Bjerrum model which we have used for so long: (1), only ions in contact are counted as pairs; (2), no quibbles about an arbitrary limit of integration arise; and (3), association is not automatically excluded beyond a critical value of the parameter b.

Another former tool must, in our opinion, also be discarded as obsolete in the analysis of conductance data. Our earlier calculations[10] of limiting conductance and "dissociation" constants by various modifications of the Ostwald dilution law were subject to the recognized (but then unknown) hazard of error due to the inclusion in K of terms of higher order arising from long range interionic forces. In solvents of low dielectric constant, the association term is the controlling one, so the error there was not very large: for example, our early analysis[4] of the data for Am_4NNO_3 in 80% dioxane gave $K = 9.0 \times 10^{-4}$ which is in almost exact agreement with the value of A^{-1} given in Table III. These earlier methods may therefore still be used as a convenient approximation for $A \geqslant 100$. But in solvents where association is less marked, and especially when it is only moderate, then the earlier methods can only lead to erroneous results.

Our present point of view is that association can in principle and does in fact occur in any solvent. The extent to which the alkali halides, for example, associate in water is presumably small, but if the limit of A as D increases is not zero, then a non-zero concentration of ion pairs must be present at any non-zero concentration. We hasten to admit that the actual amount may be quite small. The device of mixed solvents offers an experimental approach to a quantitative answer to the question, of course.

It should be mentioned that the presence of a non-vanishing A will not change the value of Λ_0 found by the Λ'''-c extrapolation method,[3] but a small change in $\mathring{a}$ will result. Likewise, inclusion of the $5\Lambda_0\delta/2$ term for most simple inorganic salts will only change $\mathring{a}$ by a small amount; since $\delta \sim R^3$ and since the alkali ions certainly have radii not greater than half that of the tetrabutylammonium ion, the δ-term will be roughly an order of magnitude smaller for the alkalies than that for the quaternaries, *i.e.*, $5\Lambda_0\delta/2 \approx 0.25\Lambda_0$. Since $J_1(a)$ is several times Λ_0 in aqueous solutions, no drastic change in $\mathring{a}$ is to be expected from inclusion of the viscosity term. Self-consistency, however, requires that if one linear term is retained, all should be.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XIX. The Effect of Internal Field upon Molecular Relaxation Times in Liquids[1]

BY ROBERT C. MILLER[2] AND CHARLES P. SMYTH

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The effect of the internal field in a liquid upon the dielectric relaxation time of its molecules is examined by comparing the macroscopic relaxation time of a highly polar liquid with that of a liquid consisting of molecules of the same size and shape as those of the polar liquid, but with very small dipole moment. Alternatively, the comparison is made between the pure polar liquid and its dilute solutions in a non-polar solvent. After correction for viscosity differences in most cases, the assumption is made that the macroscopic relaxation time of the pure liquid of low polarity or of the dilute solutions of the polar liquid is equal to the molecular relaxation time of the highly polar liquid. The molecular relaxation times thus obtained are compared graphically with those calculated by means of the various available equations. It becomes evident that the relation of the molecular relaxation time to the macroscopic relaxation time is dependent not only upon the dielectric constant of the liquid, but also, to some extent, upon the molecular shape. Consequently, no equation thus far proposed for calculating the molecular relaxation time from the directly measured macroscopic relaxation time of a polar liquid is wholly adequate, but that proposed by Powles and obtained by O'Dwyer and Sack as a first approximation is the most nearly adequate.

It has been common practice in discussing the relations between dielectric relaxation and molecular size and shape and liquid viscosity to use as the basis of discussion the macroscopic relaxation time τ_M or the critical wave length, $\lambda_m = 6\pi \times 10^{10}\tau_M$, at which the measured dielectric loss is a maximum. This is certainly justified in the case of dilute solutions and, in the case of pure polar liquids, has been commonly considered preferable to the use of a molecular relaxation time calculated by means of the Debye theory based upon the Lorentz expression for the internal field of the liquid.

