

Investigation of Phase Behavior and Water Binding in Poly(alkylene Oxide) Solutions

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Synopsis

The aqueous solution properties of alkylene oxide polymers and copolymers are related to their interaction with water. In an attempt to better understand this behavior, differential scanning calorimetry has been employed to measure phase changes and water binding in solutions of polyethylene glycol (PEG), polypropylene glycol (PPG), and a 50/50 random copolymer of ethylene oxide and propylene oxide. PEG ($\bar{M}_n = 3510$) forms a crystalline eutectic with water at 0.48 weight fraction of polymer. The liquidus curve for water can be fit accurately using the Flory-Huggins expression for solute activity with an interaction parameter of 0.05. PPG and the random copolymer do not crystallize and thus do not form a crystalline eutectic. Based on decreases in the heat of fusion of free water with added polymer, PEG binds more water than the copolymer which binds more water than PPG. The estimated hydration numbers per polymer segment are 1.5 for PPG, 2.3 for the copolymer, and 2.7 for PEG.

INTRODUCTION

The phase behavior and physical properties of polyethylene glycol (PEG) have been studied by numerous investigators.¹ However, except for rheological behavior, relatively little work has been published on the properties of polyethylene glycol-water solutions. In this study we use differential scanning calorimetry to investigate the phase behavior and water binding in aqueous solutions of PEG, polypropylene glycol (PPG), and a random copolymer of ethylene oxide and propylene oxide.

The utility of DSC for determination of phase diagrams has been demonstrated recently in several publications.²⁻⁴ Eutectic crystallization, a common occurrence in inorganic solutions, has also been reported³⁻⁶ for several polymer solutions where the polymer and solvent have similar melting points. DSC has also been used to study water binding in solutions of various biological systems.⁷⁻⁹ The nonfreezing water is determined from the decrease in heat of fusion of water at various solute levels. Reasonable agreement has been found between DSC and NMR techniques for measuring bound water^{9,10} in cellulosic materials.

EXPERIMENTAL

The poly(alkylene oxides) used in this study are commercial products of Union Carbide Corporation. The polyethylene glycol series, designated PEG 400, 1000, 4000, and 6000, are sold under the trade name Carbowax, and the polypropylene glycol, PPG 425, is sold under the trade name Niax polyol. The ethylene oxide/propylene oxide copolymer, designated PEG-PG 3520, is a random copolymer containing 50% ethylene oxide by weight and 50% propylene oxide by

weight. It is sold under the trade name Ucon 50HB-3520. The number given with each of these polyalkylene oxides is a rough indication of the number-average molecular weight. All aqueous solutions were made with freeze-dried polymers and deionized water.

For the PEG series, the weight-average molecular weights were determined in water at 25°C using a KMX-6 low-angle laser light scattering photometer (Table I). Approximate number-average molecular weights were then obtained by assuming a polydispersity of 1.1. The validity of this polydispersity was confirmed by GPC analysis using a Waters model ALC/GPC 244 liquid chromatograph operating in chloroform with five μ -Styragel columns (100, 500, 10^3 , 10^4 , and 10^5 Å).

A du Pont 990 thermal analyzer with a model 910 differential scanning calorimeter (DSC) cell base was used to measure the differential heat flux-versus-temperature curves. This instrument is interfaced¹¹ with a Digital Equipment Corporation PDP-11/40 minicomputer system to facilitate data reduction. The functions performed by the computer include (1) real time data acquisition and storage, (2) conversion of heat flux to specific heat change and integration of melting peaks to give heats of fusion, and (3) normalization and plotting of data for reporting and comparison.

The DSC scans were made on similarly sized specimens (10 ± 3 mg) sealed in hermetic DSC cups. These were used to avoid water loss through evaporation. An empty hermetic cup was used as the reference. The DSC cell was purged with dry nitrogen to avoid moisture condensation during low-temperature operation. Specimens were program cooled at 2 K/min from above the highest melting peak to 223 K by flowing dry nitrogen gas through a cooling coil immersed in liquid nitrogen and then into the DSC block through the coolant entrance. The slow cooling and heating rates were used to obtain a high degree of crystallinity and to minimize deviations from equilibrium during the DSC warm-up scans. Pure water, also run at 2 K/min, was used to calibrate the DSC temperature scale (melting onset adjusted to 273.2 K) and the enthalpic response ($\Delta H = 334$ J/g).

