Discussion

The model and approximations are obviously too crude to lend significance to exact values of parameters deduced above and to support quantitative interpretations of the interactions they represent. Several important conclusions of a qualitative nature find solid basis nevertheless in the comparison of calculations with experiment.

The inadequacy of the independent bond approximation has been demonstrated through its failure to account for values for $\langle r^2 \rangle_0/nl^2$ as large as observed. Exclusion of $g^{\pm}g^{\mp}$ neighbor pairs about both Si and O raises this ratio into the range of the experimental results. The positive temperature coefficient admits of explanation only by assignment of $\sigma < 1$. Complete exclusion of all $g^{\pm}g^{\mp}$ sequences tends to over-estimate either the temperature coefficient or the magnitude $\langle r^2 \rangle_0/nl^2$. Guided by structural considerations, we achieve a more refined agreement with experiment by relaxing the exclusion of such sequences about O (but not about Si), adopting $\delta \cong 0.06$ to this end.

The main conclusions, namely, that $g^{\pm}g^{\mp}$ sequences are largely suppressed and that the *trans* state is preferred over the *gauche* ($\sigma < 1$), are firmly established by the foregoing analysis. The calculations in support of these conclusions are insensitive to minor changes in θ' or other structural parameters. The idealization implicit in the model whereby discrete rotational states are substituted for averages over ranges of angle may distort the calculations in detail, but could scarcely affect our principal conclusions to a significant degree. The former of these conclusions finds independent basis in the structure. The latter confirms that nonbonded methyl groups attract at a distance of about 3.8 Å.; no other grounds for the preference of the *trans* state over the *gauche* is apparent.

A value of $\Delta\epsilon_\sigma$ in the range 500 to 1000 cal. mole^{-1} accords with structural considerations presented earlier. According to the numerical calculations (Table I), $\Delta\epsilon_\delta \cong 2000$ cal. mole^{-1}, which is twice the estimate for this quantity on the basis of coulombic repulsion between oxygen atoms. The sensitivity of numerical calculations (Fig. 4) to the value of δ suggests that this parameter (and therefore $\Delta\epsilon_\delta$ also) is subject to greater error than is σ from idealizations underlying the calculations. The discrepancy is well within the limits of error in either the model or in the experimental results.

If the suppression of $g^{\pm}g^{\mp}$ sequences about O is indeed to be accounted for by coulombic repulsions, a decrease in the polarity of the medium should further diminish δ. To the extent that σ also is influenced by electrostatic effects associated with the slightly closer proximity of the pairs of atoms, Si and O, separated by three bonds in the chain (see above), it should increase with decrease in polarity of the medium. Both changes should increase $\langle r^2 \rangle_0/nl^2$. Results for the fluorocarbon mixture,[28] in which $\langle r^2 \rangle_0/nl^2$ was found to be 7.7, are qualitatively in accord with this deduction.

A satisfactory account of the spatial configurations of the siloxane chain in terms of structural considerations appears to have been achieved.

Microwave Absorption and Molecular Structure in Liquids. LIII. Hydrogen Bonding and Dielectric Properties in Chloroform Mixtures[1,2]

BY ARTHUR A. ANTONY[3] AND CHARLES P. SMYTH

Dielectric constant and loss measurements are reported on mixtures of chloroform with cyclohexane, dioxane, and diazabicyclo[2.2.2]octane, and of trichlorofluoromethane with dioxane. The data are used to calculate relaxation times and distribution functions. Dipole moments are calculated for chloroform–dioxane mixtures. Viscosities, densities, and refractive indices of the four series of mixtures are also reported. The relaxation times are compared with those previously obtained in other solvents and interpreted in terms of hydrogen bonds between chloroform and the various proton acceptors. Trichlorofluoromethane is discussed because of its similarity to chloroform in size and shape and its inability to hydrogen bond. Two relaxation times are obtained for the chloroform–diazabicyclo[2.2.2]octane mixtures, one of which is attributed to chloroform rotation, the other to rotation of the complex formed between chloroform and the amine.

This work was undertaken in order to study the effect of hydrogen bonding on dielectric relaxation processes in simple systems. Chloroform was selected because it was expected to behave as a rigid, nearly spherical molecule with a dipole moment of 1.1 D. in solution.[4] The dielectric relaxation of trichlorofluoromethane was also studied because this is a compound similar to chloroform in its molecular shape, but incapable of forming hydrogen bonds by proton donation.

