1835 cm.$^{-1}$ were assigned by rather complex combinations deriving intensity through resonance from the 1803 cm.$^{-1}$ fundamental. The 835 cm.$^{-1}$ matrix band has a shoulder on the high frequency side of the band whose origin remains obscure.

All band contours as observed by Nielsen, *et al.*,[4] agree with those predicted in the Table I assignment with the one exception of the 440 cm.$^{-1}$ band already mentioned.

The spectroscopic entropy has been calculated using the assignment in Table I and the microwave rotational constants of Robinson.[16]

At 280.66°K. (b.p.) $S = 66.99$ cal./deg. mole
298.16°K. $S = 67.82$ cal./deg. mole

This reduces the apparent third law discrepancy between calorimetric and spectroscopic entropy to 0.36 cal./deg. mole. In the calorimetric measurements,[6] an unusual expansion of the sample near the melting point stretched and eventually broke the resistance thermometer. There are also unresolved questions about the possible presence of a second crystalline form. Consequently the accuracy of the calorimetric entropy is questionable. Professor Giauque has told us of his intention to repeat the heat capacity measurements to firmly settle the third law value.

Acknowledgment.—We wish to thank Mr. Dolphus E. Milligan for aid in performing the matrix experiments.

BERKELEY 4, CALIFORNIA

(16) G. W. Robinson, *J. Chem. Phys.*, **21**, 1741 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXI. Relaxation Times, Viscosities and Molecular Shapes of Substituted Pyridines, Quinolines and Naphthalenes[1,2]

BY ROBERT W. RAMPOLLA AND CHARLES P. SMYTH

RECEIVED SEPTEMBER 5, 1957

Dielectric constant and loss measurements at wave lengths of 1.25, 3.22 and 10.0 cm. and 300 m. have been carried out at 20, 40 and 60° on 1- and 2-methylnaphthalene, 1,2,3,4-tetrahydronaphthalene, 1-nitronaphthalene, 2-, 4-, 6- and 8-methylquinoline and 2,4- and 2,6-dimethylpyridine in the pure liquid state, and also on 1-nitronaphthalene in dilute benzene solution. These data have been used to construct arc plots from which were obtained the critical wave length, distribution coefficient and optical dielectric constant at each temperature. A change in the direction of the dipolar vector for similarly shaped, non-spherical molecules is found to have a marked effect on relaxation time but not on viscosity. A rough proportionality between relaxation time and viscosity is observed for molecules of not too different size and shape provided the direction of their dipolar vectors does not vary appreciably.

The investigation into the relations between dielectric relaxation and other molecular properties, such as size, shape and viscosity, has been extended to include a series of ten aromatic compounds, all but two of which are modifications of the basic naphthalene nucleus. The rigidity of the molecules eliminates some of the difficulties involved in the interpretation of these relations when internal rotation and bending are possible,[3,4] while the similarity in their sizes and shapes should afford a convenient basis for comparison. All the compounds have been measured in the pure liquid state, and, in addition, 1-nitronaphthalene has been investigated in dilute benzene solutions. The methods used in measuring the dielectric constants and losses of liquids and in calculating critical wave lengths have been described in previous papers of this series.[5-11]

Purification of Materials.—The 1,2,3,4-tetrahydronaphthalene and 4-methylquinoline used were obtained from Matheson, Coleman and Bell, Inc., the 6- and 8-methylquinoline from the Eastman Kodak Co., while the remaining six compounds were from Brothers Chemical Co. 2-Methylnaphthalene was fractionally crystallized at the melting point and distilled at reduced pressure. 1-Nitronaphthalene was fractionated at reduced pressure and recrystallized twice from heptane. The other compounds were refluxed over barium oxide for 24 hr. and then fractionally distilled. Analytical reagent grade benzene from the General Chemical Co. was used for the solution measurements without further purification. Although the boiling point of the 1-methylnaphthalene sample agreed well with the literature value, the fact that it was obtained from "Practical" grade material would seem to account for the anomalously high dipole moment value obtained for it in Table III. Boiling or melting points and refractive indices are tabulated below, together with values taken from the literature.

