Two Characteristic H-bonded O–H Stretching Bands for the Compounds Containing Ether Oxygen and Hydroxyl Oxygen

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The two characteristic H-bonded OH stretching bands of α-monoalkyl-ω-hydroxyorigo(oxyethylene)s, (C_nE_m), have been observed at about 3460 and 3330 cm^{-1} in the liquid state; the former is due to the localized OH···O hydrogen bonds and the latter, the OH···OH···O hydrogen bonds of chain structures. The two bands were applied to the investigation of the phase transition process from the liquid to the solid for $C_{12}E_3$.

Self-organization of amphiphilic molecules which is one of the fundamental processes in solution chemistry is of great importance in biotechnology. Suitable probes are desired for elucidating those processes. In this paper, we report that the H-bonded OH stretching bands are usable as key bands for monitoring the structural behavior of nonionic surfactants, α-monoalkyl-ω-hydroxyorigo(oxyethylene)s (abbreviated as C_nE_m) even in states of complicated aggregation such as the liquid state. In the infrared spectra of C_nE_m, the sharp free OH stretching band is observed at about 3640 cm^{-1} in CCl_4 in analogy with primary alcohols.[1] The H-bonded OH stretching wavenumbers of 3460–3400 cm^{-1} of C_nE_m in the liquid state, however, differ clearly from those of the alcohols, as given in Figure 1, indicating that the hydrogen bond of C_nE_m may be different from that of the alcohols in the liquid state. For all the alcohols, the H-bonded OH stretching bands are observed at about 3330 cm^{-1} in the liquid state. It is well known that the free OH stretching band is shifted to lower wavenumbers upon the formation of hydrogen bonds and the magnitude of the red-shift is proportional to the strength of the hydrogen bond.[2] For C_nE_m, the band shape shows the overlapping of two major components. In fact, the broad bands can be resolved into two components, for example, the bands at 3460 and 3330 cm^{-1} for $C_{12}E_3$ and C_1E_1 (B and C of Figure 1), by Gaussian–Lorentzian functions, though the broad band would be composed of many types of H-bonded OH vibrations. The relative intensity of the band at about 3460 cm^{-1} increases with increasing the oxyethylene unit, m, of C_nE_m. This is interpreted that the population of the molecules concerned with the 3460 cm^{-1} band increases compared to that concerned with the 3330 cm^{-1} band. Recently, theoretical calculations such as B3LYP and MP2 methods give in general precise harmonic vibrational wavenumbers.[3] In order to confirm the above results, theoretical calculations by the B3LYP/6-311++G(d,p) method were performed for several H-bonded models.[4] In the calculations, diethyl ether (R_2O) and ethyl alcohol (ROH) were used as the simple model compounds for $CH_2CH_2OCH_2CH_2$– part and the –CH_2CH_2OH part of C_nE_m, respectively. The optimized geometries are shown in Figures 2 and 3. The harmonic OH stretching wavenumbers calculated are scaled by 0.93, because the calculated harmonic values are higher by about 10% than the observed unharmonic values.[3] The calculated H-bonded OH stretching wavenumbers are divided into two groups. One is 3412 (538) cm^{-1} for R_2O···HOR (Figure 2a), 3424 (443) cm^{-1} for R(H)O···HOR (Figure 2b), 3457 (371) and 3431 (511) cm^{-1} for ROH···(R_2)O···HOR (Figure 2c), and 3459 (360) and 3442 (511) cm^{-1} for ROH···(RH)O···HOR

