[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXVII. The Mutual Viscosities and Dielectric Relaxation Times of Several Polar Aromatic Compounds in Solution[1,2]

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The viscosities of dilute solutions of seven polar solutes in two non-polar solvents have been measured at 20, 40 and 60°, and the slopes of the viscosity–concentration plots have been used to calculate the mutual viscosities. The use of these values in an equation developed by Hill for the calculation of the relaxation times of the solutions gives values considerably higher than the observed.

The dielectric relaxation time of a polar molecule in solution is dependent on the solute size and shape, on the position of the dipole moment within the solute molecule and on the viscous interaction of the solute and solvent molecules during the orientation process. A measure of the solute–solvent interaction[3–9] is the mutual viscosity coefficient proposed to account for the viscosities of binary liquid mixtures. The theory of N. E. Hill has aroused some interest in the recent literature in regard to the calculation of dielectric relaxation times, but it has been tested only for smaller molecules.[5] In this study, we have evaluated the mutual viscosities of polar solutes having a considerable variation in molecular size and shape. The relationship of the mutual viscosity and of the relaxation time calculated therefrom to the observed relaxation times will be discussed.

Experimental

The solutes and solvents were prepared and purified according to procedures reported elsewhere. Their properties are tabulated below for comparison with literature values.

	M.p., °C.	M.p., °C. (lit.)
Acenaphthenequinone[10]	252	260–261[11]
Acepleiadylene[12]	162	156–162[13]
Anthrone[14]	155	154–155[15]
Benzene[12]	B.p. 79.9 (757.8 mm.)	B.p. 80.1[16]
Dioxane[10]	B.p. 101.2 (760.8 mm.)	B.p. 101.4[16]
Fluorenone[14]	84	84[17]
Phenanthrenequinone[10,14]	208	208[17]

Two complex compounds, chlorophenyl-heptaphenyl-porphyrazine and ferric octaphenyl-porphyrazine chloride, have high and indefinite melting points and do not sublime.[18]

The viscosities of dilute solutions of the above substances and of their solvents were measured in an Ostwald–Fenske–Cannon[19] viscometer immersed in a water-bath held to ±0.01° with a mercury–toluene type regulator. The times of efflux for solutions in benzene were approximately 260, 200 and 160 sec., and for solutions in dioxane 470, 340 and 260 sec., at 20, 40 and 60°, respectively. The average deviation in measured efflux time was ±0.2 sec. To assure internal consistency of the viscosity results, one viscometer was used for all determinations.

The densities of the solutions were measured in an Ostwald–Sprengel type pycnometer[20] with an accuracy of ±0.002%.

Within the experimental error, the viscosities of solutions of the above polar substances were linear with solute concentrations, x_2, in mole fraction. The values of the slope $d\eta_{12}/dx_2$ are given in Table I.

Treatment of Data

The Hill relation[5] is given by eq. 1, where the subscripts 1 and 2 refer to the components of the solution, and the subscript 12 refers to the solution.

$$\eta_{12} = x_1^2\eta_1\sigma_1/\sigma_{12} + 2x_1x_2\eta_m\sigma_m/\sigma_{12} + x_2^2\eta_2\sigma_2/\sigma_{12} \quad (1)$$

The quantities η are the respective viscosities in a mixture of mole fractions x_1 and x_2, and the σ values represent average intermolecular distances. These may be obtained from

$$\sigma_1 = (M_1/d_1N)^{1/3} \quad (2)$$

$$\sigma_2 = (M_2/d_2N)^{1/3} \quad (3)$$

$$\sigma_{12} = [(x_1M_1 + x_2M_2)/d_{12}N]^{1/3} \quad (4)$$

where M refers to the molecular weight, d to the density and N is the Avogadro number. The average separation of solute and solvent molecules, σ_m, is given by $(\sigma_1 + \sigma_2)/2$. The viscous interaction of components 1 and 2 is described by η_m, the mutual viscosity.