Experimental Methods

Purification of Materials.—The chloroform used was washed with concentrated sulfuric acid, then with distilled water, and then was distilled from phosphorus pentoxide. Trichlorofluoromethane obtained from Matheson Coleman and Bell was fractionally distilled. The dioxane was distilled from sodium, and its purity verified by measuring the static dielectric constant at 25°. Cyclohexane purchased from Matheson Coleman and Bell was used without further purification. Diazabicyclo[2.2.2]octane obtained from Aldrich Chemical Co. was recrystallized from ether; m.p. 157–158°.

Apparatus.—Dielectric constants and losses were measured by methods previously described.[5-9] Viscosity measurements were made with an Ostwald viscometer, calibrated with distilled water and benzene.

Experimental Results

Calculations of the dielectric constants and losses for the high-loss solutions were made with the aid of an

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(2) This paper represents part of the work submitted by A. A. Antony to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Allied Chemical Fellow, 1961–1962; Woodrow Wilson Fellow 1959–1960.

(4) A. N. Campbell, E. M. Kartzmark, and H. Triesen, *Can. J. Chem.*, **39**, 735 (1961).

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(8) F. H. Branin and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).

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TABLE I
DIELECTRIC CONSTANTS AND LOSSES OF MIXTURES AT 20°

M.f. CHCl₃	Wave length, cm.	ϵ'	ϵ''
Chloroform–dioxane			
0.0494	1.25	2.2623	0.0346
	3.26	2.2934	0.0475
	57500	2.3409	
0.099	57500	2.4575	
.199	57500	2.6834	
.300	57500	2.9039	
.400	1.25	2.2566	0.348
	3.22	2.8578	.366
	9.96	3.0854	.155
	57500	3.1115	
0.495	1.25	2.6621	0.452
	3.22	3.0457	0.433
	57500	3.3099	
0.591	1.25	2.7889	0.572
	3.22	3.2394	.487
	9.96	3.4885	.188
	57500	3.5110	
0.700	1.25	2.9582	0.714
	3.22	3.4774	.549
	9.96	3.7355	.202
	57500	3.7652	
0.805	1.25	3.1484	0.878
	3.22	3.7702	0.604
	57500	4.0493	
0.903	1.25	3.4184	1.023
	3.22	4.0958	0.683
	9.96	4.3494	0.241
	57500	4.3378	
1.000	1.25	3.6518	1.28
	3.22	4.5720	0.775
	57500	4.8170	
Chloroform–cyclohexane			
0.044	57500	2.0829	
0.077	1.25	2.1123	0.0275
	3.22	2.1252	0.0198
	57500	2.1279	
0.287	1.25	2.3857	0.182
	3.22	2.4573	0.088
0.421	57500	2.7477	
0.462	1.25	2.6357	0.349
	3.22	2.8058	0.189
	57500	2.8544	
0.668	1.25	2.9135	0.578
	3.22	3.2776	0.340
	57500	3.3747	
0.874	1.25	3.3403	0.919
	3.22	3.8946	0.574
Chloroform–diazabicyclo[2.2.2]octane			
0.609	57500	3.6215	
0.629	1.25	2.6948	0.306
	3.22	2.9551	.416
	9.96	3.3455	.338
0.909	1.25	3.3564	.899
	3.22	4.0468	.695
	9.96	4.3334	.346
0.933	57500	4.5250	
Trichlorofluoromethane–dioxane			
0.121	57500	2.2514	
0.185	1.25	2.2465	0.0230
	3.22	2.2623	0.0145
	57500	2.2669	
0.301	1.25	2.2613	0.0293
	3.22	2.2824	0.0188
	57500	2.2877	
0.351	1.25	2.2681	0.0318
	3.22	2.2893	0.0215
	57500	2.2960	

