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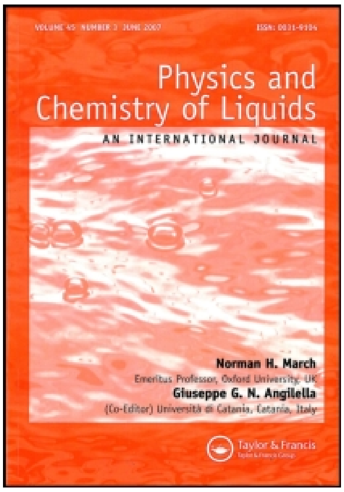

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Small Angle X-Ray Scattering from *Tertiary*-Butyl Alcohol-Water Mixtures

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Abstract—Small angle x-ray scattering measurements have been made on a number of *t*-butanol-water mixtures. The scattering is concentration dependent and has a maximum intensity for the solution with 0.11 mole fraction of alcohol. The zero angle scattering from this solution is temperature dependent and increases by a factor of 2.5 when the temperature changes from 5° to 56°C. Theoretical zero angle intensities, calculated from thermodynamic data in terms of the Kirkwood and Buff solution theory, were found to be in agreement with the experimental results. Thermodynamic data were also used to show that the solutions that give rise to appreciable small angle scattering also tend to form clusters of like molecules.

Introduction

Study of alcohol–water mixtures has continued for a number of years. Much of the work has recently been reviewed by Frank and Ives.[1] Of particular interest has been the study of properties which exhibit extrema at some intermediate alcohol concentration. The ultrasonic absorption, for example, shows a very pronounced maximum in the case of *t*-butanol–water mixtures at 0.12 mole fraction of alcohol.[2] The anomalous properties are thought to be a consequence of structural units or "clusters" in the solution. Knight believes that the positive deviation from Raoult's law, which is observed over most of the concentration range, is due to the association of large numbers of alcohol molecules and not to the association of pairs or triplets of alcohol molecules.[3] *t*-Butanol is the last of the simple aliphatic alcohols which is completely miscible with water, and consequently it is not surprising that a number of the anomalies seem to be particularly pronounced in the *t*-butanol–water system.

A small angle x-ray scattering study of an alcohol–water mixture is of

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special significance because it affords a test of the applicability of the Kirkwood and Buff fluctuation theory[4] to solutions where clustering is present. Shaffer[5] has shown how this theory can be used to relate the zero angle x-ray scattering to thermodynamic parameters for a binary mixture. The theory has been shown to be in essential agreement with experiment for solutions of both large and small molecules.[5,6] No work has been reported, however, for solutions where appreciable clustering is present. Sufficient thermodynamic data[7,8] are available for *t*-butanol–water mixtures so that a fair approximation of the zero angle scattering can be calculated over a broad concentration range.

Theory

The expression for the scattered intensity, $I(h)$, for a two-component system contains three radial distribution functions, $P_{ij}(r)$, which in general are not known.[9] However, a calculation of the zero angle intensity, I_T, requires a knowledge only of the integrals of these radial distribution functions.

$$G_{ij} = \int_V [P_{ij}(r) - 1]\,dv$$

Shaffer[5] has pointed out that these are the same integrals that are related to thermodynamic parameters by the Kirkwood and Buff solution theory. The zero angle intensity for a binary solution follows directly from the intensity equation for a multi-component system given by Guinier and Fournet.[9]

$$\frac{I_T}{I_e(0)V} = c_1 n_1^2(1 + c_1 G_{11}) + c_2 n_2^2(1 + c_2 G_{22}) + 2c_1 c_2 n_1 n_2 G_{12} \qquad (1)$$

c_i is the number of i type particles per unit volume and n_i is the number of electrons in each particle of type i. $I_e(0)$ is the zero angle intensity scattered by a single electron and V is the total sample volume. In Eq. (1) the probability that one particle is of type i has been set equal to vc_i where v is the average volume offered to each particle regardless of type. By using the Kirkwood and Buff relations for the partial molecular volume of particles of type 2, and the isothermal compressibility, κ; G_{12} and G_{22} can be eliminated from Eq. (1). Shaffer collected terms to obtain an expression containing I_2, the zero angle scattering from pure component 2.