At temperatures where both components are liquid, and hence have measurable viscosities, the mutual viscosity may be evaluated from a knowledge of η_{12} at one or more concentrations. The precision of the solution for η_m may be improved by graphic presentation of the data. The Hill equation may be rearranged to the form in eq. 5

$$(\eta_{12}\sigma_{12} - x_1^2\eta_1\sigma_1)/x_2^2\sigma_2 = \eta_2 + (2x_1\sigma_m/x_2\sigma_2)\eta_m \quad (5)$$

The experimental viscosity and density data may be used to construct a plot with $(\eta_{12}\sigma_{12} - x_1^2\eta_1\sigma_1)/x_2^2\sigma_2$ on the ordinate axis, and $2x_1\sigma_m/x_2\sigma_2$ on the abscissa axis. The intercept at the axis of ordi-

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

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TABLE I

SLOPES FOR THE DEPENDENCE OF SOLUTION VISCOSITY ON MOLE FRACTION OF SOLUTE AND MUTUAL VISCOSITY COEFFICIENT

Solute	Solvent	$d\eta_{12}/dx_2$ 20°	40°	60°	η_m 20°	40°	60°
Acenaphthenequinone	Dioxane	2.59[a]	1.61[a]	1.12[a]	2.27	1.52	1.11
Acepleiadylene	Benzene	3.35[b]			1.94[b]		
Anthrone	Benzene	2.41	1.67	1.26	1.61	1.16	0.89
Metal-free porphyrazine	Benzene	16.6	10.4	8.0	5.02	3.20	2.46
Ferric porphyrazine chloride	Benzene	18.5	12.5	10.8	5.46	3.71	3.21
Fluorenone	Benzene	2.50	1.77	1.31	1.70	1.23	0.94
Phenanthrenequinone	Benzene	2.60	1.83	1.38	1.71	1.24	0.95
Phenanthrenequinone	Dioxane	8.86	5.16	3.72	4.86	2.99	2.18

[a] Preliminary data of Mr. K. H. Illinger. [b] Data at 30°.

TABLE II

THE MUTUAL VISCOSITIES (CP.) OF BINARY LIQUID SYSTEMS AND THE VISCOSITIES (CP.) OF THE PURE COMPONENTS

Ref.	Component 1	2	t, °C.	η_m Eq. 5	Eq. 8	η_1	η_2
[a]	Benzene	Ethyl diethylacetoacetate	25	0.802	0.800	0.6145	2.793
[a]	Pyridine	Ethyl diethylacetoacetate	25	1.144	1.319	.8805	2.793
[b]	Benzene	Phenol	20	1.101	1.169	.629	11.04
[b]	Chlorobenzene	Phenol	20	1.236	1.321	.768	11.04
[b]	Nitrobenzene	Phenol	20	2.307	2.466	1.931	11.04

[a] A. E. Dunstan and J. A. Stubbs, *J. Chem. Soc.*, 1919 (1908). [b] A. Bramley, *ibid.*, 10 (1916).

nates is seen to be η_2 and the slope is η_m. This method of calculation is equally applicable to systems in which component 2 is solid at the temperature of measurement, the quantity η_2 being a second unknown.

The mutual viscosity of a polar solid solute 2 in a non-polar solvent 1 may be evaluated by an alternate method in dilute solutions. With the approximation that $\sigma_{12} = \sigma_1$, the differentiation of eq. 1 with respect to x_2 yields

$$\mathrm{d}\eta_{12}/\mathrm{d}x_2 = 2x_2\eta_2\sigma_2/\sigma_1 - 2x_1\eta_1 + 2(x_1 - x_2)\eta_m\sigma_m/\sigma_1 \quad (6)$$

For solutions of sufficient dilution, $x_2 << x_1 \cong 1$, so that

$$\mathrm{d}\eta_{12}/\mathrm{d}x_2 \cong 2x_2\eta_2\sigma_2/\sigma_1 - 2\eta_1 + 2\eta_m\sigma_m/\sigma_1 \quad (7)$$

and

$$\eta_m \cong [\sigma_1(\mathrm{d}\eta_{12}/\mathrm{d}x_2 + 2\eta_1) - 2x_2\eta_2\sigma_2]/2\sigma_m$$
$$\cong \sigma_1(\mathrm{d}\eta_{12}/\mathrm{d}x_2 + 2\eta_1)/2\sigma_m \quad (8)$$

To determine the validity of these equations, the mutual viscosities of five binary liquid systems in the literature have been calculated by the graphic solution of eq. 5 and from eq. 8. The values are shown in Table II. In the approximate method, $\mathrm{d}\eta_{12}/\mathrm{d}x_2$ was determined from the viscosities of the solvent and the most dilute solution reported (1–2 mole % for the solutions of ethyl diethylacetoacetate, and 5-6 mole % for the phenol solutions). The mutual viscosity of veratrole:benzene at three temperatures was determined at low concentrations of veratrole by Mr. D. M. Roberti of this Laboratory, and discrepancies of less than 2% between the results of eq. 5 and 8 were noted. For ethyl diethylacetoacetate in pyridine, a $^1/_2$% variation of the solution viscosity gives rise to a 15% change in the mutual viscosity value from eq. 8, and it is possible that the differences between the two methods of calculation are ascribable to experimental error.