TABLE II
DENSITIES, VISCOSITIES, AND REFRACTIVE INDICES OF MIXTURES AT 20°

M.f. CHCl₃	Density, g./cc.	Viscosity, cp.	Refractive index
Chloroform–dioxane			
0.0787	1.0650	1.220	1.42402
.1999	1.1197	1.16	1.42675
.2911	1.1598	1.103	1.42898
.4199	1.2185	1.047	1.43239
.4859	1.2492	0.998	
.5981	1.3021	.931	1.4371
.7124	1.3558	.832	1.43995
.8224	1.4075	.747	1.44215
Chloroform–cyclohexane			
0.077	0.8165	0.909	1.42632
.287	0.9364	.770	1.42836
.462	1.0494	.704	1.43134
.668	1.2001	.644	1.43627
.874	1.3765	.605	1.44215
Chloroform–diazabicyclo[2.2.2]octane			
0.625	1.2882	2.024	1.47391
.657	1.3034	1.862	1.47222
.889	1.4301	0.875	1.45643
.940	1.4542	0.738	1.45193
Cyclohexane–diazabicyclo[2 2.2]octane			
M.f. C₆H₁₂			
0.950	0.7860	1.023	
.972	.7827	1.007	
.979	.7802	0.988	
Trichlorofluoromethane–dioxane			
0.121	1.0903	1.154	1.41922
.185	1.1206	1.087	1.41721
.301	1.1733	0.975	1.41495
.351	1.1967	.931	1.41426

IBM 650 computer. Cole–Cole arc plots[10] were used to calculate the relaxation times and distribution parameters. Dielectric constants and losses are presented in Table I, while Table II gives densities, viscosities, and refractive indices. Table III gives the values of the relaxation times, ratios of relaxation times to viscosities (reduced relaxation times), and Cole–Cole distribution parameters, α, which were calculated from the experimental data. Dipole moments of chloroform in dioxane (Table IV) were calculated using the Debye equation. For the pure liquid and for one solution, the dipole moment was also calculated using the Onsager equation, but this leads to a value which is too high for the pure liquid, and is, therefore, considered to be less appropriate than the Debye equation. The optical dielectric constant used in this equation was obtained from the Cole–Cole arc plots.

Discussion

Aromatic systems, for which hydrogen bonding to the solvent can affect the mesomeric moment, have significantly different dipole moments in benzene and dioxane. These differences are not usually observed for nonaromatic molecules, even when these molecules are capable of hydrogen bonding to the solvent.[11-14] The dipole moment variation with concentration of chloroform in dioxane is not as large as the differences be-

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(13) E. Hertel, *Z. Elektrochem.*, **47**, 813 (1941).
(14) W. Wassiliew and J. Syrkin, *Acta Physicochim. U.R.S.S.*, **14**, 414 (1941).
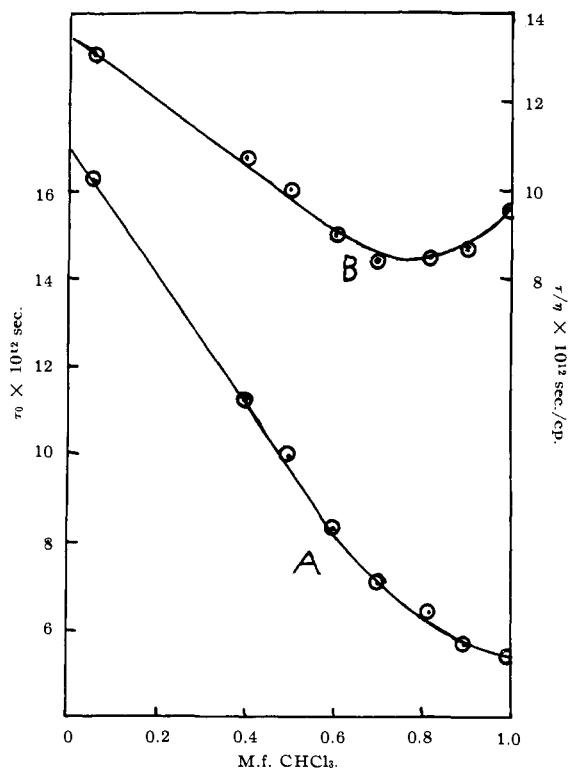
Fig. 1.—Relaxation time (A) and reduced relaxation time (B) of chloroform in dioxane at 20°.

tween dipole moments of aromatic amines in benzene and dioxane.

