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Discovery and Modeling of Upper Critical Solution Behavior in the Poly(ethylene oxide)/Water System at Elevated Pressure

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I. Introduction

Nonionic, water-soluble polymer systems can exhibit properties not seen in typical hydrocarbon systems. Examples are extraordinarily large second virial coefficients,[1] polymer aggregation under good-solvent conditions,[2−6] and unusual phase behavior.[7−9] An example of such a polymer is poly(ethylene oxide), hereafter PEO. PEO is a particularly simple water-soluble polymer which exhibits all of the above-mentioned behavior. This paper concerns its phase behavior in water.

In typical hydrocarbon systems, the temperature−concentration ($T-C$) phase diagram exhibits an upper critical solution temperature (UCST) above which the polymer and solvent are in a single phase. In contrast, many water-soluble polymer systems exhibit an inverted coexistence curve, or equivalently, a lower critical solution temperature (LCST) above which there is coexistence between two phases.[10] PEO in water exhibits such behavior; the LCSTs range from 371.8 to 448.7 K for molecular weights ranging from 1020 to 2.18 kg/mol, respectively.[7] Molecular weights lower than 2.29 kg/mol exhibit a closed loop behavior in which a UCST exists at temperatures above the LCST. The $T-C$ phase behavior was modeled by Matsuyama and Tanaka (M−T) using a modified Flory−Huggins theory which specifically includes temperature effects on the hydrogen bonds.[8]

In this paper we present new experimental data on the temperature−pressure−concentration ($T-P-C$) phase behavior of PEO in water under pressure. Hydrogen bonds are known to weaken under pressure;[11−13] therefore, by applying pressure to a water-soluble polymer system the hydrogen bond strengths can be varied reversibly. Prior work[9] on the pressure behavior of the LCST found a previously unknown decline in the LCST with pressure. However, this work is limited in several ways: (a) the work was done with a diamond anvil cell, which has inherently large pressure uncertainties, (b) the temperatures were limited to $T > 23$ °C, and (c) study of the concentration dependence was not feasible. Furthermore, there was no adequate model to explain the unusual behavior. In this paper, we find that in addition to a declining LCST, PEO in water exhibits $P-T$ reentrant behavior with pressure, in which the polymer is soluble in an intermediate temperature range, but insoluble above and below this range. This is similar to protein denaturation under pressure.[14] This is the first clear indication for a UCST below the ambient-pressure freezing point of water; although previous viscometry measurements have hinted at the presence of this UCST.[10] Previous work on poly(*N*-vinylpyrrolidone), hereafter PVP, in water has also shown such behavior, implying that such behavior may be common to water-soluble polymers.[3] This reentrant phase behavior is fit to a modified version of Matsuyama and Tanaka's theory which includes the effect of pressure on hydrogen bond strength and hydrophobic interactions.

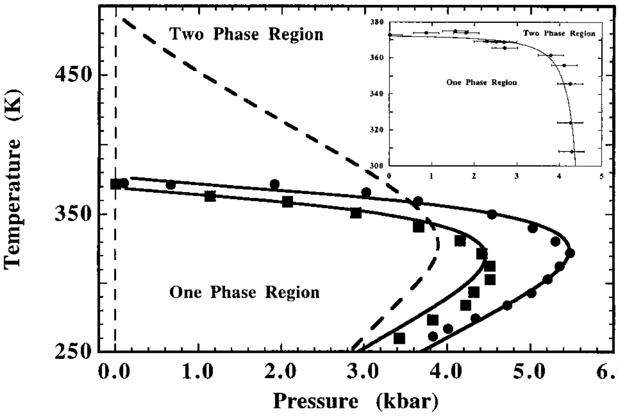

Figure 1. Phase separation temperatures as a function of pressure for PEO in water. The circles and squares are experimental data points for $M_w = 21$ and 1390 kg/mol at concentrations of $C = 50$ and 10 mg/mL respectively. The solid lines are the fitted binodal boundaries. The dashed line is the binodal phase boundary for PVP ($M_w = 389$ kg/mol, $C = 60$ mg/mL) in water.[3] The inset shows the data obtained by Cook et al. for $M_w = 270$ kg/mol at $C = 10$ mg/mL.[9]

