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Dipole Moments of the Iodine Compounds Complexed with Some Aliphatic Amines

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Synopsis. The dipole moments of some iodine compounds complexed with some aliphatic amines in benzene solution were obtained: 6.81D for EtH_2N–I_2; 6.78D for Et_2HN–I_2; 6.72D for Me_3N–ICl; 7.22D for Me_3N–IBr; 6.46D for Me_3N–ICN.

One of the present authors has recently reported the dipole moments of the electron-donor-acceptor (EDA) complexes between iodine and two aliphatic amines as follows: 12.4D in dioxane,[1] 6.78D in benzene,[2] 5.49D in cyclohexane,[2] for the triethylamine–iodine (Et_3N–I_2) complex, and 10.0D in dioxane,[1] 6.32D in benzene,[3] 5.25D in cyclohexane,[3] for the trimethylamine–iodine (Me_3N–I_2) complex. It was found that the experimental values of the dipole moments for these two complexes were strongly dependent on the solvents. The dipole moment of the Et_3N–I_2 complex was found to be time-dependent after mixing the two components. From the dipole moment of the Me_3N–I_2 complex in cyclohexane and the X-ray analysis data by Stroemme,[4] the contribution of the charge transfer (CT) structure in the ground state (b^2+abS) was evaluated to be about 0.30. Recently ESCA[5] and NQR[6] of pyridine–ICl (Py–ICl), for the gas phase and the solid state respectively, were measured. The charge distribution densities on each N, I, and Cl atoms has been directly evaluated from these data under certain assumptions. The dipole momemt measurement in solution at room temperature, however, is one of the most useful methods by which a direct measure for (b^2+abS) could be supplied. (b^2+abS) is one of the most basic constants of EDA complexes. The importance of the complex as a typical example is so great that extra efforts to obtain accurate data are justified.

Experimental

Cyclohexane, benzene, iodine, and Me_3N were purified by the method reported previously.[2,3] Ethylamine(EtH_2N) and diethylamine (Et_2HN) were purified by Nagakura's method.[7] ICl and IBr were prepared by the methods reported by Cornog and Karges,[8] and Popov and Skelly,[9] respectively. ICN, which was prepared by the method of Bak and Hillebert,[10] was colorless and melted at 145 °C in a sealed capillary. The apparatus for the measurements of dielectric constants, the picnometer for the measurements of densities, and the procedure of handling have been reported previously.[2] The temperature was kept constant at 25.00 ± 0.05 °C or 20.00 ± 0.05 °C throughout the series of measurements. The dipole moment of nitrobenzene obtained by means of this apparatus was 4.03D in a benzene solution at 25 °C. In each series of measurements, benzene solutions containing a fixed concentration of the amines and various concentrations of iodine, ICl, IBr, and ICN were used. The concentrations of the iodine compounds ranged from 0 to 1.8×10^{-3} mol/l in the benzene solution and did not exceed a tenth of that of amine in the solution. The dipole moments of the complexes were obtained by use of the Kobinata-Nagakura method.[11]

Results and Discussion

The experimentally observed dielectric constants (ε_{123}) and the densities (d_{123}) of the solutions were found to be linearly dependent upon the weight fractions (w_3) of the molecular complexes, as previously described.[2,3] The dipole moments of the complexes were evaluated from the slopes of these lines using only the first term of the Kobinata-Nagakura equation.[11] In spite of the low concentrations of the complexes, which were $(1.5-6)\times10^{-3}$ for EtH_2N–I_2 and $(1.8-7)\times10^{-3}$ for Et_2HN–I_2 in weight fraction and corresponded to about a tenth of the values in Nagakura's experiments,[11] the same results were obtained. As seen in Table 1, the dipole moments of the complexes increased with an increase in the amine concentration in a mixed solvent containing benzene and amine.

