that ($\sim 10^3$) reported by Katzenellenbogen,[10] also obtained by measurements on the variation of the ultraviolet absorption band of $Co(NH_3)_6^{+++}$ with ($S_2O_3^=$).

The simplest interpretation of the experiments with $Mg(ClO_4)_2$ added in small amount is that the affinity of Mg^{++} and $SO_4^=$ is small with an equilibrium quotient for the association reaction probably of the order of magnitude of unity at $\mu = 0.091$ and 25°. At higher concentrations, $Mg(ClO_4)_2$ exerts a remarkable effect, enhancing D rather than reducing it as would be expected if depletion of $SO_4^=$ were its only effect. The effect appears whether a series at constant μ (expts. 2–6 in Table III) or at constant (ClO_4^-) (expts. 7–10, Table III) is followed and increases sharply in the $Mg(ClO_4)_2$-rich end of the concentration range. It cannot be explained merely by assuming that $Mg(ClO_4)_2$ shifts equilibrium (1), for the different wave lengths respond differently.

There is the possibility that cations of high field intensity can affect the u.v. spectra of forms such as $Co(NH_3)_5^{+++}\cdot SO_4^=$; if so, the spectral method is not suited to very refined measurements. Alternatively, the effect may merely be to change the distribution between the 1:1 complex, and higher order ones.

Acknowledgment.—This work was given financial support by the Office of Naval Research under Contract N6-Ori-02026.

CHICAGO 37, ILLINOIS

(10) E. R. Katzenellenbogen, Paper No. 23, Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, September, 1950.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XI. The Relaxation Times of Three Nearly Spherical Molecules in the Pure Liquid and in Solution[1,2]

BY RUSSELL S. HOLLAND,[3a] GEORGE N. ROBERTS[3b] AND CHARLES P. SMYTH

RECEIVED JUNE 27, 1955

The dielectric constants and losses of 1,1,1-trichloroethane, 2,2-dichloropropane and 2,2-dinitropropane and of their dilute solutions in heptane, a paraffin oil and carbon tetrachloride have been measured at wave lengths of 1.22, 3.22, 6.6, 10.7 and 30 cm. and temperatures between 2 and 60°. The data have been used to calculate the critical wave lengths, the corresponding dielectric relaxation times of the liquids, and the approximate molecular relaxation times. The results indicate a rough proportionality between molecular relaxation time and the macroscopic viscosity of the liquid when molecules of not very different sizes and shapes are compared within a narrow range of viscosity. This is in contrast to the extreme deviations from proportionality previously reported in this series of papers for liquids varying over a wide range of viscosity.

In earlier papers of this series[4-13] the critical wave lengths of *t*-butyl bromide[6], *t*-butyl chloride[10] in the pure liquid and in solution, and 1,1,1-trichloroethane[10] in solution in heptane and nujol have been studied. In a recent paper,[14] the critical wave lengths of these three substances and of 2,2-dichloropropane, dibromodichloromethane and 2,2-dinitropropane have been considered with reference to their molecular relaxation times, τ_μ, and the microscopic or internal viscosities, η_μ, of the liquids. It is the purpose of the present paper to present as briefly as possible the dielectric constants and losses of three of these substances at different temperatures in the pure state and in solution in different solvents and to consider the significance of their relaxation times. These substances have been chosen for consideration together because of the roughly spherical shapes of their molecules.

Experimental Methods and Results

n-Heptane from the Phillips Petroleum Company was used without further purification; n^{20}_D 1.3881 (lit. values 1.3877–1.3882). The viscous paraffin oil used was Nujol purchased at a drugstore. Carbon tetrachloride was refluxed over mercury for two hours, washed with concentrated sulfuric acid, distilled water, dilute sodium hydroxide solution and distilled water, dried over anhydrous calcium chloride, and twice fractionated; b.p. 76.2–76.4° (lit. 76.7–76.8°), n^{20}_D 1.4602 (lit. 1.4604–1.4608). 1,1,1-Trichloroethane, or methylchloroform, from Matheson, Coleman and Bell was washed three times with concentrated sulfuric acid, distilled water, sodium bicarbonate solution and distilled water, dried over anhydrous calcium chloride, and twice fractionated; b.p. 74.0–74.3° (lit. 73.9–74.1°), n^{20}_D 1.4383 (lit. 1.4384). 2,2-Dichloropropane from the Halogen Chemical Company was washed twice with sodium carbonate solution and distilled water, dried over anhydrous calcium chloride, and fractionally distilled; b.p. 69.2–69.5° (lit. 69.3°), n^{20}_D 1.4150 ("International Critical Tables," 1.4093). 2,2-Dinitropropane, kindly given us by the Commercial Solvents Corporation, was fractionally crystallized

---

(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 R. S. Holland to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) Procter and Gamble Fellow in Chemistry, 1953–1954; (b) supported by a Grant-in-Aid to the Chemistry Department of Princeton University from E. I. du Pont de Nemours and Company.

