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# Ultrasonic Relaxation Due to Complexation Reaction between *β*-Cyclodextrin and Alkylammonium Ions

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Ultrasonic absorption coefficients in an aqueous solution of propylammonium chloride (PACL) and butylammonium chloride (BACL) (pH ≈ 7.2) were measured in the presence and absence of *β*-cyclodextrin (*β*-CD) at 25 °C in the frequency range 0.8−220 MHz. There was no relaxation in the solution of individual alkylammonium chloride or *β*-CD. Also, in the solution with PACL and *β*-CD, the relaxation was not observed. However, a single relaxational absorption was found in the solution of BACL when *β*-CD coexisted. The cause of the relaxation was attributed to a perturbation of a chemical equilibrium associated with an interaction between *β*-CD and the butylammonium ion from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. The rate and thermodynamic constants were determined for the association and dissociation reactions of the complex in the system of BACL with *β*-CD. The results obtained were compared with those for other similar systems, e.g., propionate ion or propionic acid and alcohols with *β*-CD. It was ascertained that the stability of the complex formed between BACL and *β*-CD is relatively lower than those between other guests and *β*-CD.

## Introduction

Cyclodextrins are well-known to form inclusion complexes with a variety of inorganic and organic molecules in aqueous solution. There are numerous reports on observations related to the stability of the inclusion complexes by various methods.[1−3] However, depending upon the experimental tools, some restrictions are imposed on the experimental conditions, such as a special solvent and additions of indicators. To understand the structural characteristics of the solutions on a molecular scale, the application of wave techniques with ultrasonic vibrations is very appropriate. This is because the weak pressure waves are utilized to receive the response from the observation system directly.[4]

In our series of ultrasonic studies[5−8] for molecular recognition kinetics of several guest molecules (guest) by cyclodextrins (host), it has been proposed from the dynamic point of view that the inclusion complex formation between host and guest is controlled mainly by the rate of the departure of the guest molecule from the cavity of the host molecule. In the study for propionic acid or propionate ion as the guest for *β*-CD, the complex formation process is surely observed at around 10 MHz and the sufficiently effective difference was not found in these solutions.[7] To examine the effect of the charge difference or functional groups on the complex formation, alkylammonium salts are expected to be appropriate as the guest because the charge of the ammonium group has a considerable difference from that of the carboxylate group. This kind of information is not obtained from solutions of amino acids because they are ampholytes.[5,6] Therefore, propylammonium chloride (PACL) and butylammonium chloride (BACL) were chosen as guests for the host, *β*-CD, and the ultrasonic study was extended to obtain the information on the molecular kinetic recognition for the complexation reactions.

## Experimental Section

**Chemicals.** *β*-Cyclodextrin (*β*-CD) was purchased from Wako Pure Chemical Co. Ltd. The purification procedure of *β*-CD was reported previously.[8] Propylamine and butylamine were also purchased from Wako Pure Chemical Co. Ltd. as the purest grade and were used without further purification. The sample solutions of *β*-CD were prepared by weighting and the solutions of the amines were from their stock solutions. Distilled and filtered water from the MilliQ SP-TOC system of Japan Millipore Ltd. was used as a solvent. The alkylammonium chloride solutions were obtained by adding concentrated hydrochloric acid solution to adjust at pH ≈ 7.2.

**Apparatus.** The ultrasonic absorption coefficient, α, was measured in the frequency range from 0.8 to 9 MHz by a resonance apparatus, which consists of three cells with 3, 5, and 7 MHz x-cut fundamental crystals. The temperature for these resonator cells was controlled within ±0.01 °C (Lauda RM20). A pulse method with 5 and 20 MHz quartz crystals was applied in the frequency range from 25 to 220 MHz and the temperature of the cells for the pulse equipment was maintained within ±0.1 °C (EYEYA UNI ACE BATH NCB-2200). More details about the absorption apparatus and the procedure for determining the absorption coefficient are described elsewhere.[9,10] Sound velocity values were obtained by the resonator at around 3 MHz and solution densities were by a vibrating density meter (Anton Paar NMA 60/602). The solution pH was measured by a glass electrode with HM-60S Toa Denpa pH meter. All measurements were performed at 25 °C.

