occupancies. Thus, while not relevant to the plait point, the orientational constraints imposed by the model may play an important role in the antiferromagnetic-like ordering, and the details of this phase transition might well be model dependent in a way that the plait-point phenomenon is not.

The Dielectric Constants of Mixtures and of the Supercritical Region of Some Hydrogen-Bonded Fluids

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Abstract: Recently, the domain theory of the dielectric constants of hydrogen-bonded liquids proposed by Hobbs, Jhon, and Eyring has been successfully applied to the system of light and heavy water, various forms of ice, and to the lower aliphatic alcohols. In this paper, we apply the theory to the supercritical region of water. The theory is also developed for the calculation of the dielectric constant of mixtures such as water–methanol and water–dioxane. The model is quite satisfactory in all cases.

Recently, Hobbs, Jhon, and Eyring[2a] developed the domain theory of the dielectric constants of hydrogen-bonded liquids in which the following assumptions were made.

(1) Liquid water and other hydrogen-bonded liquids are made up of a mosaic of roughly bricklike domains with the dipoles in a particular domain having an average resultant moment $\mu \cos \theta$ along the direction of maximum polarization for the domain, while the direction of maximum polarization of neighboring domains tend to be rotated through 180° with respect to the first in the same way magnets juxtapose south poles against north poles. For perfect tetrahedral bonding $\cos \theta$ gives the value of 1, while for bent hydrogen bonds[2b] $\cos \theta$ is correspondingly smaller.

(2) Under the electric field, those domains which are favorably oriented with respect to the field grow at the expense of the less favorably oriented domains until the steady state is reached. The relaxation process involves only the molecules at the interface between domains.

The resulting mean dipole moment for solid-like molecules is then $\bar{\mu} = \mu^2 \cos^2 \theta F/kT$, while for the gas-like molecules, $\bar{\mu} = \mu^2 F/3kT$ since such molecules orient freely in the local field F.[3]

The use of the foregoing assumptions and the concept of the significant structure theory of liquids[4] lead to the following equation for the dielectric constants of hydrogen-bonded liquids such as liquid water.

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V}\left(\frac{n^2 + 2}{3}\right)^2 \left(\frac{V_s \mu^2 G}{V\,kT} + \frac{V - V_s}{V}\frac{\mu^2}{3kT}\right) \quad (1)$$

Here ϵ, n, and μ are the dielectric constant, the index of refraction, and the dipole moment, respectively, and V_s and V are the molar volume of the solid-like structure in the liquid and the molar volume of the liquid, respectively.

This model differs from the Onsager[5] and Kirkwood[6] models in an essential point. This is in the account taken of the forces due to neighboring molecules. Equation 1 was tested for the dielectric constants[2a] of the various forms of ice and of light and heavy water where excellent agreement between experiment and theory was found.

The fact that the values found for G are nearly equal to unity is an extremely satisfying result in conjunction with the proposed model.

Following our early work, Jhon, *et al.*,[7] calculated the dielectric constants of various lower aliphatic alcohols by a similar scheme to that used for liquid water, and G values which were found to be slightly greater than unity were interpreted as indicating a slight degree of polymerization of alcohol molecules.

In this paper, we extend the theory to the supercritical regions of hydrogen-bonded liquids for which no satisfactory theoretical studies appear to have been made; second, the theory of the dielectric constant of some of the hydrogen-bonded liquid mixtures is developed.

Dielectric Constant of Water in the Supercritical Region

For the calculation of the dielectric constant of steam at supercritical temperatures under high pressure, we have to consider the pressure effect in eq 1.

In a compressed region of dense gas or liquid, the pressure effect[8] on V_s is not negligible, since some solids are fairly compressible. Thus, the pressure dependence

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of the solid volume is

$$V_s' = V_s(1 - \beta\Delta p) \tag{2}$$

where V_s' indicates the solid volume under pressure, β is the solid compressibility, Δp is the pressure minus the vapor pressure at the melting temperature, T_m, and V_s has already been defined. If Δp is not large, V_s is equal to V_s', since β for ice is 12×10^{-6} atm^{-1},[9] but at pressures in excess of 100 atm, V_s gives noticeable changes as indicated in eq 2.