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

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

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

(7) W. M. Heston, Jr., and C. P. Smyth, *ibid.*, **72**, 99 (1950).

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

(11) P. L. McGeer, A. J. Curtis, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 3541 (1952).

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

(13) R. S. Holland and C. P. Smyth, *J. Phys. Chem.*, **59**, 1088 (1955).

(14) C. P. Smyth, *ibid.*, **58**, 580 (1954).

TABLE I

DIELECTRIC CONSTANTS AND LOSSES OF PURE POLAR LIQUIDS

	1.24 cm.		3.22 cm.		10 cm.					
t, °C.	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	(n^2D)	ϵ_0	λ_m	α
					2,2-Dichloropropane					
2	6.427	5.3	10.77	4.05	....	...	2.031	12.58	1.47	0.00
20	6.766	4.7	10.12	3.10	....	...	2.004	11.42	1.23	.00
40	6.993	4.1	9.54	2.27	....	...	1.973	10.24	0.99	.00
					2,2-Dinitropropane					
60	...	..	22.4 23.3[a]	15.7 ± 2 16.3[a]	33.6[b]	8.0[b]	2.002	35.0[c]	2.6	0.0
					1,1,1-Trichloroethane[d]					
4	4.891	2.70	6.981	1.95	....	...	...	7.71	1.25	0.05
20	5.007	2.49	6.720	1.52	7.242	0.449	2.070	7.20	1.04	.03
40	5.165	2.15	6.309	1.16	6.605	0.370	...	6.57	0.84	.01

[a] J. G. Powles, D. E. Williams and C. P. Smyth, *J. Chem. Phys.*, **21**, 136 (1953). [b] Measurements by Dr. J. H. Calderwood in this Laboratory. [c] R. W. Crowe and C. P. Smyth, THIS JOURNAL, **72**, 4009 (1950). [d] Measurements by A. A. Anderson in this Laboratory.

TABLE II

SLOPES OF DIELECTRIC CONSTANT AND LOSS *versus* CONCENTRATION

		1.24 cm.		3.22 cm.		6.6 cm.		10.7 cm.		30 cm.				
t, °C.	a_∞	a'	a''	a'	a''	a'	a''	a'	a''	a'	a''	a_0	λ_m	α
							2,2-Dinitropropane–nujol							
20	−0.11	5.7	4.33	9.6	2.84	11.3	2.44	11.2	1.78	11.7	0.62	..	1.35	0.22
40	− .21	6.2	4.10	9.6	2.22	11.0	1.82	11.0	1.27	11.1	.44	..	1.06	.21
60	− .14	6.7	3.81	9.0	1.44	9.8	1.26	10.2	0.97	10.4	.32	..	0.78	.17
							2,2-Dinitropropane–heptane							
2	....	7.9	4.46	..	..	10.8	1.44	11.4	0.95	10.9	0.26	..	0.73	0.06
20	0.06	8.2	3.69	9.50	2.14	9.9	1.05	10.2	.70	10.2	.20	..	.56	.04
40	0.06	7.9	3.15	..	..	9.1	0.76	9.10	.55	9.15	.15	..	.50	.00
							2,2-Dichloropropane–nujol							
20	0.17	3.24	1.53	4.00	0.83	3.87	0.52	3.96	0.35	3.81	0.13	..	0.64	0.0
40	.17	2.78	1.22	3.68	.55	3.68	.44	3.70	.28	3.51	.10	..	.51	.0
60	.17	2.98	1.08	3.02	.34	3.15	.31	3.17	.22	3.04	.07	..	.41	.0
							2,2-Dichloropropane-heptane							
2	....	3.18	1.22	..	..	4.10	0.33	4.05	0.19	4.20	0.07	4.20	0.48	0.21
20	0.04	2.90	1.05	..	..	3.70	.22	3.68	.15	3.79	.05	3.80	.45	.22
40	0.05	2.82	0.84	..	..	3.30	.17	3.30	.11	3.42	.04	3.42	.34	.20
							1,1,1-Trichloroethane–carbon tetrachloride							
4	0.00	2.54	1.63	..	..	...	..	3.66	0.18	...	..	4.48	0.86	0.10
20	− .09	2.66	1.41	..	..	...	..	3.62	.16	3.60	0.09	3.58	.67	.07
40	0.00	2.68	1.29	..	..	...	..	3.18	.13	...	..	3.18	.58	.00

from ethyl alcohol and dried over anhydrous calcium chloride.

