

The influence of hindered molecular rotation on the dielectric constants of alcohols: A comment upon a little recognized error of Oster and Kirkwood

Arnold V. Lesikar

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The influence of hindered molecular rotation on the dielectric constants of alcohols: A comment upon a little recognized error of Oster and Kirkwood

Arnold V. Lesikar

Department of Physics, St. Cloud State University, St. Cloud, Minnesota 56301
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It is shown that the calculation of the alcohol correlation parameter g made by Oster and Kirkwood is in error as the result of an averaging procedure since proved to be invalid. A correct calculation is carried out on the basis of the same model of the alcohol self-association as used by Oster and Kirkwood, yielding a value of 2.0 for g . Literature dielectric data is discussed in relation to this result. It is suggested that the large g values observed in the less sterically hindered alcohols are due mainly to the increment of the dipole moment occurring as a result of hydrogen bond formation. Rotation around the hydrogen bond in these materials is probably almost free.

The work of Oster and Kirkwood¹ evaluating the electric dipole correlation parameter g for various polar liquids has become a citation classic. In this paper the alcohols are pictured as hydrogen bonded chains of infinite length, each molecule being bonded to two neighbors. Free rotation around each hydrogen bond is assumed but the ROH bond angle θ is assumed to be constant. The correlation parameter is calculated from the formula

$$g = 1 + 2 \sum_{n=1}^{\infty} (\cos \gamma_n)_{av}, \quad (1)$$

where γ_n is the angle between the dipole moments of a molecule and a chain neighbor separated from it by n bonds. The average of Eq. (1) is calculated by a procedure developed by Fuoss and Kirkwood² upon the basis of a suggestion by Eyring.³ This procedure results in the value

$$g = 1 + 2f \cot^2(\theta/2), \quad (2)$$

where

$$f = \frac{(\mu_H + \mu_R)(\mu_H + \mu_R \cos \theta)}{\mu_H^2 + \mu_R^2 + 2\mu_H \mu_R \cos \theta} \quad (3)$$

and μ_H and μ_R are the dipole moments of the OH and OR bonds, respectively.

Several authors^{4,5} have pointed out that the Fuoss-Kirkwood averaging procedure is in error. Consequently Eqs. (2) and (3) are invalid. There seems to be little awareness of this fact among workers studying the dielectric properties of the alcohols. Several studies⁶⁻⁹ have cited the g factor of Oster and Kirkwood. In one case it was attempted to extend the Oster-Kirkwood theory to alcohol associates of finite length.⁷ The Oster and Kirkwood calculation has been cited without comment in at least two recent reviews.^{10,11}

The Oster and Kirkwood calculations may seem of little importance since there is a great deal of evidence in the literature indicating that the alcohol self-association is a great deal more complicated than Oster and Kirkwood had assumed.¹² Indeed, the existence of association chains has been strongly questioned.¹³ The attempts of Cole, Dannhauser, and co-workers⁶⁻⁹ to draw quantitative structural information from the com-

parison of measured and calculated g factors has been criticized on the basis of our ignorance of the nature of the alcohol associates.¹⁴ In this context the calculation of g factors on the basis of a simple chain model has little relevance. Recent Raman studies, however, offer stronger evidence for the association of the primary alcohols into chains both at room temperature and below.^{15,16} These chains seem to become very long in the supercooled liquid.^{17,18} In the light of this work, a correct calculation of the alcohol g factor on the basis of a chain model of the self-association can offer interesting and useful information. We would hope to be able to derive estimates of the energy difference between rotational isomeric states¹⁹ of the hydrogen bonded chain from the low temperature g factors⁶⁻⁹ for comparison with the "bond flex energy"²⁰ derived from glass studies.¹⁸ A correct calculation of the g factor on the Oster-Kirkwood model is a useful step in this direction.

