[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XVIII. The Relaxation Times of Four Rigid Polar Molecules Surrounded by Non-polar Molecules of Similar Sizes and Shapes[1]

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RECEIVED SEPTEMBER 10, 1956

Measurements of dielectric constant at 300 meters wave length and of dielectric constant and loss at 10.66 cm. wave length have been carried out upon quinoline and isoquinoline over a range of temperature. The results have been combined with those of previous measurements to revise critical wave length values previously reported. The corrected values agree well with the earlier values for quinoline and differ somewhat from those for isoquinoline. Similar measurements have also been carried out upon dilute solutions of pyridine and *s*-trioxane in benzene and of quinoline and isoquinoline in naphthalene at 577 m., 3.22 and 1.244 cm. Comparison of the values of the molecular relaxation times calculated for the four substances in the pure liquid state with the relaxation times for the solutions indicates that, for these molecules, the method of calculating the molecular relaxation time and the assumption of its proportionality to liquid viscosity are not bad approximations. The closeness of the molecular relaxation times of pyridine and trioxane to each other suggest that the pyridine molecule may rotate with almost equal ease around axes in the plane of the ring and perpendicular to this plane. The relaxation times of the benzene and naphthalene molecules are considered in the light of those of pyridine and trioxane in benzene solution and of quinoline and isoquinoline in naphthalene solution, respectively. The difference between the relaxation times of quinoline and isoquinoline shows the existence of a considerable amount of orientation of both molecules by rotation out of the plane of the rings.

In previous work the critical wave lengths or dielectric relaxation times have been determined for pyridine,[3,4] *s*-trioxane,[4] quinoline[3] and isoquinoline[3] in the pure liquid state. Important factors in the interpretation of the results for the pure liquids are the effects of the viscosities and of the internal fields due to the large molecular dipole moments (2.0–2.5 $\times$ 10^{-18}). Measurements of solutions in non-polar solvents have been used in the past to minimize these effects. In the present work, solvents with non-polar molecules identical in size and shape with the solute molecules have been selected for the further investigation of pyridine, quinoline and isoquinoline, and rather similar in size and shape for the study of trioxane. It was further hoped that the relaxation times obtained for the polar molecules surrounded by non-polar molecules of identical size and shape might be taken as approximate relaxation times for the non-polar molecules, which cannot be determined directly by dielectric measurements.

Experimental Methods and Results

The solutes were obtained in a pure state by methods previously described,[3,4] except that trioxane was further purified by crystallization from benzene. Benzene was dried with calcium hydride and distilled. U.S.P. naphthalene was purified by distillation.

Dielectric constants ϵ' and losses ϵ'' at wave lengths of 1.24 and 3.22 cm. and the so-called static dielectric constant ϵ_0 at a wave length of 577 meters were measured by methods described or referred to in an earlier paper.[3] The slopes a of the linear plots of ϵ' and ϵ'' against weight fraction of polar solute are used to obtain the critical wave lengths and relaxation times.[5,6] In addition, measurements were made upon pure quinoline and isoquinoline in order to improve the accuracy of the results obtained on them previously.[3] These additional measurements were the determination of dielectric constant and loss at 10.66 cm. wave length and of static dielectric constant at 300 meters with a twin-T impedance apparatus.

TABLE I

DIELECTRIC CONSTANTS AND LOSSES OF PURE LIQUIDS

t, °C.	ϵ_0 (300 m.)	ϵ' (10.66 cm.)	ϵ'' (10.66 cm.)
	Quinoline		
20	9.19	6.84	2.53
40	8.57	7.16	2.06
60	7.95	7.27	1.62
	Isoquinoline		
25	10.70	6.76	3.30
40	10.16	7.62	3.10
60	9.43	8.01	2.58

TABLE II

MOLAR VOLUMES, VISCOSITIES, CRITICAL WAVE LENGTHS, RELAXATION TIMES AND DISTRIBUTION COEFFICIENTS

t, °C.	V(cc.)[a]	η(c.p.s.)[a]	λ_m(cm.)	$\tau_M(10^{-11}$ sec.)	α
	Quinoline				
20	118.2	3.79	8.3	4.40	0.11
40	119.8	2.47	5.60	2.97	.10
60	121.5	1.67	3.73	1.98	.09
85[b]	123.8	1.11	2.5	1.33	..
	Isoquinoline				
25	117.9	3.53	10.7	5.68	0.09
40	119.3	2.60	8.4	4.46	.06
60	121.0	1.79	5.95	3.16	.03
85[b]	123.4	1.24	3.9	2.07	..

[a] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishers, New York, N. Y., 1950, pp. 571–573. [b] Extrapolated from measurements at lower temperatures.

Discussion of Results

The redetermination of the critical wave lengths of quinoline and isoquinoline gave results for quinoline in good agreement with the earlier measurements.[3] For isoquinoline, the new and more accurate values are somewhat different from the old, but the differences are too small to affect the conclusions drawn previously.[3]

(1) This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) Supported by a Grant-in-Aid to the Chemistry Department, Princeton University, from E. I. du Pont de Nemours and Company.

