Solvation Characteristics of a Model Water-Soluble Polymer

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ABSTRACT: The model water-soluble polymer poly(ethylene oxide) was used to investigate solvation characteristics in mixtures of *d*-water (deuterated water) and *d*-alcohols (deuterated alcohols). Three *d*-alcohols have been used: *d*-methanol, *d*-ethanol, and *d*-ethylene glycol. Small angle neutron scattering was used to monitor the solvation properties of poly(ethylene oxide) in the *d*-solvent mixtures. Nonideal solvent mixing was observed throughout. Solvent mixtures were found to be more effective solvating agents than individual solvents. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 3195–3199, 2006

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INTRODUCTION

The class of "water-soluble polymers" covers a wide range of macromolecular systems including biopolymers such as DNA and synthetic polymers such as poly(ethylene oxide) (PEO). Understanding hydrophobic and hydrophilic interactions is crucial for the understanding of phase transitions, micelle formation, and biological function. The simplest water-soluble polymer, PEO, is used here as a template for studying such interactions. A few other investigations also used PEO.[1–3]

The chemical structure of the PEO monomer $—CH_2CH_2O—$ contains an oxygen atom, which attracts water molecules (through hydrogen bonding) making PEO soluble in water. Its homologues, poly(methylene oxide)(PMO) and poly (propylene oxide) (PPO), do not dissolve in water. This is due to the delicate balance between hydrophobic ($—CH_2—$ groups) and hydrophilic forces in PEO. The oxygen–oxygen interdistance along the PEO backbone (4.7 Å) matches that in the structure of water.[4] Oxygen–oxygen interdistance in the water structure is 2.85 Å for the nearest neighbor and 4.7 Å for the next nearest neighbor.[4,5] This balance is not achieved in other members of the homologous series (PMO and PPO). Dissolved PEO macromolecules are surrounded by a water shell whereby water bridges and shields the hydrophobic $—CH_2—$ groups; it effectively "dresses" the PEO chain.

Water-soluble polymers are characterized by a local "solvation" structure and a long-range "clustering" structure. Water molecules interact with the individual monomers and form a hydration (or solvation) sheath around the polymer. In these hydrophilic interactions, solvent–monomer attractive interactions (mostly hydrogen bonding) are stronger than monomer–monomer interactions. On the other hand, clustering interactions take place when monomer–monomer interactions are stronger than monomer–solvent interactions. Hydrophobic groups, for instance, cannot stay dissolved. They seek other hydrophobic groups and stick to them to become shielded

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from contact with water. This results in large clusters.

SMALL-ANGLE NEUTRON SCATTERING

Small-angle neutron scattering (SANS) scans a wide enough size scale to cover both the solvation structure range (nanometer sizes) and the clustering structure range (micrometer sizes). When used on partially deuterated samples, SANS is uniquely sensitive to density and composition fluctuations and can therefore detect slight changes in structure and/or interactions within the sample.

A typical SANS spectrum from 4% (mass-fraction) PEO in *d*-water (deuterated water) is shown in Figure 1. It has two main features: a low-Q part characterizing clustering and a high-Q part characterizing solvation properties. A simple functional form that catches these two features is used throughout to fit the SANS data. The SANS intensity is fit to the form:[3]

$$\mathrm{I}(Q) = A/Q^n + C/\{1 + (QL)^m\} + B \qquad (1)$$

the first term describes Porod scattering from clusters and the second term describes scattering from polymer chains. This second term characterizes the polymer/solvent interactions and therefore the chain solvation characteristics. The two multiplicative factors A and C, the incoherent background B and the two exponents n and m are used as fitting parameters. The final parameter L is a correlation length for the polymer chains. Q is the scattering variable. Fits to the SANS data of Figure 1 gave $L = 16.48 \pm 0.19$ Å, $n = 2.39 \pm 0.06$, and $m = 2.06 \pm 0.02$. C represents the solvation (high-Q) feature. C is used here to monitor basic monomer–solvent interactions. A lower value of C represents a more effective solvation and therefore a less-stressed solvation sheath around polymer chains.

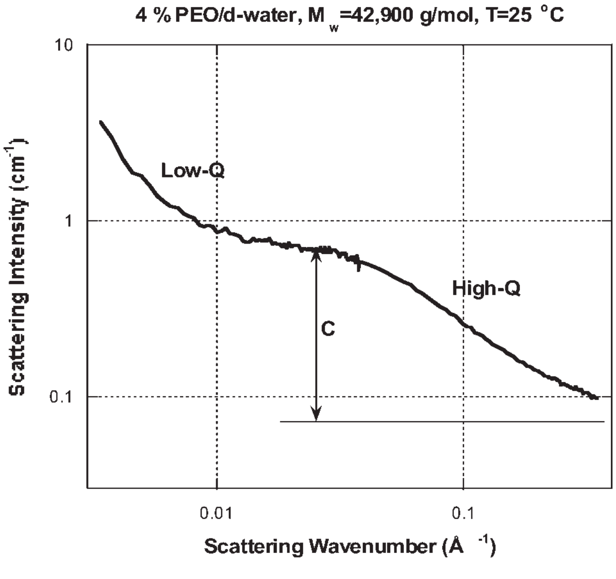

Figure 1. SANS from 4% PEO/*d*-water at 25 °C.

