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On the Application of the Raman–Krishnan Theory to Dipole Moment Measurements by the Dilute Solution Method

BY H. O. JENKINS AND S. H. BAUER

It has been suggested by Le Fèvre and Le Fèvre[1] that the Raman–Krishnan theory of anisotropic dielectrics[2] provides an explanation of the effect of the medium on the determination of the moment by the dilute solution method. We wish to point out that strong theoretical objections to the Raman–Krishnan treatment itself can be raised and to demonstrate empirically that the particular application is not useful since accurate predictions cannot be made by means of it.

To begin with, it is difficult to justify the expression given by the latter investigators for the local field (equation 11, note 2) when the parameters are given the meaning they intend them to have. An extended argument for the model they had in mind is presented by Krishnan and Rao,[3] who attempt to show that the field at the center of an ellipsoidal cavity of the dimensions of a single molecule immersed in a medium of uniform polarizability is the proper value to be taken for the local field. We should like to draw attention to the restrictions to which the equations used in obtaining the field in a cavity are subjected, *viz.:* the cavity must be so large that it contains many of the volume elements over which the necessary integrations are to be performed and hence must contain many molecules, while at the same time it must be sufficiently small so that the polarization does not vary appreciably across it. As the cavity is made smaller quadrupole and higher order terms should be taken into consideration, and when its dimensions approach those of a single molecule the integration of the polarization over the surface of the cavity should further be replaced by a summation. If these latter troublesome evaluations are to be avoided, the cavity must be made of dimensions of the order of thousands of molecules and then, obviously, the local field will be independent of the shape chosen.

Hence, as far as we can see, for solutions one cannot escape calculating the contribution to the local field of the material inside the cavity (called $\mathbf{F}_3$), which requires that special assumptions be made regarding the distribution of charges around the dipole in question. To emphasize the complexity of the situation we shall list the factors which must be taken into consideration in expressing the mean volume polarization of a sufficiently dilute solution (one in which dipole–dipole interactions may be neglected) in terms of molecular constants: (a) the effect of the impressed field upon the solvent molecules; (b) the effect of the dipoles on the solvent molecules in their immediate vicinity; (c) the effects of solvent molecules on each other (usually quite small); (d) the effect of the impressed field upon the solute molecules; (e) the effect of the polarization of the solvent on the solute molecules (due to factors a, b and c); (f) the statistical fluctuations in the above effects (those of a and c are usually considered; the others are neglected). Since a rigorous treatment of all the above factors would be indeed a formidable task,[4] an empirical or semi-empirical method of approach seems the most promising at present. It is encouraging to note that F. E. Hoecker[5] has obtained highly accurate measurements on extremely dilute solutions of ethyl alcohol in various non-polar solvents and found that in the usual treatment an apparently anomalous behavior often takes place at great dilutions. By slightly modifying the analysis he was able to perform the extrapolation to zero concentration to obtain for the electric moment a value which agreed very well with the accepted one for the gas.

Since the ultimate value of a theory may best be ascertained by investigating its usefulness in predicting the results of experiments, we assumed the final form of the R–K formula (equation 23) and made the following empirical test. It was, however, first necessary to derive from the latter an expression which is applicable to a dilute solution. [We here wish to indicate that the Le Fèvre equation is not the one which is obtained

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[1] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1747 (1935), and subsequent papers in the same journal.

[2] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.* (London), **A117**, 589 (1927).

[3] K. S. Krishnan and S. R. Rao, *Indian J. Physics*, **4**, 39 (1929).

[4] Lars Onsager, THIS JOURNAL, **58**, 1486 (1936), considered some of these factors but restricted his discussion to spherical isotropic molecules immersed in an isotropic medium.

[5] F. E. Hoecker, *J. Chem. Phys.*, **4**, 431 (1936).

through the strict application of the theory since it gives only the most significant term but omits others which may be appreciable (see tables below); also that one should keep in mind that two assumptions must be made in attempting the suggested application: (a) the volume polarizations of the components are additive (*i. e.*, no interactions between solute and solvent molecule takes place which will alter their moments); (b) the new constants entering into the formulation are to be characteristic of the molecules themselves and not of the state of aggregation.] Under this circumstance

$$\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,\frac{M_1f_1+M_2f_2}{\rho_{12}} = \frac{4\pi N}{3}\left\{\left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_1 f_1 + \left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_2 f_2\right\} + N\,\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,(\psi_1f_1+\psi_2f_2) + \frac{N}{3kT}\left\{\frac{4\pi}{3}\,\mu^2 + \frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,\theta_2\right\} f_2 \quad (1)$$

(suffix $_1$ refers to solvent; $_2$ to solute; $_{12}$ to solution), and M, f, N, ρ, k, T have their usual significance.