Figure 1 shows the DSC scans obtained for a series of PEG 4000 solutions. As can be seen, isolated and overlapping peaks are encountered. Heats of fusion (Table II) for isolated peaks were computed by constructing a linear baseline from the peak onset to completion and numerically integrating the enclosed area. For overlapping peaks, the baseline was constructed from the onset of the first peak to completion of the second peak and the integration was carried out in two

TABLE I
DSC Results for PEG 400, 1000, 4000, and 6000 (100% Polymer)

Sample	\bar{M}_w	\bar{M}_n^a	Polymer melting transition	
			T_m, K^b	$\Delta H_p, J/g$
PEG 400	450	409	276.1	61
PEG 1000	1150	1050	303.5	108
PEG 4000	3860	3510	328.3	180
PEG 6000	10300	9360	332.7	180

^a \bar{M}_n estimated from a polydispersity of 1.1.

^b T_m = melting peak temperature after adjusting for sample temperature lag.

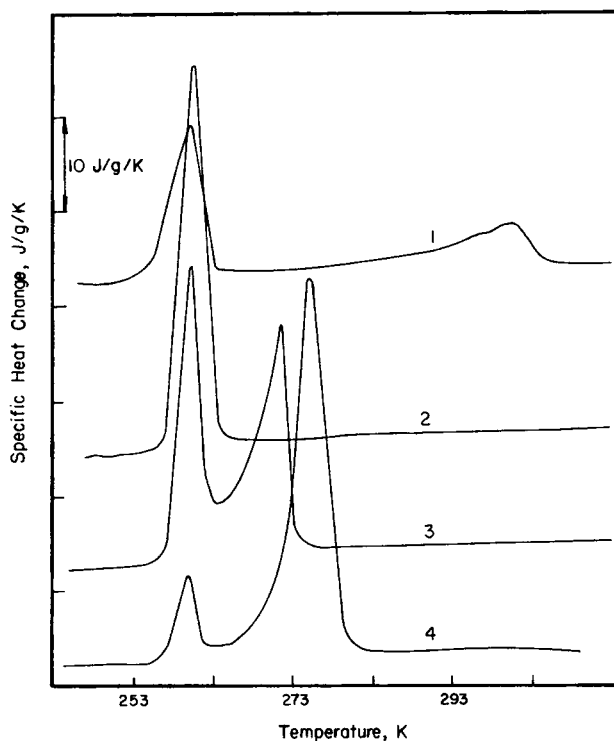


Fig. 1. DSC curves for PEG 4000 in aqueous solution at various concentrations: (1) 0.7 polymer weight fraction (W_1); (2) $W_1 = 0.5$; (3) $W_1 = 0.3$; (4) $W_1 = 0.1$.

parts, below and above the valley between the peaks. All baseline constructions and integrations were done on time-based data using the computer.

Melting temperatures listed in the tables are the measured peak temperatures adjusted for sample temperature lag during melting. The temperature lag, difference between onset and peak temperature, found for pure water (3.5 K) was used in making the adjustment.

TABLE II
DSC Results for Aqueous Solutions of PEG 4000

Weight fraction polymer	Polymer melting		Free-water melting		Eutectic melting	
	T_m , K ^a	ΔH_p , J/g	T_m , K ^a	ΔH_{fw} , J/g	T_m , K ^a	ΔH_e , J/g
0.0	—	0	273.2	334 ^b	—	0
0.10	—	0	272.2	228	256.9	26
0.20	—	0	270.8	180	256.9	54
0.30	—	0	268.3	114	257.0	92
0.40	—	0	264.4	44	257.2	123
0.45	—	0	261.6	18	256.7	128
0.50	—	0	—	0	257.4	143
0.60	284.9	15	—	0	258.7	106
0.70	298.4	54	—	0	257.2	61
1.00	328.3	180	—	0	—	0

^a T_m = melting peak temperature after adjusting for sample temperature lag.

^b Instrument was calibrated so that measured heat of fusion of pure water was 334 J/g.

DISCUSSION

DSC Results for PEG Solutions

The DSC data obtained for aqueous solutions of PEG 4000 (polyethylene glycol, $\bar{M}_n = 3510$) are summarized in Table II for $W_1 = 0.1, 0.2, 0.3, 0.4, 0.45, 0.5, 0.6, 0.7$, and 1.0, where W_1 is the polymer weight fraction. Figure 1 shows the DSC curves for $W_1 = 0.1, 0.3, 0.5$, and 0.7.

Two endothermic peaks are detected at polymer weight fractions above and below ~ 0.5 . A single peak is seen at $W_1 = 0.5$ and for pure PEG ($W_1 = 1$) and water ($W_1 = 0$). Below $W_1 = 0.5$, the higher-temperature peak is due to melting of free water. The peak temperature (melting point) and peak size (ΔH) are depressed as the polymer concentration is increased until only the single low-temperature peak is observed at $W_1 \simeq 0.5$. Similarly, above $W_1 = 0.5$ the high-temperature peak is due to the depressed melting point of polyethylene glycol. The lower-temperature peak shows a melting point (257 K) which is independent of polymer concentration. This behavior is characteristic of binary eutectic systems and indicates that PEG and water reach a eutectic composition at 257 K.