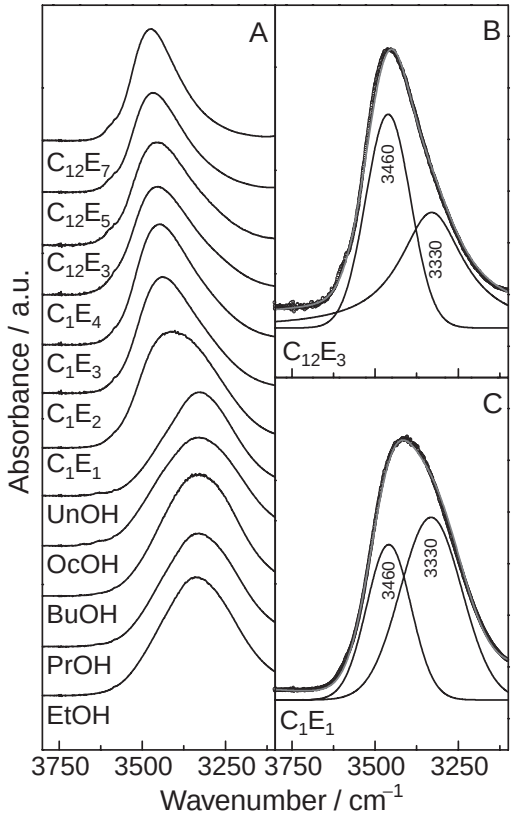

Figure 1. The H-bonded OH stretching bands of C_nE_m and primary alcohols in the liquid state.

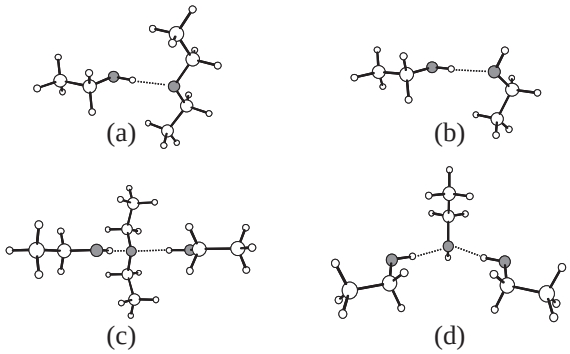

Figure 2. The localized OH···O hydrogen bonds optimized by the B3LYP/6-311++G(d,p).

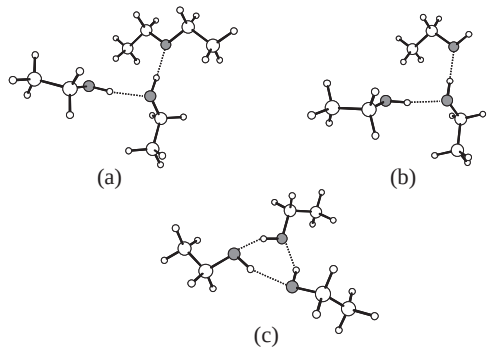

Figure 3. The OH···OH···O hydrogen bonds optimized by the B3LYP/6-311++G(d,p).

(Figure 2d), where the intensity, km mol^{-1}, is indicated in parentheses. Another is 3355 (626) and 3320 (787) cm^{-1} for R_2O···HO(R)···HOR (Figure 3a), 3360 (737) and 3323 (684) cm^{-1} for R(H)O···HO(R)···HOR (Figure 3b), and 3360 (754), 3348 (957), and 3301 (58) cm^{-1} for the cyclic trimer of ROH (Figure 3c). Thus, the calculated results indicate that the 3460 cm^{-1} band is associated with the localized OH···O hydrogen bond or the OH···O···HO hydrogen bond (the localized OH···O hydrogen bonds), as is likely to occur mainly for the hydrogen bond between OH and ether oxygen of C_nE_m. This band is experimentally found at about 3470 cm^{-1} for the cyclic dimer of C_1E_m ($n = 1$ and 2)[5] and at about 3480 cm^{-1} for the 8-menbered-ring monomer of C_1E_m ($n = 2$ and 3) in CCl_4.[6] The 3330 cm^{-1} band is associated with the OH···OH···O hydrogen bonds, as is likely to occur for hydrogen-bonding networks among hydroxyl groups of alcohols and also C_nE_m. It is therefore interpreted that for C_nE_m two characteristic bands are present in the liquid state; the localized OH···O hydrogen band at about 3460 cm^{-1} and the OH···OH···O hydrogen band of chain structures at about 3330 cm^{-1}.

