# Carbon-13 NMR and Raman Scattering Studies of Potassium Propoxybenzoate and Potassium Butoxybenzoate. Conformational Change Due to Micellization

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Carbon-13 NMR chemical shifts and carbon-13 spin-lattice relaxation times of potassium propoxybenzoate and potassium butoxybenzoate in deuterium oxide solution were measured at various concentrations.

For the alkoxy group, the carbon-13 resonance peak of the O-$CH_2$ segment is shifted rapidly up-field upon micellization, while the resonance peaks of other methylene groups are shifted downfield. This observation is ascribed to the conformational change of the alkoxy group on micellization.

In the monomolecular solution of potassium butoxybenzoate, the restricted state of the O-$CH_2$ bond was estimated by carbon-13 spin-lattice relaxation time measurement. It was also found that micellization brings about a further restricted internal rotation about the O-$CH_2$ bond.

## Introduction

Surfactant molecules form a variety of structures in the presence of water, such as liquid crystals, micelles, bilayers and monolayers. Studies of such structures are an important topic of molecular biology, biophysics and chemistry, and are also the subject of much discussion.

A series of 4-*n*-alkoxybenzoic acids ($n = 7-12$) are known as compounds forming smectic and nematic liquid crystals [1–3]. Potassium salts of these compounds are soluble in water and form micelles. Conformational studies of these surfactants in aqueous solution aid in understanding the liquid crystal structure.

We have reported Raman, proton and carbon-13 NMR studies of sufactants having short hydrocarbon chains. A conformational change upon micellization has been demonstrated for some simple surfactants. In N-acylsarcosinate ions existing in both the cis and trans forms about the C-N bond of a peptide group, micellization leads to an increase of the trans form [4, 5]. For alkylcarboxylate ions having short saturated hydrocarbon chains, the all-trans form predominates after micelle formation [6], while for trans-2-hexenoate ion the skew-gauche form is more stable in the micelle than in the monomer state [7].

Such conformational changes of surfactant molecules influence the carbon-13 spin-lattice relaxation times, which give information on the restricted state of the segments due to micellization [8, 9, 10].

In this paper we report on the conformational change of alkoxybenzoate ions due to micellization. The restricted state of the alkoxy segment upon micellization is discussed in view of C-13 spin-lattice relaxation times, and the Raman spectra in the accordion vibration region give direct evidence of the conformational change of the alkoxy segment.

## Experimental

### *Materials*

The samples are potassium propoxybenzoate (PPOB), potassium butoxybenzoate (PBOB), potassium hexoxybenzoate (PHOB) and potassium octoxybenzoate (POOB), which were prepared from alcoholic potassium hydroxide and the corresponding carboxylic acids (Tokyo Kasei Co.) and were purified by recrystallization.

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*NMR Measurements*

Carbon-13 NMR chemical shifts and carbon-13 $T_1$ values were measured by a JEOL PFT-60 and a JEOL PFT-100 Fourier transform spectrometer, respectively, at 15.0 MHz and 25.1 MHz and in the Fourier transform mode, at 32 °C.

For the determination of each carbon-13 chemical shift, 16384 points in the time-domain were used. TMS as an external reference was used and no susceptibility correction was made.

By the Inversion Recovery Fourier Transform method ($\pi - \tau - \pi/2$ sequence) [11], the carbon-13 spin-lattice relaxation times ($T_1$) were measured with a spectral width of 5000 Hz and 8192 points in the time domain. The pulse recycling time ($t_{pr}$) was varied to satisfy the relation of $t_{pr} \geqq 5T_1$. Measurements of C-13 chemical shifts were made in 10 mm NMR sample tubes having a 0.5 ml egg-shaped cell filled with the $D_2O$ solution of the sample. The C-13 $T_1$ measurements were carried out by use of 5 mm sample tubes.

Proton NMR measurements were made with a Hitachi-Perkin Elmer R-20B spectrometer (60 MHz), equipped with a Takeda Riken TR-3824 electronic frequency counter. The temperature of the samples was controlled within $\pm 1$ °C at 35 °C.

