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The Dipole Moment of the Trimethylamine-iodine Complex

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One of the present authors[1] reported last year that his experimental measurements of the dipole moment of the triethylamine-iodine(Et_3N-I_2) complex confirmed the value, 5.5—5.7D, previously reported by Boule[2] in a cyclohexane solution. Furthermore, the dipole moment of the Et_3N-I_2 complex in a benzene solution was found to increase with the time after the two solutions had been mixed. These experimental values of the dipole moment show a much lower value than the value,[3] 12D, obtained in a dioxane solution. One of the present authors[3] has recently reported that his experimental dipole moment of the trimethylamine-iodine(Me_3N-I_2) complex shows the very large value, 10D, in a dioxane solution. We have reinvestigated the dipole moment of the Me_3N-I_2 complex in cyclohexane and in benzene; the importance of the complex as a typical example is so great that extra efforts to obtain accurate data are justified.

Experimental

The cyclohexane, benzene, and iodine were purified and stored by the method reported previously.[1] Trimethylamine generated from its aqueous solution by adding concentrated aqueous alkali was dried by potassium hydroxide. The dry trimethylamine thus obtained was led into cyclohexane to prepare the stock solution. The I_2 and Me_3N solutions were both made up by weight. The Me_3N solutions were prepared by the use of Le Fèvre's method.[4] The apparatus for the measurements of dielectric constants and the picnometer for the measurements of densities have been reported on previously.[1] The temperature was kept constant within 25.00± 0.05°C throughout the series of measurements. The dipole moment of nitrobenzene obtained by means of this apparatus was 4.06D in a benzene solution at 25°C. In each series of measurements, benzene or cyclohexane solutions containing a fixed concentration of Me_3N and various concentrations of iodine were used. The latter concentrations ranged from 0 to 8.0×10^{-3} mol/l in benzene solutions and from 0 to 3.5×

1) A. Funatsu and K. Toyoda, This Bulletin, **43**, 279 (1970).
2) P. Boule, *J. Amer. Chem. Soc.*, **90**, 517 (1968).
3) K. Toyoda and W. B. Person, *ibid.*, **88**, 1629 (1966).
4) R. J. W. Le Fèvre and P. Russell, *Trans. Faraday Soc.*, **43**, 374 (1947).

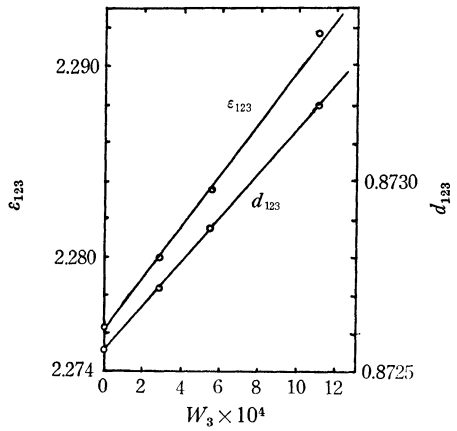

Fig. 1. In a benzene solution, the relations between the dielectric constants of solutions (ε_{123}) or the densities of solutions (d_{123}) and the weight fractions of complexes (W_3).
These straight lines are able to express
$\varepsilon_{123}=2.2763+13.3174W_3$, $d_{123}=0.87256+0.58852W_3$.

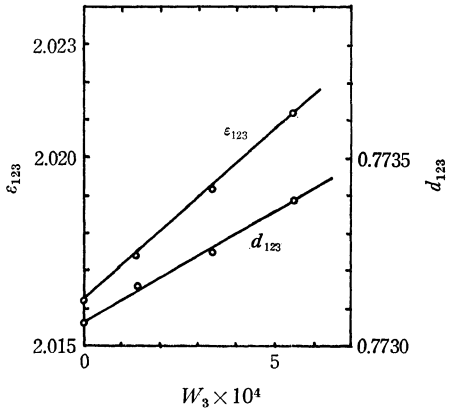

Fig. 2. In a cyclohexane solution, the relations between ε_{123} or d_{123} and W_3. These straight lines are able to express
$\varepsilon_{123}=2.0163+8.6538W_3$, $d_{123}=0.77308+0.57333W_3$.

10^{-3} mol/l in cyclohexane solutions; they never exceeded one-fifteenth 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[5] as well as by that of a previous article.[1]

Results and Discussion

The Et_3N-I_2 complex was unstable in a benzene solution, but we have found that the Me_3N-I_2 complex is stable in a benzene solution. The relations between the experimentally-observed dielectric constants or the densities of the solutions and the weight fractions of the complexes for each series of measurements are shown in Fig. 1 for benzene solutions, and in Fig. 2 for cyclohexane solutions, as examples of the measurements. The dipole moments of the complex were calculated from the slopes of these straight lines by the use of only the first term of the Kobinata-Nagakura equation.[5] In a benzene solution, the experimental values of the dipole moment of the complex thus obtained are 6.31, 6.20, 6.12, 6.63, and 6.30D; in a cyclohexane solution, they are 5.31, 4.75, 5.42, 5.53, and 5.26D. We believe these values are reasonable as compared with the values of the Et_3N-I_2 complex in a benzene or cyclohexane solution. From the dipole moment thus obtained, the contribution of the dative structure in the present complex can be estimated at 29%.

5) S. Kobinata and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 3905 (1966).