$\theta_2 = (\mu_i^2\sigma_i + \mu_j^2\sigma_j + \mu_k^2\sigma_k + \text{negligible cross terms})_2$

with $\sigma_i = p_i - \dfrac{4\pi}{3}$

$\mu_{i,j,k}$ are the components of the permanent electric moment of the solute molecule resolved along the principal axes of electric polarizability

$p_{i,j,k}$ are the factors determining the polarization field acting along any particular axis when the external field is along that axis

$\psi_2 = \dfrac{1}{3}\,(a_{ii}\sigma_i + a_{jj}\sigma_j + a_{kk}\sigma_k)_2$

and similarly for ψ_1

where $a_{ii,jj,kk}$ are the diagonal elements of the induced moment tensor.

The ψ's and θ_2 are therefore measures of the anisotropy of the molecules composing the mixture.[6] Equation (1) may be rewritten

$$(P_{12}) \equiv (P_1^g)f_1 + (P_2^g)f_2 = \frac{4\pi N}{3}\left\{\left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_1 f_1 + \left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_2 f_2 + \frac{\mu^2}{3kT} f_2\right\} = \frac{\epsilon_{12}-1}{\epsilon_{12}+2}\left\{\frac{M_1f_1+M_2f_2}{\rho_{12}} - N(\psi_1f_1+\psi_2f_2) - \frac{N}{3kT}\,\theta_2f_2\right\} \quad (2)$$

from which it may appear that one may solve for P_2^g from the value of ϵ_{12} at any concentration provided the molecular anisotropy constants are known. The molecular polarization symbols are therefore placed in parentheses to indicate that this is not legitimate as dipole–dipole and other interactions have not been taken into consideration in equation (2). The usual procedure of extrapolating to infinite dilution must be resorted to. Since in the range of concentrations used it has been experimentally verified that[7]

$$\begin{aligned}\epsilon_{12} &= \epsilon_1(1 + K_1f_2 + K_2f_2^2)\\ \rho_{12} &= \rho_1(1 + R_1f_2 + R_2f_2^2)\end{aligned} \quad (2a)$$

one finds

$$(P_2^g)_\infty = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{\frac{M_2}{M_1} - R_1 + \frac{3\epsilon_1K_1}{(\epsilon_1-1)(\epsilon_1+2)}\right\} - \frac{3\epsilon_1K_1N}{(\epsilon_1+2)^2}\,\psi_1 - \frac{\epsilon_1-1}{\epsilon_1+2}\,N\left(\psi_2 + \frac{1}{3kT}\,\theta_2\right) \quad (3)$$

which is an expression for the "gas" value of the polarization obtained by extrapolating data on dilute solutions using the R–K equation. But the first term of the right member of (3) is equal to P_2^{sol};[8] whence

$${}_\infty P_2^{\mathrm{sol}} = (P_2^g)_\infty + \frac{\epsilon_1-1}{\epsilon_1+2}\,N\left\{\psi_2 + \frac{\theta_2}{3kT}\right\} + \frac{3\epsilon_1NK_1}{(\epsilon_1+2)^2}\,\psi_1 \quad (4)$$

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(6) One may indicate at this point why the R–K equation as applied for the purpose at hand breaks down. Although in the first paper on the subject written by these authors it is stressed that the ψ's and θ's are to depend on the state of aggregation as well as on the characteristics of the particular molecules, in the subsequent work, however, these quantities were treated consistently as molecular constants and, in fact, must be so considered if their values are to be calculated theoretically.

(7) The use of a quadratic form is somewhat unusual. It is, however, a simple matter to show that this is essential in a number of cases. The authors wish to stress particularly that the graphical methods of extrapolation which are almost universally employed in this work are not sufficiently sensitive to detect deviations from linearity which may introduce as much as five per cent. error in the values of K_1 and R_1. Thus, for nitrobenzene in *n*-hexane, the K_1 derived from measurements on a solution for which $f_2 = 0.046$, was 7.566 when a linear relation was used but reduced to 7.232 when a quadratic one was assumed.

(8) With the aid of (2a), an expansion results in the following analytic expression for the quantity usually referred to as

$$P_2^{\mathrm{sol}} = \phi_0 + \phi_1f_2 + \phi_2f_2^2 + \phi_3f_2^3 + \ldots \text{ where}$$

$$\phi_0 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1} \equiv P_1^g$$

$$\phi_1 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{\frac{M_2}{M_1} - 1 - R_1 + \frac{3\epsilon_1K_1}{(\epsilon_1+2)(\epsilon_1-1)}\right\}$$

$$\phi_2 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{R_1^2 - R_1\left(\frac{M_2}{M_1} - 1\right) - R_2 + \frac{3\epsilon_1K_1}{(\epsilon_1+2)(\epsilon_1-1)}\left(\frac{K_2}{K_1} + \frac{M_2}{M_1} - 1 - R_1 - \frac{\epsilon_1K_1}{\epsilon_1+2}\right)\right\} \text{ etc.}$$

