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The dielectric constants and densities of dilute solutions of nitromethane in heptane and of chloropicrin in heptane and in benzene have been measured and used to calculate the dipole moments of the solute molecules. The values thus calculated are considerably lower than those previously obtained in the gaseous state and are not well represented by the empirical equation of Müller. Measurement of the dielectric constant of pure liquid and solid nitromethane fails to show the existence of molecular rotation in the solid state. It is concluded, therefore, that the heavier molecule of chloropicrin does not rotate in the crystal.

A S IT seemed that dielectric constant measurements on nitromethane and chloropicrin in the solid, liquid and gaseous states would be of interest, the data contained in the present paper were obtained more than two years ago. The measurements on the gases have already been considered[1] in their bearing upon the problem of the structure of these and similar molecules. The measurements upon the liquid and solid states, which were made with newly purified materials, will be used to investigate the effect of solvent upon the apparent dipole moment and the possibility of dipole rotation in the crystal. Chloropicrin was not measured as a pure liquid or solid because the failure to find molecular rotation in solid nitromethane made it appear certain that the chloropicrin molecule with its much larger moment of inertia would not rotate in the crystal. The dielectric constants and densities were measured with apparatus previously described[2] as was the dielectric constant of pure nitromethane.[3] The refractive indices were measured with a Pulfrich refractometer.

PURIFICATION OF MATERIALS

Nitromethane

Material from the Eastman Kodak Company was distilled from phosphorus pentoxide and twice fractionally redistilled; m.p. $-28.6°$; b.p. $101.5°$ (762 mm); n_D^{25} 1.37970; d_4^{25} 1.1314.

[1] C. P. Smyth and K. B. McAlpine, J. Am. Chem. Soc. **56**, 1697 (1934).

[2] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 527 (1931).

[3] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).

Chloropicrin

Material from the Eastman Kodak Company was dried with calcium chloride and fractionally distilled, then redistilled under reduced pressure, the middle fraction being used; n_D^{25} 1.45956; d_4^{25} 1.6483.

EXPERIMENTAL RESULTS

Dilute solutions of nitromethane in heptane and of chloropicrin in heptane and in benzene were measured. In Table I the first column gives the mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25° and 50° of the dielectric constants ϵ, the densities d of the solutions and the polariza-

TABLE I. *Dielectric constants, densities and polarizations.*

c_2	ϵ 25°	50°	d 25°	50°	P_2 25°	50°
			HEPTANE-NITROMETHANE			
0.00000	1.920	1.884	0.6796	0.6579	(221.5	207.0 $=P_\infty$)
.00633	1.965	1.924	.6804	.6587	216.3	203.6
.00857	1.980	1.938	.6807	.6590	212.0	201.5
.01005	1.990	1.947	.6809	.6592	210.7	199.8
.01095	1.996	1.953	.6810	.6593	209.0	200.8
.01795	2.043	1.997	.6820	.6602	203.4	197.8
.01934	2.053	2.006	.6821	.6603	203.7	197.5
.02037	2.060	2.012	.6822	.6604	203.5	196.6
.02808	2.112	2.060	.6834	.6615	198.8	193.1
.03936	2.188	2.132	.6848	.6628	193.6	189.8
			HEPTANE-CHLOROPICRIN			
0.00000	1.920	1.884	0.6796	0.6579	(95.0	87.7 $=P_\infty$)
.00835	1.941	1.902	.6850	.6633	95.7	87.3
.01752	1.964	1.922	.6911	.6692	94.5	87.7
.01852	1.966	1.924	.6917	.6698	94.0	87.6
.03866	2.017	1.968	.7050	.6827	93.3	87.2
.07103	2.103	2.042	.7268	.7038	93.0	87.3
.11071	2.213	2.141	.7542	.7305	92.0	87.4
			BENZENE-CHLOROPICRIN			
0.00000	2.274	2.224	0.8729	0.8460	(94.5	88.5 $=P_\infty$)
.00560	2.298	2.245	.8775	.8505	94.5	89.2
.01304	2.331	2.273	.8841	.8568	93.4	88.1
.02646	2.389	2.323	.8956	.8680	92.4	86.8
.04604	2.475	2.398	.9125	.8844	91.4	86.5
.06068	2.538	2.453	.9248	.8965	90.4	85.7
.08188	2.628	2.534	.9429	.9141	88.9	85.0