Calculation of Molecular Relaxation Times.—The macroscopic relaxation time may be written

$$\tau_M = \beta\tau_\mu \tag{1}$$

where τ_M is the molecular relaxation time and β a factor correcting for the effect of internal field. From the original equations of Debye[3] based on the Lorentz internal field

$$\beta = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} = 1 + \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty + 2} \tag{2}$$

where ϵ_0 is the static dielectric constant and ϵ_∞ is the optical or infinite frequency dielectric constant. Powles[4] has proposed an approximate expression for the internal field which gives

$$\beta = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} = 1 + x \tag{3}$$

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[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.

[3] P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929, Chap. V.

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

where

$$x = \frac{\epsilon_0 - \epsilon_\infty}{2\epsilon_0 + \epsilon_\infty} \tag{4}$$

O'Dwyer and Sack,[5] in a more exhaustive treatment, have obtained an expression which leads to

$$\beta = 1 + x + \frac{3x^2}{(1 - 2x)(1 + x)} = \frac{1 - 2x^3}{(1 - 2x)(1 + x)} \tag{5}$$

where x is given by eq. 4.

When ϵ_0 approaches infinity, both equations 2 and 5 require that β also approach infinity, while equation 3 requires that it approach 1.5 as a limit. As a first approximation, neglect of the third term, equation 5 becomes identical with (3). Neglect of the difference between the macroscopic and the molecular relaxation time is equivalent to taking β as equal to 1.

Consideration[6] of the relaxation times and viscosities of the closely related liquids, pyridine, γ-picoline and toluene, led to the conclusion that equation 3 was the best approximation for these liquids. It is the purpose of this paper to apply a similar approach to the considerable body of results now available for testing these equations. For toluene, the dipole moment of the molecule is so small that the internal field is too small to produce any considerable difference between the macroscopic relaxation time and the molecular, that is, $\epsilon_0 - \epsilon_\infty = 0.11$ at 20° gives $\beta = 1.025$ from equation 2, $\beta = 1.016$ from equation 3, and $\beta = 1.005$ from equation 5. When the experimental results are examined presently, it will be evident that these small departures of the values of β from 1 are negligible in comparison with other factors. It is, therefore, justifiably assumed that the macroscopic relaxation time and the molecular are indistinguishable for toluene and for other molecules of similarly small polarity. It is reasonable to assume that γ-picoline or 4-methylpyridine, which has a molecule almost identical in size and shape with that of toluene, has a molecular relaxation time practically identical with that of toluene except for the effects of viscosity. For a spherical or nearly spherical molecule, it has been found[7,8] that the effect of viscosity is small. For such molecules, it has, therefore, been neglected, as a rough approximation, in the following discussion. In previous papers of this series, it has been found that many liquids with unsymmetrical molecules show a rough proportionality between relaxation time and viscosity as indicated by the Debye theory.[3] Consequently, for the comparison of two liquids other than those with nearly spherical molecules, the relaxation time of one is multiplied by the inverse ratio of the two viscosities. If τ_1 is the observed macroscopic relaxation time for a liquid with unsymmetrical molecules of low polarity or for dilute solutions of molecules of high polarity in a non-polar solvent ($\tau_1 = \tau_{M_1} = \tau_{\mu_1}$) and τ_{M_2} is the observed macroscopic relaxation time for a liquid 2 with molecules of high polarity ($\tau_2 = \tau_{M_2}$) and size and shape similar to those of liquid 1, it is assumed that

$$\tau_{\mu_2} = \tau_{\mu_1}(\eta_2/\eta_1) \tag{6}$$

or

$$\beta = \tau_{M2}/\tau_{\mu_2} = \tau_2\eta_1/\tau_1\eta_2 \tag{7}$$

Equation 7 provides a means of obtaining approximate values of β for comparison with those calculated by means of equations 2, 3 and 5.

Experimental Results

Table I gives for the pair of liquids, 1 and 2, in the first column the difference between the static dielectric constant and the optical dielectric constant of the polar liquid, the ratio of the two observed relaxation times, and the ratio corrected by means of equation 7 for the assumed effect of viscosity. For the nearly spherical molecules, τ_{M_2}/τ_1 is taken as β. When liquid 1 is indicated as a solution, liquid 2 is the solute. In Fig. 1 these values of β are plotted against the corresponding values of $\epsilon_0 - \epsilon_\infty$, while the three curves represent the values of β calculated by each of the three equations.

