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Hydration of the Oxyethylene Chain. Hypersonic Velocities in Aqueous Solutions of α-Methyl-ω-methoxyoligo(oxyethylene)s and α-Methyl-ω-hydroxyoligo(oxyethylene)s as Studied by Brillouin Scattering

Hiroatsu MATSUURA* and Koichi FUKUHARA
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730

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Hydration of the oxyethylene chain was studied by a Brillouin-scattering method; hypersonic velocities in aqueous solutions of $CH_3(OCH_2CH_2)_mOCH_3$ with $m=1—4$ and $CH_3(OCH_2CH_2)_mOH$ with $m=2$ and 3 were measured. The concentration of the solution, at which the sound velocity gave a maximum value, led to the number of water molecules, at the highest hydration, per ether linkage in the oxyethylene chain. The experimental results showed that 1.8 water molecules take part in the hydration of each $-CH_2OCH_2-$ group and that the number of the water molecules is virtually constant independently of the oxyethylene-chain length as far as the number of the oxyethylene units is limited up to four. These findings indicate that a sort of hydration complex of approximately 1 $-OCH_2CH_2-$:2 H_2O is formed in the aqueous solution. It is suggested that the stabilization of the *gauche* conformation for the OCH_2-CH_2O group in aqueous solution, as evidenced by Raman-spectroscopic observations, is promoted greatly by the hydrogen bond of water molecules which are bridged between the adjacent ether oxygens in the oxyethylene chain.

Properties and structures of nonionic surfactants having oxyethylene chain as a hydrophilic group have been studied extensively by various experimental methods.[1)] One of the current interests in nonionic surfactant chemistry is the hydration of the oxyethylene chain,[2—9)] since the hydration structure is closely related to the size and shape of the micelles[10,11)] and the phase behavior.[12)] In order to elucidate the hydration of the oxyethylene chain in the nonionic surfactants, investigation of hydration structure is first required for simple model compounds consisting of the oxyethylene units.

In the present work, we have studied hydration of the model compounds, α-methyl-ω-methoxyoligo(oxyethylene)s $CH_3(OCH_2CH_2)_mOCH_3$ ($m=1—4$) and α-methyl-ω-hydroxyoligo(oxyethylene)s $CH_3(OCH_2CH_2)_mOH$ ($m=2$ and 3), by measuring hypersonic velocities in aqueous solutions of these compounds by a Brillouin-scattering method. Brillouin scattering from liquid gives directly the velocity of sound propagating in the medium.[13)] In the liquid medium, fluctuations of density arise from the presence of sound waves of various wavelengths associated with the thermal energy of the medium, and passing of a monochromatic light-beam through such a medium gives rise to a change of frequency in the scattered light owing to the density fluctuation, the frequency shift $\Delta\nu$ being given by[14)]

$$\Delta\nu = \pm 2\nu_i(v/c)n\sin(\theta/2), \qquad (1)$$

where ν_i is the frequency of the incident light, v is the velocity of sound in the medium, c is the velocity of light in vacuum, n is the refractive index of the medium, and θ is the angle of scattering. For usual Brillouin-scattering experiments, the sound velocities obtained are those in the hypersonic region with frequencies of 1—10 GHz.

The sound velocity is correlated with elasticity or, conversely, compressibility of the medium in which the sound propagates. Accordingly, knowledge of the sound velocity will provide useful information of the structure of liquid or solution. It is expected that, when some ordered close structure is formed in solution, the volume and the compressibility of the solution will in general change; this leads to a change in sound velocity in the medium. The composition of the solution, at which the sound velocity reaches the extreme, is often the stoichiometric composition of a complex formed between the components. We have, therefore, examined the variation of the sound velocity with concentration for the aqueous solutions of $CH_3(OCH_2CH_2)_mOCH_3$ ($m=1—4$) and $CH_3(OCH_2CH_2)_mOH$ ($m=2$ and 3). A similar procedure, by detecting the change in fluidity of solutions, has been used to investigate extent of hydration.[15)]

Experimental

$CH_3(OCH_2CH_2)_mOCH_3$ ($m=1—4$) and $CH_3(OCH_2CH_2)_mOH$ ($m=2$ and 3) supplied by Tokyo Kasei Kogyo Co., Ltd. were purified by repeated distillation under reduced pressure. Water was carefully purified by distillation and filtration. Aqueous solutions of various mole fractions of these materials were prepared for the Brillouin-scattering measurements.

