

## Entropically Driven Partitioning of Ethylene Oxide Oligomers and Polymers in Aqueous/Organic Biphasic Systems

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Partitioning of ethylene oxide oligomers and polymers (PEO) in biphasic systems of water and chloroform or dichloromethane favors transfer to the organic phase as the molecular weight increases. For systems containing chlorobenzene, partitioning into the aqueous phase is always predominant. Calorimetric determination of the enthalpies of transfer for PEO from aqueous to organic phases reveals an endothermic process for all of the systems investigated, which was ascribed to the replacement of a more energetically favored PEO solvation in water for that in the organic phase. These results indicate that spontaneous PEO transfer from water to an organic phase is driven by an entropy increase. The number of water molecules transferred to the organic phase with PEO was determined to be ca. 0.08 water molecules per EO unit, smaller than hydration numbers reported in aqueous solutions. All of these findings lead to a picture where PEO may be extracted from water to an organic phase as long as the solvation by the organic solvent is relatively strong as compared to water. The displacement of water causes an entropy increase, which drives the transfer process. Chloroform and dichloromethane are suitable solvents for PEO extraction probably because of their hydrogen bond-donating capability.

### Introduction

Poly(ethylene oxide), PEO, is one of the most studied and widely used synthetic polymers. Many important features contribute to its importance, namely, low cost, biocompatibility, high aqueous solubility, significant solubility in many polar organic solvents, commercial availability in molecular weights ranging from a few hundred to millions of  $\text{g mol}^{-1}$ , and rather monodisperse samples. Its chemical and physical properties, pure or in solution, and its application in many fields have been extensively described in textbooks.<sup>1–3</sup>

One of these books<sup>1</sup> states that PEO may be extracted from water into chloroform and dichloromethane, and accounts for this are based on an entropy increase due to the change from a helicoidal polymer configuration in water to a looser structure in the organic phase. The fact that a highly water soluble polymer like PEO may be extracted from water to an organic phase is surprising. An earlier investigation by us<sup>4</sup> proved that PEO of molecular weights greater than  $1000 \text{ g mol}^{-1}$  were almost quantitatively extracted into chloroform and dichloromethane. We discussed such a molecular weight dependence based on the magnitude of end group hydroxyl contributions, presenting evidence from partitioning, that these contributions vanish above molecular weights of  $2000\text{--}3000 \text{ g mol}^{-1}$ . Our proposition was that oligomers below this molecular weight behave like polyglycols, whereas above this value they display polyether features, placing the poly(ethylene glycol) to PEO transition at about  $2000 \text{ g mol}^{-1}$ .

A large number of investigations have been carried out on the solution behavior of PEO, from both theoretical and experimental viewpoints. Many of these investigations focused on understanding the peculiar high aqueous solubility of PEO,

especially considering that the lower homologue, poly(methylene oxide), is insoluble in water and the next higher homologue, poly(propylene oxide), displays quite limited miscibility with water.<sup>5</sup> In general, PEO high aqueous solubility has been ascribed to an exact matching of ethylene oxide units into the structure of liquid water, with a favorable configuration for enhanced hydrogen bonding.<sup>6</sup> Another interesting feature of the PEO aqueous solution is its reverse temperature dependence of solubility, displaying a lower critical solution temperature (LCST). The LCST behavior is generally attributed to a decrease in solvation due to loss of hydrogen bonding to water<sup>5</sup> and/or the attainment of a polymer configuration of lower dipole moment at higher temperatures.<sup>7</sup> A closed-loop phase diagram has been reported for aqueous solutions of PEO of certain molecular weights.<sup>8</sup> PEO presents an opposite solubility behavior of UCST (upper critical solution temperature) type in some organic solvents.<sup>8,9</sup> Some of these features have recently been addressed by Israelachvili,<sup>10</sup> commenting on “the different faces of PEO” and stressing the importance of a better understanding of its “unusual properties”, especially because of the PEO ubiquitous presence in commercial products and in industrial and biomedical processes.

This paper follows this path, reporting a thermodynamic investigation of PEO partitioning. Results of direct measurements of Gibbs energies and enthalpies for the transfer of PEO of different molecular weights between aqueous and organic phases are reported, aiming at a better description of the driving forces underlying such processes.

