Raman spectroscopic study of the hydration of short-chain poly(oxyethylene)s $C_1E_nC_1$ ($n = 1–4$)

Mircho Georgiev$^1$, Tatiana Popova$^1$, Zhorro S. Nickolov$^2$, Nikolay Goutev$^3$, Georgi Georgiev$^1$, Hiroatsu Matsuura$^4$

$^1$Department of Quantum Electronics, Faculty of Physics, Sofia University, 1164 Sofia, Bulgaria

$^2$Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, U.S.A.

$^3$CREST, Japan Science and Technology Corporation (JST), National Institute of Advanced Industrial Science and Technology (AIST), Higashi, Tsukuba, Ibaraki 305-8562, Japan

$^4$Department of Chemistry, Graduate School of Science of Hiroshima University, Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

Received 8 April 2004; accepted 21 July 2004

Abstract: The hypothesis that the degree of hydration of poly(oxyethylene) (POE) in aqueous solution depends on the mole ratio of water molecules to ether oxygen atoms in the molecule has been verified by studying the isotropic Raman spectra in the O-H stretching region for four short-chain POEs ($C_1E_nC_1$ with $n = 1–4$). Excellent coincidence of the O–H stretching Raman band for all four POEs studied in the range of mole ratio $H_2O/O_{ether}$ from 25 to 0.6 was observed, thus confirming the assumption stated above. A conclusion that all ether oxygen atoms in the POE molecule participate in hydrogen bonding with water molecules has been made.

© Central European Science Journals. All rights reserved.

Keywords: hydrogen bonding, short-chain poly(oxyethylene)s, hydrophobic hydration, raman spectroscopy

$^*$E-mail: mdg@phys.uni-sofia.bg

$^†$E-mail: znikolov@mines.utah.edu
1 Introduction

Studies of the hydration of poly(oxyethylene) (POE) \((-\text{OCH}_2\text{CH}_2-)_n\) have attracted research interest in recent years because of the opportunity to account for different intermolecular interactions, namely POE–water, POE–POE and water–water \([1,2]\). Due to its unlimited solubility in water, POE has various technological applications \([1,2]\) and presents the simplest model of water soluble polymers. The interaction of this polymer with water can be regarded as resembling the hydration of more complex biopolymers. Accordingly, clarification of the mechanism of hydrogen bonding between POE and water is most important in continuous efforts to determine the role of water structure and hydration in biological solutions and suspensions, as well as in aqueous polymer solutions in general.

In our recent studies \([3,4]\), we have explored the hydration of short-chain POE compounds, \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\) and \(\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3\), in aqueous solutions. The aim of the present study is to investigate the hydration of a series of short-chain POEs in aqueous solutions in an attempt to generalize the results from the previous studies and to establish an empirical relation between the number of water molecules hydrating one POE molecule and the number of oxygen atoms in it. The compounds studied are \(\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3\) (abbreviated as \(\text{C}_1\text{E}_n\text{C}_1\)) with \(n = 1–4\).

2 Experimental

Ethylene glycol dimethyl ether (or 1,2-dimethoxyethane) \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\) (\(\text{C}_1\text{E}_1\text{C}_1\)), diethylene glycol dimethyl ether \(\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3\) (\(\text{C}_1\text{E}_2\text{C}_1\)), triethylene glycol dimethyl ether \(\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3\) (\(\text{C}_1\text{E}_3\text{C}_1\)), and tetraethylene glycol dimethyl ether \(\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3\) (\(\text{C}_1\text{E}_4\text{C}_1\)) if analytical grade were supplied by Katayama Chemical Industries, Osaka, Japan. Doubly distilled deionized water was used to prepare aqueous solutions of the four \(\text{C}_1\text{E}_n\text{C}_1\) compounds with 17 different concentrations in the range up to mole fraction 0.47 of \(\text{C}_1\text{E}_n\text{C}_1\). The samples for Raman measurement were sealed in glass ampoules. Special care was taken to avoid dust contamination. The compositions of the aqueous solutions of the \(\text{C}_1\text{E}_n\text{C}_1\) compounds studied are given Table 1.

