

Small-angle neutron scattering study of aqueous solutions of pentanediol and hexanediol

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Aqueous solutions of 1,2-pentanediol, 1,5-pentanediol, 1,2-hexanediol and 1,6-hexanediol have been studied by small-angle neutron scattering over a wide range of concentrations and temperatures. The structure of the solutions on the mesoscopic length scale, corresponding to the intermolecular distances, was analysed with the help of the Kirkwood–Buff formalism. 1,2-Hexanediol solutions exhibited a strong attractive diol–diol interaction, a weak diol–diol attraction was found for 1,6-hexanediol and 1,2-pentanediol, and an extremely weak diol–diol attraction was found in 1,5-pentanediol solutions. The general tendencies are the following: aggregation is stronger as the length of the hydrophobic hydrocarbon chain increases and the 1,2-diols exhibit much stronger attraction than the 1, ω -diols. The temperature dependence of the aggregation is weak for the 1,2-diols but strong for the 1, ω -diols, indicating in the latter case the hydrophobic character of the interaction.

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1. Introduction

Investigations of aqueous solutions of hydroxylic compounds are of great interest as they represent convenient model systems displaying molecular self-organization induced by competing solute–solute hydrogen bonding and hydrophobic interactions. 1,2- and 1, ω -alkanediols are amphiphiles with distinct hydrophilic and hydrophobic parts in their molecules. Therefore they often behave as non-ionic surfactants in their aqueous solutions. Numerous structural and thermodynamic investigations indicate the aggregation tendency of diol molecules in water. In 1962, Kato made the first comprehensive study of aqueous diol solutions using physico-chemical methods. He found critical micelle concentrations (CMCs) for all the diols studied with at least one OH group in a terminal position, among them 1,5-pentanediol and 1,6-hexanediol (Kato, 1962). The presence of a CMC indicated the micellar structure of these solutions. In subsequent studies, this assumption was the starting point in analysing the experimental results. Thus, in light-scattering studies of 1,2-hexanediol solutions, spherical micelles with an average aggregation number of 20 were detected (Hajji *et al.*, 1989). Later studies suggested a more complex picture. Refractivity measurements on 1, ω -diol solutions revealed multiple critical concentrations, indicating that several structural rearrangements take place upon increasing the diol concentration (Durand & Coudert, 1978).

In small-angle neutron scattering (SANS) studies of aqueous solutions of several diols and triols by D'Arrigo and co-workers (D'Arrigo *et al.*, 2000, 2003), the experimental data were analysed considering various models of interacting micelles. 1,2-Pentanediol and 1,2-hexanediol were suggested to form spherical hydrated micelle-like aggregates with attractive interaction between them. In a previous SANS study we have shown, using the example of aqueous 1,7-heptanediol, that these systems can be well described by assuming statistical concentration fluctuations (Almásy *et al.*, 2005).

Results of all previous studies indicate that diol molecules aggregate in aqueous solutions, but no definitive picture of the form of this aggregation could be established until now.

In this work we investigated the structure of aqueous solutions of four representative diols aiming to find a relation between the molecular structure of the solute and the aggregation tendencies in their aqueous solutions. Small-angle neutron scattering has been employed and the experimental data were analysed using the Kirkwood–Buff formalism, giving model-free, quantitative characteristics of the interactions between the various types of molecules.

2. Experimental

The SANS experiments were carried out at the instruments Yellow Submarine at Budapest Neutron Centre, Hungary (Rosta, 2002), and KWS2 at Forschungszentrum Jülich, Germany. All samples were measured over the q range 0.08–0.5 Å^{−1}, where q is the magnitude of the scattering vector [$q = (4\pi/\lambda) \sin \theta$; λ is the neutron wavelength and 2θ is the scattering angle]. The samples were prepared by weighing from diols purchased from the companies Fluka and Aldrich with purity above 95% and from D₂O of purity 99.44 at.%. The diols were used without further purification. The samples were placed in 1 or 2 mm thick quartz cells, and were thermostated with an accuracy of ± 0.5 K. For each sample a buffer solution having identical incoherent scattering with that of the sample was prepared by mixing the required amounts of light and heavy water. Corrections were made for scattering from the empty cell, room background and transmission. Absolute scale calibration was performed using the incoherent scattering of a 1 mm thick light water sample.

