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Reorientation of ions in contact ion pairs as a factor increasing the intensity of outer-sphere charge transfer bands

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The found increase in the extinction coefficients of ion pairs at the low dielectric permittivity of solutions in binary solvents depends on the nature of a nonpolar solvent, and it is related to not only the transformation of solvate-separated ion pairs into contact ones but also the reorientation of ions in the contact ion pairs.

The solvatochromism of dyes in mixed binary solvents is widely used for characterization of both solute–solvent and solvent–solvent interactions.[1–3] This phenomenon is observed in systems both with or without specific (homoselective and heteroselective) solvation of solutes.[4–6] Most publications are focused on solvatochromic behaviour of uncharged zwitterionic dyes, while very little attention has been paid to the solvatochromic behaviour of ionic compounds. In 1958, Kosover[1] found a relationship between the frequencies of absorption bands ($\nu_{\max}$) due to outer-sphere charge transfer (OSCT) and the apparent extinction coefficients ($\varepsilon'_{\max}$) of ion pairs in individual solvents. A study of the solvatochromic behaviour of the iodides of N-heterocyclic cations [*N*-methylpyrazinium (MPz^+) and *N*-methylquinoxalinium (MQ^+)] in the acetone–dichloromethane and acetone–chloroform systems[7] under the conditions of heteroselective specific solvation did not reveal such correlation for the binary solvents. However, a relationship between $\nu_{\max}$ shifts and changes in the apparent[†] ($\varepsilon'_{\max}$) and true[‡] ($\varepsilon_{\max}$) extinction coefficients of the ion pair was established.[7] In this work, we studied the spectral behaviour of MPzI and MQI in the acetone–nonpolar solvent binary systems in order to find a $\nu_{\max}$–$\varepsilon_{\max}$ relationship in systems without specific solvation. The significant increase in $\varepsilon'_{\max}$ in binary solutions with high concentrations of nonpolar solvents was found and a possible explanation for this effect was proposed.

^{1}H NMR[§] chemical shifts of aromatic protons of MQI in acetone–CCl_4 at mole fraction of nonpolar solvent $N < 0.5$ demonstrated the linear dependence on the solution composition (Figure 1). This indicates the absence of any specific solvation of MQ^+ cations. At a higher concentration of CCl_4 [at low values of dielectric permittivity of solutions (D)], the observed deviation from linearity can be explained by the aggregation of MQ^+,I^- ion pairs into quadruples and higher aggregates.[8] In the electronic absorption spectra[¶] of MQI in the acetone–nonpolar solvent systems, the linear dependence of the $\nu_{\max} = f(N)$ was observed (Figure 2), which suggests no specific solvation of ion pairs. The observed deviation from linearity at high concentrations of a nonpolar solvent is also due to the aggregation of the MQ^+,I^- ion pairs.[8] Thus, both the MQ^+ ion and the MQ^+,I^- ion pair are not specifically solvated in the test systems.

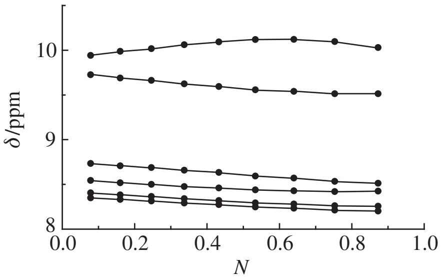

Figure 1 Dependence of the chemical shifts of the aromatic protons of MQI on the mole fraction of CCl_4 in the acetone–CCl_4 system.

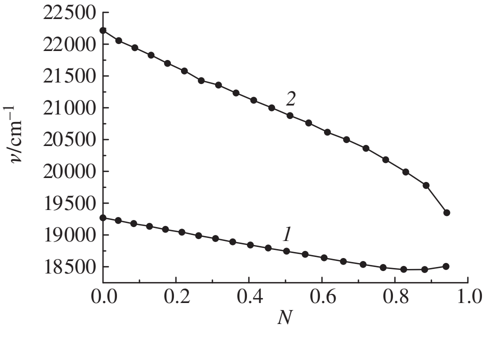

Figure 2 Dependence of the OSCT band maximum of MQI on the mole fraction of benzene in the (*1*) acetone–benzene and (*2*) isopropanol–benzene systems.