When dissolved in *d*-water, PEO coils are well described as Gaussian chains that follow random walk statistics (the exponent m in eq 1 has a value of about 2). It is noted in passing that the PEO/*d*-water system is characterized by a lower critical solution temperature; i.e., phase separation occurs upon heating.[3] A temperature scan reported previously[3] showed that C and A/Q^n vary in opposite directions when temperature is varied. Clustering (low-Q) and solvation (high-Q) are driven by opposite interactions. Solvation is driven by hydrophilic interactions while clustering is possibly driven by hydrophobic interactions.

PEO IN *d*-WATER/*d*-METHANOL SOLVENT MIXTURES

Our focus here is on the behavior of PEO in mixed solvents (i.e., in the cosolvent effect) and not on temperature effects. We have studied 4% (mass fraction) PEO solutions in mixtures of *d*-water (D_2O) and *d*-methanol (CD_3OD). The 4% PEO/*d*-water solution is amorphous for all temperatures, whereas the 4% PEO/*d*-methanol solution crystallizes for ambient temperatures. SANS data are presented for samples at 50 °C for which no crystallization occurs.

Figure 2 shows variation of the solvation intensity (parameter C in eq 1) for increasing *d*-methanol content. Lower values of C point to more effective solvation. It can be seen that mixed solvents give better solvation than either of the individual solvents.

Given our observations, a question comes to mind: Is PEO conforming to the solvent structure and therefore acting merely as a means to probe that solvent structure or is it changing it? Based on the fact that PEO dissolves in water whereas PMO and PPO do not, one can conclude that PEO does conform to the solvent structure, but it is hard to believe that it is not changing it. For

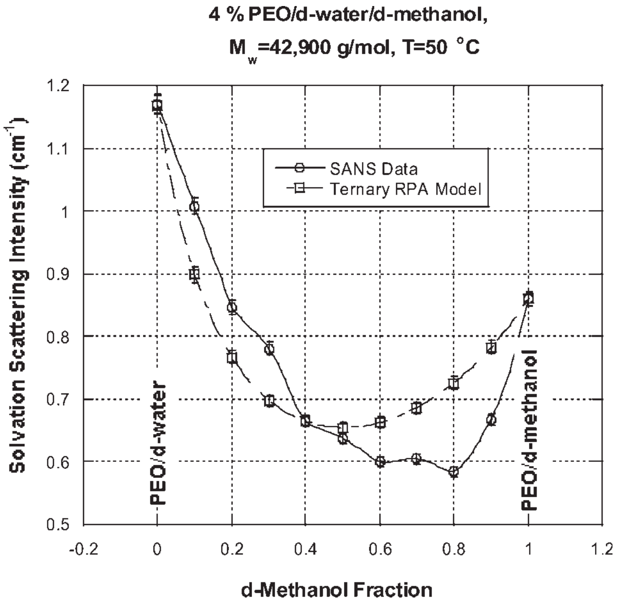

Figure 2. SANS measured solvation intensity (the parameter C in eq 1) and prediction of the ternary mixture RPA model for the 4% PEO in *d*-methanol/*d*-water mixtures. The model was forced to agree with the data at the 0, 40, and 100% *d*-methanol fractions.

example, solvent molecules are less mobile close to polymer chains because of the cage-like structures forming the solvation sheath. In general, the structures of amorphous molecular liquids (and liquid mixtures) are hard to determine because diffraction methods are not effective on noncrystalline systems. Some results using X-ray emission spectroscopy have been applied to water/methanol mixtures whereby specific cage-like structures have been reported.[6]

THE TERNARY RPA MODEL

To model the parabolic variation observed in Figure 2, we use the mean-field random phase approximation (RPA) approach for a ternary mixture (polymer and two solvents). This model is rather crude and uses the random mixing assumption and averages over molecular orientations. For instance, this RPA model is expected to reproduce the main observed trends only.

