Hydration of Short-chain Poly(oxyethylene)s in Carbon Tetrachloride Studied by Infrared Spectroscopy

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The hydration of short-chain poly(oxyethylene)s in carbon tetrachloride has been studied by infrared spectroscopy. Monodentate and bidentate hydrogen bonds of water are involved in the hydration. The latter hydrogen bond is formed between ether oxygen atoms separated by two or more oxyethylene units.

Poly(oxyethylene) (POE) is an important polymer that has diverse applications in biotechnology and biomedical sciences.[1] The primary reason for being applied to these areas is that this polymer shows practically unlimited solubility in water at moderate temperatures.[2] Among possible factors that are responsible for the high water solubility, hydrogen bonding of the POE chain with water is a prevalent one.[3,4] In fact, molecular dynamics simulations have predicted the hydration structure of a POE chain in water.[5] However, no decisive experimental observations of hydration structure of this polymer have been reported. We have therefore undertaken infrared spectroscopic studies of hydration of POE chains, aiming eventually at clarifying the peculiar properties of POE in water.[2,3]

We have sought experimental conditions under which a water molecule does not form hydrogen-bonded bridges between different POE chains. This situation enables us to study primitive hydration structure composed only of a water molecule and a single POE chain. The above conditions are satisfied if we study hydrogen bonding of water in carbon tetrachloride, where a small amount of POE is dissolved. The solubility of water in CCl_4 is 8.7×10^{-3} mol dm^{-3} at 25 °C,[6–8] which is equivalent to a mole ratio of CCl_4 to water 1:0.00084. In this work, we studied infrared spectra of water-saturated CCl_4 solutions of five short-chain POE compounds (or oligo(oxyethylene)s, OOEs), namely $CH_3(OCH_2CH_2)_mOCH_3$ ($C_1E_mC_1$) with $m = 1$–4 and 18-crown-6 (cyclo-$(OCH_2CH_2)_6$). The mole ratio of CCl_4 to water was held constant at 1:0.00084 in all experiments performed at 25 °C. The infrared spectra of solution samples with 5 mm thickness held between KBr plates were recorded on a Bruker IFS66V vacuum spectrometer. The spectral resolution was 2 cm^{-1}.

We examined the infrared spectra in the 3400–3800 cm^{-1} region where the bands due to O–H stretching modes of water are observed. The bands of the combinations and overtones of OOEs, which may disturb spectral analysis of relevant O–H stretching bands, were removed from the spectra of water-saturated CCl_4 solutions of OOEs by subtracting the spectra of the corresponding water-free CCl_4 solutions of OOEs with the same concentrations. The infrared spectra obtained this way for the five OOE compounds, along with diethyl ether as comparison, at a mole ratio of OOE:CCl_4:H_2O = 0.01:0.99:0.00083 (denoted hereafter as a mole fraction of OOE 0.01) are shown in Figure 1, where the spectrum of water-saturated CCl_4 without OOE is also given. Figure 2 shows the infrared spectra of water-saturated CCl_4 solutions of $C_1E_mC_1$ ($m = 1$–3) at various mole fractions.

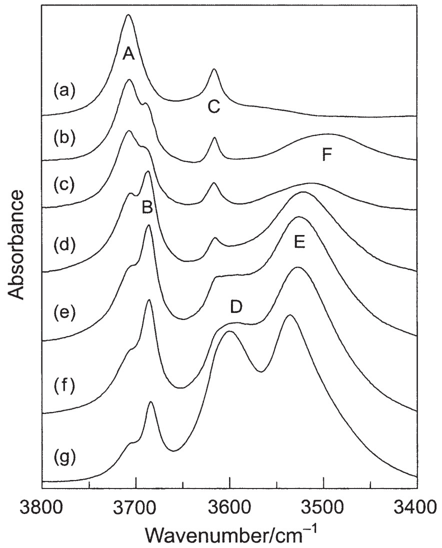

Figure 1. Infrared spectra, at 25 °C, of (a) water-saturated CCl_4 with no added OOE and water-saturated CCl_4 solutions of (b) diethyl ether, (c) $C_1E_1C_1$, (d) $C_1E_2C_1$, (e) $C_1E_3C_1$, (f) $C_1E_4C_1$, and (g) 18-crown-6, at a mole fraction 0.01.

In the spectra in Figures 1 and 2, six O–H stretching bands of water are observed at 3707 (A), 3685–3688 (B), 3615 (C), 3590–3600 (D), 3520–3535 (E), and 3495–3515 cm^{-1} (F), as summarized in Table 1. Before discussing their assignments, we should keep in mind that two types of hydrogen bonding of a water molecule with a POE chain, as shown in Figure 3, are possible; one (type I) is single hydrogen bonding in monodentate fashion, where only one of the O–H bonds of a water molecule participates in hydrogen bonding, and the other (type II) is bridging hydrogen bonding in bidentate fashion, where both of the O–H bonds of a water molecule participate in hydrogen bonding.

Bands A and C are observed for all OOEs studied and diethyl ether at a mole fraction 0.01 (Figure 1). They are assigned to the O–H stretching of free water molecules, because the spectrum of water-saturated CCl_4 with no added OOE exhibits the same bands. Band B, observed for all OOEs at a mole fraction 0.01, increases in intensity relative to bands A and C with increasing OOE fraction (Figure 2). The same band is also observed for diethyl ether, with which possible hydrogen bonding of water is only of type I in this mole fraction region. Accordingly, considering its wavenumber as well, we can assign band B to the stretching of the unbonded O–H bond of water in type I hydrogen bonding.