II. Experimental Technique

PEO samples were obtained from American Polymer Standards and Polymer Laboratories and characterized by static light scattering. The stated M_w and M_w/M_n values are 21 and 1390 kg/mol and 1.17 and 1.15, respectively. Static light scattering gives M_w values of 22 and 1523 kg/mol. The sample preparation, experimental apparatus and experimental uncertainties have been described previously.[3] Data points were obtained by equilibrating the sample to the desired temperature, and then pressurizing until critical opalescence is visually observed. The critical opalescence is reversible; the sample would clarify as the pressure is decreased below the phase separation pressure. Since we were unable to stir the solutions in situ, we used a fresh sample to obtain each data point (including the data in the $P-T$ curves). Also, since the Flory−Huggins model works best when the polymer coils overlap we chose polymer concentrations above C^* to obtain the $P-T$ curves.

III. Results and Discussion

Figures 1 and 2 respectively show the $P-T$ and the $P-C$ phase behavior for $M_w = 21$ and 1,390 kg/mol. The $P-T$ diagram shows that PEO in water exhibits pronounced reentrant behavior, indicating that PEO in water has a UCST below the ambient-pressure freezing point of water. As shown in Figure 1, this behavior is similar to that found for PVP in water, but PVP shows a more gradual decline in the LCST with pressure.[3] The $P-C$ phase behavior shows that the binodal pressure has a weak concentration dependence, particularly for the high molecular weight sample. This behavior has also been observed for PVP in water.[3]

The solid/dashed lines in Figure 2 are the predicted binodal/spinodal pressures. The model used to fit the data is based on Matsuyama and Tanaka's model for the free energy of a water-soluble polymer.[8] Bekiranov

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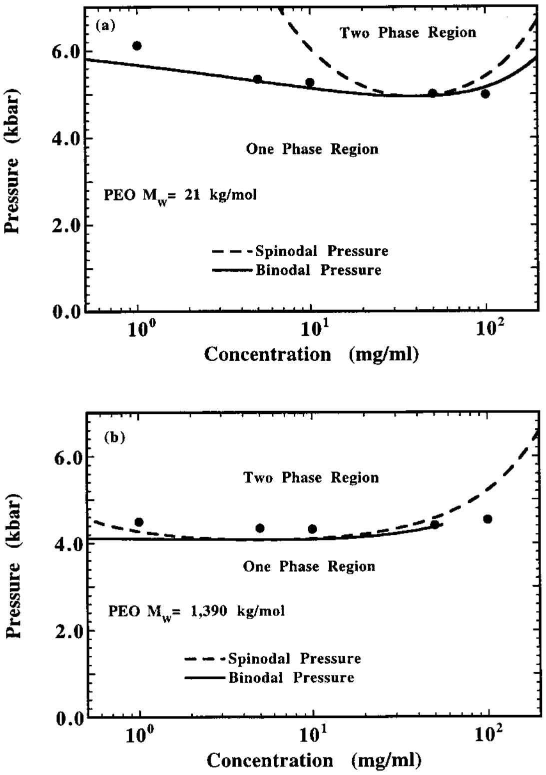

Figure 2. Phase separation pressures as a function of concentration for (a) $M_w = 21$ kg/mol and (b) $M_w = 1390$ kg/mol. The solid/dashed lines are the fit results for the binodal/spinodal pressures.

et al.[15] later showed that the M−T model can be simplified by replacing the summations over m with an average number of water molecules H-bonded to the backbone, $\bar{m}$ (see eq 3 in Sun and King.[3]). To include the effects of pressure and temperature we give the hydrogen bond strength a linear pressure dependence, $\Delta\epsilon(P) = \Delta\epsilon_o(1 - \gamma P)$, and the hydrophobic interactions a linear pressure and temperature dependence, $\chi(T,P) = (A - BT)(1 - \alpha P)$. This form of the equation was utilized in Sun and King[3] to account for the phase behavior of PVP in water. In this paper we add an additional term for the $P\Delta V$ energy by adding a term $\bar{m}P\Delta V_{HB}/T$. Here ΔV_{HB} has units of K/kbar, and describes the volume change upon formation of a hydrogen bond between a polymer unit and a water molecule. From reported dilatometery measurements at ambient pressure,[10] we calculate the volume change upon formation of a single hydrogen bond with a PEO molecule to be -3.95×10^{-24} cm^3, from which we obtain a value of $\Delta V_{HB} = -29.0$ K/kbar. We assume this value to apply across the experimental pressure range. The free energy of mixing then becomes