*Raman Scattering Measurements*

The Raman spectra of the samples, crystals and aqueous solutions, were measured at room temperature with a JASCO Raman spectrometer (Model R-800, argon ion laser, 514.5 nm).

*UV Measurements*

Ultraviolet absorption spectra were obtained by a Shimadzu Double Beam Spectrometer UV-210A in the region of 190—400 nm with a 1 cm quartz cell at room temperature.

*CMC Measurements*

The CMC's of PPOB, PBOB, PHOB and POOB, determined by a dye method, are 210, 150, 30 and 5 mg/ml, respectively.

## Results and Discussion

*Carbon-13 NMR Spectra and Concentration Dependence of Carbon-13 Chemical Shift*

Figure 1 shows the carbon-13 NMR spectra of PPOB and PBOB in the $D_2O$ solutions. The

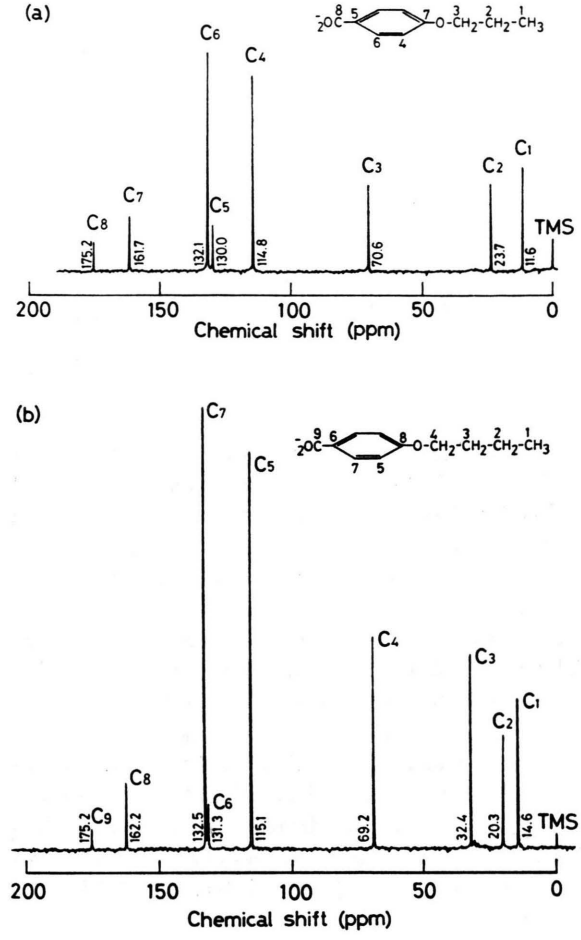


Fig. 1. Carbon-13 NMR spectra of PPOB (a) and PBOB (b) in deuterium oxide solution and their assignments. External reference: TMS.

resolved resonance peaks of each carbon-13 atom were readily assigned on the basis of chemical shift data for structurally related molecules [12]. The chemical shift of each resonance peak relative to the resonance position of TMS is also shown in Figure 1. The chemical shift of the O-$CH_2$ carbon-13 atom corresponds to a much lower magnetic field than those of other $CH_2$ carbon atoms of PPOB and PBOB.

Figure 2 shows the dependence of the chemical shifts of the alkyl carbon-13 atoms on concentration. For each carbon-13 atom of the PPOB-alkyl chain, the chemical shift is independent of the concentration below 150 mg/ml. However, above this concentration it changes rapidly until it converges at higher concentration; for the C-3 carbon it shifts