The enthalpy changes, in joules per gram of sample, for the various peaks observed by DSC, i.e., free water, eutectic, and polymer, are shown in Figure 2 as a function of polymer weight fraction. As expected the enthalpy of melting for noneutectic water decreases with increasing polymer concentration and approaches zero as W_1 approaches ~ 0.5 . That obtained for the eutectic increases as more eutectic is formed, i.e., increasing polymer concentration. It then reaches a maximum of about 148 J/g of sample at $0.45 \leq W_1 \leq 0.50$. Then, as more polymer is added, the amount of eutectic per gram of sample drops and excess polymer exists. Thus, the enthalpy of melting per gram of sample for the eutectic decreases, and the enthalpy of melting for the crystalline PEG 4000 appears and starts to increase.

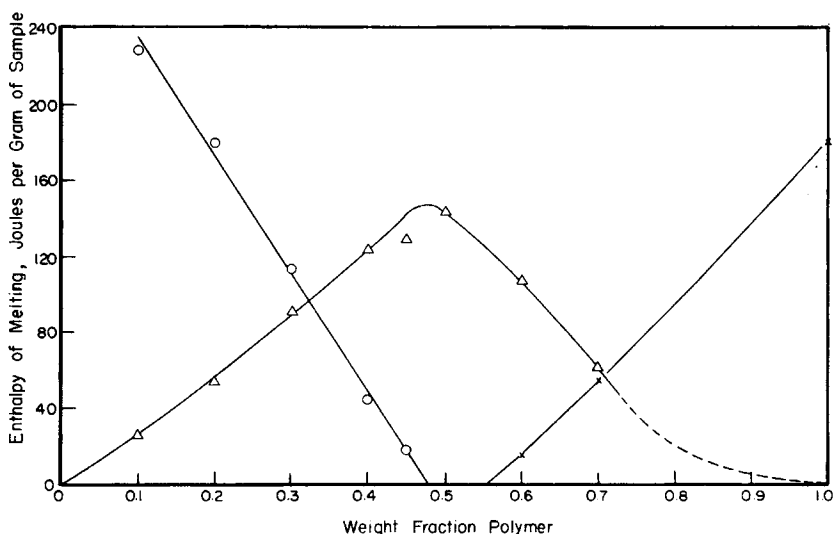


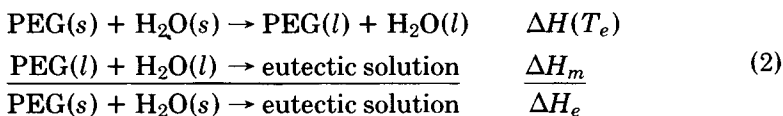
Fig. 2. Enthalpy of melting obtained by DSC plotted as a function of wt % polymer: (○) free water; (x) polymer; (Δ) eutectic.

The best values for eutectic temperature and composition, obtained by construction of the phase diagram (discussed later), are 257 ± 1 K at 48% polymer by weight (1.1 g water/g polymer). To determine the enthalpy of melting for this eutectic composition, we have plotted (Fig. 3) the enthalpy of eutectic melting (ΔH_e) per gram of sample obtained from the DSC curves as a function of grams of eutectic per gram of sample, using 1.1 g water/g polymer for the eutectic composition. The linear relationship displayed in Figure 3 yields a value of 159 J/g of eutectic, obtained from the slope. This value is significantly less than the combined enthalpies of melting (241 J/g) of pure polymer (85 J/g) plus pure water (156 J/g) estimated at the eutectic temperature and composition using

$$\Delta H(T_e) = X_{\text{PEG}}[\Delta H_{\text{PEG}}(T_m^0) - \Delta C_p(s \rightarrow l)_{\text{PEG}}\Delta T_{\text{PEG}}] + X_{\text{H}_2\text{O}}[\Delta H_{\text{H}_2\text{O}}(T_m^0) - \Delta C_p(s \rightarrow l)_{\text{H}_2\text{O}}\Delta T_{\text{H}_2\text{O}}] \quad (1)$$

where $\Delta H(T_e)$ = predicted heat of melting of eutectic, X_i = weight fraction of component i , $\Delta H_i(T_m^0)$ = heat of melting of pure component at its equilibrium melting point, $\Delta C_p(s \rightarrow l)_i$ = specific heat change for pure component (i) on melting, and $\Delta T_i = T_m^0 - T_e$ (freezing point depression). For water, $\Delta H(T_m^0)$, T_m^0 , and ΔC_p were taken as 334 J/g, 273.2 K, and 2.1 J/g/K, respectively, while for PEG 4000 $\Delta H(T_m^0)$ was measured to be 180 J/g at 328.3 K and ΔC_p was taken as 0.21 J/g/K.¹²

