

## **CALORIMETRIC INVESTIGATION OF WATER/POLYOXYETHYLENE SYSTEMS**

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Systems of water and polyoxyethylene with different molecular weights were studied calorimetrically. The enthalpies of melting of the eutectic phases, and the concentrations of bound water and polyoxyethylene were determined, depending on the composition and the POE sample.

Polyoxyethylene (POE) is known to form binary eutectic systems with water [1]. In previous papers we have presented the results of calorimetric studies of systems of water and three samples of POE with different molecular weights. Their phase diagrams on heating and cooling were drawn on the basis of these results [2, 3].

It was established that these systems tend to supercool substantially or do not crystallize at all when the POE content is about or a little higher than the eutectic concentration. This behaviour is attributed to the formation of stable complexes between water and POE.

On the basis of the results of calorimetric studies of systems of water and low molecular weight POE (from POE-400 to POE-6000), the amount of bound water was determined [1]. A non-linear relationship was found between the concentration of bound water in the system and the ratio of its components. It decreases with increasing polymer content between 0.1 and 0.2 and above 0.5 weight fraction of POE, and is constant from 0.2 to 0.5 weight fraction of POE. The higher concentration of bound water at low concentrations of POE may be explained in terms of a multilayer arrangement of water molecules around the POE unit. In the interval from 20 to 50 wt% POE, a single hydration layer is favoured, its concentration being from 1.1 to 1.15 g of bound water per gram of POE-4000. This translates to hydration numbers per polymer segment of 2.7 to 2.8.

These data agree well with the results for bound water determined by IR spectroscopy [5]. According to these results, the maximum amount of bound water

is 3 mole of water per monomer unit of POE. In the same paper the enthalpy of melting for the eutectic of water/POE-1000 system was also determined, to be 159 J/g.

The present paper, which is a continuation of our systematic investigations of the systems of water and POE with different molecular weights [2, 3], presents the results of calorimetric studies of these systems. From these results, the enthalpies of melting of the eutectic phases and the concentrations of bound water were determined, depending on the molecular weight and the amount of POE.

## Experimental

The DSC curves of melting were studied for systems of water and three samples of POE with different molecular weights: POE-1 and POE-2, commercial products of Merck, average molecular weight  $\bar{M}_n = 1000$  and  $\bar{M}_n = 20,000$ , respectively, and a high molecular weight POE (POE-3) obtained from the Central Polymer Laboratory of the Bulgarian Academy of Sciences, having an intrinsic viscosity  $[\eta] = 6.08$  dl/g in benzene at 25° ( $\bar{M}_n = 1.8 \cdot 10^6$ ). Water demineralized by double distillation was used.

Calorimetric studies of water/POE systems were carried out with a DSC-111 differential scanning calorimeter (Setaram, France) in the temperature interval from -90 to 110° with heating at a rate of 5 deg/min [2]. As shown in [2], the endotherms of melting are monomodal for systems of eutectic composition, and bimodal when the composition is different from the eutectic. The characteristic melting temperatures and the enthalpies of melting of free POE, free water and the eutectic phase were calculated in joules per gram of sample as a function of composition [2]. Table 1 presents the eutectic concentrations of the systems under study, the melting temperature of the eutectic ( $T_m^e$ ) obtained from the phase diagrams, and the maximum enthalpy of melting for the eutectic phase ( $\Delta H_m^{e,max}$ ) in joules per gram of sample at a nearly eutectic concentration of POE.

**Table 1** Compositions, melting temperatures and enthalpies of melting of the eutectic phases

No.	System	Eutectic concentration			$T_m^{e*}$ , °C	$\Delta H_m^{e,max}$ J/g of sample
		wt. fr. POE	g H <sub>2</sub> O/g POE	mol H <sub>2</sub> O/ mol POE		
1	POE-1/water	0.55	0.82	2.0	-22	115
2	POE-2/water	0.50	1.0	2.4	-11	147
3	POE-3/water	0.47	1.18	2.8	-8	142

\* Temperature of the peak maximum for eutectic melting.

