[Contribution from the Frick Chemical Laboratory of Princeton University]

Microwave Absorption and Molecular Structure in Liquids. VII. Effects of Viscosity and Dipole–Dipole Forces[1]

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The dielectric constants and losses of solutions of *t*-butyl chloride, methyl chloroform, *n*-tetradecyl bromide and α-chloronaphthalene in *n*-heptane and in a viscous paraffin oil, and of *t*-butyl chloride and *n*-tetradecyl bromide in carbon tetrachloride have been measured at wave lengths of 1, 3 and 10 cm. and temperatures between 4 and 60°. The slopes of the plots of these quantities against concentration have been used to obtain a satisfactory arc plot for each system and to calculate the critical wave length and the distribution of relaxation times. The results, in conjunction with previously published data, show that the critical wave lengths or relaxation times of spherical or nearly spherical molecules are much less dependent upon the viscosity of the medium than are those of unsymmetrical molecules, the rotation of which requires displacement of the surrounding molecules. Dipole–dipole forces are found to play an important part in hindering molecular rotation. The distribution of relaxation times tends to increase with increasing viscosity and is influenced by molecular size and shape.

When an electric field is applied to a liquid, the polar molecules of the liquid tend to orient in the field and the orientation period or relaxation time depends upon the size, shape and rigidity of the molecules and upon the viscosity of the liquid. Spherical polar molecules in a homogeneous, uniform medium should have a single relaxation time. Microwave measurements[3,4] of dielectric constant and loss have shown that the orientation of molecules in pure polar liquids occurs with a single relaxation time when the molecules are spherical or nearly spherical, while a distribution of relaxation times generally occurs when the molecular shape is very different from that of a sphere. It has been shown[5–8] previously that the relaxation time is generally not proportional to the measured macroscopic viscosity, although the Debye theory of dielectric loss requires that it be proportional to the internal or microscopic viscosity, which cannot be directly measured. In the present investigation, in order to accentuate the effect of viscosity, measurements of dielectric constant and loss have been carried out upon dilute solutions of polar molecules in *n*-heptane, in carbon tetrachloride and in a viscous paraffin oil. Measurements have also been made upon pure *t*-butyl chloride.

Experimental Results

Most of the materials have been purified by methods described in another paper.[9] Methylchloroform obtained from the Matheson Company was shaken repeatedly with concentrated sulfuric acid, followed by distilled water, 10% sodium carbonate solution and more distilled water. The material was dried over calcium chloride and fractionally distilled three times, after which a constant boiling fraction was obtained; b.p. 74.1°, $n^{20}\text{D}$ 1.4386; as compared to literature values,[10,11] b.p. 74.1°, $n^{20}\text{D}$ 1.4379, 1.4384. The viscous paraffin oil used was nujol. After attempts at low pressure fractionation of this material had proved unprofitable, it was merely subjected to vacuum to remove dissolved gas and used without further purification. The small dielectric loss, usually about 0.001, found for the liquid did not affect the slopes of the linear plots of the dielectric losses of the solutions against concentration.

An earlier paper[12] has described the methods used in measuring the dielectric constants and losses of these solutions and has shown that, in accordance with general experience, these quantities are linear functions of the concentration in dilute solution. The static dielectric constant, ϵ_0, the real part, ϵ', of the complex dielectric constant, and the imaginary part or dielectric loss, ϵ'', may thus be represented by the equations

$$\epsilon_0 = \epsilon_1 + a_0c_2$$
$$\epsilon' = \epsilon'_1 + a'c_2$$
$$\epsilon'' = \epsilon''_1 + a''c_2$$

in which subscript 1 refers to the pure solvent, c_2 is the mole fraction or weight fraction of polar solute, and a is the slope of the straight line for the dependence of the dielectric quantity upon the concentration. The dielectric loss of heptane is negligible and even for nujol it is so small that $\epsilon'_1 = \epsilon_1$, as in the case of heptane. For heptane, we may thus take $\epsilon_1'' = 0$, while the value $\epsilon''_1 = 0.001$ for the paraffin oil is of the same magnitude as the probable errors in the solution values.

