Scattering vector dependence of the small-angle scattering from mixtures of hydrogenated and deuterated organic solvents

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In connection with a contrast variation small angle neutron scattering (SANS) study of water-in-oil microemulsions, mixtures of hydrogenated and deuterated *n*-decane and similar mixtures of iso-octane have been measured as backgrounds. For the pure deuterated and hydrogenated solvents the spectra were flat but for all the mixtures the large molecular size of the alkanes give rise to a scattering vector dependence in the small angle scattering region. An explanation of this can be given based on the scattering contributions which have been identified for mixtures of water. The intensity is proportional to $x(x-1)$ where x is the volume fraction of deuterated molecules. Using the analogy to scattering from polymer blends of hydrogenated and deuterated chains, the scattering spectra are analysed using the model for random gaussian coils. For the solvent mixtures investigated in the present study, the radius of gyration was determined to be 3.8 Å for decane and 2.9 Å for iso-octane, independent of the fraction of deuterated molecules.

1. Introduction

Water is the most frequently used solvent for studies of soft materials. Water furthermore has the advantage of giving rise to a flat spectrum in the small angle scattering (SAS) region and is often used for normalization of detector efficiency and to convert the data to an absolute scale. In small angle neutron scattering (SANS), mixtures of D_2O and H_2O are widely used in contrast variation studies. Due to the exchange of H and D in such mixtures the coherent entity is almost point-like, and no scattering vector dependence is observed in the SAS region. The scattering vector qi s defined as $q = 4\pi \sin(\theta)/\lambda$, where θ is half the scattering angle and λ is the wave length. The absense of a q dependence has the consequence that the scattering from a mixture of D_2O and H_2O is simply a linear combination of the scattering spectra from pure D_2O and pure H_2O.

In connection with a contrast variation SANS study on Sodium di(2-ethyl hexyl) sulfosuccinate (AOT) microemulsion droplets, mixtures of hydrogenated and protonated decane and similar mixtures of iso-octane have been measured. The data showed that for the alkane mixtures the situation is less simple than for water. For the pure deuterated (*d*) and hydrogenated (*h*) solvents the spectra are still flat, but for all the mixtures a scattering vector dependence was observed. This was somewhat unexpected as we usually presume that solvent backgrounds are flat.

In the first analysis we assumed that the q dependence was negligible and that the backgrounds could simply be estimated as a linear combination of the scattering from the pure *h* and *d* alkanes. But when doing a careful analysis of the microemulsion spectra it became evident that the information we aimed at extracting on size distributions and shape fluctuations of the droplets was strongly influenced by the q dependent backgrounds. For this reason we decided to perform a more thorough study of the scattering from alkane mixtures.

The reasons that the small angle scattering of the alkane mixtures, contrary to water, is q dependent are that the alkane molecules are relatively large and that there is no exchange of H and D as there is for water. In the following the different contributions to the scattering from the alkane mixtures will be identified and it will be shown how the analogy to polymer blends of hydrogenated and deuterated chains allows us to make a more quantitative analysis of the SANS spectra from alkane mixtures.

2. Materials and experiments

The SANS measurements were performed at the SANS facility at Risø National Laboratory (Mortensen, 1994, Pedersen, 1995). Using different combinations of neutron wavelengths and sample-to-detector distances, a q range from 0.02 Å^{-1} to 0.26 Å^{-1} was covered. All measurements were performed at room temperature. The SANS data were azimuthally averaged and normalized by the standard approach by division of the scattering spectrum of H_2O as described by Jacrot (Jacrot,1976). Resolution effects due to the spread in wavelengths of the neutrons and the finite collimation were neglected in the present work due to the relatively weak q dependence of the spectrum (Pedersen, Posselt & Mortensen, 1990). The samples were contained in 1 mm Hellma quarts cells. We used deuterated iso-octane and *n*-decane from Cambridge Laboratories. The decane has a purity of *d* at 99% and the iso-octane has a purity of *d* at 98%.