In the calculation, the following values of $G = 0.964$ and $\mu = 1.84$ D used in a previous paper[2a] were taken, and the experimental value of approximately 250 atm was used for the pressure. The index of refraction was estimated in a similar way[2a,7] assuming the validity of the Clausius–Mosotti theorem. One sees that the changes in volume affects the index of refraction remarkably. The calculated results are summarized in Table I and show good agreement with the observed values.[10]

Table I. Dielectric Constant of Steam at Various Densities

d, g/cm^3	V, cc	n^2	ϵ_{calcd}	ϵ_{obsd}[10]
		$T = 661$°K		
0.1	180.16	1.064	1.81	1.83
0.2	90.08	1.129	3.09	2.91
0.3	60.05	1.198	4.89	. . .
0.4	45.04	1.270	7.22	7.12
0.5	36.03	1.344	10.07	9.72
		$T = 651$°K		
0.1	180.16	1.064	1.83	1.85
0.2	90.08	1.129	3.12	2.97
0.3	60.05	1.198	4.95	. . .
0.4	45.04	1.270	7.31	7.27
0.5	36.03	1.344	10.16	9.94

Dielectric Constants of Mixtures Containing Water

Here, we extend the domain theory of the dielectric constants of hydrogen-bonded liquids to mixtures. To exemplify the procedure we consider two typical mixtures: (a) water–methanol, a polar–polar mixture, and (b) water–dioxane, a polar–nonpolar mixture.

(a) Derivation of the General Equation. According to Hobbs, Jhon, and Eyring,[2a] the dielectric constant of two hydrogen-bonded liquids A and B is given by

$$\frac{(\epsilon_A - n_A^2)(2\epsilon_A + n_A^2)}{3\epsilon_A} = 4\pi\frac{N}{V_A}\left(\frac{n_A^2 + 2}{3\epsilon_A}\right)^2\left(\frac{V_{sA}}{V_A}P_{sA} + \frac{V_A - V_{sA}}{V_A}P_{gA}\right)$$

where

$$P_{sA} = \mu_A^2G_A/kT \text{ and } P_{gA} = \mu_A^2/3kT$$

and

$$\frac{(\epsilon_B - n_B^2)(2\epsilon_B + n_B^2)}{3\epsilon_B} = 4\pi\frac{N}{V_B}\left(\frac{n_B^2 + 2}{3}\right)\left(\frac{V_{sB}}{V_B}P_{sB} + \frac{V_B - V_{sB}}{V_B}P_{gB}\right)$$

where

$$P_{sB} = \mu_B^2G_B/kT \text{ and } P_{gB} = \mu_B^2/3kT \tag{3}$$

respectively, where the ϵ, n, μ, V, and V_s are as defined previously.

Similarly, the dielectric constants ϵ_M of mixtures of liquid A and B should be given by

$$\frac{(\epsilon_M - n_M^2)(2\epsilon_M + n_M^2)}{3\epsilon_M} = 4\pi\frac{N}{V_M}\left(\frac{n_M^2 + 2}{3}\right)^2\left(\frac{V_{sM}}{V_M}P_{sM} + \frac{V_M - V_{sM}}{V_M}P_{gM}\right) \tag{4}$$

where the letters with the subscript M represent the quantities for the mixture.

