Raman Spectroscopic Observations of Anomalous Conformational Behavior of Short Poly(oxyethylene) Chains in Water

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The Raman spectra of aqueous solutions of $CH_3(OCH_2CH_2)_mOCH_3$ (m = 1–4) were measured for mole fractions down to 0.005. The spectral observation for the compounds with $m \geq 2$ indicates that, on addition of water, the POE chain progressively prefers the *gauche* conformation for the OCH_2–CH_2O segment at the first stage, but this direction of the conformational preference is reversed for concentrations lower than a particular solution composition. This anomalous conformational behavior is suggestive of a new structural aspect of the POE–water system.

Poly(oxyethylene) (POE)[1] ($-OCH_2CH_2-)_m$ is soluble in water in all proportions at moderate temperatures, unlike other structurally related polymers.[2] The mechanism of the high water solubility and of a related phenomenon of the phase separation at higher temperatures[3] has attracted much attention of many investigators for a long time.[4,5] The fundamental problems relevant to the POE–water system are the interactions between the POE chain and water, the structure of water, and the conformation of the POE chain. In particular, the conformational behavior of the POE chain in water is important, because it plays a central role among others in the emergence of particular properties and functions of the POE–water system. In fact, a model based on the conformation of the POE chain has been proposed for elucidating the phase behavior of POE and POE-type nonionic surfactants in water.[6]

Conformational properties of the POE chain in water have been studied actively in recent years by a number of experimental and theoretical methods. A Raman spectroscopic study has shown the evidence that the population of the *gauche* conformation about the OC–CO bond of the POE chain increases with increasing water fraction.[7] An experimental difficulty was encountered, however, of observations of the Raman spectra for further diluted solutions. For the purpose of studying dilute aqueous solutions by Raman spectroscopy, we have recently developed a multi-reflection Raman cell.[8] Using this new device, we succeeded in the present work in obtaining the Raman spectra of aqueous solutions of short POE compounds $CH_3(OCH_2CH_2)_mOCH_3$ ($C_1E_mC_1$) with m = 1–4 for mole fractions down to 0.005 with sufficient signal-to-noise ratios and found anomalous conformational behavior of the short POE chain in low concentration regions. The experimental results indicate that the population of the *gauche* conformation about the OC–CO bond *decreases* with increasing water fraction in concentration regions lower than a particular solution composition. In this letter, we report this new experimental finding, which is highly suggestive of a new structural aspect of the POE–water system. This anomalous conformational behavior of the POE chain in water was further confirmed by infrared spectroscopy.[9]

In the present work, we focused on a spectral region between 800 and 900 cm^{-1}, where well-defined conformation-sensitive bands of the POE chain are observed. The Raman spectra of aqueous solutions of $C_1E_mC_1$ (m = 2 and 3) are shown in Figure 1. All of the compounds studied exhibit three bands in this wavenumber region. According to normal coordinate analysis,[7,10] a prominent band at 851–855 cm^{-1} and a shoulder at 832–834 cm^{-1} are associated with the OCH_2–CH_2O segment in the *gauche* conformation, while a weaker band at 808–823 cm^{-1} is associated with the same segment in the *trans* conformation. In the present analysis, we used the bands at 851–855 cm^{-1} (*gauche*) and 808–823 cm^{-1} (*trans*) to examine the conformational behavior of the POE chain. In Figure 2, the intensity ratio of the two bands, I_{gauche}/I_{trans}, is plotted against a mole fraction of $C_1E_mC_1$, where the integrated band intensities are measured as areas of the resolved Pearson components.

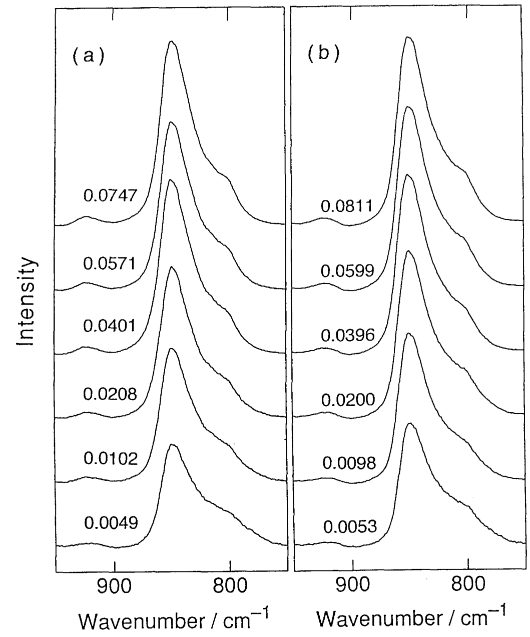

Figure 1. Raman spectra of aqueous solutions of (a) $C_1E_2C_1$ and (b) $C_1E_3C_1$. Mole fractions of the solute are indicated in the figure.

