7730 *Macromolecules* **1995,** *28,* 7730–7736

A Neutron Scattering Study of Poly(ethylene glycol) in Electrolyte Solutions[†]

P. Thiyagarajan,[‡] D. J. Chaiko,*,[§] and R. P. Hjelm, Jr.[⊥]

Intense Pulsed Neutron Source, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, and Los Alamos Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received July 17, 1995; Revised Manuscript Received August 24, 1995[⊗]

ABSTRACT: The solution microstructure of aqueous (D_2O) poly(ethylene glycol) (PEG) solutions was determined as a function of polymer concentration and molecular weight in the presence of salts such as $NaNO_3$, Na_2CO_3, and Na_3PO_4. Measurements were made by using small-angle neutron scattering (SANS). In addition, anion effects on biphase formation were investigated by cloud point measurements in H_2O and D_2O. In the presence of $NaNO_3$, PEG behaves like a random coil with no evidence of aggregation, whereas the presence of either Na_3PO_4 or Na_2CO_3 leads to aggregate formation. Furthermore, the aggregate size increased with increasing salt concentration until a discontinuity appeared at the point of biphase formation, where the polymers in the PEG-rich phase form an entangled mesh with loss of chain identity. In the monophasic regime, the aggregates were elongated with a radius of approximately 19 Å and a length which varied with salt type and concentration. Analysis of the effects of electrolytes on the cloud points of PEG in H_2O and D_2O suggests that its phase behavior in solution is entropy driven. Salt effects on cloud points follow the well-known Hofmeister series. Anions leading to increased structuring of water lower the cloud point, as does the substitution of D_2O for H_2O. The cloud point data correlate linearly with the change in water entropy upon the addition of electrolytes.

Introduction

Aqueous poly(ethylene glycol) (PEG) solutions, when combined with an appropriate salt, form heterogeneous liquid/liquid (biphase) systems. These aqueous biphasic systems contain as much as 70–90 wt % water in each of the liquid phases.[1] A variety of polymer/salt systems have been evaluated by numerous investigators for potential use in the separation of metal ions (for a recent review, see Rogers et al.[2]), ultrafine particles,[3–7] and organics.[8,9] Aqueous biphasic separation (ABS) processes could be used in place of other techniques, such as oil flotation and conventional solvent extraction with an oil/water system. We have recently begun to scale-up ABS processes for ultrafine particle/particle separation by countercurrent extraction using a pilot-scale Karr column.[10]

The physicochemical properties of aqueous poly(ethylene oxide) (PEO) solutions and its lower molecular weight analog, PEG, have been studied extensively and have been reviewed by Bailey and Koleske.[11] A host of techniques have been used to probe the aqueous solution structure of PEO, such as light scattering,[12,13] Raman spectroscopy,[14] electron microscopy,[15] small-angle neutron scattering,[16,17] viscometry,[18,19] and free volume measurements.[20] These studies have revealed many fascinating properties of aqueous PEO solutions.

In the crystalline state, PEO was shown to possess a distorted helical symmetry with a *trans,gauche,trans* (*tgt*) conformation about the (CCOC), (OCCO), and (COCC) dihedral angles, respectively.[11] In aqueous solution, PEO assumes a random coil configuration but retains a significant portion of the *tgt* conformational structure.[14] The fully hydrated polymer associates with two to three hydrogen-bonded water molecules per monomer unit.[21] Poly(ethylene oxide) exhibits an inverse solubility–temperature relationship[11] and has a lower critical solution temperature (LCST) of about 100 °C. The LCST increases slightly as the molecular weight of the polymer decreases. For example, the LCST of PEG-3400 is about 120 °C. It has been postulated that the phase separation of aqueous PEO solutions is related to changes in the *gauche–trans* equilibrium about the C–O bond.[22] A *trans* conformation about the C–O bond together with a *gauche* conformation about the C–C bond would be expected to result in a significant dipole moment and hence a strong interaction with water. Other conformations are expected to have significantly smaller dipole moments, which would lead to a reduced affinity for water.[22]

Salts containing trivalent anions such as PO_4^{3-} are known to be more effective in promoting biphase formation than salts containing divalent anions like SO_4^{2-}, which in turn are more effective than monovalent anions like OH^-.[23] However, multivalent cations tend to interact strongly with the ether oxygens of PEG and, thus, shift the biphase regime toward higher salt concentrations. In fact, the metal-complexing ability of the ether oxygens of PEG has led some authors to view PEG's as "flexible" crown ethers.[24] Metal complexation by PEG's can be quite effective in solvents having a low donor ability and moderately high dielectric constant. Consequently, water is generally not a suitable solvent for PEG complexation reactions. Nevertheless, biphase formation has been attributed to a competition between the salt anions and the ether oxygens for water of hydration, thereby leading to a partial dehydration of the polymer.[23]

The partial dehydration of PEG, by itself, is unlikely to be sufficient to lead to phase separation. The intrinsic viscosity of PEG solutions has been reported[11,25] to decrease with increases in concentration of salts like Na_2SO_4 and $MgSO_4$. This suggests that

---

* To whom correspondence should be addressed; e-mail: Dave_Chaiko@qmgate.anl.gov.

[†] Work supported by the U.S. Department of Energy, Division of Advanced Energy Projects, under Contract W-31-109-ENG-38.

[‡] Intense Pulsed Neutron Source, Argonne National Laboratory.

[§] Chemical Technology Division, Argonne National Laboratory.

[⊥] Los Alamos National Laboratory.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-7730$09.00/0

aggregation of the polymer takes place as the biphase regime is approached.

