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MANIFESTATION OF DIPOLE-DIPOLE INTERACTION IN THE INFRARED SPECTRUM OF SOLUTIONS OF TRIALKYLAMMONIUM SALTS

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An important contribution to the interaction of polar molecules is made by the interaction of dipoles, which is detected in measurements of various physicochemical properties, such as, for example, mutual solubility, dielectric polarization, lowering of the melting point of a solution, heat of mixing, etc. The manifestations of dipole-dipole interaction in vibrational spectra, however, have still been poorly studied, although the spectroscopic method could provide new possibilities in the study both of the thermodynamic properties of associations of dipolar molecules and of their structure. In work ([1]) an attempt was made to interpret the continuous frequency shift in the combination-scattering spectrum upon decreasing the concentration of dipolar molecules in inert solvents in terms of dipole-dipole interaction, and the energy of this interaction was determined for ketones ([2]). A considerable increase in the integral intensity of the νCN band in the infrared spectrum with increasing concentration of nitriles in inert solvents was likewise interpreted as a manifestation of dipole-dipole interaction ([3]). Unfortunately, the form of the concentration dependence of the frequency and intensity of bands in the spectra of solutions is determined by a whole series of factors ([4]), so that it is extremely difficult to single out from the continuous frequency shift or from the change in band intensity the part determined by dipole-dipole association. Recently ([5]) it was shown that in the vibrational spectra of liquids with large dipole moments of the molecules (nitriles) there are broad absorption bands in the region 50-150 cm^{-1}. These bands were attributed to vibrations of dipolar molecules relative to one another.

In the present work an attempt was made to detect, in infrared spectra, manifestations of dipole-dipole interaction between molecules of trialkylammonium salts R_3NHA ($R = C_8H_{17}, C_{10}H_{21}$; $A = Cl^-, Br^-$), dissolved in inactive solvents. In such solvents, even at very low salt concentrations, dissociation into ions is practically absent ([6],[7]). Cryoscopic ([6]) and dielectric ([7]) measurements, as well as extraction data ([8],[9]), convincingly show that in solutions of ammonium salts

Fig. 1 and Fig. 2: absorption spectra

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there is strong association of their molecules, apparently due to dipole–dipole interactions. A detailed investigation of the infrared spectra of solutions of tri- and dialkylammonium salts (^{10},^{11}) shows that in the molecules of these salts there is a strong hydrogen bond between the NH group of the cation and the anion, so that the stretching-vibration band νNH of trialkylammonium chloride and bromide lies at 2400 and 2550 cm^{-1}. Since it could be assumed that, upon formation of a dipolar complex, the strength of the hydrogen bond would change, we investigated the absorption of solutions in this region of the spectrum. The work was carried out on

spectrometer IKS-12 with a LiF prism, equipped with an optico-acoustic receiver OAP-1, with modulation of the light beam and AC amplification.

Figure 1 shows the absorption spectra of solutions of trioctylammonium chloride in CCl_4 as the concentration is varied from 0.1 to 0.001 mol/l. It is seen that a decrease in the salt concentration is accompanied by a decrease in the intensity of the 2400 cm^{-1} band, which apparently has structure, and by the appearance and growth of the intensity of the 2050 cm^{-1} band. The same picture is also observed in the spectra of solutions of tridecylammonium bromide in CCl_4, in which the frequencies of the νNH stretching-vibration bands have values of 2500 and

Fig. 1. Spectra of solutions of $(C_8H_{17})_3NHCl$ in CCl_4 at concentrations (in mol/l): 1 –0.001; 2 –0.004; 3 –0.016; 4 –0.048; 5 –0.096

Fig. 2. Spectra of a 0.0048 mol/l solution of $(C_8H_{17})_3NHCl$ in CCl_4 at temperatures: +6° (1), +22° (2), and −10° (3)

2300 cm^{-1}. Changing the temperature of the solution (these measurements were carried out in the cell described in (^{12})) from −10 to +60° leads to a weakening of the high-frequency band and strengthening of the low-frequency band, although the shape of the high-frequency band at −10° differs noticeably from the shape of this band at room temperature and at higher solution concentration (Fig. 2). All temperature changes are reversible in character.