Methylquinoxalinium iodide is insoluble in nonpolar solvents. Thus, in order to estimate the $\nu_{\max}$ in nonpolar solvents we extrapolated the linear parts of the curves $\nu_{\max} = f(N)$, with N from 0 to 0.8 obtained in the acetone–nonpolar solvent systems to $N = 1$.[††] The found values of $\nu_{\max}$ (Figure 3) for the studied

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[†] $\varepsilon'_{\max} = A_{\max}/C^0l$, the dissociation of ion pairs is neglected.

[‡] The dissociation of ion pairs is taken into account.

[§] The ^{1}H NMR spectra were recorded on a Bruker AVANCE-III instrument with an operating frequency of 600.31 MHz at 303 K.

[¶] The electronic absorption spectra were measured on a Specord 50PC spectrophotometer at 298 K in quartz cells with an optical path length of 1 cm in the wavelength range of 300–700 nm. The working solutions of MQI or MPzI in acetone with the concentration $C^0 = 1$ mmol dm^{-3} were diluted with nonpolar solvents.

[††] The nonlinear extrapolation with N from 0 to 0.95 to $N = 1$ allowed us to estimate the $\nu_{\max}$ of ionic aggregates.

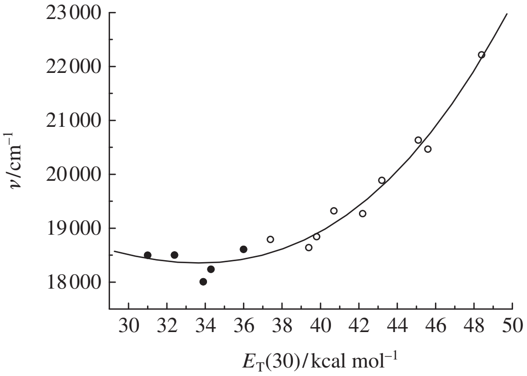

Figure 3 Dependence of the OSCT band maximum of MQ^+,I^- on the parameter $E_T(30)$.[3] Solid circles correspond to hexane, CCl_4, toluene, benzene or dioxane. Open circles correspond to THF, CH_2Br_2, cyclohexanone, CH_2Cl_2, acetone, DMF, DMSO, acetonitrile or isopropanol.

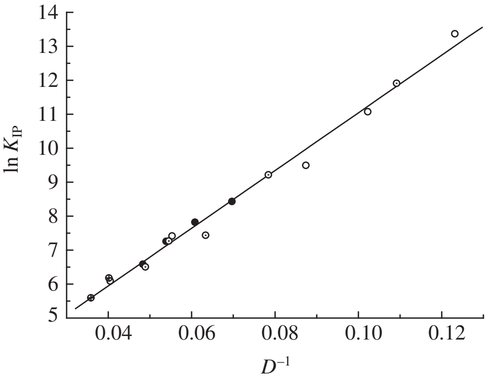

Figure 5 Dependence of the logarithm of the stability constant of MPz^+,I^- ion pair on the inverse dielectric constant for the acetone–CCl_4 system (solid circles). Different open circles correspond to the acetone–$CHCl_3$, acetone–CH_2Cl_2 and acetonitrile–$CHCl_3$ systems.

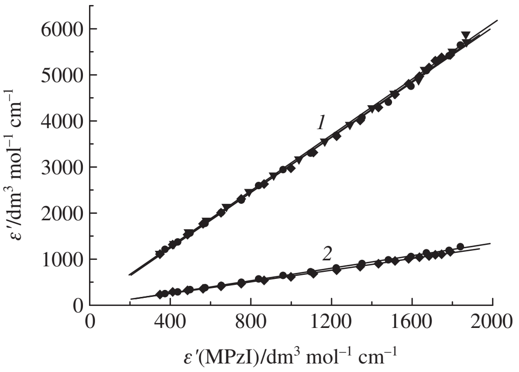

Figure 6 Dependence of the apparent extinction coefficients of (*1*) MQI and (*2*) 1,2,3-trimethylpyrazinium iodide on the apparent extinction coefficients of MPzI in solutions of the same composition in the acetone–benzene, acetone–dioxane and acetone–CCl_4 systems.

nonpolar solvents are almost constant (they vary from 18000 to 18600 cm^{-1}) and lower than the corresponding experimental values of $\nu_{max}(MQ^+,I^-)$ for polar and slightly polar solvents. Taking into account the almost linear dependence of the ν_{max} for polar solvents on the solvent polarity parameter [characterized by $E_T(30)$,[3] Figure 3], no solvation of MQ^+,I^- by nonpolar solvents can be expected.