At present, very little information is available on the solution structure of PEG/salt systems as a function of salt concentration and temperature. To further understand the molecular basis for biphase formation, we carried out SANS studies of PEG solutions as a function of polymer molecular weight, concentration, salt type, and salt concentration. Anion effects on the solution structure of PEG-3400 under static conditions were studied using the salts $NaNO_3$, Na_3PO_4, and Na_2CO_3. A few SANS experiments were done using PEG with molecular weights (M_n) of 1500, 2000, and 10 000 to establish the similarity in the structural features between the PEG used in this study and that reported previously in the literature.[26] In addition, we carried out cloud point measurements with PEG-3400 as a function of anion type in H_2O and D_2O.

Materials and Methods

Materials. Poly(ethylene glycol) and D_2O (99.6% purity) were purchased from Aldrich Chemicals. The number-average molecular weights (M_n) of the PEG used were 1500, 2000, 3400, and 10 000. Most of the SANS experiments involved PEG-3400 and were carried out using material from a single lot number (06622cw). We have used the same PEG in our solvent extraction studies[27] so that we could make correlations between the solvent extraction studies and the solution structures of PEG from SANS. A number of studies in which M_n and M_w (weight-average molecular weight) were measured for commercially available PEGs less than 50 000 Da have indicated that the ratio of M_w/M_n is between 1.0 and 1.5.[11] The salts (NaCl, $NaNO_3$, Na_3PO_4, $NaHCO_3$, and Na_2CO_3) were purchased from Fisher Scientific while Na_2SO_4 and Na_2SeO_4 were purchased from Aldrich Chemicals. All were of analytical reagent grade. Deionized (18 MΩ-cm) water was prepared using a Barnstead E-Pure ion exchange unit with activated carbon cartridges.

The appropriate PEG/salt solutions were prepared in D_2O to increase the contrast between the PEG and the solvent for neutron scattering. Both PEG and PEG/salt solutions were prepared for analysis. When the biphasic systems were prepared for study, they were equilibrated by vortexing for several minutes and then centrifuged at 3000 rpm for 10 min to ensure complete phase separation. The less dense, PEG-rich phases were separated and kept at 23 °C for more than 48 h prior to SANS measurements.

Measurements. The scattering measurements on PEG solutions were carried out with the time-of-flight small-angle diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. This instrument uses neutrons produced in pulses by spallation due to the deposition of 450 MeV protons on a depleted uranium target, followed by moderation by a solid methane moderator (22 K), yielding a wavelength range of 1−14 Å. The scattered neutrons were detected with a 20 cm × 20 cm gas-filled proportional counter having a 64 × 64 array area. The wavelength of the scattered neutrons was determined by their time of flight. This instrument can provide-useful SANS data in the momentum transfer (q) range of 0.007–0.25 $Å^{-1}$ ($q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the wavelength of the incident neutrons). The scattering data were corrected for (1) empty cell and background solution scattering, (2) incoherent scattering, (3) detector nonlinearity, (4) sample transmission, and (5) variation in the detector sensitivity.

The SANS data collected at IPNS were placed on an absolute scale of differential scattering cross section per unit volume, $d\Sigma(q)/d\Omega$ (cm^{-1}), by calibration with standard samples measured at D11 of the Institut Laue Langevin, France.[28]

Measurements were also carried out with the small-angle X-ray scattering (SAXS) instrument on the X12B beamline at the National Synchrotron Light Source (NSLS) for aqueous PEG solutions in the presence and absence of salt. These measurements failed to produce any reasonable signal with several hours of counting. The lack of an X-ray scattering signal even at the high-flux synchrotron sources indicates that the X-ray scattering cross sections per unit volume should be the same for PEG and H_2O. Thus, the electron density of PEG should be equal to that of H_2O, 9.3×10^{10} cm^{-2}, and this value can be used to calculate the density of PEG-3400 in H_2O from the following expression:

$$\psi = \sum n_i \sigma N_A \rho / M_w \tag{1}$$

where ψ is the electron density, n_i is the number of electrons in the ith atom in a PEG molecule, σ is the scattering cross section of an electron (0.28×10^{-12} cm), ρ is the density (inverse of the partial specific volume) of PEG in H_2O, N_A is the Avogadro number, and M_w is the molecular weight of the PEG polymer. Since the chemical composition of PEG and ψ are known, the density of PEG-3400 can be calculated and was found to be 1.02 g/cm³. This value is similar to that reported by Cabane and Duplessix[17] for PEO. Our contrast variation SANS studies of PEG-3400 measured at 3 wt % also agree with this value, but these data are not reported here.

Cloud point measurements were carried out in H_2O and D_2O using sealed glass test tubes which were immersed in a thermostated water bath that could be regulated to within 0.1 °C. For measurements above 100 °C, we used an oil bath. The samples were allowed to equilibrate at least 10 min between incremental adjustments in temperature. The cloud points were verified on multiple heating and cooling cycles. The solutions used in these measurements were prepared from anhydrous salts. Solutions were prepared on both weight percent and mole percent concentration scales. The later scale was used to estimate bias in solution behavior due to the molecular weight difference between H_2O and D_2O.

Analysis of SANS Data. The SANS data were analyzed in the region of $qR_g \leq 1.0$ by using standard Guinier analysis:[29]

$$d\Sigma(q)/d\Omega = d\Sigma(0)/d\Omega \exp(-q^2 R_g^2/3) \tag{2}$$

The radius of gyration, R_g is the root-mean-squared distance of all of the atoms from the centroid in the neutron scattering length density distribution of the particle. From a plot of ln-$[d\Sigma(q)/d\Omega]$ vs q^2, a linear fit can be made in the region where $qR_g \leq 1.0$, and the R_g and $d\Sigma(0)/d\Omega$ can be obtained from the slope and the y-intercept of the linear fit, respectively. While working with concentrated solutions, as in our case, the values of R_g and $d\Sigma(0)/d\Omega$ can be decreased by excluded volume effects (discussed later), and hence, the R_g values are considered apparent values.