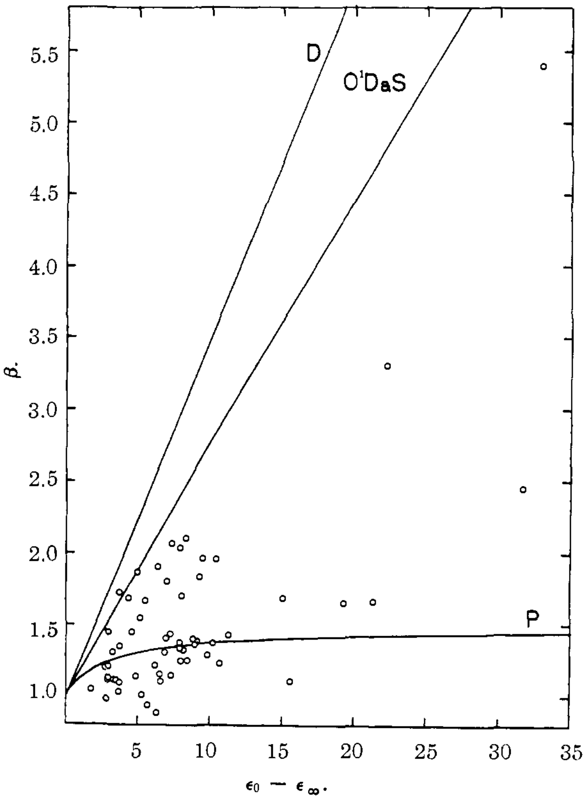

Fig. 1.—Plot of β against $\epsilon_0 - \epsilon_\infty$. Circles represent experimental values. Curve D represents values calculated by means of Debye equation 2; curve O'D & S, values calculated by means of O'Dwyer and Sack equation 5; curve P, values calculated by means of Powles equation 3.

Discussion of Results

The equations under examination by means of the data in Table I were derived for the case of a spherical molecule in a continuous medium and do not take into account the effects of differences in molecular shape and dipole location in the molecule. They may, therefore, be expected to apply with different degrees of approximation to different liq-

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Table I

Internal Field Corrections for Polar Liquids

Liquid	t, °C.	$\epsilon_0 - \epsilon_\infty$	τ_2/τ_1	β
1. Benzene soln.	20	11.3	2.09	1.43
2. Pyridine	40	10.2	2.06	1.37
	60	9.1	2.07	1.39
1. Toluene	1	10.7	2.02	1.23
2. γ-Picoline	20	9.9	2.06	1.29
	40	9.0	2.04	1.37
	60	8.2	1.96	1.33
1. Toluene	1	3.76	1.82	1.35
2. Chlorobenzene	20	3.35	1.78	1.31
	40	2.99	1.62	1.21
	60	2.79	1.62	1.20
1. Toluene	20	2.99	2.86	1.45
2. Bromobenzene				
1. Toluene	20	31.7	8.33	2.45
2. Nitrobenzene				
1. *p*-Xylene soln.	20	3.69	1.43	1.03
2. *p*-Chlorotoluene	40	3.47	1.52	1.11
	60	3.18	1.50	1.13
1. Furan	1	6.9	1.78	1.31
2. Tetrahydrofuran	20	6.2	1.64	1.22
1. Benzene soln.	60	15.1	4.08	1.69
2. Trioxane				
1. *m*-Xylene	20	5.0	2.63	1.87
2. 2,6-Dimethylpyridine	40	4.4	2.31	1.69
	60	3.8	2.24	1.73
1. Toluene				
2. Benzonitrile	20	22.3	7.41	3.31
1. Ethylbenzene	20	8.43	1.89	1.25
2. 4-Ethylpyridine	40	7.96	1.99	1.38
	60	7.27	2.04	1.44
1. Naphthalene soln.				
2. Quinoline	85	4.91	1.40	1.14
1. Naphthalene soln.	85	6.06	1.61	1.16
2. Isoquinoline				
1. Tetrahydronaphthalene	20	8.08	2.18	1.25
2. Isoquinoline	40	7.36	2.00	1.15
1. 1-Methylnaphthalene	20	6.36	1.75	0.87
2. 4-Methylquinoline	40	5.86	1.66	.94
	60	5.36	1.60	1.01
1. Methylnaphthalene	20	3.76	1.58	1.10
2. 8-Methylquinoline	40	3.33	1.51	1.11
	60	2.94	1.43	1.11
1. 1-Methylnaphthalene	20	2.8	1.05	0.98
2. 1-Chloronaphthalene	60	2.2		
1. 1-Methylnaphthalene	20	1.9	1.68	1.04
2. 1-Bromonaphthalene	60	1.5		
1. 1-Methylnaphthalene	60	15.7	2.84	1.11
2. 1-Nitronaphthalene				
	t, °C.	$\epsilon_0 - \epsilon_\infty$	τ_2/τ_1	$\tau_2\eta_1/\tau_1\eta_2$
1. CCl_4 soln.	4	5.6	1.67	1.83
2. CH_3CCl_3	20	5.2	1.55	1.79
	40	4.6	1.45	1.71
1. CCl_4 soln.	2	10.5	1.96	
2. $(CH_3)_2CCl_2$	20	9.3	1.84	2.51
	40	8.1	1.71	
1. CCl_4 soln.	4	8.9	1.41	
2. $(CH_3)_3CCl$	20	8.0	1.34	2.59
	40	7.0	1.41	
1. $CBrCl_3$	1	9.5	1.97	
2. $(CH_3)_3CBr$	20	8.4	2.11	4.19
	40	7.4	2.08	
	60	6.4	1.91	
1. CBr_2F_2	1	8.0	2.04	
2. CH_3CH_2Br	20	7.1	1.81	2.44
1. CBr_2Cl_2	60	33.0	5.4	4.3
2. $(CH_3)_2C(NO_2)_2$				
1. $CFCl_3$	1	21.4	1.67	2.31
2. $(CH_3)_2CO$	20	19.3	1.66	