A remarkable observation in Figure 2 is that the intensity ratio for $C_1E_2C_1$, $C_1E_3C_1$, and $C_1E_4C_1$ shows a maximum at solute mole fractions of 0.019±0.004, 0.030±0.006, and 0.030±0.006, respectively. For $C_1E_1C_1$, however, no maximum of the intensity ratio was observed in the concentration range studied. The spectral observation for $C_1E_mC_1$ with $m \geq 2$ indicates that, on addition of water, the POE chain progressively prefers the *gauche* conformation for the OCH_2–CH_2O segment at the first stage, but this direction of the conformational preference is reversed for concentrations lower than a particular solution composition. The decrease of the *gauche* conformation, or the increase of the *trans* conformation, with increasing water fraction

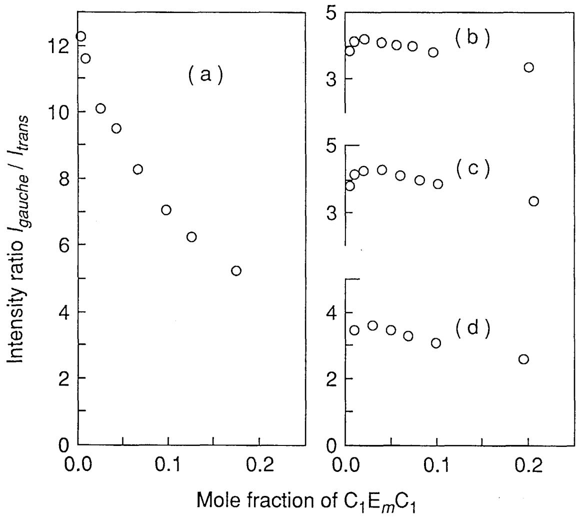

Figure 2. Intensity ratio I_{gauche}/I_{trans} for aqueous solutions of $C_1E_mC_1$ (m = 1–4) as plotted against a mole fraction of the solute: (a) $C_1E_1C_1$, (b) $C_1E_2C_1$, (c) $C_1E_3C_1$, and (d) $C_1E_4C_1$.

was observed for this binary system for the first time. The observed maximum of the *gauche* population can be interpreted either as anomalous enhancement of the stabilization of the *gauche* conformation in a limited concentration region or as substantial declination of the stabilization of the *gauche* conformation in concentration regions lower than a particular composition of the binary system.

The overall increase of the *gauche* population with increasing water fraction is explained by the dielectric effect in the medium and the effect of the hydrogen bonding between the ether oxygens of the POE chain and water. The former effect implies that the *gauche* conformation of the OCH_2–CH_2O segment with larger dipole moment is more stabilized than the *trans* conformation with smaller dipole moment in the medium of water which has higher dielectric constant than $C_1E_mC_1$.[11] It should be noted, however, that the dipole moment of the OCH_2–CH_2O segment depends also on the conformation about the CO–CC and CC–OC bonds.[12] The importance of the hydrogen bond in the stabilization of the *gauche* conformation[13] is shown by the favorable formation of hydrogen-bonded bridges of water molecules between the adjacent ether oxygens of the *gauche* OCH_2–CH_2O segment, as supported by molecular dynamics and Monte Carlo simulations.[14,15]

The dielectric effect stabilizes the *gauche* conformation steadily with increasing water fraction, while the stabilization by the hydrogen-bond effect is expected to reach its maximum when the surface of the POE chain is all covered with water molecules and will be substantially constant on further addition of water. Thus, other factors must be responsible for the observed conformational behavior showing the maximum of the *gauche* population. We may speculate on possible formation of specific structure of the POE–water system. This structural effect may change the conformation of the POE chain in a complicated manner with a change of the composition of the binary system. A related experimental observation reported is a minimum of the partial molar volume of $C_1E_mC_1$ (m = 1 and 2) in water in similar concentration regions;[16,17] the mole fraction at the point of the minimum is 0.04 for $C_1E_1C_1$ and 0.03 for $C_1E_2C_1$. These values of the mole fraction do not coincide, however, with those at the point of the maximum *gauche* population. These experimental results suggest that complicated behavior of the interactions involved most probably accounts for the peculiar properties of dilute aqueous solutions of short POE compounds. The new experimental finding in the present work obviously promotes further relevant studies for elucidating a number of interesting phenomena of the POE–water system.

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References and Notes

1 The term ‘poly(oxyethylene) (POE)’ is used in this paper to indicate the $(-OCH_2CH_2-)_m$ group irrespective of the number (m) of monomeric units.

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