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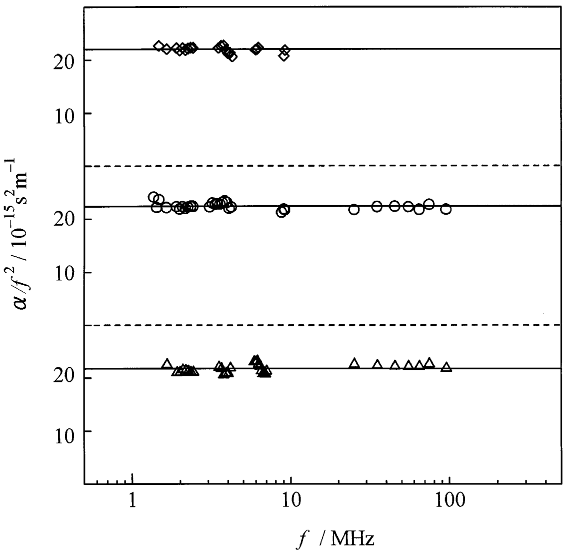

**Figure 1.** Ultrasonic absorption spectra in an aqueous solution of propylammonium chloride (PACL) and $\beta$-CD at 25 °C: (△) 0.40 mol dm$^{-3}$ PACL; (○) 0.15 mol dm$^{-3}$ PACL + 0.0087 mol dm$^{-3}$ $\beta$-CD; (◇) 0.40 mol dm$^{-3}$ PACL + 0.0087 mol dm$^{-3}$ $\beta$-CD.

## Results

It was reported that the relaxational absorption is not observed in $\beta$-CD solution in the concentration range below 0.016 mol dm$^{-3}$ with 0.1 mol dm$^{-3}$ salt.[11] Kato et al. reported a very small excess absorption at 0.013 mol dm$^{-3}$ of $\beta$-CD.[12] We confirmed that there exists no relaxation at 0.011 mol dm$^{-3}$.[13] In this study, the concentration of $\beta$-CD was kept constant at 0.0087 mol dm$^{-3}$. The observed ultrasonic absorption spectra in an aqueous solution of PACL are shown in Figure 1 in the presence and absence of $\beta$-CD. In the solution of PACL, the absorption coefficient divided by the square of the measurement frequency, $\alpha/f^2$, is independent of the frequency. The concentration range of the guest was taken below 0.40 mol dm$^{-3}$ because the ultrasonic results in other systems were in the same range or less and the present result would be compared with them. There also exists no excess absorption in the solution of PACL even if $\beta$-CD coexists. Figure 2 shows the spectra in aqueous solution of BACL in the presence and absence of $\beta$-CD. When $\beta$-CD does not coexist in the solution, the excess absorption is not observed. However, the values of $\alpha/f^2$ change with the frequency in the solution with BACL and $\beta$-CD.

Frequency dependence of absorption was conventionally tested by a Debye-type relaxational equation with a single relaxation frequency, $f_r$, as[4]

$$\alpha/f^2 = A/\{1 + (f/f_r)^2\} + B \tag{1}$$

where $A$ is the amplitude of excess absorption and $B$ is the background absorption. Because eq 1 is a monotonic decreasing function with frequency, it is slightly modified to calculate the above three parameters, $A$, $B$, and $f_r$ as follows,

$$\alpha/f = Af/\{1 + (f/f_r)^2\} + Bf \tag{1$'$}$$

A nonlinear least-mean-squares method using eq 1′ was applied so as to obtain the best fit to the experimental data, determining $f_r$, $A$, and $B$. Once these three ultrasonic relaxation parameters are obtained, it is possible to calculate the theoretical curves, which are shown in Figure 2 as solid lines. It is obvious that the Debye-type equation can reasonably be applied to the experimental data. The obtained ultrasonic relaxation parameters are listed in Table 1 along with the values of density, $\rho$, sound velocity, $v$, and pH of the solutions. The relaxational absorption observed in the system of BACL with $\beta$-CD is responsible to the interaction between the two solutes, because the relaxation is only found when both of the solutes are dissolved. Therefore, the perturbation of the following equilibrium by ultrasonic wave was proposed as a cause of the observed ultrasonic relaxation.

