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hydrocarbons (PAHs) and hence shorter analysis time. In addition, this should lead to better selectivity in the separation. The presence of the alcohols will also reduce the competition between the solvent and stationary phase for the polynuclear aromatics.

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**Registry No.**  $\gamma$ -CD-pyrene, 87832-35-7;  $\gamma$ -CD-H<sub>2</sub>O, 134970-99-3;  $\gamma$ -CD-H<sub>3</sub>CCH<sub>2</sub>OH, 134971-00-9;  $\gamma$ -CD-H<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>OH, 134971-01-0;  $\gamma$ -CD-(H<sub>3</sub>C)<sub>2</sub>CHOH, 134971-02-1;  $\gamma$ -CD-H<sub>3</sub>C(CH<sub>2</sub>)<sub>3</sub>OH, 134971-03-2;  $\gamma$ -CD-(H<sub>3</sub>C)<sub>3</sub>COH, 134971-04-3;  $\gamma$ -CD-H<sub>3</sub>C(CH<sub>2</sub>)<sub>4</sub>OH, 134971-05-4;  $\gamma$ -CD-cyclopentanol, 134971-06-5;  $\gamma$ -CD-cyclohexanol, 134971-07-6.

## Conformational Adaption of Poly(ethylene oxide). A <sup>13</sup>C NMR Study

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The <sup>13</sup>C NMR chemical shift was used as a probe for the average partition of rotational conformers around the C-C bond in the O-CH<sub>2</sub>-CH<sub>2</sub>-O segments of poly(ethylene oxide). Dividing the conformers into a large group of trans and a smaller group of gauche conformers, we concluded that the trans conformers have a higher (downfield) average chemical shift than the gauche conformers. The shift of the main PEO <sup>13</sup>C line with changing environment was interpreted as an adaption in the partition between the two groups of conformers. Furthermore, the trans conformers had nonpolar character and were favored at high temperatures, whereas the gauche conformers had polar character. The measurements were compared to the predictions of a model proposed by Karlström, and a semiquantitative agreement was found.

### Introduction

Poly(ethylene oxide) (PEO), pure or in solution, has been extensively studied as a component of nonionic surfactants and block copolymers but also in its own right. Specifically, Raman,<sup>1-4</sup> NMR,<sup>5-8</sup> and other methods<sup>9-11</sup> have been used to study the conformational changes induced by changing the solvent or the temperature. Analysis of the Raman spectra<sup>1-4</sup> suggests that the largest variation of the conformation with changing environment is due to shifting the ensemble average of rotational conformers around the C-C bond in the O-CH<sub>2</sub>-CH<sub>2</sub>-O segments. It is empirically found that decreasing the temperature or increasing the polarity (or hydrogen bonding capacity) of the solvent favors the gauche conformers. These observations are corroborated by NMR coupling constants<sup>5-8</sup> and in some respect by theoretical calculations.<sup>10,11</sup> Furthermore, the free energy of interaction between PEO and a polar solvent goes through a maximum with increasing temperature. This is manifested in the contraction of PEO coils with increasing temperature<sup>12</sup> and by the phase separation at a lower consolute point<sup>13</sup> in water and formamide.

Karlström<sup>14</sup> has proposed a model where the conformational adaption to the environment provides the mechanism of the changing free energy of interaction, thus connecting the above observations. The gist of the model is the division of the rotational conformers into two groups. Members of the smaller group (gauche) interact favorably with polar moieties, whereas members of the larger group (trans) have less favorable interaction with polar groups. The partitioning of conformers between the two groups therefore depends on the temperature and the local environment. With this extra degree of freedom extending the Flory-Huggins theory, Karlström succeeded in choosing a set of parameters that gave a reasonable reproduction of the PEO-water binary phase diagram. The simple but powerful model has been successfully incorporated in a number of calculations<sup>15,16</sup> and supported by phase behavior studies,<sup>17</sup> but its predictions of the conformational changes have never been tested directly. This is our aim.