Poly(ethylene oxide) in water has been shown to be in a random coil state.[14] Hence, in solutions that did not show polymer aggregation, the scattering was modeled over the entire scattering curve by using the Debye expression[30] for a random coil:

$$d\Sigma(q)/d\Omega = d\Sigma(0)/d\Omega(2/z^2)(e^{-z} - 1 + z) + I_{inc} \tag{3}$$

where $z = q^2R_g^2$. Nonlinear regression methods were used to obtain R_g, $d\Sigma(0)/d\Omega$, and the incoherent scattering value (I_{inc}). Since water is a good solvent for PEG, it is reasonable to assume that the polymer exhibits a swollen configuration. On this basis, it is expected that the scattering intensity of aqueous PEG solutions will vary as $q^{-1.4}$ when $qR_g > 1$, rather than q^{-2}, as predicted by eq 3. Nevertheless, the scattering model of a Debye coil is expected to yield a reasonable approximation given (1) the relatively small size of PEG used in our studies, (2) the dominance of I_{inc} for $q > 0.1$ $Å^{-1}$, and (3) the precision of the scattering measurements.

In our more concentrated samples, interparticle interactions are present, and the essential criterion for the Guinier analysis[29] (that of uncorrelated particle position) does not hold. For quasi-spherical interacting particles, the scattering intensity is $I(q) = S(q)|F(q)|^2$, where $|F(q)|^2$ is the form factor approximated by eq 2 or 3, for example, and $S(q)$ is the structure factor describing the particle interactions. The use

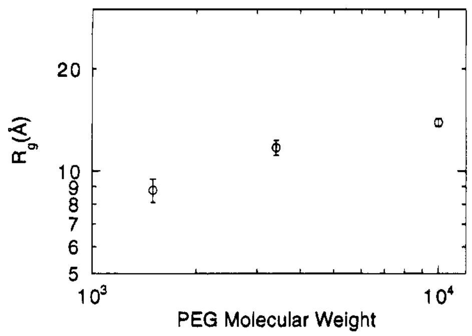

Figure 1. Plot of R_g as a function of PEG molecular weight at a polymer concentration of 8.5 wt %.

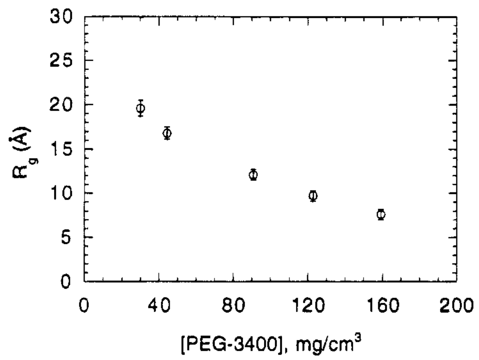

Figure 2. Effect of PEG-3400 concentration on R_g at 23 °C.

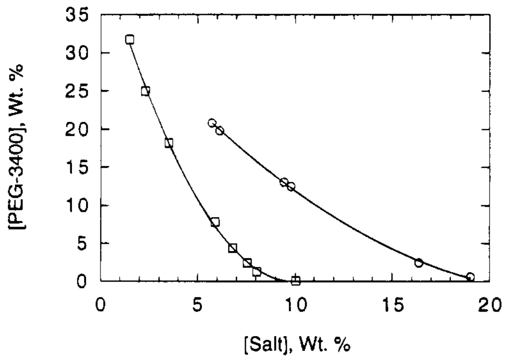

Figure 3. Phase diagram of the PEG-3400/Na_2CO_3 system at 25 °C (squares) and PEG-3400/Na_3PO_4 at 25 °C (circles).

of eqs 2 and 3 assumes that a q-domain can be found where $S(q) \rightarrow 1$. In general, such domains are present at high q but the Guinier analysis is not possible due to the constraint that $qR_g \leq 1.0$ for measuring a given value of R_g. In those cases we modeled the scattering data in the high-q region where $S(q) \rightarrow 1$ by using the Debye random coil expression (eq 3). Consequently, effects on the R_g values from interparticle interactions are minimal. The validity of this approach is supported by the fact that in the case of systems whose scattering data permitted Guinier analysis, the values of R_g and $d\Sigma(0)/d\Omega$ were consistent with those values obtained from the nonlinear regression analysis of the Debye model. For example, at a PEG concentration of 3 wt % in D_2O, the Guinier analysis yields values of 19.1 ± 1 Å and 0.26 ± 0.02 cm^{-1} for R_g and $d\Sigma(0)/d\Omega$, respectively. The corresponding values from the Debye model are 18.8 ± 0.3 Å and 0.24 ± 0.03 cm^{-1}. Thus, the agreement between the modeling approaches in the high-q region, at intermediate PEG concentrations, lends support for the analysis of the SANS data from solutions with high PEG concentrations where excluded volume effects will reduce the swollen coil configuration to one of a more compact random coil.

In principle, it should be possible to extract $S(q)$ and obtain the appropriate interaction potentials between the PEG molecules. However, the overall conformation of the PEG molecule changes with its concentration and the lack of information on these changes precludes such an attempt at this time.

In the case of polymer aggregates, whose scattering data cannot be described by the Debye model (eq 3), we fit the data using the form factor for a prolate ellipsoid of revolution:[29]

$$\frac{d\Sigma(q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega} \int_0^{2\pi} \{(3 \sin X - X \cos X)/X^3\} \cos \beta \, d\beta + I_{inc} \tag{4}$$

In eq 4, $X = qA_s\{\cos^2 \beta + (A_s/B_s)^2 \sin^2 \beta]^{1/2}$, where A_s and B_s are the major and minor axes of the prolate ellipsoid, respectively, and β is a factor that takes care of orientational averaging. From eq 4, $d\Sigma(0)/d\Omega$ and the semiaxes can be obtained.