$$\frac{\Delta F_{mix}}{kT} = \phi_O \ln \phi_O + \frac{\phi_{\bar{m}+1}}{\bar{m}+n} \ln \phi_{\bar{m}+1} + \chi\phi(1-\phi) + \frac{\phi_{\bar{m}+1}}{\bar{m}+n}\left[\frac{-\bar{m}\Delta\epsilon}{T} + \frac{\bar{m}P\Delta V_{HB}}{T} - \ln\left(\frac{n+\bar{m}}{n}\lambda_o^{\bar{m}}\right) - \ln\left(\frac{f!}{(f-\bar{m})!\bar{m}!}\right)\right] \quad (1)$$

where ϕ_o is the volume fraction of free water molecules, $\phi_{\bar{m}+1}$ is the volume fraction of m clusters (defined as a polymer molecule with $\bar{m}$ water molecules H-bonded to its backbone), ϕ is the total volume fraction of polymer, and n and f are the number of segments and hydrogen bond sites respectively on a polymer molecule. The ln(λ_o) describes the change in disorientational entropy[16] per bond upon solvation. The parameter χ accounts for poor solvent interactions such as hydrophobic interactions. The four terms within the square brackets, are respectively, (1) the enthalpy of water molecules H-bonding to the polymer backbone, (2) the dilatation energy associated with the hydrogen bond formation, (3) the change in disorientational entropy upon cluster formation, and (4) the combinatorial entropy. Collectively these four terms represent the change in free energy due to cluster formation. We use the complete form of eq 1 to fit our data, whereas Bekiranov et al.[15] used a simplified form in which the approximation ln(1 − $\bar{m}$) ≈ $\bar{m}$ is made. This approximation is acceptable at higher temperatures ($k_BT \geq \Delta\epsilon_0$) where $\bar{m}$ is significantly less than unity, but not at lower temperatures where $\bar{m} \approx 1$.

Table 1. Optimized Values and Uncertainties for Variables in Equation 1 Describing Poly(ethylene oxide) in Water[a]

fitting params	params obtained from the pressure data	params obtained from Matsuyama & Tanaka[8]
$\Delta\epsilon_o$	4180 ± 473	4380
ln(λ_o)	-11.3 ± 1.2	−11.0
A	2.5 ± 0.2	2.9
B (K^{-1})	$3.6 \times 10^{-3} \pm 0.6 \times 10^{-3}$	3.8×10^{-3}
γ (kbar^{-1})	$-8.7 \times 10^{-3} \pm 5.2 \times 10^{-3}$	-----
α (kbar^{-1})	$-9.7 \times 10^{-2} \pm 2.7 \times 10^{-2}$	-----

[a] The parameters found for a full $P-T-C$ fit agree well with those from $T-C$ fits.

The fit parameters and uncertainties are tabulated in Table 1, and compared to the parameters obtained by Matsuyama and Tanaka in their fits to the $T-C$ data obtained by Saeki et al.[7] At this point we should mention that Matsuyama and Tanaka give χ an effective temperature dependence of $\chi = B'/T - A'$ (where they find that $B' = 730$ K and $A' = 0.5$),[8] whereas we use a linear temperature dependence $\chi = A - BT$. Therefore, to obtain the values of A and B shown in the right column of Table 1, we fit the Matsuyama and Tanaka form of χ over the temperature range of the Saeki data to a straight line. In doing so we obtain values of 2.9 and 3.8×10^{-3} K^{-1} for A and B respectively, with a correlation coefficient of $R = 0.996$. Overall, we find that the parameters not associated with pressure ($\Delta\epsilon_o$, ln(λ_o), A, and B) obtained from the fit to the pressure data match the values obtained by Matsuyama and Tanaka in their fit of the $T-C$ phase data of Saeki et al.