### Experimental Section

**Materials.** Ethylene oxide oligomers and polymers used in this study were PEO 300 (Aldrich), PEO 1500 (Aldrich), PEO 3350 (Sigma), PEO 10 000 (Sigma), PEO 20 000 (Merck), PEO

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35 000 (Fluka), and PEO dimethyl ethers 500 and 2000 (Aldrich). Liquid or pasty polymers were kept over molecular sieves for drying (in some cases, after they were heated to 60 °C for 4 h). Solid polymers were dried under vacuum after they were heated. PEO dimethyl ethers were extracted from the aqueous solution with  $\text{CH}_2\text{Cl}_2$  after they were recovered from the organic phase by solvent removal under vacuum for 24 h. Number average molecular weights of PEO 500 and 2000 dimethyl ethers were determined as described elsewhere<sup>11,12</sup> by vapor pressure osmometry (using a Knauer osmometer), in toluene solutions at 55 °C providing values of  $522 \pm 55$  and  $2070 \pm 55 \text{ g mol}^{-1}$ , in good agreement with the nominal values.

Water of Milli-Q quality was used throughout, and organic solvents were treated as follows. Dichloromethane (pa, from Synth) was kept under reflux with previously activated  $\text{CaCl}_2$  for 24 h, then distilled under nitrogen, and collected over molecular sieves. Chloroform and chlorobenzene (both pa, from Synth) were washed with water, dried over  $\text{K}_2\text{CO}_3$ , refluxed with  $\text{P}_2\text{O}_5$  and  $\text{CaCl}_2$  for 2 h, distilled, and kept over molecular sieves.

**Partitioning Measurements.** The procedure for determination of PEO partition coefficients was previously described.<sup>4</sup> Briefly, equal volumes (ca. 3 mL) of aqueous and organic PEO solutions were shaken and equilibrated for at least 48 h in a temperature-controlled water bath at 298 K (with temperature stability of 0.01 K). Aliquots of each phase were removed, and the polymer content was determined by dry weight after solvent removal by heating at 60 °C for 24 h. Most partition coefficients were determined with systems containing ca. 10 wt % PEO. However, systematic measurements in systems with 1, 5, 10, and 20 wt % PEO 3350 were performed, producing essentially the same results. Because PEO 3350 is the polymer of highest molecular weight for which thermodynamic data were determined, hence the most prone to be affected by polymer–polymer interactions, the invariance of  $K$  values for experiments with different polymer contents led us to assume that these interactions do not play a significant role in the processes under investigation. Systems were prepared by loading PEO either in the aqueous or in the organic phases, with no measurable differences in the obtained partition coefficients. For systems with  $K$  values up to 100, at least three experiments were performed, with reproducibility better than 2%. For systems with larger  $K$  values, an average of 10 measurements was performed, but even then, these  $K$  values were associated with larger deviations (up to 30% in the worst cases).

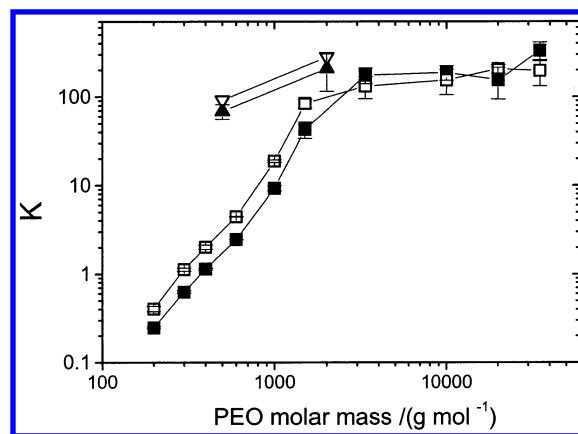
**Determination of the Water Content in the Organic Phases.** Water dragging upon PEO transfer from aqueous to organic phases was determined by assaying the water content of organic phases by Karl Fisher titration, using Orion AF 8 equipment.