Thus, we have analyzed the data in a number of ways, and the justification for their use will be made at the appropriate places in the remainder of this paper.

Results and Discussion

Neutron Scattering from Aqueous (D_2O) PEG Solutions. Equation 2 was used to analyze the scattering data from 8.5 wt % PEG solutions in pure D_2O as a function of PEG molecular weight. The R_g values obtained are shown in Figure 1. This power law behavior of R_g with M_w is typical of linear coiled polymers in good solvents. Additionally, the particle sizes agree reasonably well with those reported for low molecular weight PEG in D_2O solutions.[26]

To assess the effects of interparticle interactions on the sizes obtained by SANS, we carried out SANS measurements on PEG-3400 as a function of its concentration in D_2O at 23 °C. Figure 2 shows the R_g values as a function of concentration. The R_g values decrease with increase in concentration of PEG, and these R_g values are similar to those reported by Abbott et al.,[26] although their SANS measurements were done on PEG-4000 at higher concentrations than our studies. The interesting observation here is the nonlinearity in the increase of R_g with decreasing PEG concentration. If the three-dimensional conformation of the macromolecule does not change with concentration (e.g., as expected with proteins), the excluded volume effects would lead to a linear decrease in R_g as a function of increasing polymer concentration.[31] The nonlinear variation of R_g noted for PEG may be due to the combined effects of (1) possible changes in the three-dimensional structure of PEG with increasing concentration as indicated by Abbott et al.[26] and (2) the interparticle interaction of PEG polymers (excluded volume effects) at high concentrations. Under the concentrations studied here, PEG seems to be nonaggregated, as no concentration-dependent aggregation (shown by an increase in the slope of the Guinier plots) was seen.

Neutron Scattering from PEG/Salt Solutions. Among the four salts that we used in these measurements (NaCl, $NaNO_3$, Na_3PO_4, and Na_2CO_3), only Na_3PO_4 and Na_2CO_3 led to biphase formation.[23] The phase diagram obtained from cloud-point measurements for PEG-3400 and Na_2CO_3 in H_2O at 25 °C is shown in Figure 3. Also shown in Figure 3 are data for the PEG-3400/Na_3PO_4 system at 25 °C. Solutions whose compositions lie to the left of the binodal are monophasic, while solutions whose compositions lie to the right of the binodal are biphasic. Our purpose in carrying out the SANS measurements was (1) to determine what changes, if any, occur in the microstructure of PEG/salt solutions as the coexistence curve for biphase formation is approached by increasing the salt concentration and

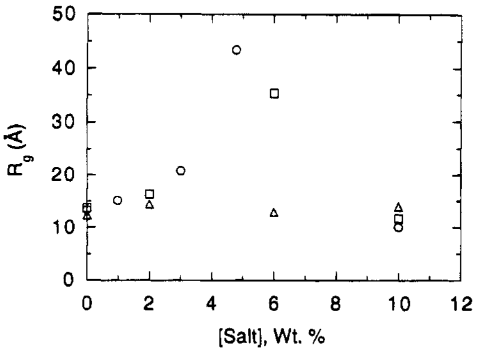

Figure 4. Apparent R_g values of 7.1 wt % PEG-3400 as a function of salt concentration: $NaNO_3$ (triangles); Na_3PO_4 (squares); Na_2CO_3 (circles). The error bars are smaller than the symbols.

(2) to compare this behavior with that occurring in PEG/electrolyte solutions that do not lead to biphase formation (e.g., $NaNO_3$). Our studies focused primarily on PEG-3400, although we performed some experiments with PEG-2000 as well. In these experiments we kept the PEG concentration constant while studying the effects of salt type and salt concentration on the solution morphology of the PEG polymer.

In Figure 4 we compare the R_g values obtained from the SANS measurements for 7.1 wt % PEG-3400 in $NaNO_3$, Na_3PO_4, and Na_2CO_3 solutions. In the PEG/$NaNO_3$ solutions, we did not see any evidence of PEG aggregation as the ionic strength of the PEG solution was increased. The effective R_g remained constant and equal to the value that we obtained for PEG-3400 in deionized D_2O (i.e., 11 Å). In contrast to the PEG/$NaNO_3$ solutions, our SANS measurements of PEG-3400 in D_2O solutions containing either Na_2CO_3 or Na_3PO_4 salts did show evidence for PEG aggregation. Thus, there appears to be a relation between PEG aggregation and biphase formation in aqueous PEG/salt solutions. The sizes of the polymer aggregates formed in PEG solutions containing Na_2CO_3 and Na_3PO_4 are shown in Figure 4 as a function of salt concentrations. There is a significant increase in R_g as the concentration of Na_2CO_3 or Na_3PO_4 increases, and the solution composition approaches the boundary between the single and biphase regions. In the biphasic region, the value for R_g in the PEG-rich phase is slightly smaller than that observed in the single-phase samples containing only PEG or PEG/$NaNO_3$. These differences are probably real and could be due to slight changes in the degree of polymer entanglement.