uids. The application of a viscosity correction in the case of non-spherical molecules and its neglect in the case of approximately spherical molecules is arbitrary, but, in view of the observed behavior of a large number of liquids, seems to be the best available approximation. An unavoidable approximation is the use of the viscosity of the solvent in place of that hindering the rotational orientation of a solute molecule completely surrounded by solvent molecules. However, when the highly polar molecule is of the same size and shape as the solvent molecule or the molecule of low polarity with which it is compared, the error resulting from this approximation is probably not serious. In the calculation of the curves in Fig. 1 a single value, 2.0, is used for the optical dielectric constant in calculating the Debye and the O'Dwyer and Sack curves, although higher values would lower the curves and give somewhat better agreement with the values of β in Table I. However, the effect of using permissibly higher values for ϵ_∞ would not be sufficient to alter the conclusions as to the applicability of the equations.

In Fig. 1, where the values of β in Table I are plotted against those of $\epsilon_0 - \epsilon_\infty$, the points scatter widely, as might be expected in view of the approximations which have been pointed out. The points lie well below the curve based on the Debye application of the Lorentz internal field and, except for four points just outside this area, between the abscissa axis corresponding to $\beta = 1$ and the O'Dwyer and Sack curve, these two lines forming approximate lower and upper limits for the values of the internal field correction. For values of $\epsilon_0 - \epsilon_\infty$ below about 16, the Powles curve seems to give a very rough average of the observed values of β. For the few points above $\epsilon_0 - \epsilon_\infty = 16$, that is, for high internal field, the Powles equation undercorrects, while that of O'Dwyer and Sack overcorrects. If the values of β in Table I are plotted against $(\epsilon_0 - \epsilon_\infty)/(\epsilon_\infty + 2)$ from equation 2 instead of against $\epsilon_0 - \epsilon_\infty$, the points do not fall as far below the curve given by equation 2 as they do in Fig. 1, but they still show clearly the inapplicability of equation 2. If they are plotted against $x = (\epsilon_0 - \epsilon_\infty)/(2\epsilon_0 + \epsilon_\infty)$ from equation 4, the points lie between the abscissa axis and the curve given by equation 5 as approximate lower and upper limits, respectively. As in Fig. 1, many of the points lie below and many above the curve given by equation 3, which may still be regarded as giving the most adequate approximation for the largest number of liquids.

