

diisopropylamine is highly dissociated in the presence of water. When R' is methyl and R'' is isopropyl (N-(2-nitroisobutyl)-N-(isopropyl)-methyamine), the equilibrium constant is approximately 300. The stability in the presence of water is much better, although it can be seen from the results in the Experimental section that the 2-nitroalkylamine dissociates readily in the presence of water. In contrast, N-(2-nitroisobutyl)-isopropylamine, in which the combined steric requirements of the groups R' and R'' are much smaller, dissociates to a much lesser extent under the same conditions.

Hydrogenation of the above 2-nitroalkylamines provides additional evidence of their instability. Each was degraded to a mixture of amines of lower molecular weights. For example, hydrogenation of N-(2-nitroisobutyl)-diisopropylamine yielded among other amines isopropylamine, diisopropylamine and N-(methyl)-diisopropylamine. The mechanism of the formation of these compounds is obscure but it seems reasonable to attribute at least some of the degradation to reaction of the 2-nitroalkylamines with water which forms as soon as some of the nitro groups are hydrogenated. Other reactions which may contribute to the degradation are hydrogenolyses of

either one or both of the methylene bonds. There is considerable strain at this location in the molecule, thus weakening the bonds and making them susceptible to cleavage by catalytic hydrogenation.

It should be noted that steric strain in the 2-nitroalkylamines does not lead to thermal instability. For example the highly hindered N-(2-nitroisobutyl)-diisopropylamine distilled at 95-97° at 5 mm. without any decomposition. Additional evidence of excellent thermal stability of 2-nitroalkylamines with bulky groups on the nitrogen can be obtained by an examination of the boiling points that are listed in Table II.

Summary

Some new 2-nitroalkylamines have been prepared from formaldehyde, 2-nitropropane and dialkylamines.

In contrast to earlier data, some of the new compounds exhibit marked instability in the presence of water, and on hydrogenation are degraded completely to amines of lower molecular weights.

The steric requirements of the alkyl groups in the dialkylamines have been considered and it is suggested that the instabilities of the 2-nitroalkylamines are attributable to steric strain.

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Dielectric Constants, Viscosities, Densities, Refractive Indices and Dipole Moment Calculations for Some Organic Halides¹

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In connection with the interpretation of data on the microwave absorption of liquids,^{2,3,4} it was necessary to measure the dielectric constants, refractive indices, densities and viscosities of a large number of organic halides. This paper presents the results of these measurements for an homologous series and related compounds, and makes use of this large body of information on closely related liquids to examine the relations between dielectric constant and dipole moment.

Purification of Materials.—The separate purification methods used are given below. In the first two columns of Table I are listed the compounds, their sources, purification procedures, and boiling points. The superscripts refer to the manufacturer and the numbers in parentheses refer to the purification procedure used. (1) The sample was shaken with three separate portions of sodium carbonate solution, washed with distilled water until free from alkali and then placed over calcium chloride to dry. When dry,

the sample was decanted and distilled. (2) The sample was shaken with three separate portions of concentrated sulfuric acid, followed by three portions of sodium carbonate solution. It was then washed with distilled water until free from alkali, dried with calcium chloride, and distilled. (3) This procedure was the same as (1), but, in addition, the distillate was placed over feathered zinc to remove the discoloration. It was then decanted and redistilled. (4) The sample was fractionally distilled as received from the manufacturer. (5) The sample was used as received from the manufacturer: (a) Columbia Organic Chemicals Company; (b) Eastman Kodak Company; (c) General Chemical Company; (d) Halogen Chemical Company; (e) Paragon Testing Laboratories.

Experimental Results

Values of the static dielectric constant, ϵ_0 , in Table I were measured at a frequency of 520 kilocycles by means of a previously described heterodyne-beat apparatus,⁵ modified by the introduction of an oscilloscope as a null point instrument. Refractive indices for the sodium D line, n_D^{25} , measured with a Pulfrich refractometer at 25° are given in the third column. The densities reported in

(1) This research was carried out with the support of the Office of Naval Research.

(2) Heston, Hennelly and Smyth, *THIS JOURNAL*, **70**, 4093 (1948).

(3) Laquer and Smyth, *ibid.*, **70**, 4097 (1948).

(4) Hennelly, Heston and Smyth, *ibid.*, **70**, 4102 (1948).

