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Strong negative synergism of ion pair extinction coefficients in chloroform–acetone and methylene dichloride–acetone mixtures

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The heteroselective preferential solvation of the iodides of N-heterocyclic aromatic cations in acetone–chloroalkane (chloroform and dichloromethane) binary mixtures results in not only a shift in the maxima of outer-sphere charge transfer absorption bands but also a considerable decrease in the molar extinction coefficients of ion pairs.

Preferential solvation in binary solvent mixtures is of considerable interest.[1–5] Studies on solvatochromic charge transfer bands in betaine dyes and ionic compounds formed by N-heterocyclic aromatic cations allowed the concept of solvent–solvent and solvent–solvate interactions to be expanded considerably.[6–10] A strong short-wave shift of the charge transfer bands of betaine dyes was observed in the mixtures of chloroform with solvents that are hydrogen bond acceptors (acetone, dimethyl sulfoxide, acetonitrile, *etc.*).[11] The greatest shift of the charge transfer band maximum was observed for mixtures with a 1:1 molar ratio between the solvents. The frequency corresponding to a dye charge transfer band maximum was higher than that in each individual solvent. This fact allowed Testoni *et al.*[11] to conclude that betaine dyes in a mixed solvent are preferentially solvated by the complex of chloroform and a co-solvent formed by hydrogen bonds. Ionic compounds colored due to outer-sphere charge transfer (OSCT) bands were not previously studied in such mixed solvents. Here, we studied the solvation of ionic compounds, *viz.*, the iodides of N-heterocyclic aromatic cations [1-methylpyrazinium (MPz^+) and 1-methylquinoxalinium (MQ^+)], in acetone–chloroform and acetone–dichloromethane binary mixtures by electronic absorption[†] and ^{1}H NMR[‡] spectroscopy.

In pure acetone, dichloromethane and chloroform, MQI in a concentration of 5×10^{-4} mol dm^{-3} displays OSCT bands at 19400 cm^{-1}. In dichloromethane and chloroform, the position of the band maximum depends on the concentration of the dissolved compound. Previously,[12] we found that the observed small shifts in the frequencies corresponding to the charge transfer band maxima are related to the aggregation of iodides of N-heterocyclic aromatic complexes as their solutions in low-polar solvents are concentrated.

In acetone–chloroform and acetone–dichloromethane mixtures with a molar ratio of 1:1 under conditions corresponding to nearly total absence of ion pair aggregation, the OSCT bands of 5×10^{-4} mol dm^{-3} MQI are recorded at 20400 and 19800 cm^{-1}, respectively [Figure 1(*a*)]. Mixing was accompanied by a considerable decrease in the color intensity. The greatest deviation of the apparent molar extinction coefficients in the maxima of OSCT absorption bands (ε'_{max}) from the expected values in an ideal solution (with correction for a volume change upon mixing[13]) is observed for the acetone–chloroform mixture near a 1:1 molar ratio; it amounts to 1400 dm^3 mol^{-1} cm^{-1} [Figure 1(*b*)]. As a result, in acetone–chloroform mixtures containing 15–20 mol% chloroform, the minimum apparent extinction coefficient that is about one-third smaller than that for the solution in acetone was observed. This effect was also detected in the acetone–dichloromethane mixture, but it was much less pronounced. A similar situation took place for methylpyrazinium iodide. Using the approach reported by Hemmes *et al.*,[14] the thermodynamic stability constants of ion pairs and the true molar extinction coefficients (ε_{max}) were determined from the concentration plots of absorption of MPz^+, I^- ion pairs in the mixed solvents. The plots of the logarithm of MPz^+, I^- ion pair stability constant in acetone–chloroform and acetone–dichloromethane mixtures *versus* the inverse dielectric constant of the solvent[15,16] (Figure 2; data from ref. 16 were converted to $T = 298$ K) are linear and nearly coincide. This allows us to conclude that (1) the molar extinction coefficients are more sensitive to changes in the ion pair geometry than the stability constants, and (2) a negative synergism is characteristic of molar extinction coefficients in mixed solutions. We found that for MPz^+, I^-, $\varepsilon_{max} = 870$ dm^{-3} mol^{-1} cm^{-1} in pure acetone, $\varepsilon_{max} = 700$ dm^{-3} mol^{-1} cm^{-1} in the solution containing 20 mol% chloroform and $\varepsilon_{max} = 1822$ dm^{-3} mol^{-1} cm^{-1} in pure chloroform. The positive deviations of the frequencies corresponding to the OSCT band maxima in acetone–dichloromethane mixture from the values expected for ideal non-specific solvation and the negative deviations of the apparent molar extinction coefficients