With the technique described in [1], the enthalpy of melting of the eutectic phase and the concentration of bound water were estimated.

The enthalpy of melting of the eutectic phase, in joules per gram of eutectic, was obtained from the slope of the curve representing the enthalpy of melting of the eutectic, in joules per gram of sample, as a function of the ratio between the weight of the eutectic phase and the sample weight.

The concentrations of bound water and bound POE expressed in weight fractions are determined in two ways: (1) analytically (calculated by using Eq. 1), and (2) graphically, by extrapolating to  $\Delta H_m^{\text{free water(POE)}} = 0$  the straight line representing the dependence of the enthalpy of melting of free water (expressed in joules per gram of POE in the system) and the enthalpy of melting of free POE (in joules per gram of water in the system), respectively, on the amount of water in the system per gram of POE and the amount of POE in the system per gram of water, respectively.

The bound water is that part of the water in the system which does not crystallize or melt with free water. The bound POE is that part of the POE in the system which does not crystallize or melt with free POE.

The concentrations ( $C$ ) of bound water and bound POE in the system, expressed in weight fractions, are calculated using

$$C = \frac{\Delta H_f(T) - \Delta H_f(m)}{\Delta H_f(T)} \quad (1)$$

where  $\Delta H_f(m)$  is the enthalpy of melting of free water or free POE (joules per gram of water or POE in the system), determined experimentally from the area of the endothermic peak of melting of free water or POE in the DSC curves of the investigated systems; and  $\Delta H_f(T)$  is the enthalpy of melting of pure water or POE at the melting temperature or free water or free POE in the system,  $T_m^{\text{free water(POE)}}$  (the maximum temperature of the exothermic peak in the DSC curves).  $\Delta H_f(T)$  is calculated using

$$\Delta H_f(T) = \Delta H_f(T^\circ) - \Delta C_{p(s \rightarrow 1)} \cdot \Delta T \quad (2)$$

where  $\Delta C_{p(s \rightarrow 1)}$  is the change in the specific heat of water or POE on melting;  $\Delta H_f(T^\circ)$  is the enthalpy of melting of the pure components, water and POE, at the corresponding temperature  $T_m^\circ$ ;  $\Delta T = T_m^\circ - T_m$  is the difference between the melting temperature of the pure component, water or POE,  $T_m^\circ$ , and the melting temperature of the free (non-eutectic) component in the water/POE system,  $T_m$ .

The values of  $\Delta C_{p(s \rightarrow 1)}$  and  $\Delta H_f(T^\circ)$  for water and POE are given in Table 2.

In the calculation of  $\Delta H_f(T)$ , the effect of the dissolution heat during the melting of free water in aqueous solutions of POE and vice versa is neglected, since it is

**Fig. 2** Melting temperatures, enthalpies of melting and changes in the specific heat of melting of the initial components

No.	Component	$T_m^\circ$ , °C	$\Delta H_f(T^\circ)$ , J/g	$\Delta C_{p(s \rightarrow l)}$ , J/g·deg
1	water	0	334	2.1
2	POE-1	38	150	0.21
3	POE-2	63	162	0.21
4	POE-3	65	130	0.21

difficult to estimate. When the content of POE is close to the eutectic, almost the whole amount of water is bound to POE, which is why the heat of mixing of free water and POE is very low and may be neglected.

## Results and discussion

### *I. Enthalpy of melting of the eutectic phase*

Figure 1(a-c) presents the enthalpy of melting of the eutectic phase,  $\Delta H_m^e$ , expressed in joules per gram of sample, as a function of the content of the eutectic phase per unit weight of sample. This relationship is plotted in the form of straight lines drawn through the experimental points [1].