**Calorimetric Measurements.** Solution enthalpies were measured with a Thermometric 2255 solution calorimeter, operating inside a Thermometric 2277 water bath at 298 K (with a temperature stability of 0.0001 K), by the ampule breaking technique. Accuracy was confirmed by the agreement of the measured solution enthalpy for KCl with literature data.<sup>13</sup>

The enthalpy changes associated with PEO transfer from aqueous to organic phases were calculated from PEO solution enthalpies, as follows

$$\Delta_{\text{t}}H_{\text{PEO}} = \Delta_{\text{sol}}H_{\text{PEO}}^{\text{org}} - \Delta_{\text{sol}}H_{\text{PEO}}^{\text{aq}} \quad (1)$$

where the superscripts org and aq refer to organic and aqueous phases.



**Figure 1.** PEO partitioning in biphasic systems at 298 K as a function of molecular weight. Squares, PEO; triangles, dimethyl PEO. Open symbols, water/chloroform; solid symbols, water/dichloromethane systems. Partition coefficients are defined as the ratio of mole fractions (calculated on a monomer basis) in organic to aqueous phases. Data taken from ref 4 (except for PEO 1500, 10 000, and 20 000, this study).

Solution enthalpies were determined both in pure solvents and in ternary mixtures containing PEO, water, and organic solvent at the same composition of the partitioning experiments. Enthalpy values obtained in pure solvents were used to estimate a hypothetical enthalpy of transfer of PEO between pure water and pure organic solvents, whereas data for ternary systems allowed the determination of enthalpy changes associated with the transfer of PEO in the same conditions at which partition coefficients were measured. In each experiment, about 0.3 g of PEO was added to ca. 80–100 mL of liquid, producing energy changes of ca. 7 J. Empty ampules (at least 10) were broken in the pure solvents or in the ternary mixtures, and the average energy was subtracted from the measurements with PEO. Such corrections were significant only for organic phases. At least two sets of three consecutive PEO additions were performed for each determination. No trend was observed for the solution enthalpies within these experiments; hence, these values were assumed to represent differential enthalpies.<sup>14</sup>

## Results and Discussion

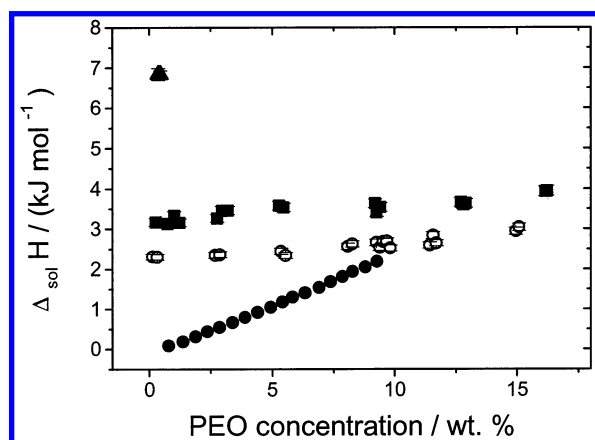
Data on the effect of PEO molecular weight on the partitioning between aqueous and organic phases from this and from a previous study<sup>4</sup> are summarized in Figure 1. These data show that end group contribution to PEO solution behavior becomes less significant as the molecular weight increases, leveling off at 2000–3000  $\text{g mol}^{-1}$ . On the basis of this interpretation, we have proposed that the transition from polyglycol to polyether character occurs around 2000  $\text{g mol}^{-1}$ . A previous investigation of PEO solubility, based on chromatography, proposed this transition at 1000  $\text{g mol}^{-1}$ .<sup>15</sup> Other properties of PEO such as melting point<sup>16</sup> and enthalpy of fusion<sup>17,18</sup> display a similar molecular weight dependency,<sup>4</sup> confirming that end group contributions affect a variety of PEO properties. Moreover, the data in Figure 1 confirm the earlier statement that PEO above a certain molecular weight may be quantitatively extracted from water to certain organic solvents.<sup>1</sup> Interestingly, chlorobenzene, in which PEO displays significant solubility (estimated as  $33.3 \pm 0.2 \text{ wt } \%$ , using the same procedure as before<sup>4</sup>), is not capable of extracting PEO within the molecular weight range studied. This finding suggests that a subtle balance between PEO solvation by water and by the organic solvents controls the partitioning process.