The experimental arrangement for the measurement of Brillouin scattering was essentially the same as that used in the previous studies.[16,17)] The light source was a helium-neon gas laser (NEC GLG5800) operated in the fundamental transverse mode at 632.8 nm with an output of about 50 mW. The light scattered from the sample at 90°

away from the incident-beam direction (θ=90°) was analyzed by a pressure-scanned Fabry-Pérot interferometer of Mizojiri Kogaku Kogyo Co., Ltd. The spacer between the interferometer etalons had a thickness of 6.075 mm, which gave the free spectral range[18] of 24.674 GHz. The Brillouin-scattering measurements were made, at least five times for each of the solutions, at 298±0.5 K by using a thermostat apparatus.

Results and Discussion

Some typical Brillouin spectra measured in this work are shown in Fig. 1. For the determination of sound velocity from the frequency shift, refractive index is required for each of the solutions studied. The refractive indices of aqueous solutions of $CH_3OCH_2CH_2OCH_3$ and $CH_3(OCH_2CH_2)_2OCH_3$ at various concentrations are available in the literature.[19,20] Therefore, the refractive indices at desired concentrations for these compounds were obtained from these data. The sound velocity thus obtained as a function of mole fraction of the solute is shown in Fig. 2. Since precise refractive-index data are not available for aqueous solutions of $CH_3(OCH_2CH_2)_3OCH_3$, $CH_3(OCH_2CH_2)_4OCH_3$, $CH_3(OCH_2CH_2)_2OH$, and $CH_3(OCH_2CH_2)_3OH$, the refractive indices were assumed to be

$$n = x_1 n_1 + x_2 n_2, \tag{2}$$

where x_1 and x_2 are mole fractions of the solution components and n_1 and n_2 are the refractive indices for their neat liquids. The sound velocities thus derived for the four compounds given above are shown in Figs. 3 and 4. In order to ensure the assumption of Eq. 2, the sound velocities for $CH_3OCH_2CH_2OCH_3$ and $CH_3(OCH_2CH_2)_2OCH_3$ are plotted, as shown in Fig. 5, against the refractive indices evaluated through Eq. 2. The plots in Figs. 2 and 5 give in fact the same value, within experimental error, of the mole fraction x_m, at which the sound velocity gives a maximum value, for each of the two compounds.

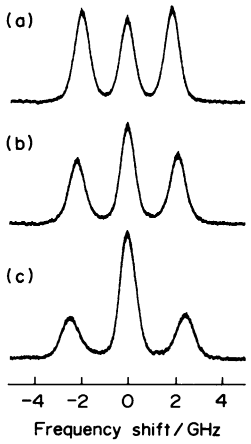

Fig. 1. Brillouin spectra of aqueous solutions of $CH_3OCH_2CH_2OCH_3$ with mole fractions of (a) 0.80, (b) 0.40, and (c) 0.125.

Figures 2—4 show that the maximum value of the sound velocity is at the mole fractions of 0.100, 0.085, 0.074, and 0.065, respectively, for the aqueous solutions of the monomer, dimer, trimer, and tetramer of $CH_3(OCH_2CH_2)_mOCH_3$ and at the mole fractions of 0.126 and 0.103, respectively, for those of the dimer and trimer of $CH_3(OCH_2CH_2)_mOH$. At these mole fractions of x_m, the aqueous solutions of