For the assignment of bands for type II hydrogen bonding, the O–H stretching bands of water in diethyl ether serve as a

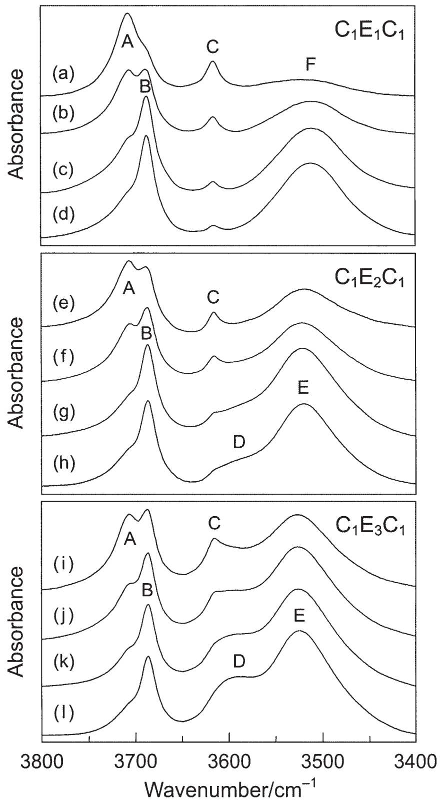

Figure 2. Infrared spectra, at 25 °C, of water-saturated CCl_4 solutions of $C_1E_1C_1$ (a–d), $C_1E_2C_1$ (e–h), and $C_1E_3C_1$ (i–l) at mole fractions (a) 0.008, (b) 0.015, (c) 0.031, and (d) 0.048; (e) 0.007, (f) 0.011, (g) 0.033, and (h) 0.057; (i) 0.005, (j) 0.011, (k) 0.021, and (l) 0.050.

Table 1. Observed O–H stretching bands of water in water-saturated CCl_4 solutions of OOEs

Band	ν_{obs}/cm^{-1}	Assignment[a]
A	3707	$\nu_{HOH(antisym)}$ of free water
B	3685–3688	$\nu_{OH(unbonded)}$ of type I water
C	3615	$\nu_{HOH(sym)}$ of free water
D	3590–3600	$\nu_{HOH(antisym)}$ of type II water
E	3520–3535	$\nu_{HOH(sym)}$ of type II water
F	3495–3515	$\nu_{OH(H\text{-}bonded)}$ of type I water

[a] The local symmetry of free and type II water molecules is C_{2v}, while that of a type I water molecule is C_s.

reference, because the water molecule forms type II bridging hydrogen bonds between different diethyl ether molecules in this solution. The wavenumbers of the relevant bands reported are 3600 (antisymmetric) and 3525 cm^{-1} (symmetric).[9] The wavenumber of band D, observed for $C_1E_2C_1$, $C_1E_3C_1$, $C_1E_4C_1$, and 18-crown-6, but not for $C_1E_1C_1$, well corresponds to the former of the wavenumbers given above. The progressive increase of the relative intensity of this band with increasing OOE fraction (Figure 2) and no observation of this band for diethyl ether (Figure 1) ensure the assignment of band D to the antisymmetric O–H stretching of water participating in type II hydrogen bonding. Band E, on the other hand, is assigned to the symmetric O–H stretching of water in type II hydrogen bonding, as evidenced by its wavenumber coinciding with the wavenumber of water in diethyl ether given above and by its intensity behavior with increasing OOE fraction.

For $C_1E_1C_1$ and diethyl ether, less prominent band F is observed (Figure 1), which is assigned to the stretching of the hydrogen-bonded O–H bond of water in type I hydrogen bonding for the reason described for band B. Band F for other OOEs is heavily overlapped with band E. The present assignments of the observed O–H stretching bands of water (Table 1) are consistent with those in a previous work on 18-crown-6 in water-saturated CCl_4.[10]

Having established the band assignments, we now discuss the hydration structure of short-chain POEs. The fact that band B is observed for all OOEs studied indicates that type I hydrogen bonding is invariably involved in the hydration of the POE chain. Band D is absent in the spectra for $C_1E_1C_1$, while the intensity of this band observed for the longer OOEs becomes stronger as the chain length increases. This observation shows that hydrogen bonding between $C_1E_1C_1$ and water is only of type I. Type II hydrogen bonding is possible for those OOE compounds that comprise two or more oxyethylene units and is more dominant for the longer compounds.

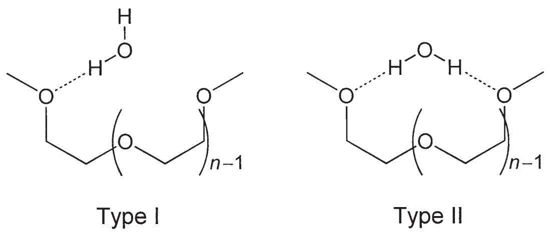

Figure 3. Two types of hydrogen bonding of a water molecule with a POE chain: type I (monodentate) and type II (bidentate).

The important finding in this work is that type II hydrogen bonds of water are not formed between adjacent ether oxygen atoms O_a and O_b in the $-O_aCH_2CH_2O_b-$ structure. A previous quantum chemical study of a 1:1 complex of $C_1E_1C_1$ with water[11] has indicated that the calculated three lowest-energy configurations all involve type I hydrogen bonding, not type II, being consistent with our experimental results. Type II hydrogen bonding is possible between ether oxygen atoms separated by two or more oxyethylene units ($n \geq 2$, Figure 3). The unaccomplished type II hydrogen bonding of a water molecule between adjacent ether oxygen atoms can be explained by presumed unfavorable geometry of lone electron pairs of the oxygen atoms for the formation of hydrogen bonds with a water molecule. The present results suggest that $C_1E_1C_1$, the shortest OOE compound, is not an adequate model compound for POE in respect of hydrogen bonding with water.

References and Notes

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