Sodium Iodide-Acetone and Zinc Bromide-Acetone Molecular Complexes

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The molecular compound between sodium iodide and acetone, known as NaI·3 acetone, can be used for the purification of acetone. The nature of the bonding, however, has not been made clear. From conductivity measurements, Rosenthal[1] suggested that the molecular compound was dissociated into Na^+ and $(I\cdot 3\ \text{acetone})^-$ in acetone. This may indicate that the compound has an ionic structure as represented by Na^+ $(I\cdot 3\ \text{acetone})^-$. By infrared studies, Slovokhotova[2] reported that acetone molecules had the enol form when sodium iodide was added, but her explanation does not seem to be plausible.

On the other hand, the complex formed by the addition of iodine or lithium perchlorate to acetone is known as the charge transfer complex stabilized by the electron donor-acceptor interaction[3,4]. The sodium compounds of salicylaldehyde and methylsalicylate[5] are also known to be formed by the same interaction between the Na^+ ion and the C-O and C=O groups, respectively. As for the NaI-acetone complex, the charge transfer force may interpret the intermolecular bonding.

The present study has been undertaken to clarify what sort of force gives rise mainly to the intermolecular bonding of the NaI-acetone and $ZnBr_2$-acetone systems.

Experimental

Guaranteed commercial anhydrous sodium iodide and zinc bromide were used without further purification. Sodium perchlorate was obtained by heating $NaClO_4\cdot H_2O$ in an air bath. The anhydrous salts were stored in the dark in a desiccator. Acetone was used after drying over anhydrous sodium sulfate and fractionating. The salts were dissolved into acetone and the thin layers of the solutions were obtained by sandwiching them between polyethylene films. The solid sample was made by cooling with the dry ice-ethanol mixture. The infrared spectra were taken with a Perkin-Elmer Model 112 infrared spectrophotometer in the region 400 cm^{-1}～4000cm^{-1}, using KBr, NaCl, CaF_2 and LiF prisms.

The composition of the complex was determined as follows. The salt was dissolved into acetone at room temperature and its concentration was determined by weighing. When the solution was cooled and the complex was crystallized, an excess of acetone was eliminated by suction and the complex was weighed.

Results and Discussion

The wave numbers of the spectra of the NaI- and $ZnBr_2$-acetone systems are shown in Table I and the curves in Figs. 1—5.

The skeletal vibrations of acetone were influenced noticeably by the addition of the salts, while the other bands were not so affected. Concerning the bands splitting into the two components, one of the components can be attributed to the complex and the other to original acetone. Although the separation of the C=O stretching band in NaI-acetone system

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[1] W. Rosenthal, *Compt. rend.*, **237**, 1537 (1953),

[2] N. A. Slovokhotova, *Zhur. Fiz. Kim.*, **25**, 768 (1951), *Chem. Abstr.*, **46**, 2396h (1952).

[3] H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82**, 1543 (1960).

[4] A. D. E. Pullin and J. McC. Pollock, *Trans. Faraday Soc.*, **54**, 11 (1958).

[5] H. Yamada, This Bulletin, **32**, 1051 (1959).

TABLE I. WAVE NUMBERS OF SPECTRA FOR ACETONE, NaI-ACETONE AND $ZnBr_2$-ACETONE

Acetone (liquid)	NaI-acetone (liquid)	NaI-acetone (solid)	$ZnBr_2$-acetone (liquid)	Assignment*
1717	1709	1708	1697(s)	A_1 C=O stretching
785	789	790	789	A_1 C-C sym. stretching
1215	1233(s)	1236(s)	1236(s)	B_1 C-C antisym. stretching
530	539(s)	540(s)	540(s)	B_1 C-C=O bending
3411	3405	3401	3401	A_1 C=O stretching overtone
1092	1093	1094	1091	
903	906	910	909	

(s) indicates the band having two components and the wave number is the value for the complex component.

* T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **74**, 915 (1953).

could not be observed, the observed band with the shifted maximum is interpreted as the complexed band closely overlapped with the non-complexed one. The fact that the band shifts observed on complex formation are small suggests that the acetone molecules in the complex are slightly perturbed. The directions and amounts of the shifts are similar to those observed for the iodine-acetone[3] and lithium perchlorate-acetone complexes[4]. These shifts may be interpreted as being due to the changes of the force constants of C=O stretching and C-C=O bending vibrations caused by the formation of the complex, similarly as the case of the iodine-acetone or lithium perchlorate-acetone complex[6].