The Raman spectra were recorded in the usual 90° scattering geometry with a polarization rotator in the exciting laser beam and an analyzer in front of the input slit of the spectrometer. The 488 nm line of an argon ion laser generating output power of 300 mW was used for excitation. The detection system was a computer-controlled optical multichannel analyzer with a spectral range of 2000 cm\(^{-1}\) that covers the whole O-H stretching bands and part of the C-H stretching bands. Every spectrum is an average of 1000 scans. The recorded spectra were corrected for the channel sensitivity of the spectrometer. The parallel \((I_{||})\) and the perpendicular \((I_{\perp})\) spectra of the scattered radiation were used to calculate the isotropic spectra \((I_{\text{iso}})\) using a relation \([5]\)

\[ I_{\text{iso}} = I_{||} - (4/3)I_{\perp}. \]
In order to account only for the influence of POE concentration all spectra are recorded at constant temperature (24 °C) and atmospheric pressure.

3 Results and discussions

Before discussing our present experiment results, we would like to review hydration of POE in water in different concentration regions.

3.1 Hydration of POE-overview

POE molecules are characterized with a well-expressed hydrophilic region at the oxygen atoms and a hydrophobic region at the ethylene groups. In contrast to structurally related polyethers with one CH2 group less or more, i.e. poly(oxyethylene) or poly(oxytrimethylene), which are practically insoluble in water, POE is strongly hydrated at ambient temperatures and is effectively hydrophilic. One of the main factors for this behavior of POE is recognized as the existence of structural similarity between the oxyethylene unit and water. Experimental results show that POE molecules in aqueous solution, where they are well hydrated, prefer the trans—gauche—trans conformation for the O-CH2—CH2—O groups. In this conformation the distances between the oxygen atoms of the O-CH2—CH2—O groups (2.9 Å) coincide essentially with those between the
oxygen atoms of neighboring water molecules in bulk water (2.85 Å), allowing proper incorporation of POE chains into the structure of liquid water [6].

The idea of a partially hydrophobic-like hydration of POE in dilute aqueous solutions is supported by the observed slightly increased partial molar volumes of water [7-9], the reduced rotational mobility of hydration water [10-12] and the improved tetrahedral coordination [3,4] of hydration water in dilute aqueous solutions of short-chain POEs compared to the case of pure water. There are, however, differences between the hydration of POE in dilute solutions and hydrophobic hydration. Generally, the hydrophobic hydration preserves or slightly increases the strength of hydrogen bonding between water molecules, while the opposite behavior is observed in the hydration of short-chain POEs, namely the strength of hydrogen bonding decreases gradually accompanied by improved tetrahedral coordination [3,4,13]. For low concentrations of POE, the weakening of the hydrogen bonds can be explained by the expansion of the inherent cavities in the water structure, required to accommodate the hydrophobic ethylene and terminal methyl groups of the polymer.

Raman and infrared spectroscopic studies have shown that the hydration of POE at higher concentrations gradually loses its hydrophobic nature, which suggests that another mechanism of hydration arises [3,4]. The most developed network of hydrogen-bonded and tetrahedrally coordinated water molecules in aqueous solutions of POE is formed for a mole ratio of water molecules to oxyethylene monomer units around 2:1. The same ratio was found to correspond to the most compact solution structure according to Brillouin scattering and ultrasonic velocity studies [14,15]. Such low number of water molecules hydrating one oxyethylene monomer unit also infers that a new type of interaction between water and POE molecules takes place instead of hydrophobic hydration in this range of concentrations.

The Raman and infrared O–H stretching spectra of aqueous solutions of POE indicate, however, that there still exist tetrahedral structures of water molecules having hydrogen bonding similar to that in bulk water [3,4,13]. Therefore, a tendency for the formation of relatively small and homogeneously distributed clusters of water molecules in the region of moderately concentrated solutions can be accepted. When water concentration is below the concentration of optimal hydration, that is 2:1 mole ratio of water molecules to oxyethylene monomer units, the tetrahedral structural pattern is broken down.

