

ture of Dry Ice and acetone; the samples were then cooled to liquid nitrogen temperature, and warming runs taken. Curves for these measurements are given in Figs. 9 and 10 for octadecyl and tetradecyl mercaptan, respectively. It is clear from the figures that dipole orientation is possible in the α -phase of these compounds. Unfortunately, the dispersion region was spread out over so wide a frequency range that it was not possible to obtain accurate loss measurements. Above the dispersion region, where measurement at 5 kc. corresponds to the static dielectric constant, the dielectric constant began to drop with increasing temperature, as it should, if molecular rotational orientation were occurring. The appearance of the low temperature dispersion region is reminiscent of that observed in the α -forms of the triglycerides^{8,9,17} where rotation of the molecule as a whole is presumably prevented by its shape, and only that of segments should be permitted, and also of that in the long-chain fatty acid esters,¹⁸ where rotation of the molecule around its long axis appears possible. Dispersion below the melting point with rise in dielectric constant above that of the liquid is commonly attributable to interfacial polarization¹⁹ between a solid phase and a more or less conducting liquid phase arising from the presence of impurities, but this behavior is not shown by the stable forms in Figs. 7 and 8. Impurities do not, therefore, appear to be the cause of the dispersion. Possibly, enough weak hydrogen bonding occurs between the mercaptan molecules in a rotator phase to give a very small effect analogous to that which is so conspicuous in the behavior of the hydrogen-bonded

(17) R. W. Crowe and C. P. Smyth, *THIS JOURNAL*, **73**, 2040 (1951).

(18) R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5401 (1951).

(19) C. P. Smyth, *ref. 8*, p. 73.

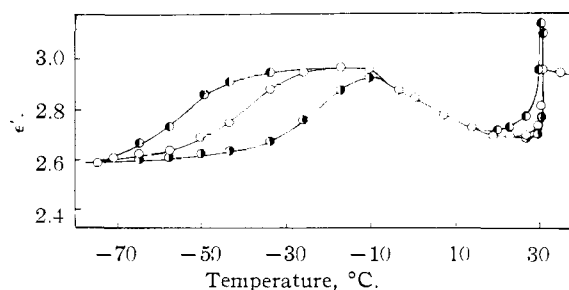


Fig. 9.—Variation of the dielectric constant of the α -form of octadecyl mercaptan with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

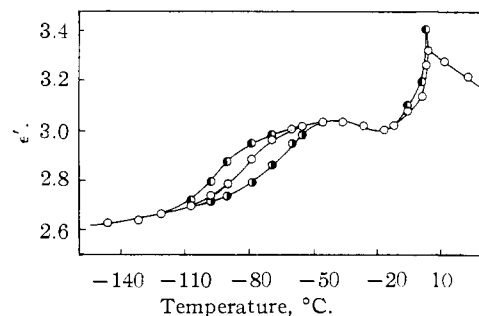


Fig. 10.—Variation of the dielectric constant of the α -form of tetradecyl mercaptan with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

alcohols. However, it is clear that strong hydrogen bonding is necessary to produce the effect observed in the long-chain alcohols.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XIV. The Apparent Critical Wave Lengths of Liquid Long Chain Alcohols¹

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RECEIVED OCTOBER 6, 1955

The dielectric constants and losses of *t*-butyl, octyl, decyl, dodecyl, tetradecyl, cetyl and octadecyl alcohols and of solutions of decyl alcohol in carbon tetrachloride and in *n*-ujol have been measured at wave lengths at 1.25, 3.22 and 10.0 cm. at temperatures between 2 and 85°. Approximate critical wave length values calculated from the results of these measurements are shown to be consistent with the explanation of measurements on shorter chain alcohols by other investigators as involving a low frequency dispersion region arising from hydrogen bonds and a high-frequency region arising from the rotational orientation of alkoxy groups.

The microwave measurements reported in the present paper were carried out some six years ago with the expectation that further measurements would be carried out at somewhat lower frequencies. Although these projected lower frequency measurements have not been carried out in this Laboratory, much additional information has been

obtained elsewhere on alcohols up to dodecyl in size. It has, therefore, seemed desirable to publish the present results in spite of the fact that absence of data at wave lengths of a few meters leaves the calculated critical wave length values very approximate.