It is found that two straight lines of almost the same slope may be drawn through the experimental points. They connect the enthalpies of melting of the eutectic phases in the systems in which the water or POE component prevails (the amount of POE in the system, expressed in weight fractions, is indicated at each experimental point in Fig. 1(a-c)). The deviation (at 0.4 and about 0.56 weight fraction of POE, respectively) has the same sign, but a different value for the three samples of POE (the broken lines in Fig. 1(a-c)) and may be attributed to supercooling and incomplete eutectic crystallization on cooling or heating before melting. Therefore, as the deviation of the experimental points is wide, it should be taken into consideration in the interpretation of the results, especially from a quantitative aspect.

If the deviations observed, which are characteristic of very narrow compositions of the systems, are neglected, the enthalpy of melting of the eutectic phase may be calculated in joules per gram of eutectic from the slopes of plots 1-2 in Fig. 1(a-c). The values obtained are given in Table 3. They are approximately the same on the left and on the right of the eutectic point, particularly for POE-1 and POE-2, and depend on the molecular weight of POE.

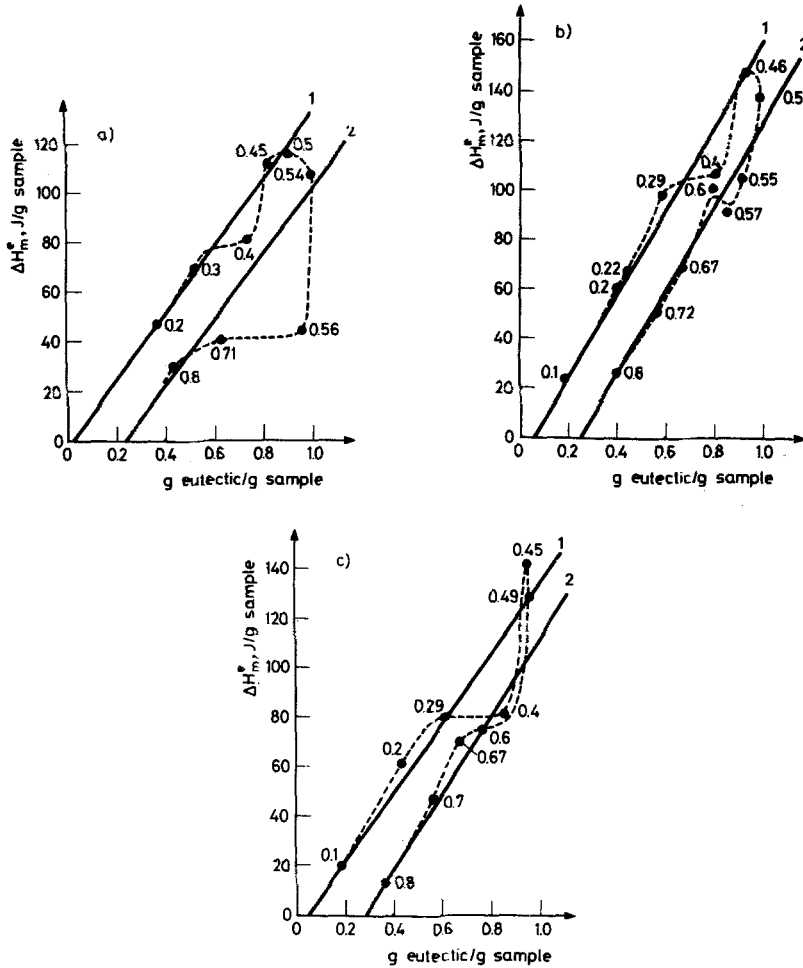


Fig. 1 Dependence of the enthalpy of melting of the eutectic ( $\Delta H_m^e$ ), in joules per gram of sample, on the amount of the eutectic per unit weight of sample calculated from the eutectic composition (Table 1). *a* – water/POE-1; *b* – water/POE-2; *c* – water/POE-3

Table 3 Enthalpies of melting of the eutectic phases

No.	System	$\Delta H_m^e$ , joules per gram of eutectic	
		For systems with POE content	
		above the eutectic	below the eutectic
1	POE-1/water	133	130
2	POE-2/water	170	172
3	POE-3/water	138	153