Ideally, the difference (-82 J/g) between the measured enthalpy of eutectic melting and the calculated value should equal the heat of mixing (ΔH_m) of the polymer and water at the eutectic composition:



Estimates of the heat of mixing from published data¹³⁻¹⁵ places this value in the -25 to -80 J/g range. Other factors that could contribute to the enthalpy difference observed in this work (-82 J/g) include uncertainty in the extrapolated

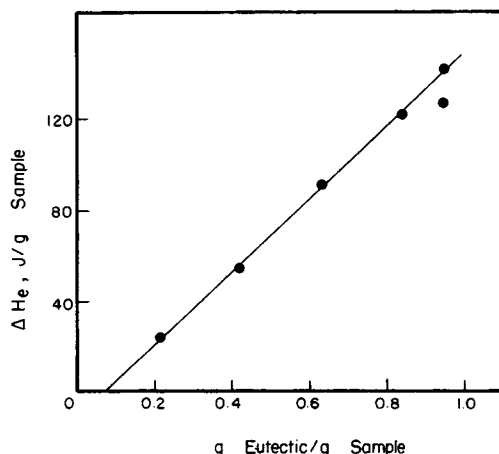


Fig. 3. Plot of enthalpy of eutectic melting (ΔH_e) per gram of sample vs. number of grams of eutectic per gram of sample, assuming a eutectic composition of 1.1 g water/g polymer.

TABLE III
DSC Results for PEG 400, 1000, 4000, and 6000 at 20% Polymer by Weight in Water

Sample	Free-water melting		Eutectic melting	
	T_m , K ^a	ΔH_{fw} , J/g	T_m , K ^a	ΔH_e , J/g
PEG 400	270.0	165	—	0
PEG 1000	270.1	172	247.5	25
PEG 4000	270.8	180	256.9	54
PEG 6000	270.8	175	258.7	54

^a T_m = melting peak temperature after adjusting for sample temperature lag.

heat of fusion of PEG and incomplete crystallization of water and polymer to form the eutectic.

To ascertain the effect of polymer molecular weight on the eutectic formation, we first determined the melting point and enthalpy of melting of pure PEG 400, 1000, and 6000. The results obtained for these polymers as well as PEG 4000 are listed in Table I. Also included are the weight-average molecular weights, obtained by light scattering measurements, and approximate number-average molecular weights, estimated by assuming a polydispersity of 1.1. The melting point for the polyethylene glycols is very molecular weight dependent. For PEG 400 it is 276.1 K, whereas for PEG 6000 it is 332.7 K. If we assume a value of $\Delta H_f = 188$ J/g for high molecular weight polyethylene oxide,¹⁶ then the two higher molecular weight samples, PEG 4000 and PEG 6000, have ΔH_f equal to 96% of the theoretical heat of fusion. The heat of fusion for PEG 1000 and PEG 400 are only 57 and 32% of the theoretical value.

Next, DSC results were obtained for aqueous solutions ($W_1 = 0.2$) of PEG 400, 1000, 4000, and 6000. They are tabulated in Table III and plotted in Figure 4. For the PEG 400 sample, no eutectic peak is detected. However, it may exhibit one below 223 K, which was the starting temperature for our studies here. As the molecular weight of the polyethylene glycol is further increased, the eutectic peak appears at progressively higher temperatures. Note that the melting point of the free-water peak has only a slight molecular weight dependence. The strong temperature dependence of the eutectic melting point on polymer molecular weight is likely related to the differences in melting point of the bulk polymers. It is interesting to note that the enthalpies of melting obtained for the eutectic in the PEG 4000 and 6000 solutions are the same and almost twice as large as those obtained for the PEG 1000 solutions. This trend is similar to that observed for the heats of fusion obtained for the bulk polymers.

Phase Diagram

By plotting the melting points obtained by DSC for the aqueous solutions of PEG 4000, it is possible to develop a phase diagram describing the behavior of polyethylene glycol in water (Fig. 5). The phase diagram obtained is similar to those recently reported for a variety of polymer solutions, including poly(ethylene oxide) in trioxane³ and poly(ethylene oxide) in glutaric acid.⁵ However, to our knowledge this is the first reported eutectic of PEG and water.

