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Formation of ionic pairs between single-charged anions and double-charged cations with separated charge

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The stability constants and extinction coefficients of ethyl viologen–iodide ionic pairs were calculated using the modified Kosover equation, and the effective cation charge was found by an analysis of the crystal structure of ethyl viologen diiodide.

Methyl viologen diiodide (1,1′-dimethyl-4,4′-bipyridinium) and ethyl viologen diiodide (1,1′-diethyl-4,4′-bipyridinium, EV^{2+}) are convenient models for the description of ionic association in solutions.[1] These commercially available compounds easily undergo crystallization and are soluble in water and in polar organic solvents. Solutions of these compounds are colored due to outer-sphere charge transfer (OSCT) bands in the visible region. Analysis of absorption *vs.* concentration plots allowed Bertolotti *et al.*[1] to obtain the characteristics of ionic pairs. However, the quantitative description of ionic association between halide ions and methyl viologen cations using the Benesi–Hildebrand method may hardly be considered successful since the measurements were carried out in solutions with a high content of halide ions. The formation of ion triplets may not be ruled out in such systems, as found[1] using halogen-selective electrodes. The Kosover method[2,3] for the description of interactions in the solutions of 1 : 1 electrolytes is an alternative method for the spectroscopic characterization of ion association processes. We suggest a modified method for describing the stability constants of ion pairs at zero solution ionic strength (K^0) and extinction coefficients (ε) at the maxima of OSCT bands for 2 : 1 electrolytes in systems where the cation charge is spatially separated, in particular, for describing the formation of EV^{2+}, I^- ion pairs. This approach is based on determining the effective cation charge and finding the values of K^0 and ε by the Kosover method. In this case, the working equation corresponds to the first association stage in the doubly charged cation – singly charged anion system, while the ionic strength of the solution and the activity coefficients are found using the effective charge of the cation.

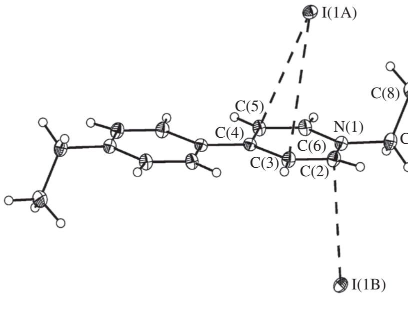

Figure 1 General view of EVI_2 representing atoms as thermal ellipsoids, showing two types of I···π interactions in a crystal. The species I(1A) and I(1B) are obtained from the basic one by the symmetry operations $-x, -y+1, -z$ and $x, -y+1.5, z-0.5$, respectively. Only the I···C interactions associated with bond critical points within AM theory are depicted as dashed lines.

According to high-resolution X-ray diffraction (XRD) data[†] for EVI_2, the dication in a crystal occupies a special position, *viz.*, the inversion center in the middle of the C(4)–C(4) bond (Figure 1). The ions are held together by C–H···I contacts [C···I varying from 3.913(1) to 4.067(1) Å] and I···π interactions, the latter forming two distinctive binding modes (Figure 1). The first one involves an iodine anion located above the carbon atom C(2) at a distance of 3.732(1) Å [the distance to the nitrogen atom is 3.832(1) Å], while the second one involves an iodine anion that is above the centroid of the pyridine ring [I···C 3.995(1)–4.047(1) Å] but slightly shifted towards the C(5) atom. Topological analysis of the electron density distribution function from the XRD experiment[‡] within Bader's 'Atoms in Molecules' (AIM) theory[4] allowed identifying only three bonding I···C interactions (with the shortest interatomic distances) between the counterions. In addition to the above C–H···I contacts, some C–H···π and H···H interactions

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[†] *Crystallographic data.* Crystals of EVI_2 ($C_{14}H_{18}I_2N_2$, $M = 468.10$) are monoclinic, space group $P2_1/c$, at 100 K: $a = 6.1926(1)$, $b = 13.0228(3)$ and $c = 10.3146(2)$ Å, $\beta = 104.527(1)°$, $V = 805.23(3)$ Å^3, $Z = 2$ ($Z' = 1/2$), $d_{\text{calc}} = 1.931$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 38.92$ cm^{-1}, $F(000) = 444$. Intensities of 149 778 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [$\lambda(\text{MoK}\alpha) = 0.71072$ Å, ω-scans, $2\theta < 120°$], and 12 166 independent reflections ($R_{\text{int}} = 0.0298$) were used in a further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of electron density and refined in the isotropic approximation. For EVI_2, the refinement converged to $wR_2 = 0.0457$ and GOF = 1.006 for all the independent reflections [$R_1 = 0.0192$ was calculated against F for 10 514 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 876566 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

