ARCHIVES OF ACOUSTICS
23, 3, 411–428 (1998)

# ABSORPTION OF ULTRASONIC WAVES IN AQUEOUS SOLUTIONS OF $\alpha$-CYCLODEXTRIN WITH ALKYLPYRIDINIUM OR ALKYLTRIMETHYLAMMONIUM BROMIDES

A. BALCERZAK, R. PŁOWIEC

Institute of Fundamental Technological Research
Polish Academy of Sciences
(00-049 Warszawa, ul. Świętokrzyska 21)

A. JUSZKIEWICZ

Department of Chemistry
Jagiellonian University
(30-060 Kraków, ul. Ingardena 3)

Measurements of the absorption coefficient, $\alpha/f^2$, of aqueous solutions of $\alpha$-cyclodextrin with alkylpyridinium bromides $C_nH_{2n+1}C_5H_4NBr$ or alkyltrimethylammonium bromides $C_nH_{2n+1}N(CH_3)_3Br$ ($n = 8$, 10, 12), were carried out at 15, 25, 35 and 45°C in the concentration range 0.01 M to 0.04 M and frequency range 1 MHz to 150 MHz. The occurrence of two ultrasonic relaxation processes has been noted. The obtained results have been compared with data published previously for sodium alkyl sulfates.

## 1. Introduction

Different molecules or their moieties can penetrate a cavity of the cyclodextrin molecule forming an inclusion complex [1, 2]. This process is caused by driving forces of several kinds, among which the hydrophobic interaction plays an important role [2–6]. Many aqueous systems containing cyclodextrins and surfactants were investigated from the hydrophobic interaction point of view [7–25].

In a work [25] published formerly, the results of ultrasonic investigations of aqueous solutions of $\alpha$-cyclodextrin ($\alpha$-CD) with sodium alkyl sulfates were presented. In this work the presentation of ultrasonic investigations of other surfactants, alkylpyridinium and alkyltrimethyl-ammonium bromides is continued. The surfactants have anionic polar heads (in comparison to the cationic ones of sodium alkyl sulfates) of different dimensions.

The manner of making measurements and calculations is similar to that presented formerly [25].

## 2. Experimental part

Measurements of the absorption coefficient, $\alpha/f^2$, in aqueous solutions of $\alpha$-CD with alkylpyridinium bromides $C_nH_{2n+1}C_5H_4NBr$ or alkyltrimethylammonium bromides $C_nH_{2n+1}N(CH_3)_3Br$ ($n$ = 8, 10, 12) were performed in the frequency range 1 MHz to 150 MHz at 15, 25, 35 and 45°C and at the concentration of 0.04 M of each of the components. At 25°C the measurements were also made for 0.01, 0.02 and 0.03 M equimolar solutions.

As previously the resonator and pulse methods were applied for the measurements [25].

The additional measurements of the speed of sound and the density for these solutions were also made. They are needed for further calculations [25]. The speed of sound was measured applying the resonator method [26–28]. The measurements of the density were performed by means of a MG-2 densimeter (Ecolab, Poland) which works on the principle of a U-shaped tube oscillator.

The parameters of the theoretical equations

$$\frac{\alpha}{f^2} = B + \sum_{i=1}^{l} \frac{A_i}{1 + (f/f_{ri})}, \tag{1}$$

$$\mu = 2\sum_{i=1}^{l} \mu_{mi} \frac{f/f_{ri}}{1 + (f/f_{ri})^2}, \tag{2}$$

were adjusted to the measured values of absorption by means of nonlinear regression. The adjusted parameters are: the relaxation frequency, $f_{ri}$, the relaxation amplitude, $A_i$, the contribution to the sound absorption from any other processes that may occur at higher frequencies beyond the frequency range measured, $B$, and the maximum of the excess absorption per wavelength, $\mu_{mi}$. $f$ is the measured frequency, $\alpha$ is the ultrasonic absorption, $\mu = (\alpha - Bf^2)\lambda$ is the excess absorption per wavelength $\lambda$ ($\lambda = c/f$, $c$ is the speed of sound), $l$ is the number of relaxation processes ($l$ = 1 or 2 in our case). The relation between $A_i$ and $\mu_{mi}$ is as follows: $\mu_{mi} = f_{ri}A_i(c/2)$.

## 3. Results and discussion

The results of the measurements are presented in Tables 1–6.

Representative plots of the dependence of the excess sound absorption per wavelength, $\mu$, on frequency, $f$, for several investigated systems are shown in Figs. 1–6.

The values of the parameters of Eqs. (1) and (2) are shown in Tables 7 and 8.