Earlier papers[4–6,8,13] have described most of the methods used in measuring the dielectric constants and losses of the pure liquids and of the solutions, but the solution measurements at 6.6, 10.7 and 30 cm. were made with a coaxial resonant cavity constructed by Mr. D. A. Pitt and not yet fully described. It has been shown[8] that the slopes of the dielectric constant and loss concentration curves for the solutions as well as the dielectric constants and losses of the pure liquids may be used to calculate critical wave lengths by means of the Cole and Cole arc plots. The values of the dielectric constants, ϵ_0 and ϵ', and losses, ϵ'', and the squares of the refractive indices n^2D of the pure liquids are given in Table I. The corresponding slopes, a, for the dependence of these quantities upon weight fraction of polar solute in nujol and mole fraction of polar solute in the other solvents at concentrations between 0.006 and 0.07 are given in Table II. The value of the constant for any particular dilute solution may be calculated from the slope and the value for the pure solvent given in a previous paper,[10] which also gives the viscosities of the solvents. The calculated values of the critical wave length, λ_m, at which the loss is a maximum, are given in Tables I and II, together with the empirical constants, α, for the distribution of the relaxation times. The errors in these values are somewhat larger than usual and occasional discrepancies between them and previously quoted values are attributable to the combined probable error.

Discussion of Results

It has been customary in much of the discussion of dielectric relaxation to use the critical wave length or the macroscopic relaxation time

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

as the basis of the discussion. In a recent paper[14] a microscopic or molecular relaxation time

$$\tau_\mu = \frac{2\epsilon_0 + \epsilon_\infty}{3\epsilon_0}\,\tau_M \qquad (2)$$

given by Powles'[15] approximate treatment of the internal field in the liquid has been used in discussing the microscopic viscosity of the liquid. In the preceding paper[13] of this series, it has been

---

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

shown that, in the cases examined, this expression for the molecular relaxation time, which is identical with one obtained as a first approximation by O'Dwyer and Sack,[16] is a better approximation to reality than that obtained by O'Dwyer and Sack as a second approximation and is far better than the much earlier expression of Debye. In the present discussion, therefore, the values of the macroscopic relaxation time given by eq. (1) and those of the molecular relaxation time given by eq. (2) will be listed in Table III and examined. The relaxation times for *t*-butyl chloride calculated from earlier measurements[10] are included in the table for comparison. The dielectric constants of the solutions are so small that the calculated values of the microscopic or molecular relaxation times differ by a negligible amount from the macroscopic relaxation times, and are, therefore, omitted from the table. For example, the macroscopic relaxation time of 1,1,1-trichloroethane in dilute solution in carbon tetrachloride at 2° is 0.47 and the calculated microscopic value is 0.46×10^{-11} sec. To facilitate discussion, the viscosities of the solvents taken from earlier work,[10] that of 2,2-dinitropropane newly measured, and those of the other three solutes extrapolated or interpolated from data in "Annual Tables of Physical Constants" are given in Table IV.

TABLE III

DIELECTRIC AND MOLECULAR RELAXATION TIMES (SEC. $\times$ 10^{11})

Solute	t, °C.	Pure solute τ_M	Pure solute τ_μ	τ_M for soln. in: C_7H_{16}	τ_M for soln. in: Nujol	τ_M for soln. in: CCl_4
CH_3CCl_3	2	0.67	0.51			0.47
	20	.55	.39	0.24[10]	0.44[10]	.36
	40	.45	.35	.21[10]	36[10]	.31
$(CH_3)_2CCl_2$	2	.78	.56	.25		
	20	.65	.47	.24	0.34	
	40	.53	.39	.18	.27	
	60				.22	
$(CH_3)_3CCl$[10]	4	0.56	0.41			0.37
	20	.48	.35	0.16	0.27	.35
	40	.43	.32	.16	.21	.32
$(CH_3)_2C(NO_2)_2$	2			39		
	20			.30	.72	
	40			.27	.56	
	60	1.4	0.96		.41	