Earlier papers³⁻⁶ in this series have described the

(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This article is based upon a thesis submitted by Dr. G. B. Rathmann in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(3) W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *THIS JOURNAL*, **70**, 4093 (1948).

(4) H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

(5) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

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

methods used in measuring the dielectric constants and losses of the liquids and in calculating the critical wave lengths.

Experimental

t-Butyl alcohol (Matheson Company, Inc.) was distilled at atmospheric pressure, dried over calcium shavings and thrice fractionally crystallized. The product of the last crystallization was fractionally distilled, b.p. 82.3–82.4° n_{25}^{25D} 1.38516, f.p. 25.4°; lit. b.p. 82.5°, n_{25}^{25D} 1.3852,⁷ f.p.⁸ 25.5°.

n-Octyl alcohol was fractionally distilled under reduced pressure and dried over small pieces of metallic sodium followed by a second fractional distillation at reduced pressure, n_{20}^{20D} 1.43018.

n-Decyl alcohol (chemically pure) from Columbia Organic Chemicals was twice distilled under reduced pressure, n_{20}^{20D} 1.43670; lit. 1.43660.⁹

n-Dodecyl alcohol was purified by Dr. R. W. Crowe, f.p. 23.5°; Beilstein (I-432) lists the f.p. as 24°.

n-Tetradecyl alcohol secured from Paragon Testing Laboratories was twice distilled under reduced pressure, f.p. 36.4°; Phillips and Mumford¹⁰ give a f.p. of 37.7°.

n-Cetyl alcohol was purified by Dr. R. W. Crowe. The conductivity as measured by Dr. A. Di Giacomo was less than 10^{-9} mhos; f.p. 48.9°; lit. 49.27°.¹¹

n-Octadecyl alcohol, crystallized from dry ether and benzene, was fractionally distilled under reduced pressure, f.p. 57.6°. Phillips and Mumford¹⁰ record a f.p. of 57.95°.

Experimental Results

Viscosities, densities and refractive indices for the *n*-sodium line measured for the alcohols are given in Table I. The dielectric constants ϵ' and losses ϵ'' measured at the indicated wave lengths and temperatures, and the so-called static dielectric constant ϵ_0 measured at 520 kilocycles are given in Tables II and III. In solution, the alcohols depart from the linear dependence upon concentration usually observed at the dilutions given in Table III. The values of the static dielectric constant of dodecyl, cetyl and octadecyl alcohols were measured by Dr. A. Di Giacomo.

TABLE I
VISCOSITIES, DENSITIES AND REFRACTIVE INDICES

Alcohol	Temp., °C.	Viscosity (centipoises)	Density	n_D
<i>t</i> -Butyl	25			1.38516
<i>n</i> -Octyl	20			1.43018
<i>n</i> -Decyl	31	9.32	0.823	1.4327
	80	2.17	.787	1.4151
<i>n</i> -Dodecyl	31	12.84	.826	
	55	5.60	.808	1.43066
	80			1.42066
<i>n</i> -Tetradecyl	40	12.03	.822	
	60	6.03	.807	1.4320
	80	3.41	.794	1.4246
<i>n</i> -Hexadecyl	55	9.50	.813	1.4371
	80	4.38	.796	1.4286
<i>n</i> -Octadecyl	60	9.74	.813	1.4388
	69	7.32	.806	1.4354
	90	4.01	.792	1.4275

(7) J. Timmermans and Y. Delcourt, *J. chim. phys.*, **31**, 85 (1934).

(8) C. J. Marsdon and E. J. Evans, *Phil. Mag.*, **24**, 377 (1937).

(9) A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

(10) J. W. C. Phillips and S. A. Mumford, *ibid.*, 235 (1933).

(11) J. D. Meyer and E. E. Reid, *THIS JOURNAL*, **55**, 1574 (1933).