It was established calorimetrically that the endothermic peaks of eutectic melting are observed only in the interval from 0.1 to 0.8 weight fraction of POE [2]. This is why plots 1 and 2 in Fig. 1(a-c), which are drawn through the experimental points, do not pass through the origin of the coordinates, but intersect the abscissa in the intervals from 0.02 to 0.06 and from 0.24 to 0.28 gram eutectic per gram of sample, respectively. These values for the concentration of the eutectic systems correspond to a POE content from 0.01 to 0.03 and from 0.85 to 0.89 weight fraction, respectively. At these concentrations of POE, the experimentally determined enthalpy of melting of the eutectic phase is zero. It is probable that in these concentration intervals the heat of eutectic melting is compensated by the heat of mixing the components of the eutectic phase, which has the same value and the opposite sign. It is also probable that water and POE do not undergo eutectic crystallization because of supercooling, or that crystallization is discontinued on heating because of their low concentration and complete solubility in free POE and free water, respectively.

To check these suppositions, the amount of the eutectic phase and the enthalpy of melting,  $\Delta H_m^e(T)$ , expressed in joules per gram of sample, were calculated for the systems with experimental zero enthalpy of melting of the euectic,  $\Delta H_m^e = 0$ . In Table 4 these values are compared with the heat of mixing,  $\Delta H_{\text{mix}}(T)$ , of the eutectic components, water and POE, calculated in joules per gram of sample on the basis of the experimental average value of the heat of mixing (50 J/g POE) of water and POE-6000 at 30° [4]. The enthalpies of mixing of POE and water (without being reduced to the corresponding temperature of melting of the eutectic phase) are seen to be opposite in sign, but considerably less in value than the calculated enthalpies of melting for the eutectic phase, i.e. the heat of eutectic melting can be compensated only partially by the heat of mixing of the eutectic components.

Therefore, the supposition is confirmed that at very low concentrations the components of the eutectic phase, POE and water, do not crystallize completely

**Table 4** Enthalpies of mixing of POE and H<sub>2</sub>O

No.	System	Amount of POE at $\Delta H_m^e = 0$ , weight fraction	Amount of eutectic phase, wt%	Calcd. $\Delta H_m^e(T)$ , J/g sample	Calcd. $\Delta H_{\text{mix}}(T)$ , J/g sample
1	POE-1/water	0.01	2	2.7	-0.55
		0.89	23.7	30.8	-6.5
2	POE-2/water	0.03	6	10.2	-1.5
		0.87	25	42.9	-6.2
3	POE-3/water	0.02	4	5.5	-0.9
		0.85	28	43	-3.6

when cooled, or heated before melting, due to complete dissolution or strong binding with the component that prevails in the system. For example, when the concentration of water is lower than 0.15 weight fraction, it is most probable that a great part of it is molecularly dissolved in the amorphous regions of POE crystals and is strongly bound to POE units through hydrogen-bonds, which hinders its crystallization.

These suppositions, of course, are also valid for cases where melting of the eutectic phase is observed over the whole concentration interval under study. Thus, for systems of water and low molecular weight POE (from POE-600 to POE-6000) it was found that the experimental enthalpies of melting of the eutectic phase are less in value than the additive enthalpies [1]. The difference between them is attributed to the compensation of the heat of melting by the heat of mixing of the components of the eutectic phase when it melts. For the systems under study, the enthalpy of melting of the eutectic phase is the combined enthalpies of melting of pure water plus POE estimated at the eutectic temperature and composition using:

$$\begin{aligned} \Delta H_{(T,e)} = & a[\Delta H_{\text{POE}(T^{\circ})} - \Delta C_{p(s \rightarrow l)}^{\text{POE}} \cdot \Delta T_{\text{POE}}] + \\ & + b[\Delta H_{\text{H}_2\text{O}(T^{\circ})} - \Delta C_{p(s \rightarrow l)}^{\text{H}_2\text{O}} \cdot \Delta T_{\text{H}_2\text{O}}] \end{aligned} \quad (3)$$