With respect to the pressure parameters, a key feature to note is that the value of γ obtained from the fit is slightly negative, although the fit error is large. This indicates that the hydrogen bond strength increases slightly with pressure, which is in contrast to what has been found for PVP in water,[3] and the generally accepted belief that hydrogen bonds weaken with pressure.[11−13] We discuss this further in the conclusions. The sign of α indicates that hydrophobic interactions increase with pressure, a feature which has been observed in other systems, including PVP in water.[3,17−19] The low-temperature UCST is due to an increase in hydrophobic interactions with declining temperature. The ambient pressure UCSTs predicted by the fit parameters are 104 and 124 K for $M_w = 21$ and 1390 kg/mol, respectively. This is significantly

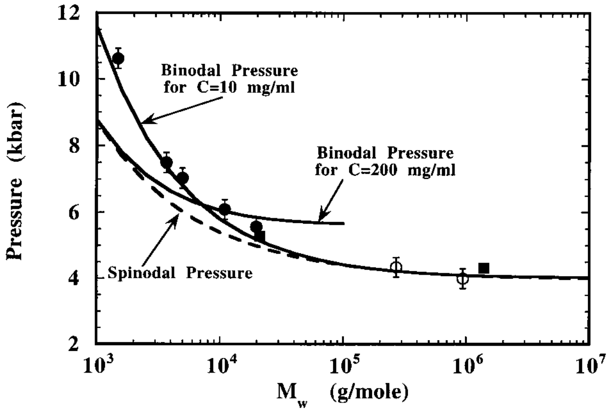

Figure 3. Comparison of the predicted and experimental molecular weight dependence of the spinodal and binodal pressures. The solid and open circles are points obtained by Cook et al. at concentrations of $C = 200$ and 10 mg/mL, respectively.[9] The solid lines are the predicted binodal pressures at the two concentrations; the dashed line is the predicted spinodal pressure at the critical concentration. The solid squares are values obtained at $M_w = 21$ and 1390 kg/mol at $C = 10$ mg/mL.

different from the value of 261 ± 3 K suggested by viscometry measurements.[10]

The unusual reentrant behavior in the $P-T$ plane evidenced by the data in Figure 1 suggests that there exists a point in $P-T-C$ space at which the critical points for the UCST and LCST meet. With experimental data alone this would be very difficult to prove, but utilizing our free energy function, eq 1, along with the parameters in Table 1, we can search for it. Calculating the critical points for the UCST and LCST with increasing pressure, we indeed find that the locus of points for the two critical concentrations approach and meet in a common point. The calculated $P-T-C$ values are (4.9 kbar, 309.6 K, 4.1 wt %) for $M_w = 21$ kg/mol and (4.0 kbar, 308.0 K, 0.5 wt %) for $M_w = 1390$ kg/mol. This thermodynamic invariant point has been designated the hypercritical point (HP) by Schneider.[20] In his review paper he categorizes the eight types of such points that exist theoretically and designates the type found here as HP $- 2T(x)$. In his Table 2, the values of several thermodynamic quantities at such a hypercritical point are listed. As can be anticipated, several derivatives which have differing signs for the UCST and LCST vanish at the hypercritical point. Among these is $(\partial^2 H^E/\partial X^2)$, where H^E is the excess enthalpy. According to his eq 8a, this ensures that dT/dP is infinite at the hypercritical point. This is a generalization of our previous observation using the Claperyron equation.[9]

In Figure 3 we compare the predicted ambient-temperature phase separation pressure to the data obtained by Cook et al.[9] (the lowest molecular weight data point may not be valid because water freezes at pressures above 10 kbar). The molecular weight dependence of these data was unexplained except to note that it exhibits a $M_w^{-1/2}$ scaling of the transition pressure. Recently, we have shown that such a scaling relationship can be obtained by assuming a linear pressure dependence to the enthalpic contributions to the free energy.[3] In the experiments, the phase separation pressures as a function of molecular weight were obtained at concentrations of $C = 200$ mg/mL for $M_w < 10^5$ g/mol and $C = 10$ mg/mL for $M_w > 10^5$ g/mol; these points are plotted as solid and open symbols, respectively. The dashed line represents the spinodal pressure at the critical concentration predicted by the parameters shown in Table 1; the solid lines represent the predicted binodal pressures at concentrations of $C = 200$ and 10 mg/mL. As shown in Figure 3, the spinodal and binodal pressures are essentially equal over a large concentration range for high molecular weights but deviate strongly for low molecular weights. Significantly, the data follow the binodal behavior. Hence, as seen in Figure 3, the spinodal and binodal pressures overlap and both agree well with the two highest molecular weight data. At lower molecular weights where the deviation of the binodal from the spinodal is much greater, the match between the predicted and experimental values for the binodal pressures is not as good; in fact, the data seem to correspond more to the predicted binodal pressure at $C = 10$ mg/mL instead of at $C = 200$ mg/mL where the data was taken. The discrepancy may be due to the conversion of polymer concentration to volume fraction; in performing this conversion, we assumed that each monomer unit has one segment length (as did Matsuyama and Tanaka).