TABLE IV

VISCOSITIES (CENTIPOISES) OF PURE LIQUIDS

	2°	20°	40°	60°
C_7H_{16}	0.52	0.42	0.34	0.28
Nujol		108	38	15
CCl_4	1.23	0.97	0.74	0.59
CH_3CCl_3	1.12	.84	.63	
$(CH_3)_2CCl_2$	0.96	.71	.54	
$(CH_3)_3CCl$	.68	.50	.39	
$(CH_3)_2C(NO_2)_2$				1.90

Because of the considerable errors in the small values for the relaxation times of these nearly spherical molecules, small differences between the values for the three methylchloromethanes may not be significant. *t*-Butyl chloride, which has the lowest viscosity of the three, has the shortest relaxation time, as it should have according to the Debye equation

$$\tau_\mu = \frac{4\pi\eta a^3}{kT} \tag{3}$$

in which η is the viscosity and a is the molecular radius, the three molecules having approximately the same van der Waals radius.[14] 1,1,1-Trichloroethane and 2,2-dichloropropane, which do not differ much from each other in viscosity, do not differ greatly in relaxation time. The highly polar 2,2-dinitropropane molecule, which has nearly the same radius as the other three molecules, has a much larger relaxation time, but the increase in the relaxation time is not proportional to the large increase in the viscosity of the liquid above those of the other three liquids.

The differences between the molecular relaxation time calculated by means of eq. 2 for the polar liquids and the indistinguishable macroscopic and molecular relaxation times for the solutions in non-polar solvents have been stated to be smaller than the difference between the macroscopic times.[14] This is evident in Table III. Indeed, the molecular relaxation times for 1,1,1-trichloroethane in the pure polar liquid, in heptane, and in carbon tetrachloride appear to be roughly proportional to the viscosities of the liquids. For 2,2-dinitropropane, the molecular relaxation time in the pure liquid at 60° is approximately four times that in heptane solution extrapolated to 60°, while the viscosity is approximately seven times as great. With the much higher viscosity of the pure polar liquid, the molecular relaxation time is not increased over that of the solution to the extent expected. This is conspicuously true for all the solutions in the very viscous paraffin oil, nujol, which show relaxation times no more than double those in heptane, although the viscosities are from 54 to 257 times as great. It would appear that the nearly spherical polar solute molecules rotate in the liquid hydrocarbon with so little displacement of the solvent molecules that the bulky, interlocking molecules of the oil hinder the rotation only a little more than do the relatively small heptane molecules, the molecules of both solvents presenting a hydrocarbon surface to the solute molecules. For these solute molecules, the microscopic or internal viscosities[14] of the two solvents would thus not be very different.

The tendency of the critical wave length or macroscopic relaxation time of a pure polar liquid to be longer than that of a dilute solution of the same polar molecules of about the same viscosity has been attributed[10,14] to hindrance of molecular rotation by dipole–dipole interaction, present in the pure liquid and largely absent in the dilute solution. The differences between the microscopic or molecular relaxation times in the pure liquid, already approximately corrected for the effect of the local field, and those in dilute solution are smaller and, in some cases, no greater than the possible effects of viscosity differences. A similar situation exists in regard to solutions in carbon tetrachloride, in which unexpectedly long critical wave lengths were indicated as possibly due to the effects of local dipole–dipole interactions.[10] Some

---

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

of the molecular relaxation times are longer than would be expected from viscosity differences alone, but some of the times are roughly proportional to the viscosities, which may themselves be influenced by dipole–dipole interaction.

The values of the distribution coefficients show no distribution of relaxation times for the nearly spherical molecules in the pure liquid state, in agreement with previous observations[6] and an apparently considerable distribution only for the solutions of 2,2-dinitropropane in the paraffin oil and 2,2-dichloropropane in heptane. This is in accord with a previously noted tendency toward distribution in solution, possibly attributable in some cases to increased experimental error.