(5) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

TABLE I

Substance	B. p. °C.	Mm.	n_{25}^D	Dielectric constants				Densities				Viscosities (in millipoises)			
				1.0°	25.0°	40.0°	55.0°	1.0°	25.0°	40.0°	55.0°	1.0°	25.0°	40.0°	55.0°
Ethyl bromide ^e (2)	38.3-38.5		1.41636	10.23	9.20					4.82	3.83
<i>n</i> -Propyl bromide ^d (1)	71.5-71.7		1.43123	8.90	8.09	7.59	7.09					6.36	4.95	4.30	3.81
<i>i</i> -Propyl bromide ^d (4)	60.2-60.3		1.42206	10.52	9.46	8.89	8.14					5.97	4.65	4.03	3.52
<i>n</i> -Butyl bromide ^d (2)	102.1-102.6		1.43776	7.57	6.93	6.57	6.24					7.82	5.97	5.09	4.42
<i>i</i> -Butyl bromide ^e (1)	91.5-92.4		1.43490	7.82	7.18	6.74	6.32					8.19	6.10	5.23	4.50
<i>s</i> -Butyl bromide ^d (1)	91.4-91.7		1.43420	9.43	8.64	8.15	7.65					7.37	5.57	4.75	4.13
<i>t</i> -Butyl bromide ^d (1)	72.7-72.9		1.42456	11.56	10.30	9.52	8.75					11.00	7.50	6.10	5.02
<i>n</i> -Amyl bromide ^e (1)	34.6-34.8	22	1.44265	6.88	6.31	6.00	5.70	1.2400	1.2095	1.1906	1.1716	10.32	7.55	6.34	5.49
<i>n</i> -Hexyl bromide ^e (1)	55.2-55.4	24	1.44606	6.30	5.82	5.56	5.30	1.1935	1.1664	1.1499	1.1325	13.14	9.36	7.80	6.62
<i>n</i> -Heptyl bromide ^e (1)	43.1-43.4	5	1.44856	5.74	5.33	5.11	4.90					17.70	11.86	9.55	7.86
<i>n</i> -Octyl bromide ^d (1)	73.8-74.1	10	1.45097	5.32	5.00	4.80	4.60					23.26	14.90	11.73	9.48
<i>n</i> -Nonyl bromide ^e (1)	76.7-76.9	6	1.45207	5.01	4.74	4.57	4.40	1.1065	1.0843	1.0705	1.0570	28.50	17.50	13.50	10.80
<i>n</i> -Decyl bromide ^e (1)	92.1-92.2	4	1.45367	4.75	4.44	4.28	4.12	1.0842	1.0621	1.0483	1.0344	38.80	22.90	17.45	13.70
<i>n</i> -Dodecyl bromide ^e (1)	154.9-157.3	19	1.45637	4.31	4.07	3.93	3.80	1.0476	1.0255	1.0117	0.9980	66.0	36.0	26.00	19.57
<i>n</i> -Tetradecyl bromide ^e (4)	162.0-165.5	17	1.45707	4.04	3.84	3.73	3.61	1.0326	1.0117	0.9989	0.9855	...	41.6	29.6	22.1
<i>n</i> -Hexadecyl bromide ^d (1)	144.8	1	1.46085	...	3.68	3.57	3.46	...	0.9949	0.9827	0.9704	...	67.3	46.6	33.2
<i>n</i> -Octyl chloride ^d (1)	44.4-44.8	4	1.42837	5.47	5.05	4.80	4.55					17.37	11.50	9.12	7.39
<i>n</i> -Octyl iodide ^e (3)	104.8-106.8	23	1.48503	4.90	4.62	4.44	4.27					32.35	19.50	15.00	11.70
<i>n</i> -Dodecyl chloride ^d (4)	130	15	1.44174	4.45	4.17	3.99	3.85					47.5	26.50	19.60	15.00
Cyclohexyl bromide ^e (5)		1.49345	8.54	7.92	7.55	7.18	1.3506	1.3215	1.3032	1.2850	32.40	20.00	15.65	12.50
Chlorobenzene ^e (1)	131.4-131.7		1.52240	6.15	5.63	5.31	5.09					10.40	7.56	6.33	5.40
Bromobenzene ^e (1)		1.55774	5.74	5.39	5.18	4.96					15.50	10.80	8.83	7.40
α -Chloronaphthalene ^e (4)	112.0-114.7	7		5.30	5.04	4.88	4.72	1.1917	1.1709	1.1581	1.1450	54.8	29.40	21.40	16.05
α -Bromonaphthalene ^e (4)	117.4	4		...	4.83	4.70	4.57	...	1.4788	1.4634	1.4480	...	45.2	32.00	23.30
Ethylene chloride ^e (4)	84.1-84.8		1.44305	11.66	10.16	9.37	8.66					11.00	7.90	6.55	5.50
Ethylene bromide ^e (1)	131.4-132.0		1.53641	...	4.76	4.67	4.58					...	16.00	13.80	10.52
Tetramethylene chloride ^b (1)	50.0-50.1	17	1.45297	9.64	8.90	8.44	7.98	1.1612	1.1340	1.1175	1.1005	19.88	13.06	10.50	8.60