To investigate the balance of solvation forces controlling PEO partitioning, we determined the enthalpy of transfer for PEO

**TABLE 1: Enthalpies of Solution for PEO in the Aqueous and Organic Phases (Ternary Systems) and Thermodynamic Functions for PEO Partitioning in Aqueous/Organic Biphasic Systems, Determined at 298 K**

	PEO 300			PEO 3350			PEO 500 dimethyl		PEO 2000 dimethyl	
	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Cl	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Cl	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>
$\Delta_r G$ (kJ mol <sup>-1</sup> ) <sup>a</sup>	-0.3 ± 0.1	1.16 ± 0.08	10 ± 1	-12.0 ± 0.7	-12.7 ± 0.9	9 ± 3	-11.2 ± 0.2	-10.5 ± 0.5	-14.0 ± 0.9	-13 ± 1
$\Delta_r H$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	1.1 ± 0.3	2.2 ± 0.4	3.4 ± 0.1	2.2 ± 0.1	2.8 ± 0.1	4.6 ± 0.7	2.3 ± 0.2	3.3 ± 0.2	1.9 ± 0.2	2.9 ± 0.3
$T\Delta_r S$ (kJ mol <sup>-1</sup> )	1.4 ± 0.3	1.1 ± 0.5	-7 ± 1	14.2 ± 0.7	15.5 ± 0.9	-4 ± 3	13.5 ± 0.2	13.8 ± 0.5	15.9 ± 0.9	16 ± 1
$\Delta_{sol} H^{aq}$ (kJ mol <sup>-1</sup> ) <sup>c</sup>	-5.57 ± 0.01	-5.5 ± 0.2	-5.65 ± 0.05	0.62 ± 0.05	0.61 ± 0.03	1.34 ± 0.07	-8.0 ± 0.2	-7.7 ± 0.1	0.06 ± 0.02	0.2 ± 0.1
$\Delta_{sol} H^{org}$ (kJ mol <sup>-1</sup> ) <sup>c</sup>	-4.5 ± 0.3	-3.3 ± 0.2	-2.29 ± 0.08	2.84 ± 0.05	3.36 ± 0.09	5.9 ± 0.6	-5.7 ± 0.4	-4.44 ± 0.06	2.0 ± 0.2	3.1 ± 0.2

<sup>a</sup>  $\Delta_r G$  calculated as  $\Delta_r G = -RT \ln K$ , where  $K$  is defined as the ratio of PEO mole fractions (calculated on basis of ethylene oxide units) in organic to aqueous phases (data taken from ref 4). <sup>b</sup>  $\Delta_r H$  calculated from PEO solution enthalpies in organic and aqueous phases (see text). <sup>c</sup> Enthalpies of PEO solution in ternary systems (aqueous and organic phases), at the same composition of the partitioning experiments.

**Figure 2.** Solution enthalpies at 298 K for PEO 3350 in different solvents, expressed per mole of ethylene oxide units. ●, water; ○, chloroform; ■, dichloromethane; and ▲, chlorobenzene.

between the two phases. A negative enthalpy of transfer indicates a more energetically favorable solvation of the transferred component at the final stage, whereas positive values reveal an opposite situation.

The determined enthalpies of solution for PEO in the different aqueous and organic phases (always ternary systems, at the same composition of the partitioning experiments) and the calculated enthalpies of transfer, determined through eq 1, are shown in Table 1 for PEO 300 and 3350 and dimethyl PEO 500 and 2000. Transfer enthalpies for all macromolecules, from water to organic phases, in all systems investigated, are positive, indicating that PEO solvation in the aqueous phase is more energetically favorable (more negative enthalpy of solvation) than in the organic phase. These values are more positive for systems containing chlorobenzene but very similar with chloroform and dichloromethane.

Enthalpy changes for the hypothetical transfer of PEO 3350 from pure aqueous to pure organic solvents were derived from the solution enthalpies determined in pure solvents displayed in Figure 2. Taking the polymer concentrations in the phases as equal to the equilibrium values of the partitioning experiments, these enthalpies of transfer were calculated as 2.4, 3.3, and 4.5 kJ mol<sup>-1</sup>, respectively, for PEO 3350 transfer from water to chloroform, dichloromethane, and chlorobenzene (for this last system, the value of solution enthalpy in water was extrapolated to ca. 15 wt % of polymer, assuming the same trend displayed in Figure 2). These values are very close to the values determined from the solution enthalpies in the actual ternary systems (see Table 1), suggesting that the presence of the other solvent does not significantly affect the energetics of PEO

solvation in either phase. This finding is consistent with a small degree of polymer solvation by organic solvent when in the aqueous phase, and also by water when the polymer is dissolved in the organic phase (an issue discussed in more detail later).

