

LINEAR DIELECTRIC EFFECT IN CONCENTRATED SOLUTIONS OF SIMPLE ALCOHOLS IN NEUTRAL SOLVENTS, BY DOMAIN THEORY OF H-BONDED LIQUIDS INCLUDING SIGNIFICANT STRUCTURES

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(Received February 23, 1972)

It is proposed that, during dilution of an alcohol with a neutral solvent, the mean number of possible orientations of Hobbs-Jhon-Eyring domains gradually increases. The necessary condition for this hypothesis is formulated: The mean number of domain orientations, at given alcohol concentration, has to be independent of temperature. The hypothesis is subjected to a verification by application to values of static dielectric permittivities in solutions of *n*-butanol-1 in *n*-hexane and in cyclohexane from 25°C to 55°C taken from the paper of Huyskens *et al.* The possibility is discussed of a uniform interpretation of static dielectric permittivities and infrared spectra in the range of stretching hydroxyl vibrations in concentrated solutions of alcohols.

1. Introduction

Recently, in a short Note [1], this author proposed the hypothesis that, in the process of diluting an alcohol with a neutral solvent, the mean number of possible orientations of Hobbs-Jhon-Eyring domains [2], increases. This hypothesis will be discussed more fully in the present paper and will be put to test by application to a vaster amount of experimental data. Domain theory of associated liquids taking into account significant structures was proposed by Hobbs, Jhon and Eyring [2, 3] in 1966. They express the mean value of the projection of the molecule's dipole moment on the external electric field direction by the relation:

$$\langle \mu \rangle = \frac{A}{V} \langle \mu \rangle_s + \frac{V-A}{V} \langle \mu \rangle_g \quad (1)$$

with: A the volume of one mole of the substance in the solid state at melting temperature, and V in the liquid state. A/V is the fraction of significant structure, represented by "solid-

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-like" molecules, whereas $(V-A)/V$ is the fraction of the other significant structure, represented by "gas-like" ones. In a liquid, according to the above-cited authors, the "solid-like" molecules are built into domains having solid phase structure: the "solid-like" molecules have vibrational degrees of freedom. In the space between domains, "gas-like" molecules are present, having rotational degrees of freedom. The directions in which the domains exhibit maximal electric polarization are not distributed randomly, but are mutually oriented with regard to one another at an angle of 180° . Hence, the mean projection of the dipole moment of the "solid-like" molecules into the direction of the field is given by the formula:

$$\begin{aligned} \langle \mu \rangle_s &= \frac{\mu \cos \theta \exp(p\mu \cos \theta F/kT) - \mu \cos \theta \exp(-p\mu \cos \theta F/kT)}{\exp(p\mu \cos \theta F/kT) + \exp(-p\mu \cos \theta F/kT)} = \\ &= \frac{\mu^2 p \cos^2 \theta F}{kT} \equiv \Pi F \quad \text{for} \quad \frac{p\mu \cos \theta F}{kT} \ll 1 \end{aligned} \quad (2)$$

with θ denoting the angle between the direction of maximal polarization of the domain and the direction of the dipole moment μ of a built-in molecule, F the local Onsager field strength, and p the number of simultaneously reorienting molecules. The mean projection of the dipole moment of "gas-like" molecules into the field direction is given by the formula [4]:

$$\langle \mu \rangle_g = \frac{\mu^2 F}{3kT} \equiv PF \quad \text{for} \quad \frac{\mu F}{kT} \ll 1. \quad (3)$$

By the assumption (1) and Eqs (2) and (3), the relation between the dielectric permittivity and dipole moment of free molecules able to form hydrogen bonds is expressed as follows [3]:

$$g = \frac{4\pi N}{V} \left(\frac{A}{V} \Pi + \frac{V-A}{V} P \right) \quad (4)$$

where n is the light refractive index and N Avogadro's number; the quantities Π and P are defined by Eqs (2) and (3), whereas g is given as:

$$g = \left(\frac{3}{n^2 + 2} \right)^2 \frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} \quad (5)$$