where  $\Delta H_{(T,e)}$  is the additive heat of melting of the eutectic phase;  $a$  and  $b$  are the eutectic concentrations of POE and water, respectively;  $\Delta H_{\text{POE}(T^{\circ})}$  and  $\Delta H_{\text{H}_2\text{O}(T^{\circ})}$  are the heats of melting of the pure components (POE and water) at the equilibrium temperature of melting ( $T^{\circ}$ ).

Table 5 shows the calculated additive enthalpies of melting of the eutectic phase, and the difference between them and the experimental eutectic enthalpies of melting, which are obtained by averaging values given in Table 3.

It can be seen that the difference between the experimental and calculated additive enthalpies of melting for the eutectic is greater than the experimental heat of mixing of water and POE ( $-50$  J/g of POE [4] or about  $-25$  J/g of eutectic). If these enthalpies are reduced to the same temperature, the difference between them will become still greater. In this case, too, the observed differences between the

**Table 5** Differences between the additive and experimental enthalpies of melting of the eutectic phases

No.	System	Additive enthalpy of melting, $\Delta H_{(T,e)}$ , J/g eutectic	$\Delta H_{(T,e)} - \Delta H_m^e$ ,* J/g eutectic
1	POE-1/water	205	73.5
2	POE-2/water	229	58
3	POE-3/water	222	76.5

\* The average of values given in Table 3.

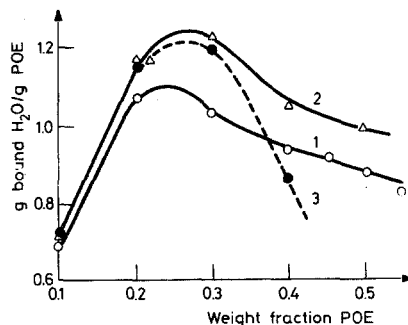
additive and experimental enthalpies of melting of the eutectic may be due to the heat of mixing of the components and also to some extent, to incomplete eutectic crystallization of the components, since these binary systems tend to supercool greatly, particularly when their composition is close to the eutectic [2, 3].

## II. Bound water and POE

The water and POE which do not melt in the intervals of melting of free water and POE when the systems under study are heated, or melt before that as eutectic components, are called here bound water and bound POE.

The concentrations of bound water and POE may be determined via Eq. (1) from the difference between the experimental heats of melting of free water and POE (estimated in joules per gram of water of POE in the system from the area of the high-temperature endothermic peak in the DSC curves) and the heats of melting of the pure initial components calculated at the same temperatures.

As noted before, at POE contents below the eutectic concentration the water/POE system contains free water and eutectic phase, while at POE contents above the eutectic concentration the system contains free POE and eutectic phase. This is why we calculate the amount of bound water in the first concentration interval and the amount of bound POE in the second interval. The results obtained are presented in Figs 2 and 3. On the whole, they show that there is no definite dependence of the concentration of bound water on the POE sample. It increases non-linearly and extremely with increasing POE content, a slight but clear maximum being exhibited at about 0.2–0.3 weight fraction of POE (Fig. 2). In this concentration interval the amount of bound water corresponding to the maximum is from 1 to 1.2 grams of water per gram of POE, which corresponds to 2.5 or 3



**Fig. 2** Dependence of the amount of bound water, in grams per gram of POE, on the concentration of POE in the water/POE-1 system (curve 1), the water/POE-2 system (curve 2) and the water/POE-3 system (curve 3)