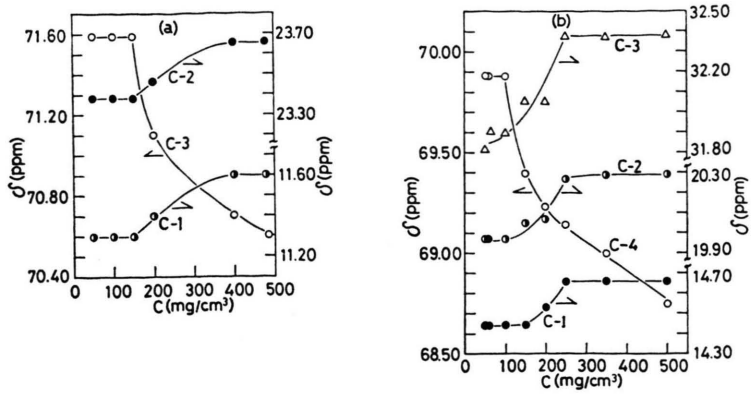


Fig. 2. Concentration depends of carbon-13 chemical shift of alkoxy-carbon atoms for PPOB (a) and PBOB (b).

toward a higher magnetic field, while for C-1 and C-2 it moves to lower magnetic fields. For the alkyl chain of PBOB, the C-13 chemical shift variation occurs at a concentration of about 100 mg/ml, and the features of the shift curves are similar to those of PPOB.

The difference between the chemical shifts at CMC and infinite concentration, which is called micellar effect, seems to be dependent on the chain length, as is seen in Table 1.

Such a marked variation of the shift curves should be due to a conformational change of the alkoxygroup upon micellization, because micellization brings about a conformational change of hydrocarbon chains, as has been pointed out [6, 7].

Persson et al. [13] have observed the concentration dependence of the carbon-13 chemical shift of nonylammonium bromide to estimate the aggregation number in the micelle. Further, they have interpreted the observed downfield shift due to micellization as caused by an increase of the trans form about the $CH_2$-$CH_2$ bond.

In the present study, the downfield shift observed in the alkoxy carbon-13 atoms may also be ascribed to an increased proportion of the all trans form on micellization. An upfield shift of the O-$CH_2$ carbon atom should be due to a conformational change about the O-$CH_2$ bond. It must be the change from the gauche to the trans form, because in the alkoxybenzoate ion the steric repulsion between the phenyl group and the alkyl group bound with the O-$CH_2$ group possibly makes the gauche form much less stable than the trans form.

Table 1. Micellar effect ($\Delta\nu$) of carbon-13 NMR chemical shift for PPOB and PBOB.

| | | | | |
|---|---|---|---|---|
| | $^1CH_3$ — | $^2CH_2$ — | $^3CH_2$—O | |
| PPOB ($\Delta\nu$)* | + 0.3 | + 0.3 | — 1.0 | |
| | $^1CH_3$ — | $^2CH_2$ — | $^3CH_2$ — | $^4CH_2$—O |
| PBOB ($\Delta\nu$)* | + 0.2 | + 0.3 | + 0.6 | — 1.2 |

* $\Delta\nu = \delta_{micelle} - \delta_{monomer}$, $\delta$: C-13 chemical shift (ppm).

The preferential stabilization of the specific rotational isomer about the O-$CH_2$ bond on micellization may bring about an increase in atomic charge density of the O-$CH_2$ carbon atom, because in such a restricted state of the O-$CH_2$ bond the lone pair electron orbitals of the oxygen atom will overlap with the $\pi$-orbitals of the benzene ring and the pseudo $\pi$-orbitals of the $CH_2$ group. The increase in atomic charge density of the O-$CH_2$ carbon atom becomes one of the dominant factors for such an up-field displacement.

For the aromatic ring and $COO^-$ carbon-13 atoms, the chemical shift variation also occurs at concentrations which are regarded as CMC's of PPOB and PBOB, obtained by carbon-13 chemical shift measurements. For the C5 and C9 carbon-13 atoms of PBOB, the resonance peaks shift toward higher magnetic fields with increasing concentration, while for the C6, C7 and C8 carbon atoms they shift toward lower magnetic fields.

The chemical shift change of the C5—C9 carbon-13 atoms may be due to the coplanarity of the $COO^-$ and benzene ring planes, which gives the maximum conjugation effect between the $\pi$-orbital systems of the two groups. This makes it possible to transfer electrons from negatively charged oxygen atoms of the $COO^-$ group to the carbonyl carbon atom.