To further understand the effect of PEG molecular weight on the aggregation phenomenon and, ultimately, the phase separation behavior, we also carried out neutron scattering measurements for PEG-2000/salt solutions. Comparison of data in Figure 5 for PEG-3400 and PEG-2000 in solutions containing Na_2CO_3 shows that PEG aggregation occurs in both cases. In the monophasic region, the particle sizes at the same PEG and salt concentrations are smaller for PEG-2000 than PEG-3400. However, in both cases, the particle sizes become similar in the top phase after biphase formation. Under these conditions, the PEG concentration exceeds the chain overlap concentration (c^*), where the polymer chains become an entangled mesh in which the identities of individual polymers are lost.[32]

Our SANS studies reveal that PEG aggregates when Na_2CO_3 is added to a 7.1 wt % PEG-3400 solution and that the aggregate size increases with increasing Na_2CO_3 concentration, as seen by the increase in SANS signal in the low-q region (Figure 6). The concentrations of Na_2CO_3 corresponding to the four curves are 0, 1, 3, and 4.78 wt %. The SANS data for the two lower concentrations of salt (1 and 3 wt %) can be fitted with the Debye function (eq 3), whereas the data corresponding to 4.78 wt % Na_2CO_3 could be fitted only with the form factor of a prolate ellipsoid of revolution (eq 4). The fits to the data are shown as lines in Figure 6. These results indicate that the PEG molecules in Na_2CO_3 solution aggregate into elongated particles as the salt concentration increases. According to the fit, the PEG-3400 aggregates in the sample with 4.78 wt % Na_2CO_3 can have a length of 240 ± 4 Å and a radius of 19 ± 1 Å (note: we also found that fitting the SANS data using the form factor for a cylinder produced similar particle dimensions). Since this result suggests long rod-shaped particles, the present fit was checked by analyzing the scattering data by a modified Guinier method, which involves plotting $\ln[qI(q)]$ as a function of q^2. The slope of a linear fit in a q region ($qR_c < 0.8$) will yield R_c, the cross-sectional radius of gyration of a rod-shaped particle.[33] The radius of the rod-shaped particle (R) is obtained from $R = 2^{1/2}R_c$. This modified Guinier analysis (Figure 7) gives a radius of 20.6 ± 0.3 Å, which confirms that the morphology of the PEG aggregate is rodlike.

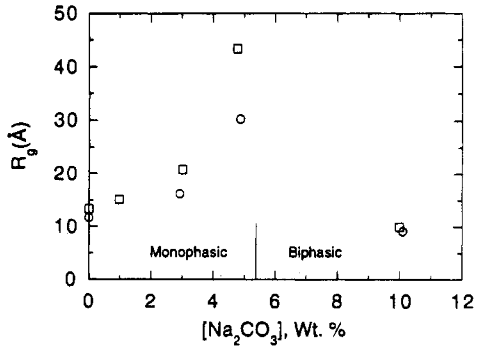

Figure 5. Effect of PEG molecular weight on apparent R_g values: M_w = 3400 (squares) and M_w = 2000 (circles). The error bars are smaller than the symbols.

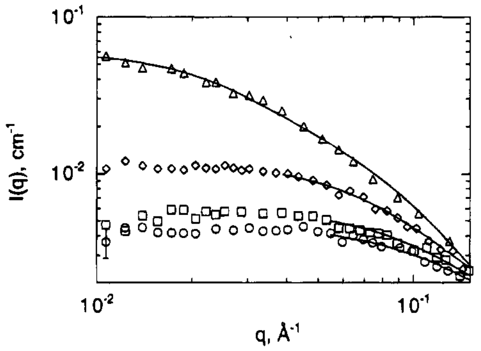

Figure 6. SANS data for 7.1 wt % PEG-3400 as a function of [Na_2CO_3]: no salt (circles); 1 wt % salt (squares); 3 wt % salt (diamonds); 4.78 wt % salt (triangles). The lines are modeling fits using eq 3 or 4 given in the text.

We found that the length of these particles, at similar PEG and salt concentrations, is proportional to the molecular weight of the individual polymer. For example, at a PEG concentration of 7.1 wt % and a Na_2CO_3 concentration of 4.8 wt %, the radius and length values are 15 ± 0.7 and 135 ± 1.5 Å for PEG-2000, while the corresponding values for PEG-3400 are 19 ± 1 and 240 ± 4 Å.

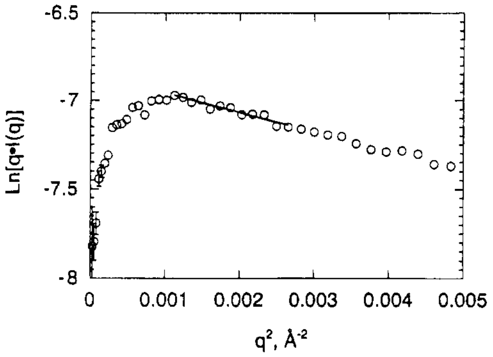

Figure 7. Modified Guinier plot of the scattering data for the 7.1 wt % PEG-3400/4.78 wt % Na_2CO_3 system in D_2O.

Similar particle growth occurs in the case of PEG-3400/Na_3PO_4 solutions (see Figure 4). However, the changes in particle size seem to be less than those for PEG-3400/Na_2CO_3 for a given change in salt concentration, and the particle sizes are smaller than those observed for PEG-3400/Na_2CO_3 at otherwise similar conditions. The significant conclusion from these studies is that, in the case of salts leading to biphase formation, there is a progressive particle growth whose size depends on the type of salt and its concentration. In addition, our data indicate the presence of a discontinuity in particle size in the regime where the PEG/salt system passes from monophasic to biphasic. The growth appears to be faster in the case of salts that lead to biphase formation at low salt concentration. The growth is slower in the case of salts that lead to biphase formation only at high salt concentration. Beyond the phase transition, the apparent size of the aggregates in the PEG-rich phase are smaller than those in the salt solutions under monophasic conditions. This apparent smaller size is due to the fact that the SANS analysis is detecting polymer segments in an entangled mesh of PEG molecules wherein the individuality of the polymer coils is lost. The salt-rich phase from the biphase system does not yield any significant scattering because of the low (<0.5 wt % from the phase diagram) PEG concentration.