Recent Raman studies [16] of the hydration of $C_1E_1C_1$ at high concentrations up to mole fraction 0.99 show that the isotropic O-H stretching band can be decomposed into two components assigned to water monomers and water molecules that participate in clusters. Further analysis of the behavior of these components with concentration and temperature show that (1) almost all water molecules realize two hydrogen bonds through their hydrogen atoms, (2) water monomers always form a bridge between oxygen atoms of $C_1E_1C_1$ molecules, and (3) clusters of water molecules still exist at higher concentration, but the lack of the collective in-phase vibration at 3200 cm$^{-1}$ shows that the water clusters are smaller than water pentamers.
3.2 Analysis of the Raman spectra

Examples of the recorded spectra are shown in Figure 1. For extracting information about the hydration of POE from the observed Raman spectra, the O-H stretching band of aqueous solutions is normally decomposed into three components [3,17-20]. The first one at ca. 3200 cm$^{-1}$ is attributed to tetra-coordinated water molecules connected with strong hydrogen bonds. The second component at ca. 3400 cm$^{-1}$ is associated with O-H stretching vibrations of water molecules taking part in weaker hydrogen bonds, i.e. water molecules with weaker coordination with their neighbors. The third component at ca. 3600 cm$^{-1}$ corresponds to weakly bound water molecules or “free” O-H oscillators. This division of the O-H stretching Raman band agrees in principle with the mixture model for interactions in water [17]. The integral intensity ratio of the 3400 cm$^{-1}$ component to the 3200 cm$^{-1}$ component calculated from the isotropic Raman spectra, $R = I_{3400}/I_{3200}$, expresses the degree of structural order (or disorder) in the hydrogen-bonded network in the solutions [3]. The ratio $R$ reflects qualitatively the changes in the structure of water; the spectra with higher (or lower) $R$ correspond to a lower (or higher) degree of coordination of water molecules in the hydrogen-bonded network.

![Fig. 1 Curve fitting example of the O-H and C-H stretching bands used to calculate the parameter $R$ of the O-H stretching Raman band of aqueous solution of C$_1$E$_3$C$_1$ with concentration 0.04 mole fraction.](image)

3.3 Elucidation of the hydration of C$_1$E$_n$C$_1$

In our previous studies [3,4], we have explored the hydration of C$_1$E$_1$C$_1$ and C$_1$E$_2$C$_1$ in dilute and moderately concentrated solutions using the parameter $R$. To complete this series of experiments, we report in this paper the studies of hydration for aqueous solutions of C$_1$E$_3$C$_1$ up to mole fraction 0.30. The concentration dependence of the parameter $R$ is
shown in Figure 2, in comparison with the same dependence for C₁E₁C₁ taken from the literature [4].

As it was discussed in detail in [4] the first minimum around mole fraction 0.05 for C₁E₁C₁ corresponds to the strengthening of water structure as a result of hydrophobic-like hydration. The second, deeper minimum at mole fraction (m.f.) ca. 0.1 corresponds to the most compact structure of the solutions, namely the most developed hydrogen-bonded network of water and POE molecules. Now we notice that the same tendency of two poorly expressed minima in R concentration dependence is observed for C₁E₃C₁ solutions as for C₁E₁C₁ solutions, but the first minimum is at ca. 0.025 m.f. and the second one is at ca. 0.5 m.f. It is clearly seen that both curves have the same shape, but the scale of mole fraction for C₁E₃C₁ is compressed twice compared to C₁E₁C₁.

This similarity of the concentration dependence of the parameter R makes us suggest that both C₁E₁C₁ and C₁E₃C₁ influence hydrogen bonding and water structure in the same way. A C₁E₃C₁ molecule contains four ether oxygen atoms, while a C₁E₁C₁ molecule contains two. Therefore, the ratio of the number of oxygen atoms in C₁E₃C₁ to the number of oxygen atoms in C₁E₁C₁ is 2, which coincides with the scaling coefficient of the R dependencies (0.05/0.025 for the first minimum and 0.1/0.05 for the second minimum). Taking this into account we may assume that the number of oxyethylene groups is a determining factor of the interaction of POE with water. The similarities in the dependencies of the parameter R on concentration for C₁EₙC₁ with different chain lengths also make us believe that there is a similarity in the hydration structure and hydration mechanism of POE in aqueous solutions.