We argue that the <sup>13</sup>C NMR chemical shift of the methylene carbons in PEO provides a measure of the ensemble average of conformers. Such an interpretation has been attempted previously by Ahlinäs et al.<sup>18</sup> The basic assumption is that the gauche group gives rise to a lower (upfield) average chemical shift than does the trans group. Rapid interconversion between the conformers produce one single peak whose shift is indicative of the partition between the groups. A number of observations support this assumption. Dioxane, which obviously is constrained in an extreme gauche conformer, has a <sup>13</sup>C chemical shift (66.5 ppm, relative to TMS)<sup>19</sup> which is considerably lower than that of the unconstrained dimethoxyethane (72.3 ppm).<sup>20</sup> Analysis of the <sup>13</sup>C shifts

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of the crown ether 1,4,7,10-tetraoxacyclododecane (12-crown-4) also shows that the conformation with trans conformers occurs at a higher average chemical shift than that with only gauche conformers.<sup>21</sup> Furthermore, IR and X-ray studies of the 12-crown-4 sandwich complex with sodium suggest that the crown ether is constrained in a all gauche conformation in the complex. Going from the uncomplexed 12-crown-4 in solution to the constrained complex changes the shift from 71.5 to 66.8 ppm.<sup>22</sup> The shift of the complex is rather insensitive to solvent, and thus most of the shift can be ascribed to conformational changes.<sup>23</sup> For alkyl chains it is well-known that the predominant changes of the <sup>13</sup>C chemical shifts are due to conformational changes rather than "medium effects".<sup>24</sup> In this investigation we have measured the <sup>13</sup>C NMR chemical shift of poly(ethylene oxide) in different environments and at different temperatures. The simple spectrum consists of three lines: a strong signal due to internal methylene groups, flanked by two small signals due to the end methylene groups near the hydroxyl group. Only the shift of the strong central signal was studied.

### Experimental Section

The measurements were performed on a Bruker MSL 100 FT NMR and a JEOL FX-100 FT NMR spectrometer operating at 25.18 MHz. The optimum resolution was approximately 0.25 Hz, or 0.01 ppm. The shifts were measured relative to hexamethyldisilane (HMDS) as external reference in a coaxial inertube. Poly(ethylene glycols) of two molecular weights were used, 6000 (Serva) and 600 (Merck), with molecular weight ranges according to the manufacturer of 6000–7500 and 570–630, respectively. All solvents and additives were of analytical grade (except NaI, which was suprapur) and were used as supplied. To provide a lock signal, the water used was a mixture of Millipore filtered water and D<sub>2</sub>O (>99%, Norsk Hydro), such that 20% wt/wt of the total sample was D<sub>2</sub>O. In the cases where no water was present, the shifts were observed on the MSL without field frequency stabilization.

### Magnetic Susceptibility Effects

Using an external standard avoids artifacts due to interactions of the reference with the sample but introduces the problem of differential shielding. The magnetic field experienced by the reference and the sample depends on the shape of the containers due to polarization near the surface. It can be shown<sup>25</sup> that for long and perfectly cylindrical vessels placed perpendicularly with respect to the field axis (i.e., in an electromagnet) the intrinsic chemical shift is related to the observed value through

$$\delta_{\text{int}} = \delta_{\text{obs}}^{\perp} - (2\pi/3)(\chi_{\text{ref}} - \chi_{\text{sample}}) \quad (1)$$

where  $\chi$  is the magnetic susceptibility. For the same vessel placed in a longitudinal field (i.e., in a superconducting solenoid) the relation is

$$\delta_{\text{int}} = \delta_{\text{obs}}^{\parallel} + (4\pi/3)(\chi_{\text{ref}} - \chi_{\text{sample}}) \quad (2)$$

Elimination of the susceptibilities gives the intrinsic chemical shift in terms of the observed shifts:

$$\delta_{\text{int}} = \frac{1}{3}(\delta_{\text{obs}}^{\parallel} + 2\delta_{\text{obs}}^{\perp}) \quad (3)$$

Settings eqs 1 and 2 equal and rearranging, we get the expected differences in chemical shift between the two types of magnets to be

$$\delta_{\text{obs}}^{\parallel} - \delta_{\text{obs}}^{\perp} = 2\pi(\chi_{\text{ref}} - \chi_{\text{sample}}) \quad (4)$$

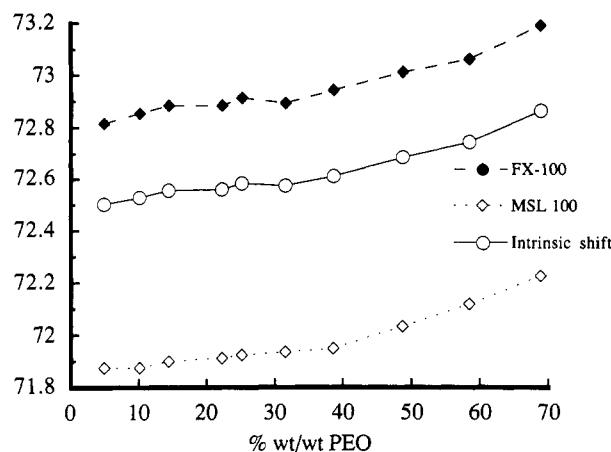


Figure 1. <sup>13</sup>C chemical shifts observed in an electromagnet (FX) and in a superconducting coil (MSL) and calculated intrinsic shift with changing weight percentage of PEO 600 in water at 25 °C.