Since the spectrum of the NaI-acetone complex exhibited a similarity to that of the $NaClO_4$-acetone complex except the absorption caused by the ClO_4^- ion, the formation of the salt-acetone complex may be due to the bonding between acetone and the Na^+ or Zn^{2+} ion.

When the NaI-acetone solution was cooled, the needle crystal was obtained. Its composition was 1 : 5 mole ratio. The spectrum of this crystal contained the original acetone bands and was similar to that of the solution. The C-C antisymmetric stretching band is shown in Fig. 2(b). This curve can be divided into the two Lorentz curves with the maxima at 1236 cm^{-1} and at 1215 cm^{-1}. Intensities were calculated from Ramsay's method[7]. It has been shown[3] that, for the iodine-acetone system, this band does not change in intensity on complex formation. The same may be true for this complex. From this property of the band and the fact that the area intensity ratio between the two bands is about 3 : 2, it follows that three acetone molecules are regarded as those of complexed acetone and the other two as those of non-complexed acetone. Probably the Na^+ ion forms the tetracoordinate compound having I^- and three acetone molecules as ligands and the other two acetone molecules will be contained in the crystal without coordinating.

The overtone band of the C=O stretching vibration showed a remarkable change. As shown in Fig. 5, this band became broad and was enhanced very much. By subtracting the two bands at 3520 cm^{-1} and at 3620 cm^{-1} from the observed curve for the NaI-acetone system, the dotted curve was obtained. This may be attributed to the overtone band of C=O stretching vibration and not the OH band, because the similar phenomenon was observed for the overtone band of the C=O stretching vibration of the iodine-acetone complex.

Relatively large shifts were observed for the skeletal vibrations belonging to the B_1 type. This differs from the phenomenon observed for the iodine-acetone complex and is probably due to the fact that the mole ratio of the NaI-acetone complex is 1 : 3 even in solution, while that of the iodine-acetone is 1 :1.

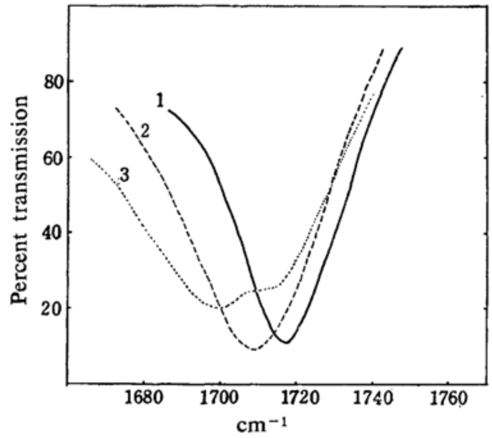

Fig. 1. C=O stretching bands for NaI- and $ZnBr_2$-acetone systems.
1. Pure acetone
2. NaI-acetone solution (saturated)
3. $ZnBr_2$-acetone solution (saturated)

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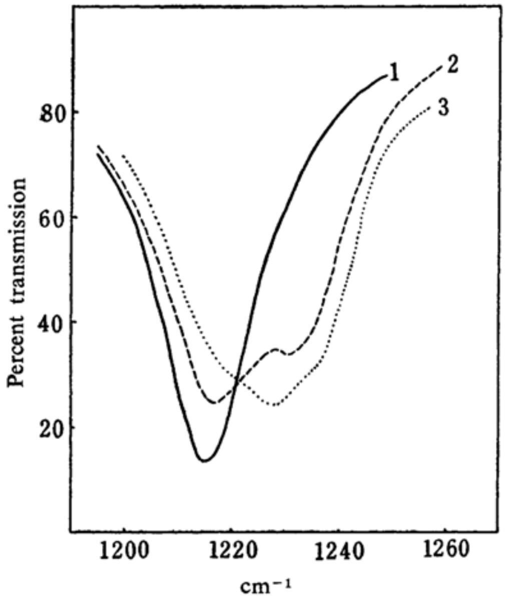
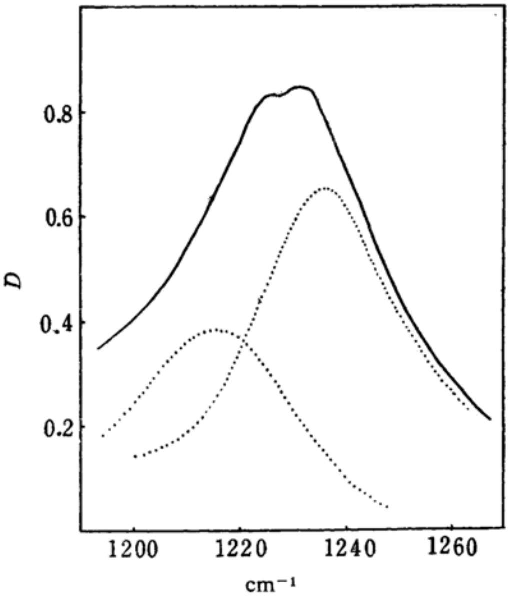
[6] K. Kozima and H. Yamada, unpublished.

