Dielectric Relaxation and Molecular Structure. XV. A Further Study of the Benzene Effect of 1,2-Dichloroethane and Related Molecules

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The dielectric relaxation times, τ, and dipole moments, μ, of 1,2-dichloroethane (A), *cis*-1,2-dichloroethylene(B), 1,3-dichloropropane(C), *o*-dichlorobenzene(D), and 1-chloro-2-propanone(E) have been measured in two aromatic and two aliphatic nonpolar solvents. The results are as follows: both the τ and μ of (A) and (E) are exceptionally large in aromatic solvents, showing the benzene effect; (B) and (C) have large τ but normal μ values in aromatic solvents, while (D) shows normal effects of the solvent upon both τ and μ in two different sets of solvents. Finally, the intetmolecular interaction between the solute and the solvent is discussed with special regard to the origin of the benzene effect.

A previous dielectric study[1] of the solvent effects of 1,2-dichloroethane was based on the measurements on the frequencies, 1 MHz and 9.33, 24.15, and 48.00 GHz. A further investigation of the same subject by the use of millimeter waves with the frequencies of 96.3—96.6 GHz will be reported here. In addition, the results of new dielectric measurements will be discussed with regard to three dichloro-compounds (one aromatic and two aliphatic) and one ketone (1-chloro-2-propanone), which exhibits the benzene effect in dipole moments.[2]

Experimental

The samples employed were all commercially available. They were carefully purified before use. The boiling points and the refractive indices were checked against the literature values. The apparatus and the experimental technique for the dielectric measurements at 96.3—96.6 GHz were described in a preceding paper.[3] The static dielectric constants were measured by the heterodyne beat method, while the refractive indices for the Na D line were measured by the use of a Pulfrich refractometer.

Results

The values of the slopes a_0, a', a'', a_D, and b obtained in this experiments for five compounds, (A), (B), (C), (D), and (E), in four solvents are collected in Table 1. The slopes a' and a'' were obtained on the assumption that the linear relationship of the dielectric constant, ε', and loss, ε'', with the concentration (weight fraction), w_2, is valid in dilute solutions:

$$\varepsilon' = \varepsilon_1' + a'w_2 \qquad \varepsilon'' = \varepsilon_1'' + a''w_2 \tag{1}$$

Further, a_0, a_D, and b represent the slopes for the static dielectric constant, ε_0, the square of the refractive index, n_D^2, and the specific volume, v, against the weight fraction respectively. (Regarding the symbols and equations in detail, see the preceding papers.[1,4,5])

Table 2 records the molecular polarization, ${}_\infty P_2$, at an infinitely dilute concentration; it was obtained from a_0 and b by the use of the following equation:[5,6]

$${}_\infty P_2 = M_2\left\{\frac{3a_0v_1}{(\varepsilon_{10}+2)^2} + (v_1+b)\frac{\varepsilon_{10}-1}{\varepsilon_{10}+2}\right\} \tag{2}$$

Table 1. The slopes a_0(static), a', a'' (96 GHz), a_D(optical), and b(volume) at 20 °C

Solvent	a_0	a'	a''	a_D	b
(A) 1,2-Dichloroethane[a]					
Benzene	3.585	0.899	1.062	−0.143	−0.331
p-Xylene	2.941	0.770	0.692	−0.133	−0.351
Carbon tetrachloride	4.074	1.353	1.432	−0.091	0.187
Cyclohexane	1.797	0.895	0.647	−0.017	−0.435
(B) *cis*-1,2-Dichloroethylene[b]					
Benzene	3.611	0.936	1.138	−0.118	−0.358
p-Xylene	3.609	0.970	0.998	−0.095	−0.387
Carbon tetrachloride	6.420	2.058	2.313	−0.053	0.154
Cyclohexane	2.991	1.408	1.122	0.013	−0.487
(C) 1,3-Dichloropropane[b]					
Benzene	4.121	0.894	1.154	−0.129	−0.292
p-Xylene	4.027	0.884	1.035	−0.102	−0.321
Carbon tetrachloride	7.460	1.814	2.228	−0.034	0.212
Cyclohexane	3.386	1.271	1.148	0.007	−0.408
(D) *o*-Dichlorobenzene[c]					
Benzene	3.565	0.285	0.567	0.102	−0.363
p-Xylene	3.467	0.322	0.519	0.118	−0.403
Carbon tetrachloride	5.972	0.534	0.843	0.353	0.148
Cyclohexane	2.919	0.414	0.512	0.213	−0.506
(E) 1-Chloro-2-propanone[c]					
Benzene	9.646	2.115	2.536	−0.184	−0.264
p-Xylene	8.538	2.017	1.967	−0.166	−0.286
Carbon tetrachloride	12.187	4.141	3.449	−0.174	0.265
Cyclohexane	5.046	2.439	1.712	−0.056	−0.344

Frequencies of measurements: a) 96.31 GHz; b) 96.46 GHz; c) 96.59 GHz.

