SPECTROSCOPIC DETERMINATION OF DIPOLE-DIPOLE INTERACTION IN SOLUTIONS OF TRIOCTYLAMMONIUM HALIDES

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Dimerization energies of trioctylammonium halides in carbon tetrachloride solution, associated as a result of dipole-dipole interaction, were calculated from the infrared absorption spectra. The values obtained were 5, 4, and 1.5 kcal/mole for the chloride, bromide, and iodide, respectively. The calculation showed that the dimers of these salts are contact dimers.

Table 1

Frequencies ν(NH) for Monomers and Associates of Trioctylammonium Halides, cm^{-1}

Compound	ν_m(NH)	ν_d(NH)	$\Delta\nu$	ν'_{assoc}(NH)	ν''_{assoc}(NH)
$(C_8H_{17})_3NHCl$	2050	2300	250	2375	2425
$(C_8H_{17})_3NHBr$	2225	2450	225	2525	2575
$(C_8H_{17})_3NHI$	2415	2510	95	2560	—

The qualitative spectroscopic manifestations of association in molecules of trialkylammonium salts in carbon tetrachloride and benzene solutions were described in [1, 2]. By analysis of the results it was possible to interpret the interaction of alkylammonium halides both with themselves and with other dipole molecules, leading to the formation of intermolecular complexes, as interactions of a dipole-dipole nature. During formation of the complex, the ν(NH) band is displaced in a discrete manner to the high-frequency region, and at a certain range of concentrations it is possible to observe simultaneous existence of the bands of monomeric molecules and associates, where the equilibrium content of these forms depends on the initial concentration of the salt. The band of the associated molecules has a complex form, which depends on the concentration of the solution. The ν(ND) band of the deuterated compounds behaves similarly [3]. Together with results from investigations of electrolytes in solvents with low dielectric constant [4], this makes it possible to speak of the existence in the solution of associates with various degrees of complexity (dimers, trimers, etc.). Variation in the temperature of the solution leads to a redistribution of intensity between these bands, which corresponds to a transition from one type of complex to another. The purpose of the present work was to measure the formation energy of the dipole—dipole complex between trioctylammonium halide molecules from the temperature dependence of the ν(NH) band intensities of the monomer and the complex.

The spectra of solutions of trioctylammonium chloride, bromide, and iodide in carbon tetrachloride at concentrations between 0.1 and 0.001 mole/l were obtained at temperatures between −10 and 60° C on an IKS-12 spectrophotometer with a lithium fluoride prism and an OAP-1 receiver in the 1800–2800 cm^{-1} region. Figure 1 shows the spectra of trioctylammonium bromide solutions.

The enthalpy value ΔH was calculated from the van't Hoff equation,

$$-\ln K = \ln A - \frac{\Delta H}{R}\frac{1}{T}.$$

Assuming that the Lambert-Beer law is satisfied for the bands of the monomers and dimers, the left-hand side of the equation for the monomer-dimer equilibrium can be expressed in experimentally determinable quantities:

$$\ln K = \ln\frac{D_d}{D_m^2} - \ln\frac{\varepsilon_d}{\varepsilon_m^2 d},$$

where D_m and D_d are the optical densities at the maxima of the monomer and dimer bands; ε_m and ε_d are the absorption coefficients of these bands at the respective frequencies; d is the thickness of the layer of solution.