We can generalize the empirical rule suggested above for C₁E₁C₁ and C₁E₃C₁ to include all of the C₁EₙC₁ compounds studied. C₁E₁C₁, C₁E₂C₁, C₁E₃C₁ and C₁E₄C₁ possess two, three, four and five ether oxygen atoms, respectively, in the molecule. This
would mean that 30 molecules of \( C_1E_1C_1 \) act as 20 molecules of \( C_1E_2C_1 \), or as 15 molecules of \( C_1E_3C_1 \), or as 12 molecules of \( C_1E_4C_1 \) with respect to the hydration structure around the molecules of these compounds. Therefore, if the mole fractions (m.f.) of these \( C_1E_nC_1 \) compounds are related as \( \text{m.f.}(C_1E_1C_1):\text{m.f.}(C_1E_2C_1):\text{m.f.}(C_1E_3C_1):\text{m.f.}(C_1E_4C_1) = 30:20:15:12 \), the structure of water in these aqueous solutions should be perturbed in an equivalent way. We should expect accordingly that the O–H stretching band of the solutions would coincide with one another. In other words, we should expect the observation of the same hydration for the four \( C_1E_nC_1 \) compounds with different chain lengths at the same mole ratio of water molecules to ether oxygen atoms contained in the \( C_1E_nC_1 \) molecule.

To verify the hypothesis stated above, we have performed a validation experiment. Because we cannot determine the error in the calculation of \( R \) with sufficient accuracy, we are not using the parameter \( R \) to prove our hypothesis. Instead, as a clear and physically uncontroversial proof with an experimental error of less than 1%, we used direct comparison of sets of Raman spectra for aqueous solutions of different \( C_1E_nC_1 \) compounds with intentionally prepared concentrations according to the mole ratios stated above. We have analyzed the isotropic Raman spectra in the O–H stretching region of aqueous solutions of \( C_1E_nC_1 \) \((n = 1-4)\) at 17 compositions in the range of mole ratio \( H_2O/O_{\text{ether}} \) from 25 to 0.6. The exact compositions of the aqueous solutions studied are given in Table 1 and the relevant Raman spectra are shown in Figure 3.

Direct comparison of the four spectra for \( C_1E_1C_1, C_1E_2C_1, C_1E_3C_1 \) and \( C_1E_4C_1 \) in each set of aqueous solutions shows total coincidence in the whole range of concentrations, and fully supports our assumption that hydration of POE does not depend on the length of the molecular chain but depends on the mole ratio of water molecules to ether oxygen atoms in the molecule. The observed slight mismatch in the low wavenumber wing arises due to the overlap with the C–H stretching bands which have specific shapes and intensities for every particular \( C_1E_nC_1 \) compound.