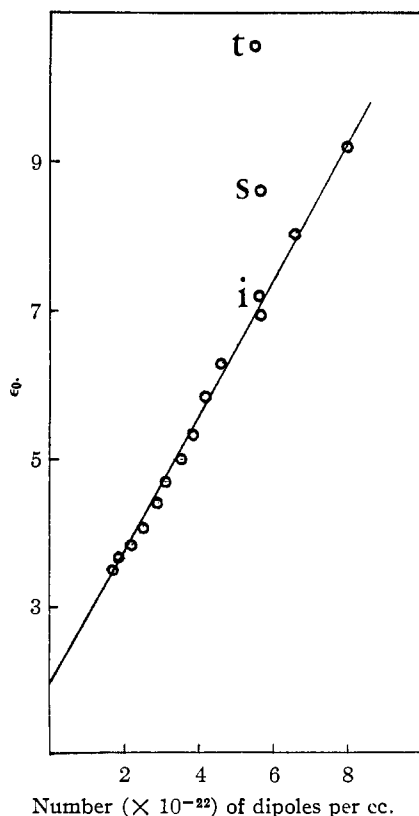


Fig. 1.—Plot of dielectric constants of alkyl bromides against number of dipoles per cc. at 25°.

Table I were determined with a chainomatic Westphal balance. Values for the other substances treated in this paper were obtained from the literature.^{6,7} The measurements in the present work were made over a 45° temperature range and interpolated or extrapolated to the desired temperatures. The accuracy of this method was more than sufficient for use in the calculation of viscosities, the probable error being $\approx 0.02\%$. The time of flow measurements used in calculating the viscosities in Table I were made with a modified Ostwald viscometer described by Cannon and Fenske.⁸ The probable error of the calculated viscosities was $\approx 0.2\%$.

Discussion of Results

The decrease of ϵ_0 with increasing chain length is due to the decrease in the number of molecular dipoles per unit volume with increasing molecular size, as shown in Fig. 1, where ϵ_0 is plotted against the number of dipoles per cc. for the alkyl bromides. The linear relationship indicates that, as the chain length increases, the C-Br dipole is merely diluted in the hydrocarbon medium provided by the chain. Extrapolation of the line to zero dipole concentration gives a dielectric constant value, 1.95, a typical value for an aliphatic hydrocarbon. The value for hexadecane is 2.04 and that for heptane is 1.92 at 25°. Also shown by Fig. 1 are the branched-chain butyl bromides, for which the dielectric constant rises as the mo-

(6) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926); Timmermans, Martin and Delcourt, *ibid.*, **25**, 411 (1928); Timmermans and Delcourt, *ibid.*, **31**, 85 (1934); Timmermans and Hennaut-Roland, *ibid.*, **34**, 693 (1937).

(7) Vogel, *J. Chem. Soc.*, **146**, 637 (1943).

(8) Cannon and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1937).

lecular shape approaches that of a sphere. Similar plots for solutions show that the dielectric constants of benzene and hexane solutions of chlorobenzene and *m*-dichlorobenzene are linear functions of the numbers of dipoles per cc. throughout the entire range of concentration up to those of the pure polar liquids. *o*-Dichlorobenzene in benzene and in hexane, ethyl bromide in hexane, heptyl bromide in heptane, and *t*-butyl chloride in heptane show a pronounced curvature in these curves.