The occurrence of two relaxation processes for the surfactants with the decyl and dodecyl hydrocarbon chains should be noticed, while one relaxation process has been found for the octyl chain. This result is similar to that for aqueous systems of $\alpha$-CD with the sodium alkyl sulfate [25]. The values of the B parameter are slightly greater then the absorption coefficient $\alpha/f^2$ for pure water at corresponding temperatures. This can be caused by a greater viscosity of the liquid systems under test than that of water. This

**Table 1.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with octylpyridinium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 44.4 | 37.3 | 24.8 | 20.1 | 24.4 | 26.5 | 30.9 |
| 1.55 | 40.7 | 34.5 | 26.1 | 20.5 | 24.8 | 27.7 | 30.5 |
| 2.04 | 41.6 | 35.6 | 26.9 | 20.0 | 24.6 | 27.1 | 32.3 |
| 3.08 | 41.2 | 33.7 | 25.1 | 21.2 | 25.1 | 27.2 | 31.2 |
| 3.57 | 42.1 | 34.2 | 25.8 | 20.5 | 24.8 | 26.8 | 31.2 |
| 4.60 | 41.0 | 35.0 | 24.8 | 20.5 | 24.6 | 27.4 | 30.7 |
| 5.58 | 41.1 | 33.9 | 25.2 | 20.2 | 24.6 | 26.8 | 31.6 |
| 6.32 | 41.2 | 34.9 | 25.5 | 20.5 | 25.0 | 27.0 | 30.9 |
| 7.06 | 39.9 | 34.6 | 25.2 | 20.3 | 24.7 | 27.0 | 31.2 |
| 8.50 | 40.7 | 33.8 | 25.7 | 20.2 | 24.8 | 26.6 | 30.4 |
| 9.35 | 40.3 | 33.5 | 25.0 | 19.9 | 24.7 | 27.1 | 30.7 |
| 10.00 | 40.4 | 33.4 | 24.7 | 19.7 | 24.7 | 26.5 | 30.5 |
| 15.00 | 38.7 | 32.5 | 23.9 | 19.0 | 24.3 | 26.2 | 29.3 |
| 20.00 | 37.4 | 31.2 | 23.4 | 18.9 | 24.3 | 25.8 | 28.8 |
| 30.00 | 35.3 | 29.4 | 21.6 | 17.4 | 23.9 | 25.0 | 27.3 |
| 40.00 | 33.4 | 28.1 | 20.7 | 16.5 | 23.5 | 24.5 | 26.2 |
| 50.00 | 32.5 | 27.3 | 19.7 | 15.8 | 23.5 | 24.1 | 25.7 |
| 60.00 | 32.0 | 26.6 | 19.4 | 15.4 | 23.3 | 23.9 | 25.2 |
| 70.00 | 31.6 | 26.3 | 19.0 | 15.1 | 23.2 | 23.7 | 24.9 |
| 80.00 | 31.3 | 26.0 | 18.7 | 14.9 | 23.2 | 23.6 | 24.8 |
| 90.00 | 31.1 | 26.0 | 18.7 | 14.7 | 23.2 | 23.5 | 24.6 |
| 100.00 | 30.9 | 25.7 | 18.5 | 14.6 | 23.1 | 23.5 | 24.5 |
| 110.00 | 30.8 | 25.6 | 18.4 | 14.5 | 23.1 | 23.4 | 24.4 |
| 120.00 | 30.7 | 25.6 | 18.3 | 14.4 | 23.1 | 23.4 | 24.4 |
| 130.00 | 30.6 | 25.5 | 18.3 | 14.3 | 23.1 | 23.4 | 24.3 |
| 140.00 | 30.6 | 25.5 | 18.2 | 14.3 | 23.1 | 23.3 | 24.3 |
| 150.00 | 30.5 | 25.4 | 18.2 | 14.3 | 23.1 | 23.3 | 24.2 |
| | speed of sound [m/s] | | | | | | |
| | 1481.3 | 1511.8 | 1531.8 | 1550.6 | 1500.5 | 1504.3 | 1508.0 |
| | density [kg/m$^3$] | | | | | | |
| | 1010.0 | 1006.1 | 1002.3 | 998.2 | 999.3 | 1001.6 | 1003.9 |