$$I_2 = n_2^2(c_2^0)^2\kappa_2^0\,kT$$

where c_2^0 is the number of particles per unit volume in pure component 2. The zero angle intensity, in a slightly more correct form than Shaffer's expression, is then

$$\frac{I_T}{I_e(0)V} = c_1(n_1 - n_0)^2(1 + c_1 G_{11}) + \frac{c_2 \kappa I_2}{(c_2^0)^2 v_2 \kappa_2^0}\left[1 + \left(\frac{2l_1}{l_2} - \frac{V_1}{V_2}\right)\frac{W_1}{W_2}\right] \qquad (2)$$

where l_i is the ratio of n_i to the molecular weight, V_i is the partial specific volume of component i and W_i is the fraction by weight of component i and $n_0 = n_2 v_1/v_2$. v_i is the partial molecular volume for particles of type i. For solutions in which the density, partial molar volume and partial vapor pressure have been determined, G_{11} can conveniently be evaluated from the expression[10]

$$\frac{G_{11}}{v_1} = -\phi_2\left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{p,T} - 1 \qquad (3)$$

where ϕ_i is the volume fraction of component i. We have neglected a term containing the compressibility because it is small for condensed systems. The activity of component 1, a_1, is approximately equal to the ratio of the partial vapor pressure of component 1 to the vapor pressure of the pure component 1. The quantity, $\phi_1 G_{11}/v_1$, called the Zimm clustering integral, represents the mean number of molecules of type 1 in excess of the random expectation in the neighborhood of a given molecule of type 1.[11] For an ideal solution the activity is proportional to the volume fraction and G_{11} is equal to minus one molecular volume. On the other hand, G_{11} will be large if the molecules tend to cluster. The term *cluster* as used here must be somewhat vague and refers to a region in the solution that contributes significantly to the average correlation fluctuations. It also follows that $\phi_1 G_{12}/v_1$ represents the mean number of molecules of type 1 in excess of the random expectation in the neighborhood of a molecule of type 2. If for a condensed system we neglect the term containing the compressibility, then[5]

$$\frac{\phi_1}{v_1} G_{12} = -\frac{\phi_1}{\phi_2}(1 + c_1 G_{11})$$

$\phi_1 G_{12}/v_1$ will be negative if like molecules cluster and positive if unlike molecules cluster.

The general expression for $I(h)$ which served as the starting point for the derivation of Eq. (2) is correct for isotropic fluids in which the orientations of molecules are not modified by the relative positions of neighboring molecules. This condition is always realized for spherically symmetric molecules and is likely to be reasonably well satisfied for other systems if the particle shapes are not too anistropic and the forces between the molecules are weak. The presence of certain types of molecular associations could no doubt lead to significant deviations from the above theory. If the orientation condition is satisfied, the presence of clusters in the solution should not invalidate the theory provided the Kirkwood and Buff expressions are still relevant.

Experimental Method

A brass sample holder of thickness 1.25 mm was used for all samples. The sample transmission for copper K_α radiation ranged from 26% for water to 55% for pure *t*-butanol. Mica windows, 67% transmission, were used without glue or gasket in contact with the solution. Sample temperature up to about 60°C could be achieved by circulating water around the top of the sample holder.

The x-ray diffractometer was the four-slit Beeman type with 50 cm between neighboring slits. The slit widths used were 0.029". The entire beam path between the slits was evacuated to reduce air scattering. Window scattering was limited to the two mica windows on the sample holder. A rotating copper anode x-ray source was operated at 65 mA and 38 kV constant potential. Monochromatization was achieved with a K_β filter and a pulse height analyzer. The data were corrected for background, slit and window scattering and also for the effect of slit height. The data-taking process was completely automated with a step scanner capable of setting steps of any integral multiple of 0.0005 radians. The scattering was observed on both sides of the incident beam.

Comparison of the experimental zero angle scattering with the theoretical values calculated from Eq. (2) was accomplished by using water as a reference sample. Chonacky[6] has made a careful comparison of the theoretical and experimental zero angle scattering of water. He has shown that the two values are in good agreement if a correction is made for double scattering. The latter contributes approximately 5% to the water scattering. We have not attempted to correct for the double scattering which is of course present in the alcohol solutions as well as the pure water, and to some extent the effect will tend to cancel. Water as the reference has certain advantages. It is possible to use the same sample holder for both the water reference and the solutions which eliminates the necessity of geometrical corrections. Also errors involved in monochromatization will tend to be small since the transmission for water and for most of the solutions is not appreciably different.