The molar refraction, R_D, of Table 2 is given by:[5]

$$R_D = M_2\left\{\frac{3a_Dv_1}{(n_{1D}^2+2)^2} + (v_1+b)\frac{n_{1D}^2-1}{n_{1D}^2+2}\right\} \tag{3}$$

The symbols M_2, ε_{10}, and n_{1D} have their usual significance.[4,5] The dipole moment, μ(D), in Table 2 is calculated from Eq. (4):

$$\mu = 0.0128\{({}_\infty P_2 - R_D)T\}^{1/2} \tag{4}$$

Table 2. Polarizations, refractions, and dipole momemts (20 °C)

Solvent	$_{\infty}P_2$ (cm^3)	R_D (cm^3)	μ (D)	μ(lit.) (D)
(A) 1,2-Dichloroethane				
Benzene	89.9	20.9	1.82	1.78,[a] 1.85[a]
p-Xylene	79.4	20.9	1.68	1.63,[b] 1.58[c]
Carbon tetrachloride	65.8	21.1	1.47	1.38,[b] 1.56[d]
Cyclohexane	63.7	21.1	1.43	1.46[c]
(B) *cis*-1,2-Dichloroethylene				
Benzene	87.7	20.1	1.80	1.76[a] (25 °C)
p-Xylene	89.2	20.2	1.82	—
Carbon tetrachloride	87.3	20.2	1.80	1.80[a] (25 °C)
Cyclohexane	88.7	20.1	1.82	—
(C) 1,3-Dichloropropane				
Benzene	115.2	25.4	2.08	2.09[a]
p-Xylene	115.2	25.5	2.08	—
Carbon tetrachloride	116.0	25.6	2.09	—
Cyclohexane	116.3	25.6	2.09	—
(D) *o*-Dichlorobenzene				
Benzene	131.6	36.4	2.14	2.26[e]
p-Xylene	130.5	35.9	2.13	—
Carbon tetrachloride	125.3	36.9	2.06	—
Cyclohexane	131.2	36.7	2.13	2.27[f] (25 °C)
(E) 1-Chloro-2-propanone				
Benzene	190.2	20.6	2.86	2.89[g] (25 °C)
p-Xylene	175.1	20.7	2.73	—
Carbon tetrachloride	142.3	20.9	2.42	2.38[a] (25 °C)
Cyclohexane	133.3	21.1	2.32	2.36[g] (25 °C)

a) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco and London (1963). b) Ref. 1. c) Ref. 22. d) J. Crossley and S. Walker, *J. Chem. Phys.*, **45**, 4733 (1966). e) B. Krishna and K. K. Srivastava, *ibid.*, **32**, 663 (1960). f) J. Crossley and W. H. Hassell, *ibid.*, **48**, 1261 (1968). g) Ref. 2.

where T is the absolute temperature. It may be seen from Table 2 that both benzene and *p*-xylene give higher dipole moments for two solutes, (A) and (E), while they provide the remaining three molecules, (B), (C), and (D), with almost the same dipole moments as those in aliphatic solvents.

Discussion

The Cole-Cole equation[7] for a dilute solution is expressed in the following form:[8]

$$\frac{(a'-ia'')-a_\infty}{a_0-a_\infty}=\frac{1}{1+(i\omega\tau_0)^{1-\alpha}} \quad (5)$$

where τ_0 is the most probable relaxation time, α is the distribution parameter, and ω is the angular frequency. Using the a' and a'' values obtained for 1,2-dichloroethane at five frequencies, 1 MHz and 9, 24, 48, and 96 GHz, three parameters, τ_0, α, and a_∞, of Eq. (5) were calculated for various solutions by the use of a computer. The results are shown in Table 3.