The relaxation time and the reduced relaxation time of chloroform in dioxane are plotted as functions of

TABLE III

RELAXATION TIMES, REDUCED RELAXATION TIMES, AND COLE–COLE DISTRIBUTION PARAMETERS OF MIXTURES AT 20°

M.f. CHCl₃	τ_0, 10^{-12} sec.	τ_0/η	α
Chloroform–dioxane
0.0494	16.2	12.9	0
.400	11.2	10.7	0
.495	9.9	10.0	0
.592	8.3	8.95	0.02
.700	7.1	8.4	.04
.805	6.5	8.5	.04
.903	5.7	8.6	.04
Chloroform–cyclohexane
0.077	3.7	4.0	0
.287	3.7	4.7	0
.462	4.4	6.2	0
.668	5.2	8.1	0
.874	5.6	9.3	0
Chloroform–diazabicyclo[2.2.2]octane
0.626	22.8	10.9	0.22
0.909	8.2	9.9	0.05
Pure chloroform
1.000	5.4	9.6ᵃ	0
Trichlorofluoromethane–dioxane
M.f. CFCl₃
0.185	6.3	5.8	0
.301	5.9	6.0	0
.351	6.0	6.4	0

ᵃ The value used for the viscosity of chloroform at 20°, 0.563 cp., is taken from the "International Critical Tables."

concentration in Fig. 1. For solutions between mole fractions (m.f.) of 0.6 to 0.9 chloroform, a very slight distribution of relaxation times (α value) is observed,
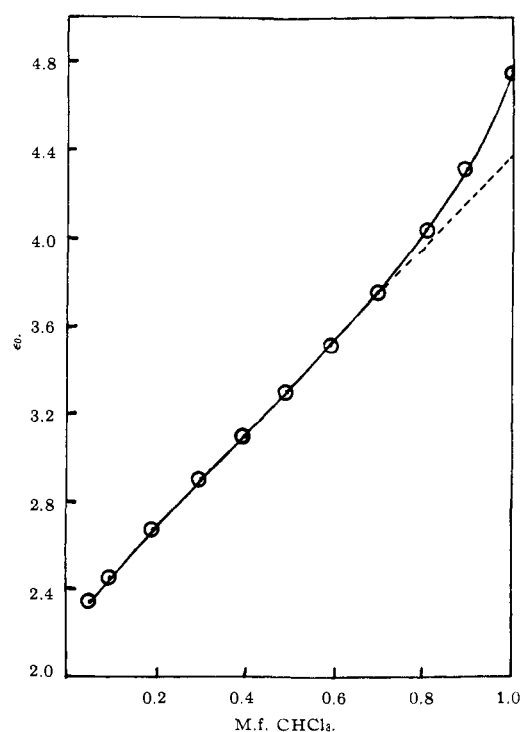

Fig. 2.—Static dielectric constant as a function of chloroform concentration for chloroform–dioxane mixtures at 20°.

while more dilute solutions and pure chloroform have single relaxation times. The very small distribution parameter appears to attain its largest value at about 0.7 to 0.8 mole fraction of chloroform, but even this maximum value is hardly distinguishable from zero. At approximately the same concentration, the plot of static dielectric constant vs. concentration (Fig. 2) de-

TABLE IV

DIPOLE MOMENT OF CHLOROFORM IN DIOXANE AT 20°

M.f. CHCl₃	μ, 10^{-18} e.s.u. × cm. Debye	Onsager	M.f. CHCl₃	μ, 10^{-18} e.s.u. × cm. Debye	Onsager
0.0494	1.13		0.700	1.02	
.400	1.02		.805	1.03	
.495	1.01	1.06	.903	1.03	
.591	1.01		1.000	1.06	1.23

parts from linearity. Attempts made with a double arc method[15] to decompose the arc plot for the 0.700-mole fraction solution into two dispersion regions were futile. It would, therefore, appear that the behavior of this solution cannot be explained on the basis of two independent relaxation times. For the other solutions, which show even less distribution, it is even less likely that two relaxation times can be obtained.

Plots of viscosity as a function of concentration of CXCl₃, where X is H or F, mixed with dioxane, cyclohexane, and diazabicyclo[2.2.2]octane, are shown in Fig. 3. The viscosity–concentration curve for the chloroform–dioxane mixtures is similar in shape to that for chloroform–diethyl ether mixtures.[16] The curve is slightly concave downward, a shape often associated with strong solute–solvent interaction.[17] In common with most nonassociated liquid mixtures, the curve (Fig 3) for the chloroform–cyclohexane mixtures is concave upward. In Fig. 3 the plot of the viscosities of mixtures of trichlorofluoromethane and dioxane is very slightly concave upward.