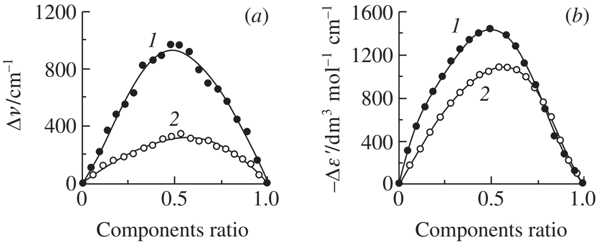

Figure 1 Plots of (*a*) positive deviations of the frequencies of OSCT band maxima for MQ^+, I^- from the values expected for ideal solvation and (*b*) negative deviations of apparent extinction coefficients in (*1*) acetone–chloroform and (*2*) acetone–dichloromethane mixtures *versus* the molar fraction of the respective chloroalkane.

[†] Electronic absorption spectra in the range of 300–700 nm were recorded with a Specord 50PC spectrophotometer at 298 K in 1 cm quartz cells.

[‡] ^{1}H NMR spectra were recorded with a Bruker Avance-III instrument at a working frequency of 600.31 MHz at 303 K at the NMR Research Centre of the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences.

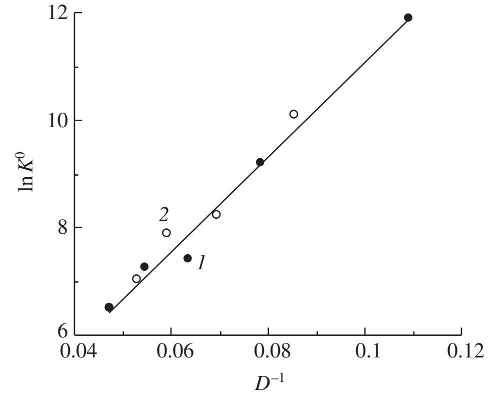

Figure 2 Plot of the logarithm of stability constant of MPz^+, I^- ion pair in (*1*) acetone–chloroform and (*2*) acetone–dichloromethane mixtures *vs.* the inverse dielectric constant of the solvent.

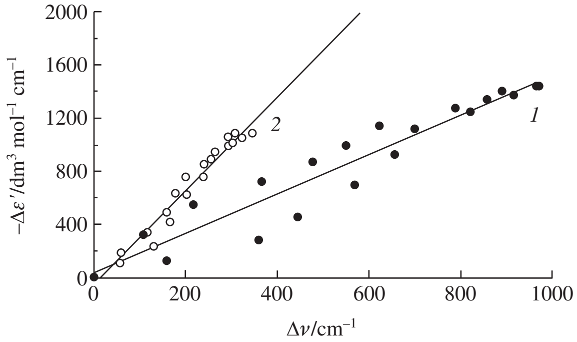

Figure 3 Relationship between the positive deviation of the frequencies of OSCT band maxima and negative deviation of apparent extinction coefficients of MQ^+, I^- from the values expected for ideal solvation in (*1*) acetone–chloroform and (*2*) acetone–dichloromethane mixtures.