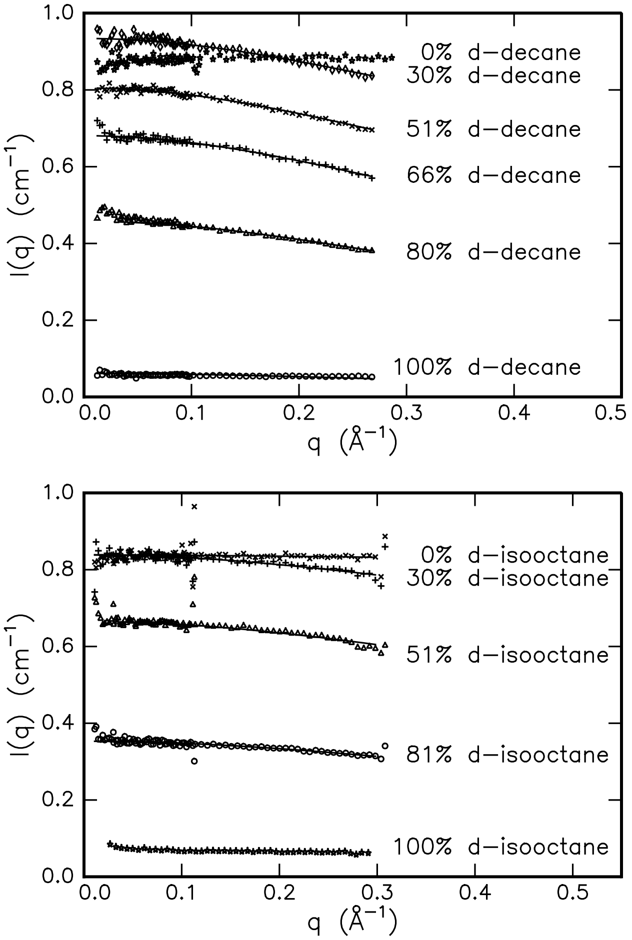

Figure 1
Small angle scattering spectra from mixtures of *h* and *d* decane (top) and *h* and *d* iso-octane (bottom). The results of fitting a Debye function to the scattering data are also shown.

3. Measurements and analysis

In Fig. 1 the scattering spectra obtained from the decane and iso-octane samples are shown. While the spectra from the pure deuterated or protonated alkanes are flat, it is clearly seen that all the mixtures of deuterated and protonated alkanes display a *q* dependence of the small angle scattering.

3.1. Analysis of $I(0)$ data

A simple explanation of the scattering intensity at zero angle from mixtures of D_2O and H_2O is given by J.P. Cotton (Cotton, 1991). The explanation is easily generalised to mixtures of deuterated and protonated alkanes. The scattering as a function of the volume fraction *x* of deuterated solvent is described by:

$$\begin{aligned} \sigma &= \frac{1}{v}(xb_{D,inc}^2 + (1-x)b_{H,inc}^2) \\ &+ \frac{1}{v^2}(xb_{D,coh} + (1-x)b_{H,coh})^2 k_B T \chi_T \\ &+ x(1-x)\,\frac{1}{v}\,(b_{H,coh} - b_{D,coh})^2, \end{aligned} \quad (1)$$

where *v* is the molecular volume, *b* is the scattering length and χ_T is the isothermal compressibility.

The first term is from the incoherent scattering and the second and third term are from the coherent scattering. The second term is the structure factor of the liquid and describes the scattering due to density fluctuations in the liquid. It is proportional to the isothermal compressibility of the liquid. The third term is due to compositional fluctuations and is proportional to $x(x-1)$. Note that this term corresponds to Laue scattering for alloy crystals.

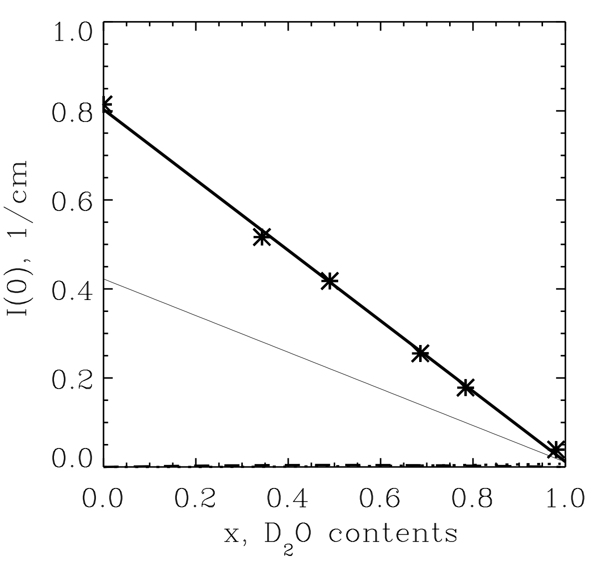

Figure 2
The scattering intensity at zero angle as a function of the D_2O contents *x* in a mixture of H_2O and D_2O. Experimental points, Composition fluctuation (bold dashed line), isothermal compressibility (thin dashed line), calculated background (thin line) and fitted background (bold line) The empirical expression for the incoherent background is based on the fit of a straight line to the experimental points shown in the figure.

For water there is exchange of H and D. For this reason the molecular volume *v* and scattering length *b* used should be for half a H_2O (D_2O) molecule. The three contributions, their sum and the corresponding experimental points are plotted in Fig. 2 for a mixture of H_2O and D_2O.