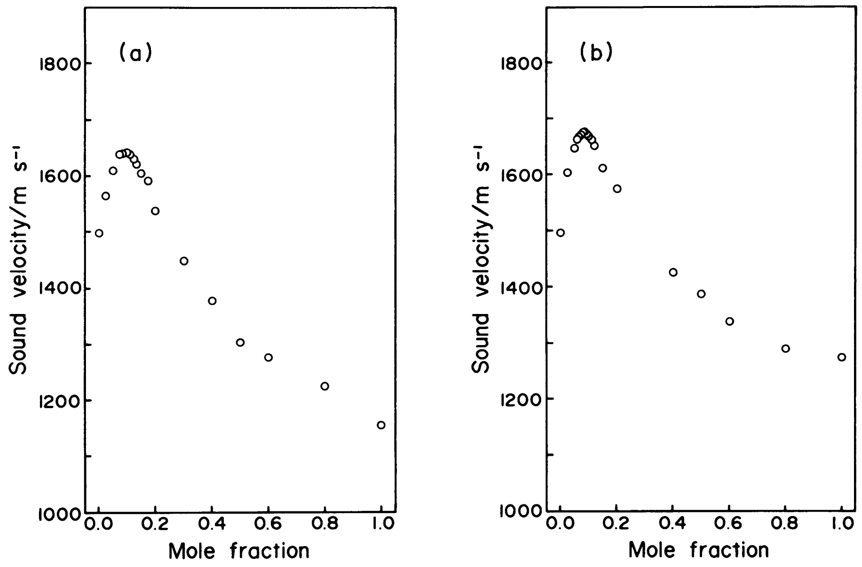

Fig. 2. Sound velocity vs. mole fraction of aqueous solutions of (a) $CH_3OCH_2CH_2OCH_3$ and (b) $CH_3(OCH_2CH_2)_2OCH_3$. Correct values for refractive index are employed.

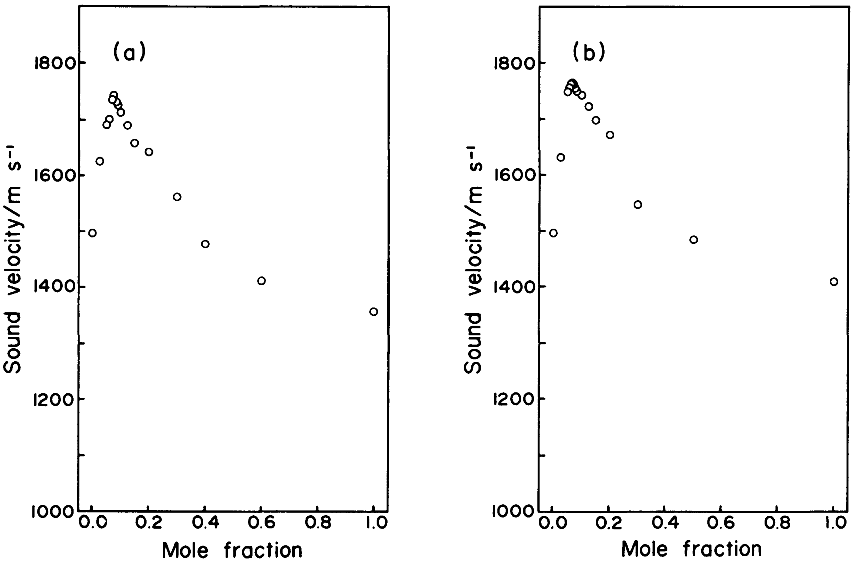

Fig. 3. Sound velocity vs. mole fraction of aqueous solutions of (a) $CH_3(OCH_2CH_2)_3OCH_3$ and (b) $CH_3(OCH_2CH_2)_4OCH_3$. A linear relation of refractive index with mole fraction is assumed.