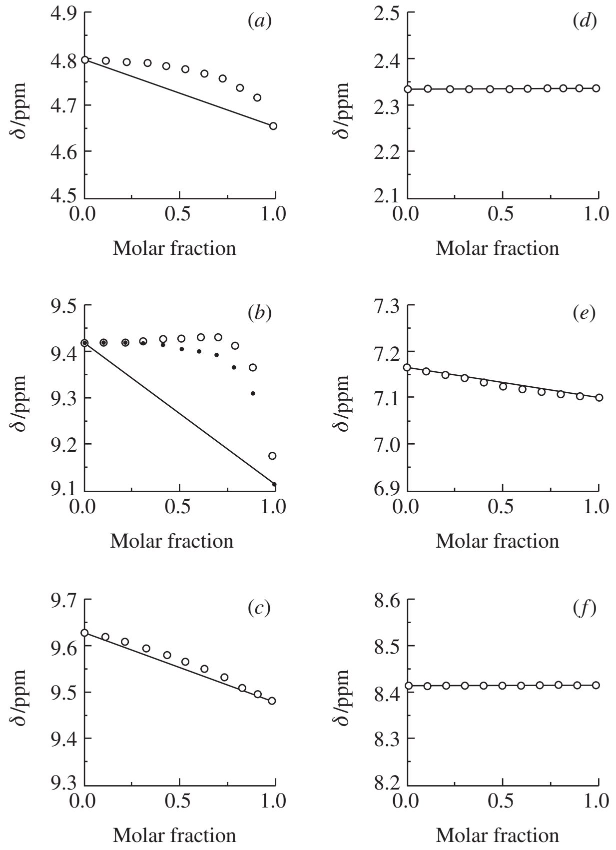

Figure 4 ^{1}H NMR chemical shifts in dichloromethane–acetone mixtures *vs.* the molar fraction of dichloromethane: (*a*)–(*c*) 1-methylpyrazinium iodide and (*d*)–(*f*) 4-methylpyridine. Small dots indicate the values corrected for the aggregation of ion pairs.[12]

of MQ^+, I^- are related almost linearly (Figure 3). A considerable deviation from linearity in acetone–chloroform is primarily due to the aggregation of the dissolved compound in chloroform and acetone–chloroform with a low acetone content. It was previously shown[12] that the changes in the positions of OSCT bands in the case of aggregation do not change the apparent extinction coefficients.

The observed decrease in the extinction coefficients allowed us to conclude that the distance between the interacting ions increases when ion pairs are formed in mixed solvents in comparison with that in the pure solvents. The geometry of the light-absorbing ion pair can change due to both ion pair solvation by a complex formed from a chloroalkane and acetone *via* hydrogen bonds and heteroselective solvation which involves the preferential solvation of cation and anion by different solvents. In order to determine the mechanism of MPzI solvation, we studied the ^{1}H NMR spectra of MPzI in dichloromethane–acetone mixtures [Figure 4(*a*)–(*c*)]. Dichloromethane was chosen because the solubility of MPzI in it is higher and the aggregation of MPzI accompanied by a considerable shift of signals of the protons involved in it[12] is less pronounced in this solvent.

According to Figure 4, all protons of 1-methylpyrazinium in acetone–dichloromethane mixtures are preferentially solvated by acetone. In a 1:1 mixture, the protons of MPz^+ are solvated with acetone by 88% (N–Me), 96% (Pz; 2,6-H) and 66% (Pz; 3,5-H). The pyrazine protons located at the 2,6-positions are solvated with acetone to the highest extent. Previously,[17] it was noted that these protons in 1-ethylpyridinium derivatives are most sensitive to changes in the solvent composition. Note that, according to ^{1}H NMR data, the preferential solvation of chloroform protons with acetone is less pronounced (58% at a 1:1 molar ratio between the solvents) than that of MPz^+ protons, while the preferential solvation of dichloromethane protons with acetone is almost not observed.

Thus, the equatorial plane of the pyrazine ring and the methyl group in MPz^+ are preferentially solvated with acetone. The negatively charged iodide ion is located on one side of the ring of the cation that is a part of the ion pair, in an axial position.[17] Most probably, the π-system of the cation on the other side of the ring is preferentially solvated by the carbonyl moieties of acetone that carry a small negative charge. In acetone–chloroform mixtures, halide anions contained in the ion pair are preferentially solvated by chloroform,[19] which forms weak complexes with them.[20] As a result, the MPz^+, I^- ion pair in the ground state is solvated heteroselectively. Apparently, the solvation of the cation and anion with different solvents results in an increase in the distance between the ions in the ion pair.

The observed increase in the energy of OSCT bands in mixed solvents in comparison with the values in the pure solvents is mainly due to the re-solvation of radicals on transition from the ground state to the excited state. A pair of radicals is formed during electron transfer in the ion pair; these are solvated in the excited state in the same way as the ions in the ion pair. A halide radical in the ground state, unlike a halide ion, is not preferentially solvated with one of the solvents in acetone–chloroform mixtures.[19] To simulate the solvation in the ground state of the MPz^+ cation one-electron reduction product, we studied the possibility of preferential solvation of 4-methylpyridine, a compound that is isoelectronic to the MPz^+ cation. According to Figure 4(*d*)–(*f*), there is no specific solvation for two types of protons in 4-methylpyridine, whereas protons of the third type (Py) are slightly more strongly solvated by chloroform. The above allows us to believe that the radical pair in the ground state is solvated non-specifically. Taking into account that the strongest short-wave shift of OSCT bands was observed for the mixtures of chloroform and dichloromethane with acetone in a 1:1 molar ratio, it can be assumed that the solvation of an ion pair involves redistribution of the solvent, and in general, the MPz^+,I^- ion pair that is not charged as a whole is solvated non-specifically, unlike its constituents.

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