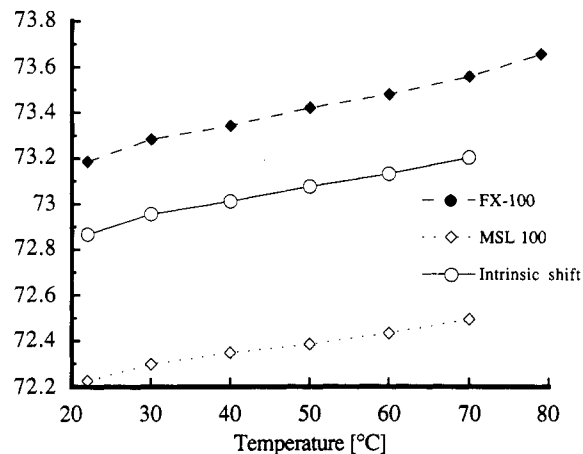


Figure 2. <sup>13</sup>C chemical shifts observed in an electromagnet (FX) and in a superconducting coil (MSL) and calculated intrinsic shift with changing temperature for a 68.9% PEO 600 in water.

We studied the susceptibility effect with changing PEO concentration (Figure 1) and with changing temperature (Figure 2). Using eq 4, assuming that the magnetic susceptibility of HMDS is similar to that of hexamethyldisiloxane (−0.560 ppm),<sup>26</sup> and taking the water susceptibility (−0.719 ppm)<sup>25</sup> for the sample yield that the MSL shifts should be approximately 1 ppm lower than the FX shifts. This is the observed difference. With changing concentration of PEO this difference is largely constant but is increasing with changing temperature. However, the susceptibility effects with increasing temperature are small and can be neglected. With increasing temperature the shift of the reference itself may change but was found to be approximately −0.07 ppm (MSL, no lock) with a 50 °C increase. This boosts the increasing shift of PEO with increasing temperature but has not been corrected for in the results given. Any shift difference due to substitution of H<sub>2</sub>O with D<sub>2</sub>O is negligible. From Figures 1 and 2 it is clear that the observed shifts follow the same trend as the intrinsic chemical shifts (with minor reservations for changing temperature) and are thus indicative of the ensemble average of rotational conformers. For simplicity, we have chosen to report the <sup>13</sup>C NMR chemical shifts relative to that of HMDS as observed on the Bruker MSL 100.

### Theoretical Model

In the extended Flory–Huggins theory proposed by Karlström,<sup>14</sup> the Helmholtz free energy of mixing can be written as

$$A = U - TS + A_{\text{int}} \quad (5)$$

(26)  $\chi/\rho$  was given in *CRC Handbook of Physics and Chemistry*, and  $\rho$  was found in the Aldrich catalogue.

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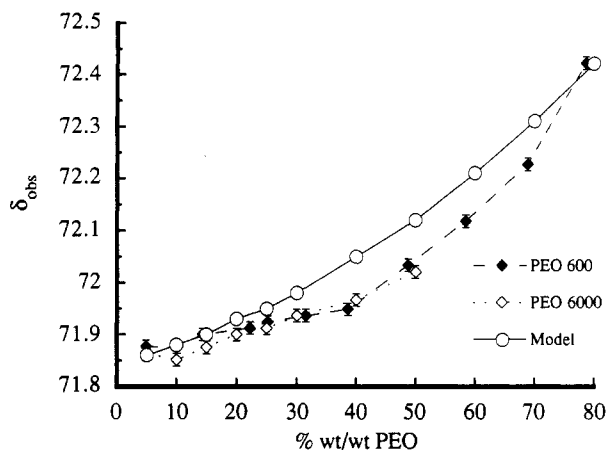


Figure 3.  $^{13}\text{C}$  chemical shifts predicted and observed (MSL) with changing PEO concentration in water at 25 °C.