Jhon and Eyring [5] applied the domain theory of liquids taking into consideration significant structures to solutions of the water-alcohol and water-dioxane types. They described the relation between the dielectric permittivity of the solution and the dipole moments of the molecules composing it by an equation of the same form as Eq. (4). If Eq. (4) is to be applied to a solution, all quantities appearing therein have to refer to the solution, thus: ϵ —dielectric permittivity of the solution, n —refractive index of the solution, V —molar volume of the solution. Henceforth we shall be denoting quantities referring to a solution by means of symbols without indices; quantities referring

to the components will be denoted by symbols with the index 1 or 2. In particular, quantities referring to "solid-like" molecules will be denoted by capital Greek letters (Π , Λ); those of "gas-like" ones — by capital Latin letters (P , V). According to Jhon and Eyring, P and Π of Eq. (4), referred to a solution, have the following meanings:

$$P = (1-f)P_1 + fP_2 \quad (6)$$

f is the molar fraction of component "2".

$$\Pi = (1-f)^2 \Pi_1 + f^2 \Pi_2 + 2f(1-f)\Pi_{12} \quad (7)$$

Π_{12} can be defined in two ways:

$$\Pi_{12} = \sqrt{\Pi_1 \Pi_2} \quad (8)$$

or

$$\Pi_{12} = \frac{\Pi_1 + \Pi_2}{2}. \quad (9)$$

When considering the solution water-alcohol, Jhon and Eyring [5] apply Eq. (8); in dealing with water-dioxane, they resort to Eq. (9). They define the molar volume of the solution in the solid state by the relation:

$$\Lambda = (1-f)\Lambda_1 + f\Lambda_2. \quad (10)$$

2. Strict formula for solutions of the water-alcohol and water-dioxane types

There is some inconsistency in applying formula (4) to solutions. Onsager's theory [6] assumes additivity of the polarizabilities of the molecules, and the formula expressing the dependence between the dielectric permittivities of solutions and the dipole moments of their components involves the refractive indices of the latter but not of the solution. Onsager's formula, particularized for the case of two-components solutions of polar liquids, is of the form:

$$lV = (1-f)V_1q_1 + fV_2q_2 + 4\pi NR \quad (11)$$

where we have introduced the notation:

$$l = \frac{(\varepsilon-1)(2\varepsilon+1)}{3\varepsilon} \quad (12)$$

$$q_i = \frac{(2\varepsilon+1)(n_i^2-1)}{2\varepsilon+n_i^2}, \quad i = 1, 2 \quad (13)$$

$$R = (1-f)R_1 + fR_2 \quad (14)$$

$$R_i = Q_iP_i, \quad i = 1, 2 \quad (15)$$

$$Q_i = \left[\frac{(2\varepsilon+1)(n_i^2+2)}{3(2\varepsilon+n_i^2)} \right]^2, \quad i = 1, 2. \quad (16)$$

Eq. (11) with the assumptions inherent in significant structure theory taken into account, becomes:

$$IV = (1-f)V_1q_1 + fV_2q_2 + 4\pi N \left(\frac{A}{V} \Omega + \frac{V-A}{V} R \right). \quad (17)$$

The quantity Ω is defined similarly to Π (Eq. (7)):

$$\Omega = (1-f)^2 \Omega_1 + f^2 \Omega_2 + 2f(1-f) \Omega_{12} \quad (18)$$

$$\Omega_i = Q_i \Pi_i, \quad i = 1, 2. \quad (19)$$

The quantity Ω_{12} can be defined in two ways, like Π_{12} :

$$\Omega_{12} = \sqrt{\Omega_1 \Omega_2} \quad (20)$$

or

$$\Omega_{12} = \frac{\Omega_1 + \Omega_2}{2}. \quad (21)$$

When describing the properties of a solution of the water-alcohol or water-dioxane type respectively, Ω_{12} can be defined by Eq. (20), or (21). Formula (17) is more accurate though at the same time much more complicated than (4). For solutions in which the refractive indices of the components differ but little (e.g. alcohols, hexane, cyclohexane), Eq. (4) renders well the properties of the solution and is considerably more handy in calculations than formula (17).

