

THEORY OF NONLINEAR DIELECTRIC EFFECT WITHIN THE CONTEXT OF SIGNIFICANT STRUCTURE THEORY OF HYDROGEN-BONDED LIQUIDS

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(Received September 25, 1971; Revised paper received November 17, 1971)

A formula for the nonlinear change in dielectric permittivity is derived in a quadratic approximation from domain theory of hydrogen-bonded liquids and significant structure concepts. For some straight-chain alcohols, the formula yields $\Delta\epsilon$ values in accordance, to within error, with experiment results.

1. Introduction

Recently, this author published a note [1] proposing a formula for the nonlinear dielectric effect in the context of significant structure of associated liquids [2]. In Ref. [1], $\Delta\epsilon$ is calculated by the method proposed by Böttcher [3]. Here, we derive a stricter formula for the change in dielectric permittivity in an intense electric field based on Kielich's paper [4] in the context of significant structure theory of associated liquids [2]. The treatment of Kielich is more accurate than that of Böttcher.

In Debye's theory [5] of molecular orientation in a strong electric field, the mean projection of the molecular dipole moment onto the field vector is:

$$\langle \mu \rangle = \mu L(\mu F/kT) \quad (1)$$

where μ is the dipole moment of the molecule, F the local field and L the Langevin function. By the definition of L , the mean projection of the moment is not a linear function of the field strength when $\mu F/kT$ is large. Thus the dielectric permittivity is no longer a constant in strong fields but is rather a function of the field strength. In a first approximation, the change in dielectric permittivity, $\Delta\epsilon$, found when applying a strong electric field E to the sample, is proportional to the square of the field strength [5]:

$$\frac{\Delta\epsilon}{E^2} = -A \frac{4\pi N\mu^4}{15k^3 T^3 V} \quad (2)$$

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where N is Avogadro's number, and V the volume of one mole of the substance. The constant A depends on the choice of the local field model; for Onsager's field [6], it becomes [4]:

$$A = \frac{3\epsilon^2}{(2\epsilon^2 + n^4)} \left(\frac{3\epsilon}{2\epsilon + n^2} \right)^2 \left(\frac{n^2 + 2}{3} \right)^4 \quad (3)$$

where ϵ is the dielectric permittivity determined in the presence of a weak electric field, and n the refractive index. The effect, described above, consisting in a decrease in dielectric permittivity in a strong field, is often referred to as dielectric saturation.

Schelma [7] derived an equation taking into account the influence of association on dielectric saturation. Resorting to Fröhlich's method [8], he assumed additionally that the molecules were endowed with a permanent dipole moment only ($n^2 = 1$). The essential difficulty when applying his formulas arises from the necessity of determining the molecular angular distributions.

The theory of dielectric saturation in solutions of alcohols is due to Piekara [9]. In his theory of the nonlinear dielectric effect in hydrogen-bonded liquids, the mean value of the dipole moment was determined by the Langevin function.

This paper is aimed at the calculation of changes in dielectric permittivity due to a strong electric field E from Hobbs', Jhon's and Eyring's [10] domain theory of hydrogen-bonded liquids and taking into account significant structure concepts [2]. The fundamental assumptions of this theory are these:

The value of any property X of the liquid is given by the equation

$$X = \frac{A}{V} X_s + \frac{V-A}{V} X_g \quad (4)$$

with X_s and X_g denoting the values of the property X in the solid and gaseous states, respectively. V and A are the molar volumes of the liquid and solid. $(V-A)/V$ is the fraction of gas-like molecules, and the remainder A/V is that of solid-like ones. (In the present paper, quantities relating to solid-like and gas-like molecules will be denoted by capital Greek letters and capital Latin letters, respectively). Another assumption concerns the structure of a hydrogen-bonded liquid, which has to be conceived of as a mosaic of domains. In each domain, the dipoles yield a mean resultant moment $\mu \cos \vartheta$ along the direction of maximum polarization of the domain. The polarization directions of neighbouring domains tend to orient at 180° . The theory under consideration assumes molecules built into domains have solid-like properties, and that the mean projection of their moment onto the field direction is given by the formula:

$$\begin{aligned} \langle \mu \rangle &= \frac{\mu \cos \vartheta \exp \frac{\mu p \cos \vartheta F}{kT} - \mu \cos \vartheta \exp \left(- \frac{\mu p \cos \vartheta F}{kT} \right)}{\exp \frac{\mu p \cos \vartheta F}{kT} + \exp \left(- \frac{\mu p \cos \vartheta F}{kT} \right)} = \\ &= \frac{\mu^2 p \cos^2 \vartheta F}{kT} \quad \text{for } \frac{\mu p \cos \vartheta F}{kT} \ll 1. \end{aligned} \quad (5)$$