3. Results and discussion

Solutions of 1,2-pentanediol (12PD), 1,5-pentanediol (15PD), 1,2-hexanediol (12HD) and 1,6-hexanediol (16HD) in heavy water were measured over the concentration range 0.5–25 mol% at the temperatures 288, 298 and 333 K. Enhanced small-angle scattering was observed for each of the studied samples. The scattering curves of 12HD and 16HD solutions are displayed in Fig. 1. The increase of the

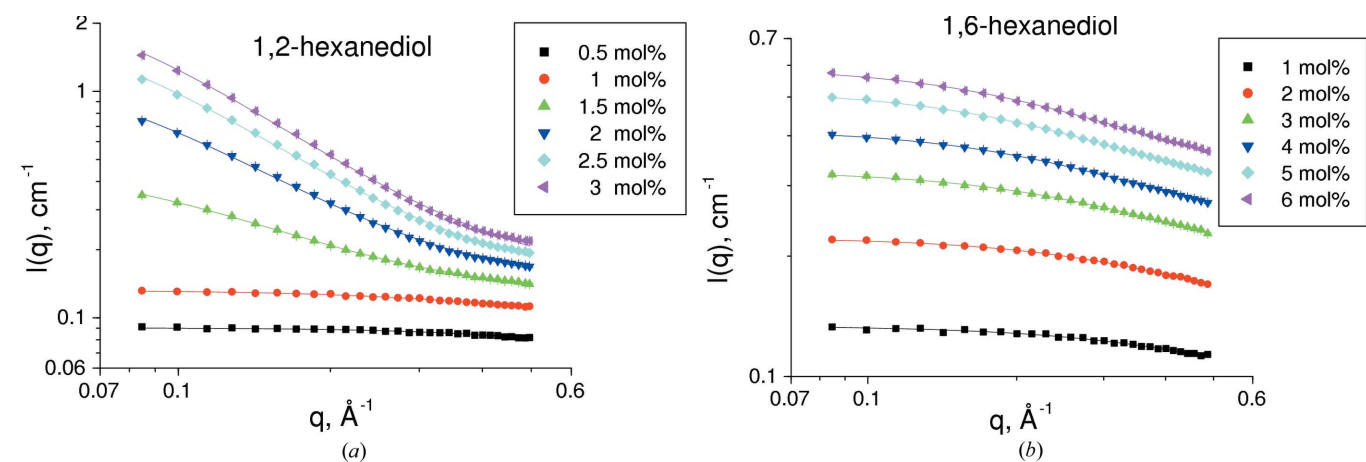


Figure 1
SANS curves for solutions of 1,2-hexanediol (a) and 1,6-hexanediol (b) in D₂O at 298 K.

Table 1
Coherent forward scattering intensities for solutions of 12PD, 15PD, 12HD and 16HD in D₂O.

X_{diol} is the diol mole fraction.

