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Effect of ion solvation in binary solvents on the stability of ion pairs

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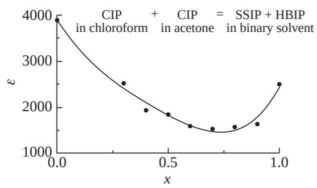
According to the UV-VIS spectroscopic data, preferential solvation in binary solvents results in the formation of less stable ion pairs MQ^+I^- as compared to those in individual solvents.



The theoretical dependence of the stability constants (K^0_{ip}) of ion pairs in solutions on the dielectric constant (D) of a solvent, the formal charge product (z_1z_2) and the contact distance (a) between ions follows the Fuoss equation[1]

$$K^0_{ip} = (4\pi N a^3/3000)\exp[-z_1z_2e^2/(kTaD)], \qquad (1)$$

where N is the Avogadro constant, e is the elementary charge, and k is the Boltzmann constant. Thus, the logarithm of stability constant of an ion pair is a linear function of the reciprocal of the solution dielectric constant at a constant temperature (T):

$$\ln K^0_{ip} = A - z_1z_2e^2/[kTa(1/D)]. \qquad (2)$$

The value of a can be calculated from the slope of the function, provided it is constant in solutions with various dielectric constants. At the same time, it is usually supposed that the value of z_1z_2 is the product of the formal charges of ions, whereas the dielectric constant is equal to a bulk dielectric constant. For real ions in real solutions, the $\ln K^0_{ip}$–$(1/T)$ linear relationship is seldom fulfilled, and it was observed only in a limited range of experimental data (Figure 1). The calculation of a from a linear range of experimental functions for binary solutions led to values that substantially differed from one another, including meaningless ones much smaller than a crystallographic distance between ions.

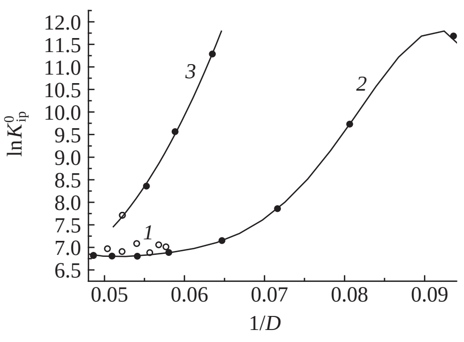


Figure 1 Logarithm of the stability constant of the ion pairs MQ^+,I^- *vs.* reciprocal dielectric constant for (*1*) isopropanol–acetone (empty circles), (*2*) chloroform–acetone, and (*3*) isopropanol–chloroform mixtures.

Possible reasons for the deviation of the values of z_1z_2, a and D for real ions and real solutions from ideal ones will be considered below. For non-spherical ions and ions with unequally distributed charges, the values of z_1z_2 can markedly differ from those of the formal charge product.[2] Contact ion pairs (CIPs) with the distance a close to crystallographic predominate in the solvents with low dielectric constants under conditions where ion solvation is small. The fraction of ion pairs stabilized by hydrogen bonds[3] (HBIP) and solvent-separated ion pairs (SSIP) increases with D when a solvent is replaced by a more polar one or when a polar solvent fraction increases in a nonpolar solvent–polar solvent binary solution. All these pairs are simultaneously present in solutions with D of about 10–25. Ions included in the ion pairs have their own absorption in the UV part of the electronic absorption spectrum (EAS). However, only the CIPs have absorption in the visible region of the spectrum associated with outer-sphere charge transfer. Thus, the fraction of CIPs in a solution can be estimated from the ratio of the ion pair extinction coefficient in a solvent to the maximal value obtained from the extrapolation of the values for binary solutions (polar solvent–nonpolar solvent) to the zero content of a polar solvent. Since the distance between ions markedly differs for different ion pairs, we can say only about the effective value of a, which is typically higher than that used in calculations. On the other hand, it is smaller than the value of a for the SSIP, obtained as a sum of the Stokes radii of ions. The dielectric constant of the solvent surrounding an ion pair is much smaller than D due to the effect of dielectric saturation.[4,5] As a result, the experimentally found product $z_1z_2/(aD)$ can be both higher and lower than a value calculated from formal parameters using $a_{calc} = a_{cryst}$, and it will be higher than the calculated value for $a_{calc} = a_{solv}$. Thus, taking into account that equation (1) was derived for the contact ion pairs, the choice of $a_{calc} = a_{cryst}$ seems more correct for a comparison of constants.