Above, p is the number of molecules orienting as a unit. This formula fails to take into account the interaction between domains and between the latter and the gas-like molecules. The mean projection of the moment of the gas-like molecules (the ones in interdomain space) is given by Eq. (1), because these molecules orient freely in the local field F . These assumptions lead to the formula of Hobbs, Jhon and Eyring for the dielectric permittivity of a hydrogen-bonded liquid:

$$g(\epsilon, n^2) = 4\pi \frac{N}{V} \left(\frac{A}{V} \Pi + \frac{V-A}{V} P \right) \quad (6)$$

where we have introduced the notation:

$$\Pi = \frac{\mu^2 p \cos^2 \vartheta}{kT} \quad (7)$$

$$P = \frac{\mu^2}{3kT} \quad (8)$$

$$g(\epsilon, n^2) = \frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} \left(\frac{3}{n^2 + 2} \right)^2 \quad (9)$$

Jhon and Eyring [11] applied this formula to the calculation of the dielectric permittivity of mixtures of liquids.

2. Nonlinear dielectric effect in quadratic approximation in pure, hydrogen-bonded liquids

In this Section, a formula will be derived for the change in dielectric permittivity in a strong electric field taking into account domain theory of liquids in the light of significant structure concepts. In our consideration relating to nonlinear changes of dielectric permittivity, we shall assume additivity of the fraction of gas-like and solid-like molecules. This means that the strong electric field does not affect the ratio of solid-like and gas-like molecules.

Usually, dielectric permittivity measurements are performed in a weak AC field; the projection of the mean moment of the solid-like molecules onto the field direction is then expressed by the quantity ΠF and that of the gas-like ones by PF , and ϵ is a constant independent of the field strength. When a strong DC electric field is applied additionally to the dielectric, its dielectric permittivity is found to change. The experimental study of the dielectric nonlinearity of the medium reduce to measurements of variations ($\Delta\epsilon$) of its permittivity in function of the applied field strength, which is commonly of the order of 10^5 V/cm, so that the dielectric nonlinearities are very small and require high accuracy of the experimental method [12, 13]. In such conditions, consequently, it is no longer sufficient to take into account only the first term of the expansion of (1) and (5); the mean moment of gas-like molecules is now expressed as [14]:

$$\langle \mu \rangle_g = \frac{\mu^2 F}{3kT} - \frac{\mu^4 F^3}{45k^3 T^3} = PF - \frac{1}{3} KF^3 \quad (10)$$

with the notation:

$$K = \frac{\mu^4}{15k^3T^3}. \quad (11)$$

For solid-like molecules, the mean value of the projection of the moment (5) calculated with accuracy to the second term of the expansion is:

$$\langle \mu \rangle = \frac{\mu^2 p \cos^2 \vartheta F}{kT} - \frac{\mu^4 p^3 \cos^4 \vartheta F^3}{3k^3 T^3} = \Pi F - \frac{1}{3} \Xi F^3 \quad (12)$$

where we have used the notation:

$$\Xi = \frac{\mu^4 p^3 \cos^4 \vartheta}{k^3 T^3}. \quad (13)$$

The quantity ε and the mean projection of the moment on the field vector are related by the well-known formula:

$$\frac{\varepsilon - 1}{4\pi} \frac{V}{N} = \frac{\partial}{\partial E} (\alpha F + \langle \mu \rangle) \quad (14)$$

with α — the polarizability.

We shall apply the formula of the Onsager local field strength in the form [8]:

$$F = \frac{s}{1 - \alpha r} E + \frac{r}{1 - \alpha r} \langle \mu \rangle \quad (15)$$

where the notation is:

$$s = \frac{3\varepsilon}{2\varepsilon + 1}; \quad r = \frac{2\varepsilon - 2}{2\varepsilon + 1} \frac{1}{a^3}.$$

a the radius of Onsager sphere, and E the external field strength. With regard to (4), (15), (10) and (12), Eq. (14) becomes:

$$\begin{aligned} \frac{(\varepsilon + \Delta\varepsilon - 1)(1 - \alpha R)}{4\pi S} \frac{V}{N} = \alpha + \frac{1}{1 - \alpha R} \left(\frac{A}{V} E_{II} + \frac{V - A}{V} P \right) + \\ - \frac{S^2}{(1 - \alpha R)^3} \left(\frac{A}{V} \Xi + \frac{V - A}{V} K \right) E^2 \end{aligned} \quad (16)$$

where the notation is:

$$S = \frac{3(\varepsilon + \Delta\varepsilon)}{2(\varepsilon + \Delta\varepsilon) + 1}$$

$$R = \frac{2(\varepsilon + \Delta\varepsilon) - 2}{2(\varepsilon + \Delta\varepsilon) + 1} \frac{1}{a^3}.$$

In the preceding formula, the possibility that Π can vary with the field strength is taken into account by introducing the notation ${}^E\Pi$.

