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Structure of the ion pairs of 1:1-electrolytes in aqueous solutions

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The association of 1:1-electrolytes in aqueous solutions proceeds with the formation of contact ion pairs and solvent-shared ion pairs.

Electrostatic models of electrolytes are widely used for describing physico-chemical processes with the participation of ion pairs (IP) in chemical and biological systems.[1–3] Three types of IP are known: contact (CIP), solvent-separated (SSIP) and solvent-shared IP (SShIP).[3,4] The CIP structure does not contain solvent molecules in space between ions, whereas ions in the SShIP and SSIP structures are separated by one and two solvent molecules, respectively.

Equilibria between the solvated free ions C^+S_n and A^-S_m (n and m are the solvation numbers) and IP were investigated by an ultrasonic method in aqueous solutions of 2:2-electrolytes,[3] $MgSO_4$ and $MnSO_4$, which form commensurable concentrations of IP of the three types:

$$\underset{\text{Free ions}}{C^+S_n + A^-S_m} \rightarrow \underset{\text{SSIP}}{C^+SSA^-\,(S_{m+n})} \rightarrow \underset{\text{SShIP}}{C^+SA^-\,(S_{m+n-1})} \rightarrow \underset{\text{CIP}}{C^+A^-\,(S_{m+n-2})}$$

The existence of SSIP, alongside with CIP, in aqueous solutions of 1:1-electrolytes was discussed previously.[5] Free ions and ion pairs can be determined by spectroscopic methods.[6]

The aim of this work was to compare the experimental association constants, K_a, for cations and anions in aqueous solutions of 1:1-electrolytes, with those calculated on a basis of the continual electrostatic model of Fuoss.[3,5] A comparison of these two series can elicit the influence of the salt structure on the structures of generated IP.

The K_a values were calculated using the equation[5]

$$K_a = (4\pi NR^3/3000)\exp(\beta/R) \qquad (1)$$

where $\beta = e^2/(DkT)$; N is the Avogadro number, e is the elementary charge, D is the permittivity of the solvent, k is the Boltzmann constant, and T is the temperature. The distance between ions, R, in the calculations of K_a for SSIP, SShIP or CIP was taken[5] equal to $a + 2d$, $a + d$ or a, respectively, where $a = r_c + r_a$ is the sum of the crystallographic radii of cation (r_c) and anion (r_a). The values of r_c and r_a (for a coordination number of 6) were taken from ref. 7. The distance d corresponds to the side of a cell occupied by a solvent molecule, H_2O or D_2O, in a liquid phase. The d values were calculated[5] as $d = [(M/(N\rho)]^{1/3}$, where M is the molecular weight of the solvent and ρ is its density.

The multiple regressions were calculated by the least-squares method using the STATGRAPHICS Plus (v. 2.1) program. The statistical performances of regressions reflect the number of compounds in subset n, standard deviation s, correlation coefficient r and Fisher statistical test F.

The applicability of a continual electrostatic model of interactions between cations and anions to the processes of SSIP, SShIP and CIP formation was ascertained by Fuoss.[5] The K_a values were determined[8–16] for a series of 1:1-electrolytes from the conductance of aqueous salts solutions. The calculations of K_a values for 1:1-electrolytes were made using equation (1) under assumptions that the IP formed in water have (1) SSIP, (2) SShIP and (3) CIP structures.

The $K_{a(SSIP)}$ values, calculated in the first variant, for all salts considerably surpassed, by a factor of 1.6–6.9, observed K_a. This implies that the formation of SSIP in aqueous solutions of the surveyed 1:1-electrolytes does not occur.

Table 1 Association constants, K_a/dm^3 mol^{-1} for the aqueous solutions of 1:1-electrolytes calculated by equation (1) for CIP and SShIP and observed values of K_a determined from the conduction of salts in water and D_2O.