The entropic contribution to the free energy is independent of the internal states and is thus given (in  $kT$  units) by the familiar

$$\beta TS = -n_0 \ln \Phi_0 - (n_1/r) \ln \Phi_1 \quad (6)$$

where  $\beta = [kT]^{-1}$ ,  $r$  is the number of monomers in the polymer chain, and  $n_0$  ( $n_1$ ) is the number of sites occupied by solvent (monomers), with  $\Phi_0$  ( $\Phi_1$ ) being the corresponding volume fraction. Taking the two internal states into account, the energy of mixing is

$$\beta U = n_0 \Phi_1 [P\chi_{0G} + (1-P)\chi_{0T}] + n_1 \Phi_1 \chi_{GT} P(1-P) \quad (7)$$

where  $\chi$  is the Flory-Huggins interaction parameter,  $P$  (and  $1-P$ ) is the probability that a monomer is in the gauche (trans) group, and the indices 0, G, T denote the "species": solvent, gauche, and trans, respectively. It is convenient to choose the internal reference such that the internal free energy is zero in the absence of internal states. Arbitrarily choosing the gauche group of internal states as reference, the internal free energy takes the form

$$\beta A_{\text{int}} = n_1 \left\{ P \ln P + (1-P)\alpha + (1-P) \ln \frac{(1-P)}{g} \right\} \quad (8)$$

where  $\alpha$  is the internal energy difference between gauche and trans, and  $g$  is the number of states in the trans group divided by the number of states in the gauche group. For a given temperature ( $T$ ), composition ( $\Phi_1$ ), and set of parameters  $\{\chi_{0G}, \chi_{0T}, \chi_{GT}, \alpha, g\}$ , the probability ( $P$ ) is chosen so that the Helmholtz free energy is minimized. Karlström<sup>14</sup> found a reasonable reproduction of the binary PEO-water system by choosing the parameters<sup>16</sup> to be  $RT\chi_{0G} = 0.6508$ ,  $RT\chi_{0T} = 5.568$ ,  $RT\chi_{GT} = 1.266$ ,  $RT\alpha = 5.086 \text{ kJ mol}^{-1}$ , and  $g = 8$ .

## Results and Discussion

Given the composition and temperature, the partition between the gauche and trans groups can be predicted by the Karlström model and the above parameters. Consequently, provided with the average shift for the gauche and the trans group the observed shift can be calculated. By fitting the model at two experimental points (5% and 80% PEO in Figure 3), the gauche shift and the trans shift are estimated to be 71.58 and 73.83 ppm, respectively. In Figures 3–5 we compare the shifts predicted by the model with the experimental results as a function of concentration and as a function of temperature at three concentrations (5%, 50%, and neat PEO 600). (The error bars on the experimental results are indicative of the optimal resolution.) A semiquantitative agreement is observed.

There are two driving forces for conformational change in the model: Since the number of trans conformers is larger than the number of gauche conformers, they are favored by increasing temperature as all possible conformers then tend to be equally populated. Moreover, giving each of the two groups different

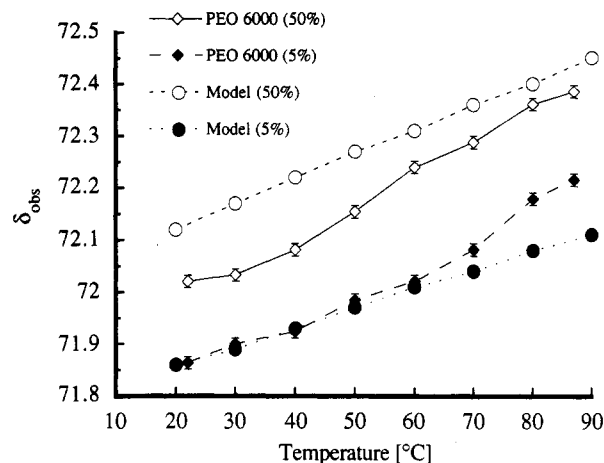


Figure 4.  $^{13}\text{C}$  chemical shifts predicted and observed (MSL) with changing temperature for two concentrations 5 and 50% of PEO 6000.