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

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TABLE III

SLOPES FOR DEPENDENCE OF DIELECTRIC CONSTANTS AND LOSSES OF SOLUTIONS UPON WEIGHT FRACTION OF SOLUTE

t, °C.	λ (cm.)	a'	a''
	Pyridine–Benzene		
20	∞	6.97	..
	3.22	6.30	1.43
	1.244	5.47	2.80
	0	0.05	..
40	∞	6.27	..
	3.22	5.93	1 13
	1.244	5.53	2 07
	0	0.05	..
60	∞	5.70	..
	3 22	5.43	0.73
	1.244	5.00	1.76
	0	0.05	..
	Trioxane–Benzene		
20	∞	5.60	..
	3.22	5.33	1 10
	1.244	4.67	1 97
	0	0.02	..
40	∞	5.10	..
	3 22	4.97	0.80
	1.244	4.63	1.63
	0	0.02	..
60	∞	4.53	..
	3.22	4.40	0.50
	1.244	4.13	1.30
	0	0.02	..
	Quinoline–Naphthalene		
85	∞	3.70	..
	3.22	2.72	1.28
	1.244	1.38	1.47
	0	0.05	..
	Isoquinoline–Naphthalene		
85	∞	4.72	..
	3.22	2.82	1.65
	1.244	1.52	1.58
	0	0.07	..

TABLE IV

MOLAR VOLUMES, DIELECTRIC CONSTANTS AND VISCOSITIES OF SOLVENTS, AND CRITICAL WAVE LENGTHS, RELAXATION TIMES AND DISTRIBUTION COEFFICIENTS OF SOLUTIONS

t, °C.	V(cc.)	ϵ	η(c.p.s.)	λ_m (cm.)	$\tau(10^{-11}$ sec.)	α
	Benzene			Pyridine–Benzene		
20	88.9	2.284	0.65	0.67	0.36	0
40	91.1	2.244	.48	.53	.28	0
60	93.5	2.204	.39	.44	.23	0
				Trioxane–Benzene		
20				0.55	0.29	0
40				.43	.23	0
60				.38	.20	0
	Naphthalene			Quinoline–Naphthalene		
85	131.4[a]	2.537	0.90[a]	1.78	0.95	0.09
				Isoquinoline–Naphthalene		
				2.42	1.28	0.14

[a] J. Timmermans, ref. *a*, Table II, p. 179.

The results on the two pairs of similar polar molecules under examination in this paper may be most conveniently examined by collecting the values for the pure liquids (Table II and ref. 4) and the solutions in Table V. An approximate microscopic or molecular relaxation time, $\tau_{\mu l}$, is calculated for the pure liquids from the equation of Powles.[3,7] Except for the effect of viscosity this should be approximately the same as the relaxation time of the solution, which, accordingly, is listed as $\tau_{\mu s}$ in Table V. Since the molar volumes of quinoline and isoquinoline (Table II) are practically identical, the quantity $\eta_S\tau_{\mu l}/\eta_l\tau_{\mu s}$ should be equal to 1, if the relaxation time is proportional to the viscosity and if the approximate equation of Powles is valid. The viscosity of the solvent is used as a sufficient approximation for the slightly different viscosities of the dilute solutions.

TABLE V

COMPARISON OF VISCOSITIES (C.P.S.) AND RELAXATION TIMES (10^{-11} SEC.)

	t, °C.	Pure liquid τ_M	Pure liquid $\tau_{\mu l}$	Pure liquid η_l	Solvent η_S	Soln. $\tau_{\mu s}$	$\eta_S\tau_{\mu l}/\eta_l\tau_{\mu s}$
Pyridine	60	0.48	0.35	0.58	0.39	0.23	1.02
s-Trioxane	60	.82	.59	.94	.39	.20	1.15
Quinoline	85	1.33	1.02	1.11	.90	.95	0.87
Isoquinoline	85	2.07	1.56	1.24	.90	1.28	.89

As the approximate correction factor[7] for changing the macroscopic relaxation time to the molecular is 0.72–0.77 for the four liquids in Table V, it is evident that the values of the expression in the last column would all exceed 1 by different amounts if the macroscopic relaxation times were used instead of the molecular. The fact that the values in the last column of Table V are not far from 1 shows that, for these four molecules, the calculation of the molecular relaxation time and the assumption of its proportionality to viscosity are not bad approximations. However, for very viscous solutions of small symmetrical molecules, the proportionality of relaxation time to viscosity is almost non-existent.[6] When the molecular relaxation time of pyridine[4,8] at 20° is multiplied by the ratio of the viscosity of benzene to that of pyridine, 0.65/0.95, the result 0.36 is identical with the value for the solution in Table IV, an agreement which parallels that observed at 60° in Table V. However, it has been pointed out[8] that the molecule of fluorobenzene also resembles the benzene molecule in shape, showing a small protrusion at the fluorine atom as contrasted to a slight indentation at the nitrogen atom in the pyridine molecule. Possibly, it is this protrusion which causes the molecular relaxation time of fluorobenzene,[8] 0.49, to be higher than the pyridine value multiplied by the viscosity ratio, $0.53 \times 0.58/0.95 = 0.32$.