### 4 Conclusions

The hydration of short-chain POEs \((C_1E_nC_1 \ (n = 1–4))\) in aqueous solution has been studied by Raman spectroscopy through the O–H stretching band as a function of POE concentration up to mole fraction 0.47. Direct comparison of the isotropic O-H stretching spectra of the four \( C_1E_nC_1 \) aqueous solutions infers that the hydration of POE does not depend on the length of the molecular chain but depends on the mole ratio of water molecules to ether oxygen atoms in the molecule. In addition, a conclusion that all ether oxygen atoms in the POE molecule participate in hydrogen bonding with water molecules has been derived.
Fig. 3 Isotropic Raman spectra in the O-H stretching band region of aqueous solutions of $C_1E_nC_1$ ($n = 1–4$) with concentrations up to mole fraction 0.47 at room temperature. The mole ratios of water molecules to ether oxygen atoms in the $C_1E_nC_1$ molecule, $H_2O/O_{ether}$, are 25.0 (a), 8.1 (b), 6.8 (c), 6.0 (d), 3.9 (e) and 1.0 (f).
Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research No. 10440176 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] F.E. Bailey, Jr. and J.V. Koleske: Poly(ethylene oxide), Academic Press, New York, 1976.
[2] P. Molyneux: Water-Soluble Synthetic Polymers: Properties and Behavior, Vol. I, CRC Press, Boca Raton, FL, 1983.
[3] N. Goutev, Zh.S. Nickolov, G. Georgiev and H. Matsuura: “Hydration of a Short Chain Poly[oxyethylene](C₁E₂C₁) Studied by Analysis of the O-H Raman Band”, J. Chem. Soc., Faraday Trans., Vol. 93, (1997), pp. 3167–3172.
[4] N. Goutev, Zh.S. Nickolov and H. Matsuura: “Hydration Structure of 1,2-Dimethoxyethane (C₁E₁C₁): O-H Raman Band Studies”, J. Mol. Liq., Vol. 76, (1998), pp. 117–124.
[5] D.A. Long: Raman Spectroscopy, McGraw-Hill, New York, 1977.
[6] M.F. Fox, E. Powell, J.W. Stafford and M.J. Blandamer: “Spectroscopic and viscosimetric studies of aqueous poly(ethylene oxide) solutions.”, Chemical Communications, Vol. 17, (1968), pp. 1022–1024.
[7] W.J. Wallace and A.L. Mathews: “Densities, Refractive Indices, Molar Refractions, and Viscosities of Ethylene Glycol Dimethyl Ether-Water Solutions at 25°”, J. Chem. Eng. Data, Vol. 8(4), (1963), pp. 496–498.
[8] W.J. Wallace and A.L. Mathews: “Densities, Refractive Indices, Molar Refractions, and Viscosities of Diethylene Glycol Dimethyl Ether-Water Solutions at 25°”, J. Chem. Eng. Data, Vol. 9(2), (1964), pp. 267–268.
[9] G. Douheret, M.I. Davis, I. Fjellanger and H. Hoiland: “Ultrasonic Speeds and Volumetric Properties of Binary-Mixtures of Water with Poly(Ethylene Glycol)S at 298.15 K”, J. Chem. Soc., Faraday Trans. 1, Vol. 93, (1997), pp. 1943–1949.
[10] J. Breen, D. Huis, J. Bleijser and J.C. Leyte: “Solvent Dynamics in Aqueous Peo-Salt Solutions Studied by Nuclear Magnetic-Relaxation”, J. Chem. Soc., Faraday Trans. 1, Vol. 84, (1988), pp. 293–307.
[11] A.C. Barnes, T.W.N. Bieze, J.E. Enderby and J.C. Leyte: “Dynamics of Water in the Poly(Ethylene Oxide) Hydration Shell - A Quasi-Elastic Neutron-Scattering Study”, J. Phys. Chem., Vol 98, (1994), pp. 11527–11532.
[12] G. Carlström and B. Halle: “The State of Water in Non-Ionic Surfactant Solutions and Lyotropic Phases - O-17 Magnetic-Relaxation Study”, J. Chem. Soc., Faraday Trans. 1, Vol. 85, (1989), pp. 1049–1063.
[13] Zh.S. Nickolov, K. Ohno and H. Matsuura: “FTIR-ATR Studies of the Hydration of 15-Crown-5 and 18-Crown-6 in Aqueous Solution”, J. Phys. Chem. A, Vol. 3, (1999), pp. 7544–7551.
[14] H. Matsuura and K. Fukuhara: “Hydration of the Oxyethylene Chain. Hypersonic Velocities in Aqueous Solutions of a-Methyl-w-ethoxyoligo(oxyethylene)s and a-Methyl-w-hydroxyoligo(oxyethylene)s as Studied by Brillouin Scattering”, Bull. Chem. Soc. Jpn., Vol. 59, (1986) pp. 763–770.
[15] Y. Miyazaki and H. Matsuura: “Hydration of Cyclic Oligo(Oxyethylene) Compounds - Ultrasonic Velocities and Compressibilities of Binary-Systems of Water with 12-Crown-4, 15-Crown-5, and 18-Crown-6”, *Bull. Chem. Soc. Jpn.*, Vol 64, (1991), pp. 288–290.

[16] Zh.S. Nickolov, N. Goutev and H. Matsuura: “Hydrogen Bonding in Concentrated Aqueous Solutions of 1,2 Dimethoxyethane: Formation of Water Clusters”, *J. Chem. Phys. A*, Vol. 105, (2001), pp. 10884–10894.

[17] G.E. Walrafen: “Water: A Comprehensive Treatise”, Vol. 1, In: F. Franks (Ed.): *Raman and Infrared Spectral Investigations of Water Structure*, Plenum, New York, 1972.

[18] G.E. Walrafen: “Structure of Water and Aqueous Solutions”, In: W.A.P. Luck (Ed.): *Spontaneous and stimulated Raman spectra from water and aqueous solutions*, Verlag Chemie, Weinheim, 1974.

[19] J.L. Green, A.R. Lacey and M.G. Sceats: “Spectroscopic Evidence for Spatial Correlations of Hydrogen Bonds in Liquid Water”, *J. Phys. Chem.*, Vol. 90, (1986), pp. 3958–3964.

[20] D.E. Hare and C.M. Sorensen: “Interoscillator coupling effects on the OH stretching band of liquid water”, *J. Chem. Phys.*, Vol. 96, (1992), pp. 13–22.