The plots of eq. 5 for ethyl diethylacetoacetate were linear over the entire range of concentration, as shown in Fig. 1, intersecting the Y-axis at the experimental value of η_2. However, the phenol data were linear only at phenol concentrations less than 0.3 to 0.4 mole fraction and were concave upwards on approaching the pure phenol viscosity. Extrapolation to the Y-axis of the linear portions of the three phenol plots of Fig. 2 leads to an apparent solute viscosity of 4-5 cp., which may correspond to the absence of association, although this value seems somewhat high.

The mutual viscosities of the solutes comprising this study were calculated from the measured values of $\mathrm{d}\eta_{12}/\mathrm{d}x_2$ by eq. 8 and are given in Table I. The molecular dimensions, Table III, were obtained from Stuart–Briegleb models.[21] The intermolecular distances are calculated as $\sigma = (ABC)^{1/3}$ where A, B and C are the lengths of the molecular ellipsoid along the principal axes. The value of σ_1 for benzene obtained by eq. 2 at 20° is approximately 1% greater than that obtained from the models.

The relaxation time of the polar solute, according to the theory of Hill, is given by

$$\tau = 3N[I_1'I_2/(I_1' + I_2)][(M_1 + M_2)/M_1M_2]\sigma_m\eta_m/kT \quad (9)$$

where I_2 is the moment of inertia of the polar solute molecule for dielectric relaxation, and I_1' is the moment of inertia of the solvent molecule about the centroid of the solute molecule at the instant of collision. In our calculations, this was approximated by

$$I_1' = [(I_a)_1 + (I_b)_1 + (I_c)_1]/3 + M_1\sigma^2_m/N$$

The moments of inertia were obtained by a direct calculation about the various axes using the best available data on intermolecular distances. In all of the solutes studied, the ellipsoidal molecular shape is symmetrical about the a-axis, and the dipole moment lies parallel to one of the principal axes. Since there is no orienting torque about the latter axis, only the remaining two moments of inertia were used in averaging for I_2. The calcu-

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(21) G. Briegleb, *Fortschr. chem. Forsch.*, **1**, 642 (1950).

TABLE III

CALCULATED AND OBSERVED DIELECTRIC RELAXATION TIMES (10^{-12} SEC.)

Solute	Solvent	$\tau_{calcd.}$ 20°	40°	60°	$\tau_{obsd.}$ 20°	40°	60°	Ref.
Acenaphthenequinone	Dioxane	106	67	46	53[a]	44[a]	28[a]	10
Acepleiadylene	Benzene	127[b]			20.7[b]			12
Anthrone	Benzene	88	60	43	24.8	18.4	13.6	14
Metal-free porphyrazine	Benzene	2670	1590	1150	302	212	159	22
Ferric porphyrazine	Benzene	2640	1680	1360	706	500	367	22
Fluorenone	Benzene	83	56	40	19.9	14.9	11.5	14
Phenanthrenequinone	Benzene	95	65	47	31.3	22.2	16.1	14
Phenanthrenequinone	Dioxane	246	142	97	91.7	60.1	42.0	10

[a] Tentative data of Mr. K. H. Illinger. [b] Data at 30°.

lated dielectric relaxation times are listed in Table III for comparison with the experimentally observed values.

Discussion of Results

A correlation between the observed dielectric relaxation time and that calculated by eq. 9 is shown by the data of Table III. The calculated values for four of the eight systems observed are three to four times the corresponding experimental relaxation times. Values for solutions in dioxane are closer to agreement, with factors of 1.5 to 2.7.