Results and Discussion

The scattering curves obtained from six alcohol–water solutions and also for the pure components are shown in Fig. 1. The zero angle intensity extrapolations, $I(0)$, relative to water, are given in Table 1. These values should be within 8% of the correct values. The largest uncertainty is involved in the use of water for the reference sample. The theoretical values, I_T, also relative to water, shown in Table 1, were calculated from Eq. (2). These values may have errors as high as 15% because of the limited available vapor pressure data over much of the concentration range between 0.05 to 0.3 mole fraction of alcohol. See Fig. 2. The close agreement between experiment and theory here is fortuitous, as can be seen by the relatively large size of the uncertainty compared to the disagreement. In

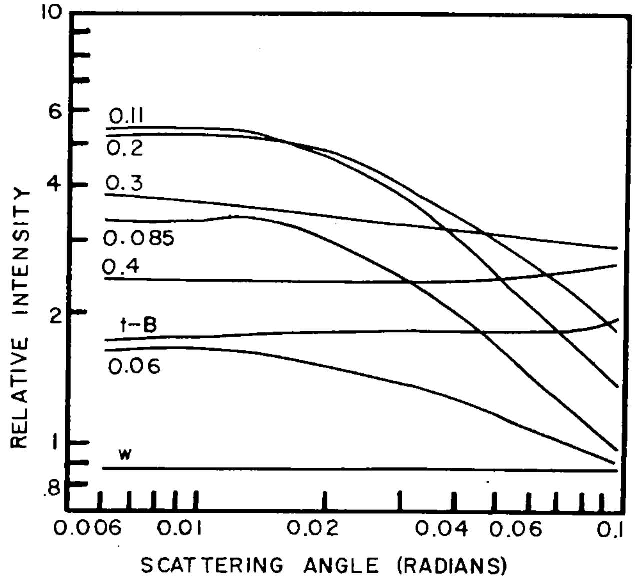

Fig. 1. Scattering curves for six solutions with different alcohol mole fractions concentrations and the two pure components, water, w, and *t*-butanol, t-B.

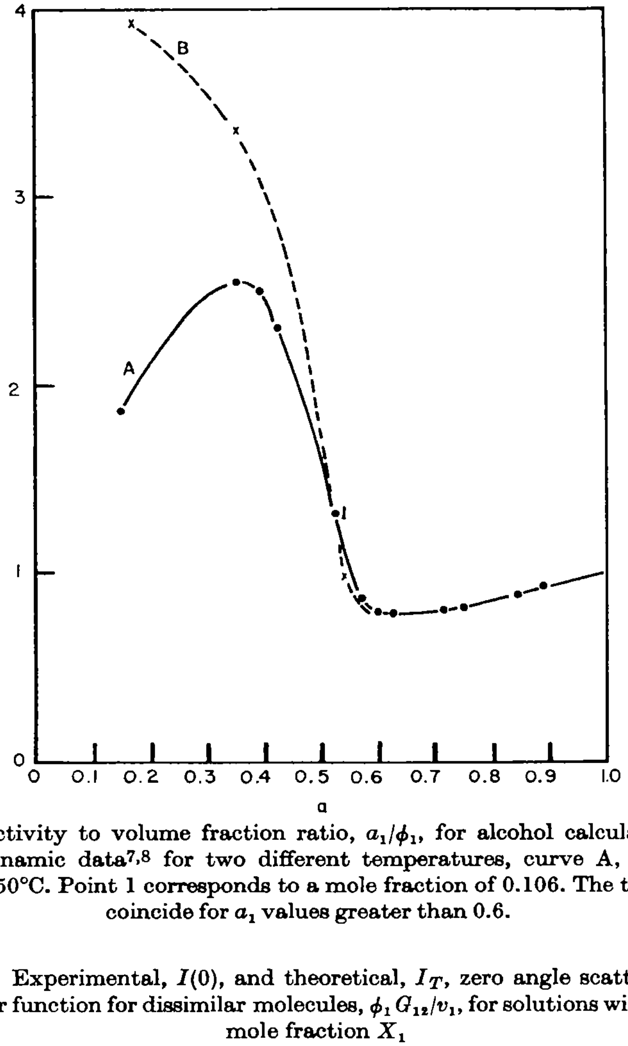

Fig. 2. Activity to volume fraction ratio, a_1/ϕ_1, for alcohol calculated from thermodynamic data[7,8] for two different temperatures, curve A, 25°C and curve B, 50°C. Point 1 corresponds to a mole fraction of 0.106. The two curves coincide for a_1 values greater than 0.6.