The extensive dielectric data in Table I can be used to calculate the molecular dipole moments. The classical Debye equation⁹ may be rearranged in a form suitable for dipole moment calculation

$$\mu^2 = \frac{M}{d} \frac{27kT}{4\pi N} \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_0 + 2)(\epsilon_\infty + 2)} \quad (1)$$

where μ is the dipole moment, M , the molecular weight, d , the density, N , Avogadro's number, k , the Boltzmann constant, ϵ_0 , the static dielectric constant, ϵ_∞ , the optical dielectric constant and T , the absolute temperature. The optical dielectric constant, which is slightly larger than n^2 because of the atomic polarization, has been calculated from the refraction in a manner previously described.⁴ The inadequacy of this equation when applied to pure polar liquids, as in this case, is well-known. It is evident in Table II, where the calculated values of the dipole moment increase with rising temperature, as shown by the differences between the 55° and the 1° moment values in the third column, and decreasing dipole concentration per unit volume, still being at least 20% low even for the largest molecule, that of hexadecyl bromide.

Several attempts have been made to correct this discrepancy^{10,11,12} by assuming that the molecules are not able to orient freely in the liquid. However, it remained for Onsager,¹³ and later Kirkwood,¹⁴ to present what appear to be the best ways to calculate moments from ϵ_0 and ϵ_∞ data.

Onsager derived an equation which presumably gave a moment corresponding to the gas moment, μ_0 , namely

$$\mu_0^2 = \frac{M}{d} \frac{9kT}{4\pi N} \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (2)$$

Moments calculated by means of equation (2) are tabulated in Table II, together with a column calculated by the Kirkwood equation and values observed by gas (g) or dilute solution measurements (s) obtained from the literature. These observed values had been calculated by means of the Debye equation.

(9) Debye, "Polar Molecules," The Chemical Catalog Company, Inc., Reinhold Publ. Corp., New York, N. Y., 1929.

(10) Debye, *Chem. Rev.*, **19**, 171 (1936).

(11) White, *J. Chem. Phys.*, **7**, 58 (1939).

(12) Wilson, *Chem. Rev.*, **25**, 377 (1939).

(13) Onsager, *THIS JOURNAL*, **58**, 1486 (1936).

(14) Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

TABLE II
DIPOLE MOMENTS ($\times 10^{18}$)

	Debye		Calculated Onsager		Kirkwood 25°	Obs.
	25°	55° -1°	25°	55° -1°		
C ₂ H ₅ Br	1.28 (0.11)		1.80 (0.02)		1.90	2.02 g ¹⁵
<i>n</i> -C ₃ H ₇ Br	1.36	.10	1.83	.02	2.02	2.15 g ¹⁶
<i>i</i> -C ₃ H ₇ Br	1.45	.12	2.06	.02	2.10	2.19 g ¹⁶
<i>n</i> -C ₄ H ₉ Br	1.41	.12	1.80	.06	1.92	2.15 g ¹⁶
<i>i</i> -C ₄ H ₉ Br	1.44	.11	1.86	.03	1.92	1.97 s ¹⁷
<i>s</i> -C ₄ H ₉ Br	1.52	.13	2.10	.05	2.14	2.20 g ¹⁶
<i>t</i> -C ₄ H ₉ Br	1.62	.14	2.39	-.02	2.40	2.21 s ¹⁷
<i>n</i> -C ₅ H ₁₁ Br	1.46	.10	1.82	.03	1.99	1.95 s ¹⁸
<i>n</i> -C ₆ H ₁₃ Br	1.51	.10	1.83	.04	1.99	1.97 s ¹⁹
<i>n</i> -C ₇ H ₁₅ Br	1.53	.09	1.81	.04	1.90	2.15 g ²⁰
<i>n</i> -C ₈ H ₁₇ Br	1.56	.10	1.81	.05	1.88	1.96 s ¹⁹
<i>n</i> -C ₉ H ₁₉ Br	1.58	.10	1.81	.06	1.89	1.89 s ²¹
<i>n</i> -C ₁₀ H ₂₁ Br	1.59	.08	1.79	.03	1.90	1.90 s ²²
<i>n</i> -C ₁₂ H ₂₅ Br	1.61	.07	1.79	.03	1.89	
<i>n</i> -C ₁₄ H ₂₉ Br	1.63	.08	1.78	.05	1.83	
<i>n</i> -C ₁₆ H ₃₃ Br	1.66	.07	1.80	(.03)	1.87	
<i>n</i> -C ₈ H ₁₇ Cl	1.58	.07	1.84	.01	2.14	
<i>n</i> -C ₈ H ₁₇ I	1.46	.07	1.65	.04	1.80	
<i>n</i> -C ₁₂ H ₂₅ Cl	1.65	.07	1.84	.03	2.11	
C ₆ H ₁₁ Br	1.52	.11	2.00	.04	2.08	2.11 s ²³
C ₆ H ₅ Cl	1.22	.06	1.45	.01	1.54	1.72 g ²⁴
C ₆ H ₅ Br	1.17	.07	1.37	.05	1.52	1.77 g ²⁴
α -C ₁₀ H ₇ Cl	1.20	.07	1.35	.05	1.33	1.50 s ²⁵
α -C ₁₀ H ₇ Br	1.13 (.06)		1.25	.05	1.29	1.48 s ²⁵
C ₂ H ₄ Cl ₂	1.31	.09	1.89	-.05	2.94	1.47 g ²⁶
C ₂ H ₄ Br ₂	0.93	.09	1.04 (.1)		1.14	1.04 g ²⁶
C ₄ H ₈ Cl ₂	1.52	.11	2.10	.04	2.13	2.22 g ²⁷