Earlier,[8] it was found that in contrast to the ν_{max} the values of ε'_{max} for the iodides of N-heterocyclic cations do not depend on the degree of aggregation of ion pairs in chloroform. As no specific solvation of MQI was detected both in nonpolar solvents and in binary solvents, it can be assumed that the solvation shell of an ion pair has the same composition as a solvent. Based on this assumption, we can expect the same linear dependence of $\varepsilon_{max} = f(\nu_{max})$ for nonpolar solvents. Figure 4 shows the dependence $\varepsilon'_{max}(\text{MPzI}) = f(\nu_{max})$ in the acetone–CCl_4 system. The nonlinear character of the dependence indicates a low degree of association of ions into ion pairs at high acetone content. The true values of ε_{max} and the stability constant of ion pairs (K_{IP}) were calculated from the concentration dependences of MPzI absorption according to a published method.[9] The found values of $\ln K_{IP}$ in acetone–CCl_4 (Figure 5) as well as in the acetone–chloroform, acetone–dichloromethane[7] and acetonitrile–chloroform systems linearly depend on the inverse dielectric constant (1/*D*), confirming the values obtained. The calculated values ε_{max}(MPzI) and ε'_{max}(MPzI) in the region of low acetone concentrations actually lie on straight line ($R^2 = 0.987$) on the $\varepsilon_{max} = f(\nu_{max})$ dependence (Figure 4), confirming the previous conclusions.

The conclusion on the absence of both the solvation of ion pairs by nonpolar solvents and their specific solvation in binary solvents can also be valid for other compounds. This generalization can be supported by the linear nature of ε'_{max} *vs.* ε'_{max}(MPzI) dependences for different compounds in solutions of identical compositions (Figure 6). On the other hand, the dependences of the ε'_{max}(MQI) on *N* are similar in all systems studied (Figure 7); this makes it possible to extend the conclusion to all acetone–nonpolar solvent systems. Surprisingly, such dependences were found to be different at high concentrations of nonpolar solvents, where ε'_{max} reaches its highest values (Figure 7). It was noted previously[10] that the solvate-separated ion pair–contact ion pair transition makes the main contribution to a change in ε_{max} with changing the composition of binary solutions. It is believed,[10] that in solvents with $D < 7$ almost all ion pairs are the contact ones and a solvent does not play a significant role in their formation. Therefore, the experimental values of ε_{max} for ion pairs in different slightly polar solvents with $D < 7$ are close to each

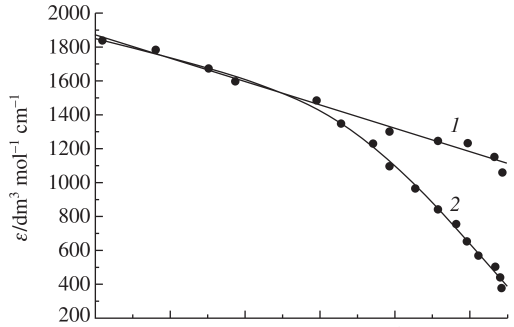

Figure 4 Dependence of the (*1*) true and (*2*) apparent extinction coefficients of MPz^+,I^- on the OSCT band maximum in the acetone–CCl_4 system.

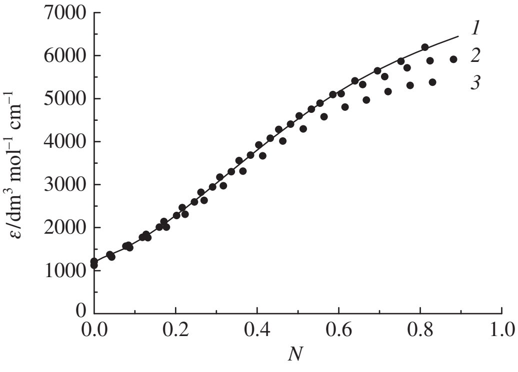

Figure 7 Dependence of the apparent extinction coefficients of MQ^+,I^- on the mole fraction of a nonpolar solvent in the (*1*) acetone–CCl_4, (*2*) acetone–benzene and (*3*) acetone–dioxane systems.