(15) F. K. Fong and C. P. Smyth, J. Phys. Chem., 67, 226 (1963).
(16) D. B. McLeod, Trans. Faraday Soc., 19, 17 (1923).
(17) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928, Chapter 9.

Table V

Summary of Relaxation Times at 20°

Compound	State	τ_0, 10^{-12} sec.	τ_0/η, 10^{-12} sec./cp.
CHCl$_3$	Dil. soln. in dioxane	16.5	13
CHCl$_3$	Dil. soln. in benzene	7.1	11.0[a]
CFCl$_3$	Dil. soln. in dioxane	6.3	5.7
CHCl$_3$	Pure	5.4	9.6
CHCl$_3$	Dil. soln. in CCl$_4$	5.0[a]	5.1[a]
CHCl$_3$	Dil. soln. in cyclohexane	3.2[a]	3.3[a]
CFCl$_3$	Concn. soln. in CCl$_4$	2.2[b]	3.3[a]
CFCl$_3$	Pure	2.0[b]	4.6[b]

[a] C. P. Smyth, "Dielectric Behavior and Structure," McGraw–Hill Book Co., Inc., New York, N. Y., 1955, p. 122.   [b] R. C. Miller and C. P. Smyth, J. Chem. Phys., 24, 814 (1956).

Table V lists some pertinent relaxation times and reduced relaxation times. The data support the evidence given by the infrared spectrum of deuterated chloroform in various solvents that chloroform forms weak hydrogen bonds by proton donation.[18] If one makes the assumption that the relaxation time of a proton donor increases as the accepting ability of the solvent increases, all other factors being equal, the order expected for the relaxation time of chloroform in various solvents should be dioxane > benzene > carbon tetrachloride > cyclohexane, for this is the order observed for the shift in the OH stretching frequency[19,20] of an alcohol mixed with these solvents. The reduced relaxation times also decrease in the same order as the proton-accepting ability of the base. In fact, the relaxation time of chloroform in benzene is greater than that in either carbon tetrachloride or cyclohexane in spite of the fact that the viscosity of benzene is smaller.

By thermodynamic methods,[21] a bond strength of about 1.8 kcal. per mole has been estimated for the hydrogen bond between chloroform and dioxane. In general, the van der Waals interaction energy is only a few tenths of a kilocalorie per mole.[22] Such interaction energies are considerably smaller than that of the hydrogen bond and would be expected to have a smaller effect on the relaxation time.

The dielectric data indicate a strong chloroform–chloroform interaction, hydrogen bonds probably making an important contribution to this interaction. Chloroform should be a better hydrogen-bonding base than carbon tetrachloride because hydrogen is less electronegative than chlorine. Therefore, one would expect that the electron density on the chlorines would be greater in chloroform than in carbon tetrachloride. Pure liquid chloroform and chloroform in a dilute solution in carbon tetrachloride have about the same relaxation time in spite of the fact that the latter has a considerably higher viscosity. For chloroform–cyclohexane mixtures, the viscosity decreases as the concentration of chloroform increases, but the relaxation time increases, probably because of interaction between the chloroform molecules. The single relaxation time observed is of the magnitude to be expected for the rotation of a single chloroform molecule. For concentrated solutions of chloroform in dioxane, in spite of the fact that the viscosity decreases very steeply in this region, the relaxation time appears nearly to level off. This

(18) R. C. Lord, B. Nolin, and H. D. Stidham, J. Am. Chem. Soc., 77, 1365 (1955).

