$$\left\langle \exp\left\langle \frac{i\mathbf{k}}{L} \sum_{\substack{p'=-\infty \\ p'\neq p}}^{\infty} \mathbf{R}_\alpha(p',t)(e^{2\pi i p' s_\alpha/L} - e^{2\pi i p' s_\alpha'/L}) \right\}\right\rangle_{\{p'\}\neq p} = \exp\left\{ -\frac{k^2}{3} \int_{-\infty}^{\infty} \frac{\mathrm{d}q}{2\pi}\, \frac{l_1(q)}{q^2} [1 - \cos q|s - s'|] \right\} = \exp(-k^2 l_1 |s - s'|/6) \quad (\text{A.8})$$

We have assumed that l_1 is dependent only on the first mode in obtaining the second equality of (A.8). Substitution of (A.8) into (A.7) gives

$$\mathcal{A} = -\frac{2k_\mathrm{B}T}{3L} \int_0^L \mathrm{d}s_\alpha \int_0^L \mathrm{d}s_\alpha' \int \frac{\mathrm{d}^3k}{(2\pi)^3}\, k^2 \Delta(k) \times \sin^2\left(\frac{q|s_\alpha - s_\alpha'|}{2}\right) e^{-k^2 l_1 |s_\alpha - s_\alpha'|/6} \mathbf{R}_\alpha(q,t) \quad (\text{A.9})$$

Combining (A.3), (A.6), and (A.9) yields

$$Lq^2\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{2}{9} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \int \frac{\mathrm{d}^3k}{(2\pi)^3}\, k^2 \Delta(k) \times \sin^2\left(\frac{q|s - s'|}{2}\right) e^{-k^2 l_1 |s - s'|/6} \quad (\text{A.10})$$

This is exactly the same equation as (4.8a) of ref 11, which was obtained by a different method using a variational procedure. Since we are here interested in the small-q limit only, we expand the sine to get

$$\frac{1}{l} - \frac{1}{l_1} = \frac{w}{18\pi^2 L} \int_0^\infty \mathrm{d}k\, \frac{k^6}{k^2 + \xi_\mathrm{s}^{-2}} \int_0^L \mathrm{d}s \int_0^s \mathrm{d}s' \,(s - s')^2 e^{-k^2 l_1 (s - s')/6} = \frac{24w}{\pi^2 l_1^3} \int_0^\infty \mathrm{d}k\, \frac{1}{k^2 + \xi_\mathrm{s}^{-2}} \quad (\text{A.11})$$

which is the same as (4.11). Equation 4.9 is used in obtaining the first equality of (A.11).

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Microcalorimetric Study of Poly(ethylene oxide) in Water and in Water–Ethanol Mixed Solvent

Hubert Daoust* and Daniel St-Cyr

Department of Chemistry, Université de Montréal, Montreal, Quebec, Canada H3C 3V1.

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ABSTRACT: Intermediate heats of dilution, heats of mixing, and heat capacities have been measured in the dilute and intermediate concentration ranges for the poly(ethylene oxide) (PEO)–water and PEO–water–ethanol systems. Heats of dilution are exothermic for all systems and pass through a minimum at 50% by weight of ethanol. Heats of fusion of PEO in water and in 50% water–ethanol calculated from the combined heat of dilution and heat of mixing results are 9564 and 10 224 J basemol^{-1}, respectively. Apparent basemolar heat capacity ($C_{p,\phi}$) has been determined for PEO. In water, results show that $C_{p,\phi}$ decreases with increasing concentration and that $C_{p,\phi}$ at infinite dilution decreases with decreasing molecular weight. The value of $C_{p,\phi}$ increases with increasing temperature. Values of $C_{p,\phi}$ in water–ethanol go through a minimum at 30% by weight of ethanol. The results do not support very strongly the existence of an ordered structure for PEO in solution in water. However, they are in very good agreement with the conclusion of a recent light scattering study of the same system assuming that aggregates coexist with molecularly dispersed PEO.

