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Determination of coherently forward scattered intensity from SANS measurements of binary liquids mixtures without resorting to structural models

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A method for the determination of the coherently forward scattered intensities from small angle neutron scattering (SANS) measurements without resorting to structure describing model functions was applied for diol-water mixtures. The coherently forward scattered intensities were determined by subtracting the incoherent scattering of backgound solutions from the scattering of the samples. The such determined coherently forward scattered intensities were used for the calculation of the Kirkwood-Buff integrals.

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1. Introduction

In the structural characterization of binary liquid mixtures, pair correlation functions, (g_{ij}), play an important role. Kirkwood and Buff developed in 1951 a theory for solutions [1] which relates thermodynamic quantities to the Kirkwood-Buff integral (KBI). The KBI is defined as the integral of the pair correlation function taken over the entire space:

$$G_{ij} = \int_0^\infty \left(g_{ij}(r) - 1\right) 4\pi r^2 dr$$

r being the distance between the centers of molecules i and j.

These integrals can be calculated from thermodynamic data, such as partial molar volumes, isothermal compressibility and the excess Gibbs free energy.

Nishikawa deduced a relationship between the intensity in small angle X-ray scattering and the KBI's and used it for alcohol-water solutions [2,3]. The advantage of this approach is that the zero angle scattered intensity takes the place of the excess Gibbs free energy in the KBI calculation, and this way the determination of the integrals becomes more precise in certain cases.

Almásy et al. adopted this method for SANS instead of SAXS data, relying on the analogy between the two methods [4,5].

SANS scattering curves contain, beside the coherently scattered intensity relating to structural information, an incoherent part mainly due to the incoherent scattering of the hydrogen present in the sample.

In most previous SANS studies the coherently forward scattered intensities were determined by fitting with a model function, which contain the incoherent background as an adjustable parameter [4,5,6,7].

The incoherent part of the scattering can also be determined by measuring background solutions containing suitable amounts of H_2O and D_2O. By subtracting this incoherent background from the scattering of the sample the coherently scattered intensity is calculated. In the present paper we describe the application of this method for studying aqueous solutions of polyfunctional alcohols, 1,2- and 1,ω-pentanediols (PD) and hexanediols (HD). Applying this method is proven to be very advantageous in this case, because no suitable model function is known to describe accurately these systems [8,9]. The Kirkwood-Buff integrals calculated using the coherently forward scattered intensities [10], allowed us to characterize the aggregation of diols in their aqueous solutions in a quantitative way, without resorting to any assumed model in the SANS data analysis.

2. Experimental

The experiments were performed at the SANS instrument “Yellow Submarine” installed at the cold neutron beam line of the Budapest Neutron Centre [11]. The D_2O was of 99.4 % isotopic purity. The alcohols were purchased from Fluka and Aldrich, and were used without further purification. The samples were prepared by weighing the required amounts of diol and water, and, for the background solution measurements, from the corresponding amounts of light and heavy water. The samples were placed in quartz cells of 1 or 2 mm thickness, depending on the transmission, in order to minimize multiple scattering and were put in a sample changer, the temperature of which was regulated with an accuracy of ±0.5°C. The sample to detector distance and the wavelength were chosen in such way, that the forward scattered intensity could be determined with high accuracy.

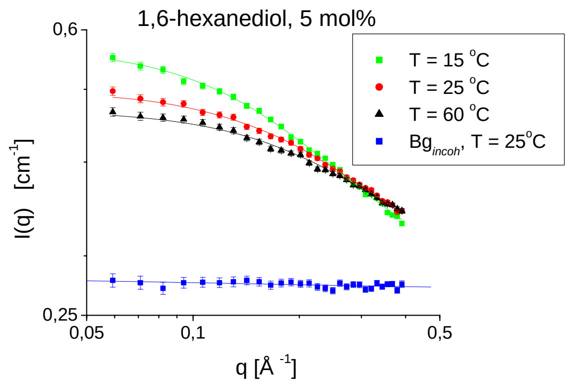

Fig. 1. SANS scattering curves of 5 mol% 16HD solution at three temperatures and the scattering curve of the corresponding background solution at T = 25 °C.

3. Analysis

The common way of analyzing SANS experimental results is the modeling of the sample structure using various theoretical models, and calculating the scattering curves of these model systems. The adjustable parameters of the model can be fitted by minimizing the deviation between the model curve and the measured data points. The validity of the models can be checked by analyzing the consistency of the fitted curves with the experimental ones.

In the case of diol-water mixtures the SANS scattering curves are rather featureless, especially in the case of 1,ω-diols. D'Arrigo et al. tried to characterize the structure of these systems using SANS [8,9]. They applied various model functions but the results obtained were not unambiguous.

For the characterization of diol-water mixtures we used the Kirkwood-Buff formalism. The utilization of a model function describing the structure was not needed.