Experimental Results

The dielectric constants ϵ' and losses ϵ'', measured at 1.25, 3.22 and 10.0 cm., the static dielectric constants ϵ_0, measured at 300 m., the densities d and the viscosities η for the pure liquids are listed in Table I. Table II contains the slopes, a_0, a' and a'' of dielectric constant and loss against mole fraction for solutions of 1-nitronaphthalene in benzene. The data in Tables I and II have been used to construct Cole and Cole arc plots[12] from which critical wave lengths λ_m, distribution parameters α and infinite frequency or optical dielectric constants ϵ_∞ were obtained. The results at

---

(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 paper represents a part of the work submitted by Mr. R. W. Rampolla to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) C. P. Smyth, *J. Phys. Chem.*, **58**, 580 (1954).

(4) C. P. Smyth, *Rec. Chem. Progr.*, **11**, 1 (1950).

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

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

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

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

(9) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3447 (1950).

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

(11) F. H. Branin, Jr., *J. Appl. Phys.*, **23**, 990 (1952).

(12) K. S. Cole and R. S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

BOILING POINTS, MELTING POINTS AND REFRACTIVE INDICES

Compound	B.p., °C.		n^{20}_D	
	Obsd.	Lit.	Obsd.	Lit.
1-Methylnaphthalene	244.4	244.6[a]	....	1.6157[a]
2-Methylnaphthalene	M.p. 34.1	34.6[a]	1.6023 (40°)	1.6026 (40°)[a]
1,2,3,4-Tetrahydronaphthalene	...	207.6[a]	1.5414	1.54135[a]
1-Nitronaphthalene	M.p. 54.5	55.8[b]	....	.....
2-Methylquinoline	246.6	246–247[b]	....	1.6126[b]
4-Methylquinoline	265.6	265.5[b]	....	1.6206[b]
6-Methylquinoline	259.2	258.6[b]	....	1.6157[b]
8-Methylquinoline	247.9	247.8[b]	....	1.6164[b]
2,4-Dimethylpyridine	157.5	157.8[b]	1.4984 (25°)	1.4985 (25°)[b]
2,6-Dimethylpyridine	142.7	142.5[b]	1.4956 (25°)	1.4953 (25°)[b]

[a] Physical and Thermodynamic Properties of Hydrocarbons," A.P.I. Res. Project 44, Carnegie Press, 1953. [b] Beilstein.

each temperature are listed in Table III, together with molar volumes V and macroscopic relaxation times τ_M, calculated from the relation

$$\tau_M = \frac{\lambda_m}{6\pi \times 10^{10}} \qquad (1)$$

Included also are dipole moments μ calculated by means of the Onsager equation[13] for the pure liquids and by means of the Halverstadt and Kumler equation[14] for the solutions. The data are similar in accuracy to those in previous papers of this series.

Discussion of Results

The use of the Onsager equation in calculating dipole moments has met with considerable success in the past, particularly when applied to symmetrical molecules for which it was intended. The moments given in Table I, however, indicate that the Onsager equation is inadequate for highly polar, unsymmetrical molecules. The values thus obtained for the methylquinolines and 1-nitronaphthalene are considerably lower than values obtained from solution measurements, the discrepancy ranging from 12% in the case of 2-methylquinoline to 22% in the case of 4-methylquinoline. The dipole moment of 0.59×10^{-18} found for 1,2,3,4-tetrahydronaphthalene, however, is in close agreement with that of *o*-xylene, 0.62×10^{-18} in the vapor state and 0.58×10^{-18} in benzene solution. On the basis of the vector model of dipole moments, the moments of these compounds should be identical and equal to 1.73 times the moment of toluene, or 0.64×10^{-18}, if one uses the vapor value 0.37 for the latter. The slight increase in moment of 2-methylnaphthalene over that of toluene is consistent with the fact that inductive effects tend to make the moments of 2-substituted naphthalenes somewhat higher than those of their benzene analogs. When compared with the values for 2-methylnaphthalene and toluene, the apparent moment value obtained for 1-methylnaphthalene, 0.51×10^{-18}, is anomalously high, probably because only "Practical" grade material was available as the source of the sample measured. Traces of polar impurities could account for this high value, although the internal consistency of the microwave results indicates that their effect on the relaxation time is negligible.

The critical wave length of 2-methylnaphthalene is considerably longer than that of 1-methylnaphthalene at 40 and 60° despite the fact that the latter has a higher viscosity. This behavior can be accounted for qualitatively, at least, in terms of the position of the molecular dipole axis and molecular shape. With the methyl group in the 2-position, the molecule is elongated, the dipolar vector making an angle of approximately 30° with the long axis of the molecule in the plane of the rings. Substitution of the methyl group in the 1-position, however, produces a structure with the dipole directed almost parallel to the shorter axis of the molecule, again in the plane of the rings. Since dielectric relaxation involves orientation through rotation about an axis perpendicular to that of the dipole, the increase in critical wave length of 2-methylnaphthalene is to be expected as a result of the effective increase in size of the orienting unit for rotations both in and out of the plane of the rings.