The calculation of the alcohol g factor in the approximation of infinite chains with free rotation about the hydrogen bonds may be carried out using the matrix methods developed for the computation of polymer configurations.¹⁹ We assume that each of the n molecules of the chain carries a dipole moment μ_0 . Then identifying the vector \mathbf{M} from Chap. 1 of Flory with the total dipole moment of an alcohol associate we find the g factor to be expressible²¹ in terms of the thermal average of M^2 :

$$g = \lim_{n \rightarrow \infty} \langle M^2 \rangle / n \mu_0^2. \quad (4)$$

This quantity can be expressed in terms of the thermally averaged transformation matrix $\langle \mathbf{T} \rangle$ between coordinate systems attached to adjacent hydrogen bonds¹⁹:

$$g = \mathbf{m}^T (\mathbf{E} + \langle \mathbf{T} \rangle) (\mathbf{E} - \langle \mathbf{T} \rangle)^{-1} \mathbf{m}. \quad (5)$$

Here $\mu_0 \mathbf{m}$ is the column vector representing the dipole moment of the i th alcohol molecule in the coordinate system of the i th bond¹⁹ and \mathbf{E} is the 3×3 identity matrix. In the case of free rotation about a bond we have

$$\langle \mathbf{T} \rangle = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (6)$$

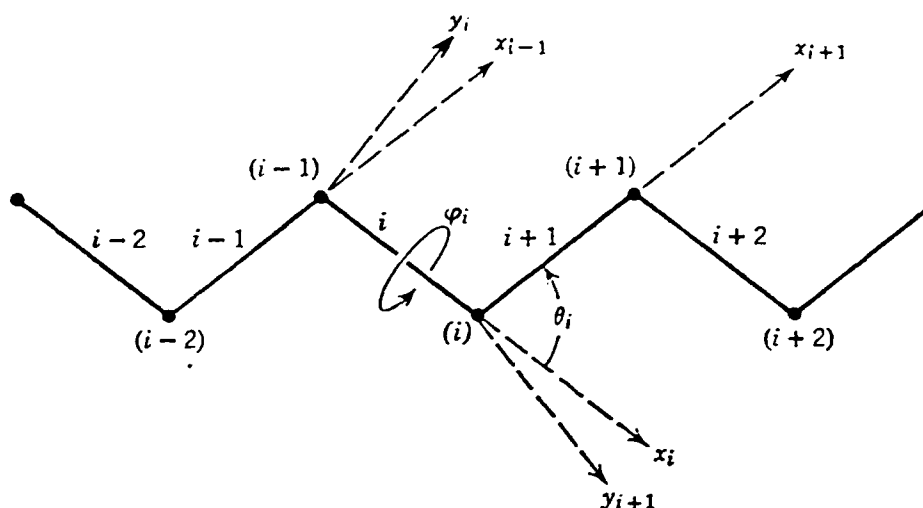


FIG. 1. Hydrogen bond coordinate systems for consecutive hydrogen bonds of an alcohol self-association chain defined following Ref. 19. The z axes, not shown, are perpendicular to the page with directions up or down chosen to give a right handed coordinate system. Here θ_i is the angle between the i th and $(i+1)$ th bond and ϕ_i represents the angle of rotation about the i th bond.

where Θ is the angle between consecutive hydrogen bonds in the chain.

We set up the local bond coordinates in analogy to the system used for polymers¹⁹ (Fig. 1). The axis x_i of the coordinate system attached to the i th hydrogen bond is taken in the direction of the bond. The y_i axis lies in the plane of bonds $i-1$ and i with a positive projection on the x_{i-1} axis. The direction of the z_i axis is then chosen to give a right handed coordinate system. The dipole moment of the molecule is assumed to form an angle γ with the OH bond. If its projection in the local $y-z$ plane forms an angle ϕ with the y axis (Fig. 2), then,

$$\mathbf{m} = \begin{pmatrix} \cos \gamma \\ \sin \gamma \cos \phi \\ \sin \gamma \sin \phi \end{pmatrix}. \quad (7)$$

Use of Eq. (5) then gives the result

$$g = \frac{1}{1 - \cos \Theta} (1 + \cos \Theta \cos 2\gamma + \sin \Theta \sin 2\gamma \cos \phi). \quad (8)$$

This is our final result to replace the incorrect Eqs. (2) and (3) derived by Oster and Kirkwood.¹