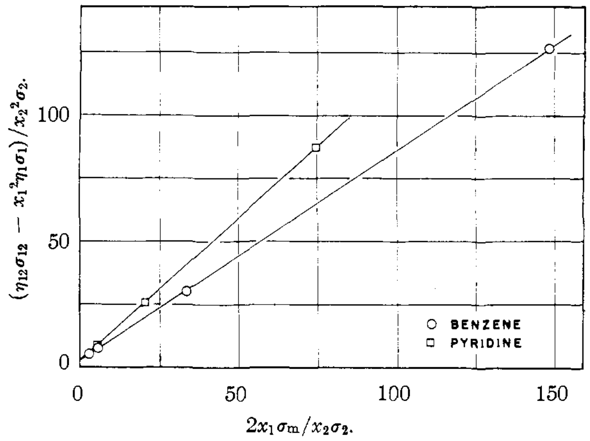

Fig. 1.—Graphic solution of eq. 5 for ethyl diethylacetoacetate in benzene and in pyridine,

The two remaining molecular systems, benzene solutions of acepleiadylene and of the metal-free porphyrazine, have factors between 6.1 and 8.9. In both cases, there exists a possibility of a preferred dielectric orientation mechanism involving rotation in the molecular plane. For these approximately disk-shaped molecules, this mode of orientation would create less disturbance of the neighboring solvent molecules than a rotation out of the plane of the molecule, and one would therefore expect a lowered value of the relaxation time. The effect of the position of the dipole moment in the solute molecule on the dielectric relaxation time is demonstrated[22] in the case of the porphyrazine complexes, since the metal-free compound has its dipole moment in the molecular plane, while in the ferric compound the dipole moment is perpendicular to the plane, and hence the molecule cannot orient by rotation in the plane. On the other hand, the molecular interaction of the viscosity process is not selective in regard to the dipole moment position.

A linear dependence of the observed dielectric relaxation time upon the mutual viscosity has been noted by Hill[5] for several systems in which the solute molecules are not large. Indeed, the two smallest relaxation times in Table III fit on the same line. However, as the molecules increase in size, the increases in moment of inertia and in intermolecular distance (eq. 9) cause the relaxation time to rise above the line corresponding to linear dependence upon mutual viscosity. Although the use of mutual viscosity instead of solvent viscosity is a logical step in the right direction, it is evident that the calculated relaxation times in Table III are still considerably higher than the observed.

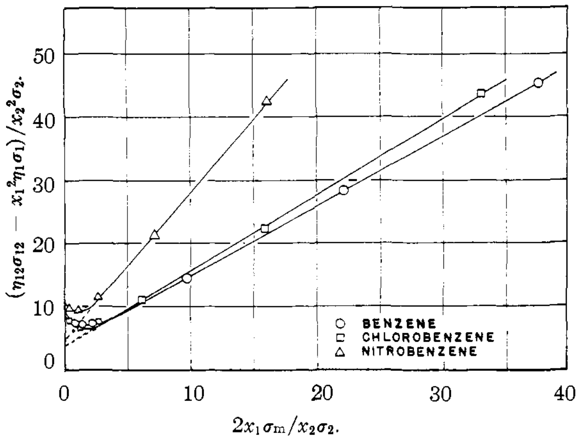

Fig. 2.—Graphic solution of eq. 5 for phenol in benzene, chlorobenzene and nitrobenzene.

Five of the seven solute molecules in Table III were selected for investigation because of their rigidities and well-defined dipole locations. The two porphyrazines were chosen[22] to see if their large sizes in comparison with the solute molecules would reduce the departure from Debye behavior generally observed for smaller molecules. In a paper published after the conclusion of the present investigation Meakins[23] found, in a number of measurements, that, when the solute molecule was at least three times as large as that of the solvent, the solutions gave good agreement with Debye's equation written in the form

$$\tau = 3V\eta/kT$$

where V is the van der Waals volume of the solute

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(22) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, in press (1959).

(23) R. J. Meakins, *Trans. Faraday Soc.*, **54**, 1160 (1958).

molecule calculated as an additive quantity.[24] With the exception of the porphyrazines, the solute molecules in Table III have volumes slightly more than twice that of the solute, *e.g.*, anthrone, 184×10^{-24} cc., phenanthrenequinone, 188×10^{-24}, and benzene, 84×10^{-24}. These volumes lead to calculated relaxation times at 20° of 86×10^{-22} sec. for anthrone and 88×10^{-12} for phenanthrenequinone, slightly lower than the values in Table III calculated by means of eq. 9 but still much higher than the observed values. These discrepancies and those for the remaining solutions in Table III, other than the porphyrazines, resemble those found by Meakins for other solutions in about the same range of solute-to-solvent molecular volume ratios. The volume of the metal-free porphyrazine molecule is calculated from "atomic increments"[24] to be 881×10^{-24} cc., about 10.5 times that of the solvent molecule. This gives a calculated value 410×10^{-12} sec., in much better agreement with the observed 302×10^{-12} than any of the calculated values in Table III, an agreement which is consistent with the conclusion of Meakins. The ferric porphyrazine molecule, having about the same volume, should have about the same relaxation time according to the simple Debye equation, but the observed value is much larger, probably, because of the extensive displacement of solvent molecules involved in the rotation out of the molecular plane. The observed value is, however, nearer to the value calculated by the Debye equation than it is to that calculated with eq. 9. It is evident that, for these solutions as for those investigated by Meakins, the agreement with observed values given by eq. 9 is better for small molecules but poorer for large molecules than that given by the Debye theory.