The iodides of N-heterocyclic cations are test materials for studying ion association and solvation processes in 1 : 1 electrolyte solutions.[6–10] Among them, *N*-methylquinoxalinium iodide

Table 1 Experimental and calculated parameters of the ion pairs MQ^+,I^- in individual and binary solvents.

Solvent	ν_{max}/cm^{-1}	ε_{max}/ dm^3 mol^{-1} cm^{-1}	K^0_{exp}/ dm^3 mol^{-1}	D^{14-16}	K^0_{calc}/ dm^3 mol^{-1}	F	F (K^0_{exp} ^{15,16})	
							Bu_4NI	Bu_4NBr
Pr^iOH (100)	22240	1463	2234	19.41	398	1.216	1.456 (1265)	1.364 (871)
Pr^iOH–acetone (80 : 20)	21700	1267	1157	17.75	841	1.037	1.210 (597)	1.155 (483)
Pr^iOH–acetone (60 : 40)	21410	1137	1109	17.39	1009	1.011	1.128 (416)	1.089 (367)
Pr^iOH–acetone (40 : 60)	20960	1183	973	17.90	782	1.025	1.114 (311)	1.087 (296)
Pr^iOH–acetone (30 : 70)	20660	1117	1191	18.38	624	1.077	–	–
Pr^iOH–acetone (20 : 80)	20300	1381	997	18.90	494	1.085	1.134 (243)	1.121 (252)
Pr^iOH–acetone (10 : 90)	19940	1571	1064	19.67	358	1.138	1.158 (215)	1.164 (248)
Acetone (100)	19430	2499	916	20.56	254	1.169	1.149 (155)	1.242 (285)
Acetone–$CHCl_3$ (90 : 10)	19710	1643	904	19.63	364	1.115	–	–
Acetone–$CHCl_3$ (80 : 20)	19960	1565	900	18.48	596	1.049	–	–
Acetone–$CHCl_3$ (70 : 30)	20100	1532	977	17.23	1096	0.987	–	–
Acetone–$CHCl_3$ (60 : 40)	20200	1595	1273	15.46	3079	0.912	–	–
Acetone–$CHCl_3$ (50 : 50)	20250	1847	2587	13.96	9065	0.887	–	–
Acetone–$CHCl_3$ (40 : 60)	20230	1943	16810	12.40	36770	0.938	–	–
Acetone–$CHCl_3$ (30 : 70)	20120	2524	118800	10.68	276600	0.942	–	–
Acetylacetone (100)	19200	1565	423	23.10	111	1.199	–	–

(MQ^+)[3,11] can be noted since it absorbs in the visible region of EAS. In this work, the solutions of MQI in acetone, acetylacetone, isopropanol, chloroform and binary solutions including these solvents were studied by EAS[†] to reveal solvation effects on the stability constants of the ion pairs MQ^+,I^- in the binary systems. The results obtained by quantum-mechanical calculations[‡] for methylpyrazinium iodide (MPzI)[12] were also used in the interpretation since it is the nearest structural analogue of MQI.

Table 1 summarizes the maxima of outer-sphere charge transfer bands (ν_{max}) for MQ^+,I^- in the individual and binary solvents, the extinction coefficients (ε_{max}), and the stability constants of ion pairs (K^0_{ip}) found from the concentration dependences of absorption in the solutions of MQI according to a published procedure.[8] The experimental values of Table 1 are compared with those calculated by equation (1). The value of a_{calc} was taken equal to 3.75 Å. This value is almost identical to the shortest NI distance in a crystal of $MPzI\cdot 0.5I_2$[12] (3.751 Å). Owing to its geometry and the absence of covalent bonding,[12] the MPzI fragment can be considered as a CIP model with the varied NI distance (along the N···I axis, Figure 2). The quantum-chemical calculations of this fragment at $D = 20$ show that the energy minimum in the E–a plot corresponds to $a = 3.70$ Å (Figure 3). Therefore, the selected model with the minimum possible a will give a maximum value of K^0_{calc}. Unlike the model ion pair, the covalent component contributes to the energy of formation of the ion pair with hydrogen bonding C–H···I.[3,12] However, according to calculations, even at $D = 20$ when the Coulomb energy component of ion interaction is markedly weakened, the model ion pair is energetically more favorable than that under consideration. The effective charge of the non-spherical ion MPz^+ of the model ion pair was obtained from the electric potential, which MPz^+ creates in the point corresponding to the iodide ion position in a crystal.[12] The value of $(z_1z_2)_{calc} = -1.04$ was estimated from a comparison of the electric potential with that created with a hydrogen cation 3.751 Å apart. With increasing a, the value of $(z_1z_2)_{calc}$ approaches –1. This little change does not allow us to consider $(z_1z_2)_{calc}$ among the main factors defining a change in K^0_{ip}. Published data[14–16] were used for $D_{calc} = D_{bulk}$.