These results and those of the preceding paper[13] of this series point to a rough proportionality between molecular relaxation time and macroscopic viscosity when molecules of similar size and shape are compared. Extreme deviations from proportionality may occur when very different molecules are involved, as in the case of the viscous paraffin oil used as solvent.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Triarylboron Anions. I. Magnetic and Cryoscopic Studies of Monovalent Trimesitylboron Anion Solutions[1a,b]

BY TING LI CHU AND THEODORE J. WEISMANN

RECEIVED JULY 11, 1955

Trimesitylboron reacts with sodium in tetrahydrofuran forming a blue solution of the monosodium salt, NaTMB, which is monomeric in the concentration range 0.05–0.15 M at 25°, having one unpaired electron. Blue crystals, which are diamagnetic, separate from a tetrahydrofuran solution of NaTMB indicating the association of ion-pairs into ion clusters by coulombic forces. NaTMB is red and diamagnetic in benzene or cyclohexane solution due to polymerization, having association numbers 5.7 ± 0.4 and 5.0 ± 0.4, respectively, as determined by molecular weight measurements. NaTMB formed in ether solution is initially monomeric but gradually associates as indicated by changes in color and magnetic susceptibility. However, NaTMB is monomeric and stable in a 1:1 by weight benzene–tetrahydrofuran mixture which has the same dielectric constant as ether, demonstrating the role of solvation in stabilization of the monomer.

The reaction of the triarylborons with the alkali metals in ether solution, involving the transfer of one or two electrons from the alkali metal atoms to one molecule of the triarylboron, forming colored salts was first studied by Krause and his co-workers.[2] In a solvent of low dielectric constant, the salt exists largely in the form of ion-pairs. The monovalent triaryl-boron anion has an odd number of electrons and is isoelectronic with the corresponding triarylmethyl radical. The sodium salt of the monovalent triphenylboron anion (hereafter NaTPB) was found to be diamagnetic in tetrahydrofuran solution by magnetic susceptibility and paramagnetic resonance absorption measurements, and exhibited no resemblance to triphenylmethyl in spectroscopic behavior.[3] In the absence of molecular weight data on NaTPB, it is assumed that the ion-pairs associate to form ion clusters such as $\left[\begin{array}{ll}(C_6H_5)_3B^- & Na^+ \\ & Na^+ \ {}^-B(C_6H_5)_3\end{array}\right]$ which are diamagnetic. Since the units are held together by electrostatic forces, the dielectric constant of the medium is an important factor in determining the extent of the association; the higher the dielectric constant, the smaller the electrostatic attraction between the ion-pairs and hence the greater the probability of the existence of NaTPB in the monomeric form. However, NaTPB is unstable in such a medium. On the other hand, the importance of the steric effect of ring substituents on the homolytic dissociation of the hexaarylethanes has been well established and would lead one to expect that the replacement of the phenyl groups of NaTPB by bulky aromatic groups may cause the ion clusters to dissociate with the formation of free radicals. In this and subsequent papers, some physico-chemical properties of a series of triarylboron anions containing large aromatic groups will be described.

Trimesitylboron (TMB) reacts readily with sodium in tetrahydrofuran, forming a dark blue solution of the monosodium salt, NaTMB. With 40% sodium amalgam, the reaction proceeds quantitatively to completion within a few minutes. It is probable that the solvation energy of the sodium ion by tetrahydrofuran and the moderate polarity of the medium (dielectric constant 7.39 at 25°), favor this electron transfer process. Unlike the sodium salt of the monovalent tri-α-naphthylboron anion,[4] NaTMB is resistant to further reaction with sodium in solutions of concentration greater than 10^{-4} M. This behavior simplifies considerably the experimental investigation of NaTMB. NaTMB is reactive toward oxygen. In the oxygen absorption experiment, 0.7198 mmole of NaTMB in tetrahydrofuran solution absorbed 0.7275 mmole of oxygen at an initial oxygen pressure of 337 mm., yielding a light yellow solution from which TMB was recovered quantitatively after hydrolysis. In another experiment, the oxygenated product, obtained from 0.7186 mmole of NaTMB under similar conditions, regenerated Na-

---

[1a] Presented before the Division of Physical and Inorganic Chemistry at the 128th A.C.S. Meeting, Minneapolis, Minn., September, 1955. (b) This paper represents a part of the dissertation to be submitted by T. J. Weismann to the Graduate School of Duquesne University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] E. Krause and H. Polack, *Ber.*, **59**, 777 (1926); **61**, 271 (1928); E. Krause and P. Nobbe, *ibid.*, **63**, 934 (1930); **64**, 2112 (1931).

[3] T. L. Chu, THIS JOURNAL, **75**, 1730 (1953).

[4] H. E. Bent and M. Dorfman, *ibid.*, **54**, 2132 (1932).