[‡] The multipole refinement was carried out within the Hansen–Coppens formalism[8] using the XD program package[9] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[10] Before the refinement, the C–H bond distances were normalised to the standard value of 1.08 Å. The level of multipole expansion was hexadecapole for iodine and octupole for carbon and nitrogen atoms. The D_{10} dipole was refined for hydrogen atoms. The refinement was carried out against F and converged to $R = 0.0122$, $Rw = 0.0142$ and GOF = 0.90 for 8080 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria.[11] The residual electron density did not exceed 0.33 eÅ^{-3}. Analysis of the topology of the $\rho(r)$ function was carried out using the WINXPRO program package.[12]

[C···C 3.444–3.965(1) Å] between EV dications were also found.[5] Their energy was estimated by the versatile Espinosa correlation.[6,7] The values obtained are 0.7–1.1, 0.6–1.9 and 0.4–1.0 kcal mol^{-1} for I···C, C–H···I and cation-cation interactions, respectively. Note that the total energy of I···π binding within the two types of ionic pairs (Figure 1) – I···centroid and I···C(2) – thus reaches 1.1 and 1.3 kcal mol^{-1}, with the same values of 8 and 4 kcal mol^{-1}, respectively, for all of the C–H···I and cation-cation interactions in an EVI$_2$ crystal (the interaction energy and charge density distribution within the species will be reported elsewhere).

According to published data,[13] the solutions of methyl viologen halides show negative deviations from the Debye–Hueckel limiting law for 2 : 1 electrolytes. Therefore, it is reasonable to determine the activity coefficients of ions and the ionic strength of solution using the effective cation charge. For this purpose, we used structure fragments including a double-charged cation and an iodide anion with N···I distances of 3.832 and 4.042 Å as models of ion pairs. It was assumed that the charge of the cation in solution is separated into two single charges localized on the nitrogen atoms of the cation. Thus, we considered the electrostatic interaction in a system of three single charges: two positive ones separated at 7.014 Å and a negative one located at distances of 3.832 and 8.026 or 4.042 and 6.759 Å from the positive charges for the first and second models, respectively. The resultant Coulombic forces for these models allowed the cation effective charge to be determined: +1.30 and +1.28. The following working equation was used:

$$2C_0^2/FA = [C_0(2+\alpha)/F]/\varepsilon + 1/(K^0\varepsilon), \qquad (1)$$

where C_0 is the total salt concentration, F is the activity coefficient, A is the optical density at the maximum of the OSCT band, and α is the dissociation degree of the ion pair.

Table 1 summarizes the characteristics of the EV^{2+},I$^-$ ion pairs in aqueous ethanol solutions. For comparison, we used the characteristics of MPz$^+$,I$^-$ ion pairs (MPz$^+$ = methylpyrazinium) in aqueous ethanol solutions of MPzI, obtained using the equation[2]

$$C_0^2/FA = [C_0(1+\alpha)/F]/\varepsilon + 1/(K^0\varepsilon), \qquad (2)$$

The stability constants of the EV^{2+},I$^-$ and MPz$^+$,I$^-$ ion pairs were plotted *versus* the dielectric constant of solvent in the Fuoss equation coordinates[14]

$$\ln K^0 = \ln(4\pi N_A a^3/3000) - z_1z_2e^2/(Dk_BTa), \qquad (3)$$

where N_A is the Avogadro number, a is the separation distance between the centers of ions (contact distance, Å), z_1 and z_2 are the charges of interacting ions, in our case z_2 is the cation effective charge, e is the electron charge, D is the static solvent dielectric constant, k_B is the Boltzmann constant, and T is the absolute temperature.

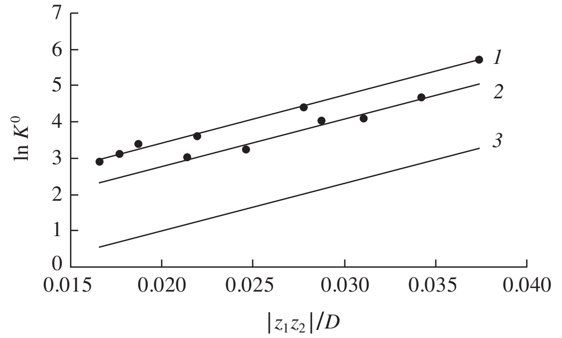

Figure 2 Stability constants of EV^{2+},I$^-$ and MPz$^+$,I$^-$ ion pairs at zero solution ionic strength *versus* the solvent static dielectric constant in the Fuoss equation coordinates.[14] (*1*) EV^{2+},I$^-$; (*2*) MPz$^+$,I$^-$; and (*3*) calculated by the Fuoss equation (a = 4.26 Å).