We find the distribution parameter, α, to be almost zero in non-aromatic solvents. We also find that α values are also small, but differ from zero in aromatic solvents. Using Budo's equation,[9] we are able to obtain, for aromatic solvents, two reasonable relaxation times (τ_1 and τ_2) and also the weight factors, C_2 and C_1 ($=1-C_2$) *viz.*, τ_1=6.81 ps, τ_2=2.75 ps, C_2=0.502 (for benzene) and τ_1=7.22 ps, τ_2=2.00 ps, C_2=0.233 (for *p*-xylene)*, but we failed to obtain any sensible results for other solvents. However, this cannot be regarded

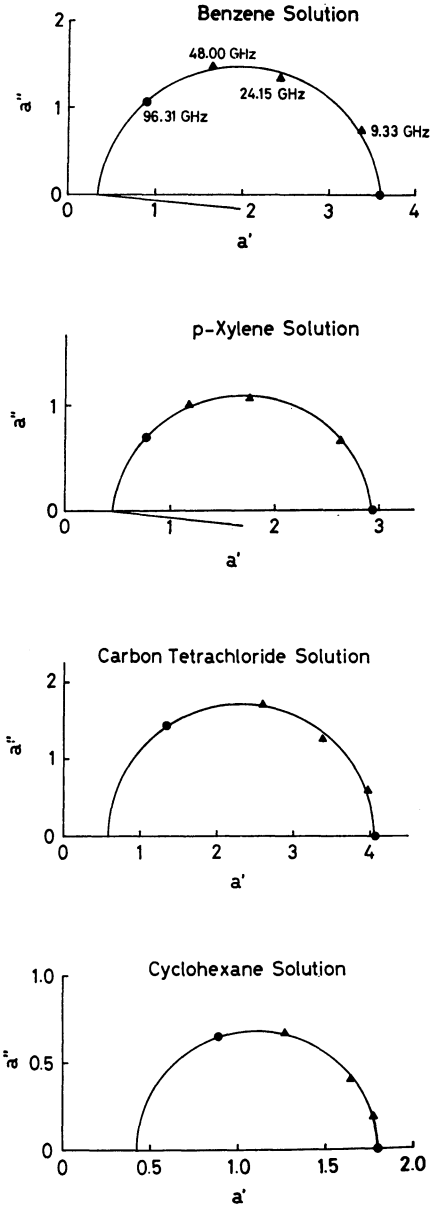

Fig. 1. The Cole-Cole plots for 1,2-dichloroethane in various solvents at 20 °C.
●: This work, ▲: A previous work (Ref. 1).

Table 3. Three cole-cole parameters for 1,2-dichloroethane at 20 °C

Solvent	a_∞	τ_0(ps)	α
Benzene	0.339	4.28	0.07
p-Xylene	0.450	5.67	0.08
Carbon tetrachloride	0.587	2.96	0.00
Cyclohexane	0.422	2.38	0.01

* This means that the number of *free gauche* isomers becomes smaller in *p*-xylene than in benzene.

TABLE 4. THE RELAXATION TIMES τ(ps) CALCULATED FROM MEASUREMENTS AT 100 GHz (20 °C)

Substance	Benzene	*p*-Xylene	Carbon tetrachloride	Cyclohexane
(A) 1,2-Dichloroethane	4.18±0.12	5.18±0.12	3.14±0.06	2.30±0.11
(B) *cis*-1,2-Dichloroethylene	3.88±0.11	4.36±0.17	3.11±0.07	2.33±0.05
(C) 1,3-Dichloropropane	4.61±0.09	5.01±0.10	4.18±0.05	3.04±0.10
(D) *o*-Dichlorobenzene	9.52±0.22	9.99±0.16	10.62±0.08	8.06±0.12
(E) 1-Chloro-2-propanone	4.89±0.05	5.46±0.08	3.84±0.07	2.51±0.17

as good evidence for complex formation[10] in the aromatic medium, since the observed α values are too small to make such an analysis reliable.

Another point of interest is that the slopes, a_∞, for the extremely high frequency were found to be unusually large.** In fact, the present work gives much higher values of a_∞ than those estimated roughly in the preceding paper.[1] Possibly this indicates some appreciable absorption in the submillimeter region; however, this point is not yet clear.

As has been reported in the preceding paper[1] the relaxation times of 1,2-dichloroethane are of a considerable magnitude in both benzene and *p*-xylene. That is, the τ_0 values in the aromatic solvent, 4.28 ps (benzene) and 5.67 ps (*p*-xylene), are about twice the τ_0 values in non-aromatic solvents, *viz.*, 2.96 ps (carbon tetrachloride) and 2.38 ps (cyclohexane), while the viscosities of the aromatic solvents are even smaller than those of the non-aromatic solvents (cyclohexane and carbon tetrachloride) by 32.4% (benzene) and 33.9% (*p*-xylene).