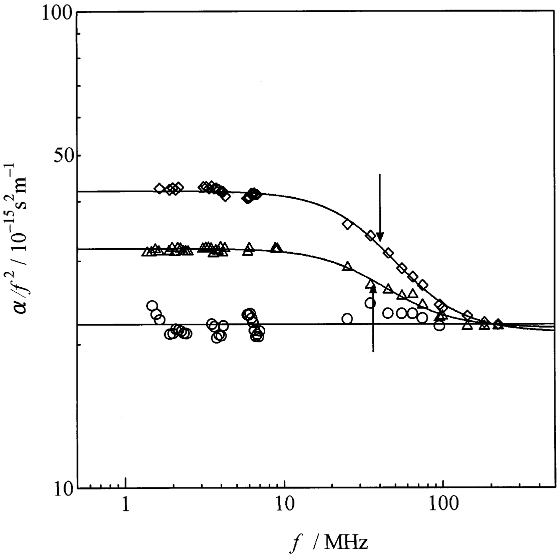

**Figure 2.** Ultrasonic absorption spectra in an aqueous solution of butylammonium chloride (BACL) and $\beta$-CD at 25 °C. The arrows show the location of the relaxation frequency. Key: (○) 0.40 mol dm$^{-3}$ BACL; (△) 0.14 mol dm$^{-3}$ BACL + 0.0087 mol dm$^{-3}$ $\beta$-CD; (◇) 0.320 mol dm$^{-3}$ BACL + 0.0087 mol dm$^{-3}$ $\beta$-CD.

$$\mathrm{CD} + \mathrm{BA}^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{CDBA}^+ \tag{2}$$

where CD is $\beta$-CD, BA$^+$ is butylammonium ion, CDBA$^+$ is the host−guest complex, $k_f$ and $k_b$ are the forward and backward rate constant, respectively. The relationship between the relaxation time, $\tau$, or the relaxation frequency, $f_r$, and the reactant concentrations can be derived as[5]

$$\tau^{-1} = 2\pi f_r = k_f\{[\mathrm{CD}] + [\mathrm{BA}^+]\} + k_b \tag{3}$$

$$= k_b\{(1 + KC_{\mathrm{CD}} + KC_{\mathrm{GST}})^2 - 4K^2C_{\mathrm{CD}}C_{\mathrm{GST}}\}^{1/2} \tag{3$'$}$$

where $C_{\mathrm{CD}}$ and $C_{\mathrm{GST}}$ are the analytical concentrations of $\beta$-CD and BACL, respectively. It is assumed that the activities of the reactants are their concentrations. The equilibrium constant, $K$, is defined as $K = k_f/k_b$. As the concentration of $\beta$-CD was fixed, the relaxation frequency, $f_r$, was only dependent on the concentration of the guest, $C_{\mathrm{GST}}$. Therefore, the parameters of $K$ and $k_b$ can be estimated by using a nonlinear least-mean-squares method. Figure 3 shows the plots of $2\pi f_r$ vs concentration term, $\{(1 + KC_{\mathrm{CD}} + KC_{\mathrm{GST}})^2 - 4K^2C_{\mathrm{CD}}C_{\mathrm{GST}}\}^{1/2}$, in eq 3′. The solid line is the one calculated by using determined $K$ and $k_b$, and it is seen that the experimental data fall on the calculated line. This agreement supports that butylammonium ion and $\beta$-CD are interacting with each other and they are considered to form the host−guest complex. The calculated rate and equilibrium constants are tabulated in Table 2 along with those for other systems reported previously.

Additional information, which can be obtained from the ultrasonic absorption measurement with the help of the densities and the sound velocities, is associated with the standard volume

**TABLE 1: Ultrasonic Relaxation and Thermodynamic Parameters for Aqueous Solutions of Butylamine with $\beta$-CD at 25 °C**