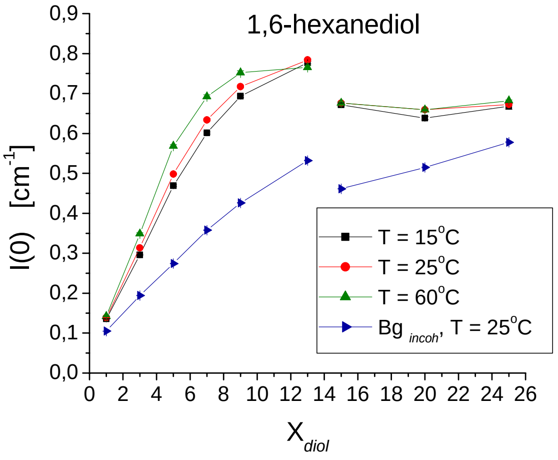

Fig. 2. SANS forward scattered intensities of 16HD and of the corresponding background solutions.

The integrals can be calculated using the coherently forward scattered intensities from SANS measurements along with partial molar volumes and isothermal compressibility data. For these calculations a precise determination of the coherently forward scattered intensity, $I_{coh}(0)$, is needed. For this purpose a so called background solution was prepared for each concentration by mixing of light and deuterated water. The compositions were chosen in such way that the background solutions give the same incoherent scattering as the sample. The sum of the incoherent scattering cross sections of all nuclei present in the sample solution was made equal to the sum of the incoherent scattering cross sections of all the hydrogen, deuterium and oxygen nuclei contained in the same volume of the background solution. The exact deuterium content of heavy water was properly taken into account. The background solutions, prepared in the way described above, were measured under the same conditions as the samples. For saving measuring time they were measured only at 25 °C. The incoherently scattered intensities were corrected for the difference caused by the volume expansion due to the temperature change. The volume expansion was found to be maximum 1% for the studied diol-D_2O mixtures. All measurements were corrected for transmission and scattering from empty cell and scaled to absolute units using the scattering of a light water sample of 1mm thickness.

The scattered intensity of the sample was extrapolated to zero angles by fitting with a model function which describes accurately the low scattering vector part of the curve (usually the Ornstein-Zernike model). The scattering from the background solution was extrapolated using a linear fit supposing homogeneous incoherent scattering. The fitted small angle scattering curves for 5 mol% 1,6-hexanediol (16HD) solution at three temperatures, and the fitted curve for the background solution are shown in Fig. 1. The extrapolated forward scattered intensities are plotted in Fig. 2 for 16HD. The breaking which can be seen on the curves is due to the change in the sample thickness. For samples with less than 13 mol% diol content quartz cells of 2 mm thickness were used. Above this concentration, in order to avoid multiple scattering, we used 1 mm cells. For the background solutions the same cell thicknesses were used as for the corresponding sample solutions. By subtracting the extrapolated incoherent backgrounds from the extrapolated forward scattered intensities of the samples the coherently scattered intensities were determined. The errors of the $I_{coh}(0)$ were calculated applying error propagation to the errors of the fits and assuming 10% uncertainty of the absolute calibration (Fig. 3.). The method described above was applied for all the studied diol-D_2O systems.

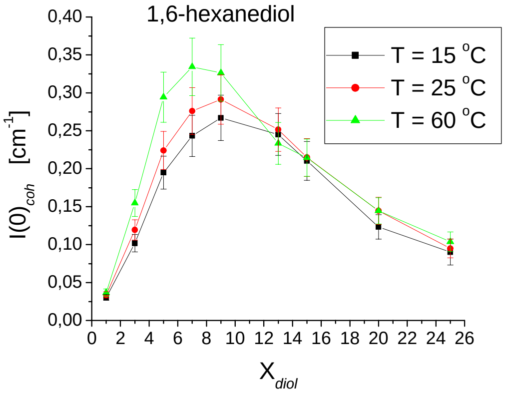

Fig. 3. Coherently forward scattered intensities for 16HD at three temperatures.

The so determined $I_{coh}(0)$ were used for the calculation of the KBI's for 12HD, 16HD, 12PD and 15PD [10]. We found that only for 12HD micelle like aggregates can occur, supporting the results obtained by D'Arrigo et al. and Hajji et al. [9,12]. For the other three systems a weaker diol-diol interaction was found. The excess numbers, which characterize the local environment of a molecule in a mixture, were calculated. The excess numbers of the same type of molecules in 16HD, 12PD and 15PD solutions vary from 0.4 to 3, and are between 1 and 29 in the 12HD-D_2O mixtures [10].

4. Conclusions

The present work demonstrates a method to calculate Kirkwood-Buff integrals from SANS data in cases where no suitable model functions are available that describe the experimental scattering curves. This could be achieved by preparing so called background solutions, which can be used for the subtraction of the incoherent part of the scattered intensity. The method was applied for the characterization of the aqueous solutions of four representative diols with the use of the Kirkwood-Buff formalism.

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