The structure of 1,2,3,4-tetrahydronaphthalene is considerably different from that of the methylnaphthalenes, due primarily to the puckering of the saturated ring, which makes the molecule smaller, but thicker. The Stuart–Briegleb model of this molecule reveals that the direction of the resultant dipole moment is normal to the carbon–carbon bond shared between the aliphatic and the aromatic ring and lies in the plane defined by the latter. As a result, the difference between the sizes of the orienting units for rotations about either of the two axes perpendicular to the dipole axis is small. The absence of any distribution of relaxation times, as evidenced by the zero value for α in Table III at all temperatures, together with the shorter critical wave length of 1,2,3,4-tetrahydronaphthalene as compared to those of the methylnaphthalenes is consistent with this model.

The rather long critical wave lengths of 1-nitronaphthalene and the methylquinolines are roughly what one would expect for molecules of this size and polarity. Unlike the methylnaphthalenes, however, the direction of the dipole moment in the latter compounds is affected very little by the position of the methyl group, amounting to a shift of less than 10° from the short axis of the molecule in the case of 2- and 6-methylquinoline. Consequently, while the size of the orienting unit for rotations in the plane of the rings is larger for the 2 and 6 isomers, the opposite is true for rotations out of the plane, and the resulting variation in critical wave length is much smaller than that found for the methylnaphthalenes. The somewhat smaller values found for 2- and 8-methylquinoline may be attributed to the partial shielding of the heterocyclic nitrogen atom by the methyl group with its attendant reduction of intermolecular attractions.

---

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

(14) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

TABLE I

DENSITIES, VISCOSITIES, DIELECTRIC CONSTANTS AND LOSSES OF SUBSTITUTED NAPHTHALENES, QUINOLINES AND PYRIDINES

				1.25		3.22		10.0 cm.	
t, °C.	d	η(cps.)	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
				1-Methylnaphthalene					
20	1.0189	3.10	2.915	2.637	0.040	2.664	0.080	2.764	0.126
40	1.0058	1.97	2.853	2.606	.053	2.656	.094	2.764	.113
60	0.9902	1.40	2.797	2.589	.059	2.648	.099	2.749	.094
				2-Methylnaphthalene					
40	.9961	1.67	2.747	2.587	.029	2.610	.052	2.671	.066
60	.9759	1.27	2.702	2.560	.034	2.589	.054	2.656	.055
				1,2,3,4-Tetrahydronaphthalene					
20	.9678	2.22	2.776	2.433	.074	2.510	.157	2.687	.151
40	.9532	1.53	2.719	2.417	.085	2.512	.161	2.672	.116
60	.9389	1.13	2.665	2.400	.094	2.527	.157	2.632	.093
				1-Nitronaphthalene					
60	1.2260	3.57	18.45	3.71	1.64	4.71	3.02	9.67	5.36
				2-Methylquinoline					
20	1.0582	4.26	7.24	2.93	0.42	3.02	0.84	4.30	1.93
40	1.0427	2.56	6.78	2.92	.59	3.21	1.16	4.94	1.83
60	1.0272	1.73	6.30	2.94	.71	3.45	1.35	5.26	1.66
				4-Methylquinoline					
20	1.0809	6.24	9.31	3.05	0.59	3.57	1.20	4.80	2.56
40	1.0665	3.46	8.81	3.08	0.78	3.49	1.51	5.85	2.61
60	1.0520	2.22	8.32	3.15	1.01	3.86	1.88	6.55	2.42
				6-Methylquinoline					
20	1.0650	4.42	8.48	3.06	0.53	3.26	1.02	4.35	2.19
40	1.0498	2.66	7.97	3.05	.74	3.41	1.42	5.13	2.39
60	1.0347	1.78	7.51	3.10	.86	3.68	1.59	5.74	2.22
				8-Methylquinoline					
20	1.0710	4.44	6.58	2.87	.38	3.02	0.75	3.84	1.59
40	1.0559	2.67	6.10	2.86	.47	3.12	0.96	4.38	1.58
60	1.0408	1.80	5.67	2.86	.56	3.32	1.11	4.76	1.41
				2,4-Dimethylpyridine					
20	0.9296	0.887	9.60	3.22	1.93	4.92	3.01		
40	.9120	.676	8.88	3.43	2.17	5.47	2.92		
60	.8945	.538	8.21	3.70	2.34	5.81	2.56		
				2,6-Dimethylpyridine					
20	.9246	.869	7.33	2.90	1.32	4.14	2.19		
40	.9072	.668	6.70	3.01	1.40	4.67	2.07		
60	.8897	.532	6.08	3.22	1.56	4.70	1.69		