On inserting into Eq. (14) the formulas (15), (5), (10) to within the first term of the expansion and taking (4) into account, we obtain:

$$\frac{(\varepsilon-1)(1-\alpha r)}{4\pi s} \frac{V}{N} = \alpha + \frac{1}{1-\alpha r} \left(\frac{A}{V} \Pi + \frac{V-A}{V} P \right). \quad (17)$$

In order to calculate the change in permittivity in a strong field, one has to subtract (17) from (16). To this aim, we resort to the simplification:

$$\psi[(\varepsilon+\Delta\varepsilon), n^2] - \psi(\varepsilon, n^2) = \frac{\partial\psi}{\partial\varepsilon} \Delta\varepsilon$$

$$\psi_1 = \frac{(\varepsilon-1)(1-\alpha r)}{s}$$

$$\psi_2 = \frac{1}{1-\alpha r}$$

and

$$\frac{\partial\psi_1}{\partial\varepsilon} = \frac{1}{n^2+2} \frac{2\varepsilon^2+n^2}{\varepsilon^2} \quad (18)$$

$$\frac{\partial\psi_2}{\partial\varepsilon} = \frac{n^2+2}{3} \frac{2(n^2-1)}{(2\varepsilon+n^2)^2} \quad (19)$$

On subtraction (17) from (16), we obtain a formula expressing the change in dielectric permittivity due to a strong electric field:

$$\Delta\varepsilon = \frac{4\pi N}{V} \left[\frac{\varepsilon^2(n^2+2)^2}{3(2\varepsilon^2+n^4)} \frac{A}{V} ({}^E\Pi - \Pi) + \right. \\ \left. - \frac{3\varepsilon^2}{2\varepsilon^2+n^4} \left(\frac{3\varepsilon}{2\varepsilon+n^2} \right)^2 \left(\frac{n^2+2}{3} \right)^4 \left(\frac{A}{V} \mathcal{E} + \frac{V-A}{V} \mathcal{K} \right) E^2 \right]. \quad (20)$$

In deriving this formula, small quantities of second order have been neglected. When solely the mechanism of molecular orientation is taken into account but other mechanisms are omitted, the equality ${}^E\Pi = \Pi$ results; this in turn leads to the following formula, which express the change in dielectric permittivity of the medium caused by reorientation of its molecules in the strong electric field:

$$\Delta\varepsilon^{\text{or}} = - \frac{4\pi N}{V} \frac{3\varepsilon^2}{2\varepsilon^2+n^4} \left(\frac{3\varepsilon}{2\varepsilon+n^2} \right)^2 \left(\frac{n^2+2}{3} \right)^4 \left(\frac{A}{V} \mathcal{E} + \frac{V-A}{V} \mathcal{K} \right) E^2. \quad (21)$$

The coefficient:

$$\frac{3\varepsilon^2}{2\varepsilon^2+n^4} \left(\frac{3\varepsilon}{2\varepsilon+n^2} \right)^2 \left(\frac{n^2+2}{3} \right)^4$$

coincides with the coefficient A of Kielich (3), [4].

3. Conclusions

Experimental studies of dielectric saturation in alcohols yield, in some cases, negative values (*n*-butanol-1, *n*-pentanol-1, *n*-hexanol-1, *n*-octanol-1) and, in others, positive values (*n*-decanol-1, *n*-dodecanol-1) (see [1] and the papers cited therein). From the fact that also variations $\Delta\epsilon > 0$ occur, it can be concluded that molecular orientation is not the only mechanism underlying the effect under investigation, since the orientation of molecules by a strong external field necessarily leads to a decrease of the dielectric permittivity. Within the framework of the above discussed theory, however, there is room for yet another mechanism, in addition to orientation. The other mechanism we have in mind causes a change in Π , and is thus related with the solid-like molecule, as is taken into account in the first term of Eq. (20), namely $4\pi NA(\epsilon^E\Pi - \Pi)/V^2f(\epsilon, n^2)$. Since Π (Eq. (7)) is related with the permanent moment of the molecule μ , the number of molecules orienting as a unit p , and the angle ϑ between the direction of the molecule's dipole moment and that of maximum polarization of the domain, variations in Π in strong electric field can be due to changes in μ , p and ϑ simultaneously or to a change in one of these quantities. A change in p or ϑ under the influence of a strong field E seems hardly plausible, since the field strengths applied to the liquid condenser are by some three orders of magnitude weaker than the strengths of the inhomogeneous fields of neighbouring polar molecules. One can, however, consider the mechanism of field stimulated proton shift proposed by Piekara [9] as a result of which the mean dipole moment to be effectively assigned to each alcohol molecule in the strong external electric field increases. Obviously, any variation of μ would entail a change not only of Π but of ϵ also. However, as the second term of (20) is by about five orders smaller than the first term, a small variation in μ in the second term can be neglected.