Analysis of Anion Effects. It has been observed that the effectiveness of inorganic salts in promoting biphase formation with PEG follows the well-known Hofmeister ion series.[23] This effect has been found to be due primarily to the nature of the anions. Lyotropic ions, like Na_2SO_4 and Na_3PO_4, tend to reduce the water solubility of hydrophilic organic compounds, while hydrotropic ions, like NO_3^- and SCN^-, tend to increase their water solubility. The fact that these relationships hold for a remarkably wide variety of organic solutes suggests that they are primarily due to interactions between the inorganic ions and water and the consequent changes that this leads to in water structure.

Spectral data[34] show that lyotropic ions lead to an increase in the self-hydration of water through H-bonding (a process often referred to as structure making), while hydrotropic ions lead to a decrease in the number of H-bonded OH groups in water (a process referred to as structure breaking). The border between structure makers and breakers varies slightly with the organic compound in question and is related to the dipole moment of the organic solute.[34,35] Chloride ion appears to be unique in that it behaves as a weak structure maker at low temperatures (e.g., <60 °C) and becomes a weak structure breaker at higher temperatures.[34]

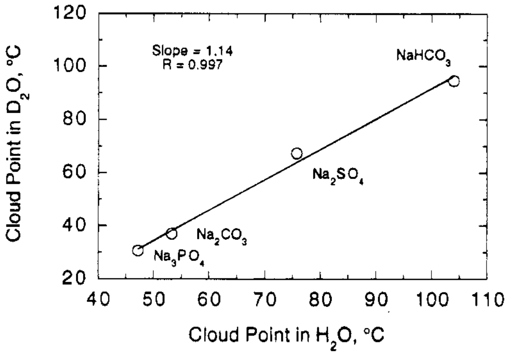

Figure 8. Cloud points of PEG-3400 in H_2O and D_2O as a function of anion type. The solution compositions were fixed at 7 wt % PEG/5 wt % salt.

The greater strength of the H-bond in D_2O, versus H_2O, leads to a lower solubility of polar compounds and a reduced critical micelle concentration (cmc) for surfactants.[34,36] Just as the addition of structure-making ions lowers the cloud point of PEG's so too does the substitution of D_2O for H_2O. This is illustrated in Figure 8, where the cloud points in H_2O and D_2O are compared for various PEG-3400/salt solutions. The linear fit of the data indicates that the effects of salt and D_2O are additive, suggesting that both influence the cloud point through a mechanism of increasing water structure. Interestingly, the difference in cloud point (ΔT_{cp}) is greater at lower temperatures and decreases with increasing temperature. This behavior mirrors the strength and magnitude of the H-bond network of D_2O as a function of temperature, which breaks down faster than that of H_2O as temperature increases.[36]

We should note that there is an additional factor which contributes to the rather large ΔT_{cp} values observed in Figure 8. And that is the fact that the molecular weight and density differences between H_2O and D_2O are large enough to significantly alter the water concentration. Thus, the mole ratio of water to ether oxygens in the polymer does not remain constant when one is substituted for the other on a constant weight percent basis. However, we have verified that a rather large ΔT_{cp} is still observed when the solutions are prepared on a fixed mole percent basis. For example, in the PEG-3400/Na_2SO_4 system, we obtained a ΔT_{cp} of 5.8 °C with a system composition of 99.243 mol % H_2O or D_2O, 0.715 mol % salt, and 0.042 mol % PEG-3400. This corresponds to a system composition of 7 wt % PEG and 5 wt % salt.

Since water structure appears to play a major role in determining the phase behavior of PEG solutions, we looked for a possible correlation between the cloud point lowering of PEG by electrolytes and the changes in water entropy. In Figure 9, we plot the cloud point data from Bailey and Koleske[11] for poly(ethylene oxide) ($M_w = 4 \times 10^6$) as a function of the change in entropy (ΔS_{II}) related to the structural changes of water during hydration of electrolytes. The PEO concentration was fixed at 0.5% and we arbitrarily selected cloud point data at a salt concentration of 0.3 M. The S_{II} values for the anions were obtained from Krestov[37] and refer to the change in entropy of water during the formation of the hydrated ion. The linear relationship in Figure 9 supports the view that the phase behavior of PEG in aqueous solutions is dominated by water structure effects.

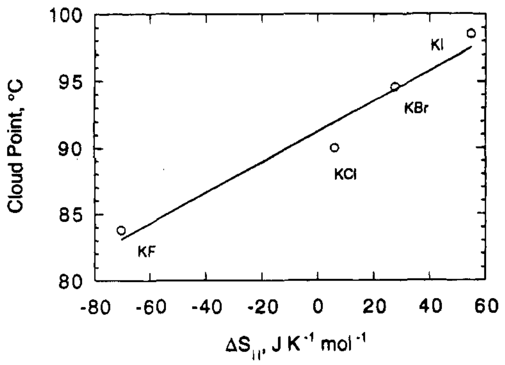

Figure 9. Effect of potassium salts on the cloud points of 5% PEO ($M_w = 4 \times 10^6$) solutions. The data are from Bailey and Koleske[11] and are at a fixed salt concentration of 0.3 M.

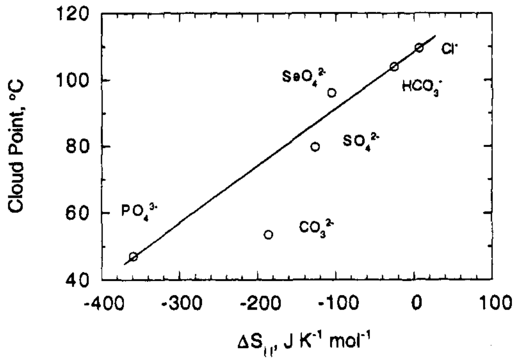

Figure 10. Effect of sodium salts on the cloud points of PEG-3400 in H_2O. The solution compositions were kept constant at 7 wt % PEG/5 wt % salt.