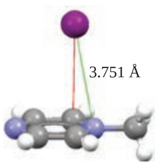


Figure 2 Fragment of the structure of $MPzI\cdot 0.5I_2$[12] used in the calculation of the ion pair MPz^+,I^-.

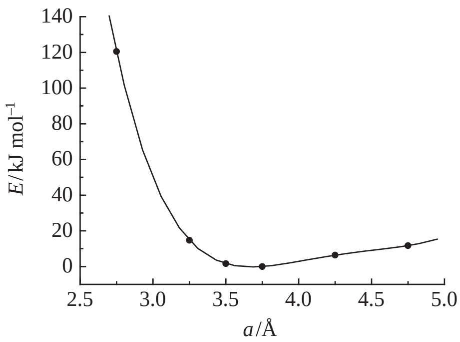


Figure 3 Energy of the contact ion pair MPz^+,I^- *vs*. distance between ions in acetone. The energy of the ion pair with a = 3.75 Å was assumed to be zero.

The values of $[z_1z_2/(aD)]_{calc}$ were compared with $[z_1z_2/(aD)]_{exp}$ found from the experimental stability constants of the ion pairs MQ^+,I^-:

$$[z_1z_2/(aD)]_{exp}/[z_1z_2/(aD)]_{calc} = F. \qquad (3)$$

The value of F represents a ratio of experimental to calculated electrostatic part of the energy. This value allows us to minimize the difference of the solvents relative to D in the comparison of the stability of ion pairs. At the same time, the nonelectrostatic part of the energy was considered to be constant, and it was calculated using equation (1) with $a_{exp} = a_{calc}$. We have also tentatively considered the possibility that a preexponential factor of the stability constant could be estimated from data on the stability of the iodide anion–uncharged tetracyanopyrazine[13] pair. However, a significant effect of the counterion (alkylammonium

[†] The electronic absorption spectra were measured on a Specord 50PC spectrophotometer at 298 K in quartz cuvettes (light path, 1 cm) in a wavelength range of 300–700 nm. The concentration of MQI in working solutions was 1 mmol dm^{-3}.

[‡] Single-point quantum chemical calculations of isolated model ion pairs with different I···N distances were performed with the Gaussian 09 software[21] making use of the B97D functional[22] and basis sets POL[23] for iodine and 6-311+G** for other atoms. Solvent effects were included using the polarizable continuum model (PCM) with acetone as a solvent.

cation) size on the stability constant of an ion pair and a significant difference in the stability constants of ion pairs including uncharged organic compounds of similar geometry (tetracyanopyrazine–tetracyanobenzene)[13] both forced us to refuse this estimation.

The values of F calculated for three individual solvents are close to one another within a range from 1.17 for acetone to 1.22 for isopropanol. Therefore, equation (1) gives understated values for the individual solvents even when $a_{calc} = a_{cryst}$. This fact allows us to conclude unambiguously that the main contribution into the increase of F, as compared with the calculated value for the ion pair formed only owing to Coulomb ion interaction, comes from a decrease in D. Previously, it was mentioned that a decrease in D is caused by the effect of dielectric saturation of ions involved in ion pairs. This circumstance also explains larger F values for isopropanol with regard to acetone because acetone mainly solvates a cation, whereas isopropanol solvates both ions involved in the ion pair. The values of ν_{max} from Table 1 are consistent with this statement.