The fairly constant value of the moment, as calculated for the straight chain aliphatic bromides, is to be expected from the constancy of the moment of the C-Br dipole and its environment. These values are lower than some which have been calculated by other workers,^{28,29} because higher values for the optical dielectric constant have been used in the present calculations. The calculated dipole moment values are generally slightly lower than those measured in solution and markedly lower than those measured in the vapor.

Kirkwood's¹⁴ treatment has been applied to associated liquids as well as to normal liquids.^{30,31} His equation for the polarization, P , is

(15) Smyth and McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

(16) Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

(17) Parts, *Z. physik. Chem.*, **B7**, 327 (1930).

(18) Cowley and Partington, *J. Chem. Soc.*, 130 (1937).

(19) Henrlon, *Bull. soc. roy. sci. Liège*, **8**, 36 (1939).

(20) Smyth and McAlpine, *J. Chem. Phys.*, **3**, 347 (1935).

(21) Hertel and Schinzel, *Z. physik. Chem.*, **B48**, 289 (1941).

(22) Henrlon, *Bull. soc. roy. sci. Liège*, **10**, 414 (1941).

(23) Hassel and Naeshagen, *Z. physik. Chem.*, **B15**, 373 (1932).

(24) Hurdis and Smyth, *THIS JOURNAL*, **64**, 2212 (1942).

(25) Nakata, *Bull. Chem. Soc. Japan*, **10**, 318 (1935).

(26) Bloom and Sutton, *J. Chem. Soc.*, 727 (1941).

(27) Oriani and Smyth, to be published.

(28) Böttcher, *Physica*, **6**, 59 (1939).

(29) Watanabe, Mizushima and Morino, *Sci. Rep. Inst. Phys. Chem. Res.*, **39**, 401 (1942).

(30) Oster and Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

(31) Oster, *THIS JOURNAL*, **68**, 2036 (1946).

TABLE III
 DIPOLE MOMENTS CALCULATED WITH KIRKWOOD EQUATION

	$g^{1/2}\mu_0$	$\mu_0(\text{obs.})$		$g^{1/2}\mu_0$	$\mu_0(\text{obs.})$
Methyl bromide ³²	1.65	1.78 g ¹⁵	Chlorobenzene ³⁶	1.54	1.72 g ³⁹
Ethyl iodide ³³	1.66	1.90 g ¹⁵	$c_2 = 0.6$ in benzene ³⁶	1.65	
1-Bromo-2-chloroethane ³⁴	1.53	1.09-1.28 g ³⁵		1.70	
Ethyl bromide ³⁶	1.90	2.02 g ¹⁵		1.75	
$c_2 = 0.7$ in hexane ³⁶	1.92		<i>o</i> -Dichlorobenzene ⁴⁰	2.26	2.51 g ³⁹
0.5	1.80		$c_2 = 0.5$ in benzene ⁴⁰	2.32	
0.3	1.86			2.45	
0.2	1.90		<i>m</i> -Dichlorobenzene ⁴⁰	1.42	1.67 g ⁴¹
<i>t</i> -Butyl chloride ³⁷	2.39	2.13 g ³⁸			
$c_2 = 0.2$ in heptane ³⁷	2.42				

$$P = \frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{9\epsilon_0} \frac{M}{d} = \frac{4\pi N}{3} \left(\alpha + \frac{g\mu^2}{3kT} \right) \quad (3)$$