Table 1 Characteristics of the EV^{2+},I$^-$ and MPz$^+$,I$^-$ ion pairs in aqueous ethanol solutions.

Ion pair	Ethanol (vol%)	$\nu_{\max}$/cm^{-1}	K^0/dm^3 mol^{-1} (ε/dm^3 mol^{-1} cm^{-1})	
			Model 1	Model 2
EV^{2+},I$^-$	0	29650	18.6 (610)	18.3 (622)
	10	29310	22.9 (587)	22.6 (579)
	20	28750	30.2 (514)	29.8 (523)
	40	27870	37.9 (526)	37.3 (536)
	60	27300	83.8 (522)	82.6 (532)
	80	26400	309 (561)	306 (569)
MPz$^+$,I$^-$	60	28170	20.4 (485)	
	70	27770	25.5 (569)	
	80	27350	56.8 (486)	
	85	27110	60.8 (592)	
	90	26890	108 (588)	

These straight lines correspond to the distances of 4.26 Å for MPz$^+$,I$^-$ and EV^{2+},I$^-$ according to the first model (Figure 2) and 4.20 Å for EV^{2+},I$^-$ according to the second model. The resulting values are close to 4.19 Å calculated[3] for the MPy$^+$,I$^-$ ion pair in the aqueous ethanol solutions of methylpyridinium iodide and are just a little higher than the separation distance between the ions in a crystal. Note that the linear dependence obtained allows one to assess the contact distance in ion pairs only if it remains unchanged. The extinction coefficients for aqueous and ethanolic solutions are close. In a mixed solvent, a small decrease in ε was observed for solutions with an ethanol content of 20–60 vol%. A concentration of 40% also corresponds to a maximum synergistic effect of an increase in the energy at the OSCT band maximum in the system (Figure 3), suggesting that preferential solvation of the ion pair by the mixed solvent occurs to result in a small increase in the separation distance between the ions. However, the ε values change insignificantly (Table 1), which indicates that the values of a are relatively close. Figure 3 was prepared using the OSCT band maxima at 25 140 and 24 500 cm^{-1} in 95% ethanol and pure ethanol, respectively. Under these conditions, ion triplets are formed in considerable amounts along with ion pairs. Therefore, we do not show the results of concentration analysis of absorption for these solutions.

Using the equation[15]

$$\breve{a}^2 = 0.00042\,\varepsilon\,\nu_{1/2}/(\nu_{\max}a^2), \qquad (4)$$

where $\nu_{1/2}$ is the half-width of the absorption band, we found the degree of electron density transfer in ion pairs in the ground

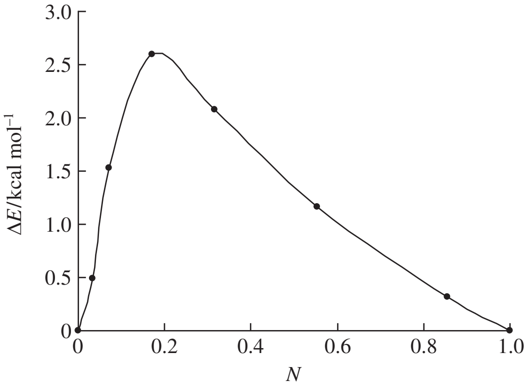

Figure 3 Synergistic effect of an increase in the energy at the OSCT band maximum for EV^{2+},I$^-$ in aqueous ethanol solutions *versus* the molar fraction of ethanol.

state: $\breve{a}$ = 0.052–0.055. The value thus obtained is typical of ion pairs in solutions.

The stability constants of the MPz^+,I^- and EV^{2+},I^- ionic pairs obtained here are somewhat higher than those calculated using the Fuoss equation (Figure 2). The differences in the constants correspond to the energies of 1.0 and 1.4 kcal mol^{-1}, respectively. This energy difference may be due to the entropy factor (cation non-sphericity) or the enthalpy factor that does not depend on the solvent dielectric constant. Note that this value is close to the total energy of I···C interactions in the two types of ion pairs in the EVI_2 crystal (1.1 and 1.3 kcal mol^{-1}).

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