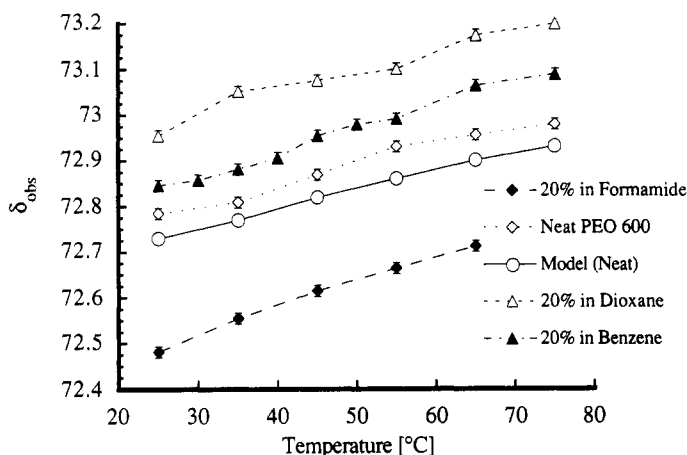


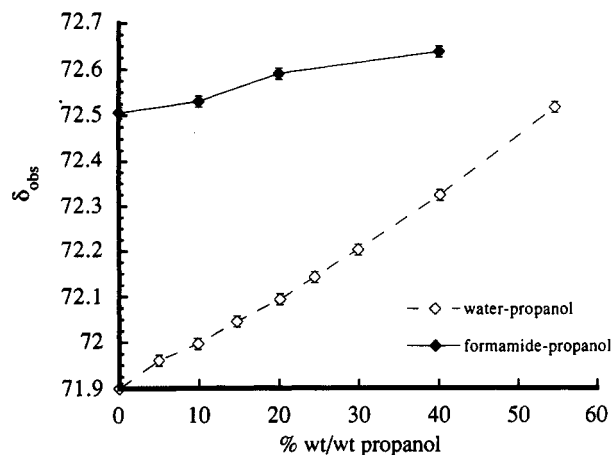
Figure 5.  $^{13}\text{C}$  chemical shifts predicted and observed (MSL) with changing temperature for neat PEO 600 and for 20% PEO 6000 in formamide, benzene, and dioxane.

interaction with the immediate surrounding will segregate the groups. Two other (interrelated) model for the temperature-dependent interaction between PEO and water, hydrogen bonding<sup>4,13</sup> and "water-structure",<sup>27</sup> could potentially rationalize the conformational changes as a secondary effect. However, since conformational changes do occur with changing temperature even though no water is present (Figure 5), models invoking "water structure" arguments seem less plausible as a single mechanism. Furthermore, solvent-structure arguments are difficult to quantify.<sup>28</sup> Predicting conformational changes with hydrogen bonding will become rather complicated since it requires temperature-dependent interaction with the different conformers. Furthermore, it cannot explain the conformational changes in neat PEO 600. Apart from the conformational predictions, the advantage of the Karlström model is that the temperature and concentration dependence of the PEO-water interaction is not introduced ad hoc but through standard statistical mechanical functions with easily interpretable parameters. While the other mechanisms cannot be excluded, the above model thus seems to be the simplest plausible model for the behavior of PEO in solution. A minor limitation due to cooperative interactions not included in the model is manifested by crystallized PEO, which is reported<sup>1</sup> to have mainly gauche conformers (indicating a helical arrangement).

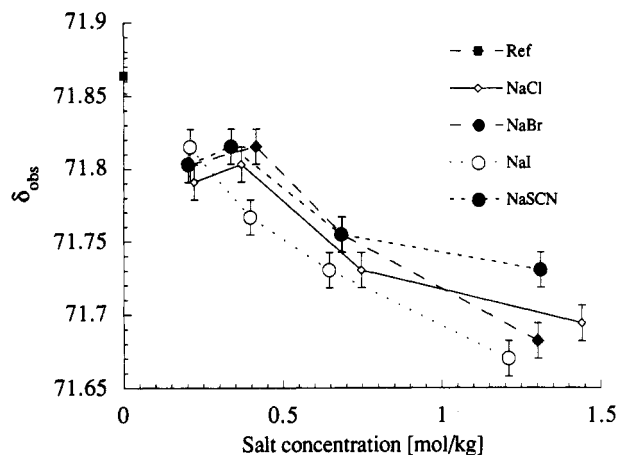
Increasing the relative amount of propanol in a mixed solvent (Figure 6) favors the trans conformers, which seems to confirm the nonpolar character of that group. This character is of course also confirmed in Figure 3, by the increasing shift with increasing

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**Figure 6.**  $^{13}\text{C}$  chemical shifts observed (MSL) for 20% PEO 6000 in mixed solvents, water-propanol and formamide-propanol, at 25 °C.