The facts presented indicate the existence in the solution of an equilibrium between different molecular forms such that, on going from one form to another, the frequency of the $\nu NH \cdots A$ band changes discretely. Taking into account the results of physicochemical studies of such solutions, it is natural to assume that the cause of the observed changes in the spectrum upon changes in concentration and temperature is association of trialkylammonium salt molecules. Thus, the low-frequency νNH band belongs to monomeric salt molecules, while the high-frequency band belongs to dimeric and, possibly, polymeric forms of more complex composition; the change in the intensity of these bands with concen-

Fig. 3 and Fig. 4 spectra

Figure 2: Fig. 3 and Fig. 4 spectra

tration and temperature is due to a shift of the monomer—polymer equilibrium. The complex structure of the high-frequency band, the noticeable shift of its maximum upon changing concentration—probably caused by redistribution of intensity among the individual components of this band—and the peculiar change in the shape of the band upon changing temperature confirm the assumption of the existence of associates more complex than dimers. We emphasize that in the spectrum of solid trioctylammonium chloride (a layer of about 10 μ, deposited from the melt onto a CaF_2 plate) there is one band with a maximum in the region of 2450 cm^{-1}, strongly broadened toward high frequencies.

The temperature dependence of the band intensities was used to estimate the energy of the complex formed. In processing the data, assumptions were made that a single monomer dimer equilibrium exists in the system and that the absorption coefficients of the monomer and dimer bands are independent of temperature. In coordinates $\ln(D_\mathrm{d}/D_\mathrm{m}^2)$, $1/T$ ($D_\mathrm{m,d}$ are the optical densities at the maxima of the monomer and dimer bands), the points lay well on a straight line, from the slope of which the dissociation energy of trioctylammonium chloride was determined, equal to 6 kcal/mol.

Since the most probable mechanism of association of salt molecules is dipole-dipole interaction, it was expedient to study the influence of the dipole moment of partner molecules on the magnitude of the shift of the νNH band upon formation of associates. For this purpose we attempted to obtain spectra of mixed complexes of trialkylammonium halides with other polar molecules. Spectra were obtained for 0.0048 mol/l solutions in CCl_4 of trioctylammonium chloride and tridecylammonium bromide with addition, respectively, of tetradecylammonium chloride and bromide, which have a dipole moment of 12-15 D (Fig. 3). It is seen from the spectra that already at a concentration ratio of the molecules of the tertiary and quaternary salts of 1 : 1, a band appears in the high-frequency region which rapidly increases in intensity with increasing concentration of the quaternary salt at the expense of the low-frequency

Fig. 3. Spectra of a 0.0048 mol/l solution of $(C_8H_{17})_3NHCl$ in CCl_4, containing $(C_{10}H_{21})_4NCl$ at concentrations (in mol/l): 1 —0; 2 —0.005; 3 —0.01; 4 —0.024; 5 —0.05

Fig. 4. Spectra of a 0.0075 mol/l solution of $(C_{10}H_{21})_3NHCl$ in CCl_4 (1) and in CCl_4 containing 0.75 mol/l acetone (2) and 0.75 mol/l acetonitrile (3)

bands, and at a concentration ratio of 1 : 10 the low-frequency bands (monomer and dimer of the trialkylammonium salts) have negligibly small intensity. The new band is shifted to the high-frequency region relative to the dimer band by $\sim$ 200 cm^{-1} and has a distinctly expressed structure. This band may reasonably be assigned to associates of trialkylammonium halide molecules with molecules of the corresponding tetraalkylammonium halides. Addition to a solution of tridecylammonium chloride of substances whose molecules have a dipole moment smaller than the dipole moment of the salt molecule—acetonitrile ($\mu = 3.8$ D) and acetone ($\mu = 2.8$ D)—leads to a change in the shape of the νNH ... A band, and at high concentrations of the dipolar molecules added to the solution (1 : 100), the band becomes rather simple and its maximum is located between the maxima of the monomer and dimer of the salt, at 2250 cm^{-1} upon addition of acetonitrile and 2150 cm^{-1} upon addition of acetone (Fig. 4). If, as may be supposed, these bands belong to salt molecules forming with the molecules of the added substance a dipole-dipole complex, then an interesting regularity is found: the larger the dipole moment of the molecule interacting with the trialkylammonium chloride molecule, the greater the shift to high frequencies experienced by the νNH band of the salt monomer upon formation of the complex. This shift increases in the series: acetone, acetonitrile, tridecylammonium chloride (dimer), tetradecylammonium chloride. Such a regularity serves as confirmation of the proposed explanation of the observed picture.