X_{diol}	288 K	298 K	333 K
1,2-pentanediol			
0.02	0.043 ± 0.005	0.061 ± 0.008	0.047 ± 0.005
0.03	0.061 ± 0.007	0.109 ± 0.012	0.118 ± 0.014
0.05	0.167 ± 0.019	0.204 ± 0.023	0.264 ± 0.030
0.08	0.352 ± 0.038	0.371 ± 0.040	0.369 ± 0.102
0.1	0.368 ± 0.039	0.376 ± 0.040	0.348 ± 0.037
0.15	0.240 ± 0.027	0.240 ± 0.027	0.212 ± 0.024
0.2	0.136 ± 0.016	0.137 ± 0.016	0.117 ± 0.014
0.25	0.101 ± 0.013	0.095 ± 0.013	0.074 ± 0.012
0.3	0.095 ± 0.012	0.092 ± 0.012	0.067 ± 0.010
1,5-pentanediol			
0.02	0.034 ± 0.004	0.037 ± 0.004	0.045 ± 0.005
0.03	0.051 ± 0.006	0.055 ± 0.006	0.069 ± 0.008
0.04	0.064 ± 0.007	0.070 ± 0.008	0.089 ± 0.010
0.05	0.068 ± 0.008	0.076 ± 0.008	0.098 ± 0.011
0.07	0.084 ± 0.009	0.092 ± 0.010	0.114 ± 0.013
0.08	0.098 ± 0.012	0.107 ± 0.013	0.126 ± 0.015
0.1	0.101 ± 0.012	0.110 ± 0.013	0.126 ± 0.016
0.15	0.103 ± 0.014	0.102 ± 0.013	0.101 ± 0.013
1,2-hexanediol			
0.005	0.02 ± 0.02	0.03 ± 0.01	0.03 ± 0.01
0.01	0.03 ± 0.01	0.04 ± 0.01	0.07 ± 0.01
0.015	0.16 ± 0.02	0.34 ± 0.04	0.52 ± 0.06
0.02	0.81 ± 0.09	1.20 ± 0.13	1.25 ± 0.14
0.025	1.76 ± 0.19	2.30 ± 0.26	2.16 ± 0.24
0.03	2.36 ± 0.26	2.76 ± 0.30	2.49 ± 0.27
0.05	2.55 ± 0.27	2.64 ± 0.28	2.22 ± 0.24
0.025	1.76 ± 0.19	2.30 ± 0.26	2.16 ± 0.24
0.07	2.10 ± 0.22	2.11 ± 0.22	1.81 ± 0.19
0.08	1.96 ± 0.20	1.96 ± 0.20	1.74 ± 0.18
0.09	1.48 ± 0.15	1.48 ± 0.16	1.28 ± 0.14
0.095	1.38 ± 0.14	1.37 ± 0.14	1.17 ± 0.12
0.13	0.51 ± 0.06	0.48 ± 0.05	0.48 ± 0.05
0.15	0.40 ± 0.04	0.37 ± 0.04	0.38 ± 0.04
0.2	0.21 ± 0.02	0.21 ± 0.02	0.19 ± 0.02
0.25	0.12 ± 0.01	0.11 ± 0.01	0.10 ± 0.01
1,6-hexanediol			
0.01	0.031 ± 0.004	0.034 ± 0.004	0.038 ± 0.005
0.02	0.064 ± 0.007	0.075 ± 0.008	0.099 ± 0.011
0.03	0.111 ± 0.013	0.129 ± 0.015	0.171 ± 0.020
0.04	0.157 ± 0.017	0.183 ± 0.019	0.242 ± 0.026
0.05	0.203 ± 0.023	0.236 ± 0.027	0.305 ± 0.035
0.06	0.246 ± 0.026	0.281 ± 0.030	0.347 ± 0.037
0.07	0.251 ± 0.028	0.286 ± 0.032	0.342 ± 0.039
0.09	0.267 ± 0.030	0.291 ± 0.033	0.326 ± 0.037
0.13	0.245 ± 0.028	0.252 ± 0.029	0.233 ± 0.028
0.15	0.210 ± 0.025	0.215 ± 0.025	0.214 ± 0.025
0.2	0.123 ± 0.016	0.145 ± 0.018	0.145 ± 0.017
0.25	0.090 ± 0.017	0.095 ± 0.012	0.104 ± 0.013

intensity at small angles indicates that the mixtures are not homogeneous on the length of tens of ångströms. The scattering is generally more intense for the 1,2-diols than for the 1,ω-diols. This behaviour is expected, since the hydrophobic part of the 1,2-diols is more pronounced and their shape resembles that of typical surfactant molecules. Therefore, micelle-like aggregates may be expected to form in the solutions.