For the test binary solutions, the values of F are lower than those for the individual solvents. Therefore, in the acetone–isopropanol system with 40 vol% acetone, F is as high as 1.01 [Figure 4(*b*)], whereas F decreases to 0.89 in the acetone–chloroform system with 50 vol% acetone [Figure 4(*a*)]. From changes in ν_{max}, we can conclude that solvation in the binary solutions is much higher than the additive contribution from solvation with two solvents (in particular, for the acetone–chloroform system, acetone mainly solvates a cation, whereas chloroform solvates an anion[11]). Therefore, the effect of dielectric saturation is higher for the binary solvents than that for individual ones, and it leads to an increase in F. When the local dielectric constant decreases, the decrease in F can be caused by both an increase in the effective value of a owing to ion solvation and an increase in the fraction of SSIP and HBIP. Increasing the fraction of such pairs in the system leads to a decrease in ε_{max}. A significant negative deviation of ε_{max} from ideal behaviour was observed in

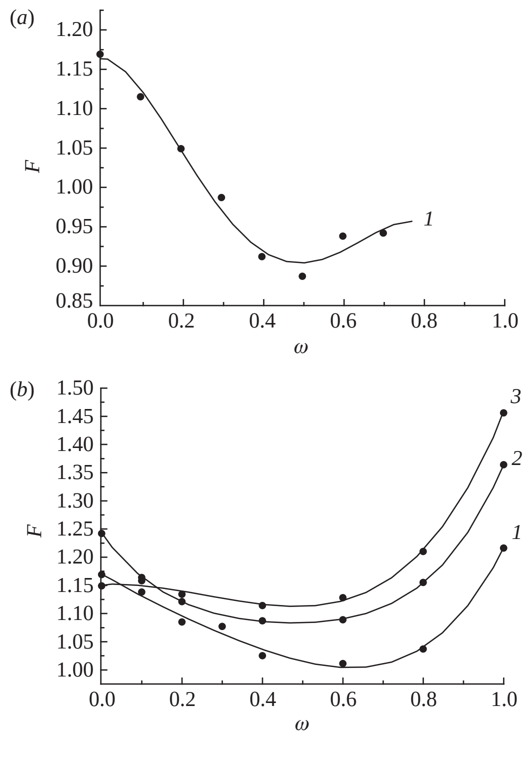


Figure 4 Values of F *vs.* the volume fraction of a second solvent in the (*a*) acetone–chloroform and (*b*) acetone–isopropanol systems: (*1*) MQ^+I^-, (*2*) $NBu_4^+Br^-$ (according to refs. 15, 16), and (*3*) $NBu_4^+I^-$ (according to refs. 15, 16).

Table 2 The values of F for the ion pairs $NBu_4^+I^-$ in individual solvents.

Solvent	$D^{14,20}$	F (K^0_{exp} ^{17,20})
EtOH	24.3	1.31 (123)
PrOH	20.1	1.30 (407)
BuOH	17.1	1.29 (1360)
Pentanol	14.4	1.21 (3220)
Pr^iOH (283 K, 1 atm)	20.62	1.43 (1092)
Pr^iOH (298 K, 1 atm)	19.41	1.44 (1247)
Pr^iOH (313 K, 1 atm)	17.30	1.39 (1535)
Pr^iOH (298 K, 529 atm)	20.54	1.45 (830)
Pr^iOH (298 K, 1004 atm)	21.02	1.44 (643)

the dependence of ε_{max} on the volume fraction of a solvent (ω) in the isopropanol–chloroform system, whereas a minimum appeared in the ε_{max}–ω plots for the acetone–chloroform and acetone–isopropanol systems (Table 1).

The selective solvation of unequally charged reagents strongly depends on a particular charge distribution, which can be qualitatively different from that for MQ^+. Therefore, the results obtained for the ion pair MQ^+,I^- were compared with published data obtained[15,16] in a conductometric study of ion association in acetone–isopropanol NBu_4I and NBu_4Br solutions and NBu_4I in individual alcohols.[17,20] We used a_{calc} = 5.05 Å for $NBu_4^+I^-$ in the calculations (the shortest NI distance in a crystal[18] was 5.048 Å, and the parameter a obtained from the conductivity data in acetone was 5.00±0.10 Å). The value of $(z_1z_2)_{calc}$ was taken equal to –1.