Two different approaches have been made to the benzene effect of 1,2-dichloroethane. One was made by Wada and Morino,[11] who showed that the *gauche* isomers are stabilized in the medium of benzene for an unspecified reason, resulting in a higher dipole moment. The other, by Kubo,[12] is that 1,2-dichloroethane forms a 1:1 complex with benzene, from which an increase in the relaxation time can be predicted. Morita *et al.*[10] reached Kubo's conclusion by repeating the same experiment and further confirmed that the 1:1 complex of 1,2-dichloroethane has the dipole moment of the *gauche* isomer, 2.55 D.[13]

However, there are some difficulties with the Kubo-Morita's conclusion, First. thermodynamical studies have failed in producing any evidence for the complex formation.[14] Secondly, the equilibrium constant for the complex formation has been found to depend upon the inert solvent,*** K_c (ml/mol) is 30.0 in carbon tetrachloride, 90.7 in *n*-hexane, and 139 in cyclohexane; further, the dipole moment of the complex is affected also by the solvent, μ(D)=2.54 in carbon tetrachloride, 2.11 in *n*-hexane, and 1.99 in cyclohexane.[10,15] Probably, benzene interacts with 1,2-dichloroethane in such a way that the configuration of the *gauche* isomer is more favored; however, this interaction is not strong enough to produce an aggregate with a structure rigid enough at room temperature to be unaffected by the surrounding molecules of the inert solvent.

The interaction between 1,2-dichloroethane and *p*-xylene is somewhat similar to, but stronger than, that of 1,2-dichloroethane and benzene, since the τ_0 value (5.67 ps) in *p*-xylene is larger than that (4.28 ps) in benzene—compare this change with the change in the weight factor, C_2, and its related footnote. The above findings are in accord with the changes in the equilibrium constants—*e.g.*, K_c=30.0 ml/mol in benzene and 51.0 ml/mol in *p*-xylene (in the inert solvent CCl_4).[10,15] On the other hand, the dipole moment, or the configuration itself, of the *gauche* isomer might be changed in the 1:1 complex. In fact, the polarity of the complex becomes smaller upon a change in solvent from benzene to *p*-xylene, *e.g.*, μ=2.54 D in benzene and 2.04 D in *p*-xylene (in the inert solvent CCl_4).

In Table 4 the relaxation times, τ, for five molecules, (A), (B), (C), (D), and (E), are collected. The values were all obtained by the use of the following Debye equation:

$$\tau = \frac{1}{w}\frac{a_0 - a'}{a''} \tag{6}$$

in which a' and a'' at 96 GHz are employed for the calculation.[8] In Table 4 we find the relaxation times of all the five solutes in carbon tetrachloride to be larger by 32—53% than the corresponding ones in cyclohexane. This is surprising because the two solvents have practically the same viscosity at room temperature; the two τ values should, then, be equal to each other for any solute if the usual Debye equation[18] were valid. The unusual rise in the relaxation time in carbon tetrachloride indicates, therefore, that the Debye approach is wrong. The alternative interpretation[19] after Eyring would indicate that particularly strong forces exist between all the solutes and carbon tetrachloride, by which the rotation of the solute molecules is hindered.

The skeleton of *cis*-1,2-dichloroethylene (B) is flat, and its C=C bond is slightly shorter than the C–C bond in 1,2-dichloroethane (A); the dipole moment, 1.80—1.82 D, for (B) is smaller than the *gauche* isomer of (A) 2.55 D. In other respects, however, the configuration of (B) may well compare with that the *gauche* isomer of (A). The relaxation times in the last two solvents are almost the same for the two molecules, (A) and (B). Although they differ in magnitude, the relaxation times of (B) are similarly high in aromatic solvents in spite of the fact that (A) has rotational isomers, while (B) has none. Perphaps this suggests that the relaxation

** If a_D is used instead of a_∞, we obtain a skewed arc, as has been pointed out by some Indian workers. For instance, see, for the benzene solutions, S. Chandra and R. A. Yadav, This Bulletin, **46**, 1900 (1973), and for a liquid, S. Chandra and R. A. Yadav, *J. Chim. Phys.*, **69**, 1018 (1972).

*** Similar variations in K with inert solvents were observed on charge-transfer complexes.[16,17] Possibly, the inert solvent is not ideal, but it interacts with either the solute or the solvent, or with both.

time is affected mostly by forces acting between the solute and the solvents in the first approximation.

The solvent interaction of 1,3-dichloropropane (C) with aromatic solvents is similar to, but somewhat weaker than, that of *cis*-1,2-dichloroethylene (B), while the corresponding interactions of (D) in aromatic solvents are the least pronounced of all. On the other hand, the interactions of 1-chloro-2-propanone (E) may well compare with those of 1,2-dichloroethane (A); both molecules have two rotational isomers, one strongly polar and the other nonpolar or at least less polar.