In our calculations, n_M^2 and V_M are taken from the references indicated. For the evaluation of the value of P_{gM}, we assume that the interaction between A and B molecules in the gas-like degrees of freedom is negligible. Accordingly

$$P_{gM} = \frac{\mu_A^2}{3kT}X_A + \frac{\mu_B^2}{3kT}X_B \tag{5}$$

On the other hand, for the evaluation of P_{sM}, we have to consider the A–B-type interaction. If we represent the mole fractions of each component by X_A and X_B, the probabilities of occurring of A–A, B–B, and A–B contacts of molecules are given by X_A^2, X_B^2 and $2X_AX_B$, respectively, under the condition of random mixing. Then

$$P_{sM} = X_A^2P_{sA} + X_B^2P_{sB} + 2X_AX_BP_{sAB} \tag{6}$$

where P_{sAB} can be defined as

$$\sqrt{P_{sA}P_{sB}} \tag{6a}$$

or

$$\frac{P_{sA} + P_{sB}}{2} \tag{6b}$$

and for simplicity, we use the following relation for V_{sM}

$$V_{sM} = V_{sA}X_A + V_{sB}X_B \tag{7}$$

(b) Dielectric Constants of the Methanol–Water System. Now, we investigate the validity of eq 4 for the mixture. Substituting eq 5, 6a, 6, and 7 into eq 4, and rearranging eq 4 for convenience, one obtains

$$\epsilon_M = \frac{n_M^2}{2} + \frac{n_M^4}{2\epsilon_M} + \frac{3}{2}(4\pi)\frac{N}{V_M}\left(\frac{n_M^2 + 2}{3}\right)^2\left[\frac{V_{sA}X_A + V_{sB}X_B}{V_M}\left(X_A^2\frac{\mu_B^2G_B}{kT} + X_B^2\frac{\mu_B^2G_B}{kT} + 2X_AX_B\frac{\sqrt{G_AG_B}\mu_A\mu_B}{kT}\right) + \frac{V_M - V_{sA}X_A - V_{sB}X_B}{V_M}\left(\frac{\mu_A^2}{3kT}X_A + \frac{\mu_B^2}{3kT}X_B\right)\right] \tag{8}$$

where A and B represent water and methanol, respectively. In the calculation, the following values were used: $G_A = 0.964$,[2a] $G_B = 1.202$,[7] $\mu_A = 1.840$,[2a] $\mu_B = 1.690$,[7] and $n^2 = 1.77$.[2a,7]

For simplicity, we used $n^2 = 1.77$ throughout since its value is not affected significantly within the temperature ranges in our calculations. The values of V_M are

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[9] E. W. Washborn, *et al.*, "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p 51.

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Table II. Dielectric Constant of Water–Methanol System at Various Compositions

Mole % MeOH	283°K		298°K		313°K	
	ϵ_{calcd}	ϵ_{obsd}[11]	ϵ_{calcd}	ϵ_{obsd}[13]	ϵ_{calcd}	ϵ_{obsd}[11]
0	83.02	83.83	78.52	78.48	74.18	73.15
0.2432	...	...	62.72	65.55	...	...
0.2725	63.79	66.05	...	...	55.84	56.20
0.4575	54.09	56.20	50.40	51.67	46.96	47.40
0.8350	39.86	41.55	35.89	37.91	34.12	34.60
1.0000	34.75	35.75	32.68	32.61	30.37	29.80

obtained from the density data[11,12] using the following relation, $V_M = (M_A X_A + M_B X_B)/\rho_M$, where M_A, M_B, and ρ_M represent the molecular weights of A and of B, and the density of the mixture, respectively.

Calculated values of the dielectric constants of the water–methanol system at several temperatures for compositions varying from 0 to 100% are compared with experiment in Table II.[11–13] The calculated results are in excellent agreement with experiment[11–13] over the entire composition range.

(c) The Dielectric Constant for the Water–Dioxane System. The study of the dielectric constant of this system is important in distinguishing between various theories and in interpreting experiments reported in recent years.[14] The addition of dioxane to water should change the liquid structure and, consequently, the dielectric behavior. Recently, Smith, *et al.*,[15] explained their experimental results in which the mixtures have two dielectric relaxation times in contrast to the single time found for water. Two structures can also be understood in terms of the domain model.

One relaxation is the rapid rotation of the individual molecules at the interface between pure water domains, and the second is that due to the rotation of islands of P water molecules giving a second relaxation time. The addition of dioxane to water tends to increase the number of small islands of water.