SANS experimental data are usually analysed by comparing or fitting the scattering curves with various model functions. This procedure has been followed by D'Arrigo for analysing the scattering curves for diol solutions (D'Arrigo *et al.*, 2000, 2003). As the scattering curves for these systems are rather featureless, using model functions with more than four parameters was not always reliable (D'Arrigo *et al.*, 2000). Therefore, in the present work we restricted our analysis to the determination of the coherent forward scattering intensity $I_{\text{coh}}(0)$, and made further interpretations using the Kirkwood–Buff formalism (Kirkwood & Buff, 1951).

3.1. Forward scattering intensity

The total forward scattering intensity was determined by extrapolating the measured data using various model functions which

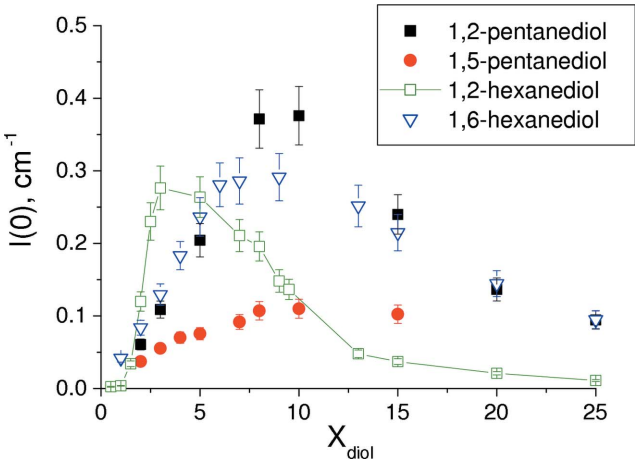


Figure 2
Coherent forward scattering intensities for aqueous solutions of 12PD, 15PD, 12HD and 16HD at 298 K as a function of diol mole fraction (X_{diol}). The intensity values for 12HD solutions are divided by 10.

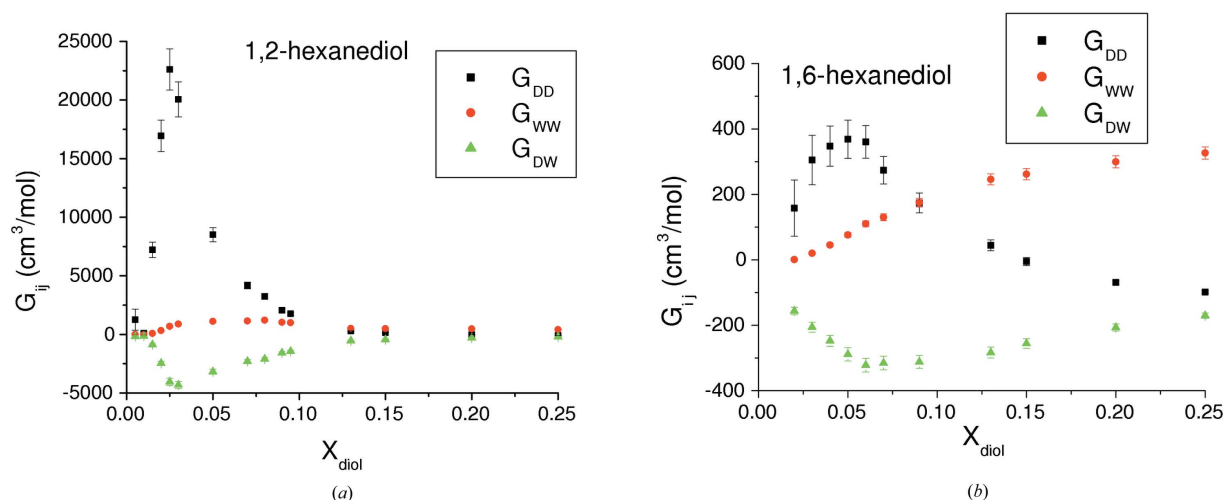


Figure 3
The Kirkwood–Buff integrals for aqueous solutions of 1,2-hexanediol (a) and 1,6-hexanediol (b). $T = 298 \text{ K}$.