**Table 2.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with decylpyridinium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 59.6 | 52.1 | 35.7 | 39.3 | 29.6 | 37.9 | 42.4 |
| 1.55 | 63.6 | 52.6 | 45.0 | 34.2 | 28.2 | 35.4 | 44.2 |
| 2.05 | 63.9 | 50.1 | 41.2 | 35.6 | 29.6 | 37.3 | 43.0 |
| 3.08 | 54.7 | 49.6 | 38.9 | 35.0 | 28.3 | 36.9 | 40.8 |
| 3.55 | 55.7 | 48.3 | 39.7 | 33.4 | 28.6 | 35.5 | 41.2 |
| 4.36 | 53.4 | 46.4 | 37.8 | 32.6 | 27.6 | 34.0 | 39.2 |
| 5.61 | 50.0 | 44.1 | 35.8 | 31.3 | 27.1 | 33.3 | 37.4 |
| 6.31 | 49.1 | 42.6 | 35.2 | 30.8 | 26.5 | 32.8 | 36.4 |
| 7.09 | 47.2 | 41.0 | 33.6 | 29.2 | 26.7 | 31.8 | 36.0 |
| 8.50 | 45.4 | 39.5 | 31.8 | 28.1 | 26.2 | 30.6 | 34.0 |
| 9.25 | 44.4 | 38.8 | 31.4 | 27.3 | 26.0 | 30.2 | 33.3 |
| 10.00 | 44.1 | 38.2 | 30.7 | 26.4 | 25.9 | 29.9 | 33.1 |
| 15.00 | 40.3 | 34.4 | 27.1 | 23.2 | 25.2 | 28.4 | 30.5 |
| 20.00 | 38.9 | 32.6 | 25.1 | 21.1 | 24.6 | 27.3 | 29.2 |
| 30.00 | 36.2 | 30.2 | 22.8 | 18.9 | 24.2 | 26.2 | 27.4 |
| 40.00 | 34.6 | 28.6 | 21.2 | 17.5 | 23.8 | 25.2 | 26.4 |
| 50.00 | 33.5 | 27.7 | 20.4 | 16.6 | 23.5 | 24.8 | 25.8 |
| 60.00 | 32.7 | 26.9 | 19.7 | 16.0 | 23.4 | 24.4 | 25.3 |
| 70.00 | 32.3 | 26.5 | 19.2 | 15.6 | 23.3 | 24.2 | 24.9 |
| 80.00 | 31.9 | 26.1 | 18.9 | 15.3 | 23.2 | 24.0 | 24.7 |
| 90.00 | 31.6 | 25.9 | 18.7 | 15.1 | 23.1 | 23.9 | 24.5 |
| 100.00 | 31.5 | 25.7 | 18.5 | 14.9 | 23.1 | 23.8 | 24.4 |
| 110.00 | 31.2 | 25.6 | 18.3 | 14.8 | 23.1 | 23.7 | 24.3 |
| 120.00 | 31.2 | 25.4 | 18.2 | 14.7 | 23.0 | 23.6 | 24.2 |
| 130.00 | 31.1 | 25.4 | 18.1 | 14.6 | 23.0 | 23.6 | 24.2 |
| 140.00 | 31.0 | 25.3 | 18.1 | 14.6 | 23.0 | 23.6 | 24.1 |
| 150.00 | 30.9 | 25.2 | 18.0 | 14.5 | 23.0 | 23.5 | 24.1 |
| | speed of sound [m/s] | | | | | | |
| | 1481.4 | 1511.9 | 1532.0 | 1550.8 | 1500.6 | 1504.4 | 1508.2 |
| | density [kg/m$^3$] | | | | | | |
| | 1011.3 | 1007.6 | 1003.5 | 999.4 | 999.8 | 1002.3 | 1004.9 |

**Table 3.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with dodecylpyridinium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 66.2 | 78.8 | 56.9 | 54.1 | 29.9 | 42.8 | 54.0 |
| 1.55 | 76.0 | 69.2 | 53.6 | 50.5 | 34.0 | 42.5 | 55.7 |
| 2.05 | 73.4 | 66.3 | 58.8 | 52.0 | 32.5 | 45.0 | 56.7 |
| 3.08 | 69.6 | 65.5 | 55.4 | 50.3 | 31.5 | 42.0 | 52.2 |
| 3.55 | 69.4 | 63.2 | 54.5 | 48.8 | 31.6 | 41.4 | 52.4 |
| 4.36 | 65.4 | 61.3 | 51.4 | 48.3 | 31.5 | 39.7 | 50.2 |
| 5.61 | 61.1 | 55.8 | 48.2 | 45.1 | 30.3 | 38.5 | 47.6 |
| 6.31 | 58.3 | 54.7 | 46.3 | 43.5 | 29.9 | 37.5 | 45.6 |
| 7.09 | 57.2 | 52.2 | 44.9 | 42.1 | 29.4 | 36.4 | 44.4 |
| 8.50 | 53.1 | 48.8 | 41.1 | 38.7 | 28.5 | 34.9 | 41.6 |
| 9.25 | 51.6 | 47.1 | 39.6 | 37.6 | 28.4 | 34.3 | 40.5 |
| 10.00 | 50.5 | 45.5 | 38.4 | 35.9 | 28.0 | 33.5 | 39.6 |
| 15.00 | 44.2 | 39.1 | 31.8 | 29.6 | 26.6 | 30.5 | 34.5 |
| 20.00 | 41.3 | 35.7 | 28.1 | 25.4 | 25.9 | 29.1 | 31.9 |
| 30.00 | 37.8 | 31.9 | 24.5 | 21.2 | 25.0 | 27.2 | 29.1 |
| 40.00 | 35.7 | 30.0 | 22.5 | 19.1 | 24.5 | 26.2 | 27.7 |
| 50.00 | 34.4 | 28.7 | 21.2 | 17.9 | 24.1 | 25.5 | 26.7 |
| 60.00 | 33.4 | 27.8 | 20.4 | 17.0 | 23.9 | 25.0 | 26.1 |
| 70.00 | 32.9 | 27.2 | 19.8 | 16.5 | 23.7 | 24.7 | 25.6 |
| 80.00 | 32.4 | 26.8 | 19.4 | 16.0 | 23.6 | 24.5 | 25.3 |
| 90.00 | 32.0 | 26.4 | 19.1 | 15.7 | 23.5 | 24.3 | 25.1 |
| 100.00 | 31.9 | 26.2 | 18.9 | 15.5 | 23.4 | 24.2 | 24.9 |
| 110.00 | 31.6 | 26.0 | 18.7 | 15.3 | 23.4 | 24.0 | 24.7 |
| 120.00 | 31.5 | 25.9 | 18.6 | 15.1 | 23.3 | 24.0 | 24.6 |
| 130.00 | 31.4 | 25.7 | 18.4 | 15.0 | 23.3 | 23.9 | 24.5 |
| 140.00 | 31.3 | 25.7 | 18.3 | 14.9 | 23.3 | 23.8 | 24.5 |
| 150.00 | 31.2 | 25.5 | 18.3 | 14.8 | 23.3 | 23.8 | 24.4 |
| | speed of sound [m/s] | | | | | | |
| | 1482.2 | 1512.3 | 1532.4 | 1551.6 | 1500.6 | 1504.5 | 1508.4 |
| | density [kg/m$^3$] | | | | | | |
| | 1013.4 | 1009.6 | 1005.3 | 1001.4 | 1000.2 | 1003.3 | 1006.5 |