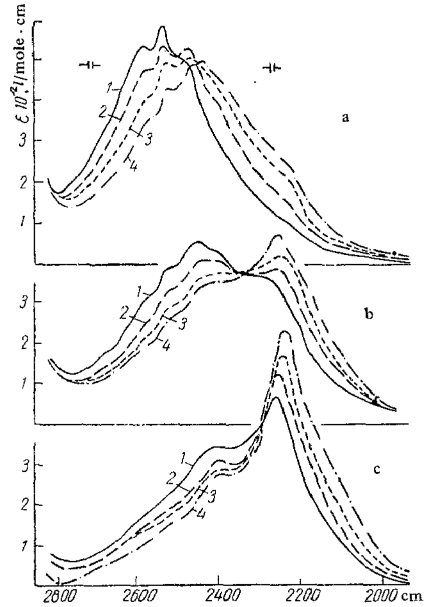

Fig. 1. Spectra of solutions of trioctylammonium bromide in carbon tetrachloride in the ν(NH) region: a) C = 0.049 mole/l; 1) 7° C; 2) 24° C; 3) 38° C; 4) 50° C; b) C = 0.0049 mole/l; 1) 6° C; 2) 14° C; 3) 38° C; 4) 50° C; c) C = 0.001 mole/l; 1) 9° C; 2) 24° C; 3) 38° C; 4) 50° C.

In the spectra of salts at the lowest concentrations which can still be investigated with satisfactory trans-

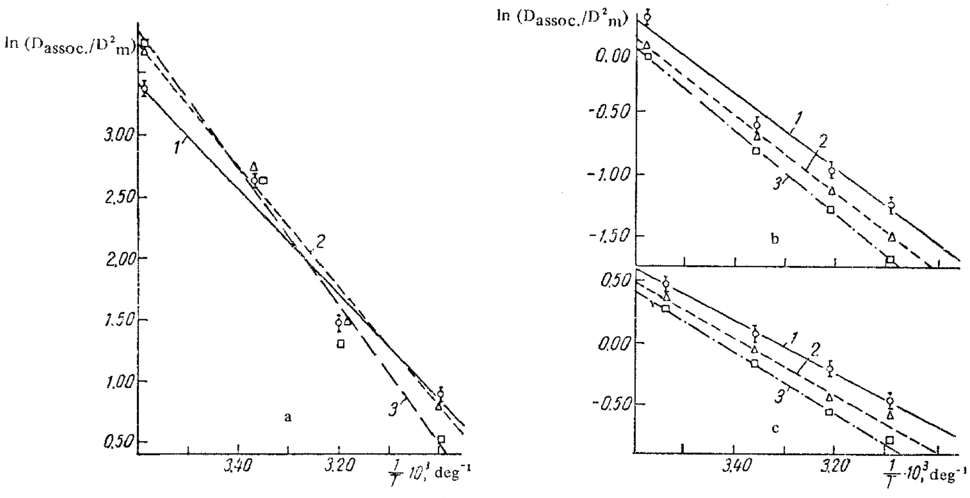

Fig. 2. Dependence of ln (D_d/D^2_m) on 1/T for trioctylammonium bromide: a) C = 0.049 mole/l; 1) $\nu_{assoc.}$ = 2450 cm^{-1}, ΔH = 8.4 kcal/mole; 2) $\nu_{assoc.}$ = = 2525 cm^{-1}, ΔH = 9.6 kcal/mole; 3) $\nu_{assoc.}$ = 2575 cm^{-1}, ΔH = 10.9 kcal/mole. b) C = 0.0049 mole/l: 1) $\nu_{assoc.}$ = 2450 cm^{-1}, ΔH = 5.5 kcal/mole; 2) $\nu_{assoc.}$ = = 2525 cm^{-1}, ΔH = 5.9 kcal/mole; 3) $\nu_{assoc.}$ = 2575 cm^{-1}, ΔH = 6.3 kcal/mole. c) C = 0.001 mole/l: 1) $\nu_{assoc.}$ = 2450 cm^{-1}, ΔH = 4.2 kcal/mole; 2) $\nu_{assoc.}$ = = 2525 cm^{-1}, ΔH = 4.4 kcal/mole; 3) $\nu_{assoc.}$ = 2575 cm^{-1}, ΔH = 4.5 kcal/mole.