[7] D A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1956).



(a) Liquid state
1. Pure acetone
2. NaI-acetone in 1 : 10 mole ratio
3. NaI-acetone in 1 : 6 mole ratio



(b) Solid state
Unbroken curve is observed for NaI-acetone solid in 1 : 5 mole ratio. Dotted curves are Lorentz curves.

Fig. 2. C–C antisym. stretching bands of NaI-acetone system.

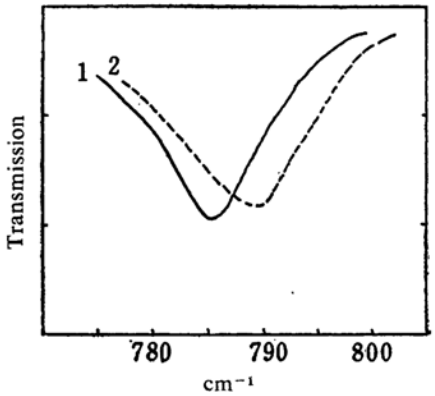


Fig. 3. C–C sym. stretching bands.
1. Pure acetone
2. NaI-acetone solution (saturated)

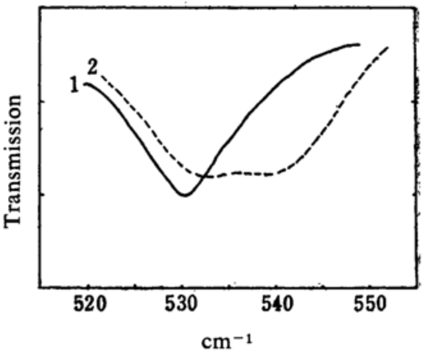


Fig. 4. C–C=O bending bands.
1. Pure acetone
2. NaI-acetone solution (saturated)

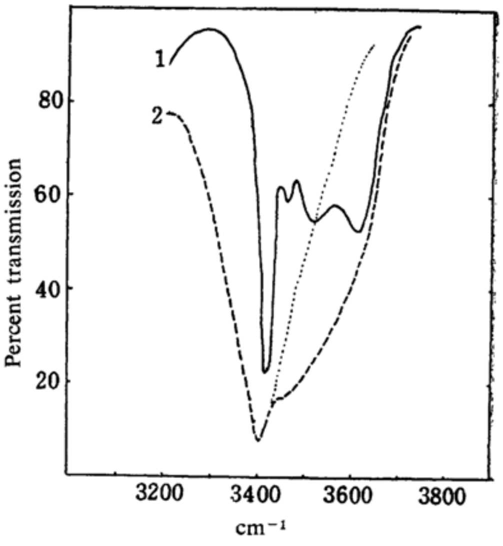
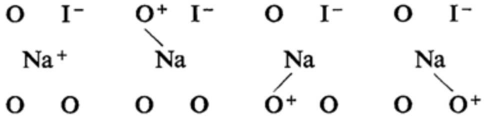


Fig. 5. Overtone bands of C=O stretching vibration.
1. Pure acetone (0.1 mm. cell)
2. NaI-acetone solution (0.1 mm. cell)

From the fact that the frequencies of the acetone band maxima do not vary continuously with salt concentration but the bands show the contour of two components and from the fact that observed shifts are similar to those for the iodine-acetone charge transfer complex, it may be concluded that the formation of the complex is due to the coordination of the lone pair electrons of oxygen atom to the Na^+ or Zn^{2+} ion. No evidence for the enolization of acetone was found. As for the intermolecular bonding of these complexes, the charge transfer force, besides ion-dipole interaction etc., should be taken into account. The wave function of the normal state for the complex may be written by

$$\Psi_N = a\phi_A + b(\phi_{BI} + \phi_{BII} + \phi_{BIII}).$$

Here ϕ_A expresses the no-bond structure and ϕ_{BI}, ϕ_{BII} and ϕ_{BIII} following dative structures.



ϕ_A ϕ_{BI} ϕ_{BII} ϕ_{BIII}

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