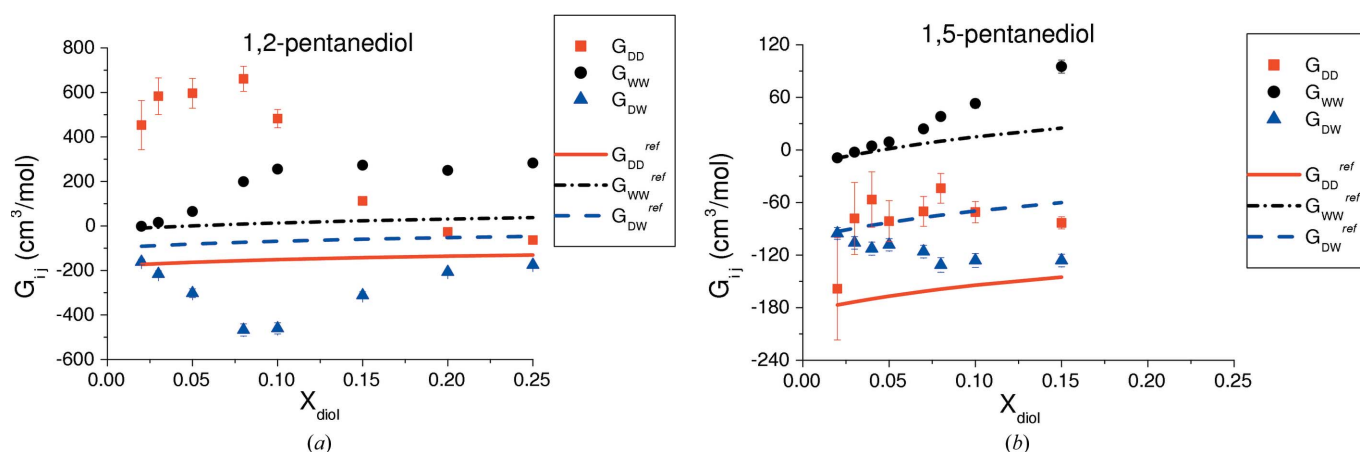


Figure 4
The Kirkwood–Buff integrals for aqueous solutions of 1,2-pentanediol (a) and 1,5-pentanediol (b). The lines are the KBIs assuming ideal mixing of the components (see text). $T = 298 \text{ K}$.

describe accurately the low- q part of the scattering curve – the Ornstein–Zernike structure factor (Almási, Cser & Jancsó, 2002; Yoshida *et al.*, 2005) or a polynomial with even powers. The incoherent background that contributes to the measured signal but does not carry structural information was determined by measuring appropriate mixtures of H_2O and D_2O . The coherent forward scattering intensities, $I_{\text{coh}}(0)$, were calculated by subtracting the measured incoherent scattering of these mixtures from the extrapolated forward scattering of the sample solutions. The accuracy of the $I_{\text{coh}}(0)$ values obtained was estimated by taking into account the errors of the fits and assuming 10% uncertainty in the absolute scale calibration. The values of $I_{\text{coh}}(0)$ obtained are summarized in Table 1 for all the studied mixtures and temperatures, and are displayed as a function of the diol mole fraction (X_{diol}) in Fig. 2.

3.2. Kirkwood–Buff integrals

The Kirkwood–Buff integrals (KBIs) are defined as integrals of the partial pair correlation functions taken over the whole space (Kirkwood & Buff, 1951):

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr, \quad (1)$$

where $g_{ij}(r)$ are correlation functions between species i and j . G_{ij} gives the tendency of molecules j to cluster around a central molecule i and therefore provides information on the solute–solute, solute–solvent and solvent–solvent interactions.

The method of determination of KBIs using small-angle X-ray scattering was introduced by Nishikawa and used extensively for studying aqueous solutions of simple alcohols (Nishikawa, 1986; Nishikawa *et al.*, 1989). Neutron scattering allows the application of this method to a much broader range of binary mixtures, due to the possibility of contrast variation using deuterated species of one of the components.