To support this idea, UV-absorption spectra of POOB in aqueous solution were also measured at

various concentrations. The UV-spectrum has two absorption maxima at 197 and 248 nm in the 190—400 nm region. In the monomer solution of POOB (0.1 mg/ml), the molar extinction coefficients ($\varepsilon$) at 197 and 248 nm are 1600 and 2900, respectively. Below CMC (5 mg/ml) the concentration dependence of $\varepsilon$ is not so marked. However, above CMC the $\varepsilon$ value rapidly increases. Further, with increasing concentration, the maximum position of 197 nm tends to shift toward longer wave-lengths. These observations should be ascribed to the $\pi$-electronic state variation upon the coplanarity mentioned above. This results in a change of the atomic charge density of the POOB benzene ring.

Thus, we suggest that the coplanarity and conformational change on micellization cause higher or lower magnetic field displacements of carbon-13 resonance peaks.

A similar observation has been made for potassium trans-2-hexenoate in aqueous solution [10].

### *Concentration Dependence of Carbon-13 Spin-lattice Relaxation Time*

The $^{13}C$ spin-lattice relaxation times ($T_1$) can be used to determine segmental motions in a surfactant [8, 9], because $NT_1$ ($N$ = number of directly attached hydrogens) is inversely proportional to the effective correlation time ($\tau_{eff}$).

Table 2 shows the concentration dependence of $T_1$ for the PBOB-alkyl carbon atoms. At the concentration of 60 mg/ml the PBOB ions are in the monomeric state, because the CMC is 150 mg/ml. In the monomeric solution of PBOB, the $T_1$ values show a progressive decrease from the $CH_3$ end to the polar group.

A similar trend in the $T_1$ values has already been observed for the monomolecular solutions of *n*-hexyl- and *n*-octyltrimethylammonium bromide [8], and sodium *n*-hexanoate [9]. In these monomer solutions, the $T_1$ values of the methylene carbon-13 atom adjacent to the polar end are in the region of 1.0—2.0 sec.

However, for the monomer solution of PBOB the $T_1$ value of 0.7 sec is small compared to those of the above other surfactants in monomer solutions. This observation shows that the rotation about the $CH_2$-O bond is restricted even in the monomolecular state. In the micellar solution of PBOB the carbon-13 $T_1$ values exhibit a severer immobilization of the $CH_2$-O segment in addition to the restriction of the mobility of the entire chain.

For sodium alkylsulfates and sodium alkylsulfonates, having short hydrocarbon chains, observations similar to PBOB were made lately by authors. For example, the ethyl sulfate ion was found to exist primarily in the trans form about the $CH_2$-O bond in the monomolecular solution. This led to a marked increase of the carbon-13 spin-lattice relaxation rate (to be reported separately).

Table 2. Concentration dependence of C-13 spin-lattice relaxation time ($T_1$, sec) and effective correlation time ($\tau_{eff}$, picosec) for the PBOB-alkyl chain.

| $C$, $M^{-1}$ | | $^1CH_3$ — | $^2CH_2$ — | $^3CH_2$ — | $^4CH_2$—O |
|---|---|---|---|---|---|
| 2.15 | $T_1$ | 1.5 | 0.8 | 0.5 | 0.4 |
| | $\tau_{eff}$ | 10.3 | 28.4 | 45.5 | 56.8 |
| 0.30 | $T_1$ | 3.0 | 1.6 | 1.1 | 0.7 |
| | $\tau_{eff}$ | 5.1 | 14.2 | 20.7 | 32.5 |