Introduction

Poly(ethylene oxide) (PEO) is a well-known polymer, and its high solubility in water makes it a very interesting industrial material. It is known to be crystalline[1,2] and to have a 7_2-helical conformation in the solid state.[3] Most of the experimental results on PEO solutions lead to the conclusion that the polymer is in its disordered or coiled form in organic solvents.[1,2,4-7] However, the situation is not as clear when water is used as solvent. Some experimental results indicate that PEO in aqueous solutions retains some of its crystalline structure[1] or sees its helical structure changed to a new, less ordered but not completely disordered one.[2] Other experimental results indicate a behavior of PEO molecules in aqueous solution similar to that in organic media, at least for low molecular weight samples.[4,6] The chain expansion of PEO in water is believed to be due to the formation of H bonds between water molecules and oxygen atoms of the chain.[8-10] Experimental results seem to indicate that three water molecules are bound to each PEO oxygen.[1,2,4,10]

Other investigators[11] have assumed a non-free-draining coil model for PEO in aqueous media and they have shown that the chain adopts a more compact conformation as the temperature increases. This is probably due to an increase in the free rotation of chain links accompanied by a weakening of polymer–solvent interactions, leading to a chain contraction. Viscosimetric results[12] support these last observations. Finally, density measurements[13] have shown that the partial molar volume of PEO repeating units in water is the same as for the free monomer. These results indicate that the polymer chain is highly extended, thus giving water molecules free access to the backbone. More recently, a static light scattering study on PEO aqueous solutions leads to the conclusion that aggregates

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of high and low density coexist with molecularly dispersed chains.[14] The high-density aggregates are assumed to be spherulites and the low-density aggregates, noncrystalline microgel particles.

Many calorimetric studies of PEO in solution in aqueous and organic media are reported in the literature. Endothermic heats of dilution have been observed for solutions of ethylene glycol and oligomers of molecular weight up to 600 in different alcohols.[15] Heats of dilution of aqueous solutions of PEO as a function of molecular weight have been shown to be exothermic and to increase in absolute value as molecular weight decreases.[16] Heats of solution and heats of dilution of PEO in water and in organic solvents have been measured,[7] and the results show that the heat of fusion of PEO has the same value in two different organic solvents but is much lower in water. This difference has been attributed to the helical structure, which would be retained in part in water. However, the reported value for the enthalpy of formation of this structure is about twice as large as those estimated for the enthalpy of formation of the α-helix.[17,18] Recently, heats of dilution and heat capacities of aqueous solutions of PEO have been measured with a modified Tian–Calvet microcalorimeter.[19]

Heat capacity measurements have been of great interest in the thermodynamic investigation of systems containing small molecules[20] and of systems containing biopolymers.[21,22] However, results from heat capacity measurements of solutions by themselves are not of great interest for an investigation of molecular behavior in solution. The apparent molar heat capacity at constant pressure ($C_{p,\phi}$) is of much greater interest since its value is much more sensitive to the molecular structure. A great precision on heat capacity measurements of solutions is needed in order to calculate $C_{p,\phi}$, which is defined by

$$C_{p,\phi} = (C_{p_{12}} - n_1 C^\circ_{p_1})/n_2 \qquad (1)$$

where $C_{p_{12}}$ is the heat capacity at constant pressure for the solution, $C^\circ_{p_1}$ is the same quantity for the pure solvent, and n_1 and n_2 are the number of moles of the solvent and the solute, respectively. Reliable $C_{p,\phi}$ values have been obtained with a Picker flow microcalorimeter for ethylene glycol, its oligomers, and polymers with degree of polymerization up to 136 in solution in water and in aqueous solutions of urea.[23]

In the present work is reported a microcalorimetric study including heat of mixing, heat of dilution, and heat capacity measurements of PEO in solution in water and in water–ethanol mixed solvent. These measurements have been done in order to learn more about the energy related to the controversial structure of PEO in aqueous media.

Experimental Section

Chemicals. Three commercial samples of PEO (PEG 2000, 4000, and 20 000, Dow Chemical Co.) were used as received. Each polymer sample has been analyzed by thermogravimetry for water content before its use. Distilled deionized water and distilled azeotropic water–ethanol mixture were used as solvents. Solutions were prepared gravimetrically.

Calorimetry. Heats of solution and heats of dilution were measured with a Tian–Calvet microcalorimeter[24] equipped with 25-mm-diameter cells. The thermoelectric piles were made of 750 thermocouples. The dilution cell of 30-mL capacity and the dilution technique have been described elsewhere.[25] About 10 g of a solution whose initial polymer concentration varied from 20 to 1.5% by weight was introduced in the inner tube of the cell and about 20 g of solvent was introduced in the outer tube. Heats of solution were measured in the same type of cell; the dry polymer was introduced in the inner tube, which was plugged with a hollow Teflon cap filled with mercury. The solvent was introduced in the outer tube; the mixing was simply done by tilting the microcalorimeter.