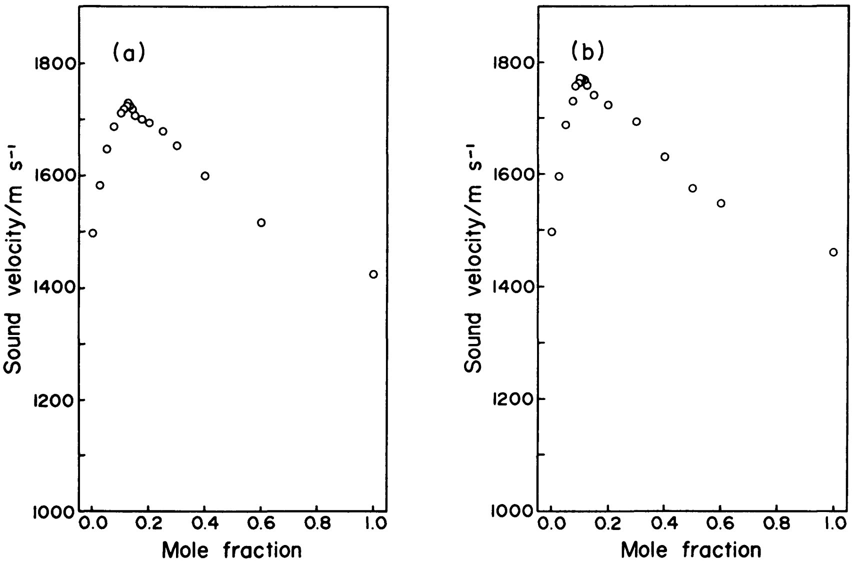

Fig. 4. Sound velocity vs. mole fraction of aqueous solutions of (a) $CH_3(OCH_2CH_2)_2OH$ and (b) $CH_3(OCH_2CH_2)_3OH$. A linear relation of refractive index with mole fraction is assumed.

the oligo(oxyethylene) compounds form the most compressed structure and all of the water molecules are expected to be involved in the hydration. For mole fractions of the solute larger than x_m, amount of water molecules is not enough to form the most close-packed solution structure; molecules of the oligo(oxyethylene) compounds themselves do not tend to form close structure as indicated by the fact that these molecules take rather disordered conformation in the neat liquid.[21] For mole fractions smaller than x_m, on the other hand, water molecules are more than enough for the highest hydration and the excess water molecules separate molecules of the oligo(oxyethylene) compounds from one another in solution, leading to less close solution structure.

The number of the water molecules, which are involved in the highest hydration, per each molecule of the oligo(oxyethylene) compounds is evaluated from their mole fractions x_m, at which the sound velocity is the maximum. The numbers obtained for

$CH_3(OCH_2CH_2)_mOCH_3$ with m=1, 2, 3, and 4 are 9.0_0, 10.7_6, 12.5_1, and 14.3_8, respectively, and those for $CH_3(OCH_2CH_2)_mOH$ with m=2 and 3 are 6.9_4 and 8.7_1, respectively. These results are summarized in Table 1.

The number of water molecules, at the highest hydration, per inner ether linkage $-CH_2OCH_2-$ in the molecular chain can be evaluated from the experimental results. If we assume that the corresponding number per terminal CH_3OCH_2- group is given by a half of the number of water molecules per molecule of $CH_3OCH_2CH_2OCH_3$. Thus, by using the number of 4.5 (=9.0/2) water molecules for the terminal CH_3OCH_2- part, the numbers of water molecules of hydration per $-CH_2OCH_2-$ group, $N_{CH_2OCH_2}$, are derived for the series of $CH_3(OCH_2CH_2)_mOCH_3$ compounds by the following equation:

$$N_{CH_2OCH_2} = (N_{mol} - 2\times 4.5)/n_{CH_2OCH_2}, \qquad (3)$$

where N_{mol} is the number of water molecules, at the highest hydration, per molecule and $n_{CH_2OCH_2}$ is the number of the $-CH_2OCH_2-$ group in the molecule. The values obtained are 1.7_6, 1.7_6, and 1.7_9 for the compounds of m=2, 3, and 4, respectively, which contain one, two, and three $-CH_2OCH_2-$ groups in the molecule. For the series of $CH_3(OCH_2CH_2)_mOH$ compounds, the number of hydration water molecules per $-CH_2OCH_2-$, $N_{CH_2OCH_2}$, may be given as a difference between the numbers of water molecules per molecule of $CH_3(OCH_2CH_2)_3OH$ (8.7_1) and $CH_3(OCH_2CH_2)_2OH$ (6.9_4); the number derived is 1.7_7.