Smith and Pennings⁴ have employed a procedure for predicting the melting temperature–composition behavior of a polymer–solvent binary system. The activity of either of the components in the mixture a_i is expressed in the following

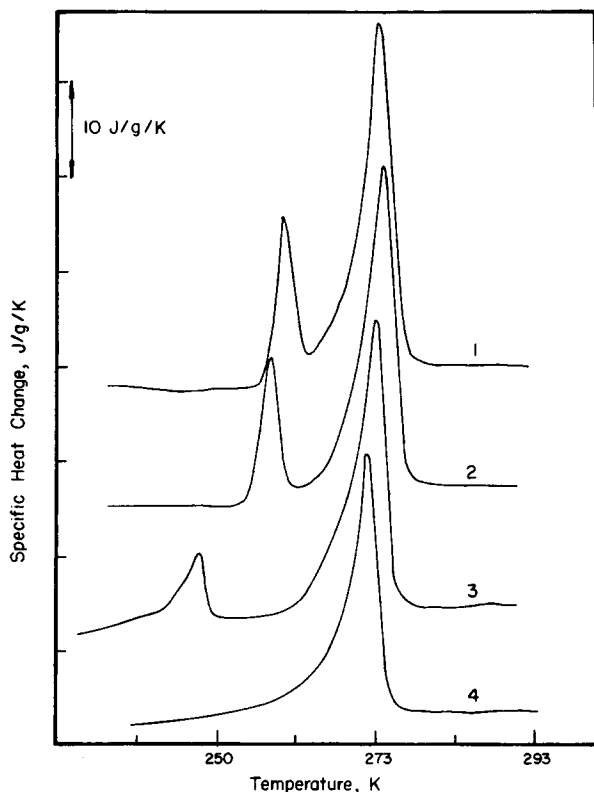


Fig. 4. DSC curves for PEGs of various molecular weights in aqueous solution at $W_1 = 0.2$: (1) PEG 6000; (2) PEG 4000; (3) PEG 1000; (4) PEG 400.

form:

$$R \ln a_i = \Delta H_i \left[\frac{1}{T_{m,i}^0} - \frac{1}{T_{m,i}} \right] - \Delta C_{p,i} \ln \frac{T_{m,i}^0}{T_{m,i}} - \Delta C_{p,i} T_{m,i}^0 \left[\frac{1}{T_{m,i}^0} - \frac{1}{T_{m,i}} \right] \quad (3)$$

where ΔH_i is the molar heat of fusion at the melting temperature $T_{m,i}^0$ of pure component i , $T_{m,i}$ is the observed melting temperature in the mixture, and $\Delta C_{p,i}$ is the difference between the molar heat capacity of component i as a solid and in solution. For the solvent ($i = 2$) the Flory-Huggins expression¹⁷ may be used for expressing the activity in terms of the solvent volume fraction ϕ_2 and the interaction parameter χ :

$$R \ln a_2 = R [\ln \phi_2 + (1 - 1/x)(1 - \phi_2) + \chi(1 - \phi_2)^2] \quad (4)$$

where x is the ratio of the molar volume of polymer and solvent. For the polymer, the activity of the structural repeat unit a_u is expressed as¹⁸

$$R \ln a_u = R \left(\frac{V_u}{V_2} \right) \left[\ln (1 - \phi_2) \frac{1}{x} - (1 - 1/x)\phi_2 + \chi \phi_2^2 \right] \quad (5)$$

where V_u and V_2 are the molar volumes of the structural unit of the polymer and the solvent, respectively. From a knowledge of the molar heats of fusion, $T_{m,i}^0$ and $\Delta C_{p,i}$ of the solvent and polymer, it is possible to calculate $T_{m,i}$ as a function of volume fraction by combining these three equations and assuming a value of

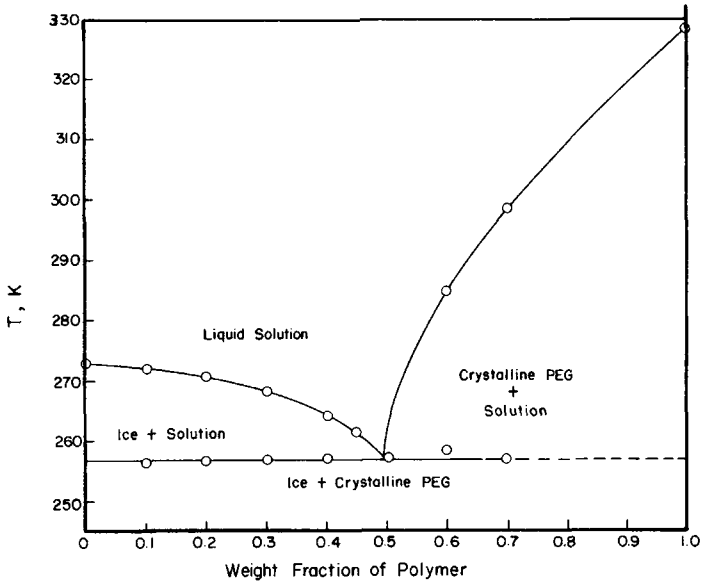


Fig. 5. Phase diagram for the PEG-4000/water binary system.