Table III. Dielectric Constants of Water–Dioxane Systems at Various Compositions

Mole % dioxane	V(cc)[a]		n[a]		298°K		313°K	
	298°K	313°K	298°K	313°K	ϵ_{calcd}	ϵ_{obsd}[a]	ϵ_{calcd}	ϵ_{obsd}[a]
0	18.08	18.17	1.3325	1.3309	78.61	78.5	74.03	73.12
20	30.97	31.31	1.3869	1.3820	59.72	60.4	55.01	56.26
40	44.47	45.00	1.4035	1.3978	41.92	42.9	38.80	39.54
60	58.24	59.03	1.4127	1.4050	27.04	25.9	24.91	23.72
80	72.03	73.13	1.4173	1.4095	13.76	10.7	12.68	9.91
100	85.83	87.23	1.4204	1.4126	2.02	2.101	1.995	2.098

[a] From J. Timmermans, "Physicochemical Constants of Binary System in Concentrated Solutions," Vol. IV, Interscience Publishers, Inc., New York, N. Y.

For the estimation of P_{sAB}, we use eq 6b since the dioxane has a negligibly small dipole moment in the liquid.[16] In this particular system, the polarizability due to the permanent dipole $P_{sA}{}^*$ in the A–B contact is different from P_{sA} in an A–A contact, since the former involves the simultaneous rotation of the P molecules of A. In this case, the mean dipole moment per molecule will be $(P\mu)^2/P = P\mu^2$. Here A, B, and $P_{sA}{}^*$ represent the water, the dioxane, and the P_{sA} term in the P_{sAB} expression. Then

$$P_{sA}{}^* = \mu_A{}^2 G_A{}^*/kT \tag{9}$$

Substituting eq 5, 6, 6b, and 9 into eq 4 and using zero for μ_B as a close approximation, we obtain

$$\epsilon_M = \frac{n_M{}^2}{2} + \frac{n_M{}^2}{2\epsilon_M} + \frac{3}{2}(4\pi)\frac{N}{V_M}\left[\frac{V_{sA}X_A + V_{sB}X_B}{V_M}\left(X_A{}^2\frac{\mu_A{}^2 G_A}{kT} + X_A X_B \frac{\mu_A{}^2 G_A{}^*}{kT}\right) + \frac{V_M - V_{sA}X_A - V_{sB}X_B}{V_M} \times \left(\frac{\mu_A{}^2}{3kT}X_A\right)\right]\left(\frac{n_M{}^2+2}{3}\right)^2 \tag{10}$$

In the calculation, the following values were used: $G_A = 0.964$, $G_A{}^* = 3.47$, $\mu_A = 1.84$ D,[2a] $V_{sA} = 17.65$[2a] cc, and $V_{sB} = 76.84$ cc.[17] The values of V_M and n_{M^2} are obtained from ref 18. The calculated results of the dielectric constants of the water–dioxane mixtures are compared with experiment[18] in Table III. Calculation and experiment are in good agreement.[18] The only significant deviation which occurs in the range of high concentration of the dioxane can be explained by considering that $G_{sA}{}^*$ may decrease because of depolymerization of the water in high concentrations of dioxane.

Conclusion

In this paper, we have tested the applicability of the domain theory of pure hydrogen-bonded liquid into the supercritical region where the system is under high pressures and under a wide range of densities of the liquid. The theory is also extended to calculate the dielectric constant of mixtures such as water–methanol and water–dioxane. The results are quite satisfactory.

It is extremely encouraging to find that the significant structure theory with the concept of gas-like and solid-like molecules leads to an explanation of the dielectric constant in the supercritical region and over a widely

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(16) C. P. Smith, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(17) Estimated from the extrapolation of the density data in the article of F. Hovorka, R. A. Schaeter, and D. Dreisbach, *J. Am. Chem. Soc.*, **58**, 2264 (1936), assuming 10% expansion on melting.