Kirkwood–Buff integrals can be calculated using the value of the coherent forward scattering intensity, the partial molar volumes of the components and the isothermal compressibility, following the procedures outlined in Almási, Cser & Jancsó (2002) and Almási, Jancsó & Cser (2002). First, the concentration fluctuations $S_{\text{CC}}(0)$ are calculated:

$$S_{\text{CC}}(0) = \frac{I_{\text{coh}}(0) + \rho x_i x_j (b_i - b_j)^2}{\rho [\bar{b}\delta - (b_i - b_j)]^2}, \quad (2)$$

where ρ is the number density of the molecules, b_i and b_j are the sums of the coherent scattering lengths of the nuclei forming the molecules

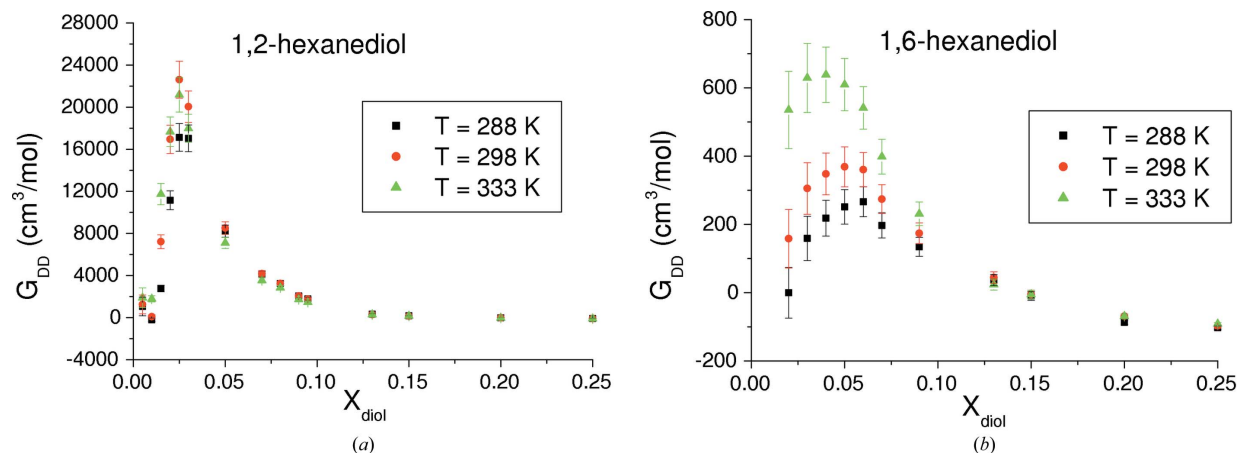


Figure 5
Temperature dependence of G_{DD} in aqueous solutions of 1,2-hexanediol (a) and 1,6-hexanediol (b).

of the two components of the mixture, $\bar{b} = x_i b_i + x_j b_j$, $\delta = (V_i - V_j)/V_{\text{mol}}$ is the dilatation factor, V_i and V_j are the partial molar volumes of the components, and V_{mol} is the molar volume of the mixture.

Then, the Kirkwood–Buff integrals are obtained as follows:

$$G_{ii} = N_A \left[-\frac{1}{x_i \rho} + k_B T \kappa_T + \frac{1}{\rho} \left(\delta - \frac{1}{x_i} \right)^2 S_{CC}(0) \right], \quad (3)$$

$$G_{jj} = N_A \left[-\frac{1}{x_j \rho} + k_B T \kappa_T + \frac{1}{\rho} \left(\delta + \frac{1}{x_j} \right)^2 S_{CC}(0) \right], \quad (4)$$

$$G_{ij} = N_A \left[k_B T \kappa_T + \frac{1}{\rho} \left(\delta - \frac{1}{x_i} \right) \left(\delta + \frac{1}{x_j} \right) S_{CC}(0) \right], \quad (5)$$

where N_A is the Avogadro number and κ_T is the isothermal compressibility.

$I_{\text{coh}}(0)$ was determined as explained in the preceding section, the isothermal compressibility was interpolated from the values of the pure constituents, and the molar volumes and partial molar volumes were calculated from experimental density data. Densities for 1,2-pentanediol solution were as published by Piekarski & Pietrzak

(2005), those for 1,5-pentanediol solutions were as published by Czechowski *et al.* (1988) and densities of hexanediol solutions were measured by us. KBIs obtained for $T = 298$ K are displayed in Figs. 3 and 4.