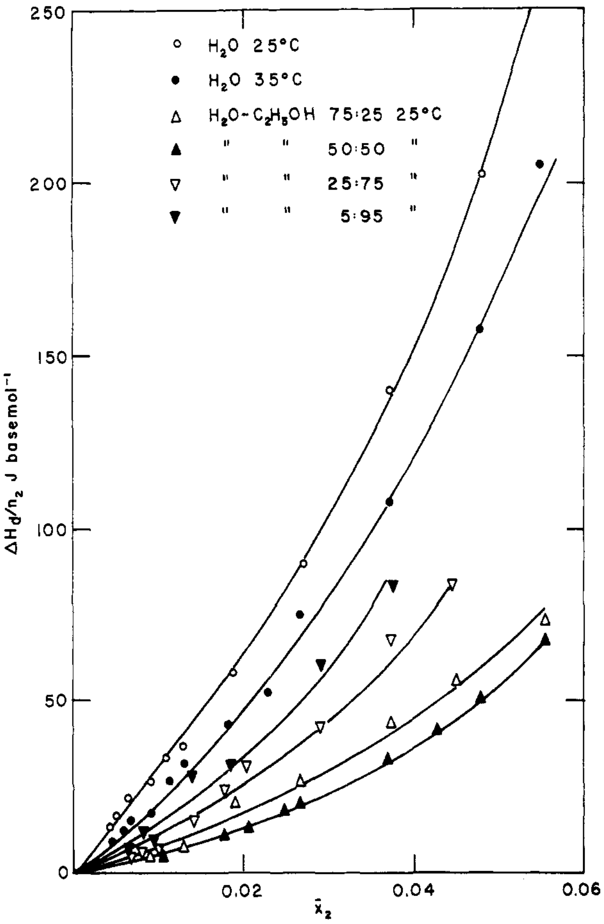

Figure 1. Variation of the intermediate heat of dilution with the average basemolar fraction for PEG 20 000 solutions. The mixed-solvent composition is defined on a weight percent basis.

Volumetric heat capacities were measured with a Picker flow microcalorimeter Model CP-D of high sensitivity (5×10^{-5} J K^{-1} mL^{-1}) with a precision of ±0.3% up to the limit of sensitivity.[26] The instrument is basically a thermal balance made of twin flow cells. Under similar conditions of heat and liquid flow, any difference in heat capacities of the liquids in the cell will cause a difference in the final equilibrium temperature. The solvent was pumped through the instrument first followed by the solution so that the flow rate was kept strictly the same in the twin cells. In order to avoid any heat effect from the large dilution front due to the high viscosity of concentrated polymer solutions, a 5-m-long line connecting the cells was used. Volumetric heat capacities were converted to specific heat capacities by dividing them by the densities of the solutions measured with a Picker flow densimeter Model 03D.[27] A high precision is needed in the determination of $C_{p_{12}}$ in order to obtain an acceptable value for $C_{p,\phi}$ for any solute. For instance, for a 0.1 m solution of PEG 20 000, an absolute error of ±0.0002 in $C_{p_{12}}$ produces an error of ±2 in $C_{p,\phi}$. In the dilute range (~0.02 m), the same error in $C_{p_{12}}$ produces an error of ±16 in $C_{p,\phi}$. For these reasons, we believe the flow microcalorimeter to be more suitable than the modified Tian–Calvet microcalorimeter for $C_{p_{12}}$ measurements.

Results and Discussion

The variation of the basemolar intermediate heat of dilution with the average polymer basemole fraction ($\bar{x}_2$) for PEG 20 000 in solution in water and in water–ethanol mixed solvent is shown for different ethanol contents in Figure 1. All dilutions are exothermic and they show an increase with the polymer concentration of the Flory–Huggins enthalpic interaction parameter, defined by[28]

$$\kappa = \Delta H_d/RTn_2(x_2 - x_2') \qquad (2)$$

Table I
Heats of Solution and Heats of Fusion for PEG 20 000 at 25 °C

w_2, g	w_1, g	ΔH_s, J	ΔH_m, J basemol^{-1}	ΔH_f, J basemol^{-1}
		H_2O		
0.257_7	13.939_2	2.28_0	-9182	9573
0.197_7	9.871_6	0.81_1	-9181	9361
0.784_7	10.439_1	12.28_1	-9083	9772
1.010_8	10.095_6	12.55_3	-9031	9579
1.522_3	10.185_1	21.90_7	-8921	9555
2.000_3	9.995_5	33.72_9	-8797	9544
		50:50 H_2O-C_2H_5OH by Weight		
0.101_0	12.807_0	2.09_9	-4368	10390
0.158_4	10.099_4	6.69_6	-6025	10119
0.505_2	10.102_9	65.25_6	-4361	10051
0.751_7	10.002_0	99.28_3	-4352	10170
0.994_0	9.929_4	136.33_7	-4344	10386