As seen in the figure the experimental points follows a straight line which lies far above the theoretical prediction for $I(0)$. We believe that the reason for the difference is that the experimental incoherent background also has contributions from multiple scattering and thermalization effects which are not included in the theoretical expression.

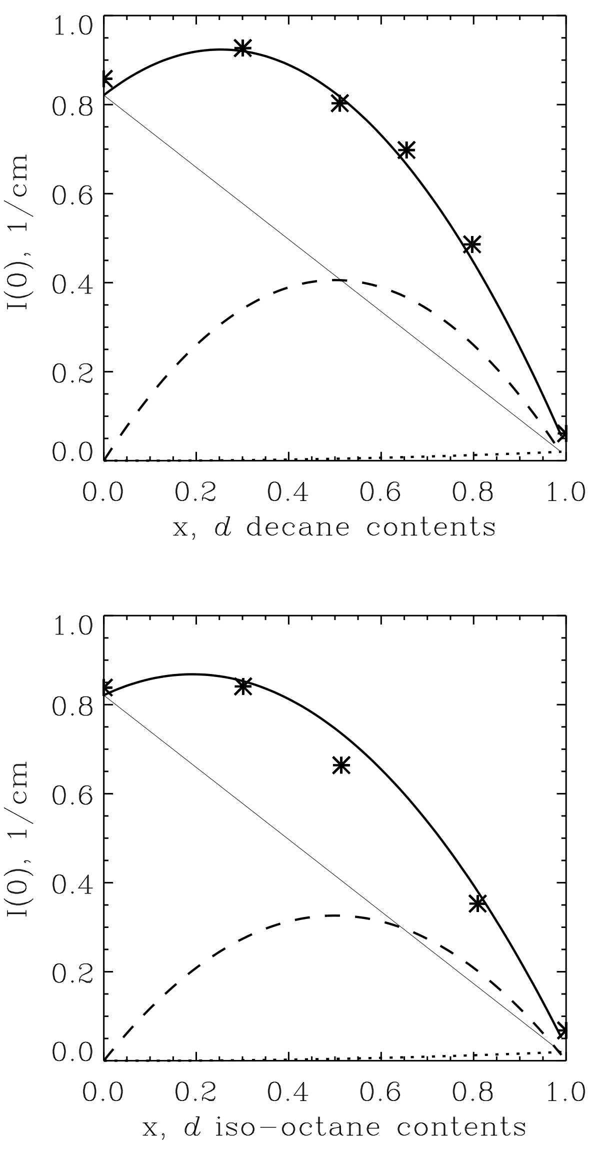

Figure 3
The scattering intensity at zero angle as a function of the *d* contents *x* in mixtures of *h* and *d* decane (top) and *h* and *d* iso-octane (bottom). Experimental points, Composition fluctuation (bold dashed line), isothermal compressibility (thin dashed line), empirical background (thin line) and calculated $I(0)$ (bold line)

For the analysis of the $I(0)$ data for the alkane solutions we decided to use an empirical description of the incoherent background, which is based on the measurements of the H_2O/D_2O mixtures. The coherent contributions are negligible for water and it is therefore assumed that the experimental $I(0)$ data shown in Fig. 2 are basically the incoherent background as a function of the H_2O contents. Since only the hydrogen give rise to incoherent background for both water and alkane, a good estimate of the incoherent background for the alkane mixtures can be obtained by scaling the measurements for water with the difference in hydrogen density ν_H between water and alkane. We did this by fitting a straight line to the experimental points from the water mixtures and multiplying the slope of this line with $\nu_{H,alkane}/\nu_{H,water}$. The estimates of the incoherent backgrounds obtained by this procedure are plotted in Fig. 3. The two coherent contributions are calculated according to expression (1), and added to the empirically determined incoherent background. We used the following table values for the isothermal compressibilities (Weast, 1982): $\chi_{T,decane} = 0.001163\,\mathrm{cm}^3/\mathrm{J}$ and $\chi_{T,iso-octane} = 0.001198\,\mathrm{cm}^3/\mathrm{J}$[1]. The terms, their sum and the experimental points are plotted in Fig. 3. There is a very good agreement between the experimental values for $I(0)$ and the calculated ones.