The solution enthalpies shown in Figure 2, expressed on monomer basis, are in good agreement with those reported by Maron and Filisko<sup>19</sup> for PEO 6000 in the same solvents. The solution enthalpies reflect the balance of a series of processes involved in PEO dissolution that may be summarized as follows:

$$\Delta_{sol} H = \Delta_{p/p} H + \Delta_{s/s} H + \Delta_{p/s} H \quad (2)$$

where (p/p) represents the disruption of PEO–PEO interaction, (s/s) represents the disruption of solvent–solvent interaction, and (p/s) represents polymer solvation. The first two terms are positive (endothermic processes), whereas the last one is expected to be negative. For polymers with some degree of crystallinity, as PEO, it has been shown<sup>18</sup> that the process (p/p), hence the determined enthalpy of solution, depends on the thermal history of the polymer sample as it affects the sample crystallinity. As polymer concentration increases, an interaction between polymer chains in solution may appear, giving rise to an extra process in eq 2, causing a variation of solution enthalpy with PEO concentration, as can be seen in the data for aqueous solutions in Figure 2.

Because all experiments were conducted with the same sample of PEO, the (p/p) term in eq 2 is constant; therefore, the smaller the solution enthalpy, the more energetically favorable the dissolution of PEO should be (the same trend expected for PEO solvation). The data shown in Figure 2 thus suggest that PEO solvation is more enthalpically favored by water, followed by chloroform, dichloromethane, and chlorobenzene.

Because PEO transfer from the aqueous to organic phase is associated with an increase in enthalpy, for systems where this transfer is favorable (with CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, for molecular weights >300–400 g mol<sup>-1</sup>), the transfer process must be directed by an entropy increase large enough to overcome the unfavorable enthalpic contribution. The values for the thermodynamic functions of PEO transfer from aqueous to organic phases, listed in Table 1, show that a significant entropy increase is associated with the spontaneous transfer of PEO 3350 and dimethyl PEO 500 and 2000 from aqueous to chloroform and dichloromethane phases, whereas an entropy decrease accompanies the transfer of PEO 300 and 3350 to chlorobenzene.

At this point, it is not possible to ascribe the causes for the entropy increase. The entropy increase was earlier attributed to a looser PEO conformation in organic phases.<sup>1</sup> PEO configuration in the solid state is well-established as a helix containing



**TABLE 2: Amount of Water, Expressed as Weight %, in the Organic Phases after PEO Partitioning**

	H <sub>2</sub> O in the CHCl <sub>3</sub> phase	( <i>N<sub>w</sub></i> / <i>N<sub>EO</sub></i> ) in CHCl <sub>3</sub> <sup>a</sup>	H <sub>2</sub> O in the CH <sub>2</sub> Cl <sub>2</sub> phase	( <i>N<sub>w</sub></i> / <i>N<sub>EO</sub></i> ) in CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>
no polymer	0.101 ± 0.003		0.178 ± 0.004	
PEO 300	0.32 ± 0.06	0.18 ± 0.04	0.44 ± 0.06	0.27 ± 0.07
PEO 3350	0.51 ± 0.01	0.078 ± 0.001	0.55 ± 0.03	0.06 ± 0.05
PEO 35 000	0.51 ± 0.01	0.08 ± 0.01	0.60 ± 0.01	0.07 ± 0.01
PEO 500 dimethyl	0.56 ± 0.03	0.086 ± 0.001	0.61 ± 0.01	0.09 ± 0.01
PEO 2000 dimethyl	0.680 ± 0.009	0.088 ± 0.003	0.57 ± 0.02	0.09 ± 0.02

<sup>a</sup> Number of moles of water per mole of EO unit. Calculated assuming the excess amount of water, discounting the solubility of water in the pure organic solvent from the total amount of water.