3. Concentrated solutions of alcohols in neutral solvents

It is our aim to find the relationship between the dielectric permittivity, determined in concentrated solutions of alcohols in neutral solvents, and the dipole moment of the isolated molecule of the alcohol. As stated in the Introduction to this paper, the authors of domain significant structure theory of associated liquids postulate, in pure liquid alcohols a 180°-array of the solid-structure domains with respect to one another. Thus, only two orientations of domains are possible. In this paper, we postulate that, as dilution of the alcohol with a neutral solvent proceeds, the mean number of possible orientations of these domains increases. That is to say, it is our suggestion that the rotation of Hobbs-Jhon-Eyring domains can be set free in the process of dilution. We shall be denoting the mean number of possible domain orientations by "I". Thus, in the pure alcohol, $I = 2$, whereas, by our hypothesis, I tends gradually upwards with growing dilution of the alcohol by addition of a neutral solvent. This process of growth of the mean number of possible orientations of the domains can be presumed to be accompanied by another process, leading to destruction of the domains. It cannot be ruled out that this latter process can lead to the formation of cyclic forms of associates. The existence of such associates, in the range of low concentrations of alcohols in neutral solvents, has been postulated by Huyskens, Henry and Gillerot [7]. In the present paper, we shall consider solely the first process. We derive the relationship between the dielectric permittivity of the solution and the dipole moment of the alcohol molecule (we denote the alcohol com-

ponent by the index "2") from Eq. (17) with (14), (18) and (21), keeping in mind that obviously $\mu_1 = 0$. The hypothesis concerning the change in mean number of possible orientations of Hobbs-Jhon-Eyring domains with dilution will be given expression by the introduction in the term in Ω_2 of a coefficient b , dependent on the number H of molecules present in 1 cm^3 of the solution. We thus obtain the following formula:

$$IV = (1-f)V_1q_1 + fV_2q_2 + 4\pi N \left[\frac{A}{V}fb(H)\Omega_2 + \frac{V-A}{V}fR_2 \right]. \quad (22)$$

Eq. (22) permits the calculation of the dependence of b on the number of molecules per 1 cm^3 of the solution. Since the mean projection of the dipole moment in the external electric field direction is always, in a first approximation, inversely proportional to the Kelvin temperature, irrespective of the number of possible orientations, hence the shape of the dependence of b on H has to be the same at all temperatures. This temperature-

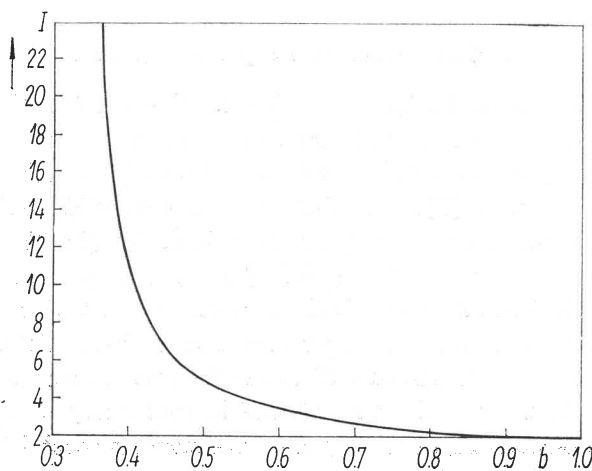


Fig. 1. Coefficient b vs average number of possible domain orientations I

independence of $b(H)$ is at the same time a necessary condition for our hypothesis. The factor $b(H)$ is thus a parameter of Eq. (22) differing from one concentration to another but, for a given concentration, constant at varying temperatures. To each b -value calculated from Eq. (22) at a given concentration, there can be assigned a mean number I of possible domain orientations. Fig. 1 shows the curve according to which I -values can be assigned to b -values. It was obtained by connecting the discrete points derived from the dependence between the numerical coefficients at the first terms of the expansion of successive Brillouin functions, and the number of quantal orientations. In this description, we used Brillouin functions for successive spins since they are intermediate between the Langevin function and that of Brillouin for spin $1/2$; the latter had been used by Hobbs, Jhon and Eyring [3] in their domain theory of associated liquids taking into account significant structures (Eq. (2)). The above method yields the values of I corresponding to the values of b calculated from Eq. (22). The physical meaning of a number I can be obtained by one of the following two interpretations: (i) With increasing dilution of the alcohol,