parency in the solvent, the optical densities of the bands for the monomer and dimer were comparable in magnitude. It was not, therefore, possible to obtain a sufficiently accurate ε_m value by extrapolation to infinite dilution and consequently to determine ε_d. It was, therefore, necessary to give up determination of the equilibrium constant and, by postulating constancy of ε_m and ε_d in the investigated temperature range, to determine the value of ΔH directly from the equation

$$\ln \frac{D_d}{D^2_m} = \ln A' - \frac{\Delta H}{R}\frac{1}{T}. \qquad (1)$$

Analysis of the results was substantially complicated by overlapping of the bands for the various molecular forms. The most isolated was the band of the monomer, and its position hardly changed with change in the concentration of the solution. The band of the dimer was largely overlapped by the bands of the more complex polymeric forms, so that the frequency of its maximum could only be reliably determined at the lowest concentrations of the salt. The frequencies of the bands for the monomer and the dimer are given in Table 1. The ΔH value was calculated for several cases by graphical separation of the bands. The use of a simplified procedure, in which the optical densities taken directly from the spectrum for the frequencies shown in Table 1 are introduced into Eq. (1), give practically the same value for ΔH. The rest of the analysis was therefore carried out by the simplified procedure without separating the bands. To assess the reliability of the data obtained, ΔH values were also determined by using the optical density values measured at two frequencies in the high-frequency region of the ν(NH) band as D_d in Eq. (1). These frequencies correspond to poorly defined maxima in the broad ν(NH) band and are also given in Table 1 ($\nu'_{assoc.}$ and $\nu''_{assoc.}$).

The first experiments showed that the measured enthalpy value depended strongly on the concentration of the solution and decreased with dilution. By way of an example, Fig. 2 shows the dependence of ln (D_d/D^2_m) on 1/T for trioctylammonium bromide at various concentrations. The points conform closely to straight lines, but the slopes are different. Similar results

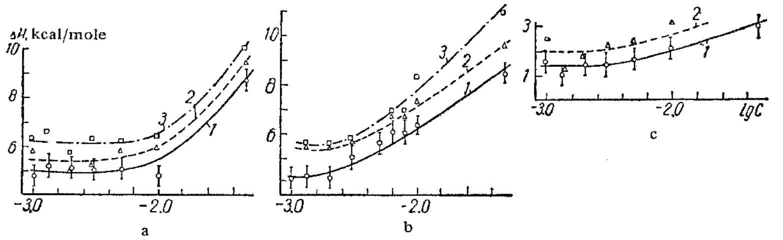

Fig. 3. Dependence of measured ΔH values on concentration of ammonium salt in CCl_4 solution: a) Oct_3NHCl, ν_m = 2050 cm^{-1}: 1) $\nu_{assoc.}$ = 2300 cm^{-1}; 2) $\nu_{assoc.}$ = 2375 cm^{-1}; 3) $\nu_{assoc.}$ = 2425 cm^{-1}. b) Oct_3NHBr, ν_m = 2225 cm^{-1}; 1) $\nu_{assoc.}$ = 2450 cm^{-1}; 2) $\nu_{assoc.}$ = 2525 cm^{-1}; 3) $\nu_{assoc.}$ = 2575 cm^{-1}. c) Oct_3NHI, ν_m = 2415 cm^{-1}: 1) $\nu_{assoc.}$ = 2510 cm^{-1}; 2) $\nu_{assoc.}$ = 2560 cm^{-1}.

were obtained for trioctylammonium chloride and iodide.

The increase in the calculated ΔH value with concentration is doubtless determined by the procedure selected for its experimental determination and evidently arises from an increase in the contribution from the bands of polymeric forms, more complicated than dimers, to the measured optical density at the frequency of the dimer maximum. This contribution decreases with decrease in the concentration of the solution, where the monomer-dimer equilibrium becomes dominant. The true value of the formation energy of the dimer can, therefore, be obtained by extrapolation of the measured ΔH values to infinite dilution.