**Table 4.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with octyltrimethylammonium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 40.7 | 32.1 | 26.3 | 22.1 | 23.6 | 26.5 | 30.5 |
| 1.55 | 40.9 | 33.5 | 24.8 | 19.8 | 25.0 | 27.0 | 31.4 |
| 2.04 | 41.8 | 34.3 | 24.0 | 20.4 | 24.8 | 28.1 | 31.2 |
| 3.08 | 40.0 | 33.5 | 24.3 | 20.6 | 24.8 | 27.1 | 31.0 |
| 3.57 | 42.5 | 33.5 | 24.8 | 20.3 | 24.5 | 26.8 | 30.8 |
| 4.60 | 40.5 | 33.0 | 24.9 | 20.3 | 24.8 | 26.9 | 30.8 |
| 5.58 | 42.0 | 33.5 | 23.9 | 20.3 | 24.9 | 26.8 | 31.4 |
| 6.32 | 40.7 | 33.0 | 24.5 | 19.7 | 24.8 | 27.2 | 30.6 |
| 7.06 | 40.9 | 33.0 | 24.8 | 20.2 | 24.6 | 26.8 | 30.3 |
| 8.50 | 40.4 | 32.7 | 24.6 | 20.3 | 24.6 | 26.7 | 30.3 |
| 9.35 | 40.2 | 32.9 | 24.1 | 20.0 | 24.6 | 26.6 | 30.2 |
| 10.00 | 39.9 | 32.4 | 23.9 | 19.9 | 24.6 | 26.9 | 29.9 |
| 15.00 | 38.9 | 31.5 | 23.2 | 19.3 | 24.2 | 26.0 | 29.3 |
| 20.00 | 37.1 | 30.4 | 22.4 | 18.6 | 24.3 | 25.6 | 28.5 |
| 30.00 | 35.0 | 28.6 | 20.9 | 17.4 | 23.8 | 24.8 | 27.2 |
| 40.00 | 33.4 | 27.1 | 19.8 | 16.4 | 23.6 | 24.2 | 26.2 |
| 50.00 | 32.4 | 26.4 | 19.1 | 15.8 | 23.4 | 23.9 | 25.5 |
| 60.00 | 31.7 | 25.8 | 18.5 | 15.2 | 23.2 | 23.7 | 25.2 |
| 70.00 | 31.4 | 25.3 | 18.3 | 15.0 | 23.2 | 23.5 | 24.9 |
| 80.00 | 31.0 | 25.1 | 17.9 | 14.7 | 23.1 | 23.4 | 24.6 |
| 90.00 | 30.8 | 25.0 | 17.8 | 14.5 | 23.1 | 23.3 | 24.5 |
| 100.00 | 30.7 | 24.8 | 17.7 | 14.4 | 23.0 | 23.3 | 24.4 |
| 110.00 | 30.5 | 24.7 | 17.5 | 14.3 | 23.0 | 23.2 | 24.3 |
| 120.00 | 30.4 | 24.6 | 17.5 | 14.3 | 23.0 | 23.2 | 24.3 |
| 130.00 | 30.4 | 24.5 | 17.4 | 14.1 | 23.0 | 23.2 | 24.2 |
| 140.00 | 30.3 | 24.5 | 17.3 | 14.1 | 23.0 | 23.1 | 24.2 |
| 150.00 | 30.2 | 24.4 | 17.3 | 14.1 | 23.0 | 23.1 | 24.1 |
| | speed of sound [m/s] | | | | | | |
| | 1481.2 | 1511.7 | 1531.8 | 1531.6 | 1550.4 | 1504.3 | 1507.9 |
| | density [kg/m$^3$] | | | | | | |
| | 1009.7 | 1005.8 | 1001.9 | 997.9 | 999.2 | 1001.4 | 1003.6 |