Measurements at each frequency were carried out on at least three and often six or seven solutions of concentration less than mole fraction 0.08 for each solute and the results are tabulated in condensed form in Table I as the slopes of the dielectric constants and losses plotted against concentration expressed in mole fraction for the *n*-heptane and carbon tetrachloride solutions and in weight fraction for the paraffin oil solutions. It has been shown[8] that these slopes may be substituted for the appropriate dielectric quantities in the equations describing these properties. Each value of a in Table I may be combined with the appropriate value of ϵ_1 for the solvent in Table III to calculate ϵ for a dilute solution of any desired concentration at a wave length λ_0 cm. It was observed that on taking into account the small correction for the atomic polarization in calculating the optical dielectric constants, ϵ_∞, somewhat more consistent results were obtainable. The results listed for a_∞, the slopes of the optical dielectric constants, have, therefore, been corrected as far as possible to include the effects of atomic polarization.[4,8] Data for pure *t*-butyl chloride are given in Table II. The values of the dielectric constant, ϵ_1, of the pure solvents and their viscosities are given in Table III.

Discussion of Results

It has been shown[8] that, when the values of the slope, a'', of the loss curve are plotted as ordinates against those of a' as abscissas, the arc of a circle is obtained, as in the Cole and Cole plot[13] of ϵ'' against ϵ'. When the dipole orientation process responsible for the dielectric loss involves only a single relaxation time, the arc is a semicircle with its diameter in the abscissa axis. When the orientation process in-

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[2] This article is based upon a thesis submitted by Mr. A. J. Curtis in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[3] W. P. Conner and C. P. Smyth, This Journal, **65**, 382 (1943).

[4] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *ibid.*, **70**, 4102 (1948).

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[6] D. H. Whiffen and H. W. Thompson, *ibid.*, **42A**, 114 (1946).

[7] C. P. Smyth, *Bull. soc. chim. France*, 336 (1949); *Record of Chemical Progress*, **11**, 1 (1950); *Electrical Eng.*, **69**, 975 (1950).

[8] A. D. Franklin, W. M. Heston, Jr., and C. P. Smyth, This Journal, **72**, 3447 (1950).

[9] W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 2071 (1950).

[10] International Critical Tables.

[11] Annual Tables of Physical Constants.

[12] W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, This Journal, **72**, 3443 (1950).

[13] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

volves a distribution of relaxation times, the diameter of the semicircle is rotated through an angle $\alpha\pi/2$ below the abscissa axis, the constant α being an empirical measure of the breadth of the distribution. This is illustrated in Figs. 1 and 2, in which the values of a'' for α-chloronaphthalene are plotted against those of a'. The values of α are determined from the arc plots and the values of the critical wave length λ_m, at which ϵ'' or a'' is a maximum, are calculated by the methods used previously.[8] The results, which include previous measurements[8] on t-butyl chloride in heptane for comparison, are given in Table IV. In earlier investigations, the viscosity of each solution was measured, but this procedure was abandoned when it became evident that the dielectric behavior was not generally sufficiently sensitive to viscosity to make it worthwhile.