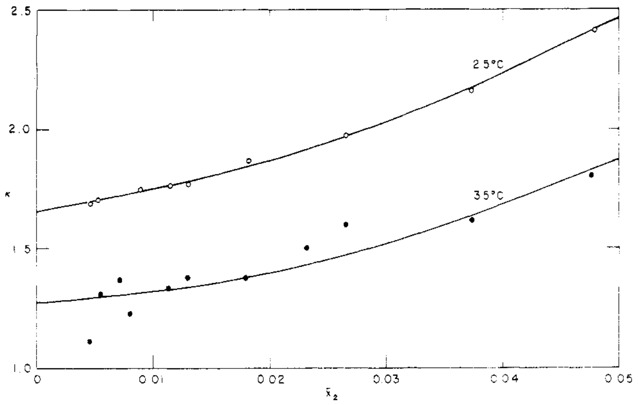

Figure 2. Concentration dependence of the enthalpic interaction parameter for PEG 20 000 in water.

where ΔH_d is the measured heat of dilution, n_2 is the number of moles of polymer segments, and x_2 and x_2' are the mole fractions of segments before and after the dilution. This concentration effect on κ is shown in Figure 2 for PEO in water at 25 and 35 °C; on the volume fraction basis (ϕ_2), κ values are about half those given here since $x_2 \simeq 2\phi_2$ for this system. Results of Kagemoto et al.[16] on the same system show also a concentration effect but their values for κ are about an order of magnitude smaller than those reported here; they also found the absolute value of κ to increase rapidly with decreasing molecular weight, especially for short chains. Experimental results of Maron and Filisko at 30 °C,[7] when treated according to eq 2, give κ values intermediate between ours at 25 and 35 °C and show also a concentration effect. Schönert and Monshaussen[19] have calculated an average value of −2.38 for κ at 25 °C over the concentration range they investigated ($\bar{x}_2$ = 0.016–0.1) for the two PEO samples they used compared to −1.9 for the concentration range covered in the present work. When κ values calculated at the same $\bar{x}_2$ value from the two sets of data are compared, the agreement is very good.

The increase of κ with the polymer concentration may be explained by the fact that at higher concentration, chain entanglement is important and segment–segment contacts are many. Upon dilution in this concentration range chains are separated, and more energetically favorable segment–solvent contacts per chain are created. As dilution progresses, less segment–solvent contacts per chain are formed, leading to lower absolute values for κ. An equivalent explanation for this concentration effect may be found in the results of Polik and Burchard.[14] Since, according to their conclusion, an equilibrium between microgel particles and molecularly dispersed PEO exists in the dilute range for the PEO–water pair, one can expect to find the existence of this gel at much higher polymer concentration. The dilution of the gel favors the access of water molecules to the polymer chains, enhancing the formation of H bonds and hydrophobic hyration. The formation of H bonds is known to be strongly exothermic,[29] whereas the sign of the contribution of hydrophobic hydration to the enthalpy of dilution depends on temperature.[30,31] At room temperature, the latter contribution is exothermic and, of course, the combined effect of the two phenomena becomes less important as concentration decreases.

When ethanol is added to the system, there is a rapid decrease in the absolute values of heats of dilution, followed by an increase as the ethanol content further increases. These results can be explained by the existence of the strong interaction between water and ethanol. The high exothermic heat of mixing of the two liquids is mainly due to the formation of H bonds between the two protic solvent molecules. This mixed solvent at low ethanol content is a poorer solvent for PEO than water since both PEO and ethanol compete with each other to form H bonds with water molecules. Moreover, the formation of microgels is probably less important in the presence of ethanol, leading to a less structured system, which implies a less exothermic enthalpy of dilution. As the ethanol content increases, more free ethanol molecules are available to interact with PEO segments, creating H bonds between the two species. This is why heats of dilution become more exothermic as ethanol content increases beyond 50% by weight.