3.2. Analysis of $I(q)$ data

A simple analysis of the data in the full q-range can be carried out by regarding the alkane mixtures as a polymer blend. For a mixture of fully deuterated and fully protonated polymers and assuming incompressibility of the blend it can be shown that the coherent scattering is given by (see e.g. King et al, 1985):

$$I(q) = (b_H - b_D)^2\, x(1-x)\frac{1}{v}S_s(q), \tag{2}$$

where the single-chain structure factor $S_s(q)$ is normalised to unity at $q = 0$. This means that the measured small angle scattering from a polymer blend is proportional to the scattering from a single chain and that the best choice for measuring the single chain scattering function is at $x = 0.5$ where there is a maximum of scattering intensity. The Gaussian random coil model is widely used to model the structure of polymers. The small angle scattering from such a coil is given by the Debye function (Debye, 1947):

$$F_D(x) = \frac{2}{x^2}(x - 1 + e^{-x}) \tag{3}$$

where $x = q^2 R_G^2$ and R_G is the radius of gyration.

Following the above considerations we decided to fit the following expression to the experimental data:

$$I(q) = c_1 F_D(x) + c_2, \tag{4}$$

where c_1 and c_2 are, in principle, fitting parameters. We took the prefactor c_1 and the radius of gyration R_G to be fitting parameters. c_1 could in principle be calculated from eq. (2), but was fitted in order to compensate for uncertainties on the absolute scale of the data. The constant c_2 is the incoherent background. We fixed it to the one obtained from the analysis of the $I(0)$ data. The radius of gyration is expected to be the same for all mixtures. Therefore the data obtained for the different mixtures of iso-octane and decane, respectively, can be fitted simultaneously with one common radius of gyration but separate scale parameters (c_1) and values for the backgrounds (c_2). The result of the fit is shown with the experimental data in Fig. 1. We obtained a radius of gyration of 3.8 Å for the decane and 2.9 Å for the iso-octane.

These values should be compared to the radii of gyration that can be calculated directly from the molecular structure of decane and iso-octane. We calculate the radius of gyration of a scattering object as:

$$R_g = \sqrt{\frac{\sum_i b_i(\mathbf{r_i} - \mathbf{R})^2}{B}}, \tag{5}$$

where b_i is the scattering length of the i'th atom, $\mathbf{r_i}$ is the position of the i'th atom, $\mathbf{R} = \sum_i b_i\mathbf{r_i}/B$ is the center of mass of the molecule and B is the total scattering length of the molecule. We take the molecules as having a regular structure on a diamond lattice with bond angles of 109.5°. The C-C bond length was taken as 1.54 Å, whereas the hydrogen atoms were displaced along the bonds to a distance of 1.11 Å (March, 1985) from the C atom to which they bond. In the calculation the scattering length of D was used for the hydrogens and the decane molecule was taken as being straight. We obtain $R_{g,theo}$=4.0 Å for decane and $R_{g,theo}$=2.6 Å for iso-octane. These are in reasonable agreement with the observed values.

4. Conclusion

The relatively large size of the decane and iso-octane molecules results in a q dependence in mixtures of heavy and light alkanes. For water there is exchange of H and D and the coherent entity is therefore almost point-like, and thus no q dependence is observed in the small angle scattering region.

The coherent scattering intensity at zero angle can be analysed using a simple model. The scattering is descibed as the sum of coherent and incoherent scattering. We used an empirical approach for describing for the incoherent background based on the observed scattering from water mixtures. The coherent background is a sum of scattering due to density fluctuations, which is proportional to the isothermal compressibility, and scattering due to composition fluctuations, which is proportional to $x(x-1)$, where x is the volume fraction of the deuterated alkane. For the studied alkane mixtures the term due to composition fluctuations is by far the dominating of the two coherent terms.

References

Cotton, J. P. (1991). *Neutron, X-ray and Light Scattering: Introduction to an Investigative Tool for Colloid and Polymeric Systems'*, edited by P. Lindner and T. Zemb, pp. 19-21. Amsterdam: North Holland.

Debye, F. (1947). *J. Phys. Colloid. Chem.* **51**, 18-32.

Jacrot, B. (1976). *Rep. Prog. Phys.* **39**, 911-953

King, J. S., Boyer, W., Wignall, G. D. & Ullman, R. (1985). *Macromolecules* **518**, 709-718.

March, J. (1985). *Advanced Organic Chemistry*, pp. 19, New York: Wiley & Sons, Inc.

Mortensen, K. (1994). *Nukleonika* **39(1-2)**, 1659-184.

Pedersen, J.S. (1995). *Modern Aspects of Small Angle Scattering* Edited by H. Brumberger, pp. 57-91. Dordrecht: Kluwer Academic Publishers.

Pedersen, J.S., Posselt, D. & Mortensen, K. (1990). *J. Appl. Cryst.* **23**, 321-333.

Weast, R. C. (1982) *Handbook of Physical Chemistry*, pp. F-14-18. Florida: CRC press, Inc.

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[1] The value used for iso-octane is the value stated for *n*-octane. We have not succeeded in finding the isothermal compressibility of iso-octane.

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