Inspecting the behaviour of the KBIs, one can see that, in general, solutions of pentanediols behave similarly to solutions of hexanediols, but the absolute values of the integrals for pentanediol solutions are smaller. In three systems, the 12HD, 16HD and 12PD solutions, the values of G_{DD} have a maximum and the values of G_{DW} have a minimum at an intermediate composition (D stands for diol, and W for water). This indicates the clustering of diol molecules in those solutions, like *e.g.* aqueous mono-ol solutions (Nishikawa, 1986; Nishikawa *et al.*, 1989; Almásy, Jancsó & Cser, 2002; Perera *et al.*, 2006). For 15PD solutions, however, there are no well defined extrema of the KBIs and their magnitudes are very small compared to those for the other three systems.

In order to obtain information on the preferential aggregation in the studied mixtures, the Kirkwood–Buff integrals should be compared to so-called reference state KBIs, G_{ij}^{ref} . The lines in Fig. 4 correspond to the behaviour of G_{ij}^{ref} for hypothetical ideal pentanediol solutions, which do not have intermolecular interactions besides the excluded volume repulsion (Shulgin & Ruckenstein, 1999). The experimental KBIs for the 1,5-pentanediol solutions are rather close to these lines for concentrations up to 0.1 molar fraction, showing almost random mixing. At higher concentrations, some water clustering is detected, like the case of 1,6-hexanediol solutions.

Comparing the KBIs of the studied diol–water systems, the general trends are the following: for 1,2-diols a stronger aggregation occurs than for 1, ω -diols, and the aggregation becomes stronger with increasing hydrocarbon chain length. For diols with shorter hydrocarbon chains (propane- and butanediols), no excess small-angle scattering was detected in preliminary measurements, while diols larger than heptanediol are only partially soluble in water.

3.3. Temperature behaviour

The temperature dependence of the Kirkwood–Buff integrals (and thus the aggregation) for the 1, ω -diols is much stronger than that for the 1,2-diols, which is illustrated in Fig. 5 for 12HD and 16HD solutions. The absolute values of the solute–solute KBIs increase with increasing temperature in the lower concentration range, while at higher concentrations the temperature dependence is not significant. Such behaviour indicates a characteristic hydrophobic type of inter-

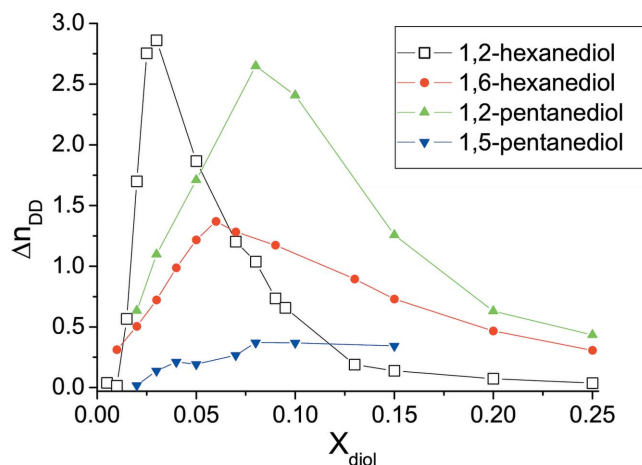


Figure 6
Clustering of diol molecules around a central diol molecule, Δn_{DD} . The excess numbers for 1,2-hexanediol are divided by a factor of 10. $T = 298$ K.

action for the dilute solutions. The maximum of G_{DD} shifts towards lower concentrations with increasing temperature, resembling the lowering of the CMC in micellar systems with increasing temperature.