It is clear then that although in the final value of ${}_\infty P_2^{\mathrm{sol}}$ the second order coefficients of f_2 do not appear, they do make a contribution to P_2^{sol} and their non-vanishing may introduce significant changes in the values of K_1 and R_1 which will affect the limiting value. Again, for nitrobenzene in *n*-hexane, ϕ_2 varies by approximately 12% in going from $f_2 = 0.046$ to 0.015 (H. O. Jenkins, *J. Chem. Soc.*, 480 (1934)). It is thus of interest to raise the question whether the extrapolations made heretofore on the assumption of a linear variation of P_2^{sol} with f_2 are valid in the range of concentrations investigated. Apparently, even though the slope of the line may vary by large amounts as indicated above, the limiting value actually changes slightly due to the fact that the ratio $\phi_2f_2/(\phi_0 + \phi_1)$ is a small quantity.

As a rule, the $\frac{\epsilon_1 - 1}{\epsilon_1 + 2} N\psi_2$ term is of the order of a cc. and may be neglected.[9]

In making the test of the applicability of the theory we calculated values of θ_2 for a number of polar solutes and compared them with the values which one must assume in order to explain the solvent effect. To obtain ψ_1 and θ_2, one must first compute the appropriate σ and a terms. There are several possible sources for these: (1) x-ray diffraction data for the liquid, giving closest distances of approach, as recommended by Krishnan and Rao. We desire to stress that such values are only significant when derived through the use of the Ehrenfest–Keesom equation, within the limitations indicated by Warren;[10] (2) light scattering data on the liquids; (3) the variation of the polarization of the liquids with pressure;[11] (4) molecular geometry as derived through the use of tables of covalent radii[12] and electron diffraction data (published by Pauling, Brockway and others). The eccentricity of the ellipsoidal cavity produced by the removal of the molecule of interest from the body of the medium which is considered as continuous may be assumed to be determined by the molecular dimensions only; the formulas given by Lord Rayleigh[13] are to be used. Method (4) enabled the authors to calculate the σ's while the a's were determined from light scattering data according to the procedure outlined by Krishnan and Rao. The following values were obtained.

TABLE I

Compound	ψ_1	a_{ii}	a_{jj} ($\times 10^{24}$)	a_{kk}	σ_1	σ_2	σ_3
n-Hexane	-2.1×10^{-24}	13.9	10.8	10.8	−1.68	0.82	0.82
Cyclohexane	−1.3	12.0	12.0	10.0	−0.58	−0.58	1.12
Carbon tetrachloride	−0.0						
Benzene	−5.2	12.9	12.9	6.38	−1.18	−1.18	2.32
Carbon disulfide	−7.0	5.74	5.74	13.0	1.47	1.47	−2.92

	θ_2	σ*
Nitrobenzene	-43.4×10^{-36}	−2.46
Chlorobenzene	− 7.6	−2.36
4-Chlorodiphenyl	− 8.9	−3.48
4-Nitrodiphenyl	−68.2	−3.52
α-Nitronaphthalene	−31.6	−1.88
β-Nitronaphthalene	−49.5	−2.46

* In making these calculations, the coördinate system was so chosen as to orient one of the major axes parallel to the direction of the resultant dipole. Then only one σ term appears in the expression for θ_2. The appropriate ones are listed.

By analogy with the corresponding chloro compounds the gas electric moments of α- and β-nitronaphthalene have been assumed to be 4.1 *D* and 4.5 *D*, respectively. The shape of the β-compound was considered to be approximately ellipsoidal while that of the α an oblate spheroid.

The following two tables give the values of θ_2 which are required to explain the experimental facts for nitrobenzene and chlorobenzene. The total polarization of these at 25° in the gas phase are 400 cc. and 91 cc., respectively.[14]

TABLE II

NITROBENZENE IN VARIOUS SOLVENTS

Solvent	${}_\infty P^{\text{sol}}$	$\frac{3N\psi_1 K_1\epsilon_1}{(\epsilon_1 + 2)^2}$	$\theta_2 \times 10^{36}$	$\theta'_2 \times 10^{36}$
n-Hexane	372.5	− 3.4	−21.4	−24.4
Cyclohexane	360.0	− 2.4	−30.1	−32.0
Carbon tetrachloride	353.1	− 0.0	−32.7	−32.7
Benzene	353.8	−11.6	−23.5	−31.4
Carbon disulfide	310.0	−19.3	−40.6	−51.6
CHLOROBENZENE IN VARIOUS SOLVENTS				
n-Hexane	86	− 0.7	− 3.8	− 4.4
Cyclohexane	84	− 0.7	− 5.0	− 5.6
Carbon tetrachloride	81	− 0.0	− 7.0	− 7.0
Benzene	81	− 1.7	− 5.6	− 6.8
Carbon disulfide	75	− 2.3	− 7.6	− 9.0

From Table II it can be seen that whether the effect of the solvent has been taken into consideration in the ψ_1 term (column 3) or whether it has been neglected (column 4), within the range of 50% θ_2 is not a molecular constant.[6]

Experiments also indicate that the polarizations of many substances are closely alike in benzene and carbon tetrachloride solutions but since ψ_1 is 5.2×10^{-24} for the former and zero for the

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[9] Le Fèvre and Le Fèvre neglected the term involving ψ_1 as well.