TABLE II

SLOPES (a) FOR THE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS OF SOLUTIONS UPON MOLE FRACTION OF 1-NITRONAPHTHALENE IN BENZENE

t, °C.	a_0	λ_0 (cm.)	a'	a''
20	23.70	1.25	4.19	5.90
		3.22	10.12	9.16
40	21.42	1.25	5.10	6.60
		3.22	11.49	8.57
60	19.20	1.25	6.38	7.06
		3.22	11.58	7.66

The lutidines or dimethylpyridines have by far the shortest critical wave lengths and lowest viscosities of any of the compounds investigated, a result which is consistent with their smaller size and more nearly spherical shape. Since the molecules of the 2,4- and 2,6-isomers are virtually identical in shape, their critical wave lengths should not differ appreciably, as is, indeed, the case.

It would seem, from what has been said above, that considerations of molecular size, shape and dipole direction can account quite successfully for the observed differences in the dielectric behavior of many substances provided they do not differ considerably in polarity and viscosity. In order to extend our discussion to a comparison of the behavior of the methylnaphthalenes with that of their highly polar analogs, it is first necessary to take these differences into account.

In Table IV are given the viscosities η, measured relaxation times τ_M, and the ratios τ_M/η and τ_μ/η, where τ_μ is the microscopic or proper relaxation time of the molecule as obtained from the expression proposed by Powles.[15] The significance of the internal field factor, which forms the basis

---

[15] J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).

TABLE III

OPTICAL DIELECTRIC CONSTANTS, DISTRIBUTION PARAMETERS, CRITICAL WAVE LENGTHS, RELAXATION TIMES, MOLAR VOLUMES AND DIPOLE MOMENTS OF SUBSTITUTED NAPHTHALENES, QUINOLINES AND PYRIDINES

t, °C.	ϵ_∞	α	λ_m (cm.)	τ_M ($\times 10^{11}$ sec.)	V(cc.)	μ($\times 10^{18}$)
			1-Methylnaphthalene			
20	2.62	0.10	10.5	5.57	139.6	(0.51)
40	2.60	.08	6.76	3.59	141.6	
60	2.57	.05	4.62	2.45	143.6	
			2-Methylnaphthalene			
40	2.57	0.16	8.67	4.60	142.7	0.42
60	2.54	0.17	5.43	2.88	145.2	
			1,2,3,4-Tetrahydronaphthalene			
20	2.42	0.00	5.52	2.93	136.6	0.59
40	2.39	.00	4.27	2.27	138.7	
60	2.37	.00	3.29	1.75	140.8	
			1-Nitronaphthalene			
60	2.86	0.23	13.1	6.95	141.2	3.31
			2-Methylquinoline			
20	2.81	0.04	16.1	8.55	135.3	1.71
40	2.81	.025	9.97	5.29	137.3	
60	2.81	.00	6.67	3.54	139.4	
			4-Methylquinoline			
20	2.95	0.08	18.4	9.77	132.5	1.95
40	2.95	.06	11.2	5.95	134.3	
60	2.95	.03	7.39	3.92	136.1	
			6-Methylquinoline			
20	2.97	0.05	18.2	9.66	134.4	1.84
40	2.95	.03	11.2	5.95	136.4	
60	2.93	.00	7.49	3.98	138.4	
			8-Methylquinoline			
20	2.82	0.03	16.6	8.81	133.7	1.58
40	2.77	.02	10.2	5.42	135.6	
60	2.73	.02	6.58	3.49	137.6	
			2,4-Dimethylpyridine			
20	2.28	0.10	4.55	2.42	115.3	2.24
40	2.25	.08	3.26	1.73	117.5	
60	2.20	.07	2.44	1.30	119.8	
			2,6-Dimethylpyridine			
20	2.42	0.03	4.37	2.32	115.9	1.78
40	2.40	.02	3.11	1.65	118.1	
60	2.38	.00	2.39	1.27	120.4	
			1-Nitronaphthalene in benzene			
20		0.11	4.30	2.28		4.00
40		.10	3.15	1.67		
60		.09	2.45	1.30		