TABLE I

SLOPES FOR DEPENDENCE OF DIELECTRIC CONSTANTS AND LOSSES UPON CONCENTRATION

t, °C.	a_∞	a_0	λ_0	a'	a''
t-C$_4$H$_9$Cl—Paraffin					
20	−0.19	4.89	1	3.39	1.65
			3	4.40	0.90
			10	4.73	.41
40	−0.19	4.43	1	3.27	1.48
			3	4.04	0.68
			10	4.21	.32
t-C$_4$H$_9$Cl—CCl$_4$					
4	−0.19		3	5.96	1.40
			10	6.20	0.27
20	− .19	5.75	1	4.17	2.60
			3	5.42	1.16
			10	5.81	0.23
40	− .19	5.11	1	3.89	2.08
			3	4.93	0.86
			10	5.09	.17
CH$_3$CCl$_3$—C$_7$H$_{16}$					
20	0.19	2.50	1	1.97	0.76
			3	2.4	.32
40	.19	2.23	1	1.85	.63
			3	2.12	.26
60	.19	1.99	1	1.73	.52
			3	1.95	.20
CH$_3$CCl$_3$—Paraffin					
20	0.04	2.43	1	1.45	0.90
			3	2.16	.54
			10	2.25	.23
40	.04	2.18	1	1.38	.82
			3	1.98	.42
			10	2.08	.17
60	.04	2.00	1	1.14	.74
			3	1.82	.33
			10	1.92	.15
n-C$_{14}$H$_{29}$Br—C$_7$H$_{16}$					
4	0.59	3.40	5	2.52	0.92
			10	2.62	1.00
20	.59	3.22	1	1.00	0.71
			3	1.72	.96
			5	2.38	.89
			10	2.60	.83
40	.59	3.00	3	1.82	.86
			5	2.28	.76
			10	2.55	.70
60	.59	2.79	1	1.23	.81
			3	1.94	.76
			5	2.16	.66
			10	2.53	.65
n-C$_{14}$H$_{29}$Br—Paraffin					
4	0.11	1.60	1	0.22	0.12
			3	.27	.21
20	.11	1.46	1	.21	.16
			3	.31	.25
			5	.51	.34
			10	.59	.36
40	.11	1.32	1	.20	.21
			3	.33	.30
			5	.59	.32
			10	.66	.34
60	.11	1.15	1	.20	.24
			3	.42	.32
			5	.68	.35
			10	.73	.32
n-C$_{14}$H$_{29}$Br—CCl$_4$					
20	0.0	4.20	1	0.41	0.90
			3	1.18	1.27
			10	2.68	1.46
40	.0	3.76	1	0.54	0.95
			3	1.46	1.28
			10	2.70	1.20
60	.0	3.34	3	1.60	1.18
			10	2.76	0.98
α-C$_{10}$H$_7$Cl—C$_7$H$_{16}$					
20	0.65	2.48	1	1.20	0.71
			3	1.90	.78
			10	2.42	.38
40	.65	2.31	1	1.26	.71
			3	1.90	.66
			10	2.29	.28
60	.65	2.13	1	1.34	.71
			3	1.90	.55
			10	2.12	.22
α-C$_{10}$H$_7$Cl—Paraffin					
2.5	0.37	1.98	1	0.51	0.17
			3	.55	.26
			10	.91	.44
20	.37	1.88	1	.53	.23
			3	.63	.32
			10	1.05	.51
40	.37	1.77	1	0.53	.26
			3	.71	.38
			10	1.19	.50
60	.37	1.65	1	0.55	.30
			3	.78	.43
			10	1.33	.43

TABLE II

DIELECTRIC PROPERTIES OF PURE t-BUTYL CHLORIDE

t, °C.	λ_0	ϵ'	ϵ''	α	λm
4	10.1	11.02	0.903	0.0	1.06
	3.22	10.11	2.6		
	1.25	7.04	4.68		
	Optical	1.94			
20	10.1	10.06	0.704	0.0	0.90
	3.22	9.48	2.0		
	1.25	7.17	4.12		
	Optical	1.92			
40	10.1	9.01	0.536	0.0	0.82
	3.22	8.82	1.5		
	1.25	7.25	3.41		
	Optical	1.89			

TABLE III

DIELECTRIC CONSTANTS AND VISCOSITIES (CENTIPOISES) OF NON-POLAR SOLVENTS

	t, °C.	ϵ_1	η
n-Heptane	4	1.944	0.510
	20	1.922	.420
	40	1.895	.339
	60	1.866	.280
Paraffin	4	2.195	279
	20	2.177	108
	40	2.157	38
	60	2.138	15
Carbon tetrachloride	4	2.270	1.231
	20	2.238	0.969
	40	2.202	.741
	60	2.160	.587

Orientation of a polar molecule in an externally applied field merely requires rotation of the molecule, while the process of viscous flow requires both rotation and translation. It has been suggested previously[7] that, if the shape of the molecule undergoing dipole orientation departs little from that of a sphere, it can rotate without any considerable displacement of the surrounding molecules. In this case, its relaxation time should be relatively insensitive to the macroscopic viscosity of the medium measured by the usual methods. If, however, the molecule is unsymmetrical in shape, its rotation, around at least one axis, must involve the displacement of neighboring molecules, and the corresponding relaxation time should depend markedly upon the viscosity of the medium. Indications of this behavior were given by the results of previous measurements,[7,8] but the critical wave lengths in Table IV make it more evident.