Compound		CH_3NO_2	CCl_3NO_2	CCl_3NO_2
Solvent		C_7H_{16}	C_7H_{16}	C_6H_6
MR_D		12.49	27.29	27.29
$P_\infty - MR_D$	25°	209.0	67.7	67.2
	50°	194.5	60.4	61.2
$\mu_{sol.}(\times10^{18})$obs.	25°	3.17	1.80	1.80
	50°	3.18	1.78	1.79
$\mu_{gas}(\times10^{18})$calc.	25°	3.28	1.86	1.92
	50°	3.28	1.84	1.90
$\mu_{gas}(\times10^{18})$obs.		3.42	1.88	1.88

tions P_2 of the polar substance. P_2 is obtained by use of the usual equations,

$$P_{12} = (\epsilon - 1)(c_1 M_1 + c_2 M_2)/(\epsilon + 2)d$$

and

$$P_2 = P_1 + (P_{12} - P_1)/c_2,$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. These values of P_2 are extrapolated to infinite dilution to obtain P_∞, from which the dipole moment μ is obtained by means of the equation $\mu = 0.0127 \times 10^{-18} [(P_\infty - MR_D)T]^{\frac{1}{2}}$, in which T is the absolute temperature and MR_D, the molar refraction, for the D sodium line, is calculated from the experimental values of n_D^{25} and d given under the "Purification of Materials." The values thus obtained are given in Table II together with moment values calculated from them for the gaseous state by an empirical equation and the previously observed values for the gaseous state. The dielectric constant values for solid and liquid nitromethane are shown in

TABLE III. *Dielectric constant of pure nitromethane.*

Kc	70	30	12	7	3	1	0.7	0.4	0.3
$t(°C)$					SOLID (m.p. $-28.6°$)				
−90	3.39	3.39	3.39	3.39	3.39	3.39	3.39	3.39	3.39
−80	3.43	3.43	3.43	3.43	3.43	3.43	3.44	3.44	3.44
−70	3.48	3.48	3.47	3.48	3.48	3.48	3.49	3.49	3.49
−60	3.53	3.53	3.53	3.53	3.53	3.54	3.54	3.55	3.55
−50	3.59	3.59	3.59	3.59	3.59	3.60	3.61	3.63	3.63
−40	3.66	3.66	3.67	3.67	3.68	3.72	3.74	3.79	3.79
−35	3.72	3.72	3.73	3.74	3.75	3.82	3.85	3.90	3.91
−33	3.74	3.75	3.77	3.79	3.81	3.90	3.95	3.99	4.02
−31	3.78	3.80	3.83	3.86	3.94	4.05	4.13	4.22	4.28
−30	3.80	3.84	3.89	3.96	4.02	4.14	4.28	4.46	4.56
−29	3.93	3.93	3.99	4.05	4.15	4.36	4.56	4.87	5.02
		LIQUID							
−31.1	45.51	45.53	45.69						
−26.7	44.46	44.50	44.67						
−22.0	43.43	43.50	43.65						
−15.3	41.99	42.04	42.26						
−8.5	40.66	40.76	40.98						
2.9	38.57	38.68	38.97						
10.3	37.21	37.34	37.70						
19.0	35.79	35.95	36.35						
27.4	34.48	34.68	35.12						

Table III, the frequency in kilocycles at which the measurement was made being given at the top of each column. Nearly half of the measurements are omitted for the sake of brevity. The conductance of the liquid was sufficient to cause some variation of the apparent dielectric constant with frequency, from which one would conclude that the values at 70 kc may be about 1 or 2 percent high, although they are considerably lower than those in *International Critical Tables*. The values for the solid are presumably low because of the presence of small cavities.