The heat of fusion of PEO was reported to be 3280, 10 451, and 10 598 J basemol^{-1} in water, chloroform, and methylene chloride, respectively, by Maron and Filisko.[7] According to these results, the heat of formation of the helix in water would be −7243 J basemol^{-1} as compared to the value of −3000 to −4000 J basemol^{-1} for the α-helix,[17,18] which is a much more stable helix than the one assumed for PEO. This result is rather surprising. The present data on heat of dilution for PEG 20 000 in solution in water and in 50:50 water–ethanol mixed solvent have been treated according to Maron and Filisko's treatment, and the results are shown in Figure 3, where X_d is the heat of dilution parameter and ϕ_2 and ϕ_2' are the polymer volume fractions before and after the dilution. Contrary to Maron and Filisko's results in water, there is an important concentration effect on X_d in both solvents. In order to determine the heat of fusion (ΔH_f) of the polymer, heats of solution (ΔH_s) have been measured. The results are given in Table I, where ΔH_m is the calculated heat of mixing according to Maron and Filisko's treatment. The calculations give

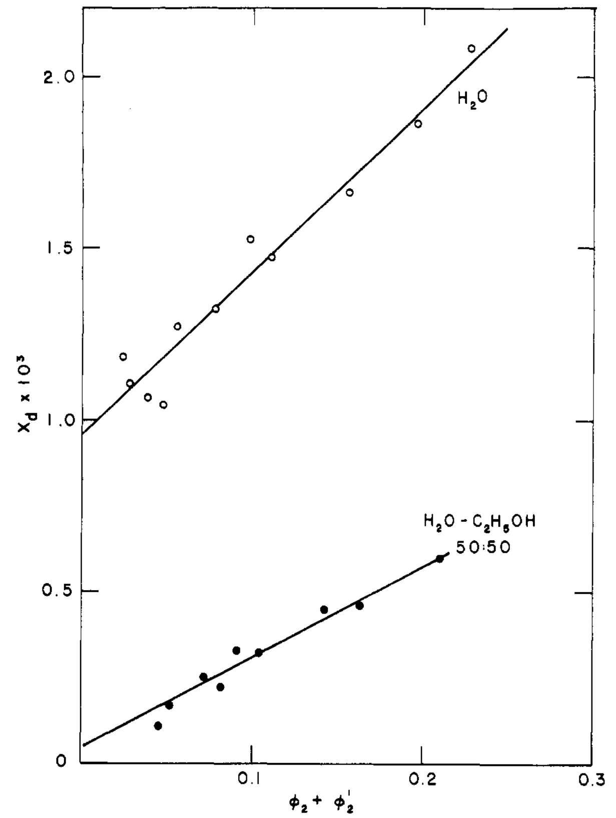

Figure 3. Concentration dependence of the heat of dilution parameter for PEG 20 000 at 25 °C.

9564 and 10 224 J basemol^{-1} for water and for the water-ethanol pair, respectively. The value for ΔH_f in the latter solvent agrees very well with those reported by Maron and Filisko for organic solvents. The difference between the heat of mixing in water and in the mixed solvent (−660 J basemol^{-1}) would be due to the residual helical structure retained by PEO in water,[1] to the formation of a new, less ordered structure,[2] or to the enthalpy of formation of the PEO–water complex,[1,2,4,10] which implies, of course, a partial destruction of the water structure in order to form this complex. The formation of microgel particles in water[14] is probably more important in water than in the mixed solvent, and this can also explain the difference in the heats of mixing of PEO in each media.

Values of $C_{p_{12}}$ for all three PEO samples in water almost fall on the same curve for all concentrations. Results obtained for PEG 20 000 are compared with those obtained by Schönert and Monshaussen[19] for a lower molecular weight (2000) in Figure 4. Obviously, the Picker system is more appropriate than the Tian–Calvet modified system to measure $C_{p_{12}}$ of high-polymer solutions. Values of $C_{p,\phi}$ (defined for a basemole) as a function of the basemole fraction of the polymer are given in Figure 5 for the three polymer samples. Extrapolation of the results to infinite dilution indicates a small variation as a function of the molecular weight, the effect being more noticeable for the shorter chains. The absolute value of the negative slope of $C_{p,\phi}(x_2)$ is also lower for the lower molecular weight sample. These facts are due to a combination of many factors. The enthalpy of mixing comes first to mind since

$$C_{p_{12}} = \left(\frac{\partial H_{12}}{\partial T}\right)_p = n_1\left(\frac{\partial H^\circ{}_1}{\partial T}\right)_p + n_2\left(\frac{\partial H^\circ{}_2}{\partial T}\right)_p + \left(\frac{\partial \Delta H_m}{\partial T}\right)_p \quad (3)$$

where H_{12} is the enthalpy of the solution and $H^\circ{}_1$ and $H^\circ{}_2$ are the molar heat contents of the pure solvent and of the pure solute, respectively, in their liquid states. For nonelectrolyte solutions, ΔH_m can be defined by[32]

