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Origin of the Blue Shift of the CH Stretching Band for 2-Butoxyethanol in Water

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A wavenumber shift of the CH stretching (ν_{CH}) band gives insight into the molecular interaction occurring in the system under study.[1−5] In particular, the shift to higher wavenumber ("blue shift") of the ν_{CH} band of alcohols,[6,7] polar organic compounds,[8,9] and surfactants[10] observed for aqueous solutions has attracted keen interest. Onori et al.[6] reported that the concentration dependence of the ν_{CH} band of alcohols in water is correlated with the variation of macroscopic properties of the solution, such as the partial molar volume and the adiabatic compressibility. There are several origins of the blue shift: direct interaction of the CH bond with solvent molecules,[1−5,7] conformational change,[11,12] indirect effect from interaction of adjacent functional atoms with solvent molecules,[12] accidental Fermi resonance,[13] steric effect,[13] electrostatic effect such as dipole−dipole interaction,[13] and so on. For direct CH⋯O hydrogen bonding, Alabugin et al.[5] gave a clear description of the mechanism of the blue shift in detail. For alcohols in water, however, the origin of the blue shift of the ν_{CH} band has not been clarified yet. An ambiguous assignment of the ν_{CH} band may make it difficult to discuss the nature of the blue shift, because the ν_{CH} bands in the 3100−2700 cm^{-1} region are severely overlapped and Fermi resonance often occurs. Mono-deuterium labeling of an alkyl group of interest is one sophisticated technique to remove the overlapping among the ν_{CH} bands. The ν_{CD} mode of the alkyl group is ideally decoupled with other ν_{CH} modes and is conformationally sensitive.[11] This technique is applicable to investigate the shift of the ν_{CD} band of a specified methyl or methylene group. In this study, the blue shift of the isolated ν_{CD} band for the monodeuterated 2-butoxyethanol (C_4E_1) in water is investigated by infrared (IR) spectroscopy combined with quantum chemical calculations. The C_4E_1/water mixture is one of the most interesting alcohol/water systems; it exhibits a closed-loop phase diagram[14] and is a model of nonionic surfactants.[15]

Figure 1 shows the chemical structures of monodeuterated C_4E_1's, i.e., C_4-α-d_1-E_1, C_4-β-d_1-E_1, and C_4-δ-d_1-E_1. The preparation of the samples was described previously.[11] IR spectra were measured at a resolution of 2 cm^{-1} by a Nicolet 6700 Fourier transform IR spectrometer using an attenuated total reflection (ATR) method.[16] The temperature of the ATR cell was kept at 298 ± 0.1 K by a thermoelectric device (LT230, CHINO). Theoretical calculations were carried out with density functional theory using Gaussian 03.[17]

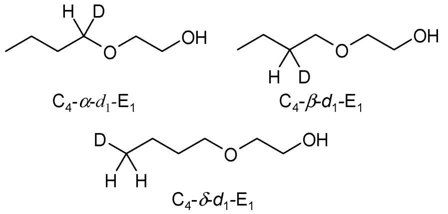

Figure 1. Chemical structures of C_4-α-d_1-E_1, C_4-β-d_1-E_1, and C_4-δ-d_1-E_1.

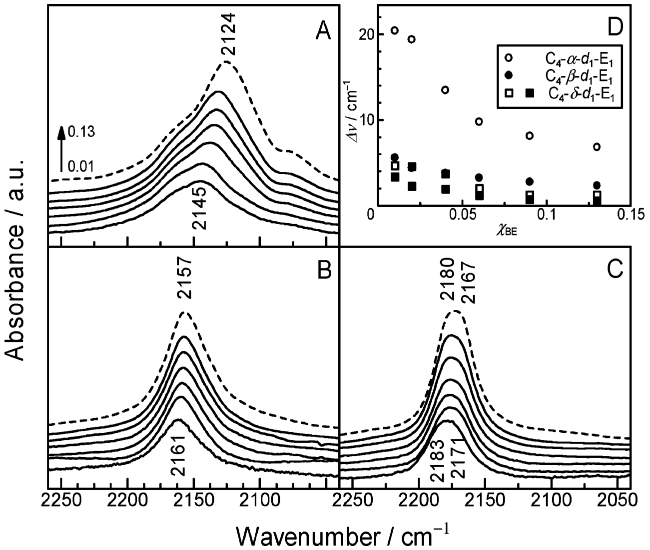

Figure 2. ν_{CD} bands of (A) C_4-α-d_1-E_1, (B) C_4-β-d_1-E_1, and (C) C_4-δ-d_1-E_1 in aqueous solutions at mole fraction of C_4E_1 from 0.13 to 0.01 (solid lines). IR spectrum for the pure liquid of each compound is represented by the dotted line. (D) Peak position estimated by second derivatives, plotted as a function of mole fraction of C_4E_1.