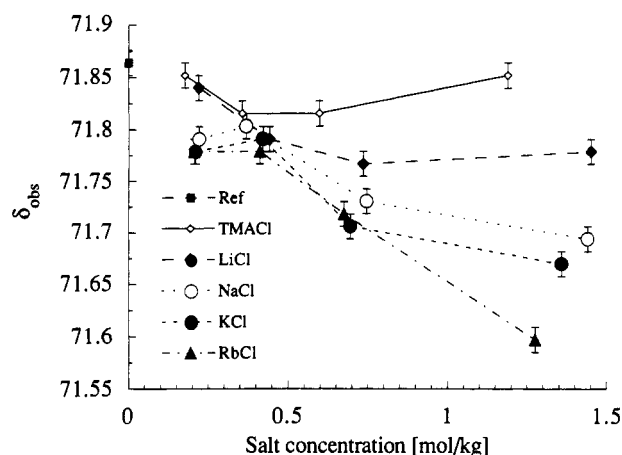


**Figure 7.**  $^{13}\text{C}$  chemical shifts observed (MSL) for 20% PEO 6000 in water with different anions at 25 °C.

concentration of PEO. By elevating the temperature, the bias toward the trans conformers thus leads to less advantageous interactions with polar solvents as discussed above. Similarly, the addition of salts favors the gauche conformers, but the effects in terms of shift are much smaller. The ability of the ion to change the shift seems to follow the Hofmeister series<sup>29</sup> for both anions (Figure 7) and cations (Figure 8) (except for NaSCN, perhaps due to susceptibility effects).

The effect of additives, in terms of chemical shift, is dependent on how far from the internal entropy maximum the starting point is. Thus additives that favor the conformers further away from the internal entropy maximum will be less "effective" in changing the chemical shift. In water we expect the gauche conformers to be highly populated and any further increase of that population is accompanied by a comparatively large free energy cost. Thus, the effect of 1.5 *m* NaI in formamide gives a decrease in the shift by 0.3 ppm, whereas in water the decrease is 0.2 ppm. A similar effect upon addition of propanol is seen in Figure 6.

An additional phenomenon affecting the shift in mixed solvents may be due to preferential solvation or adsorption of additives.<sup>30</sup> For the water-propanol system the combined effect of removing propanol-solvent and PEO-solvent contact in favor of propanol-PEO and solvent-solvent contact clearly would bias the latter



**Figure 8.**  $^{13}\text{C}$  chemical shifts observed (MSL) for 20% PEO 6000 in water with different cations at 25 °C (TMA = tetramethylammonium).

arrangement at low propanol content and thus increase the shift further.

A similar conceptual model may be used to support the Hofmeister effect for ions. Clearly, the ions suffer from decreased and anisotropic solvation near the PEO. However, some of this loss may be regained by replacing water-PEO contacts with water-water contacts. Moreover, if the ions are polarizable the anisotropic solvation may be made more favorable. Thus, if ions are polarizable and large (where solvation gives a smaller gain in free energy and where more water is replaced), they are more likely (or less unlikely) to be close to the PEO chains and therefore change the conformations more effectively. The larger effect on the shift by the cations as compared to the anions is probably due to specific interactions with the ether oxygens.

We conclude that the model of Karlström satisfactorily reproduces both the phase behavior and the conformational changes of PEO semiquantitatively. The study supports the idea that conformational changes is one important mechanism in the thermodynamic behavior of PEO. The knowledge that the increasing  $^{13}\text{C}$  chemical shift is related to a less polar environment can be used to interpret more complex systems. In the study of the interaction of PEO and sodium dodecyl sulfate (SDS), Cabane<sup>31</sup> found an increasing  $^{13}\text{C}$  shift for PEO upon addition of SDS as the chains wrapped around the micelles in the proposed "pearl necklace." Our observations support the interpretation that the PEO segments replace water near the hydrophobic micellar core. Similarly, Almgren et al.<sup>32</sup> found an increase of the PEO chemical shift in PEO-poly(propylene oxide)-PEO triblock copolymers upon addition of SDS. The decreased polarity of the environment may be due to either the induced mixed micelle formation or direct interaction with SDS as above, or both.

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**Registry No.** PEO, 25322-68-3; TMAcI, 75-57-0;  $\text{HC(O)NH}_2$ , 75-12-7;  $\text{H}_2\text{O}$ , 7732-18-5; NaCl, 7647-14-5; NaBr, 7647-15-6; NaI, 7681-82-5; NaSCN, 540-72-7; LiCl, 7447-41-8; KCl, 7447-40-7; RbCl, 7791-11-9; dioxane, 123-91-1; benzene, 71-43-2; propanol, 62309-51-7.

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