From the literature data,[15–17,20] we have obtained that the value of F for $NBu_4^+I^-$ in normal alcohols decreased from 1.31 for ethanol to 1.21 for pentanol (Table 2), and it was consistent with a decrease in the solvating ability of alcohols with longer carbon chains. Temperature and pressure changes did almost not affect the value of F (Table 2). The F–ω functions (Figure 4) for MQI, NBu_4I and NBu_4Br in acetone–isopropanol mixtures were similar to each other. The following conclusions can be drawn from the experimental data.

For the individual solvents, equation (1) gives the understated values of K^0_{ip} when crystallographic distances between the ions and the dielectric constants of solvents are used. Deviation of $\ln K^0_{ip}$ from the experimental values is higher for ion pairs with longer contact distances.

For the binary solvents under the conditions of preferential solvation, the sizes of the ions participating in the formation of ion pairs (from conductivity measurement[15,16]) and ion pairs formed (from EAS data) both expand. This leads to a decrease in difference between the experimental values of K^0_{ip} and those calculated according to equation (1) ignoring a change in the effective value of a. For the systems with the pronounced preferential solvation of ion pairs with a binary solvent, it is possible to obtain by equation (1) the overestimated values of K^0_{ip} compared with the experimental ones.

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References

1 R. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.
2 D. S. Dunin, V. Yu. Kotov, V. S. Kuleshov and Yu. V. Nelyubina, *Mendeleev Commun.*, 2012, **22**, 138.
3 M. V. Tolstykh, K. P. Birin, Yu. V. Nelyubina and V. Yu. Kotov, *Mendeleev Commun.*, 2014, **24**, 47.
4 Y. Hatano, T. Kakitani, A. Yoshimori, M. Saito and N. Mataga, *J. Phys. Soc. Jpn.*, 1990, **59**, 1104.
5 W. R. Fawcett, *Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details*, Oxford University Press, New York, 2004.

6 E. M. Kosover, *J. Am. Chem. Soc.*, 1958, **80**, 3253.
7 E. M. Kosover and J. A. Skorcz, *J. Am. Chem. Soc*., 1956, **82**, 2195.
8 P. Hemmes, J. N. Constanzo and F. Jordan, *J. Phys. Chem*., 1978, **82**, 387.
9 J.-G. Jee, Y.-H. Lee, E.-H. Woo and K.-H. Lee, *Bull. Korean Chem. Soc.*, 1983, **4**, 115.
10 O. C. Kwun and J. G. Jee, *Bull. Korean Chem. Soc*., 1985, **6**, 37.
11 K. P. Birin, D. S. Dunin, M. V. Tolstykh and V. Yu. Kotov, *Mendeleev Commun*., 2012, **22**, 320.
12 Y. V. Nelyubina, M. Y. Antipin, D. S. Dunin, V. Y. Kotov and K. A. Lyssenko, *Chem. Commun.*, 2010, **46**, 5325.
13 Y. S. Rosokha, S. V. Lindeman, S. V. Rosokha and J. K. Kochi, *Angew. Chem. Int. Ed.*, 2004, **43**, 4650.
14 (*a*) *Handbook of Solvents*, ed. G. Wypych, ChemTec Publishing, Toronto, and William Andrew Publishing, New York, 2001; (*b*) Y. Y. Akhadov, *Dielectric Properties of Binary Solutions*, Pergamon Press, Oxford, 1981.
15 D. F. Evans and M. I. McElroy, *J. Solution Chem.*, 1975, **4**, 413.
16 D. F. Evans, J. Thomas, J. A. Nadas and M. A. Matesich, *J. Phys. Chem*., 1971, **75**, 1714.
17 B. S. Krumgalz, *J. Solution Chem*., 1982, **11**, 283.
18 W. Prukała, B. Morciniec and M. Kubicki, *Acta Crystallogr., Sect. E*, 2007, **63**, o1464.
19 Q. Wang, A. Habenshuss, A. Xenopoulos and B. Wunderlich, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1995, **264**, 115.
20 S. L. Wellington and D. F. Evans, *J. Solution Chem.*, 1983, **12**, 815.
21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford CT, 2009.
22 S. Grimme, *J. Comput. Chem*., 2006, **27**, 1787.
23 A. J. Sadlej, *Collect. Czech. Chem. Commun.*, 1988, **53**, 1995.

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