TABLE II
DIELECTRIC CONSTANTS AND LOSSES OF ALCOHOLS

Temp., °C.	1.25 cm.		3.22 cm.		10.0 cm.		520 kc.	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ_0	ϵ_0
<i>t</i> -Butyl								
30	2.77	0.38	2.966	0.670	3.55	1.56		
50	2.96	.65	3.327	1.12	4.77			
70	3.20	.93	3.923	1.54	5.67	1.79		
Octyl								
2.5					(9.04 cm.)	(12.5 cm.)		
					2.644	0.324	2.683	0.382
6	2.38	0.135						
25	2.56	.22	2.584	0.323	2.736	0.513	2.841	0.603
50	2.65	.34	2.662	.496	2.976	.855	3.172	1.02
87	2.76	.56						
Decyl								
2.5					2.54	0.231		
8.4	2.353	0.105						
20	2.365	.134	2.48	0.29	2.68	.34		
40	2.41	.20	2.574	.356	2.92	.527		
60	2.47	.29	2.672	.481	3.21	.747		
82	2.58	.41						
Dodecyl								
25	2.347	0.121	2.446	0.192	2.575	0.300		
55	2.427	.201	2.585	.327	2.844	.525	4.56	
85	2.539	.312	2.80	.44	3.323	.644	4.00	
Tetradecyl								
40	2.381	0.132	2.45	0.18	2.632	0.320	4.66	
60	2.43	.16						
80	2.515	.26			3.01	.44	3.69	
Cetyl								
55	2.37	0.163	2.482	0.234	2.689	0.338	3.77	
70	2.41	.209	2.573	.287	2.837	.390	3.50	
82	2.44	.241						
Octadecyl								
60	2.356	0.152			2.661	0.293	3.34	
85	2.448	.214			2.853	.285	3.124	

Discussion of Results

Measurements of dielectric constant and loss have been summarized and interpreted^{12,13} as showing two and occasionally three dispersion regions for the liquid alcohols. The critical wave length for the lowest frequency region increases¹³ from 11.0 cm. for methyl alcohol at 20° to 375 cm. for nonyl alcohol and then appears to drop to 316 cm. for decyl. These first critical wave lengths are much too long to correspond to rotational orientation of a monomeric alcohol molecule and have been attributed to the relaxation times required for the destruction of quasi-crystalline molecular complexes stabilized by hydrogen bonding. Alternatively, it has been suggested¹⁴ that this absorption region is due to a hydrogen-bonded chain mechanism like that proposed¹⁵ for crystalline alcohols, shorter chains in the liquids accounting for relatively higher frequencies of absorption. In both cases, the proposed hypothesis involves the breaking of hydrogen bonds. A second critical wave length reported¹³ as starting at 4.0 cm. for hexyl alcohol and increasing to 10.0 cm. for decyl alcohol at 20° with a questionable value of about 3 cm. for dodecyl alcohol was attributed¹³ to the relaxation

(12) Mme. Dalbert, M. Magat and A. Surdut, *Bull. soc. chim. France*, D 345 (1949).

(13) C. Brot, M. Magat and L. Reinisch, *Kolloid-Z.*, **134**, 101 (1953).

(14) B. V. Hamond and R. J. Meakins, *Aust. J. Sci. Res.*, **A5**, 671 (1952).

(15) R. A. Sack, *ibid.*, **A5**, 135 (1952).

TABLE III
 DIELECTRIC CONSTANTS, DIELECTRIC LOSSES AND REFRACTIVE INDICES SQUARED FOR DECYL ALCOHOL SOLUTIONS

Solvent	Concn.	<i>t</i> , °C.	1.25 cm.		3.22 cm.		10 cm.		520 kc.	<i>n</i> ² _D
			ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ_0	
Carbon tetra- chloride	0.0	20	2.238	0.0015	2.237	0.0012	2.238	0.0015	2.240	2.1326
	m.fr.	40	2.202	0.0015	2.200	0.0012	2.202	.0015	2.202	
	0.04057	20	2.289	.0293	2.305	.0243	2.323	.0182	2.339	2.1280
	m.fr.	40	2.265	.0336	2.285	.0240	2.301	.0168	2.309	
	0.0536	20	2.294	.0362	2.316	.0316	2.340	.0253	2.3658	2.1260
	m.fr.	40	2.282	.0417	2.305	.0320	2.327	.0223	2.3451	
Nujol	0.06507	20	2.300	.0411	2.325	.0374	2.355	.0318	2.3804	2.1245
	m.fr.	40	2.294	.049	2.317	.0387	2.344	.0283	2.3578	
	0.0	20	2.177	.0015	2.177	.001	2.177	.0015	2.1789	2.1901
	wt.fr.	40	2.157	.0015	2.157	.001	2.157	.0015	2.1592	2.1707
		60	2.136	.0015	2.136	.001	2.137	.0015	2.1354	
	0.1025	20	2.212	.0181	2.219	.0203	2.238	.0257	2.2917	2.1753
wt.fr.	40	2.208	.0268	2.226	.0256	2.241	.0271	2.2807	2.1557	
	60	2.211	.0323	2.225	.0284			2.2662		
	0.1625	20	2.223	.0278					2.1683	
wt.fr.	40	2.226	.0362							
	60	2.233	.0487							