where α is the molecular polarizability, and g is a semi-empirical parameter whose difference from unity is a measure of the hindering effect of a molecule on its neighbors. If P is plotted against $1/T$, the slope should be proportional to $g\mu^2$. Therefore, we may write

$$g^{1/2}\mu = 0.0128b^{1/2} \times 10^{-18} \quad (4)$$

where b equals the slope. $g^{1/2}\mu$ can be calculated from Onsager's work as

$$g^{1/2}\mu_0 = \frac{3(2\epsilon_0 + \epsilon_\infty)}{(\epsilon_\infty + 2)(2\epsilon_0 + 1)} g^{1/2}\mu \quad (5)$$

A plot of ϵ_0 vs. $3(2\epsilon_0 + \epsilon_\infty)/(\epsilon_\infty + 2)(2\epsilon_0 + 1)$ for different values of ϵ_∞ makes the calculations simpler and also shows that, in normal cases, the calculated moment value should rise with increasing temperature if $g^{1/2}\mu$ remained constant, because ϵ_0 and ϵ_∞ decrease with rising temperature, thus giving higher values of $g^{1/2}\mu_0$.

The results of additional calculations with the Kirkwood equation made upon data in the literature are listed in Table III. Data on solutions have been examined by means of the equation

$$P_2 - \frac{c_1}{c_2} P_1 = \frac{(\epsilon_{12} - 1)(2\epsilon_{12} + 1)}{9\epsilon_{12}} \frac{c_1 M_1 + c_2 M_2}{c_2 d_{12}} \quad (6)$$

in which c is mole fraction and subscript 1 refers to the non-polar liquid, 2 to the polar substance, and 12 to the mixture. If the right side of equation (6) is plotted against $1/T$, the slope of the line obtained gives $g^{1/2}\mu$ by means of equation (4) just as for the pure liquids.

The Kirkwood polarization when plotted against $1/T$ for each of the substances or solutions listed in Tables II and III and for a number of substances and solutions not listed gives a straight line except for a slight curvature in the cases of *n*-butyl chloride and *n*-butyl bromide,

(32) Morgan and Lowry, *J. Phys. Chem.*, **39**, 2385 (1930).

(33) Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929).

(34) Smyth, Dornte and Wilson, *ibid.*, **53**, 4342 (1931).

(35) Zahn, *Phys. Rev.*, **40**, 291 (1932).

(36) Smyth and Morgan, *THIS JOURNAL*, **50**, 1547 (1928).

(37) Smyth and Dornte, *ibid.*, **53**, 545 (1931).

(38) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

(39) Hurdis and Smyth, *THIS JOURNAL*, **64**, 2212 (1942).

(40) Smyth and Morgan, *ibid.*, **49**, 1030 (1927).

(41) Groves and Sugden, *J. Chem. Soc.*, 1782 (1937).

possibly too slight to be significant. Curvature or discontinuity and, frequently, high values of g have been observed in the case of several highly polar or associated alcohols and ketones not included in the tables. In these latter cases, some change in the structure of the liquid presumably occurs with change of temperature. The linearity found for the other substances does not necessarily mean constancy of structure and dipole moment, for ethylene chloride, bromide and chlorobromide, whose moments vary with temperature, show the linear relationship. Molecules of this type which possess movable dipoles and may exist in the form of rotational isomers will be discussed in detail in connection with other measurements. The branched chain bromides in Table II and *t*-butyl chloride and *o*-dichlorobenzene in Table III give polarization values less than the induced polarization when their P vs. $1/T$ lines are extrapolated to $1/T = 0$. This would result if $g\mu^2$ increased as a linear function of temperature. The Debye polarization, too, even for a pure polar liquid⁴⁰ or solid,⁴² is often a linear function of $1/T$.

The values of $g^{1/2}\mu_0$ for the straight-chain alkyl bromides in Table II are so close to the gas values where available and to the less accurate solution values that the deviation of g from 1 is seemingly much less than the error involved in any attempt to calculate g by theoretical means. The values of $g^{1/2}\mu_0$ or μ_0 , g being taken as 1, are slightly closer to the so-called observed values than are those calculated by the Onsager equation, but the difference is not significant since the $g^{1/2}\mu_0$ values were calculated from the slopes of the P vs. $1/T$ curves, which accounts for the greater variations from one member of the series to the next.

