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Dipole Moments of 1,2-Dihalogeno- and 1,1,2,2-Tetrahalogenoethanes in Aromatic and Non-Aromatic Solvents

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A weak interaction between 1,2-dichloroethane and aromatic solvents has been detected by studies of the dielectric relaxation times and dipole moments.[1] In the present study measurements were made of the dipole moments of 1,2-dihalogeno- and 1,1,2,2-tetrahalogenoethanes in various solvents (Table 1). The observed moment of 1,2-diiodoethane in benzene, 0.5_3D, is considerably lower than the literature value, 1.3 D,[2] which was obtained in the very early stage of dipole moment studies.

The interaction between 1,2-dichloroethane and an aromatic solvent has been believed to occur through hydrogen-bonding; the hydrogen atoms of dichloroethane have been assumed to interact with π-electrons of an aromatic solvent.[3] However, this hydrogen-bonding mechanism can not explain the "benzene effect" of 2,3-dihalogeno-2,3-dimethylbutane[4] and that of chloroacetone,[5] because this effect appears when hydrogen atoms are replaced by methyl groups.

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TABLE 1. DIPOLE MOMENTS OF 1,2-DIHALOGENO- AND 1,1,2,2-TETRAHALOGENOETHANES
(Debye unit. 20°C)

Solvent	ε	Solute				
		CH_2Cl-CH_2Cl	CH_2Br-CH_2Br	CH_2I-CH_2I	$CHCl_2-CHCl_2$	$CHBr_2-CHBr_2$
Benzene + Naphthalene (0.177 mol%)	2.360	—	—	—	1.72	—
Benzene	2.284	1.83	1.19	0.5_3	1.71	1.42
Toluene	2.385	1.71	1.09	0.5_0	1.68	1.40
p-Xylene	2.270	1.62	1.04	0.4_7	1.67	1.40
Cyclohexene	2.219	1.51	0.93	—	1.64	1.38
Amylene	2.015	1.44	0.89	—	—	—
Carbon disulfide	2.641	1.43	0.90	—	1.51	1.26
Carbon tetrachloride	2.238	1.41[a]	—	0.4_2	1.59	—
Cyclohexane	2.024	1.45	0.89	0.4_1	1.55	1.26
n-Hexane	1.898	1.39[a]	0.96(25°C)[b]	0.4_1	1.54	1.24
$P_E+P_A=1.05R_D$ (cc)		22.06	28.35	38.89	32.12	43.92

a) Recalcd. from Ref. 1.
b) Recalcd. from K. Kojima and S. Mizushiam, *Sci. Papers Inst. Phys.-Chem. Res.* (*Tokyo*), **31**, 296 (1937).

As an alternative mechanism, the chlorine atoms of 1,2-dichloroethane have been considered to play an important role in the complex formation between the solute and the aromatic solvent.[1,6] If this mechanism were true, one might expect to find some regular changes upon the replacement of Cl by Br or by I, which have smaller electronegativities than that of the chlorine atom. The results collected in Table 1 do not offer any definitive evidence for this, however.

It was pointed out by Sutton[7] to one of the present authors that the benzene effect might be due to the hyperpolarizability[8] of the aromatic solvent in the very strong field of the solute dipole. This hyperpolarizability effect is not necessarily restricted to an aromatic solvent. It is interesting to find that the dipole moments of dihalogeno- and tetrahalogenoethanes are higher in cyclohexene than those in cyclohexane and other non-aromatic solvents. However, those in amylene are not much different from the moments in cyclohexane. The effect of hyperpolarizability seems to need further study.

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