TABLE IV

DEPENDENCE OF RELAXATION TIME ($\times 10^{11}$ SEC.) ON INTERNAL FIELD AND VISCOSITY AT 60°

	η	τ_M	τ_M/η	τ_μ/η
1-Methylnaphthalene	1.40	2.45	1.75	1.70
4-Methylquinoline	2.22	3.92	1.77	1.40
8-Methylquinoline	1.80	3.49	1.94	1.61
1-Nitronaphthalene	3.57	6.95	1.95	1.41
2-Methylnaphthalene	1.27	2.88	2.27	2.22
2-Methylquinoline	1.73	3.54	2.05	1.67
6-Methylquinoline	1.78	3.98	2.24	1.78

for the calculation of τ_μ, lies in the fact that molecules of similar size and shape, but differing in polarity, should, aside from possible difference in viscosity, have approximately equal microscopic relaxation times. The compounds have been separated into two groups on the basis of similarity in molecular shape.

It is to be expected that viscosity should be a more important factor in determining the relaxation properties of large, unsymmetrical molecules, than in the case of nearly spherical molecules.[3] The influence of viscosity on the observed relaxation times of the naphthalene and quinoline derivatives under investigation is evident from a comparison of the values of τ_M and τ_M/η in Table IV. As opposed to an average deviation of about 23% among the various τ_M values, the deviation among the τ_M/η values amounts to only 8%. The agreement is particularly significant in the case of 1-nitronaphthalene whose relaxation time is 2.8 times larger than that of 1-methylnaphthalene, an increase which is closely paralleled by the ratio of their viscosities, 2.6. The effect of viscosity on the analogous benzene derivatives, nitrobenzene and toluene, is much less apparent. While the ratio of the relaxation times of these more nearly spherical molecules at 20° is 8.3, the ratio of their viscosities is only 3.4. A similar lack of proportionality between these two properties is to be found on comparing 2,6-dimethylpyridine with *m*-xylene, the ratio of relaxation times being 2.7 as opposed to a viscosity ratio of only 1.4. In general, the farther the molecules comprising a substance depart from spherical symmetry, the greater is the interdependence of its relaxation and viscous properties.

The ratio of τ_M/η, when corrected for the effects of the internal field by means of the equation of Powles, leads to the values in the last column of Table IV. It will be noted that the resulting τ_μ/η values of the more polar compounds in each group are less than the values found for the corresponding methylnaphthalenes, which are of such low polarity as to make the internal field corrections negligible. This apparent overcorrection is, however, quite small when one considers the wide range of polarities involved.

It may be questioned, nevertheless, whether the calculation of τ_μ may better be made using some alternative expression for the internal field. Use of the Debye[16] correction factor results in an almost complete lack of correspondence between either the τ_μ or τ_μ/η values for these compounds. Application of the O'Dwyer and Sack[17] relation, while giving considerably better agreement among the microscopic relaxation times themselves, destroys the correlation between viscosity and relaxation time observed for both the uncorrected τ_M/η ratios and those corrected by means of the expression of Powles. In view of the virtual non-existence of effects due to viscosity and to the interactions of neighboring dipoles implied in the agreement ob-

---

(16) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929, Chap. V.

(17) J. J. O'Dwyer and R. A. Sack, *Australian J. Sci. Research*, **A5**, 647 (1952).

tained by using the O'Dwyer and Sack expression, the correspondence obtained by using the Powles expression and then correcting for viscous effects seems more reasonable.

With the notable exception of 2-methylnaphthalene, the agreement among the τ_μ/η values is comparable to that in column 3 of Table IV. The apparent anomaly in the high τ_μ/η value for 2-methylnaphthalene is significant in that it is the only compound listed in which the direction of the dipolar axis is not nearly parallel to the carbon–carbon bond held in common by the two rings. For this reason, therefore, the first six compounds in the table could equally well be grouped together on the basis of "electrical shape," in which case the use of τ_μ/η for purposes of comparison is to be preferred over the use of τ_M/η.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXII. The Dielectric Relaxation Times of Three Prolate Ellipsoidal Molecules in Benzene Solution[1,2]

BY DONALD A. PITT AND CHARLES P. SMYTH

RECEIVED SEPTEMBER 17, 1957

The dielectric constants of benzene solutions of anthrone, fluorenone and phenanthrenequinone have been measured at 1.25, 3.22, 10.0, 25.0 and 50.0 cm. wave length at temperatures of 20, 40 and 60°. The relaxation time and its distribution parameter for each solute have been determined from arc plots of the slopes at each wave length of the curves for the dependence of dielectric constant and loss upon the concentration of the solute. Anthrone and fluorenone have values of relaxation time which would be anticipated from their molecular sizes and shapes, but the value for phenanthrenequinone is anomalously high. This may be due to a greater volume swept out by this molecule in orienting about its long axis.