According to Piekara [9], the mechanism of field stimulated proton shift does not affect the values of $\Delta\epsilon$ measured in pure, strongly associated alcohols (e. g. *n*-butanol-1, *n*-pentanol-1, *n*-hexanol-1). The quantity $\Delta\epsilon$ measured in such alcohols is due only to the mechanism of orientation, once one neglects the influence of nonlinear changes in polarizability, electrocaloric effect and electrostriction on the value of ϵ in the presence of strong field E . Thus in this case, the values $\Delta\epsilon^{or}$ derived from formula (21) are well adapted

TABLE I

alcohol	$\Delta\epsilon \cdot 10^4$ (60 kV/cm) experimental result	$\Delta\epsilon^{or} \cdot 10^4$ (60 kV/cm)	
		calculated from Eqs (2) and (3)	calculated from Eq. (21)
<i>n</i> -butanol-1	$\begin{cases} -79.2 & [13] \\ -76 & [15] \end{cases}$	-2.5	-64
<i>n</i> -pentanol-1	$\begin{cases} -68.4 & [13] \\ -69 & [15] \end{cases}$	-2.2	-48
<i>n</i> -hexanol-1	$\begin{cases} -60 & [13] \end{cases}$	-1.9	-36
<i>n</i> -octanol-1	$\begin{cases} -38 & [16] \\ -24 & [20] \end{cases}$	-1.5	-26

for a comparison with the values yielded by experiment. As an example, we adduce (Table I) the values of $\Delta\epsilon$ for some straight-chain alcohols at normal conditions in a field of $E = 60 \text{ kV/cm}$. Assuming a domain to be a chain-wise associate, we took $\vartheta = 0^\circ$ and $\mu = 1.7 D$. It is noteworthy that Eq. (21), derived by domain theory of associated liquids and significant structure concepts leads to a value being in satisfactory agreement with experiment. It is the opinion of this author that error in measuring $\Delta\epsilon$ is very large. The literature contains widely discrepant experimental $\Delta\epsilon$ -values for one and the same liquid; e. g. $\Delta\epsilon$ for ethyl ether measured by Chełkowski [12] at normal conditions in a field of $E = 60 \text{ kV/cm}$ is given as -1.32×10^{-4} , whereas if calculated from Thiebaut's measurements, it amounts to -0.564×10^{-4} [17]. Presumably, perfected methods of measurement will some day permit the obtaining of results above doubt, and the inclusion of nonlinear changes in polarizability will improve the theory. Nevertheless, the effect of nonlinear changes in dielectric permittivity can even now be said to have provided one more argument in favour of the Eyring-Jhon theory.

In concluding, it should be stated that this is by no means the first attempt to calculate $\Delta\epsilon$ in alcohols. To Małeckı [19] is due an earlier method of calculating the changes in polarization of associated liquids in strong electric fields. He deals with the associated liquid as a mixture of multimers, each of which is situated in an Onsager cavity. The mean projection of the dipole moments of these multimers onto the field direction is determined by the Langevin function. Obviously, that method together with Eqs (2) and (3) yield $\Delta\epsilon$ -values in accordance with experiment — one need only chose a multimer with sufficiently large dipole moment and resort to Małeckı's assumption regarding additivity of the molar volumes. It is the present author's opinion that, if the Onsager cavity is to contain an associate, the moment of such a cavity cannot be accounted for by the dipole moment alone, as assumed by Małeckı [19], but that other moments will have to be taken into consideration. However, the true distribution of the electric charges in cavity of this kind is unknown, and it would be extremely difficult to achieve a description of the real situation by the method in question. Yet another controversial assumption of Małeckı concerns the reorientation of an n -mer as a whole. In the opinion of others [18, 2], reorientation of n -mers is preceded by rupture of hydrogen bond, and only molecules or (at the most) dimers undergo reorientation, as can be concluded from Ref. [2].

The author wishes to thank Professor S. Kielich for reading the first version of this paper and for his valuable critical remarks. The author is deeply indebted to Professor Z. Pająk for his discussion of the present paper. Thanks are also due to Dr A. R. Ferchmin for his advice and numerous hints throughout this investigation and to K. Flatau, M. Sc., for his remarks concerning the presentation of the results.

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