The ternary RPA model is described here briefly. More details can be found elsewhere.[7,8] Define the three components as A = PEO, B = *d*-methanol, and C = *d*-water and the degrees of polymerization N_A, N_B, and N_C, the volume fractions ϕ_A, ϕ_B, and ϕ_C, and the specific volumes V_A, V_B, and V_C for the three components. These specific volumes are assumed to be temperature independent. The bare structure factors (with no interactions) are expressed in the thermodynamic limit (scattering momentum transfer $Q = 0$) as

$$S^0_{AA} = N_A \phi_A V_A, \quad S^0_{BB} = N_B \phi_B V_B, \text{ and } S^0_{CC} = N_C \phi_C V_C. \tag{2}$$

Note that all cross terms (S^0_{AB}, etc) are zero. These cross terms are nonzero only when copolymers are present. Define the Flory–Huggins χ parameters χ_{AB}, χ_{AC}, and χ_{BC} and the following quantities:

$$\begin{aligned} V_{AA} &= 1/S^0_{CC} - 2\chi_{AC}/V_0 \\ V_{BB} &= 1/S^0_{CC} - 2\chi_{BC}/V_0 \\ V_{AB} &= 1/S^0_{CC} + \chi_{AB}/V_0 - \chi_{AC}/V_0 - \chi_{BC}/V_0 \end{aligned} \tag{3}$$

where V_0 is a “reference volume.” The fully interacting system structure factors can be expressed as

$$\begin{aligned} S_{AA} &= S^0_{AA}(1 + V_{BB}S^0_{BB})/\Delta \\ S_{BB} &= S^0_{BB}(1 + V_{AA}S^0_{AA})/\Delta \\ S_{AB} &= -S^0_{AA}V_{AB}S^0_{BB}/\Delta \end{aligned} \tag{4}$$

The denominator is given by $\Delta = (1 + V_{AA}S^0_{AA}) \times (1 + V_{BB}\, S^0_{BB}) - (V^2_{AB}\, S^0_{AA}S^0_{BB})$. The relation $\Delta = 0$ yields the spinodal condition. The SANS macroscopic scattering cross section (in units of cm^{-1}) in the thermodynamic limit ($Q = 0$) is given by

$$\begin{aligned} d\Sigma/d\Omega = {} & (b_A/V_A - b_C/V_C)^2 S_{AA} \\ & + (b_B/V_B - b_C/V_C)^2 S_{BB} \\ & + 2(b_A/V_A - b_C/V_C)(b_B/V_B - b_C/V_C) S_{AB} \end{aligned} \tag{5}$$

Here b_A, b_B, and b_C are the neutron scattering lengths.

For the system PEO/*d*-methanol/*d*-water, the following parameters were used

$N_A = 975$; $N_B = N_C = 1$; $V_A N_{av} = 38.94\ \mathrm{cm^3/mol}$; $V_B N_{av} = 40.54\ \mathrm{cm^3/mol}$; $V_C N_{av} = 18.07\ \mathrm{cm^3/mol}$; $b_A = 4.1326 \times 10^{-13}$ cm; $b_B = 3.9133 \times 10^{-12}$ cm, $b_C = 1.9145 \times 10^{-12}$ cm.

Note that Avogadro’s number ($N_{av} = 6.02 \times 10^{23}$/mol) was used to multiply the specific volumes. Remember that A = PEO, B = *d*-methanol, and C = *d*-water.

FITS TO THE TERNARY RPA MODEL

The two limiting cases of binary mixtures 4% PEO/*d*-water and 4% PEO/*d*-methanol (at $T = 50\ ^{\circ}\mathrm{C}$) are considered first. For the case of 100% *d*-water ($\phi_B = 0$), the fit to the SANS data gives $\mathrm{d}\Sigma/\mathrm{d}\Omega = C = 1.171\ \mathrm{cm}^{-1}$, which yields $\chi_{AC}/V_0 = \chi_{\mathrm{PEO}/d\text{-water}}/V_0 = 0.0106\ \mathrm{mol/cm}^3$. For the case of 100% *d*-methanol ($\phi_C = 0$), the fit to the SANS data gives $\mathrm{d}\Sigma/\mathrm{d}\Omega = C = 0.860\ \mathrm{cm}^{-1}$, which yields $\chi_{AB}/V_0 = \chi_{\mathrm{PEO}/d\text{-methanol}}/V_0 = 0.0268\ \mathrm{mol/cm}^3$. The third Flory–Huggins interaction parameter χ_{BC}/V_0 is obtained (for example) from the case of 4% PEO in 40% *d*-methanol/60% *d*-water solvent ($\phi_A = 0.04$, $\phi_B = 0.96 \times 0.4 = 0.384$, and $\phi_C = 0.96 \times 0.6 = 0.576$). For this case $\mathrm{d}\Sigma/\mathrm{d}\Omega = C = 0.6648\ \mathrm{cm}^{-1}$ which yields $\chi_{BC}/V_0 = \chi_{d\text{-methanol}/d\text{-water}}/V_0 = 0.0099\ \mathrm{mol/cm}^3$. Note that these Flory–Huggins interaction parameters (for example, χ_{AB}) are related to the monomer–monomer, monomer/solvent and solvent/solvent interaction potentials (W_{AA}, W_{AB}, and W_{BB} respectively) as $\chi_{AB}\ k_BT = W_{AB} - (W_{AA} + W_{BB})/2$ (where k_BT is the temperature in energy units).