the interaction parameter. Some theoretical liquidus curves obtained in this manner are shown in Figure 6. The experimental data (Fig. 5) were converted from weight fraction to volume fraction using a density ratio of 1.14 for PEG/

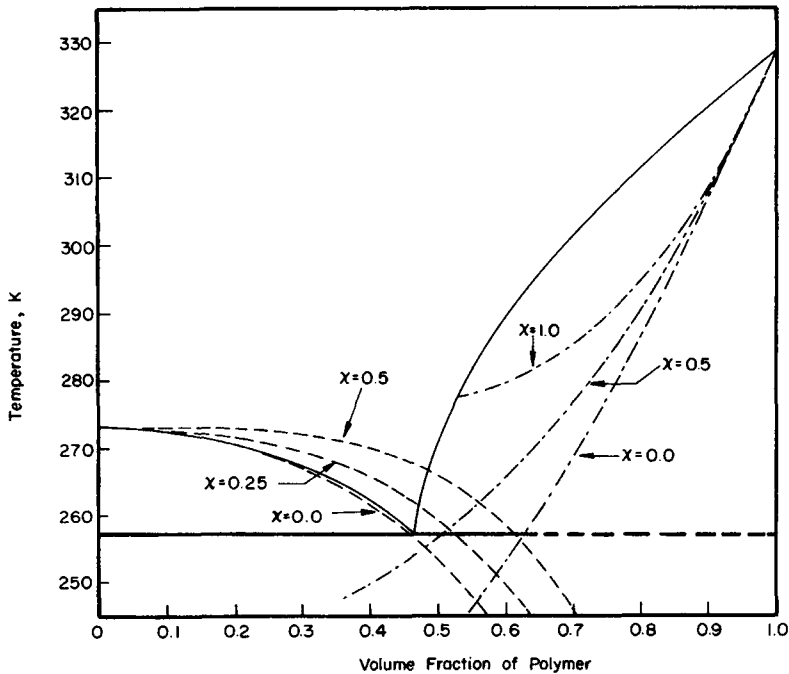


Fig. 6. Comparison of experimental and predicted freezing point depressions for the PEG-4000/water system. Solid curves represent experimental data. Other curves are labeled as follows: (—) obtained using eqs. (3) and (4) with $\chi = 0.0, 0.25,$ and $0.50,$ respectively; (---) obtained using eqs. (3) and (5) with $\chi = 0.0, 0.5,$ and $1.0.$

H₂O. This ratio is based on published values for water and extrapolation of densities measured between 60 and 100°C for pure PEG 4000. Molar heat capacity differences of 37.7 J/mole/K and 9.2 J/mole/K were used in eq. (3) for water and PEG 4000, respectively. The melting temperature curve of free water as a function of volume fraction of polymer is described reasonably well by employing a value of $\chi = 0.05$. In an unpublished study,¹⁹ fitting of activity coefficient data obtained from vapor pressure measurements of water in aqueous PEG 4000 solutions ($\phi_1 = 0.396$) to the Flory-Huggins model resulted in $\chi = 0.22$ at 303 K and 0.66 at 338 K. Thus, the low value of the interaction parameter obtained in this work at temperatures below 273 K is not unreasonable.

The theoretically predicted curves for the melting temperature of the polymer, calculated using eqs. (3) and (5) with χ values between 0.0 and 1.0, do not agree with the experimental curve. Whereas the experimental curve is concave downward, the theoretical curves predict substantially lower melting temperatures and are concave upward. Similar discrepancies have been encountered by other investigators^{3,4} in fitting polymer liquidus curves using activities obtained from eq. (5). The source of these differences is as yet unresolved.

DSC Results for PPG and Copolymer

Water solutions of polypropylene glycol (PPG 425) or a random copolymer of ethylene oxide and propylene oxide (PEG-PG 3520) do not produce crystalline eutectics. This is expected since neither of the polymers are crystalline. Instead, a single melting peak due to free water is observed in the DSC scan (Fig. 7). As indicated in Table IV, this peak decreases with increasing polymer concentration until it disappears above about 60% polymer.