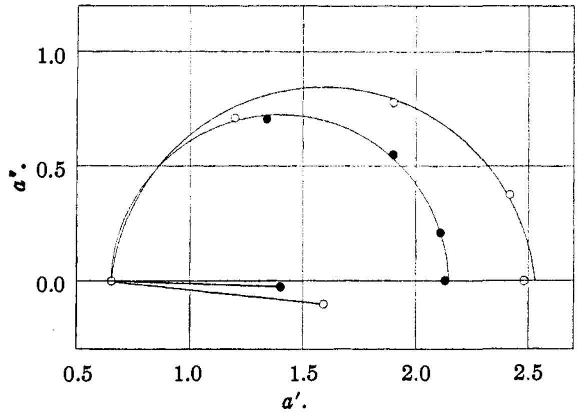

Fig. 1.—Arc plots for solutions of α-chloronaphthalene in n-heptane; hollow circles, values at 20°; filled circles, values at 60°.

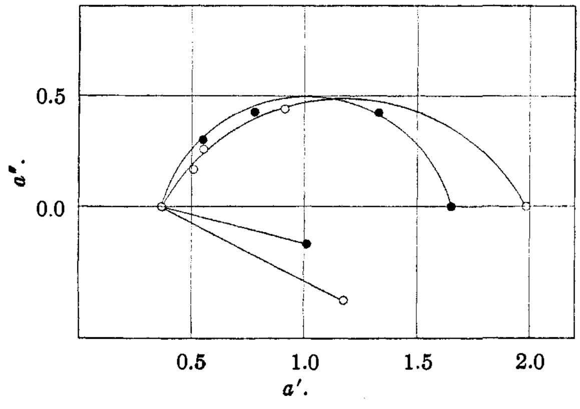

Fig. 2.—Arc plots for solutions of α-chloronaphthalene in viscous paraffin oil; hollow circles, values at 2.5°; filled circles, values at 60°.

TABLE IV

DISTRIBUTION CONSTANTS AND CRITICAL WAVE LENGTHS (CM.) OF SOLUTIONS

Solute	Solvent	t, °C.	α	λ_m
t-C_4H_9Cl	n-C_7H_{16}	20	0.2	0.3
		40	.2	.3
	CCl_4	4	.02	.70
		20	.02	.65
		40	.04	.60
	Paraffin	20	.19	.5
		40	.21	.4
CH_3CCl_3	n-C_7H_{16}	20	.12	.45
		40	.12	.40
		60	.11	.34
	Paraffin	20	.16	.83
		40	.17	.67
		60	.17	.56
n-$C_{14}H_{29}Br$	C_7H_{16}	20	.18	4.1
		40	.18	3.1
		60	.19	2.4
	CCl_4	20	.20	6.7
		40	.19	4.7
		60	.18	3.3
	Paraffin	4	.38	35
		20	.36	19
		40	.32	12
		60	.27	6.6
α-$C_{10}H_7Cl$	C_7H_{16}	20	.07	2.0
		40	.04	1.7
		60	.02	1.35
	Paraffin	4	.31	21
		20	.25	12
		40	.22	7.4
		60	.16	5.0

For the almost spherical molecule of t-butyl chloride, the critical wave length at 20° is only $^2/_3$ greater in the viscous nujol than in heptane, although the viscosity of the nujol is 257 times that of heptane. At 40°, the critical wave length in nujol is $^1/_3$ greater, although the viscosity of the nujol is 112 times that of heptane. For the methylchloroform molecule, which is similar in size and shape to the t-butyl chloride molecule, the critical wave length is slightly higher in heptane and increases a little more from heptane to nujol than does t-butyl chloride. The small differences between the values for the two solute molecules may be due to the slightly greater polarizability of the methylchloroform molecule with consequently greater intermolecular attraction and frictional forces.