Using these parameters, the RPA ternary mixture model is used to calculate the predicted values as shown in Figure 2 (together with the measured values). The overall parabolic trend for the solvation intensity observed by SANS can be reproduced. The approach used here averages over molecular orientations at the outset. The major assumptions made are mean-field RPA, incompressible polymer solutions, and composition independent χ parameters. Deviation between measurements and model predictions are due to the crude nature of our model that does not account for the specific packing of the solvent molecules around the polymer chains. We do not know of any model that would do better short of a full-fledged computer simulation that would treat molecular orientations explicitly.

PEO IN OTHER SOLVENT MIXTURES

SANS measurements have been conducted on 4% PEO in the following three solvent mixtures: *d*-water/*d*-methanol (CD_3OD), *d*-water/*d*-ethanol (CD_3CD_2OD), and *d*-water/*d*-ethylene glycol ($DOCD_2CD_2OD$). Results of the fits to eq 1 gave the solvation scattering intensity (the parameter C in eq 1), which is plotted in Figure 3 for varying solvent fractions. This figure summarizes the most significant results presented in this article.

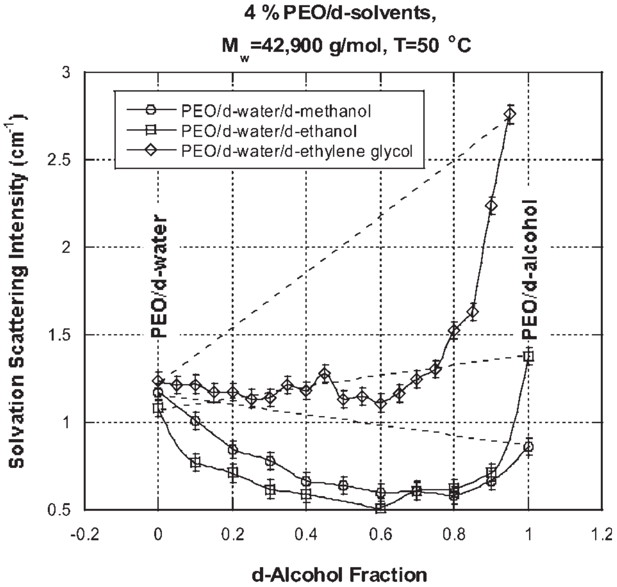

Figure 3. SANS measured solvation intensity (the parameter C in eq 1) for the case of 4% PEO in the three solvent mixtures: *d*-water/*d*-methanol, *d*-water/*d*-ethanol, and *d*-water/*d*-ethylene glycol. The ideal solvent mixing (dashed) lines are also shown.

Listed here are some observations and possible implications. For cases where *d*-water is the major component, *d*-ethanol is the best solvent, then *d*-methanol, then *d*-ethylene glycol. This may be due to the fact that the ethanol structure is the closest to that of the PEO monomer. When the *d*-alcohol fraction increases, the *d*-ethanol and *d*-methanol curves crossover (around 70% *d*-alcohol fraction as shown in Fig. 3). This is probably due to the fact that the PEO/*d*-ethanol solution tends to stay crystalline up to higher temperatures than the PEO/*d*-methanol solution.

Figure 3 shows that the solvation intensity (the parameter C in eq 1) for solvent mixtures is always smaller than the ideal mixing condition (dashed line), which is an interpolation between the two limiting cases of 0% alcohol fraction and 100% alcohol fraction. This seems to be a general result. Solvent mixtures are better solvating agents for water-soluble polymers than any of the individual solvents.

CONCLUSIONS

SANS is a valuable characterization method to probe local solvation in polymer solutions. This technique is used here to investigate the solvation of a model-polymer in a semidilute solution of *d*-water and *d*-alcohol. The SANS signal was separated into a (low-Q) clustering part and a (high-Q) solvation part. The focus in this work was put on the solvation characteristics. The solvation intensity shows a parabolic variation with changing *d*-alcohol content. Solvent mixtures are more effective at solvating polymer chains than individual solvents. A model based on the ternary RPA model reproduces this parabolic variation. This simple mean-field RPA model can reproduce only the overall (parabolic) trend observed in the data.

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