Water Binding

The disappearance of a melting peak due to free water in the PPG and copolymer systems, and the reduction in heat of fusion of free water to less than that resulting from simple dilution demonstrates that a significant amount of water does not freeze. This is presumably due to interaction (binding) of water molecules with the polymer. Figure 8 shows the amount of nonfreezing water

TABLE IV
Comparison of DSC Results for PEG, PPG, and a 50/50 Random Copolymer

Wt % Polymer	Polymer	Free-water melting	
		T_m , K	ΔH_{fw} , J/g
20	PEG 4000	270.8	180
	PPG 425	271.4	234
	PEG-PG 3520	271.7	196
40	PEG	264.4	44
	PPG	264.5	127
	PEG-PG	265.0	81
60	PEG	—	0
	PPG	257.9	42
	PEG-PG	258.2	20

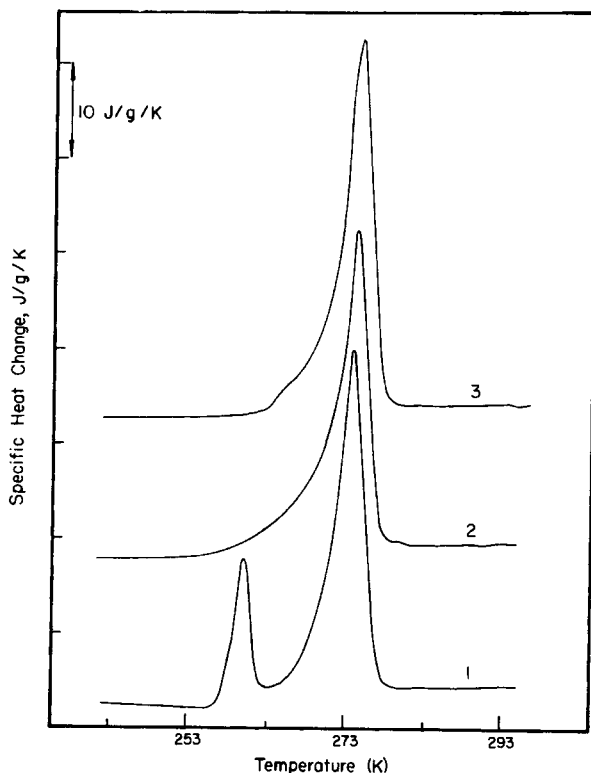


Fig. 7. DSC curves for PEG 4000 (1), PPG 425 (2), and PEG-PG 3520 (3) at $W_1 = 0.2$.

per gram of polymer as a function of polymer concentration for PEG, PPG, and the random copolymer. The amount of nonfreezing water was obtained from the heat of fusion measured by DSC using

$$\text{fraction of water that is nonfreezing} = \frac{\Delta H_f - \Delta H_{fm}}{\Delta H_f} \quad (6)$$

where ΔH_{fm} is the measured heat of fusion per gram of water present in the sample and ΔH_f is the theoretical heat of fusion for the water at the observed freezing point. The theoretical value was obtained from

$$\Delta H_f(T) = \Delta H_f(273.2 \text{ K}) - [C_{p, \text{H}_2\text{O}} - C_{p, \text{ice}}] \Delta T \quad (7)$$

where $\Delta H_f(273.2 \text{ K})$ was taken as 334 J/g, and the specific heat change from water to ice was -2.1 J/g/K . This procedure for estimating bound water has been used by several investigators (see refs. 7 and 8); however, it does neglect contributions from the heat of dilution during melting of the free water. We also have neglected this term since no data are available in the temperature and concentration range of interest for these systems. Contributions are likely to be negligible near the polymer concentration needed to bind all the water since little dilution occurs on melting of the free water. For PEG 4000, the nonfreezing water was based on the heat of fusion obtained from the area of the free-water peak down to the valley between the free-water and eutectic peaks which occurs near the onset of eutectic melting. This leads to some uncertainty in the free-

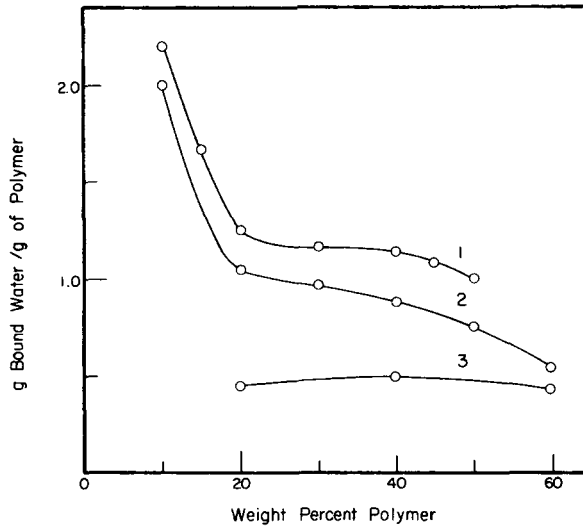


Fig. 8. Plot of bound water as function of wt % polymer for PEG 4000 (1), PEG-PG 3520 (2), and PPG 425 (3).

water content, especially at polymer fractions above 20% because of overlap of the two peaks. Comparisons of PEG 4000 solutions with lower MW PEG solutions where the eutectic peak is much better resolved or absent (PEG 400) reveals similar values of the enthalpy change for the free-water melting peaks, thereby adding weight to this method of data reduction.