We found that a similar, linear relationship exists between the cloud point and ΔS_{II} for PEG-3400 and a variety of single and multiple charged anions (see Figure 10). Interestingly, chloride acts as a weak structure maker even at the rather high cloud point of around 110 °C. While the linear fit to the data is quite good, the cloud point for the PEG/Na_2CO_3 system does deviate somewhat from the behavior of the other sodium salts. The reason for this is not known at this time, but the behavior of the carbonate system is peculiar in more than one regard. Examination of the neutron scattering data in Figure 4 shows a more rapid rate of PEG aggregate growth in the presence of increasing carbonate concentration than in the presence of phosphate, suggesting that carbonate is more efficient at biphase formation. However, this contradicts the cloud point data in Figure 8, which indicate that phosphate is more efficient at promoting the phase separation of PEG. The cloud point data indicate that at higher temperatures (e.g., 40–50 °C) sodium phosphate is more effective than sodium carbonate at promoting biphase formation.

In a qualitative sense, the ΔS_{II} values can be used to predict which salts will promote biphase formation with low molecular weight PEGs at room temperature—a feature of importance in developing separation processes. In our experience,[38] it is not possible to get biphase formation with PEG-3400 and Na_2CO_3 at pHs below about 9–10. Thus, significant concentrations of a nonbiphase forming salt, (e.g., $NaHCO_3$) can inhibit PEG phase separation in concentrated salt solutions at room temperature. It appears that a characteristic of biphase-forming salts is that they provide a minimum entropy contribution of about −65 J K^{-1} mol^{-1} (estimated from the fractional contributions of ΔS_{II} for CO_3^{2-} + ΔS_{II} for HCO_3^- at pH 9.5).

Using published thermodynamic data, it should also be possible to predict, at least qualitatively, the partitioning behavior of tracer-level ions in PEG/salt systems. We would expect that ions with highly negative ΔS_{II} values would exhibit partition coefficients (D) that are either equal to or less than those of the biphase-forming salts (e.g., $D \sim 0.1$–0.2). For example, we have found that the partition coefficient of monomeric Pu(IV) (ΔS_{II} for Pu(IV) = −462.3 J K^{-1} mol^{-1}) in the PEG-3400/Na_2SO_4 system at 25 °C is about 0.17, while that of polymeric Pu(IV) under the same conditions is about 0.001.[5] Similarly, low partition coefficients (i.e., 0.004) were obtained for uranyl carbonate (ΔS_{II} for UO_2^{2+} = −106.3 J K^{-1} mol^{-1}) complexes in the PEG-3400/Na_2CO_3 system.[38] The extremely low partition coefficients for complex species like uranyl carbonate and polymeric plutonium reflect an additional entropy loss due to a large rotational contribution.[37]

Conclusions

Low molecular weight PEG in aqueous solutions exists as random coiled monomers, as evidenced by the small variation in the sizes of the particles as a function of PEG molecular weight. On the one hand, PEG in $NaNO_3$ solutions does not aggregate. On the other hand, in solutions containing Na_3PO_4 and Na_2CO_3, PEG aggregates into rodlike particles whose length progressively increases with increasing salt concentration up to the consolute point. The apparent size of the particles becomes smaller after the biphasic regime is entered. At room temperature, the particle growth is faster and the particle sizes are larger for Na_2CO_3 than they are for Na_3PO_4 at the same concentration of salt. In the case of salt solutions leading to biphase formation, the particle sizes prior to the phase separation are directly proportional to the molecular weight of the PEG molecule. It appears that biphase formation in PEG/salt systems proceeds from the initial aggregation of the polymer molecules into aggregates, which can be viewed as phase-separated microdomains. These microdomains continue to grow in size with increasing salt concentration until phase separation on a macroscale occurs. It should be recognized that the aggregation process need not necessarily result from specific interactions between polymer segments. Increased structuring of water by lyotropic ions can provide the necessary driving force behind aggregation and phase separation.

Small-angle X-ray scattering measurements show that the polymer aggregates have an electron density identical to that of water, indicating that the polymer molecules remain highly hydrated throughout the aggregation process, again pointing toward a change in water structure as the driving force behind the aggregation process. The effects of anions on the phase behavior of PEG correlate well with the water-structure-making character of the biphase-forming salts. This confirms earlier studies which concluded that biphase formation in these types of polymer systems is an entropy-driven process.[34,39]

Past attempts to approximate the PEG molecule as a noninteracting, hard sphere when modeling partition behavior in aqueous biphase systems will have to be reevaluated. Future development of thermodynamic models of partitioning behavior will need to explicitly account for the heretofore unrecognized effects of salt on PEG aggregation.

Acknowledgment. This work benefited from the use of the Intense Pulsed Neutron Source, which is funded by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38 to the University of Chicago. We thank D. G. Wozniak (IPNS) for his technical help. We also thank Dr. Malcolm Capel (NSLS) for helping in the SAXS experiments on the X12B beamline.

References and Notes

(1) Albertsson, P.-Å. *Partition of Cell Particles and Macromolecules*; Wiley: New York, 1986.

(2) Rogers, R. D.; Bond, A. H.; Bauer, C. B. *Sep. Sci. Technol.* **1993**, *28*, 1091.

(3) Ananthapadmanabhan, K. P.; Goddard, E. D. U.S. Patent 4,725,358, 1988.

(4) Chaiko, D. J.; Mensah-Biney, R. U.S. Patent 5,411,149, 1995.