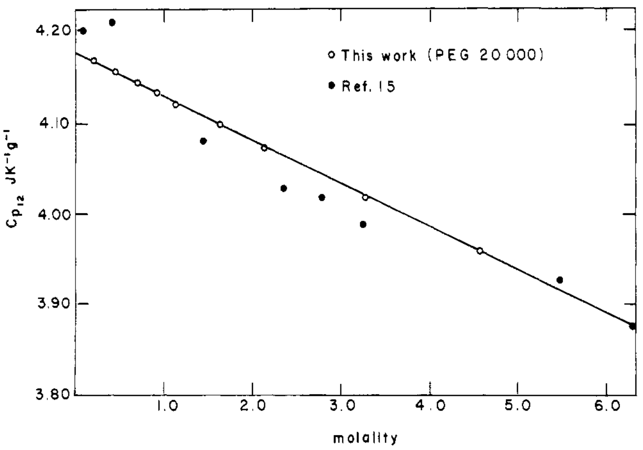

Figure 4. Comparison between values of the specific heat capacity for PEO solutions in water at 25 °C as measured by two different experimental techniques.

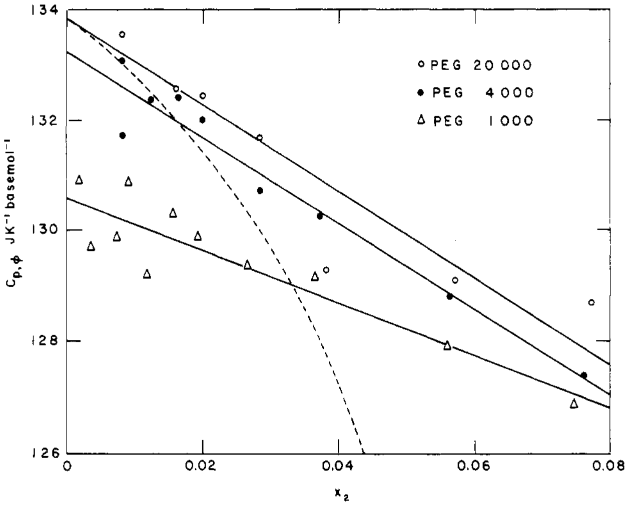

Figure 5. Concentration dependence of the apparent molar heat capacity of PEO in water at 25 °C. Values calculated according to eq 8 are represented by the broken line.

$$\Delta H_m = RT\kappa n_2 x_1 \quad (4)$$

Then from eq 3 and 4

$$C_{p_{12}} = n_1 C^\circ{}_{p_1} + n_2 C^\circ{}_{p_2} + n_2 x_1 R\left[\kappa + T\left(\frac{\partial\kappa}{\partial T}\right)\right] \quad (5)$$

$$= n_1 C^\circ{}_{p_1} + n_2 C^*{}_{p_2} - n_2 x_2 R\left[\kappa + T\left(\frac{\partial\kappa}{\partial T}\right)\right] \quad (6)$$

where

$$C^*{}_{p_2} = C^\circ{}_{p_2} + R\left[\kappa + T\left(\frac{\partial\kappa}{\partial T}\right)\right]_{x_2=0} \quad (7)$$

is the heat capacity of the polymer at infinite dilution in a given solvent. The quantity $C^\circ{}_{p_2}$ is the same quantity for the pure polymer in its liquid or disordered state. Since κ is concentration dependent for many polymer–solvent systems, it is then necessary to calculate the second term on the right-hand side of eq 7 at infinite dilution. Finally, from eq 1 and 6

$$C_{p,\phi} = C^*{}_{p_2} - x_2 R\left[\kappa + T\left(\frac{\partial\kappa}{\partial T}\right)\right] \quad (8)$$