seven EO units per period.<sup>20–22</sup> The population of *trans*–*gauche*–*trans* conformers, respectively, for O–CH<sub>2</sub>, H<sub>2</sub>C–CH<sub>2</sub>, and H<sub>2</sub>C–O bonds is proposed to be responsible for this helicoidal structure. Much of the helix structure is somewhat lost upon melting the solid, and *trans*–*trans*–*trans* conformers are present in the liquid.<sup>23</sup> Both experimental and theoretical investigations have shown that in water and in hydrogen-bonding organic solvents the preference for *trans*–*gauche*–*trans* conformation is maintained.<sup>24–26</sup> Specifically in chloroform solutions, the PEO conformation has been proposed to resemble that of the molten state, although a significant population of *trans*–*gauche*–*trans* conformers may be present. This has been ascribed to formation of bifurcated hydrogen bonds by chloroform molecules and oxygen atoms of the EO units.<sup>24</sup>

Therefore, it is possible that some entropic gain is associated with a looser configuration of PEO in organic solutions, with respect to aqueous ones. However, the change in configuration entropy would be expected to be greater for larger PEO chains, especially considering that ca. seven EO units are needed to assemble each step in the helix. The finding that even the transfer of dimethyl PEO 500, an oligomer with only 12 EO units, is associated with an entropy increase per EO unit that is similar to the increases observed for PEO 3350 and dimethyl PEO 2000 (ca. 76 and 45 EO units) suggests that the entropy change is not only associated with polymer configuration. Moreover, this line of thought would imply that the negative values obtained for the entropy of transfer from aqueous to chlorobenzene phases be attributed to a more constrained PEO chain configuration in this organic phase, an idea that has no support in the current literature.

On the other hand, an entropic control over processes involving solvation in aqueous systems is not unique, as this is the basis for the hydrophobic effect, which invokes large entropy increases associated with the release of water of solvation around apolar moieties of a solute.<sup>27</sup> We recently established that the process of phase separation in PEO aqueous solutions induced by some electrolytes, leading to formation of aqueous two phase systems, is entropy driven.<sup>28</sup> The entropic contribution was related to PEO hydration, being ascribed to the release of water molecules on separation of PEO. Other spontaneous processes involving nonionic hydrophilic polymers like PEO, such as their binding to anionic surfactants like sodium dodecyl sulfate, are also endothermic and, hence, driven by an entropy increase,<sup>29</sup> which is related to displacement of water solvation molecules from PEO. In all of these processes, release of water solvation molecules from PEO vicinity produces an entropy increase large enough to overcome the loss of solvation energy represented by the enthalpy increase. The increase in entropy upon dehydration of PEO implies a stronger entropic restriction for hydrogen bonding between water and PEO than for the water–water interaction. Although no direct assessment on this subject could be found, such a conclusion is suggested by theoretical investigations of PEO aqueous solutions.<sup>5,30</sup>

To assess changes in the solvation of PEO, we determined the amount of water transferred with each EO unit from the aqueous to the organic phases. This was done by assaying the water content in saturated organic solvents and in the mutually saturated phases obtained in the presence of PEO 300 and 3350 and dimethyl PEO 500 and 2000. The first finding is that there is an extra amount of water dissolved in the organic phase due to the presence of PEO. Hence, it is reasonable to assume that these extra water molecules are involved in PEO solvation, bound strongly enough to be transferred with PEO and not replaced with molecules of the organic solvent. These results are summarized in Table 2.

It is noteworthy that the numbers of extra water molecules per EO unit are very close (ca. 0.08 mol of water per mol of EO) for the transfer of PEO 3350 and dimethyl PEO 500 and 2000 to both chloroform and dichloromethane. Considering earlier evidence that for PEO above 3000 g mol<sup>−1</sup> the contribution of hydroxyl end groups is not significant,<sup>4</sup> this constant ratio indicates that EO solvation in these solutions involves the same number of water molecules. Assuming that solvation of EO units for the smaller PEO 300 is similar to that for the other polymers, the number of water molecules involved in the solvation of the hydroxyl end groups may be estimated as 0.3 and 0.6 water molecules per OH group, respectively, in chloroform and dichloromethane. Interestingly, hydration numbers found for EO and OH groups are quite low and much smaller than numbers commonly reported for hydration of PEO in water, which may vary from one to six water molecules per EO unit, depending on the techniques and definitions employed.<sup>5,31–33</sup> Such a remarkable reduction in the number of water molecules involved in solvation of both EO and hydroxyl groups confirms a significant water displacement due to competition with chloroform and dichloromethane. The release of water molecules caused by this displacement accounts for the entropy increase involved in PEO transfer, previously proposed as the driving force controlling this process.