It is useful to compare the phase behavior of PEO in water to that of PVP in water. Both polymers exhibit reentrant behavior in their $P-T$ phase behavior. A key difference, however, is in the pressure dependence of their LCSTs. For pressures up to 3 kbar the LCST of PVP declines much more rapidly than that of PEO (see Figure 1).[3] As a result, the fitted pressure dependence of the hydrogen bond strength, $\Delta\epsilon \propto 1 - \gamma P$, is much larger for PVP than PEO ($\gamma = 2.6 \times 10^{-2}$ kbar^{-1} for PVP as opposed to -8.7×10^{-3} kbar^{-1} for PEO). The physical reason for this difference is not presently understood. The hydrogen bond strength, $\Delta\epsilon_0$, for PEO is 14.3 k_BT, as opposed to 26.7 k_BT for PVP. This is consistent with the generally accepted belief that ether groups (as on PEO) form weaker hydrogen bonds than amide groups (as on PVP). The values of $-\ln(\lambda_o)$, which may be thought of as the change in ΔF_{mix} due to hydrophobic hydration, for PEO and PVP are $11.3k_B$ and $17.8k_B$ respectively, consistent with the smaller hydrophobic component per monomer unit for PEO than PVP. Thus we see that the values from the fits using this model are in accord with our chemical intuition. This suggests that this model's parametrization of the hydration effects for nonionic polymers could be widely applicable.

IV. Conclusion

In conclusion, by using pressure we have observed the presence of a low temperature UCST for PEO in water. Previous viscometry measurements have hinted at the presence of this UCST. The LCST declines with pressure, albeit more slowly than for PVP in water. The concentration dependence of the phase separation pressure is weak, especially for the higher molecular weight sample. We fit these data to a modified Flory–Huggins model which includes a linear pressure dependence to the hydrogen bond strength, and a linear temperature and pressure dependence to the hydrophobic interactions. The parameters obtained from the fit indicate that (a) the effective hydrogen bond strength weakly increases with pressure, (b) the low-temperature UCST is due to an increase in hydrophobic interactions with decreasing temperature, and (c) hydrophobic interactions increase with pressure. The last two conclusions are in accordance with results found for PVP in water; however, the first is contrary to what has been found for PVP in water. The differences in both sign and magnitude cause the large qualitative difference in the $P-T$ phase behavior at higher temperatures seen in Figure 1.

In trying to understand the origin of this difference in behavior, we note that the effective hydrogen bond strength, $\Delta\epsilon$, is given by $\Delta\epsilon = \epsilon_{pw} - (\epsilon_{ww} + \epsilon_{pp})/2$, where ϵ_{pw}, ϵ_{ww}, and ϵ_{pp} are the polymer−water, water−water, and polymer−polymer hydrogen bond strengths. In fitting the data we assigned a linear pressure dependence to the quantity $\Delta\epsilon$ and found that for PEO in water it increases with pressure. It is conceivable, however, that ϵ_{pw} and ϵ_{ww} exhibit different pressure dependencies. For instance, if both ϵ_{pw} and ϵ_{ww} decrease with pressure, but ϵ_{ww} decreases more rapidly, the net result may be that $\Delta\epsilon$ increases with pressure. In this situation the hydrogen bond would indeed weaken with pressure, as expected,[11] but the effective hydrogen bond strength would increase, as indicated by the fit to the PEO data. Another point to consider is that PEO in water is considered unusual even among water-soluble polymers. Neither poly(oxymethylene), which is chemically similar to PEO, but has one fewer carbon molecule per monomer unit, nor poly(propylene oxide), which has one more carbon molecule per monomer unit, is soluble in water.[10] It has been suggested[21] that this unusual solubility is due to a unique packing arrangement of PEO molecules in the water structure. If true, this packing arrangement could be disrupted by application of pressure, an effect not accounted for by our modified Flory−Huggins model used above.

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