $[FeNO(CN)_5]^{2-}$ and SO_3^{2-} (see Refs. 45 and 46) manifest themselves in a similar way. The observed differences in the dependence of the absorption of the anion pairs on the nature of the alkali-metal ions can be associated with different types of rearrangement of the second coordination sphere of the metal atoms at the formation of the anion pair. The formation of inner-sphere anion pairs is accompanied by a considerable charge transfer, which can not fail to affect the state of the ionic environment of interacting anions. The observed narrowing and shift of the bands is due to the decrease in the corresponding rearrangement energies of the system.

Conclusion

The totality of data considered in this review suggests that anion-anion association is a particular case of ion association. The major distinctions between cation-anion and anion-anion pairs are that the latter are less stable and that the outer-sphere interaction between the anions is observed in the spectra only in the case of concentrated aqueous solutions of electrolytes. In this case each of the interacting anions is surrounded by one or several cations. Under these conditions Coulomb interaction is no longer a determining factor, and the size of the ions becomes mainly responsible for the possibility of contact outer-sphere interaction.[14,47]

Investigation of the behavior of complex ions in concentrated solutions of supporting electrolytes using spectroscopic methods is of importance for the description of the properties of both the complex ions capable of forming dianionic associates and concentrated electrolyte solutions themselves. The properties of the latter are much less studied than those of dilute solutions. The reasons for such unusual behavior of complex ions in electron transfer processes occurring in highly concentrated solutions of supporting electrolytes remain unclear as yet. Attempts to explain the unusual behavior of anions in the redox reactions by the formation of associates containing two anions had been made long before anion pairs were detected and their properties were described.[48] Attempts at interpreting experimental data on the kinetics of homogeneous redox reactions between anions and heterogeneous processes of the reduction of anions taking into account the actual properties of anion pairs[39,49] have appeared to be very successful. This suggests that interest in the study of outersphere interactions between like ions will grow in the future.

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