The unusual spectroscopic manifestation of association of trialkylammonium salts in solutions, consisting in an increase in the frequency of the νNH ... HAL vibration upon formation of an associate, finds a simple interpretation on the basis of ideas about the electrostatic interaction of dipoles. Namely, upon formation of a dipole-dipole complex, polarization of the anion occurs in the field of the cation of the neighboring molecule, and the hydrogen bond NH ... HAL is weakened.

On the basis of the spectroscopic material described, it is hardly possible to construct a model of the dimer; however, measurements of the dielectric pro-

permittivity (7) show that in similar systems (solutions of tetraalkylammonium salts in benzene) the average dipole moment of the salt molecule increases as the concentration decreases. This means that the dipole moment of the dimer is smaller than that of the monomer and, consequently, it may be thought that the dimer has the form of a quadrupole with antiparallel dipoles. In work (7) it was established that the degree of association of quaternary ammonium salts in benzene is close to 0.5 at a salt concentration of 0.0002 mole/liter. Our measurement of the integrated intensity of the total νNH band of trioctylammonium chloride in CCl_4 shows that this quantity changes hardly at all with concentration, so that the integrated absorption coefficients of the νNH ... Cl bands of the monomer and dimer of the salt differ only slightly. Since the widths of the monomer and dimer bands are close, the ratio of the optical densities at the maxima of the monomer and dimer bands can be used as a measure of the ratio of their concentrations. From Fig. 2 it can be seen that a degree of association of 0.5 is attained at ~ 0.005 mole/liter. This result is not in contradiction with the data of (7), since the dipole moment of trialkylammonium salt molecules is smaller than that of tetraalkylammonium salts.

Our comparison of the spectra of solutions of tridecylammonium chloride in CCl_4 and in benzene shows that the positions of the monomer and dimer bands in these solvents are the same, but that a degree of dissociation of 0.5 is reached in benzene at 0.02-0.04 mole/liter, i.e., at somewhat higher concentrations than in CCl_4. Similar results were obtained in work (6), whose authors, by the cryoscopic method, found that a degree of dissociation of 0.5 for trihexylammonium nitrate in benzene solution is reached at a concentration of ~ 0.05 mole/liter.

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CITED LITERATURE

1. H. Wolf, *Zs. Elektrochem.*, **56**, 965 (1952).
2. K. Schäfer, H. Wolf, *Zs. Elektrochem.*, **57**, 38 (1953).
3. E. L. Zhukova, *Optics and Spectroscopy*, **4**, 750 (1958).
4. O. P. Girin, N. G. Bakhshiev, *UFN*, **79**, 235 (1963).
5. R. J. Jakobsen, J. W. Brasch, *J. Am. Chem. Soc.*, **86**, 3571 (1964).
6. V. M. Vdovenko, B. Ya. Galin, A. A. Chaikovskii, *Radiokhimiya*, **3**, 448 (1961).
7. K. Range, J. W. Smith, *J. Chem. Soc.*, 1964, 4246.
8. F. F. Kolleman, N. B. Bravaya et al., Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Reports of Foreign Scientists, **7**, 1959, p. 352.
9. W. Smulek, S. Siekierski, *J. Inorg. and Nucl. Chem.*, **24**, 1651 (1962).
10. V. M. Vdovenko, A. A. Lipovskii et al., *Ukr. Fiz. Zhurn.*, **9**, 453 (1964).
11. V. M. Vdovenko, A. A. Lipovskii, S. A. Nikitina, *Radiokhimiya*, **6**, 56 (1964).
12. D. N. Shchepkin, *Optics and Spectroscopy*, **19**, No. 6 (1965).

Note: Figure translations are in progress. See original paper for figures.