Next, we shall turn to the problem of the nature of the interaction between aromatic solvents and 1,2-dichloroethane. The mechanism of complex formation through hydrogen bonds was first proposed by Neckel and Volk[20] and later examined by Crossley and Walker[21] and Smyth.[22] However, this hypothesis of hydrogen bonding is not supported by the fact that the benzene effect in the dipole moment exists[23] even when all the hydrogen atoms of 1,2-dichloroethane are replaced by methyl groups. The alternative hypothesis is that the interaction originates from the chlorine atoms of 1,2-dichloroethane or, rather, from the C–Cl bonds. In other words, because of the large dipole moments of the C–Cl bonds and the large hyperpolarizability[24] of the aromatic solvent, the dipole-polarizability effect is possibly the origin of the benzene effect. The second explanation, however, has not yet been provided with any definitive proof.

Concluding Remarks on the Benzene Effect

The following conclusions are reached on the basis of the present investigation, together with the three preceding ones:[1,10,15]

1) 1,2-Dichloroethane and aromatic hydrocarbon molecules seem to interact in such a way as to form a loosely bound 1:1 complex in which 1,2-dichloroethane maintains its *gauche* configuration without much distortion.

2) Extra stabilization energy which cannot be explained by a simple electrostatic model[11] is gained by the *gauche* isomers in the medium of an aromatic solvent as a result of the above complex formation. Also, the Raman lines for the *gauche* isomer become stronger[11,25] in the presence of aromatic hydrocarbon molecules.

3) The apparent dipole moment of (A) becomes larger, since the number of the *gauche* isomers increases in the aromatic medium.[1] The dielectric relaxation time of (A) becomes high in the medium of an aromatic solvent because the rotation of the polar solute molecules becomes hindered in this medium.

4) The benzene effect for 1,2-dichloroethane (A) described above will be found even when another aromatic solvent is used instead of benzene. The benzene effect will also be found for some other polar molecules, *e.g.*, 1-chloro-2-propanone (E).

5) The dielectroric-relaxation-time method is useful for detecting the weakest intermolecular interaction. The dipole-polarization and other forces in the solute-solvent intraction are important in this effect.

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References

1) K. Chitoku and K. Higasi, This Bulletin, **40**, 773 (1967).
2) A. Abadie, C. Michel, and P. Mauret, *C. R. Acad. Sci. Paris*, **264C**, 1433 (1967).
3) K. Chitoku, K. Higasi, M. Nakamura, Y. Koga, and H. Takahashi, This Bulletin, **44**, 992 (1971).
4) Y. Koga, H. Takahashi, and K. Higasi, *ibid.*, **46**, 3359 (1973).
5) Y. Koga, H. Takahashi, and K. Higasi, *ibid.*, **47**, 84 (1974).
6) I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).
7) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
8) K. Higasi, This Bulletin, **39**, 2157 (1966).
9) A. Budo, *Phys. Z.*, **39**, 706 (1938).
10) A. Morita, H. Takahashi, and K. Higasi, This Bulletin, **45**, 1045 (1972).
11) A. Wada, and Y. Morino, *J. Chem. Phys.*, **22**, 1276 (1954).
12) M. Kubo, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 1221 (1934).
13) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954), p. 35.
14) O. Kiyohara and K. Arakawa, This Bulletin, **43**, 3037 (1970).
15) K. Higasi, H. Takahashi, K. Chitoku, and A. Morita, *Memo. Sch. Sci. Eng., Waseda Univ.*, **35**, 75 (1971).
16) C. C. Thompson, Jr., and P. A. D. de Maine, *J. Phys. Chem.*, **69**, 2766 (1965).
17) R. Foster, *J. Chem. Soc.*, **1960**, 1075.
18) P. Debye, "Polare Molekeln," S. Hirzel, Leipzig (1929), Eqs. (50) and (52), pp. 96—97.
19) K. Chitoku and K. Higasi, This Bulletin, **39**, 2160 (1966).
20) A. Neckel and H. Volk, *Z. Electrochem.*, **62**, 1104 (1958).
21) J. Crossley and S. Walker, *J. Chem. Phys.*, **48**, 4742 (1968).
22) J. Crossley and C. P. Smyth, *J. Amer. Chem. Soc.*, **91**, 2482 (1969).
23) Y. Morino, I. Miyagawa, Y. Haga, and S. Mizushima, This Bulletin, **28**, 165 (1955).
24) C. A. Coulson, A. Maccoll, and L. E. Sutton, *Trans. Faraday Soc.*, **48**, 106 (1952).
25) S. Mizushima, Y. Morino, and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **25**, 159 (1934).