The long flexible molecule of n-tetradecyl bromide in heptane has a much longer critical wave length than the two smaller, nearly spherical molecules just considered and shows a nearly fivefold increase from heptane to nujol at 20°, much larger than the relative increase for the two nearly spherical molecules. Although the longer molecule of n-docosyl bromide, n-$C_{22}H_{45}Br$, gives dipole orientation in the crystal, presumably by rotation about the long axis in a cylindrical volume,[14] the molecules of the long-chain bromides in the liquid state are probably less regular in form. Consequently, dipole orientation by rotation either of the entire molecule or of a molecular segment about a carbon–carbon bond should involve some displacement of the surrounding molecules and, hence, the greater dependence upon viscosity which has been noted. The somewhat flattened, rigid molecule of α-chloronaphthalene shows a critical wave length in heptane at 20° half as long as that of n-tetradecyl bromide,

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(14) J. D. Hoffman and C. P. Smyth, THIS JOURNAL, 72, 171 (1950).

but the value in nujol is six times that in heptane, a relative increase slightly larger than that in the case of the long, flexible molecule and much larger than those for the nearly spherical molecules. This sixfold increase would seem to indicate a considerable amount of translational displacement of the surrounding molecules when the polar molecule orients, but the sixfold increase in relaxation time is still very small in comparison to the 257-fold increase in viscosity, the relaxation time being supposed to be proportional to the internal viscosity. In spite of the parallelism between the mechanism of dipole orientation and that of viscous flow as indicated by the dependence of both upon temperature and molecular size,[4] there would still appear to be considerable quantitative differences between the two processes.

The significance of the results in Table IV is more evident when they are combined with the values compiled in a previous paper,[8] together with a few others taken from the literature. In Table V, the second and third columns give the viscosities and critical wave lengths of the pure, liquid solutes listed in the first column and the subsequent columns give the critical wave lengths of the solutions in the solvent listed at the top of each column, the viscosity of each solvent being given below its formula.

TABLE V

CRITICAL WAVE LENGTHS (CM.) AND VISCOSITIES (CENTIPOISES) AT 20°

	Pure solute			λ_m for solutions in				
			C_7H_{16}	$C_{16}H_{34}$	Nujol	C_6H_{12}	C_6H_6	CCl_4
				η =				
Solute	η	λ_m	0.42	3.6	108	0.97	0.65	0.97
t-C_4H_9Cl	0.53	0.90	0.3		0.5	0.3		0.65
CH_3CCl_3			.45		~ .8			
$CHCl_3$	.56	1.4	.58			.60	1.34	.94
C_2H_5Br	.40	0.8	.3	0.4		.4	0.6	
$C_8H_{17}Br$	1.65	4.6	2.1	3.6		3.1		
$C_{14}H_{29}Br$	4.67	12.3	4.1		19			6.7
C_6H_5Cl	0.80	2.1				1.47	1.56	
C_6H_5Br	1.16	3.4				2.0	2.0	
$C_6H_5CH_3$	0.59	1.4[8]						
$C_6H_5NO_2$	2.01	9[15]	1.3			1.8	2.4	2.9
α-$C_{10}H_7Cl$	3.33	11.0	2.0		12			
α-$C_{10}H_7Br$	4.98	17.6	2.7					

The measurements in the viscous paraffin (nujol) solutions already discussed seem to provide strong confirmation of the hypothesis that the critical wave lengths or relaxation times of nearly spherical molecules are much less dependent upon the viscosity of the medium than are those of unsymmetrical molecules, the rotation of which requires displacement of the surrounding molecules. This is shown also in Table V by the greater viscosity dependence of the critical wave length for *n*-octyl bromide than of that for ethyl bromide.

While both viscous flow and dipole orientation in liquids are dependent upon the van der Waals forces acting between the molecules, the differences between the mechanisms of the two processes may result in relatively different effects of the van der Waals forces. Since the medium surrounding the dipolar molecule is not continuous, but consists of other molecules with fluctuating gaps of various sizes between them, the effects of the van der Waals forces upon dipole orientation will depend somewhat upon their type. Of the three types of interaction, in terms of which van der Waals attractive forces may be described, the dispersion or London forces act in all liquids; the dipole-induced dipole forces act between the dipolar molecule and the molecules surrounding it; and, if the latter are dipolar as in a pure polar liquid, dipole–dipole forces also act. Since the potential energy of a dipolar molecule due to these latter forces should change rapidly as the dipole is rotated, they should contribute considerably to the potential barrier hindering rotation and thus increase the critical wave length. As the other two types of van der Waals force are dependent upon molecular polarizability, this quantity, which is proportional to the refraction, should be an important factor in determining the relaxation time or critical wave length.