It appears that the calculated values for the straight-chain alkyl bromides are lower than the gas values by amounts, in the case of $g^{1/2}\mu_0$, no greater than the "solvent effects." The nearly spherical molecules of *t*-butyl chloride and bromide, which have almost zero "solvent effect" and might be expected to conform particularly well to theory, give calculated moments about 10% high. The considerable variation in mo-

(42) Smyth and Hitchcock, *THIS JOURNAL*, **55**, 1830 (1933).

lecular shape among the straight-chain bromides has very little effect upon the calculated moment. The values of $g^{1/2}\mu_0$ for the more dilute solutions of chlorobenzene and *o*-dichlorobenzene are remarkably close to the gas values, but the solution values for ethyl bromide differ in no consistent manner from that for the pure liquid.

Summary

The dielectric constants at 520 kilocycles, the viscosities, and the densities not available in the literature have been measured at temperatures from 1 to 55° for twenty-seven liquid organic

halides. The refractive indices for the sodium D line of the liquids have been measured at 25°.

The dielectric constants of the straight-chain alkyl bromides are a linear function of the number of dipoles per cc. of liquid.

The Onsager and Kirkwood equations have been used with some success to calculate dipole moment values from these dielectric constants and others taken from the literature. The discrepancies between observed and calculated values seem to be not closely related to molecular structure.

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The Dielectric Constants of Water, Hydrogen Peroxide and Hydrogen Peroxide-Water Mixtures^{1,2}

BY PAUL M. GROSS, JR.,³ AND ROBERT C. TAYLOR⁴

I. Introduction

The dielectric constants of most polar liquids at room temperature lie below 20 but in the case of certain compounds such as water, some alcohols, hydrogen peroxide, hydrogen fluoride and a few others, much higher values are found. These high values of the dielectric constant are greatly in excess of those to be expected even for large values of the molecular dipole moments and are characteristic of liquids in which molecular orientation and short range structure exist as a result of hydrogen bonding. Inasmuch as many properties, and in particular the electrical properties, are markedly affected by such factors, an accurate knowledge of the dielectric constants is of general interest in connection with the study of associated liquids. Of this group of liquids, water has received the greatest attention, both experimentally and theoretically. Hydrogen peroxide being the liquid most closely related to water would seem to merit a corresponding amount of consideration in the study of how specific factors modify the general behavior. Unfortunately, however, the rather appreciable experimental difficulties involved in dealing with the compound have discouraged any extensive amount of work.

Only two sources of information are available in the literature concerning the dielectric constant of hydrogen peroxide. Calvert⁵ in 1900 reported the dielectric constant of an aqueous (40%) hy-

drogen peroxide solution, while a number of years later Cuthbertson^{6a} and Maass^{6b} published a more extensive series of measurements at 0° for a range of concentrations varying from pure water up to 99.45% hydrogen peroxide. These latter data until now have provided the only information on the pure compound.

The dielectric constants presented in this paper cover the concentration range from 0 to 99.2% hydrogen peroxide and the temperature range from approximately -65 to 30°; data for pure hydrogen peroxide were obtained by a short extrapolation. The measurements are of moderate precision and were made mostly at a frequency of 200 Kc. using a bridge circuit of a new design. As a preliminary to the measurements on hydrogen peroxide, the dielectric constant of pure water was measured as a function of temperature with excellent agreement with the results given by Wyman.⁷ The important problem of decomposition, which is always present when working with hydrogen peroxide, was overcome by selection of suitable materials and proper pretreatment.

II. Apparatus and Procedure

Apparatus.—The design, construction and residual errors of the bridge and associated equipment with which the measurements were made have been described recently by Cole and Gross⁸ and will not be discussed in detail in this paper. Certain features, however, are pertinent to the experimental procedure and will be discussed briefly. The bridge design is such that admittances due to guard ring circuits have a negligible effect on the bridge balance. This important feature eliminates the second balance usually necessary when guard rings are incorporated into a cell design and greatly simplifies the measurements. One of the chief advantages resulting was that a

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(5) H. L. Calvert, *Ann. phys.*, [4] 1, 483 (1900).

(6) (a) A. C. Cuthbertson and O. Maass, *THIS JOURNAL*, **52**, 489 (1930); (b) E. P. Linton and O. Maass, *ibid.*, **53**, 957 (1931).

(7) J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

(8) R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Instruments*, **20**, 252 (1949).