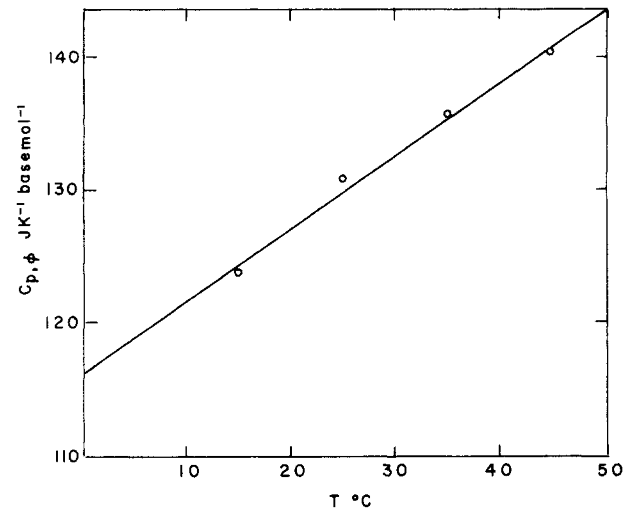

Figure 6. Effect of the temperature on the apparent molar heat capacity of PEG 20000 in water. Polymer concentration: 2% by weight.

As seen from Figure 2, κ is negative and $\partial\kappa/\partial T$ is positive; the quantity $R[\kappa + T(\partial\kappa/\partial T)]$ is then positive and is concentration dependent. Calculated $C_{p,\phi}$ values from eq 8 are compared to experimental ones for PEG 20000 in Figure 5, and the results show a strong negative effect due to the heat of mixing. According to Kagemoto et al.,[16] the value for κ for aqueous PEO solutions becomes more negative as the molecular weight of the polymer decreases. The same observation has been obtained from indirect determination of heats of dilution for PEO in water by vapor pressure measurements in the high-concentration range.[33] Assuming that $\partial\kappa/\partial T$ does not vary appreciably with the chain length, the value of $C^*_{p_2}$ should decrease as the molecular weight decreases according to eq 6, in agreement with experimental results.

Another important factor affecting $C_{p,\phi}$ values as the polymer concentration increases is the chain entanglement, which reduces the degree of freedom of the chain segments. Alternatively, if the gel structure prevails in the case of PEO in water, its negative effect on the heat capacity of the system[34] would be more severe as the polymer concentration increases. This follows from assuming that gelification and micellization in aqueous media basically involve the same type of molecular interactions, that is, the formation of hydrophobic bonds between solute molecules and hydrophilic contacts between the solute and the water molecules. However, the combined negative contributions of the heat of mixing and of the chain entanglement or of the increase in the gelification process should affect $C_{p,\phi}$ values more severely in the negative direction than shown experimentally. This might be due to the increase in the number of "free" water molecules per chain segment as the concentration increases. In fact, the accessibility of segments to water molecules decreases with increasing concentration, reducing the number of contacts between water molecules and polymer segments to finally give a higher value than expected for $C_{p_{12}}$.

The variation of $C_{p,\phi}$ with the temperature for PEG 20000 in water at a fixed concentration is shown in Figure 6. Results show that $C_{p,\phi}$ increases rapidly with the temperature, in apparent contradiction with the results of Polik and Burchard.[14] The enthalpy parameter κ can be related to the second virial coefficient A_2 through the relation $\kappa = KT(\partial A_2/\partial T)_p$, where K is a proportionality constant depending on the way the composition of the solution is defined. In dilute polymer solution, A_2 is a direct function of the volume excluded by the chain and then $C_{p,\phi}$ increases as A_2 increases since the rotational contribution to the heat capacity is proportional to the average moment of inertia of the chain. Polik and Burchard have shown that as the radius of gyration stays constant between 20 and about 50 °C, A_2 decreases. The apparent contradiction is probably due to the existence of aggregates of high density (spherulites) in equilibrium with aggregates of low density (noncrystalline microgel particles) in the dilute range.[14] As temperature increases from 20 to 60 °C, spherulites partially melt and the equilibrium is displaced in favor of the microgels. So, the structure of the whole system becomes less ordered, leading to an increase in its heat capacity.