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(22) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 2.
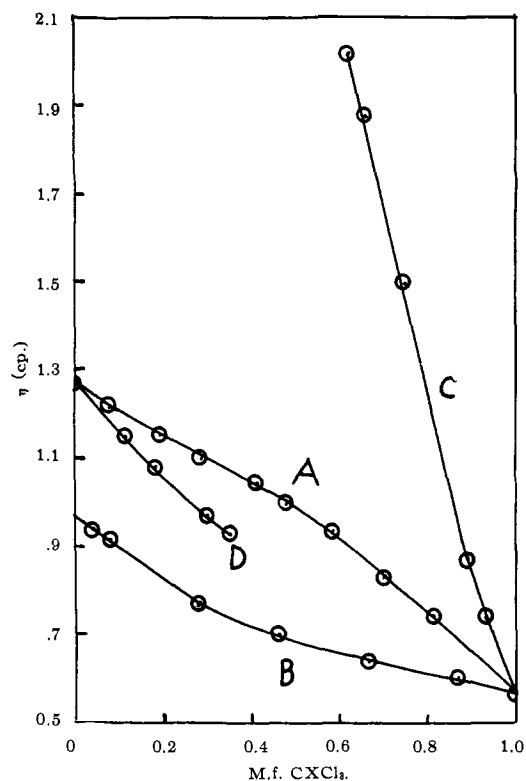
Fig. 3.—Viscosity of mixtures as a function of the mole fraction of CXCl$_3$ at 20°: A, CHCl$_3$–dioxane; B, CHCl$_3$–cyclohexane; C, CHCl$_3$–diazabicyclo[2.2.2]octane; D, CFCl$_3$–dioxane.

results in a minimum in the reduced relaxation time–concentration curve, indicating strong chloroform–chloroform interaction.

Additional evidence that hydrogen bonding is a major factor in the dielectric relaxation of chloroform comes from the fact that chloroform has a relaxation time in dioxane more than twice that of trichlorofluoromethane in dioxane, although the molecule of trichlorofluoromethane is similar in shape to that of chloroform and slightly larger. It is also noteworthy that the reduced relaxation time of pure chloroform is greater than that of pure trichlorofluoromethane.

If the relaxation mechanism in the chloroform–dioxane mixtures involves the rotation of an actual chloroform–dioxane complex, for mole fractions of chloroform above 0.67, where some uncomplexed chloroform molecules should be present, we should be able to obtain two relaxation times, one for chloroform molecules and one for the complexes. The impossibility of analyzing the data into two relaxation times has been pointed out. This is in contrast to the case discussed below, for which rotation of a complex evidently contributes to the relaxation. In the chloroform–dioxane mixtures, the relaxation mechanism involved seems to be primarily rotation of single chloroform molecules. The large relaxation time at infinite dilution results mainly from the fact that the potential barrier to rotation is high because of hydrogen bonding between chloroform and dioxane. It is possible that a very small polarization results from the orientation of complexes, which could account for the apparent small distribution of relaxation times observed, but the number of complexes is so small that it is impossible to separate the results into two relaxation times.

The dielectric behavior of chloroform–diazabicyclo[2.2.2]octane, N(CH$_2$CH$_2$)$_3$N, mixtures is quite different from that of the other mixtures. Of special significance is the fact that, as the concentration of the
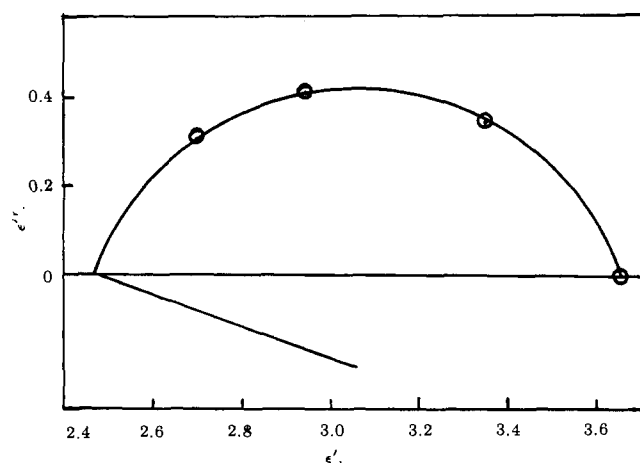
Fig. 4.—Cole–Cole arc plot for 0.626-mole fraction of chloroform with diazabicyclo[2.2.2]octane at 20°.

amine is increased, a large distribution of relaxation times is observed. The heat of formation[23] for the chloroform–triethylamine complex is −4 kcal. per mole. The heat of formation of the chloroform–diazabicyclo-[2.2.2]octane complex should be of similar magnitude, which would mean a hydrogen bond of greater strength than in the chloroform–dioxane complex. The large distribution in the relaxation times for the chloroform–diazabicyclo[2.2.2]octane mixture can be accounted for by assuming that rotation of both the uncomplexed chloroform and the chloroform–amine complex contribute to the relaxation.