Entry	Salt	D^{8-16}	T/°C	$K_{a(CIP)}$	$K_{a(SShIP)}$	K_a
1	LiCl	78.35	25	0.69	1.59	0.81[8]
2	LiI	78.35	25	0.72	1.80	0.62[8]
3	NaCl	78.35	25	0.72	1.76	0.92[9]
4	KCl	78.35	25	0.77	1.97	0.80[9]
5	$KClO_4$	78.35	25	0.90	2.31	0.98[10]
6	RbI	78.35	25	0.88	2.28	1.10[11]
7	$RbClO_4$	78.35	25	0.93	2.38	1.35[10]
8	CsBr	78.35	25	0.87	2.24	0.88,[12] 0.70[8]
9	CsI	78.35	25	0.94	2.41	0.93[12]
10	$CsClO_4$	78.35	25	0.98	2.52	1.69[10]
11	Me_4NCl	78.35	25	1.17	2.93	0.80, 1.0[13]
12	Me_4NCl	83.96	10	1.14	2.88	0.93[13]
13	Me_4NBr	71.51	45	1.27	3.11	1.25[13]
14	Me_4NBr	78.35	25	1.22	3.04	1.26[13]
15	Me_4NBr	83.96	10	1.19	2.99	1.41[13]
16	Me_4NI	71.51	45	1.38	3.33	1.52[13]
17	Me_4NI	78.35	25	1.32	3.26	1.47[13]
18	Me_4NI	83.96	10	1.29	3.21	1.79[13]
19	Et_4NBr	71.51	45	1.51	3.61	1.60[13]
20	Et_4NBr	78.35	25	1.46	3.53	1.72[13]
21	Et_4NBr	83.96	10	1.43	3.47	1.99[13]
22	Et_4NClO_4	78.35	25	1.66	3.92	2.65[13]
23	Pr_4NBr	71.51	45	1.72	4.00	2.18[13]
24	Pr_4NBr	78.35	25	1.66	3.92	2.26, 2.39[13]
25	Pr_4NBr	83.96	10	1.63	3.86	2.65[13]
26	Pr_4NI	71.51	45	1.86	4.27	3.50,[13] 3[14]
27	Pr_4NI	78.35	25	1.80	4.18	3.87, 3.0,[13] 2.1, 1.0[15]
28	Pr_4NI	83.96	10	1.76	4.12	4.29, 4.05[13]
29	Bu_4NCl	78.35	25	1.76	4.12	1.80[13]
30	Bu_4NCl	83.96	10	1.73	4.06	1.58, 2.03[13]
31	Bu_4NBr	71.51	45	1.90	4.35	2.45 [13]
32	Bu_4NBr	78.35	25	1.84	4.26	2.70, 2.84[13]
33	Bu_4NBr	83.96	10	1.80	4.20	3.40[13]
34	Bu_4NI	71.51	45	2.05	4.63	4.67,[13] 5.0[14]
35	Bu_4NI	78.35	25	1.99	4.53	5.13, 5.12,[13] 3.1, 2.0[15]
36	Bu_4NI	83.96	10	1.95	4.47	5.6, 5.6,[13] 5.0, 2.5[16]
37	Bu_4NClO_4	78.35	25	2.08	4.71	5.59[13]
38	Me_4NBr[a]	78.06	25	1.23	3.05	1.38[13]
39	Et_4NBr[a]	78.06	25	1.47	3.54	1.81[13]
40	Bu_4NBr[a]	78.06	25	1.85	4.27	2.94[13]
41	Me_4NI[a]	78.06	25	1.33	3.27	1.76[13]
42	Pr_4NI[a]	78.06	25	1.80	4.19	2.43[13]
43	Bu_4NI[a]	78.06	25	2.00	4.55	5.46,[13] 4[16]

[a] In D_2O.

The values of $K_{a(SShIP)}$ and $K_{a(CIP)}$ obtained in the second and third cases are given in Table 1 together with the observed K_a values. For the majority of salts, the second variant of calculation gives $K_{a(SShIP)}$, which is higher than the empirical K_a values by a factor of 1.5–3.3. However, in 8 systems (26, 28, 33–37, 43, Table 1), for the salts with large radii of the cations and anions, r_c and r_a, ($a > 0.6$ nm) the calculated $K_{a(SShIP)}$ values are in agreement with the experimental K_a:

$$\lg K_a = (1.048 \pm 0.040) \lg K_{a(SShIP)};$$
$$n = 8,\ r = 0.995,\ s = 0.070,\ F = 673.$$

For the same 8 systems, the $K_{a(CIP)}$ values calculated by the third variant were 1.9–2.7 times lower than the observed K_a.

For 22 systems (1–6, 8, 9, 11–17, 19, 20, 23, 29, 30, 38, 39, Table 1), the observed K_a and calculated $K_{a(CIP)}$ values are similar ($|K_a - K_{a(CIP)}| < 30\%$):

$$\lg K_a = (1.03\pm0.10)\lg K_{a(CIP)} + (0.025\pm0.014);$$
$$n = 22,\ r = 0.911,\ s = 0.061,\ F = 104.$$

It can be seen that IP generated in these systems are the mainly CIP. The specified 22 systems include salts with the relatively small sum of ionic radii, $a < 0.6$ nm, as distinct from the above 8 systems.

The calculations based on the Debye–Huckel theory and a model for incompletely dissociated 1:1-electrolytes using the sum $r_c + r_a$ as the least distance between ions adequately described the aqueous solutions of CsBr and CsI with the K_a values[17] that are consistent with the $K_{a(CIP)}$ values.

For other 13 systems (7, 10, 18, 21, 22, 24, 25, 27, 31, 32, 40–42, Table 1), including salts with the sum $r_c + r_a$ from 0.387 to 0.609 nm, the observed K_a values surpassed the $K_{a(CIP)}$ by 30–60% but they did not achieve the magnitudes of $K_{a(SShIP)}$. Obviously, in solutions of these salts the commensurable quantities of the CIP and SShIP are formed.

Thus, the calculations of K_a values carried out using the continual Fuoss model[5] and their comparison with the experimental data have shown that the association of 1:1-electrolytes, in water and D_2O, can result in CIP and SShIP; unlike 2:2-electrolytes, SSIP are not formed. The increase in the sum of the ionic radii results in the displacement of equilibrium between CIP and SShIP in the direction of SShIP. In solutions of the salts containing ions with the small sum of ionic radii, $a < 0.4$ nm, there is a preferred formation of CIP, and at $a > 0.6$ nm, there is a preferred formation SShIP.

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