The absence of any distribution of relaxation times for pure pyridine or for its solutions is consistent with the conclusion of Perrin[9] that, if the dipole moment of an ellipsoidal molecule lies along one axis of the ellipsoid, the dispersion is the same as if the molecule were spherical. However, the

(7) J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).
(8) C. P. Smyth, *Proc. Natl. Acad. Sci.*, **42**, 234 (1956).
(9) F. Perrin, *J. Phys. Radium*, [VII] **5**, 497 (1934).

quinoline solutions show some distribution of relaxation times, as evidenced by the values of α in Tables II and IV, although the dipole moment of the molecule is almost parallel to the symmetry axis in the carbon–carbon bond shared between the two rings, and should, in terms of the Perrin treatment, give a negligibly small distribution. Some distribution of relaxation times also has been found for even more symmetrical molecules in solution.[5,6] Since the dipole moment of the isoquinoline molecule does not lie in a symmetry axis, some distribution of relaxation times is to be expected, but not as large as that observed.

Similarity of the ratio of the critical wave lengths of pure pyridine and trioxane to that of the viscosities has been pointed out previously.[4] Although the approximate molecular relaxation time of the more viscous trioxane is much higher than that of pyridine, the value for the molecule in benzene solution is slightly lower than that of pyridine in benzene, possibly, because of the slightly smaller departure of the trioxane molecule from spherical form.[4] The considerable difference between the relaxation times of quinoline and isoquinoline, which have molecules of practically identical size and shape, persists in solution, although here it is relatively smaller. The larger value for isoquinoline is attributable to the considerable amount of molecular orientation by rotation around the axis in the carbon–carbon bond held in common by the two rings, an orientation practically absent in quinoline, where the molecular dipole is almost parallel to this axis. Rotational orientation around the axis in the carbon–carbon bond shared between the two rings should occur with greater difficulty than that around the other two axes and thus cause the relaxation time of isoquinoline to be longer than that of quinoline, the molecule of which orients almost entirely by turning about the other two axes.

Perrin[9] has shown that the relaxation times of an ellipsoidal molecule may be described in terms of three friction constants, C_1, C_2 and C_3 as

$$\frac{1}{\tau_1} = kT\left(\frac{1}{C_2} + \frac{1}{C_3}\right)$$

$$\frac{1}{\tau_2} = kT\left(\frac{1}{C_1} + \frac{1}{C_3}\right)$$

$$\frac{1}{\tau_3} = kT\left(\frac{1}{C_1} + \frac{1}{C_2}\right)$$

Since the benzene molecule may be considered as an ellipsoid of revolution, two of the friction constants will be equal. Pyridine is nearly the same size and shape as benzene and, since its moment lies in the plane of the ring, the relaxation time measured for a benzene solution may be taken as the relaxation time, τ_1, for benzene, that is, $\tau_1 = 0.36 \times 10^{-11}$ sec. at 20°. Similarly, the relaxation time of the benzene solutions of trioxane, which has its moment normal to the ring,[4] may be taken as the second relaxation time of benzene, that is, $\tau_2 = \tau_3 = 0.29 \times 10^{-11}$ sec. at 20°, although to a somewhat poorer approximation because of the differences in shape. The closeness of the two relaxation times and hence the friction constants suggests that a benzene molecule may rotate with almost equal ease about any axis.

The naphthalene molecule may be considered as an ellipsoid with three unequal axes and three relaxation times. Since the quinoline molecule is the same size and shape as that of naphthalene and has its moment nearly parallel to the molecular axis in the carbon–carbon bond common to the two rings, the relaxation time measured in naphthalene solutions may be taken as the first relaxation time, τ_1, of naphthalene, that is, $\tau_1 = 0.95 \times 10^{-11}$ sec. at 85°. In isoquinoline the moment is at an angle of about 30° to the long axis of the ellipsoid and it would be expected that two relaxation times would be observed for a solution in naphthalene. However, as noted above only a slightly larger distribution was found for isoquinoline than for quinoline and thus the relaxation time can only be taken as a lower limit for the second relaxation time, τ_2, of naphthalene, that is, τ_2 is greater than 1.28×10^{-11} sec. at 85°. The third relaxation time and hence the friction constants cannot be obtained without measurements on a compound of the same size and shape as naphthalene and having its moment normal to the plane of the ring. The third friction constant cannot be much smaller than C_1 and C_2 because if this were so τ_1 would be equal to τ_2 which is not the case. Thus it appears that for these molecules a considerable amount of orientation takes place out of the plane of the ring.

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