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Dipole Moment of the Triethylamine-Iodine Complex

Akinobu FUNATSU[*1] and Koichi TOYODA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto

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One of the present authors[1] has recently reported that his experimental measurements of the dipole moment of the triethylamine-iodine (Et_3N-I_2) complex have confirmed the value previously reported by Tsubomura and Nagakura[2] in a dioxane solution. The very large value, 12D, for the experimental dipole moment of this complex in a dioxane solution, combined with the ultraviolet spectra, suggests very strongly that the predominant species in this solution is an ion pair such as triethylamine hydroiodide ($Et_3N \cdot HI$). Kobinata and Nagakura[3] measured the dipole moment of the $EtNH_2$-I_2 and Et_2NH-I_2 complexes and obtained the following results: 6.2—6.5 and 6.2D in benzene, and 7.0D for the Et_2NH-I_2 complex in dioxane. We believe these experimental results support the foregoing suggestion. Subsequently, Boule[4] has been able to measure the dipole moment of this complex in *n*-heptane and has found a much lower value, 5.5—5.7D. We have reinvestigated the dipole moment of the Et_3N-I_2 complex in cyclohexane and in benzene, whose importance as a typical example is so great that extra efforts to obtain accurate data are justified.

Experimental

The Et_3N and cyclohexane were purified by the procedure given by Nagakura and Gouterman.[5] They were stored under an N_2 atmosphere in a desicator before use. The iodine was resublimed and stored in a dark bottle until use. The benzene for "Chromatographic Purposes" was used after having been dried over sodium and distilled under a N_2 atmosphere. The dielectric constants of the solutions were measured with a home-

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[*1] Present address: The Chemo-Sero-Therapeutic Research Institute, Kumamoto.

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[2] H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

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made resonance-method apparatus which used the electric circuit reported by Nakagawa.[6] A dielectric-constant-measurement cell with cylindrical platinum electrodes was used. The densities of the solutions were measured by the use of a pycnometer[7] for volatile liquids. The temperature was kept constant within 25.00 ± 0.05°C during the series of measurements. The dipole moment of nitrobenzene obtained by means of this apparatus was 4.12D in a benzene solution at 25°C. In each series of measurements, benzene or cyclohexane solutions containing a fixed concentration of Et_3N and various concentrations of iodine were used. The latter concentrations ranged from 0 to 3×10^{-3} mol/l in benzene solutions and from 0 to 7.2×10^{-4} mol/l in cyclohexane solutions; they never exceeded a 15th of that of amine in the solution. The dipole moments of the complex increased with an increase in the amine concentration in a mixed solvent containing benzene or cyclohexane and an amine. The dipole moments of the complexes were obtained by the use of the Kobinata-Nagakura method[3] modified by the ordinary Halverstadt-Kumler method.[8] Nagakura[9] noticed that a white precipitate appears at sufficiently high concentrations when there is a large excess of amine. These white crystals have been identified as $Et_3N\cdot HI$ by means of a comparison between the infrared spectrum of the white crystals and that of a synthetic salt.

Results and Discussion

We found that the present complex is unstable in a benzene solution as well as in a dioxane solution. As is shown in Fig. 1, the dielectric constants of the benzene solutions increase with the time minutes after the two solutions are mixed. Furthermore, each time, the relationship between the weight fractions of the complex and the dielectric constants or the densities of the solutions is linear. These linearities seem to show that, under the present experimental conditions, the dipole-dipole interaction between the complexes or ions is negligibly small. The dipole moments of the complex were calculated from the slopes of these straight lines on each run by the use of only the first term of the Kobinata-Nagakura equation,[3] for the residual terms were negligibly small compared with the first term. Figure 2 shows the relation between the time and the dipole moments of the present complex obtained in this way. In a benzene solution, the values of the dipole moment of the complex obtained by extrapolating the results to zero time are 6.55, 6.85, and 6.94D. We were not able to find that the dielectric constants and the densities of the solutions change with the time in cyclohexane within 30 min

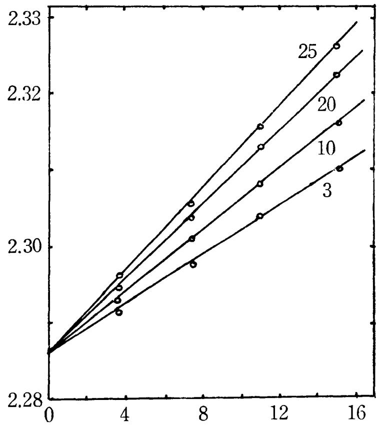

Fig. 1. The relation between the dielectric constant of the solutions (ε_{123}) and the weight fraction of complexes (W_3) in benzene. The Arabic numerals in the figure show the times passed in minutes starting from mixing the solutions.

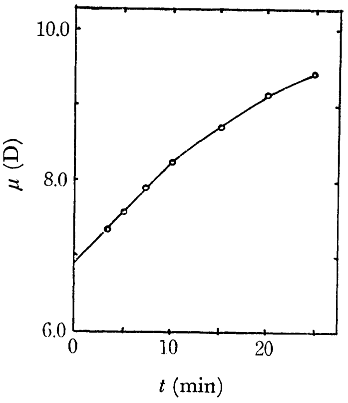

Fig. 2. The relation between the dipole moment (μ) and the time (t) in benzene.

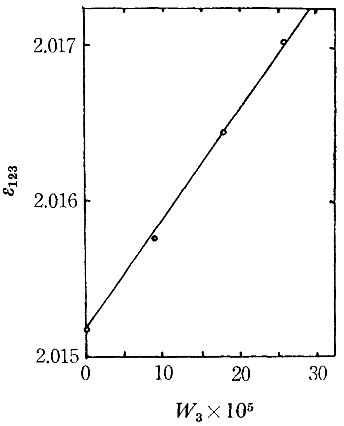

Fig. 3. The relation between ε_{123} and W_3 in cyclohexane. This straight line is able to express $\varepsilon_{123}=2.01516+7.467W_3$.

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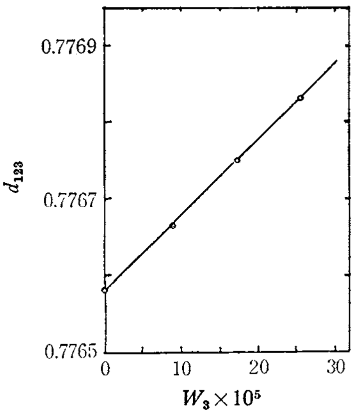

Fig. 4. The relation between the density of the solutions (d_{123}) and the weight fraction of the complexes (W_3) in cyclohexane. This straight line is able to express

$$d_{123}=0.77658+1.020W_3.$$

after the two solutions were mixed. In cyclohexane solutions, the relations between the observed dielectric constants or the densities of the solutions and the weight fraction of the complexes for a series of measurements within 30 min after the mixing of the two solutions are shown in Figs. 3 and 4. The experimental values of the dipole moment of the complex thus obtained in a cyclohexane solution are 5.23, 5.60, and 5.65D. These values are in good agreement with the Boule values.[4]

From the dipole moment thus obtained, the contribution of the dative structure in the present complex can be estimated at 30%, assuming that it takes a geometrical configuration of the trimethylamine-iodine complex[10] and that the negative charge in the dative structure is on the center of the iodine molecule.

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[10] K. O. Stømme, *Acta Chem. Scand.*, **13**, 268 (1959).