3.4. Excess coordination numbers

An illustrative parameter that characterizes the local environment of a molecule in the mixture is the excess number of molecules j around a central molecule i (Shulgin & Ruckenstein, 1999):

$$\Delta n_{ij} = (x_i/V_{\text{mol}})(G_{ij} - G_{ij}^{\text{ref}}). \quad (6)$$

These numbers give the excess of the surrounding molecules of a given type in the whole space, following the definition of the Kirkwood–Buff integrals [equation (1)]. These excess numbers are often considered to give the excess not in the whole space, but in a certain correlation volume around the central molecule, which may extend up to a few coordination shells (Marcus, 2002). Such an approximation allows the calculation of the local composition around the central molecule if the excess numbers are sufficiently small. For binary systems with long-range fluctuations, several coordination shells need to be considered and the local concentrations obtained are less reliable.

For a micellar system with uniform distribution of the micelles, a clearer meaning can be attributed to the solute–solute excess numbers, Δn_{DD} – they should be similar to the number of surfactant molecules in one micelle. The excess numbers Δn_{DD} for all the systems studied at 298 K are plotted in Fig. 6. The Δn_{DD} values for aqueous 1,2-hexanediol are divided by a factor of 10 for better visibility. It can be seen that only the 1,2-hexanediol solutions show excess numbers larger than 10.

For 1,6-hexanediol and 1,2-pentanediol the maximum values of Δn_{DD} are between 1 and 3, respectively, and for 1,5-pentanediol solutions the Δn_{DD} values are always smaller than 0.5. These values indicate that only 1,2-hexanediol solutions may be expected to contain micelles, which should consist of dozens of molecules. In 1,6-hexanediol and 1,2-pentanediol solutions there is a definite tendency for self-aggregation. However, the small values of the excess numbers ($\Delta n_{DD} = 1$ –3) show that no micelles exist in these solutions. In the 1,5-pentanediol solutions, the aggregation is extremely weak and the system is close to a random mixture. Such behaviour can be understood considering the molecular structure: in this diol, the central hydrophobic part of the molecule is partially screened by the two terminal OH groups, balancing the hydrophobic and hydrophilic properties of the molecule.

It is remarkable that in the 12HD solutions at low concentrations, when the system may contain micelles, the diol–diol excess numbers are similar to the aggregation numbers found in the previous studies. Thus, for $X_{\text{diol}} = 0.03$ and 0.05 , $\Delta n_{DD} = 29$ and 19 , respectively (Fig. 6). For X_{diol} greater than 0.025 , Hajji *et al.* obtained aggregation number of about 20 (Hajji *et al.*, 1989), and D'Arrigo *et al.* reported aggregation numbers between 8 and 14 for $X_{\text{diol}} = 0.03$, and between 11 and 17 for $X_{\text{diol}} = 0.05$, the differences being due to different micelle models used for fitting the experimental scattering curves (D'Arrigo *et al.*, 2000). A reasonable agreement is seen between these aggregation numbers and the excess numbers of diol molecules obtained in the present study using the Kirkwood–Buff approach, without assuming explicitly micellar or any other kind of structures.

4. Conclusions

Small-angle neutron scattering was used for studying the structure of several aqueous diol solutions on the mesoscopic length scale. Kirkwood–Buff integrals and excess coordination numbers were calculated from the forward scattering intensity and thermodynamic data. Strong diol–diol interactions were observed for 1,2-hexanediol, 1,2-pentanediol and 1,6-hexanediol solutions, while the 1,5-pentanediol solution behaves almost like an ideal mixture with a very weak enhancement of interactions for the similar species.

The 1,2-hexanediol solutions exhibit the strongest diol aggregation, which is by an order of magnitude larger than that in the other systems studied. The excess diol–diol coordination numbers in 1,2-hexanediol solutions are similar to aggregation numbers typical for micellar systems, suggesting that micelles may form in these solutions. The three other systems exhibit weak solute–solute attraction, and no micelles are suggested to be present in these mixtures. In the 1, ω -diol solutions the solute aggregation has a strong temperature dependence indicating the hydrophobic character of the interaction in these systems.

The aggregation tendencies in aqueous solutions of the selected diols were characterized in a quantitative way using Kirkwood–Buff integrals, without resorting to any kind of aggregate models used earlier for analysing SANS data.

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