DISCUSSION OF RESULTS

The differences between the dipole moment values in Table II at 25° and at 50° are no greater than the experimental errors. These apparent values of the moments are considerably lower than those found for the molecules in the gaseous state as commonly observed.[4] Various more or less empirical equations have been developed to represent the relation of the dielectric constant ϵ_1 of the solvent to the apparent polarization of the solute or the ratio of the moment $\mu_{sol.}$ found in solution to the moment μ_{gas} of the gas. The equation of Müller,[4] $\mu_{sol.}/\mu_{gas} = 1 - 0.038(\epsilon_1 - 1)^2$, gives the calculated values in Table II. As the experimentally observed values of chloropicrin in the two solvents are indistinguishable, the equation gives a difference of 0.06 between the two values calculated for the gas, which is unsatisfactory. The mean of the gas values calculated from the two sets of solutions is identical with the value observed for the gas. The equation seems, therefore, to be a not bad approximation for chloropicrin. For nitromethane, the equation gives a calculated gas value less than half of the way up to the observed value for the gas and must, accordingly, be regarded as inadequate in this case. As a matter of fact, this is not at all surprising since its applicability has been known to be limited[5] and Müller and Mortier[6] in a recent paper show several different types of solvent effect upon polarization. The equation works admirably for nitrobenzene,[7] but the exceptionally

[4] See H. Müller, Physik. Zeits. **34**, 689 (1933) and others.
[5] Cf. C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **3**, 347 (1935).
[6] Müller and Mortier, Physik. Zeits. **36**, 371 (1935).
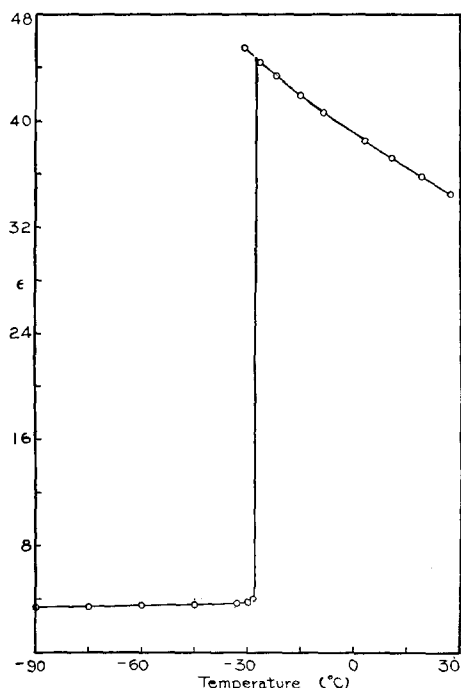[7] K. B. McAlpine and C. P. Smyth, J. Chem. Phys. **3**, 55 (1935).

strong field of force which must exist around the small nitromethane molecule with its large dipole moment may well cause behavior different from that of a molecule larger in size or smaller in moment.

The variation with temperature of the dielectric constant of pure nitromethane shown in Table III and Fig. 1, which gives the values at a frequency of 70 kc, is very similar to that previously found for nitrobenzene and leads to similar conclusions. What looks, at first glance, like a slight anomalous dispersion in the values in Table III is presumably the effect of the presence of a small quantity of impurity, which causes traces of liquid to remain in the solid near the

melting point. As in the case of nitrobenzene, there is no change in the course of the curve for the liquid in the neighborhood of the freezing point, even when supercooled as much as 2.5° below it, which indicates that there is no suddenly increased formation of molecular aggregates in this region, since such formation would almost certainly alter greatly the effect of the large dipoles in the molecules and so radically affect the curve. The tremendous drop in dielectric constant on solidification to a value normal for a solid in which there is no appreciable effect of dipoles or ionic charges indicates that there is little or no dipole rotation in the solid. This proves the absence in the crystal of rotation of the molecule about any axis perpendicular to the line passing through the carbon and nitrogen nuclei, in which the molecular dipole lies, but does not prove the absence of rotation around this line as axis, about which the molecule would have its smallest moment of inertia. The methyl alcohol molecule, which must have a much smaller moment of inertia around an axis close to the line through the carbon and oxygen nuclei, shows dipole rotation between $-114.0°$ and the melting point,[8] which further measurements indicate to be rotation of the entire molecule.[9] As the moment of inertia of the nitromethane molecule around an axis perpendicular to the carbon-nitrogen line is much larger than most, if not all, of the moments of inertia involved where the existence of molecular rotation has been clearly established and as the large dipole moment of the molecule should also tend to make the energy necessary for rotation around such an axis large, the failure to find rotation in this case is in conformity with our ideas of molecular rotation in solids. In other words, molecular rotation in a solid is very improbable unless the moment of inertia involved in the rotation is small and the internal field weak.

[8] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. 56, 1084 (1934).
[9] Paper by S. A. McNeight and C. P. Smyth presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society, New York, April 26, 1935.