**Table 5.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with decyltrimethylammonium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 63.6 | 52.0 | 38.8 | 36.8 | 27.3 | 36.7 | 44.0 |
| 1.55 | 59.5 | 52.0 | 40.5 | 34.5 | 29.1 | 37.6 | 43.7 |
| 2.05 | 60.0 | 50.4 | 40.8 | 34.9 | 29.3 | 36.0 | 42.4 |
| 3.08 | 57.1 | 49.4 | 38.7 | 33.5 | 28.1 | 35.6 | 41.7 |
| 3.55 | 54.2 | 46.7 | 38.4 | 33.5 | 27.9 | 35.0 | 40.6 |
| 4.36 | 52.7 | 46.1 | 36.0 | 32.4 | 27.2 | 34.6 | 39.2 |
| 5.61 | 49.2 | 43.3 | 34.3 | 30.6 | 27.4 | 32.6 | 37.4 |
| 6.31 | 48.4 | 42.1 | 33.9 | 30.3 | 26.8 | 32.3 | 36.1 |
| 7.09 | 46.5 | 41.2 | 32.7 | 28.9 | 26.5 | 31.9 | 35.8 |
| 8.50 | 45.0 | 38.8 | 30.8 | 27.6 | 26.2 | 31.0 | 34.2 |
| 9.25 | 44.0 | 38.2 | 30.1 | 26.6 | 26.0 | 30.6 | 33.5 |
| 10.00 | 43.3 | 37.5 | 29.4 | 26.0 | 25.9 | 30.1 | 33.0 |
| 15.00 | 39.9 | 34.2 | 26.0 | 22.5 | 25.3 | 28.3 | 30.8 |
| 20.00 | 38.5 | 32.6 | 24.4 | 20.8 | 24.9 | 27.5 | 29.4 |
| 30.00 | 36.0 | 30.2 | 22.1 | 18.5 | 24.3 | 26.2 | 27.7 |
| 40.00 | 34.4 | 28.7 | 20.7 | 17.3 | 23.9 | 25.4 | 26.7 |
| 50.00 | 33.3 | 27.8 | 19.8 | 16.4 | 23.7 | 24.9 | 26.0 |
| 60.00 | 32.7 | 27.0 | 19.2 | 15.8 | 23.5 | 24.6 | 25.5 |
| 70.00 | 32.1 | 26.6 | 18.9 | 15.4 | 23.4 | 24.3 | 25.2 |
| 80.00 | 31.8 | 26.2 | 18.5 | 15.1 | 23.3 | 24.1 | 24.9 |
| 90.00 | 31.5 | 26.0 | 18.3 | 14.9 | 23.3 | 24.0 | 24.7 |
| 100.00 | 31.3 | 25.8 | 18.1 | 14.7 | 23.2 | 23.9 | 24.6 |
| 110.00 | 31.1 | 25.7 | 18.0 | 14.6 | 23.2 | 23.8 | 24.5 |
| 120.00 | 31.1 | 25.6 | 17.9 | 14.5 | 23.2 | 23.7 | 24.5 |
| 130.00 | 31.0 | 25.4 | 17.8 | 14.4 | 23.1 | 23.7 | 24.4 |
| 140.00 | 30.9 | 25.4 | 17.8 | 14.3 | 23.1 | 23.7 | 24.3 |
| 150.00 | 30.8 | 25.3 | 17.7 | 14.3 | 23.1 | 23.6 | 24.3 |
| | speed of sound [m/s] | | | | | | |
| | 1481.2 | 1511.8 | 1532.0 | 1550.7 | 1500.5 | 1504.4 | 1508.1 |
| | density [kg/m$^3$] | | | | | | |
| | 1011.1 | 1007.5 | 1003.3 | 999.2 | 999.7 | 1002.3 | 1004.9 |

**Table 6.** Ultrasound absorption, speed of sound and density for aqueous solutions of $\alpha$-cyclodextrin with dodecyltrimethylammonium bromide.