The results are shown in Fig. 3. At low concentrations the ΔH values become practically constant. The extrapolated values are equal to: $(C_8H_{17})_3NHCl$ 5.0 ± ±0.5 kcal/mole; $(C_8H_{17})_3NHBr$ 4.0 ± 0.5 kcal/mole; $(C_8H_{17})_3NHI$ 1.5 ± 0.5 kcal/mole. The error in the determination of the energy was evaluated from the spread of the ΔH values in the region of low concentrations. These values are close to the ΔH value of 6.5 kcal/mole for dimerization of tetrabutylammonium bromide dissolved in benzene, obtained from dielectric measurements in [5].

Figure 3 also shows ΔH values obtained using measurements of the optical density in the high-frequency part of the ν(NH) band as the D_d value. They were found to be noticeably high, which provides an additional argument in favor of the suggestion that the complex nature of the associated ν(NH) band is due to superposition of bands for polymeric forms of a different composition. The high-frequency shift is greatest with the monomer-dimer transition and decreases on passing from the dimer to more complex aggregates.

It is seen from the results that increase in the radius of the anion in the order Cl^-, Br^-, I^- leads to a decrease in the energy of the dimer, and this is also accompanied by a decrease in the shift of the ν(NH) band for the monomer during formation of the dimer (Table 1). In [4] it was noticed that association of ionic pairs in media with low dielectric constant is greater, the greater the difference between the radii of the anion and cation. Our own results confirm this relationship; the difference in radius between the anion A and cation K decreases from trioctylammonium chloride to the iodide. In fact the crystallographic radii of the halogens are $r_{Cl^-} = 2.16$ Å. $r_{Cl^-} = 1.81$ Å, $r_{I^-} = 2.16$ Å. According to data from [4], the radius of the $(C_4H_9)_4N^+$ cation amounts to 2.3 Å, which is substantially less than the length of the alkyl radicals. This means that the anion in the ion pair penetrates within the framework of the tetrabutylammonium cation, and increase in the length of the alkyl chains should not substantially change the K-A distance. Examination of molecular models leads to a similar conclusion [6]. In the dimer, therefore, the radius r_c of the trioctylammonium cation in the direction of the anion of the adjacent ion pair may have a value of 2.3 Å or more. The radius of the trialkylammonium cation is of course smaller in the direction of the NH...A bond and is equal to 1.74 Å for $(C_4H_9)_3NH^+$ [4].

The enthalpy values obtained were used to evaluate the parameters which determine the geometrical structure of the complex. We will examine a model of the dimer in which the centers of the charges of the monomeric molecules (ion pairs) are disposed in a plane at the corners of a parallelogram. As shown by calculation [7] and electron-diffraction experiment [8], dimers of alkali halides in the gas phase have such a structure. According to measurements of dielectric polarization in solutions of tetraalkylammonium halides in benzene [9], the average dipole moment of the ion pair increases with decrease in the concentration of the solution, and the nature of this dependence allowed the authors in [9] to suppose that the dipole moment of the dimer is zero. These facts confirm the selected model.

We will consider the cycle

$$CCl_4 \quad \varepsilon = 2.24$$

$$\begin{tikzcd}
2K_{gas} + 2A_{gas} \arrow[r, "\Delta H_3"'] & (KA)_{2\,gas} \arrow[dd, "\Delta H_4"] \\
2KA_{gas} \arrow[u, "\Delta H_2"] & \\
2KA_{sol} \arrow[u, "\Delta H_1"] \arrow[r, "\Delta H"'] & (KA)_{2\,sol}
\end{tikzcd}$$

$$\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 \qquad (2)$$

(ΔH is the experimentally determined value.)