| $C_{CD}$, mol dm$^{-3}$ | $C_{GST}$, mol dm$^{-3}$ | $f_r$, MHz | $A$, $10^{-15}$ s$^2$ m$^{-1}$ | $B$, $10^{-15}$ s$^2$ m$^{-1}$ | $\rho$, kg m$^{-3}$ | $v$, m s$^{-1}$ | pH |
|---|---|---|---|---|---|---|---|
| 0.0087 | 0.100 | 38.9 ± 1.6 | 9.1 ± 0.4 | 21.72 ± 0.04 | 1001.54 ± 0.01 | 1509.2 ± 0.5 | 7.23 |
| 0.0087 | 0.140 | 40.1 ± 2.8 | 10.2 ± 0.7 | 21.6 ± 0.1 | 1001.61 ± 0.01 | 1513.3 ± 0.5 | 7.36 |
| 0.0087 | 0.180 | 41.9 ± 1.9 | 12.9 ± 0.6 | 20.6 ± 0.1 | 1001.69 ± 0.01 | 1519.2 ± 0.9 | 7.16 |
| 0.0087 | 0.200 | 42.0 ± 1.3 | 16.6 ± 0.5 | 21.4 ± 0.1 | 1001.54 ± 0.01 | 1518.0 ± 0.7 | 7.10 |
| 0.0087 | 0.252 | 42.2 ± 1.0 | 20.4 ± 0.4 | 21.1 ± 0.1 | 1002.17 ± 0.01 | 1525.4 ± 0.4 | 7.33 |
| 0.0087 | 0.300 | 44.4 ± 1.4 | 19.0 ± 0.6 | 21.0 ± 0.1 | 1002.85 ± 0.01 | 1530.1 ± 0.6 | 7.24 |
| 0.0087 | 0.320 | 42.3 ± 0.8 | 20.8 ± 0.4 | 21.2 ± 0.1 | 1003.04 ± 0.01 | 1533.8 ± 0.4 | 7.15 |
| 0.0087 | 0.380 | 43.6 ± 1.9 | 28.3 ± 1.3 | 20.7 ± 0.1 | 1003.25 ± 0.01 | 1538.6 ± 0.4 | 7.45 |
| 0.0087 | 0.400 | 42.4 ± 1.1 | 22.7 ± 0.6 | 21.3 ± 0.1 | 1003.85 ± 0.01 | 1539.1 ± 0.4 | 7.21 |

**TABLE 2: Rate and Thermodynamic Constants for Host−Guest Complexation at 25 °C**

| guest | $k_f$, $10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$ | $k_b$, $10^7$ s$^{-1}$ | $K$, mol$^{-1}$ dm$^3$ | $\Delta V$, $10^{-6}$ m$^3$ mol$^{-1}$ |
|---|---|---|---|---|
| butylammonium ion<br>$CH_3CH_2CH_2CH_2NH_3^+$ | 0.8 ± 0.1 | 24.3 ± 0.1 | 0.33 ± 0.02 | 25.6 ± 4.2 |
| 1-propanol<br>$CH_3CH_2CH_2OH$ | 5.1 ± 0.7 | 12.1 ± 0.7 | 4.2 ± 0.6 | 12.5 ± 0.3 |
| 1-butanol<br>$CH_3CH_2CH_2CH_2OH$ | 2.8 ± 0.8 | 3.8 ± 0.6 | 7.2 ± 2.0 | 11.1 ± 1.0 |
| propionate ion<br>$CH_3CH_2COO^-$ | 1.9 ± 0.1 | 8.19 ± 0.04 | 2.4 ± 0.1 | 16.2 ± 0.1 |

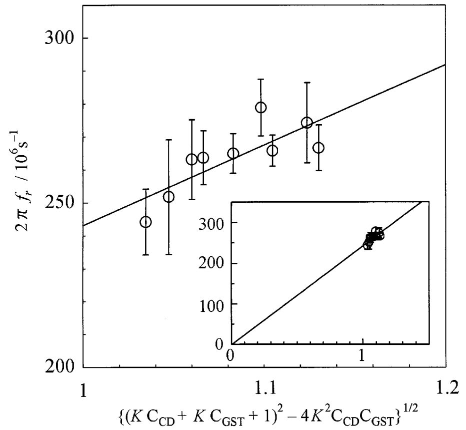

**Figure 3.** Plots of $2\pi f_r$ vs $\{(KC_{CD} + KC_{GST} + 1)^2 - 4K^2C_{CD}C_{GST}\}^{1/2}$ for an aqueous solution of BACL and $\beta$-CD at 25 °C.

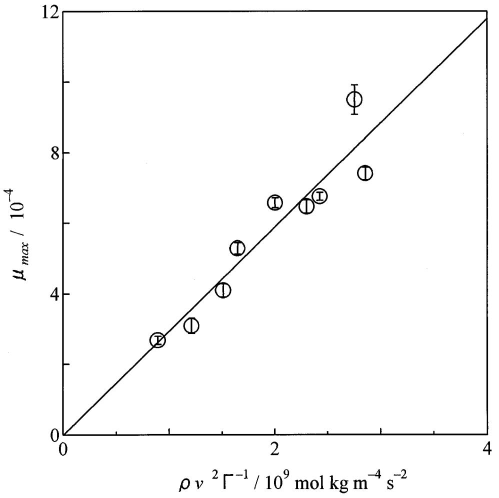

**Figure 4.** Plot of $\mu_{max}$ vs $\rho v^2\Gamma^{-1}$ for an aqueous solution of BACL and $\beta$-CD at 25 °C.

change of the reaction, $\Delta V$. Maximum absorption per wavelength, $\mu_{max}$, is conventionally used in the ultrasonic relaxation study and it is expressed for the system under considerations as