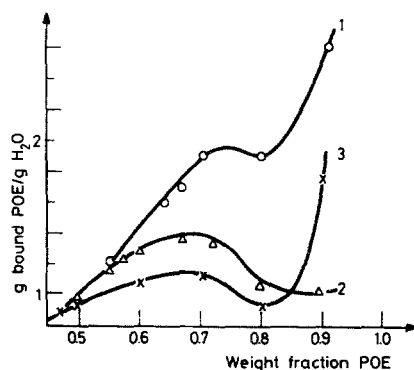


Fig. 3 Dependence of the amount of bound POE, in grams per gram of water, on the concentration of POE in the water/POE-1 system (curve 1), the water/POE-2 system (curve 2) and the water/POE-3 system (curve 3)

molecules of water to one monomer unit of POE. These values coincide with the maximum hydrogen bound numbers of POE determined by other authors [1, 5].

As noted before, on the basis of the results of similar studies of water/POE-4000 systems [1], the amount of bound water at 0.1 weight fraction of POE in the system was found to be considerably higher than the results presented in Fig. 2 for the same composition of the systems under study. It is difficult to explain this non-coincidence between the calculated values of the concentration of bound water in terms of the deviation of the experimental results and the differences in the accuracy of the measurements or in the experimental conditions, since they are commensurable. Besides, there is good agreement between the values for the concentration of bound water at a higher POE content in the system (from 0.2 to 0.5 weight fraction of POE) obtained here and in [1].

In our opinion, Fig. 2 shows that when free water prevails, crystallization of free water and partial crystallization of eutectic (bound) water takes place. The reasons for this behaviour are as yet unresolved, but it is probable that the crystals formed when free water cools serve as nuclei initiating crystallization of part of the bound water at a higher temperature than that of the crystallization of the eutectic phase, which tends to supercool greatly.

The calculated concentration of bound POE on the right of the eutectic depends on the polymer sample. It increases with decreasing molecular weight and increasing content of POE, as the plots in Fig. 3 show.

At about 0.6–0.7 weight fraction of POE, a slight maximum is observed in the curves for the concentration-dependence of bound POE, while at 0.8 weight fraction of POE a clear minimum is exhibited.

The calculated higher concentration of bound low molecular POE-1 is probably

due to the higher concentration of final hydroxy groups than is the case with POE-2 and POE-3, at the same polymer content in the system.

It has already been suggested that when the amount of water is low (less than 10 wt%) it probably stays dissolved (complex bound) in the amorphous regions of the crystal polymer component and does not crystallize eutectically. Hence, no endothermic peak of melting of the eutectic phase is observed in the DSC curves during heating. This fact may account for the increase of bound POE with increasing total concentration of POE in the system.

It should be noted that the maxima in the plots for the concentration-dependence of bound water and POE (Figs 2 and 3, respectively) coincide with the concentration of the polymer component at which a deviation from the linear slope is observed in the plots in Figs 1-3, i.e. they coincide with the POE content at which an increased tendency of the systems to supercool is observed.

The concentrations of bound water and POE are shown in Table 6. They are determined graphically by extrapolating to  $\Delta H_m = 0$  the straight lines showing the enthalpy of melting of free water or POE (expressed in joules per gram of POE or water, respectively) as a function of the component weight (Figs 4 and 5). These values are compared with the average values for the concentrations of bound water and POE calculated with Eq. (1) and presented in Figs 2 and 3 for the corresponding compositions of the system.

**Table 6** Concentrations of bound water and bound POE

No.	System	Bound water, g/g POE		Bound POE, g/g water	
		graphically determined from Fig. 4	analytically determined average values from Fig. 2	graphically determined from Fig. 5	analytically determined average values from Fig. 3
1	POE-1/water	1	0.92	1.9	1.8
2	POE-2/water	1.1	1.07	1.2	1.2
3	POE-3/water	1.2	0.98	1.17	0.9

It can be seen that there is satisfactory agreement between them for the water/POE-1 and water/POE-2 systems. In the case of the water/POE-3 system, the graphically determined concentrations of bound water and POE and the analytically calculated concentrations have the same value at about 0.2 and 0.6 weight fraction of POE, respectively, i.e. they coincide with the maxima observed in this interval in the curves in Figs 2 and 3 representing the concentration-dependence of bound water and POE.