For the complexes between Me_3N and ICl, IBr, or ICN the dipole moments in benzene solution are presented in Table 1. The measurements in cyclohexane and hexane solution gave dispersed plots because the solubility in these solvents was a tenth of that in benzene. The geometries of the Et_2HN–I_2 and EtH_2N–I_2 complexes were assumed to be the same as that of Me_3N–I_2 by Nagakura *et al.*[11] Thus μ_1 was estimated to be 17.7D in the equation, $\mu_N=\mu_1(b^2+abS)$.[12] The X-ray diffraction study of Me_3N–ICl has been already reported

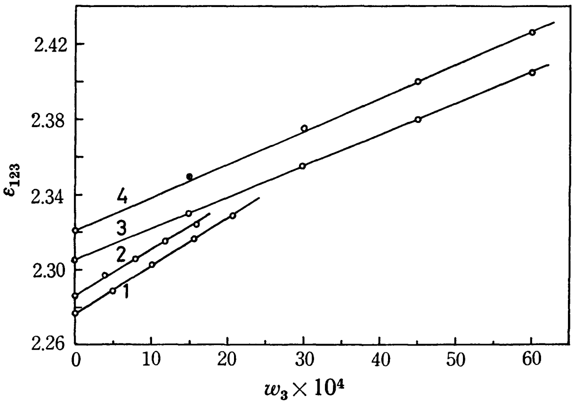

Fig. 1. The relation between the dielectric constant of benzene solutions (ε_{123}) and the weight fraction of complexes (w_3); (1) Me_3N–ICl; (2) Me_3N–ICN; (3) Et_2HN–I_2; (4) EtH_2N–I_2.

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Table 1. Dipole moments (μ_N in debye units) and dielectric constants of mixed solvents (ε_{12})

Complex	Solvent	t°C	μ_N	ε_{12}	b^2+abS	
					I[a]	II[b]
$EtH_2N–I_2$	benzene	20	6.67	2.3235	0.38	
			6.72	2.3590	0.38	
			6.76	2.3309	0.38	
			7.10	2.4350	0.40	
$Et_2HN–I_2$	benzene	20	6.60	2.3100	0.37	
			6.86	2.3050	0.39	
			6.89	2.3383	0.39	
$Me_3N–ICl$	benzene	25	6.42	2.2798	0.38	0.28
			6.82	2.2804	0.40	0.30
			6.92	2.2812	0.41	0.30
$Me_3N–IBr$	benzene	20	7.21	2.2869	0.42	0.31
			7.23	2.2885	0.42	0.31
$Me_3N–ICN$	benzene	20	6.43	2.2880		
			6.46	2.2890		
			6.50	2.2886		
$Py–I_2$[c]	cyclohexane		4.50		0.25	

a) Assuming that a negative charge is located on the center of the I–X molecule. b) Assuming that a negative charge is located on the X-atom of the I–X molecule. c) C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 3869 (1954).

by Hassel *et al*,[13] in which the bond lengths of I–Cl and N–I were 2.52Å and 2.30Å, respectively. Then the estimated values of (b^2+abS) are shown in Table 1. The assumption was made that μ_1 of $Me_3N–IBr$ was equal to μ_1 of $Me_3N–ICl$. According to the NQR study on solid Py–ICl by Hanna *et al*,[6] negative charge concentrates upon the Cl atom. Assuming that the positive charge concentrates upon the N atom, the (b^2+abS) values are obtained; these are shown in II of Table 1.

Several authors[14,16] have recently pointed out the importance of the induced polarization in the observed dipole moments of the molecular complexes. The (b^2+abS) values in Table 1, however, are estimated by the conventional procedure without giving any allowance for the polarization effects. The amounts of charge transfer Δq at the Py–ICl complex were estimated to be 0.1 for the gas phase by the ESCA[5] and 0.16 for the solid state by the NQR.[6] The (b^2+abS) in the solid state, in general, gives larger values than in the gas phase.[15] Δq obtained by the ESCA and NQR for the Py–ICl complex are the same order to the ionic character, which was estimated by considering the dipole moments of the two components in the $Py–I_2$ complex. These experimental Δq's were quite large as compared with those calculated (Δq, 0.018) for the $NH_3–I_2$ complex[16] by the MINDO/2.

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