TABLE 1 Experimental, $I(0)$, and theoretical, I_T, zero angle scattering and the cluster function for dissimilar molecules, $\phi_1 G_{12}/v_1$, for solutions with alcohol mole fraction X_1

X_1	$I(0)$	I_T	$\frac{I(0)-I_T}{I_T}100$	$\frac{\phi_1 G_{12}}{v_1}$
0.06	1.87	1.92	—2.6%	-0.55
0.085	3.75	3.60	4.2	-1.45
0.11	6.10	5.82	4.8	-2.72
0.2	6.00	6.13	-2.1	-3.06
0.3	4.22	4.28	-1.4	-2.41
0.4	2.70	2.61	3.4	-1.42

any case it seems reasonable to conclude that the agreement between x-ray results and the Kirkwood and Buff theory is within the error limits imposed by the existing data.

The Zimm cluster integrals, Fig. 3, have their largest values for solutions with alcohol mole fraction, X_1, in the range between 0.1 and 0.2. In the same region the function $\phi_1 G_{12}/v_1$ has its minimum value, Table 1. Thus it appears that in this concentration range the two phases have a tendency to cluster into groups of like molecules.

The density fluctuations resulting from the clustering are no doubt the cause of the observed small angle scattering. It is of interest to note that ultrasonic absorption also peaks in the same region, $X_1 = 0.12$. The exact cause of the maximum in the ultrasonic absorption is not known; however, there is little doubt that some type of relaxation process connected with

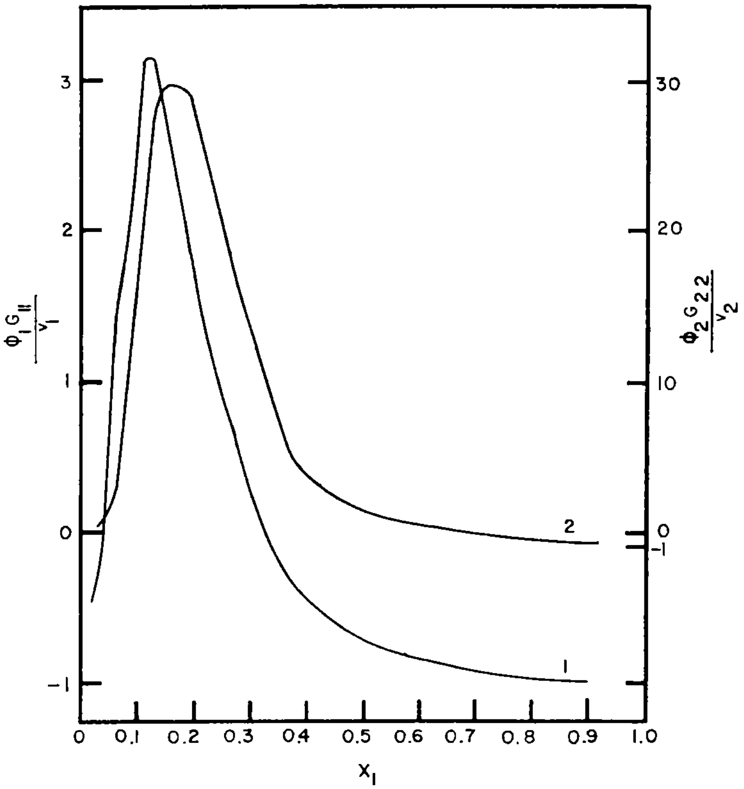

Fig. 3. Zimm cluster integrals for the two components, curve 1 for *t*-butanol and 2 for water plotted as a function of alcohol mole fraction, X_1.