The amount of bound water per gram of polymer determined from the heats of fusion varies with polymer concentration (Fig. 8). Increasing the PEG 4000 or PEG-PG 3520 concentration from 10 to 20% decreases the water binding by approximately 50%. Above 20%, the binding remains relatively constant until

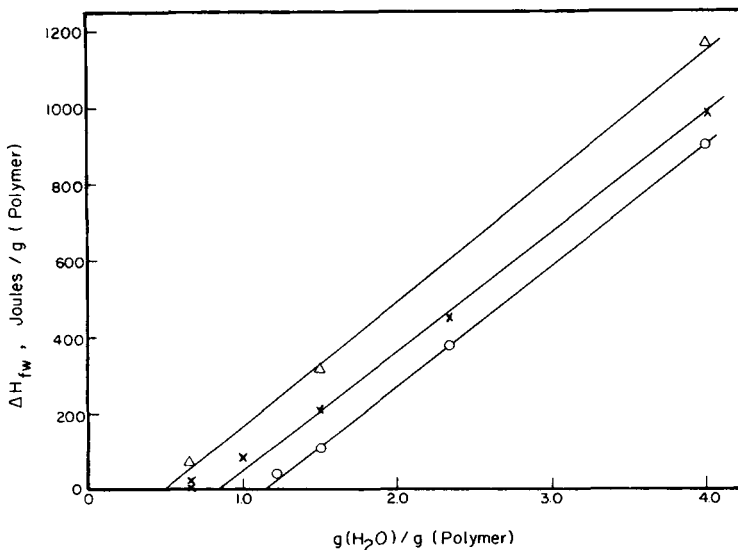


Fig. 9. Plot of enthalpy of melting of free water (ΔH_{fw}) vs. g water/g polymer for PEG 4000 (O), PEG-PG 3520 (X), and PPG 425 (Δ).

it gradually drops above 50% polymer content. Similar curves have been observed for various carbohydrate-water solutions.⁸ Increased binding at low polymer concentrations has been attributed⁸ to multilayer arrangements of water around the polymer solute. The approximately constant binding between 20 and 50% may indicate that a single hydration layer is favored. Decreases above 50% indicate insufficient water to hydrate all of the polymer segments.

The amount of bound water per gram of polymer is highest for PEG 4000, followed by PEG-PG 3520 and then PPG 425. PEG 400 binds the same amount of water as PEG 4000 (within experimental error). Thus, molecular weight is not responsible for this trend. At 40% polymer the grams of bound water per gram of polymer are 1.15, 0.88, and 0.5 for PEG 4000, PEG-PG 3520, and PPG 425, respectively. This translates to hydration numbers per polymer segment of 2.8, 2.4, and 1.6. The value for PEG 4000 is in good agreement with hydration numbers obtained by various other techniques.²⁰⁻²² Another method of estimating the bound water is to plot the heat of fusion of free water per gram of polymer versus the total weight of water per gram of polymer and extrapolate to zero for ΔH_f (Fig. 9). The water binding obtained in this manner for PEG 4000, PEG-PG 3520, and PPG 425 are 1.1, 0.85, and 0.48 g/g polymer, or 2.7, 2.3, and 1.5 molecule H_2O /polymer segment. In the case of constant water binding per gram polymer over the concentration range employed, the slope of this plot should yield the heat of fusion of pure water. The slope of the lines in Figure 9 are ~ 300 J/g, in reasonable agreement with the theoretical value (334 J/g) for pure water at 273 K.

CONCLUSIONS

Differential scanning calorimetry was used to investigate the phase behavior of aqueous solutions of polyethylene glycol, polypropylene glycol, and a 50% by weight random copolymer of ethylene oxide and propylene oxide. PEG forms a crystalline eutectic with water at about 48% by weight of polymer. The liquidus curve for the freezing point depression of water in the presence of PEG can be fit using the Flory-Huggins expression for solute activity with an interaction parameter of 0.05. Attempts at fitting the liquidus curve of PEG were not successful. Polypropylene glycol and the random copolymer do not form crystalline eutectics since the pure polymers are not crystalline.

The amount of nonfreezing water per gram added polymer increases in the order PPG < PEG-PG < PEG. Hydration numbers per polymer segment are estimated to be 1.5 for PPG, 2.3 for the random copolymer, and 2.7 for PEG.

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