| | temperature | | | | concentration | | |
|---|---|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | 45°C | 0.01 M | 0.02 M | 0.03 M |
| | concentration 0.04 M | | | | temperature 25°C | | |
| $f$ [MHz] | absorption $\alpha/f^2$ [$10^{-15}$ s$^2$m$^{-1}$] | | | | | | |
| 1.00 | 73.8 | 71.6 | 60.6 | 52.4 | 33.6 | 41.5 | 59.4 |
| 1.55 | 77.8 | 65.7 | 60.4 | 50.4 | 35.0 | 45.0 | 55.8 |
| 2.05 | 76.3 | 66.6 | 57.7 | 53.6 | 35.1 | 43.7 | 56.1 |
| 3.08 | 70.4 | 64.7 | 55.2 | 50.4 | 33.7 | 43.6 | 53.0 |
| 3.55 | 68.8 | 62.3 | 55.2 | 48.5 | 33.4 | 42.0 | 52.0 |
| 4.36 | 64.9 | 59.4 | 52.6 | 47.0 | 32.6 | 40.5 | 49.0 |
| 5.61 | 60.8 | 54.6 | 48.3 | 43.0 | 31.1 | 38.5 | 46.1 |
| 6.31 | 58.0 | 53.5 | 46.8 | 42.5 | 30.8 | 37.8 | 44.7 |
| 7.09 | 55.8 | 50.8 | 44.7 | 40.3 | 30.2 | 36.3 | 42.7 |
| 8.50 | 52.4 | 47.2 | 41.1 | 37.3 | 29.3 | 34.5 | 40.3 |
| 9.25 | 50.6 | 46.0 | 40.0 | 35.5 | 28.8 | 33.9 | 39.0 |
| 10.00 | 49.8 | 44.5 | 38.2 | 34.4 | 28.4 | 33.3 | 38.0 |
| 15.00 | 44.2 | 38.2 | 31.9 | 27.8 | 26.9 | 30.3 | 33.8 |
| 20.00 | 41.3 | 35.1 | 28.3 | 24.1 | 26.0 | 28.7 | 31.6 |
| 30.00 | 38.1 | 31.6 | 24.6 | 20.6 | 25.1 | 27.1 | 29.2 |
| 40.00 | 36.1 | 29.9 | 22.6 | 18.7 | 24.5 | 26.1 | 27.8 |
| 50.00 | 34.9 | 28.6 | 21.4 | 17.4 | 24.1 | 25.4 | 26.9 |
| 60.00 | 34.0 | 27.8 | 20.6 | 16.8 | 23.9 | 25.1 | 26.3 |
| 70.00 | 33.4 | 27.2 | 20.1 | 16.2 | 23.7 | 24.7 | 25.8 |
| 80.00 | 33.0 | 26.8 | 19.6 | 15.8 | 23.6 | 24.5 | 25.5 |
| 90.00 | 32.7 | 26.4 | 19.3 | 15.5 | 23.5 | 24.4 | 25.3 |
| 100.00 | 32.4 | 26.2 | 19.1 | 15.3 | 23.4 | 24.3 | 25.1 |
| 110.00 | 32.2 | 26.0 | 18.9 | 15.1 | 23.3 | 24.1 | 25.0 |
| 120.00 | 32.1 | 25.9 | 18.7 | 15.0 | 23.3 | 24.0 | 24.8 |
| 130.00 | 31.9 | 25.7 | 18.6 | 14.9 | 23.2 | 24.0 | 24.8 |
| 140.00 | 31.8 | 25.6 | 18.5 | 14.8 | 23.2 | 23.9 | 24.7 |
| 150.00 | 31.8 | 25.6 | 18.4 | 14.7 | 23.2 | 23.9 | 24.6 |
| | speed of sound [m/s] | | | | | | |
| | 1482.1 | 1512.3 | 1532.3 | 1551.5 | 1500.6 | 1504.5 | 1508.4 |
| | density [kg/m$^3$] | | | | | | |
| | 1013.4 | 1009.5 | 1005.2 | 1001.3 | 1000.1 | 1003.3 | 1006.4 |

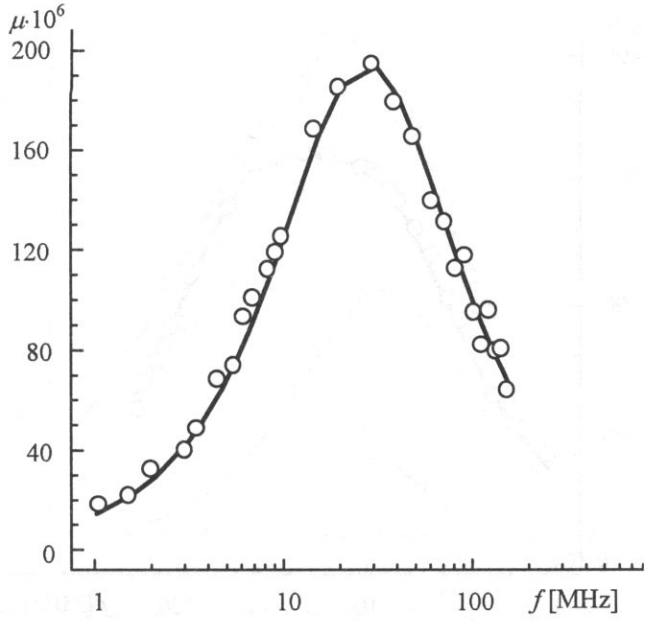


Fig. 1. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and octylpyridinium bromide. Temperature: 25°C, concentration: 0.04 M.