[10] B. E. Warren, *Phys. Rev.*, **44**, 969 (1933).

[11] Data for a number of hydrocarbons are given by Ch. Francke, *Ann. phys.*, **77**, 177 (1925).

[12] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[13] Scientific Papers, Vol. 4, p. 307.

[14] H. Müller, *Physik. Z.*, **34**, 689 (1933); H. O. Jenkins, *J. Chem. Soc.*, 480 (1934).

latter, the theory predicts that a difference should always exist. For nitrobenzene this difference is predicted to be 11 cc. but only 1 cc. has been found experimentally. The theory also indicates the presence of considerable divergences in the behavior of substituted diphenyl and naphthalene derivatives from that of the corresponding benzene compounds. That this is unlikely is demonstrated by the fact that the polarization of 4-chlorodiphenyl in benzene is close to that of chlorobenzene; further experimental work will be undertaken shortly to test this point.

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Summary

Theoretical objections to the Raman–Krishnan theory of anisotropic dielectrics are raised.[15] Empirical tests further indicate that the application of the above theory to dielectric constant measurements of dilute solutions of polar solutes in non-polar media would enable one to predict the difference between the moments as determined by the dilute solution method and those derived from gas measurements only as to order of magnitude.

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(15) Subsequent to the submittal of this manuscript to the Editor a paper by Hans Mueller appeared [*Phys. Rev.*, **50**, 547 (1936)] in which essentially similar conclusions were reached through the use of arguments quite unlike those presented here.

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. V. Rotatory Dispersion of Gelatin in Sodium Bromide Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Previous work from this Laboratory[2] has shown that a single term Drude equation $[a]_\lambda = k/(\lambda^2 - \lambda_0^2)$ expressed the rotatory dispersion of gelatin dissolved in sodium iodide solutions and that the dispersion was governed by an absorption band at 2200 Å. At 40° the rotatory dispersion constant k was linearly related to sodium iodide concentration and at 0.5° was found to be expressed by the sum of two equations, $C_{\mathrm{NaI}} = k \log [a/(1 - a)] - \log (1/K)$ and the linear equation $K_{0.5°} = K - k_0 C_{\mathrm{NaI}}$. It was concluded that the tremendous effect of sodium iodide on the rotation of gelatin at 0.5° was due to an association or dissociation of the gelatin molecule.

The purpose of the present investigation was to continue the rotatory dispersion studies using sodium bromide solutions as solvent and ascertain if the above equations were applicable to other alkali metal halide systems.

Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, *p*H, etc., was the same as has been described before.[3]

The specific rotations of gelatin solutions at 0.5 and 40° were measured at five different wave lengths in the visible spectrum, *viz.:* red lithium line, λ = 6707.86 Å.; sodium D line, λ = 5892.617 Å. (optical mean); yellow mercury line, λ = 5780.13 Å. (optical mean); green mercury line, λ = 5460.73 Å.; and the deep blue mercury line, λ = 4358.34 Å. The various light filters employed have been described. The gelatin concentration of the solutions was 0.7824 g. per 100 g. of solution.

Discussion and Conclusions

In Tables I and II are given our data for 0.5 and 40°, respectively, for the wave lengths employed. In Figs. 1 and 2 these data are graphed, plotting the reciprocal of specific rotation against the squares of the wave lengths at which the rotations were obtained. The relationship is linear, which means that a single-term Drude equation adequately expresses the results.

As with sodium iodide solutions of gelatin, the straight lines cut the x-axis at the same point, corresponding to λ_0 = 2200 Å., the location of the absorption band of gelatin. The same value for λ_0 was obtained by solving our data mathematically by the method used before. The values of k, numerator in the Drude equation, were calculated for each concentration of sodium bromide and appear in Table III and are graphed in Fig. 3. At 40° the k values bear a linear relation to

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(1) Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 153.

(2) Carpenter and Lovelace, THIS JOURNAL, **57**, 2342 (1935).

(3) Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927); Carpenter and Kucera, *ibid.*, **35**, 2619 (1931); Carpenter and Lovelace, THIS JOURNAL, **57**, 2337 (1935).