 TABLE IV
 DISTRIBUTION PARAMETERS AND CRITICAL WAVE LENGTHS

Alcohol	<i>t</i> , °C.	α	λ_m
Dodecyl	25	0(assumed)	127 (calcd. from 10 cm.)
	55	0(assumed)	33 (calcd. from 10 cm.)
	85	0(assumed)	11 (calcd. from 10 cm.)
Tetradecyl	40	0(assumed)	62 (calcd. from 10 cm.)
	80	0(assumed)	14 (calcd. from 10 cm.)
Cetyl	55	0.34	27 (3.22 cm.) 32 (10.0 cm.)
	70	.24	12 (3.22 cm.) 18 (10.0 cm.)
Octadecyl	60	.32	15 (1.25 cm.) 16 (10.0 cm.)
	85	.26	4.3(1.25 cm.) 5.0(10.0 cm.)
Decyl			(1.25 cm.) (3.22 cm.) (10.0 cm.)
0.04057 m.f. in CCl ₄	20	.39	0.9 1.0 0.9
	40	.34	.7 0.6 .6
.0536 m.f. in CCl ₄	20	.42	1.3 1.4 1.3
	40	.37	0.7 0.8 0.5
.06507 m.f. in CCl ₄	20	.40	1.2 1.4 1.6
	40	.34	0.7 0.8 0.9
.1025 w.f. in Nujol	20	.52	5.7 8.2 8.0
	40	.50	2.2 2.2 2.8
	60	.40	0.9 1.2

time for the rotational orientation of molecules not taking part in the quasi-crystalline complexes. The importance of this second mechanism relative to that of the first was believed¹⁸ to increase with increasing chain length and increasing temperature. However, very recent work¹⁶ indicates that the amplitude of the high frequency dispersion increases instead of decreasing with decreasing temperature and suggests that, instead of involving entire single molecules, this dispersion is "the result of reorientation of the oxygen-alkyl group moment during the shift of the hydrogen bond from one electron orbital of the bridged oxygen atom to the other."

If the decrease in the first critical wave length from nonyl to decyl alcohol is real, the value 127 cm. calculated for dodecyl alcohol (Table IV) from the present 10 cm. measurements at 25° is of a reasonable magnitude, although it might be expected to be short because of contribution of a second dispersion region to the loss. The decrease in apparent

(16) F. X. Hassion and R. H. Cole, *J. Chem. Phys.*, **23**, 1756 (1955).

critical wave length continues through tetradecyl and cetyl to octadecyl alcohol, where the critical wave length is of the magnitude to be expected for the high frequency dispersion region, due allowance being made for the higher temperatures of observation necessitated by high melting points. For tetradecyl alcohol, the rate of decrease of the apparent critical wave length with temperature is about the same as that of the viscosity, but, for cetyl alcohol, it is somewhat more rapid, and, for octadecyl alcohol, it is twice as great.

For dodecyl and tetradecyl alcohols, only the 10 cm. wave length results were used to calculate the critical wave length, as these were nearer to the low frequency absorption region. For cetyl and octadecyl alcohols, the critical wave length values calculated from the 10 cm. measurements are longer than those calculated from the measurements at shorter wave lengths, but the difference is not very great. It would appear that these values correspond roughly to the high frequency dispersion region,