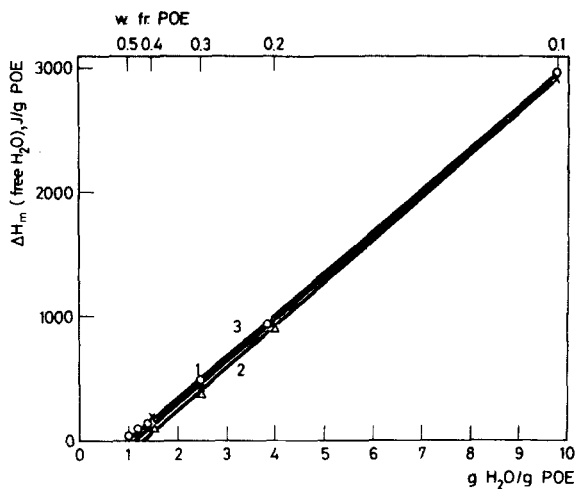


Fig. 4 Dependence of the enthalpy of melting of free water ( $\Delta H_m^{\text{free water}}$ ), in joules per gram of POE, on the amount of water, in grams per gram of POE, in the water/POE-1 system ( $\circ$ ), the water/POE-2 system ( $\Delta$ ) and the water/POE-3 system ( $\times$ )

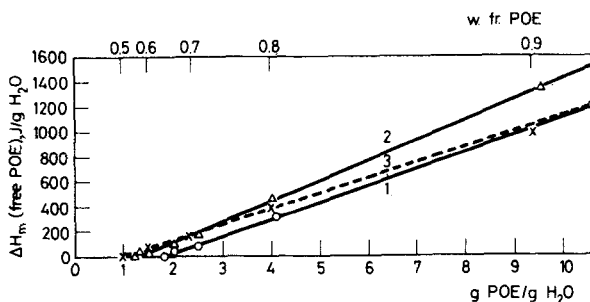


Fig. 5 Dependence of the enthalpy of melting of free POE ( $\Delta H_m^{\text{free POE}}$ ), in joules per gram of water, on the amount of POE, in grams per gram of water, in the water/POE-1 system ( $\circ$ ), the water/POE-2 system ( $\Delta$ ) and the water/POE-3 system ( $\times$ )

Table 7 Enthalpies of melting of free water and free POE, determined graphically

No.	System	$\Delta H_m^{\text{H}_2\text{O}}$ , J/g	$\Delta H_m^{\text{POE}}$ , J/g
1	POE-1/water	329	146 (150.5)*
2	POE-2/water	336	159 (162)*
3	POE-3/water	333	125 (130)*

\* Experimental enthalpy of melting of pure, initial POE

If we assume that the amount of bound water per gram of polymer is constant (i.e. it does not depend on the composition of the system), we can determine the enthalpies of melting of free water and POE from the slopes of the lines representing the dependences in Figs 4 and 5 (Table 7).

As shown in Table 7, there is good agreement between the enthalpy of melting of free water in the water/POE systems (from 329 to 336 J/g) and the enthalpy of melting of pure water at 0° (334 J/g). The enthalpy of melting of free POE in the system also agrees well with the enthalpies of pure POEs, which are determined experimentally from the DSC curves.

These results show that the free components in the systems under study behave like the initial components when they crystallize and melt.

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**Zusammenfassung** — Systeme von Wasser und Polyoxyethylenen unterschiedlichen Molekulargewichts wurden untersucht. Die Schmelzenthalpien der eutektischen Phasen und die Konzentrationen von gebundenem Wasser und Polyoxyethylen wurden bestimmt.

**Резюме** — Методом калориметрии изучены системы вода — полиоксиэтилен различного молекулярного веса. Определены энтальпии плавления эвтектических фаз и концентрация связанной воды и полиоксиэтилена в зависимости от состава и образца полимера.