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[24] J. T. Edward, *Chem. and Ind.*, 774 (1956).

[CONTRIBUTION FROM THE MEMORIAL UNIVERSITY OF NEWFOUNDLAND]

Electronic Spectra and Molecular Dimensions. III.[1] Steric Effects in Methyl-substituted α,β-Unsaturated Aldehydes

BY W. F. FORBES AND R. SHILTON

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The spectra of acrolein and of its methyl-substituted analogs are investigated. The compounds provide examples of some of the simplest conjugated systems in which steric interactions can be detected, and the spectra are therefore discussed with reference to current theories of steric effects in electronic spectra. Previously obtained effective interference radii for atoms in solution, as determined for aromatic systems, provide a consistent interpretation of steric effects in this series.

Introduction

Earlier parts of this series have shown how a steric interpretation of certain spectral effects[2] may be used to obtain values for the effective interference radii of atoms in solution. Examples were then chosen from aromatic compounds. In order to be able to extend the argument to aliphatic conjugated systems, the spectra of acrolein and of its methyl-substituted analogs have been determined. Acrolein provides one of the simplest examples of a conjugated system, and methyl-substituents are known frequently to cause appreciable steric interactions.

Previous work on the spectral properties of α,β-unsaturated carbonyl compounds includes the development of some useful relations concerning the positions of maximal wave length in the ultraviolet region.[3] The effect of structure on the extinction coefficients is less well understood, but it has been assumed that the maximal extinction coefficient ($\epsilon_{\max}$) differs depending on whether the system exists in the *s-cis* or *s-trans* conformation[4] (for nomenclature used, see ref. 5).

Experimental

The ultraviolet absorption spectra were determined at least in duplicate by standard methods in 1 cm. and 2 mm. quartz cells using a Unicam SP500 spectrophotometer. Some of the values were also checked on a Beckman Model DU spectrophotometer and on another SP500 spectrophotometer. The absorption curves obtained in cyclohexane media are shown in Fig. 1.

Since the band shapes are similar for the series of compounds shown in Fig. 1, the extinction coefficients at maximal absorption ($\epsilon_{\max}$) are used as a semi-quantitative measure of the actual absorption intensities. The similarity of band shape as shown in Fig. 1 for solutions in cyclohexane is also obtained for solutions in ethanol. The values of $\lambda_{\max}$ and $\epsilon_{\max}$ are listed in Table II. Most of the spectra have been reported previously, but frequently our values are not in good agreement with the reported data. We attribute previous low values to instrumental and weighing errors; our values are in good agreement with recent determinations. The only satisfactory weighing technique we could find was that of Forbes and Mueller.[6] The precision of $\lambda_{\max}$ values is estimated to be ±0.5 mμ, and the precision of $\epsilon_{\max}$ values ±5% or better. Values were reproducible in most cases to ±2%. Intensities can therefore be considered satisfactory for comparison purposes, since the data were obtained under identical conditions.

It was also found that the spectrum of a solution of crotonaldehyde in ethanol remained unaltered on standing for 24 hr. and showed only a 3% drop in $\epsilon_{\max}$ on standing for 14 days. This indicates that no formation of hemiacetal takes place, and this view also receives support since addition of small amounts of hydrochloric acid to the solution, which may facilitate hemiacetal formation, causes an immediate decrease in the absorption intensity.

All the compounds used were commercially available or prepared by methods as described in the literature. After

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[1] Part II, THIS JOURNAL, **79**, 6495 (1957).

[2] W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957), and preceding papers in that series.

[3] (a) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); (b) **64**, 76 (1942); (c) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[4] R. B. Turner and D. M. Voitle, THIS JOURNAL, **73**, 1403 (1951).

[5] W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1347 (1956).

[6] W. F. Forbes and W. A. Mueller, *ibid.*, **34**, 1542 (1956).