molecular associations plays an essential role. One is led to suspect that both the zero angle x-ray scattering and the ultrasonic absorption are closely related to a common structure formation in the solution. An interesting complication arises when we consider the temperature dependence of the two phenomena. The small angle scattering curves obtained at three different temperatures are shown in Fig. 4. It is seen that the scattering increases quite sharply with a temperature rise. Ultrasonic absorption measurements have been performed only at 27°C; however, there are strong indications [12,13] that the absorption would increase with decreasing temperature. This difference in the temperature dependence points out the fact that the zero angle scattering and the ultrasonic absorption have quite different causation. The x-ray scattering is a measure of density fluctuations in the solutions and will be large if the clustering gives rise to large density fluctuations. The ultrasonic absorption process is a consequence of energy transfer to the solution. This transfer can be large if structural changes in the molecular associations can be accomplished by the ultrasonic wave. Thus a situation could arise where one feature of

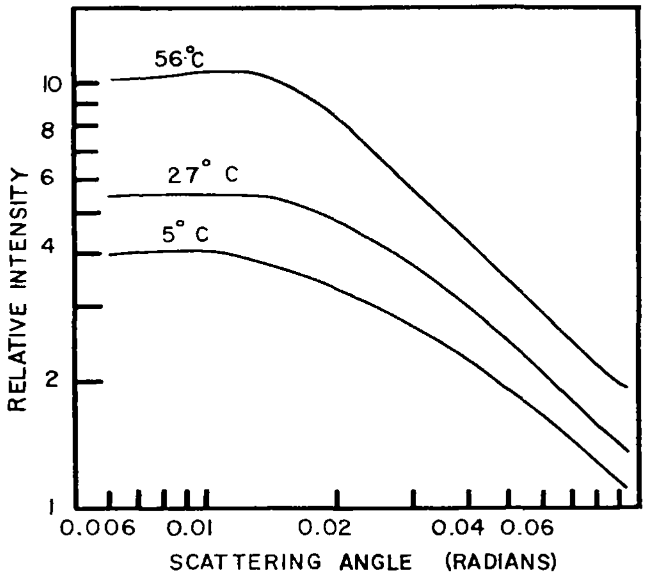

Fig. 4. Scattering curves obtained from 0.11 alcohol mole fraction solution for three different temperatures.

the cluster were all important to the ultrasonic absorption but contributes little to the x-ray scattering.

There is not sufficient thermodynamic data available to determine the complete temperature dependence of I_T. The only thermodynamic results that have been reported[8] are for temperatures of 25°, 50° and 75°C. Unfortunately there are only a few data points in the concentration range of primary interest here. The calculated activity data are shown in Fig. 2. The two curves shown are almost identical for activity values greater than 0.6, which corresponds to the region in X_1 greater than about 0.3. Primary interest is near point 1 on the curves which corresponds to $X_1 = 0.106$. The negative slope of this graph, which is related to G_{11} by Eq. (3) is clearly greater at 50°C than 25°C. All other temperature dependent factors in Eq. (2) also increase, which make it likely that the temperature dependence of the observed zero angle scattering is in agreement with the Kirkwood and Buff theory.

Additional information concerning the scattering structure is in principle contained in the angular dependence of the experimental scattering curve. Unfortunately there is, at the present time, no theory that can be used to determine perfectly general parameters from the angular dependence of the data. The usual procedure followed is to adopt some suitable model for which theoretical parameters can be determined. The validity of such an approach is of course limited by the relevancy of the assumption involved. The cluster functions discussed above indicate that both the alcohol and water molecules tend to cluster. One might assume that the two phases are distributed in a somewhat arbitrary manner. This model can be dealt with theoretically if we assume that the density of each cluster is perfectly uniform. This neglect of fluctuations of density on an atomic level is justified as long as the small angle scattering from the solution is much greater than the scattering from the pure components. In the case at hand this is not true. Attempts to make corrections in terms of the pure component scattering can not be justified in this study because the arrangement of molecules in the binary solution is likely to be quite different than what is present in the pure components. A very rough estimate of the cluster size can be obtained from the angle at which the scattering curve breaks from the horizontal region. "The rule of thumb" would lead one to expect this transition in a region where the product of h times cluster size is roughly unity, where $h = 4\pi \sin \theta/\lambda$. Thus the 0.11 mole fraction solution is likely to contain clusters of at least 20 angstroms in size.

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