Figure 2 shows the concentration dependence of the ν_{CD} band in aqueous solution. For C_4-α-d_1-E_1, the peak of the ν_{CD} envelope located at 2124 cm^{-1} in the pure liquid is shifted to a higher wavenumber with decreasing mole fraction of C_4E_1 (χ_{BE}), which results in a blue shift by ca. 20 cm^{-1} (2145 cm^{-1} at $\chi_{BE} = 0.01$). The large blue shift of the ν_{CD} band of C_4-α-d_1-E_1 is similar to that of the ν_{CH} band of C_4E_1 reported previously.[6] Similar shifts of the ν_{CD} and ν_{CH} bands indicate that the blue shift being due to the accidental Fermi resonance can be ruled out. The peak band at 2124 cm^{-1} and the shoulder band at 2168 cm^{-1} are due to its rotational isomers; the latter band, increasing in intensity with decreasing concentration, is associated with the conformers with the gauche CC−OC conformation.[11] As both bands show similar blue shifts, the large blue shift does not arise from the conformational change. For the pure liquid of C_4-β-d_1-E_1, the ν_{CD} band appears at 2157 cm^{-1} as a unimodal band. When the concentration of C_4-β-d_1-E_1 decreases, the ν_{CD} band is shifted slightly (by ∼4 cm^{-1}) to a higher wavenumber. For the pure liquid of C_4-δ-d_1-E_1, the ν_{CD} envelope consists of two bands at 2180 and 2167 cm^{-1}, which can be identified by the second derivative, and is shifted to a higher wavenumber by 3−4 cm^{-1} in the aqueous solution at $\chi_{BE} = 0.01$. According to the quantum chemical calculation for the all-trans conformer of C_4-δ-d_1-E_1, the out-of-plane ν_{CD} band (δ_g) of the methyl group is expected at 2174 cm^{-1}, whereas the in-plane ν_{CD} band (δ_t) is expected at 2182 cm^{-1} (see Table 1).[18] A conformational change may cause the changes in the relative intensity of the two bands through an intramolecular steric repulsion between the CD and C_αH bonds.[18] Therefore, we conclude that the large blue shift of the ν_{CH} band does not arise from changes in the ν_{CH} modes of the β-methylene and the methyl group but originates mainly from the change in the ν_{CH} mode of the α-methylene in the butoxy group.

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Table 1. Observed and Calculated ν_{CD} Wavenumbers (cm^{-1}) of Monodeuterated C_4E_1's

	ν_{CD} (obs)/cm^{-1}		ν_{CD} (calc[a])/cm^{-1}		
	CCl_4 [b]	water[b,e]		+ 1 H_2O[f]	+ 2 H_2O[f]
α	2126	2145(+19)	2111	2129(+18)	2136(+25)
β	2157	2161(+4)	2165	2168(+6)	2172(+7)
δ	2167	2171(+4)	2174[c]	2176(+2)[c]	2179(+5)[c]
	2180	2183(+3)	2182[d]	2184(+2)[d]	2186(+4)[d]

[a] Calculated wavenumbers are scaled by a factor of 0.965. [b] Mole fraction of C_4E_1 is 0.01. [c] ν_{CD} of the δ_g confomer. [d] ν_{CD} of the δ_t confomer. [e] $\Delta\nu_{CD}$ (= ν_{CD}(water) − ν_{CD}(CCl_4)) indicated in parentheses. [f] $\Delta\nu_{CD}$ (= ν_{CD}(complex) − ν_{CD}(monomer)) indicated in parentheses.

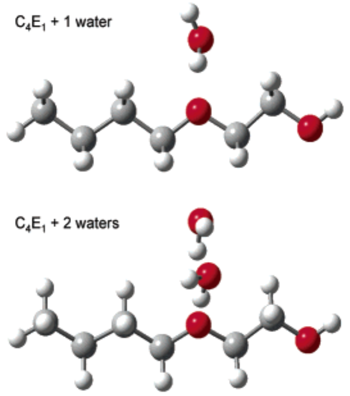

Figure 3. Simulation models for hydration of the ether oxygen atom of C_4E_1. The structures are optimized at the B3LYP/6-31+G** level.