all the domains gradually give up their orientations parallel and antiparallel to the applied field and assume three, four and more orientations; (ii) With increasing dilution of the alcohol, some of the domains persist in their orientations parallel and anti-parallel to the field, whereas the other domains orient themselves in a manner characterized by an infinite number of possible directions with respect to the field. The higher the concentration of the alcohol, the larger is the number of domains at parallel/anti-parallel orientation to the field. Obviously, dielectric measurements yielding mean values do not permit a decision as to which of these interpretations is the correct one.

A simpler, though less strict form of Eq. (22) is obtained from Eq. (4) with (6), (7), (9) ($\mu_1 = 0$) and on introducing the factor $b(H)$ at Π_2 . We now have:

$$g = \frac{4\pi N}{V} \left[\frac{A}{V} f b(H) \Pi_2 + \frac{V-A}{V} f P_2 \right]. \quad (23)$$

4. Comparison with experimental data

In this subsection, we shall subject available experimental data to a treatment by the above proposed method, for solutions of *n*-butanol-1 in *n*-hexane and cyclohexane. We take, as dielectric permittivity and molar volume values for these solutions, those interpolated from data given by Hyuskens *et al.* [7] for the four temperatures: +25, +35, +45 and +55°C. The refractive index values are from Spravochnik Khimika [8]. The dipole moment of the *n*-butanol-1 molecules is assumed as 1.66 D [9]. Infrared spectra in the range of stretching vibrations of the hydroxyl were obtained by this author with an IR "Zeiss" UR 10 spectrograph. Numerical calculations are performed on the basis of Eq. (23). The approximation of formula (23) was considered sufficient in the case of such solutions. The factor b was assumed equal to unity in the pure alcohol in conformity with Eyring and Jhon's theory [3]. In pure *n*-butanol-1, the Eyring-Jhon parameter $p \cdot \cos^2 \theta$ (denoted in Ref. [3] by G) depends on temperature. We presume that, with varying temperature, the number p of simultaneously orienting molecules changes. In Table I, we list values of the product $p \cdot \cos^2 \theta$ for the above four temperatures.

TABLE I

Values of the Eyring-Jhon parameter $G = p \cdot \cos^2 \theta$ for *n*-butanol-1 in function of temperature

Temperature	25°C	35°C	45°C	55°C
$p \cdot \cos^2 \theta$	1.292	1.238	1.215	1.170

This temperature-dependence of G is alarming, since it raises the number of parameters of the theory: for each temperature, a different value of G has to be taken. Eyring and Jhon, when applying the theory of significant structures to measurements of ϵ in water, obtained good agreement between the calculated and measured values throughout a very wide range of temperatures using always the same value of $G = 0.964$ [3]. In water, it can be presumed that single molecules only undergo reorientation. The situation is not

the same in alcohols, in which the number p of simultaneously orienting molecules differs from unity and depends on the temperature. However, X-ray scattering data from liquid alcohols [10] permit the conclusion that the calculated G -values are not devoid of physical meaning. This is apparent from the data in Table II. The number m of nearest neighbours

TABLE II
Values of the parameter G and of the number m of nearest neighbours at a distance equal to the length of the hydrogen bond, in the homologous alcohol series

Alcohol	G 55°C	G 20°C	m 20°C [10]	m -25°C [10]
methanol	—	1.202 [3]	0.86	—
ethanol	—	1.237 [3]	1.03	—
<i>n</i> -propanol-1	—	1.312 [3]	1.18	1.4
<i>n</i> -butanol-1	1.17	1.305 ¹	1.09	1.2
<i>n</i> -pentanol-1	—	1.206 ²	—	—

¹ value calculated from extrapolated data of [7].

² calculated from data of [11].