The two bands were applied to the investigation of the phase transition process from the liquid to the solid for $C_{12}E_3$ at temperatures of 301 to 270 K. Figure 4 shows that the intensity of 3460-cm^{-1} band decreases, while that of the shoulder 3330-cm^{-1} band increases with decreasing temperature and then the 3330-cm^{-1} band is dominant and two new sharp bands appear, which are observed at 3323 and 3250 cm^{-1} at 270 K. The 3323- and 3250-cm^{-1} bands should be assigned to the in-phase and out-of-phase modes, respectively, of the ordered (···OH···OH···OH)$_n$ zigzag chain structures in the solid on the basis of the results of alcohols.[7] Thus, the above results indicate that the population of the hydrogen bond between OH and ether oxygen (the 3460-cm^{-1} band) decreases and that between OH and hydroxy oxygen with chain structures (3330 cm^{-1}) increases with decreasing temperature. The latter is predominant at the temperature immediately before solidification shown in 5 and 6 of Figure 4 (mp of $C_{12}E_3$ is 289.5–290 K[8]), and the latter with more strong intermolecular hydrogen bonds leads to the formation of the solid with the ordered (···OH···OH···OH)$_n$ zigzag chain structures at the melting point or lower.

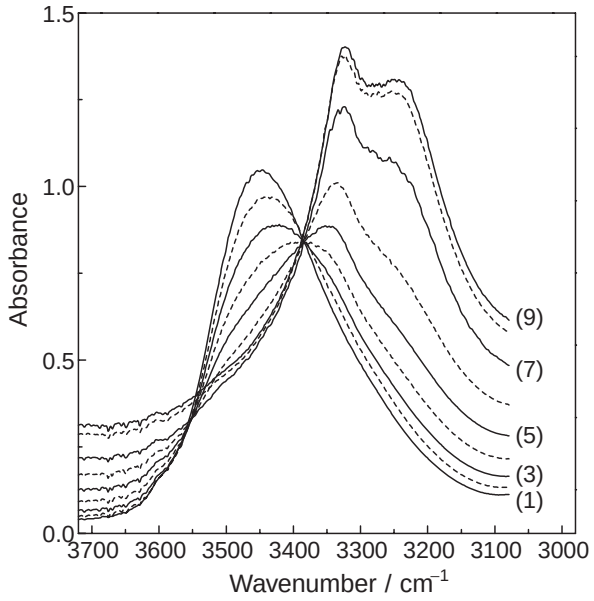

Figure 4. The spectral change in the phase transition from the liquid (1–4) to the solid (8, 9).

In conclusion, the two characteristic H-bonded OH stretching bands are present for C_nE_m; the localized OH···O hydrogen band at about 3460 cm^{-1} and the OH···OH···O hydrogen band of chain structures at about 3330 cm^{-1}. The two key bands are useful for investigating the structural behavior of the compounds containing ether oxygen and hydroxyl oxygen such as C_nE_m in states of aggregation.

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References

1 E. Nodland, *Appl. Spectrosc.*, **54**, 1339 (2000).
2 G. A. Jeffrey and W. Saenger, "Hydrogen Bonding in Biological Structures," Springer, Berlin (1994).
3 H. Yoshida, K. Takeda, J. Okamura, A. Ehara, and H. Matuura, *J. Phys. Chem. A*, **106**, 3580 (2002).
4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, "Gaussian 98, Revision A.5," Gaussian, Inc., Pittsburgh, PA (1998).
5 T. Masuda, H. Takao, Y. Katsumoto, H. Sugeta, and K. Ohno, unpublished data.
6 F. A. J. Singelenberg, E. T. G. Lutz, J. H. van der Maas, and G. Jalsovszky, *J. Mol. Struct.*, **235**, 173 (1991).
7 D. Schioberg, T. Mentel, and W. A. P. Luck, *J. Mol. Struct.*, **129**, 237 (1985) and references cited therein.
8 Y. Abe and S. Watanabe, *Kagaku Kogaku*, **66**, 86 (1963).

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