It was previously suggested[8] very tentatively that "the apparent tendency of the critical wave length of the pure polar liquid to be longer than that of the solution of about the same viscosity may be due to hindrance of molecular rotation by dipole–dipole interaction, which is present in the pure liquid and largely absent in the dilute solution." This hypothesis receives strong support from Table V, in which only the very viscous nujol solutions show critical wave lengths longer than those of the corresponding, pure polar liquids. Indeed, the nearly spherical *t*-butyl chloride molecule, whose orientation is relatively independent of the viscosity of the medium, shows almost twice as great a critical wave length in the pure liquid state as it does in solution in nujol, which has 200 times the viscosity. An essentially similar result of dipole–dipole forces is shown by the solutions in carbon tetrachloride, which has no molecular dipole moment, but contains four compensating C–Cl dipoles in the molecule. The critical wave lengths of *t*-butyl chloride, chloroform and nitrobenzene are higher in carbon tetrachloride than in cyclohexane solution, although carbon tetrachloride has the same viscosity as cyclohexane at 20°. It is reasonable to attribute this behavior to the force between the solute dipole and a C–Cl dipole, whose local force field is not cancelled by the other three C–Cl dipoles in the carbon tetrachloride molecule. The question may be raised whether the effect of carbon tetrachloride in lengthening the critical wave length may be due not to its local dipoles, but rather to its high polarizability, which undoubtedly contributes to the intermolecular forces. If, however, the polarizability had more effect than the local dipoles, the critical wave length of *t*-butyl chloride should be higher in carbon tetrachloride, which is more viscous, than in the pure liquid state. The higher critical wave length in the pure liquid state seems to confirm the importance of dipole–dipole forces.

The data for the four monosubstituted benzenes in Table V give further evidence in support of these views. The small increases in molecular volume and polarizability from the chloro to the bromo compound in both the substituted benzenes and naphthalenes cause increases in viscosity and critical wave length somewhat larger than would be expected. The toluene molecule is identical in size and shape with that of bromobenzene, but its dipole moment is only $^1/_4$ as large. The viscosity of bromobenzene is twice as large, but the critical wave length is 2.4 times as great, presumably, because of greater dipole–dipole forces. Nitrobenzene has a dipole moment about 2.7 times that of bromobenzene and a viscosity about 1.7 times as great, but a critical wave length, estimated approximately from the loss curve given by Girard and Abadie,[15] about 2.6 times that of bromobenzene. The high criti-

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(15) P. Girard and P. Abadie, *Trans. Faraday Soc.*, **42A**, 40 (1946).

cal wave length of nitrobenzene in the pure liquid state is evidently due to dipole–dipole forces since, in cyclohexane and benzene solutions, where dipole–dipole forces are unimportant, its values are close to those of bromobenzene.

The critical wave lengths of the solutions in benzene are generally higher than would be expected from the viscosity of the liquid. Benzene is a better solvent than aliphatic hydrocarbons. It has been found[16] to have an abnormal effect upon the dipole moment of ethylene chloride, raising it above the values observed in other non-polar solvents. Although the benzene molecule has no dipole moment as a whole, it has six symmetrically located C–H dipoles, which, on the basis of comparative boiling points, Van Arkel[17] has proposed to have moments of the same magnitude as the highly polar C–F bonds. Such a moment value (about 1.4×10^{-18}) is far larger than that ordinarily attributed to the C–H bond, 0.3 to 0.5×10^{-18}, in both aromatic and aliphatic compounds.[18] However, from the intensities of vibration bands, Cole and Thompson[19] have obtained a mean value of about 0.57×10^{-18} with the hydrogen atom positive with respect to the carbon. If the relatively small size of the hydrogen atom permits these dipoles to come close to neighboring molecules, they may well give sufficiently strong dipole–dipole forces to account for the abnormality of benzene.