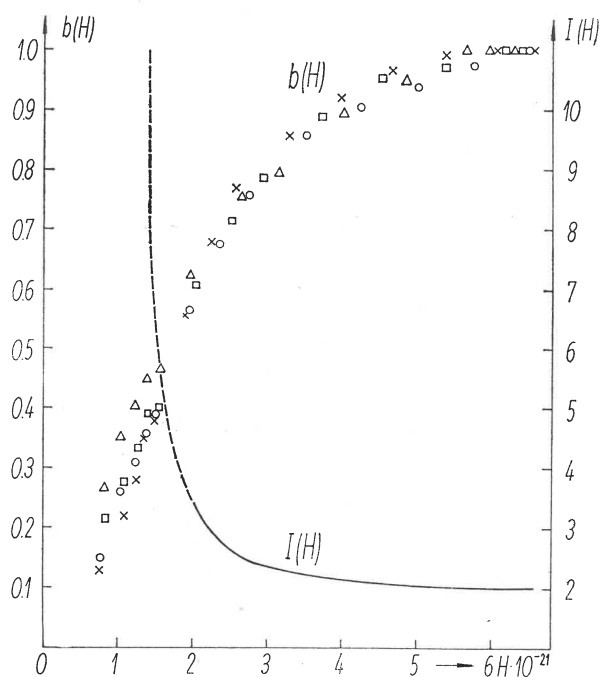


Fig. 2. Solutions of *n*-butanol-1 in *n*-hexane. Points denote values of coefficients b vs the number of molecules per 1 cm³ of solution H , calculated for temperatures: \times — +25°C, \circ — +35°C, \square — +45°C, Δ — +55°C. Full curve shows the average number of possible domain orientations I vs the number of molecules per 1 cm³ of the solution H . Dashed curve is plotted in the concentration region where presumably the domain structure undergoes destruction

at a distance equal to the length of the hydrogen bond is taken from Ref. [10]. In the series of homologous alcohols m at first increases, and then decreases from n -butanol-1 onwards, similarly to the values of G . Changes in temperature, in either case, provoke changes in G and m tending in the same direction.

In our further calculations, we shall assume G not to vary with concentration. In Figs 2 and 3 the points, different for different temperatures, denote the values of the factor b , calculated for solutions of n -butanol-1 in n -hexane and, respectively, in cyclohexane. We maintain that these points are disposed along one curve in the concentration range

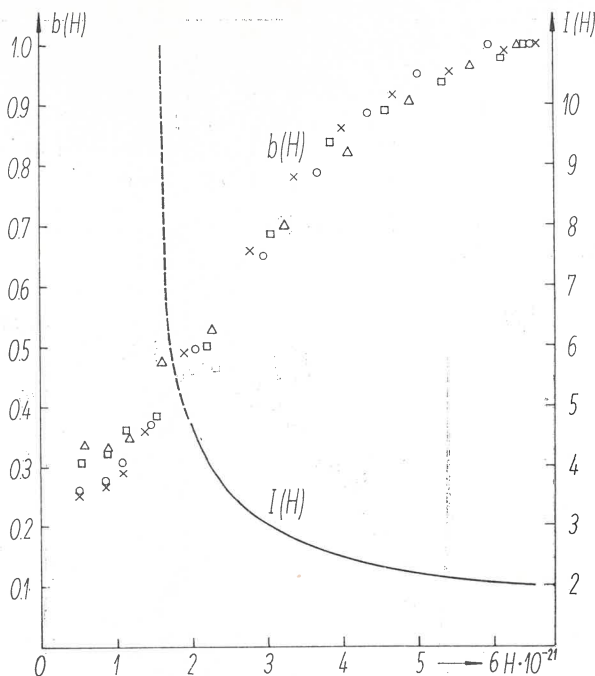


Fig 3. Solutions of n -butanol-1 in cyclohexane. Explanation as for Fig. 2

$2 \cdot 10^{21} < H \leq 6.53 \cdot 10^{21}$ to within experimental error which, as unknown to us, has not been shown in the graphs. A very important source of error in temperature measurements resides in uncontrollable variations of concentration with temperature. In the low concentration range, the b -values at constant concentration depend on temperature and are the larger the higher is the latter. Presumably, in the low concentration range $0 \leq H < 2 \cdot 10^{21}$ the domain structure of the alcohol is destroyed. In Figs 2 and 3, the full curve shows the dependence of the mean number of possible orientations of the Hobbs-Jhon-Eyring domains on the concentration of the alcohol. The curve was obtained by assigning I -values to the b -values in accordance with the method explained in Fig. 1.