other. In all our systems, the values of $\varepsilon'_{\max}$ increased with N at $D < 7$ (Figure 7). The values of $\varepsilon_{\max}$ in these solutions are higher than those in analogous solutions in slightly polar individual solvents, *e.g.*, chloroform[8] ($D = 4.86$). The extrapolation to an individual nonpolar solvent leads to substantially different $\varepsilon'_{\max}(\mathrm{MQ}^+,\mathrm{I}^-)$ values: 5900, 6300 and 6750 dm^3 mol^{-1} cm^{-1} for dioxane, benzene and $\mathrm{CCl_4}$, respectively. This cannot be due to aggregation of ion pairs because the $\varepsilon'_{\max}$ of the iodides of N-heterocyclic cations are independent of the degree of aggregation.[8] The three solvents used in this work have almost the same values of D. However, the dependences $D(N)$ for their binary solutions with acetone are significantly different.[11] In this case, the order of decreasing D in the binary solutions with the same amount of acetone in the system[11] is consistent with the corresponding increase in $\varepsilon'_{\max}(\mathrm{MQ}^+,\mathrm{I}^-)$ over the entire range of N. This allows one to conclude that processes related to changes in D are responsible for differences in $\varepsilon'_{\max}$, however, no direct impact of the solvent molecules was observed. Taking into account the non-sphericity of N-heterocyclic compounds, the reorientation of ions in the contact ion pairs seems to be responsible for the changes in the extinction coefficients. Both the Coulomb interaction of ions and the interaction of ions with the formation of the C–H···I hydrogen bond can stabilize the ion pair. In this case, the Coulomb energy depends on D to a greater extent. We calculated[‡‡] the energies of four possible geometric isomers of the $\mathrm{MPz}^+,\mathrm{I}^-$ ion pairs, which were detected[12] in $\mathrm{MPzI{\cdot}0.5\,I_2}$ at different D (Figure 8, Table 1). Based on the found energies of isomerization, we calculated the equilibrium distribution of the geometric forms of model ion pairs at 298 K neglecting the entropy component of processes. At $D = 1$, contact ion pairs almost completely (99%) occur in the most stable form, where the iodide anion is located above the π system of the pyrazine ring. This form is responsible for the appearance of OSCT bands in the visible range of the spectrum.[1] At $D = 10$, the fraction of such ion pairs in an equilibrium was only 80% of the total number of ion pairs; therefore, $\varepsilon'_{\max}$ can undergo 20% decrease upon transfer to a solvent with a greater dielectric constant; this was observed experimentally.

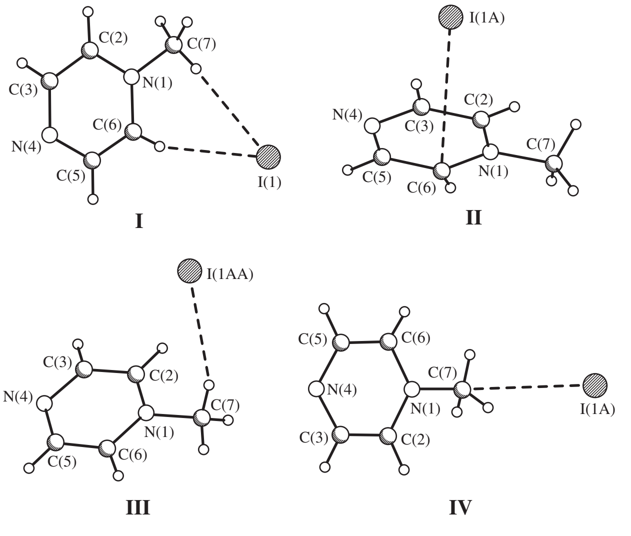

Figure 8 Possible geometric isomers of the $\mathrm{MPz}^+,\mathrm{I}^-$ ion pairs.

Table 1 Relative energies (hartree) of the isomers of MPzI ion pairs.

Ion pair isomer[8]	*D*		
	1	2.024	10
I	0.0091	0.0074	0.0031
II	0	0	0
III	0.0043	0.0032	0.0015
IV	0.0148	0.0126	0.0058

Thus, an increase in the mole fraction of a nonpolar solvent results in the decrease in the $\nu_{\max}$ and an increase in the $\varepsilon_{\max}$. The latter depend not only on the solution composition but also on D. The discovered phenomenon is explained based on the reorientation of ions in the contact ion pairs.

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[‡‡] The quantum-chemical calculations of the isolated model ion pairs without geometry optimization were performed with the use of the Gaussian 09[13] software and the B97D functional.[14] The POL[15] and 6-311+G** basis sets were chosen for the iodine atom and all of the other atoms, respectively.