The values of the distribution constant α in Table IV resemble those previously found[4] for pure liquids in that they tend to increase with increasing viscosity. The temperature dependence of α for the solutions of low viscosity is within the large experimental error in the parameter. The nearly spherical molecule of *t*-butyl chloride shows a distribution constant indistinguishable from zero in the pure liquid state and in solution among the nearly spherical molecules of carbon tetrachloride. The large and somewhat unsymmetrical molecules of α-chloronaphthalene and α-bromonaphthalene[8] in heptane solution similarly show little or no distribution, and only a small distribution in the pure state.[4] All of the solutes show a considerable distribution in the viscous paraffin oil, the distribution being greater, the larger the molecules. More data are needed before definite conclusions may be drawn, but the few available results suggest that when the solvent molecules are sufficiently large in comparison to those of the solute, their distribution may not average out sufficiently during the orientation process to give uniform environment to the solute molecules. Variation of molecular shape and segment orientation should give distribution in the tetradecyl bromide solutions, irrespective of the solvent molecules.

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[16] A. E. Stearn and C. P. Smyth, THIS JOURNAL, **56**, 1667 (1934).

[17] A. E. Van Arkel, *Trans. Faraday Soc.*, **42B**, 81 (1946); see also J. H. van Santen, *ibid.*, **42A**, 165 (1946).

[18] W. L. G. Gent, *Quart. Rev.*, **2**, 383 (1948); C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

[19] A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Formation of Arylsilylpotassium Compounds

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Organosilylpotassium compounds have been prepared by the reaction of substances containing the $\geq$Si–H or $\geq$Si–OR linkages with a 1:5 Na/K alloy. Thus triphenylmethoxysilane, triphenylsilane and tri-*p*-xenylsilane all react with this alloy and the resultant organometallics can be coupled with bromobenzene, triethylchlorosilane, methyl iodide and *p*-bromobiphenyl. Diphenylsilane and phenylsilane also react with Na/K alloy and the product can be coupled with bromobenzene to yield tetraphenylsilane. Triethylsilane does not seem to react with the alloy under the conditions of the experiment.

In a previous publication from this Laboratory[1] triphenylsilylpotassium was prepared in ethyl ether by the cleavage of phenylisopropyltriphenylsilane with liquid Na/K alloy (1:5 by weight).[2] We are now reporting the preparation of arylsilylpotassium compounds by the reaction of Na/K alloy with compounds containing the $\geq$SiH or $\geq$Si-OR linkages. The following reactions were carried out.

$$(C_6H_5)_3SiOCH_3 \xrightarrow[(2)\ (C_2H_5)_3SiCl]{(1)\ Na/K} (C_6H_5)_3SiSi(C_2H_5)_3 \quad (a)$$

$$(C_6H_5)_3SiH \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \quad (b)$$

$$(C_6H_5)_3SiH \xrightarrow[(2)\ CH_3I]{(1)\ Na/K} (C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_3SiCH_3 \quad (c)$$

$$(p\text{-}C_6H_5C_6H_4)_3SiH \xrightarrow[(2)\ p\text{-}C_6H_5C_6H_4Br]{(1)\ Na/K} (p\text{-}C_6H_5C_6H_4)_4Si \quad (d)$$

$$(C_6H_5)_2SiH_2 \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \quad (e)$$

$$(C_6H_5)SiH_3 \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \quad (f)$$

$$(C_2H_5)_3SiH \xrightarrow{Na/K} \text{N.R.} \quad (g)$$

It is to be noted that in reaction (c) two products were obtained. In fact the hexaphenyldisilane was formed in larger yield than the expected coupling product. This is in contrast to the previous report[3] that triphenylsilylsodium reacts with methyl

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[1] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[2] In a private communication to us Dr. Henry Gilman reported that potassium alone will undergo similar reactions. Thus far we have not been successful with sodium alone but have continued with the use of the Na/K alloy because of the convenience involved in pipetting it into the reaction flask.

[3] C. A. Kraus and H. Eatough, THIS JOURNAL, **55**, 5008 (1933).