In Fig. 4 we list the infrared absorption lines for stretching hydroxyl vibrations and various concentrations of n -butanol-1 in cyclohexane at 27°C in order to remind that

IR absorption provides no evidence for a concentration-dependent involvement of the hydroxyl in proton-donor and acceptor action in the range of high concentrations. Concentrated solutions of the alcohol, irrespective of the concentration, exhibit an unvaryingly wide absorption line attributed to the hydroxyl acting as proton donor and acceptor

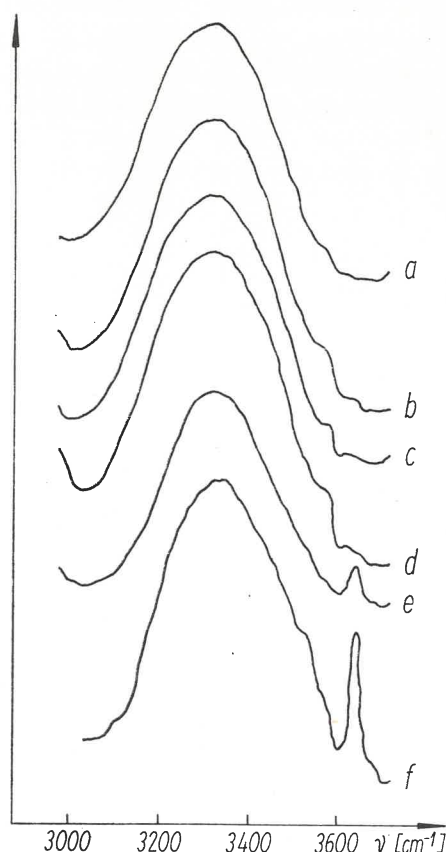


Fig. 4. Infrared absorption bands of solutions of *n*-butanol-1 in cyclohexane in the range of stretching vibrations of the hydroxyl group. Curve *a*: number of molecules of the alcohol per 1 cm³ of solution *H* is $6.55 \cdot 10^{21}$, layer thickness *d* is 0.008 mm. Curve *b*: $H = 4.21 \cdot 10^{21}$; $d = 0.009$ mm. Curve *c*: $H = 3.18 \cdot 10^{21}$; $d = 0.015$ mm. Curve *d*: $H = 2.81 \cdot 10^{21}$; $d = 0.016$ mm. Curve *e*: $H = 0.32 \cdot 10^{21}$; $d = 0.118$ mm. Curve *f*: $H = 0.16 \cdot 10^{21}$; $d = 0.513$ mm

simultaneously [12] (lines *a*, *b*, *c* and *d* in Fig. 4). This information from IR absorption does not contradict the interpretation of static dielectric permittivities proposed in the present paper. If indeed the experimentally observed changes in static dielectric permittivities with concentration are due to changes in the mean number of possible domain orientations, then these changes must not be accompanied by changes in the involvement of the hydroxyl in processes of the proton-donor and proton-acceptor types. At low concentrations, the IR spectra exhibit a line attributed to the free hydroxyl and to the latter acting exclusively as proton-acceptor [12] (lines *e* and *f* in Fig. 4). On the other

hand, at these low concentrations, the necessary condition for the correctness of the hypothesis concerning the change in mean number of possible orientations of the domains is not fulfilled — the values of b are temperature-dependent in this range of concentrations.

The author is deeply indebted to Dr J. Albrycht, Director of the Laboratory of Numerical Calculations, Institute of Mathematics, A. Mickiewicz University, Poznań, as well as to L. Mierzyński, M. Sci., for their disinterested help in tabulating g vs ε and n with the "Odra 1204" computer. Thanks are due to Professor M. Szafran and Dr J. Żarnowski, of the Institute of Chemistry of the Polish Academy of Sciences at Poznań, for making available the IR "Zeiss" UR 10 spectrograph. The author wishes to thank K. Flatau, M. Sci., for the English translation of the present paper.

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