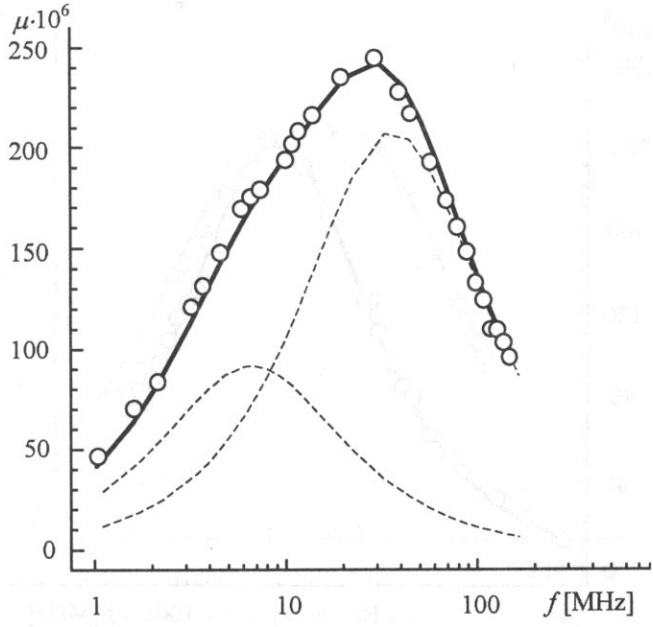


Fig. 2. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and decylpyridinium bromide. Temperature: 25°C, concentration: 0.04 M.

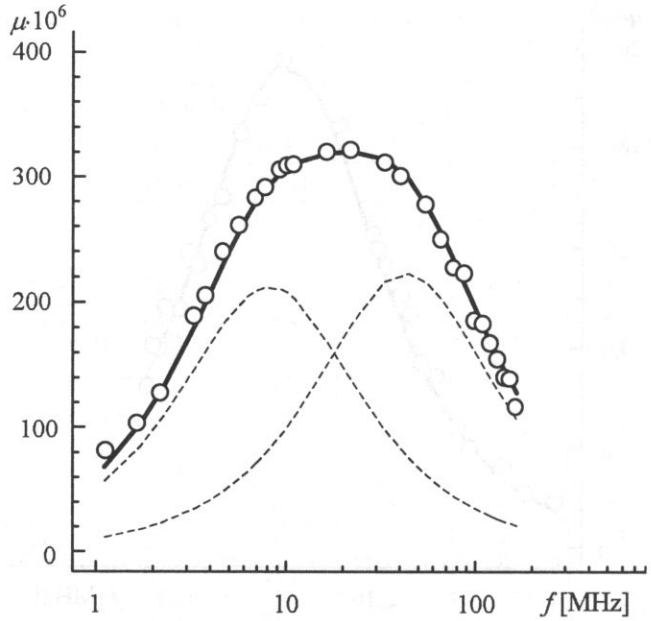


Fig. 3. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and dodecylpyridinium bromide. Temperature: 25°C, concentration: 0.04 M.

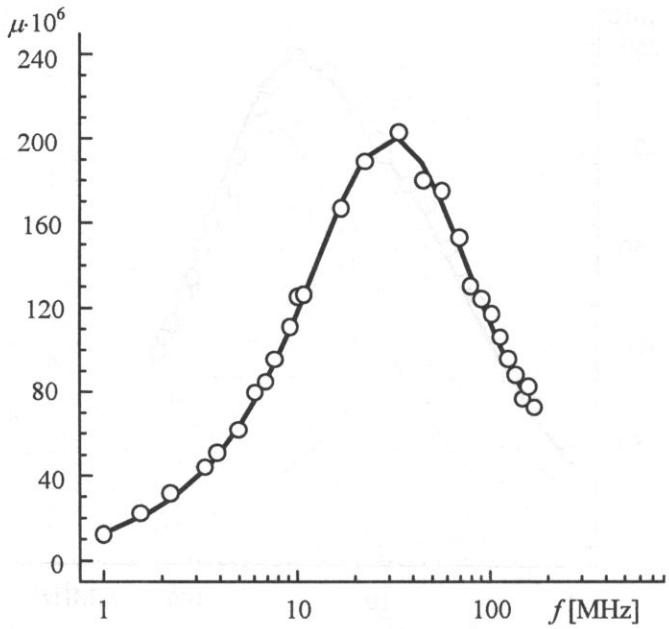


Fig. 4. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and octyltrimethylammonium bromide. Temperature: 25°C, concentration: 0.04 M.