It is worthy to note that the number of water molecules per ether linkage in the inner part of the oxyethylene chain, when the highest hydration is attained, is essentially the same for all of the model compounds treated in the present work. This experimental finding indicates that extent of hydration of the oxyethylene chain is virtually constant independently of the chain length as far as the number of the oxyethylene unit is limited up to four. The composition of a maximum of 1.8 water molecules per inner ether linkage, or equivalently per inner oxyethylene group, determined in the present work indicates that a sort of hydration complex of

Table 1. Mole Fractions x_m[a] and Ratios of the Numbers of Molecules and/or Group at x_m for Aqueous Solutions of $CH_3(OCH_2CH_2)_mOCH_3$ (m=1—4) and $CH_3(OCH_2CH_2)_mOH$ (m=2 and 3)

m	x_m	Ratios of the numbers of molecules and/or group at x_m	
		Solute : H_2O	$-CH_2OCH_2-$: H_2O
$CH_3(OCH_2CH_2)_mOCH_3$			
1	0.100	1 : 9.0_0	—
2	0.085	1 : 10.7_6	1 : 1.7_6[b]
3	0.074	1 : 12.5_1	1 : 1.7_6[b]
4	0.065	1 : 14.3_8	1 : 1.7_9[b]
$CH_3(OCH_2CH_2)_mOH$			
2	0.126	1 : 6.9_4	—
3	0.103	1 : 8.7_1	1 : 1.7_7[b]

a) Mole fraction of the solute, $CH_3(OCH_2CH_2)_mOCH_3$ or $CH_3(OCH_2CH_2)_mOH$, at which the sound velocity gives a maximum value. b) For evaluation of the ratio, see text.

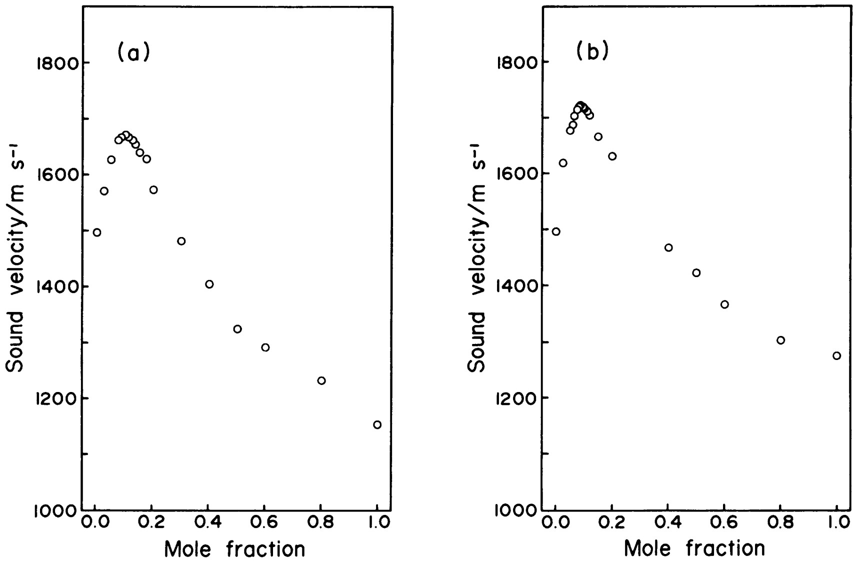

Fig. 5. Sound velocity vs. mole fraction of aqueous solutions of (a) $CH_3OCH_2CH_2OCH_3$ and (b) $CH_3(OCH_2CH_2)_2OCH_3$. A linear relation of refractive index with mole fraction is assumed.

approximately 1 $-OCH_2CH_2-:2\,H_2O$ is formed in the aqueous solution. The oxyethylene chain is incorporated with the water molecules in the formation of the structured hydration framework.