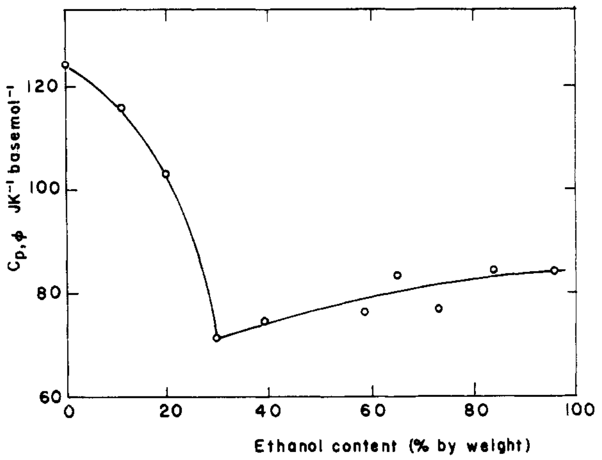

Figure 7. Effect of the ethanol content on the apparent molar heat capacity of PEG 20000 in water–ethanol mixed solvent at 25 °C. Polymer concentration: 2% by weight.

The variation of $C_{p,\phi}$ of PEG 20000 in water–ethanol mixed solvent as a function of ethanol content is shown in Figure 7. The rapid decrease in $C_{p,\phi}$ down to a value slightly above that reported for PEG 20000 in its pure solid state (65.9 J K^{-1} basemol^{-1})[35] at low ethanol content may be explained by a more compact structure of PEO in the presence of the organic solvent, in agreement with many experimental results mentioned in the Introduction. This change in the polymer structure may be explained by the lowering of the solvent power of the water–ethanol pair due to the formation of H bonds between water and ethanol molecules, which compete with the polymer–solvent interactions. Further addition of ethanol beyond the minimum value of $C_{p,\phi}$ appearing at 30% by weight of ethanol seems to contribute to increase the solvent quality. The organic solvent molecules not implicated in water–ethanol interactions would be available to interact with the polymer chain by the formation of H bonds between ethanol molecules and chain segments. This explanation is supported by the results obtained from heat of dilution measurements. Recent results obtained for PEO[36] in 1-propanol show that the polymer chain presents a more compact structure than in water due to a much lower H-bonding capacity of propanol.

Conclusion

The microcalorimetric results reported in this work do not support very strongly the existence of an ordered structure for the PEO chain in water. However, they are in good agreement with the conclusion reached by Polik and Burchard[14] that crystalline aggregates coexist with noncrystalline microgel particles. This equilibrium is displaced in favor of microgels as temperature is increased to 45 °C, the maximum temperature at which heat capacity measurements have been done. The PEO water complex is probably responsible for the formation of the aggregates;

these aggregates may results from cross-links between PEO chains through the hydrated oxygen atoms.

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Registry No. PEO, 25322-68-3.

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Distribution of Random-Flight Polymer Chains in Solution near a Barrier[†]

Edward F. Casassa

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.
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ABSTRACT: The problem of the equilibrium distribution of polymer chains in solution near an impenetrable but otherwise passive plane boundary is investigated with the assumption of random-flight statistics. Explicit expressions are obtained for the distributions of segments from specified positions (e.g., end segments and middle segments) along the contours of linear chains. A numerical integration leads to the total segment concentration profile in the depletion layer near the boundary. Some analytic properties of the segment profiles are discussed.

Introduction

When a flexible polymer chain in solution is placed near a nonabsorbing but impenetrable barrier, it is in an unfavorable entropy situation with respect to the bulk solution phase in that it is denied conformations that would be available to it in the absence of the barrier. The chain thereby experiences an effective repulsion from the barrier, and at equilibrium there exists near the barrier a depletion layer, in which the polymer chain-segment concentration increases from zero at the surface to approach the uniform value in the bulk phase. In the years since Asakura and Oosawa[1] first described this phenomenon, it has been invoked as the basis for the effect of dissolved polymer on stability of colloids[2-10] and for polymer fractionation by liquid size-exclusion (gel permeation) chromatography.[11,12] In chromatography, the net rejection of polymer chains from a micropore (the change in equilibrium polymer concentration between the pore and the bulk phase) and its dependence on chain length are of primary concern; but discussions of colloid effects focus more specifically on the character of the depletion layer. Another reason for interest in the depletion layer is that it is currently being studied directly by optical methods.[13]

In recent years several investigators have used computer simulation of lattice walks to model polymer chains in the depletion layer.[7-9] Such numerical approaches have the advantage that it is relatively simple to introduce the realistic complications of adsorption of polymer at the surface and interactions between chain segments. They have the disadvantage of not always affording the basic insight and revelation of subtle effects that even an extremely idealized analytic theory may provide.

In the following, we describe calculations of concentration profiles of polymer segments near a plane barrier (or large smooth colloidal particle). Since the derivation assumes random-flight statistics, the model can be applied rigorously only to a polymer in a Θ solvent. It has apparently not been noted that some simple analytic results

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