The influence of molecular shape upon the internal field is evident in the values of β in Table I and the points in Fig. 1. For the roughly spherical molecules of the substituted methanes, the effect of the internal field is greater than that calculated by means of the Powles equation, a discrepancy which would be still greater if the correction for the effect of viscosity were not omitted. The flattening of the sphere to the roughly oblate spheroidal form of the substituted benzene and pyridine molecules reduces the effects of the field to amounts close to those calculated by means of the Powles equation, an apparent exception being 2,6-dimethylpyridine, the points for which lie close to the O'Dwyer and Sack curve. Elongation of the flattened structure as in the quinoline, isoquinoline and substituted naphthalene molecules reduces the effects of the field below those calculated by the Powles equation. That the decrease in field effect is not merely the result of increase in molecular volume is shown by the fact that pyridine and the monomethyl and monohalogenated pyridines and benzenes have about the same molar volumes as the tetrasubstituted methanes under consideration. The strong local fields of the highly polar cyanide and nitro groups raise the effects of field well above those calculated by the Powles equation for nitrobenzene and benzonitrile, but the effect is much smaller in the case of the larger 1-nitronaphthalene.

It is evident that the macroscopic dielectric relaxation time of a polar liquid is usually greater than the molecular relaxation time but not nearly as much greater as is indicated by calculation based on the Lorentz internal field. The Powles equation and the identical first approximation obtained by O'Dwyer and Sack seems to be the best approximation for the calculation of the molecular relaxation time from the macroscopic, but it is a very rough approximation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes.[1a,b] XII. The Characteristic NH_3 Deformation Vibrations of Solid Inorganic Complexes

BY G. F. SVATOS, D. M. SWEENY, SAN-ICHIRO MIZUSHIMA,[2] COLUMBA CURRAN AND J. V. QUAGLIANO

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The infrared spectra of a number of solid metal ammine complexes have been investigated. It has been possible to determine the three deformation vibrations of the ligated molecules in these complexes. The NH_3 degenerate deformation is observed in the region of 1650–1560 cm.$^{-1}$; the NH_3 symmetric deformation in the region of 1350–1150 cm.$^{-1}$; and the NH_3 rocking frequency in the region of 950–650 cm.$^{-1}$. Each of these absorption bands has a characteristic absorption profile. A theoretical explanation for the range of these deformation frequencies is presented.

Introduction

Infrared spectra of solid ammine coördination compounds of the transition metals have been subject to several investigations.[3–7] The comparative ease of preparation and the wide diversity of substituents possible in this series have emphasized the importance of a definite characterization of the absorption bands, which may be attributed to the NH_3 grouping upon complex formation.

Mizushima, Nakagawa and Quagliano have recently characterized the deformation vibrations of coördinated ammonia molecules in Co(III) ammines.[8] Using a Urey–Bradley type potential function, the frequencies of the degenerate and symmetric deformations and the rocking vibrations have been calculated for the $Co(NH_3)_6^{+++}$ ion. These calculated values were shown to be in good agreement with frequencies observed for a number of Co(III) ammines containing coördinated ammonia molecules and, furthermore, the values calculated for the deuterated hexammine cobalt(III) chloride, using the same set of force constants, agreed with the observed frequencies.

The infrared spectra of a number of ammines have now been obtained to determine the effect of the nature and the oxidation state of the central metal atom on the frequencies of the three characteristic deformation vibrations of the coördinated ammonia molecules.

Experimental

Preparation of Compounds.—The compounds listed in Table I were prepared by methods similar to those given in the references in the last column. Most of the compounds were dried by heating under reduced pressure in an Abderhalden apparatus for several hours at 110°. All other compounds listed in Table II were supplied by Dr. D. N. Sen.[9]

Absorption Measurements.—Spectra were obtained by means of a Perkin–Elmer Infrared Spectrophotometer Model 21 with a sodium chloride prism. Preparation of the potassium bromide disks was carried out according to the procedure of Stimson and O'Donnell[10] as described in a previous article.[4]

The frequency values for the NH_3 deformation vibrations are listed in Table II.

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[1] (a) Paper XI in series, *Spectrochim. Acta.* in press. (b) Abstracted from the Ph.D. theses of G. F. Svatos, 1954, and D. M. Sweeny, 1955. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb., 1955.

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