The present result of the extent of hydration appears to be consistent with the previous result, by means of the fluidity measurement, of 2.0 water molecules per ether linkage in $CH_3OCH_2CH_2OCH_3$ and $CH_3(OCH_2CH_2)_2OCH_3$.[15] The previous study[15] showed, however, that the extent of hydration was not different between the terminal CH_3OCH_2- group and the inner $-CH_2OCH_2-$ group. This inconsistency with the present result may be associated in part with the inherencies in the two different physical properties. It may be instructive to mention that the NMR measurements on α-hydro-ω-hydroxypoly(oxyethylene) with average molecular weight of 400, which corresponds to approximately nine oxyethylene units in the molecule, showed that three molecules of water were required for the hydration of each oxyethylene unit.[22]

The present observations show that more water molecules are involved in the hydration at the terminal CH_3OCH_2- group than at the inner $-CH_2OCH_2-$ group. This may be accounted for by possible existence of additional water molecules in the vicinity of the terminal methoxyl group. These water molecules will contribute, incorporated with the water molecules involved in the hydration at the inner ether linkages, to the formation of the structured hydration framework. This means that additional water molecules are necessary to close up an open end of the hydration framework at the CH_3O- terminal. For the compounds with the hydroxyl terminal, on the other hand, the $HOCH_2-$ group with hydrogen-bonding affinity can participate, in conjunction with the water molecules of hydration, in forming the hydration framework, and accordingly less water molecules of hydration will suffice for the terminal $HOCH_2-$ group. In fact, the results, shown in Table 1, on $CH_3(OCH_2CH_2)_mOH$ suggest that less than one water molecule is responsible for the hydration at the $HOCH_2-$ group.

The conformation of the oxyethylene chain in aqueous solution has been examined by a Raman-spectroscopic method[21,23,24]; further investigations are now in progress in our recent series of studies.[25,26] According to the analysis of Raman spectra,[21] the oxyethylene chain in aqueous solution becomes more ordered as the solution is diluted down to the mole fraction x_m, at which the hydration is completed. The dominant ordered structure is described by the *gauche* conformation of the OCH_2-OCH_2 group. On dilution with water, the *trans-gauche* conformation for the $O-CH_2-CH_2O$ group is most predominantly stabilized as compared with other possible conformations, and the *gauche-gauche* conformation follows the *trans-gauche*. The *gauche-trans* and *trans-trans* conformations are, however, much less stabilized than the above two, when the solution is diluted with water.[21]

These spectroscopic findings indicate that the stabilization of the *gauche* conformation for the OCH_2-CH_2O group is promoted greatly by the hydrogen bond formed between the ether oxygens and water molecules of hydration. Further speculation is possible that the water molecules are bridged between the immediately adjacent ether oxygens in the oxyethylene chain, in conformity with the stabilized *gauche* conformation of the OCH_2-CH_2O group. Various hydration models of the oxyethylene chain have been in fact proposed previously.[27–29] It seems, however, that further comprehensive experimental efforts are required for establishing more sophisticated hydration structures. The bridging hydrogen bonding mentioned above is nevertheless one of the most essential factors to maintain the *gauche* OCH_2-CH_2O structure in the oxyethylene chain.

It has been reported that the extent of hydration changes with increasing oxyethylene-chain length in α-n-alkyl-ω-hydroxypoly(oxyethylene)s, $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$, where the n-alkyl group is relatively long ($n>10$).[1] For these nonionic surfactant molecules, the effect of the alkyl chain seems to be significantly important in forming favorable hydration structures. The present result, obtained from the simpler model compounds, will be a basis for studying more complicated interactions between the hydrophilic moiety of the nonionic surfactants and water molecules.

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