$$\mu_{max} = 0.5Af_rv$$
$$= \pi\, \rho\, v^2\, \Gamma^{-1}\, (\Delta V)^2/2RT \qquad (4)$$

where $\Gamma = 1/[\mathrm{CD}] + 1/[\mathrm{GST}] + 1/[\mathrm{CDGST}]$ and $R$ and $T$ are the gas constant and absolute temperature, respectively. Once the equilibrium constant is obtained, the individual equilibrium concentrations of the reactants can be calculated by using the analytical concentrations of the solutes, $C_{CD}$ and $C_{GST}$. Figure 4 shows the plots of $\mu_{max}$ vs $\rho v^2\Gamma^{-1}$, the slope of which provided the standard volume change of the reaction, $\Delta V$, and the obtained value is also listed in Table 2.

## Discussion

The frequency dependence of the absorption coefficient divided by the square of the measurement frequency, $\alpha/f^2$, was not observed in aqueous solutions of PACL and BACL, as can be seen in Figures 1 and 2. This means that the ultrasonic relaxation due to the proton-transfer reaction at neutral pH is far beyond over the utilized frequency range in this study. It should be noticed that the relaxation is not observed in the solution with PACL and $\beta$-CD, as is seen in Figure 1, although it is clearly found in the solution with propionic acid or propionate ion and $\beta$-CD.[7] On the other hand, the ultrasonic relaxation is definitely observed in the solution of BACL when $\beta$-CD coexists in the solution as is shown in Figure 2. It is considered that the inclusion complex between the propylammonium ion and $\beta$-CD may not be formed. The result is speculated to be due to the fact that the polarity of the $NH_3^+$ group is too high to enter into $\beta$-CD, of which the cavity is a fairly hydrophobic environment and the propylammonium ions prefer to exist in bulk phase. Kano et al.[14] reported the stability constant for propylamine and $\beta$-CD system to be 9 ± 4 mol$^{-1}$ dm$^3$ and that for butylamine and $\beta$-CD as 10 ± 5 mol$^{-1}$ dm$^3$. However, the stability may be lower for the complexation between the propylammonium or butylammonium ion and $\beta$-CD. Further, Rekharsky et al.[15] determined the constants for pentylamine, hexylamine, and octylamine with $\beta$-CD in phosphate buffer (pH = 6.90), and these amines are ionized to form alkylammonium ions. The increment of the standard free energy change with the number of methylene units, $d\Delta G_r/dN_c$, is estimated to be −3.3 kJ mol$^{-1}$. If this value were applicable to BACL and PACL solution systems, we obtained $K = 2$ mol$^{-1}$ dm$^3$ for the BACL solution and $K = 0.9$ mol$^{-1}$ dm$^3$ for the PACL solution by use of the relationship $K = \exp(-\Delta G_r/RT)$.

Although the stability constants depend on the solvent characteristics, they are considerably smaller when compared with those for other nonelectrolytes systems.[2] It is considered that the result obtained for the BACL and $\beta$-CD system in this study is not so far from the above estimated value.

According to our previous studies, the rate constant for the formation of the complex, $k_f$ , does not much depend on the structure of the guest molecule because the size of the cavity of $\beta$-CD is regarded to be large enough to incorporate such guest molecules. It was well interpreted through the Smoluchowiski equation that the association reaction is a diffusion controlled one when taking into account all of the surface area and that of the inner torus of $\beta$-CD. The calculation indicated that the forward rate constant, $k_f$, is approximated to be of the order of $10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$.[6] However, the obtained value, $k_f$, for the BACL and $\beta$-CD system is still slightly smaller than those for other systems. The diffusion coefficient for the ethylammonuim ion in water is $1.19 \times 10^{-5}$ cm$^2$ s$^{-1}$, and it is reported that the coefficient decreases as the molecular size increases.[16] Although the diffusion coefficient for butylammonium ion in water is not reported, it may be smaller than that for the ethylammonium ion, and therefore the smaller value for $k_f$ might be obtained in this study.