Water dragging in the transfer of solutes from aqueous to organic phases is a well-studied phenomenon. Tsai and co-workers<sup>34</sup> have analyzed this phenomenon in connection with solute–water interaction for the partitioning of a series of structurally diverse compounds in water/*di-n*-butyl ether biphasic systems.<sup>34</sup> They report (excess water/solute) ratios in the organic phase between ca. 0.03 and 0.8, proposing that the water-dragging effect is primarily due to the H-bond donor capacity of the solutes and, secondarily, to their H-bond-accepting capabilities. Although a direct comparison of these data with results obtained with (CH<sub>2</sub>CH<sub>2</sub>O)<sub>*n*</sub> may be difficult, the smaller water-dragging effect of EO units may be ascribed to the H-bond-accepting features of PEO and, possibly, a more effective EO solvation by chloroform and dichloromethane than by *di-n*-butyl ether.

An earlier investigation of the thermodynamics of partitioning of a homologous series of alkoxyphenols between aqueous and

organic phases<sup>35</sup> provides data that support the same proposition. In that study, Beezer and co-workers estimated entropies of transfer for the methylene unit ( $\text{CH}_2$ ) and a "parent structure", in that case,  $\text{HO}(\text{C}_6\text{H}_4)\text{O}$ , between mutually saturated phases produced by mixing water with heptane, octanol, or propylene carbonate. The solubility of water in the organic phases follows the sequence: heptane < octanol < propylene carbonate. The entropies of transfer for  $\text{CH}_2$  were positive, being smaller with propylene carbonate ( $3.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and larger with heptane ( $13.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ), consistent with the view that the release of water molecules in the vicinity of apolar solutes is larger for a less hydrated system (heptane). It is noteworthy that the entropies of transfer for the polar moiety, the parent structure, are quite different, with values of 69.0, 1.8, and  $-38 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively, for systems containing heptane, octanol, and propylene carbonate. Once more, these values point out that the transfer of moderately polar moieties from water produces a large entropy increase when the final phase is significantly dehydrated but may be associated with a negative entropy change if the amount of water in the organic phase is large enough (this being the case in propylene carbonate) so that hydration does not greatly differ between the organic and the aqueous phases.

It was not possible to determine the amount of water molecules dragged by PEO into chlorobenzene-containing phases due to the small amount of polymer transferred. These data would be important to confirm, or disprove, the hypothesis for such a driving force. Chloroform and dichloromethane differ from chlorobenzene due to their hydrogen bond-donating capability, a feature already recognized as important to PEO solvation.<sup>15</sup> Therefore, although capable of dissolving a significant amount of PEO, chlorobenzene may not interact strongly enough with PEO to displace water. Such an interaction should involve hydrogen bonding of solvent molecules with oxygen of PEO ether groups (especially for larger polymers where end group contribution is not relevant). It would be interesting to check the hypothesis of hydrogen-bonding capability as a key factor in PEO solvation for other organic solvents. Preliminary experiments show that solvents such as tetrahydrofuran and ethyl acetate, which are hydrogen bond acceptors but not donors, are incapable of extracting significant amounts of PEO 3350 from water.

It would also be relevant to test whether such a hypothesis may be pertinent for other hydrophilic polymers. In general, if polymer hydration is strong enough to restrain a large amount of water molecules and an organic solvent is capable of displacing a significant fraction of these water molecules, the entropy gain may overcome the less energetic enthalpy of solvation by the organic solvent, driving polymer transfer to the organic phase.

## Conclusion

The picture that arises from such data is that PEO may be extracted from water to organic phases, as long as some requirements are fulfilled as follows: the organic solvent must have significant hydrogen bond-donating capability in order to interact strongly enough with EO units. If prevailing, this interaction would release water solvation molecules, an event associated with considerable entropy increase, that may be large enough to overcome the loss in solvation energy (represented by a positive enthalpy of transfer), driving the transfer process. Such a transfer becomes more favorable as the polymer

molecular weight increases, due to the relative decrease in the contribution of hydroxyl end groups. In this respect, for PEO, the transfer from water to chloroform and dichloromethane becomes predominant for molecular weights above 300–400  $\text{g mol}^{-1}$ .

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