According to the theory of ionic interactions in solutions [4], in which the polarization of the ions and medium, and also the forces of repulsions, are taken more or less satisfactorily into consideration,

$$\Delta H_1 = \frac{\mu^2}{R^3_{eff}} \frac{\varepsilon - 1}{2\varepsilon + 1}. \qquad (3)$$

$$\Delta H_2 = 0.9\frac{e^2}{a} + 0.3\frac{e^2}{a^4}(\alpha_K + \alpha_A), \qquad (4)$$

$$\Delta H_3 = 0.9e^2\left(\frac{1}{a} + \frac{1}{a'} - \frac{1}{\sqrt{a^2 + a'^2}}\right) + $$
$$+ 0.3e(\alpha_K + \alpha_A)\left[\sqrt{\frac{1}{a^4} + \frac{1}{a'^4}} - \frac{1}{a^2 + a'^2}\right]^2. \qquad (5)$$

The quadrupole polarization energy ΔH_4 of the medium can be taken as zero. All the ΔH_i values are related to 1 mole of salt. In Eqs. (3)-(5), a is the equilibrium distance R_{KA} in the ion pair KA; a is the equilibrium distance between the centers of the ion pairs in the dimer $(KA)_2$; α_A and α_K are the polarizabilities of the anion and cation; μ is the dipole moment of the ion pair KA; ε is the dielectric constant of the solvent (for CCl_4 ε = 2.24); e is the charge of the electron; R_{eff} is the effective radius of the ion pair. It is possible to obtain a' after substituion of Eqs. (3)-(5) in Eq. (2).

Apart from the original premises of the theory in [4] the following assumptions were made in the calculation: 1) The interionic distances in the Oct_3NHA ion pairs are the same as in $(C_4H_9)_3NHA$; 2) The Oct_3NHA ion pairs are characterized by the same dipole moments as $(C_4H_9)_3NHA$; 3) In the dimer the ions are dis-

Table 2

Interionic Distances in Monomers and Dimers of Trioctylammonium Halides

Compound	a, Å	μ, D	R_{eff}, Å	$\alpha_A+\alpha_K(\mathrm{I})\times$ $\times 10^{24}$ см^3	a'(I), Å	$\alpha_A+\alpha_K(\mathrm{II})\times$ $\times 10^{24}$ см^3	a'(II), Å
$(C_8H_{17})_3NHCl$	3.57	7.17	3.0	35.7	4.3	19.7	4.65
$(C_8H_{17})_3NHBr$	3.70	7.61	3.15	36.8	4.55	20.8	4.9
$(C_8H_{17})_3NHI$	3.94	8.09	3.26	39.1	5.0	23.1	5.5

posed at the corners of a parallelogram with sides of a and a'; 4) The R_{eff} value was determined as the mean radius of the ion pair KA. Table 2 gives the a, μ, $\alpha_K + \alpha_A$, and R_{eff} values used in the calculation and the a' values obtained.

There are no experimental data on the polarizability of trialkylammonium cations. Therefore, following [4], we determined α_K as the sum of the polarizabilities of the groups of atoms which make up the cation, reduced by 33% on account of the presence of unit positive charge (Variant I). In this way, $\alpha_K = 32 \cdot 10^{-24}$ cm^3. In the other variant it was supposed that, roughly speaking, only half of each alkyl chain was subject to the polarizing action of the adjacent ions, while the other half was outside their zone of influence. In this case, $\alpha_K = 16 \cdot 10^{-24}$ cm^3. The α_A values were taken from [10]. Even such a significant change in $\alpha_A + \alpha_K$ has little effect on a'.

The results show that the dipolar dimers are contact dimers. In fact, by using $r_K = 2.3$ Å (in the direction of the adjacent ion pair) and the ionic radii of the anions, we obtain the following values of $a' - (r_K + r_A)$ for the chloride, bromide, and iodide, respectively: 0.2; 0.3; 0.64 Å (Variant I) or 0.54; 0.65; 1.04 Å (Variant II). This is substantially less than the diameter of the carbon tetrachloride molecule, which can be determined as 5.5 Å.

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