On the other hand, the rate constant for the departure of the guest molecule from the host cavity, $k_b$, is considerably dependent on the structure of the guest molecule. It also relates to the balance between hydrophobicity and hydrophilicity of guest molecules. The internal cavity of $\beta$-CD is considerably in the hydrophobic environment. That is to say, when the incorporated guest molecule is bearing a small hydrophobic part, it is relatively easy to leave from the $\beta$-CD cavity, which results in the increase of dissociation rate constant, $k_b$. The obtained $k_b$ value for the BACL solution is appreciably greater than those for other guests listed in Table 2. It is interesting to notice that the value is still greater than that for the propionate ion system. In fact, the complex between the butylammonium ion and $\beta$-CD is not stable when compared with other systems, and this is reflected on the stability constant, $K$. Therefore, the most important factor to control the stability of the inclusion complex is concluded to be associated with the backward rate constant, $k_b$.

Next, the result of the standard volume change of the reaction, $\Delta V$, is taken into account. The most likely mode of the complexation of guest to cyclodextrins is an insertion of the hydrophobic portion of the guest into the cyclodextrin cavity while the polar group of the guest remains in solvent exposed at the wide top end of the cavity.[15] It is said that there exist several water molecules in the $\beta$-CD cavity and they are released when the guest molecule is enclosed in the cavity. Leduc et al.[17] reported the apparent molar volume of butylammonium bromide in water as $110.2 \times 10^{-6}$ m$^3$ mol$^{-1}$. However, the obtained standard volume change of the reaction is considerably small, as seen in Table 2. Therefore, the participation of the released water molecules should be taken into account for the interpretation of the standard volume change. Wilson and Verrall[18,19] calculated semiquantitatively the transfer volume of surfactant from water to aqueous solution of cyclodextrin and reported the group contributions to the van der Waals volume ($V_{CH_3}'$, the contribution of the volume for the methyl group; $V_{CH_2}'$, that for the methylene group) and the apparent molar volume at infinite dilution ($V_{CH_3}$ and $V_{CH_2}$). If $n$ water molecules are expelled from the $\beta$-CD cavity when the guest is incorporated, the standard volume change of the reaction, $\Delta V$, is approximated as$\Delta V = V_{comp} + nV_{H_2O} - (V_{CD} + V_G)$, where $V_{comp}$ is the apparent molar volume of the complex at infinite dilution, $V_{H_2O}$ is the molar volume of water, and $V_{CD}$ and $V_G$ are the apparent molar volumes of cyclodextrin and the guest molecule at infinite dilution, respectively. The individual volumes are expressed by the following equations: $V_{comp} = V_{CD} + V_{CH_3}' + mV_{CH_2}' + (k - m)V_{CH_2} + V_{NH_3^+}$ and $V_G = V_{CH_3} + kV_{CH_2} + V_{NH_{3+}}$. In these equations, the number of methylene groups is designated by $k$ and it is considered that $m$ methylene groups and a methyl group are incorporated into the cavity, and the ammonium ion is assumed not to be included. It is also assumed that the volume of $\beta$-CD is not affected during the complexation and the obtained volume change of the reaction is positive because several water molecules are expelled from the CD cavity. The methyl and methylene groups included in the cavity may not contribute to the volume of the complex, and therefore, the term, $V_{CH_3}' + mV_{CH_2}'$, should be ignored. Then, we have a simple relation as $\Delta V = nV_{H_2O} - mV_{CH_2} - V_{CH_3}$. This means that the standard volume change of the reaction is estimated from the number of water molecules expelled from the cavity and the number of incorporated methylene groups. We utilize the reported values for $V_{CH_2} = 15.7 \times 10^{-6}$ m$^3$ mol$^{-1}$, $V_{CH_3} = 27.1 \times 10^{-6}$ m$^3$ mol$^{-1}$, and $V_{H_2O} = 18 \times 10^{-6}$ m$^3$ mol$^{-1}$. The experimental volume change in the present study, $25.6 \times 10^{-6}$ m$^3$ mol$^{-1}$, for the butylammonium ion is applied to the above equation. When $n = 4$, the number of methylene groups incorporated is about 1.2, and the number increases to $m \approx 2.4$ when $n = 5$. Wilson and Verrall[18] also explained reasonably the transfer volume change of surfactant using the displacement of 4−5 water molecules from the cavity to bulk water. The small number of $m$ indicates that only a part of the hydrophobic group in the BACL molecule is incorporated into the host cavity.

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