### *Concentration Dependence of $^1H$ NMR Chemical Shift*

Proton NMR spectra of PPOB in $D_2O$ solutions were measured at various concentrations. Observations similar to the above C-13 NMR results were obtained in the $^1H$ chemical shift of the alkoxy group relative to the HOD frequency (Figure 3). The resonance peak of the O-$CH_2$ protons shifts rapidly toward higher magnetic fields with increasing concentration until its chemical shift becomes constant above the concentration of 200 mg/ml, which is close to the CMC of PPOB. The resonance peaks of the terminal $CH_3$ and its neighboring $CH_2$ group shift toward higher magnetic fields below 200 mg/ml, and have a maximum shift in the concentration region of 200—300 mg/ml. However, above this region they have a trend to shift toward lower magnetic fields. In the $^1H$ NMR spectra of PBOB and PHOB, similar shift curves were also

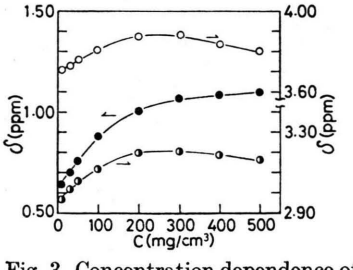


Fig. 3. Concentration dependence of proton NMR chemical shift for PPOB ($^1CH_3$, —○—; $^2CH_2$, —◑— and O—$^3CH_2$, —●—). Reference: HDO.

obtained for the O-$CH_2$, $(CH_2)_n$ and terminal $CH_3$ groups.

For proton signals of 2-phenyl propanoate ion incorporated in cetyltrimethylammonium bromide micelles, similar observations have been reported by Bunton et al. [14].

For aromatic protons of PPOB and PBOB, the concentration dependence of the chemical shifts was also found. The resonance peaks of meta-protons are shifted rapidly to higher magnetic fields with an increase in concentration until they converge at the CMC. The ortho proton resonance peaks are also shifted up-field, but the feature of the shift variation is not so marked.

Evidently, association leads to higher magnetic field shift of the aromatic and O-$CH_2$ proton signals and down-field shift of the methylene and terminal $CH_3$ proton signals.

The up-field shift should be due to the anisotropy of the aromatic ring of adjacent surfactant ions. However, the down-field shift may be correlated to a conformational change of alkyl segment, as will be discussed later.

*Raman Spectra of PBOB in Accordion Vibrational Region and Conformational Change due to Micellization*

To confirm the conformational change upon micellar formation, Raman spectra of PBOB in crystal and aqueous solution were measured.

Figure 4 shows the Raman spectra of PBOB in the accordion vibrational region. The Raman line of the crystal appears at 315 $cm^{-1}$, and is assigned to the accordion vibration of the butyl group. The accordion frequency is lower than that of *n*-butane [15], but it cosely corresponds to that of sodium *n*-butyl sulfate [6]. The accordion vibration of

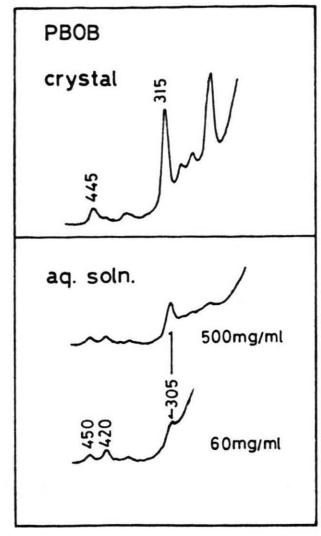


Fig. 4. Raman spectra of PBOB in the crystal and aqueous solutions.

PBOB in aqueous solution is observed at 305 $cm^{-1}$ and provides a measure of the conformational change on micellization. The Raman line of the PBOB solution at 420 $cm^{-1}$ should be assigned to the gauche isomers of the PBOB ions.

Figure 4 also shows the concentration dependence of Raman lines in the accordion vibrational region. Below the CMC, the Raman intensity of the 305 $cm^{-1}$ line is very weak. However, it increases relative to that of the 420 $cm^{-1}$ line with an increase in concentration. This observation directly shows that the all-trans form of the PBOB-butyl group is stabilized with the formation of micelles.

Thus, the carbon-13 and proton NMR chemical shift change of the alkoxy group observed in the present study should be due to the conformational change of this segment upon micellization.

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