(5) Chaiko, D. J.; Mensah-Biney, R.; Mertz, C. J.; Rollins, A. N. *Actinide Recovery Using Aqueous Biphasic Extraction: Initial Developmental Studies*, Argonne National Laboratory Report ANL-92/36, 1992.

(6) Chaiko, D. J.; Mensah-Biney, R.; Mertz, C. J.; Rollins, A. N. *Sep. Sci. Technol.* **1993**, *28*, 765.

(7) Chaiko, D. J.; Mensah-Biney, R.; Deepak, Soil Decontamination Using Aqueous Biphasic Separation. In *Proceedings of the Symposium on Waste Management, WM94*; Post, R. G.; Wacks, M. E., Eds.; Lazer Options, Inc.: Tucson, AZ, 1994; p 2257.

(8) Gullickson, N. D.; Scamehorn, J. F.; Harwell, J. H. In *Surfactant-Based Separation Processes*; Scamehorn, J. F., Harwell, J. H., Eds.; Marcel Dekker: New York, 1989; p 305.

(9) Chaiko, D. J.; Reichley-Yinger, L.; Orth, E. R.; Van Deventer, E. H.; Vandegrift, G. F.; Krumpolc, M.; Helt, J. E.; Coleman, R. D.; Kakar, S. N.; Tasi, T. S.; Horken, K.; Killian, W.; Sather, N. F. Development of a Process for Treating Red Water by Organic/Inorganic Separation and Biodegradation. In *Proceedings of the 14th Annual Army Environmental R&D Symposium*, USATHAMA Report CETHA-TE-TR-900055, 1989; p 303.

(10) Chaiko, D. J.; Deepak; Gartelmann, J.; Vojta, Y.; Thuillet, E.; Mertz, C. J. Issues in the Scale-up of Aqueous Biphasic Extraction of Uranium from Contaminated Soils. In *Separations of f-Elements*; Nash, K. L., Choppin, G. R., Eds.; Plenum Press: New York, 1995; p 225.

(11) Bailey, F. E., Jr.; Koleske, J. V. *Poly(ethylene oxide)*; Academic Press: New York, 1976.

(12) Devanand, K.; Selser, J. C. *Nature* **1990**, *343*, 739.

(13) Devanand, K.; Selser, J. C. *Macromolecules* **1991**, *24*, 5943.

(14) Maxfield, J.; Shepard, I. W. *Polymer* **1975**, *16*, 505.

(15) Cuniberti, C.; Ferrando, R. *Polymer* **1972**, *13*, 379.

(16) Abbott, N. L.; Blanchard, D.; Hatton, T. A. *Macromolecules* **1992**, *25*, 3917.

(17) Cabane, B.; Duplessix, R. *J. Phys.* **1982**, *43*, 1529.

(18) Woodley, D. M.; Dam, D.; Lam, H.; LeCave, M.; Devanand, K.; Selser, J. C. *Macromolecules* **1992**, *25*, 5283.

(19) Cuniberti, C. *Polymer* **1975**, *16*, 306.

(20) Grossman, P. D.; Gainer, J. L. *Biotechnol. Prog.* **1988**, *4*, 6.

(21) Liu, K. J.; Parsons, J. L. *Macromolecules* **1969**, *2*, 529.

(22) Karlstrom, C. *J. Phys. Chem.* **1985**, *89*, 4962.

(23) Ananthapadmanabhan, K. P.; Goddard, E. D. *Langmuir* **1987**, *3*, 25.

(24) Harris, J. M.; Hundley, N. H.; Shannon, T. G.; Struck, E. C. In *Crown Ethers and Phase-Transfer Catalysis in Polymer Science*; Mathias, L. J., Carraher, C. E., Eds.; Plenum: New York, 1984; p 371.

(25) Bailey, F. E., Jr.; Collard, R. W. *J. Appl. Polym. Sci.* **1959**, *1*, 56.

(26) Abbott, N. L.; Blanchard, D.; Hatton, T. A. *Macromolecules* **1992**, *25*, 3932.

(27) Chaiko, D. J., unpublished results.

(28) Hjelm, R. P., Jr.; Seeger, P. A.; Thiyagarajan, P. Small-Angle Neutron Scattering at Pulsed Sources Compared to Reactor Sources, In *Proeedings of the 11th Meeting of the International Collaboration on Advanced Neutron Sources*, October 22–26, 1990, Tsukuba, Japan, KEK Report 90-25, 1991; pp 673–676.

(29) Guinier, A.; Fournet, G. *Small Angle Scattering of X-rays*; John Wiley & Sons: New York, 1955.

(30) Debye, P. J. *Phys. Colloid Chem.* **1947**, *51*, 18.

(31) Porod, G. In *Small Angle X-ray Scattering*; Glatter, O., Kratky, O., Eds.; Academic Press: New York, 1982; Chapter 2.

(32) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1988.

(33) Hjelm, R. P. *J. Appl. Crystallogr.* **1985**, *18*, 452.

(34) Luck, W. A. P. *Top. Curr. Chem.* **1976**, *64*, 113.

(35) Kahlweit, M.; Lessner, E.; Strey, R. *J. Phys. Chem.* **1984**, *88*, 1937.

(36) Pandit, N. K.; Caronia, J. *J. Colloid Interface Sci.* **1988**, *122*, 100.

(37) Krestov, G. A. *Thermodynamics of Solvation*; Ellis Horwood: New York, 1991.

(38) Chaiko, D. J.; Mensah-Biney, R.; Van Deventer, E. In *Removal of Uranium from Uranium-Contaminated Soils Phase 1: Bench-Scale Testing*; Oak Ridge National Laboratory Report ORNL-6762, 1993.

(39) Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2053.

MA951036S