The Cole–Cole arc obtained for the 0.626-mole fraction of chloroform–diazabicyclo[2.2.2]octane mixture is

(23) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

presented in Fig. 4. As indicated in Table III, the mixture with a higher mole fraction of chloroform showed a smaller distribution. For the 0.626-mole fraction of chloroform mixture, it was possible to obtain two relaxation times by using a double arc method.[15] The relaxation time attributed to the rotation of the complex was 80×10^{-12} sec., for which the reduced relaxation time is 39. The relaxation time of the uncom-complexed chloroform molecules is 14×10^{-12} sec., for which the reduced relaxation time is 7, and the relative contribution, C_1, of the uncomplexed molecules to the total relaxation process is 0.65. For the mixture with 0.909-mole fraction of chloroform, the fraction of complexed chloroform molecules would be expected to be much smaller. With such a small value for C_2, it is impossible to obtain a good separation. For a value of 7×10^{-12} sec. for uncomplexed chloroform molecules, good fit was obtained by assuming values for the complex between 20×10^{-12} and 35×10^{-12} sec. The latter value gives a reduced relaxation time close to that of the complex in the mixture discussed above.

The measurements on chloroform mixed with various substances indicate that hydrogen bonding influences the dielectric relaxation in several ways. In dilute solutions, the relaxation time is increased by hydrogen bonding to the solvent. This is evident from comparison of the behaviors of chloroform in cyclohexane, carbon tetrachloride, benzene, and dioxane. As the concentration of chloroform is increased, there is competition between the solvent and chloroform for the hydrogen bond. In all of these solvents, the results are consistent with a mechanism involving the rotation of the chloroform molecule, but in the mixtures of chloroform with diazabicyclo[2.2.2]octane, an additional relaxation mechanism involves the rotation of a complex between the amine and chloroform.

Microwave Absorption and Molecular Structure in Liquids. LIV. Dielectric Relaxation and Intramolecular Hydrogen Bonding in Hydroxy- and Methoxyacetophenones[1,2]

BY ARTHUR A. ANTONY[3] AND CHARLES P. SMYTH

Dielectric constants and losses at microwave frequencies as well as static dielectric constants and refractive indices of solutions are reported for *o*-hydroxyacetophenone and *o*-methoxyacetophenone in cyclohexane and dioxane solution, and for *m*-methoxyacetophenone in dioxane. These values were used to calculate dielectric relaxation times and Cole–Cole distribution parameters. Infrared carbonyl stretching frequencies are reported for *o*-hydroxyacetophenone and *o*-methoxyacetophenone in cyclohexane, carbon tetrachloride, and dioxane. *o*-Hydroxyacetophenone behaves as a rigid molecule because of the intramolecular hydrogen bond between the hydroxyl and acetyl groups. Resonance between the substituents and the benzene ring as well as steric inhibition to group rotation causes *o*-methoxyacetophenone also to behave as a rigid molecule. Group rotation is observed for *m*-methoxyacetophenone, for which steric repulsion is absent.

This study of substituted acetophenones is a continuation of that by Antony, Fong, and Smyth[4] on the dielectric relaxation and intramolecular hydrogen bonding in the halophenols. Substituents *ortho* to the hydroxy group on the benzene ring are capable of forming intramolecular hydrogen bonds with that group. A stronger hydrogen bond is expected for an acetyl group

ortho to the hydroxy than for a chlorine or bromine atom, because oxygen is a better proton acceptor than chlorine or bromine, and because the intramolecular hydrogen bond is sterically more favored in *o*-hydroxyacetophenone. The dielectric relaxation time of *o*-hydroxyacetophenone was measured in cyclohexane and in dioxane, the former solvent being considered incapable of participating in hydrogen bonding, the latter solvent being a fairly strong proton acceptor. Measurements were also made on *o*-methoxyacetophenone in cyclohexane and dioxane, because the methoxy compound is in many ways similar to the hydroxy compound but does not form hydrogen bonds. The infrared spectra in the region of the carbonyl stretching frequency were measured for these two compounds in cyclohexane, car-