It is unlikely that direct CD···OH_2 hydrogen bonding is the origin of the large blue shift of the ν_{CH} bands for a C_4E_1/water mixture, because the wavenumber shift of the ν_{CD} band of C_4-α-d_1-E_1 is extremely different from that of C_4-β-d_1-E_1 or C_4-δ-d_1-E_1. The above interpretation may be supported by the simulation of hydrophobic hydration around methane, in which all the lone pairs of the oxygen atoms of water molecules are directed not to a methane molecule but to water molecules incorporated in the hydrate shell, and the driving force for the orientation of the hydrate is the water−water interaction rather than the water−solute interaction.[19]

To reveal the origin of the blue shift of the ν_{CD} band for a C_4E_1/water mixture, we carried out spectral simulations using quantum chemical calculations. First, the solvent effect on the ν_{CD} wavenumber was examined in terms of the self-consistent reaction field (SCRF) approach, such as an Onsager model[20] and a polarized continuum method with a cavity determined self-consistently from an isodensity surface (SCI-PCM).[21] The SCRF approach, however, did not reproduce the large blue shift of the ν_{CD} band observed experimentally.[22] Second, we considered C_4E_1/H_2O complexes as a hydration model in which the ether oxygen atom directly forms a H-bond with water molecule(s) as an acceptor. Figure 3 shows the optimized structures for the C_4E_1/H_2O complexes. The all-trans conformation was assumed for C_4E_1. The calculated ν_{CD} wavenumbers of monodeuterated C_4E_1's are compiled in Table 1. The ν_{CD} wavenumbers of the C_4-α-d_1-E_1/H_2O (+1 H_2O) and C_4-α-d_1-E_1/2H_2O (+2 H_2O) complexes are higher by 18 and 25 cm^{-1} than those of the C_4-α-d_1-E_1 monomer, respectively. On the other hand, the ν_{CD} wavenumber of the complexes of C_4-β-d_1-E_1 or C_4-δ-d_1-E_1 with H_2O(s) shows smaller blue shift by 2−7 cm^{-1}. The simulation results of the hydration model are in excellent agreement with the experimental results, as can be seen in Table 1. In addition, the CD band in the butoxy group is not sensitive to the hydration around the OH group of C_4E_1.[22]

To obtain a detailed description of intra- and intermolecular electron transfer within the complexes, we performed the natural bond orbital (NBO) analysis at the B3LYP/6-31+G** level.[23] The occupancies of Lewis NBO for the ether oxygen lone pairs are lower than those for the other Lewis NBOs, indicating that the ether lone pairs are delocalized.[24] The NBO result for C_4E_1 in vacuo clearly indicates that there is an intramolecular $n(O)_{ether} \rightarrow \sigma^*(C_\alpha H)$ interaction, with a stabilization energy of 24.5 kJ mol^{-1}. When the ether oxygen of C_4E_1 forms a H-bond with water, an intermolecular $n(O)_{ether} \rightarrow \sigma^*(OH)_{water}$ hyperconjugative interaction occurs between the ether oxygen and the OH group of water. As a consequence, the intramolecular $n(O)_{ether} \rightarrow \sigma^*(C_\alpha H)$ interaction is indirectly weakened,[24] which may lead to shrinkage of the $C_\alpha D$ bond. This causes the large blue shift of the $C_\alpha D$ band shown in the spectral simulation. Note that there is no intermolecular interaction between NBOs of water and those of $C_\alpha H$. These results indicate that the blue shift of the ν_{CH} bands due to the butoxy group of C_4E_1 originates mainly from the formation of H-bonds between the ether oxygen atom and water molecules. The present work suggests that the mono-deuterium labeling of alkoxy alcohols or nonionic surfactant and monitoring the blue shift of the ν_{CD} band provides fruitful information on the hydration state around ether groups.

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Supporting Information Available: Complete ref 17; conformation and ν_{CD} band of C_4-δ-d_1-E_1; second derivatives of the ν_{CD} bands for pure C_4E_1's; results with the SCRF approach; optimized geometries and absolute energies for the calculated structures; and results of the NBO analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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