(18) J. Timmermans, "Physicochemical Constants of Binary System in Concentrated Solutions," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1959.

varying density range. In subsequent publications, the dielectric constants of the other well-known mixtures such as aliphatic alcohols with water, alcohols with dioxane, and alcohol–alcohol systems will be investigated using our extended model for mixtures.

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Rupture of Thin Liquid Films Due to Spontaneous Fluctuations in Thickness

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Abstract: The surfaces of thin liquid films are slightly corrugated because of thermal fluctuations. These corrugations show up in the light scattered by these films. It can be shown that corrugations having wavelengths larger than a critical wavelength will grow spontaneously, because of the action of van der Waals forces, and will cause the film to become rapidly thinner and break (or be stabilized as a black film, if sufficiently strong repulsive forces keep the two faces of the film separated). The critical wavelength $\Lambda_{\mathrm{crit}} = [-2\pi^2\gamma/(\mathrm{d}^2G/\mathrm{d}h^2)]^{1/2}$, in which γ is the surface tension, G the Gibbs energy of interaction among the molecules per unit area of the film, and h the thickness of the film. The rate at which fluctuations above the critical wavelength grow depends on the viscosity of the liquid, and it can be shown that the combination of regular drainage and spontaneous growth of fluctuations leads to a critical thickness and a lifetime for the film of the same order as those found in experiments.

It is well known that Professor Debye had a vivid interest in fluctuation phenomena as manifested, *e.g.*, in light scattering. He also was interested and fascinated by the measurements of van der Waals forces between macroscopic bodies. It is therefore fitting that in this volume a paper is dedicated to his memory, which deals with a case where the combination of a fluctuation phenomenon and van der Waals forces leads to an explanation of the kinetics of breaking of thin films.

The ultimate lack of stability of foams and emulsions is not difficult to understand. These structures have a very large interfacial area, and decrease of this area is accompanied by a decrease in free energy. The mechanisms, however, by which this decrease in interfacial area is obtained, are less well understood. This is particularly true of the most efficient mechanism for coarsening foams and emulsions, *in casu*, the breaking of thin liquid lamellae between two foam bubbles or emulsion droplets. It appears as if at a "critical thickness" of the order of 0.1 μm these lamellae may become unstable and break suddenly. On the other hand, about 10 years ago de Vries[1] calculated that the energy of activation required to form a hole in a thin film is on the order of γh^2, where γ is the interfacial tension and h the thickness of the film. The film is not expected to burst until its thickness is down to a value for which the energy of activation for hole formation is a small multiple of the equipartition energy, kT, that is, for an interfacial tension of about 10 dynes/cm, down to about 20 Å.

A solution of this apparent paradox can be based upon the natural roughness of all interfaces. Although the existence of a surface tension tends to make the surface as flat as possible, thermal motions will cause a certain roughness. This roughness can be observed experimentally, because a surface that is not completely flat not only reflects but also scatters some of the light falling on it (see Figure 1).

The profile of the surface can always be represented as a sum of Fourier waves. Since each of these Fourier terms can be considered as an independent degree of freedom of the system, the average amplitude of each wave is fixed by the condition that the increase in surface Gibbs energy (surface tension multiplied by the increase in area) caused by this wave is just equal to the equipartition energy, $^1/_2kT$. The theory of surface light scattering has been given by Mandelstam[2] in 1913 and was further developed by Gans[3] (1924) and Andronow and Leontowicz[4] (1926). Experiments by Raman and Ramdas[5] (1925) and by a few others confirmed the theory, but the phenomenon was more or less forgotten, presumably as a consequence of the experimental difficulty caused by the simultaneous occurrence of bulk light scattering which is usually stronger than the scattering by the surface.

A few years ago, one of us[6] considered the possibility of calculating and measuring surface light scattering by thin liquid films. Here the bulk scattering is negligible, making experimentation easier. The theory is more complicated because of the optical interference of light scattered by the two surfaces of the thin films. But there is a third aspect which makes the investigation of

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