arising from rotational orientation of the alkoxy groups. The measurements on solutions of decyl alcohol in carbon tetrachloride give critical wave length values much shorter than the high frequency region value tabulated by Brot, Magat and Reinisch.¹³ It is reasonable to suppose that the single molecules existing in the solutions are responsible for the short critical wave length, and the viscosities of the moderately dilute solutions in carbon tetrachloride are so much lower than that of the pure alcohol that the critical wave lengths should be much lower. The critical wave lengths in the highly viscous Nujol solution are much higher than those in carbon tetrachloride, although the increase in critical wave length from one solvent to the other is much less than the increase in viscosity. The general behavior of the high frequency critical wave length of decyl alcohol in the pure state and in solution seems to parallel that of the alkyl bromide critical wave lengths,¹⁷ in particular, that of tetradecyl bromide, which has been investigated in the same solvents¹⁸ as well as in the pure state.¹⁷ However, the apparent critical wave length values for decyl alcohol are somewhat shorter than would be expected for a molecule of this size and the values of the distribution coefficient α are very large, probably as a result of the persistence of molecular association in the solutions.¹⁹

The seemingly curious absence of any considerable distribution of relaxation times for the low frequency dispersion region of the pure alcohols is

(17) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *THIS JOURNAL*, **70**, 4102 (1948).

(18) A. J. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 644 (1952).

(19) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 80-84.

possibly explicable if the rate controlling process is the destruction of quasi-crystalline complexes by the breaking of hydrogen bonds. In the calculation of the critical wave lengths of dodecyl and tetradecyl alcohol in Table IV the distribution of relaxation times was arbitrarily neglected because of the uncertainty introduced by the probable contributions of two different dispersion regions. The effect of two dispersion regions may possibly account for the large values of the distribution parameters α (Table IV) given by the Cole and Cole arc plots for cetyl and octadecyl alcohols.

The dielectric constant and loss values for *t*-butyl, octyl and decyl alcohols in Table II appear to be fairly accurate, but they are too far from the low frequency dispersion region to give information concerning the critical wave lengths corresponding to this region and contain contributions from this region which make calculation of the high frequency critical wave lengths too uncertain for inclusion in Table IV. The values for pure octyl and decyl alcohols have been analyzed in detail elsewhere.²⁰

As previously stated, the apparent critical wave lengths calculated for long chain alcohols from the measurements of dielectric constant and loss in the microwave region reported in this paper must be regarded as approximate because of the absence of measurements at somewhat lower frequencies. However, the results are consistent with the explanation of measurements on shorter chain alcohols by other investigators as involving a low frequency dispersion region arising from hydrogen bonds and a high-frequency region arising from rotational orientation of the alkoxy groups.

(20) G. B. Rathmann, Ph.D. Thesis, Princeton University, 1951. PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

Internal Rotation in N-Methylchloroacetamide

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RECEIVED APRIL 18, 1955

Infrared and Raman spectra and dipole moments of N-methylchloroacetamide have been observed. From the experimental results it has been concluded that in the liquid state the molecules are in both the *trans* and *gauche* forms, of which only the *gauche* form persists in the solid state. In solutions the *trans* molecules become less in number with decreasing dielectric constant of the solvent until they become hardly detectable spectroscopically in non-polar solutions and in the gaseous state. Based on these experimental data, as well as those previously obtained for halogenoacetyl halides and chloroacetone, the nature of the hindering potential to internal rotation about the CH₂-CO axis is discussed.

In a series of investigations we have been interested in the determination of the configuration of the polypeptide chain in relation to the internal rotation about single bonds as axes.¹ The present experiment has been made with the object of determining the molecular structure of N-methylchloroacetamide in order to obtain more information on the internal rotation about the CH₂-CO axis, which is one of the three internal rotation axes contained in the main chain of polypeptides.

(1) For the summary see S. Mizushima, "Advances in Protein Chemistry," Vol. IX, Academic Press, New York, N. Y., 1954.

Experimental

N-Methylchloroacetamide was prepared by adding aqueous sodium hydroxide solution and chloroacetyl chloride to the aqueous solution of methylamine.² The reaction product was extracted with chloroform and the pure sample was obtained by vacuum distillation, m.p. 46°.

The Raman spectra were measured in the solid state at room temperature and in the liquid state at 60°. The result is shown in Table I. Saturated aqueous solution of sodium nitrite and carbon tetrachloride solution of iodine were used as filters in the measurement in the solid state.

(2) W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **21**, 145 (1915).