The dielectric relaxation of dipolar molecules in solution provides a means of investigating the viscous drag forces which hinder the rotation of the polar solute molecules. The quantitative effects of solvent viscosity, of the volume and shape of the solute molecule and of position of the dipole moment within the solute molecule are not yet wholly clear. To further the study of the latter factors, the dielectric relaxation properties of three roughly ellipsoidal polar molecules have been examined.

Materials.—Anthrone from Brothers Chemical Co. was successively crystallized from benzene and ethanol and thoroughly dried in an Abderhalden pistol. The purified material retained a pale yellow tint; m.p. 155°; lit.[3] 154–155°.

9-Fluorenone obtained from Brothers Chemical Co., was recrystallized from absolute ethanol, forming flat needles having a bright yellow color. After drying, these melted sharply at 84°; lit.[4] 84°.

9,10-Phenanthrenequinone obtained from Eastman Kodak Organic Chemicals was twice recrystallized from dioxane and dried *in vacuo*. The orange needles melted at 208°; lit.[4] 207°.

Benzene of analytical reagent grade, Merck and Co., was used without purification. The dielectric loss at 20° and 1.25 cm. wave length was less than 10% higher than that obtained with benzene dried over sodium hydride and fractionally distilled immediately before use. The static dielectric constants were 2.2854, 2.2454 and 2.2055 at 20, 40 and 60°, and the refractive indices were 1.5009, 1.4889 and 1.4776.

Methods of Measurement.—The static dielectric constant was measured at a frequency of 520 kilocycles/sec., using heterodyne-beat equipment.[5–7] Microwave measurements of dielectric constant and loss at 1.25 and 3.22 cm. wave lengths were carried out with wave guide apparatus.[8,9] The standing-wave method of evaluating dielectric loss was applicable for all solutions. A coaxial resonant cavity apparatus[10] was employed with radiation of 10.0, 25.0 and 50.0 cm. wave length. The concentrations of solutions used in this apparatus were considerably lower than for the wave guide equipment to keep the loaded cavity loss tangent below 0.02.

Refractive indices were measured with a Pulfrich refractometer for the sodium-D line, and densities were determined with a graduated pycnometer, as described by Robertson.[11]

Experimental Results

The dielectric constant, ϵ', and loss, ϵ'', of dilute solutions of polar molecules in non-polar solvents have been shown[12] to be linear functions of concentration for non-associated solutes, that is

$$\epsilon' = \epsilon_1 + a'c_2$$
$$\epsilon'' = a''c_2$$

where c_2 is the mole fraction of the polar solute, and the subscripts 1 and 2 refer to solvent and solute, respectively. Similarly

$$\epsilon_0 = \epsilon_1 + a_0c_2$$
$$n_D^2 = (n_D)_1^2 + a_Dc_2$$
$$v = v_1 + \beta'c_2$$

where ϵ_0, n_D^2 and v are the static dielectric constants, the square of the refractive index and the specific volume of the solution, respectively.

These experimental data, obtained from measurements of two to five solutions at each frequency, are given in Table I. Heterodyne-beat measurements of ϵ_1 were used in the calculation of a' at all frequencies. Measurements of the dielectric loss of the pure solvent were used to correct the ϵ'' data of solutions for combined wall and solvent losses.

---

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

(2) This article represents a portion of the work submitted by Mr. Donald A. Pitt to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) K. H. Meyer, *Ann. Chem., Justus Liebigs*, **379**, 37 (1911).

(4) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926.

(5) C. P. Smyth and S. O. Morgan, THIS JOURNAL, **50**, 1547 (1928).

(6) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(7) L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

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

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

(10) D. A. Pitt and C. P. Smyth, unpublished.

(11) G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 464 (1939).

(12) A. D. Franklin, W. M. Heston, E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **72**, 3447 (1950).