The original paper of Oster and Kirkwood¹ yielded a g factor of 2.57 assuming bond moments of 1.6 and 0.7 D for the OH and OR bonds, respectively, and an ROH bond angle of 105° . Hassion and Cole⁶ revised this calculation by using 1.2 D as the OR bond moment. Then by taking the angle between adjacent hydrogen bonds to be equal to the ROH bond angle they found 2.39 as the value of g . We will use the bond moments of Hassion and Cole as they lead to a dipole moment of 1.73 D for the methanol molecule, which is very near to the value recommended in the tabulation of McClellan.²² These bond moments give $\gamma = 42^\circ$. Since these angles are near the tetrahedral bond angles we will take $\phi = 60^\circ$. Inserting these values in (8) yields a value of 2.03 for g . If we assume that all bonds occur exactly at tetrahedral angles and that the alcohol dipole moment lies on the bisector of the ROH bond angle, then we find $g = 2.0$ exactly.

Values of g much larger than 2.0 have been reported for several of the alcohols at room temperature and below.⁶⁻⁹ The value of g derived from experimental data depends on the value assumed for the limiting high frequency dielectric constant ϵ_∞ characteristic of induced polarization. Although the well-known uncertainty²³ in the value of ϵ_∞ introduces some uncertainty in the numerical value of g , there is little doubt that g is large. These large values of g have been attributed to the hindrance of rotation about the intermolecular hydrogen bond. These authors, however, have failed to take into account the increment in dipole moment $\Delta\mu$ produced by the formation of a hydrogen bond.²⁴ For hydrogen bond strengths typical of the alcohols $\Delta\mu$ lies in the range 0.3–0.6 D.²⁴ When the correlation parameter is calculated from experimental data using the unchanged monomer dipole moment μ_M as μ_0 , the increment $\Delta\mu$ will produce an apparent increase in g in the ratio $(\mu_M + \Delta\mu)^2 / \mu_M^2$. Indeed, we find that we can reproduce the observed low temperature g value of methanol and ethanol by assuming an increment of 0.55 D per mole-

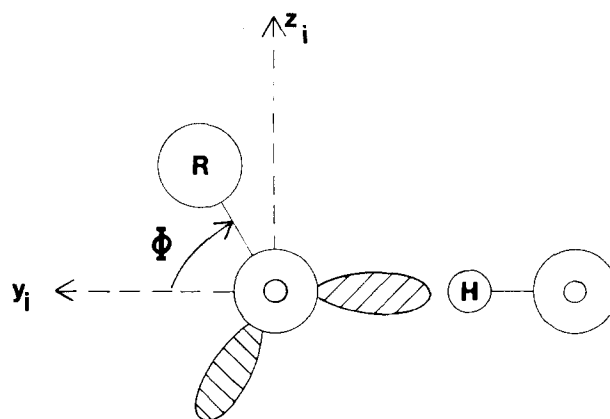


FIG. 2. Definition of the angle ϕ . Here R represents the alkyl group, O is the hydroxyl oxygen, and H is the bonding proton. The shaded areas represent lone pair orbitals. The positive x_i axis runs into the page. The dipole moment of the molecule is assumed to be the sum of the OR and OH group moments.

cule along the hydrogen bond without any hindrance of rotation around the bond whatsoever. This increases the total dipole moment of each molecule in the association chain to 2.17 D and leads to 3.3 as the apparent value of g . This increment in dipole moment is very plausible in view of the results found in other hydrogen bonding system.²⁴ Thus, we believe that there is almost free rotation about the hydrogen bond in these two alcohols even at the lowest temperatures reported in the dielectric studies.⁷ Consequently the rotation about the intermolecular hydrogen bond must be much less hindered than had been assumed⁶⁻⁹ when the alkyl group of the molecule is relatively small. Undoubtedly, however, hindrance of the bond rotation is much more important when the alkyl backbone is very bulky.

The flexibility of the alcohol hydrogen bond is very important in relation to the glass transition in these materials.^{17,18} It would be very useful to have an estimate of this quantity independent of glass measurements. We believe dielectric studies in the vicinity of the glass transition can offer valuable information in this connection. We are planning such measurements in the near future.

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