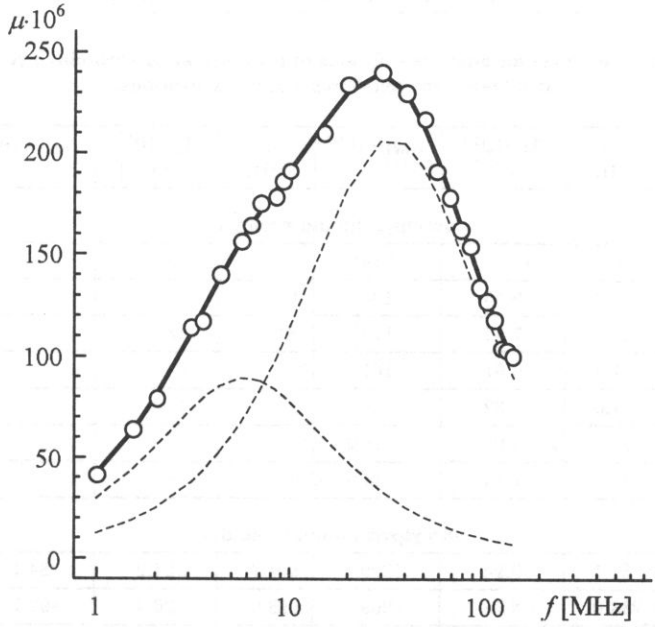


Fig. 5. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and decyltrimethylammonium bromide. Temperature: 25°C, concentration: 0.04 M.

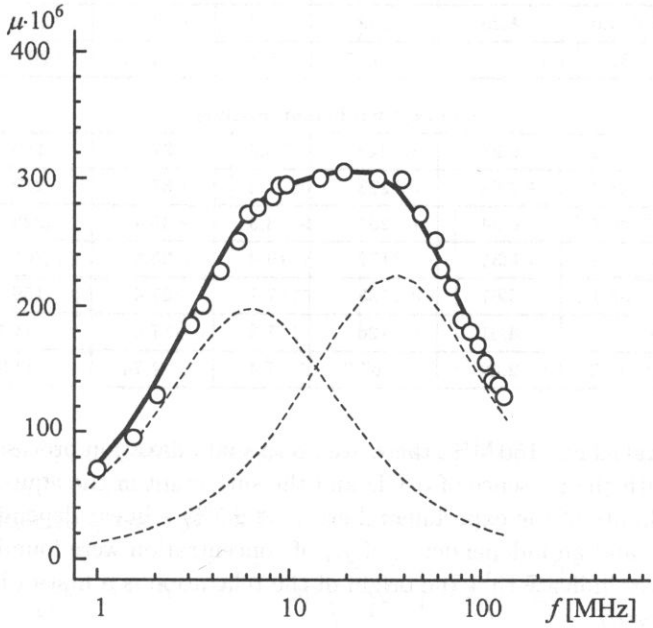


Fig. 6. Plot of the excess sound absorption per wavelength, $\mu$, vs. frequency, $f$, for the aqueous solution of $\alpha$-cyclodextrin and dodecyltrimethylammonium bromide. Temperature: 25°C, concentration: 0.04 M.

**Table 7.** Relaxation parameters for aqueous solutions of $\alpha$-cyclodextrin with alkylpyridinium bromides at different temperatures and concentrations.

| $t$ [°C] | $C$ [M] | $f_{r1}$ [MHz] | $A_1 \cdot 10^{15}$ [$s^2m^{-1}$] | $\mu_{m1} \cdot 10^6$ | $f_{r2}$ [MHz] | $A_2 \cdot 10^{15}$ [$s^2m^{-1}$] | $\mu_{m2} \cdot 10^6$ | $B \cdot 10^{15}$ [$s^2m^{-1}$] |
|---|---|---|---|---|---|---|---|---|
| octylpyridinium bromide | | | | | | | | |
| 15 | 0.04 | 25.7 | 11.5 | 219 | | | | 30.2 |
| 25 | 0.04 | 27.0 | 9.55 | 195 | | | | 25.1 |
| 35 | 0.04 | 28.9 | 7.82 | 173 | | | | 17.9 |
| 45 | 0.04 | 31.4 | 6.61 | 161 | | | | 14.0 |
| 25 | 0.03 | 27.0 | 7.32 | 149 | | | | 24.0 |
| 25 | 0.02 | 26.8 | 4.03 | 81.2 | | | | 23.2 |
| 25 | 0.01 | 27.9 | 1.84 | 38.6 | | | | 23.0 |
| decylpyridinium bromide | | | | | | | | |
| 15 | 0.04 | 31.1 | 9.94 | 229 | 4.7 | 24.2 | 84.1 | 30.5 |
| 25 | 0.04 | 33.0 | 8.38 | 209 | 6.0 | 20.4 | 92.7 | 24.8 |
| 35 | 0.04 | 35.3 | 7.06 | 191 | 7.6 | 17.5 | 102 | 17.6 |
| 45 | 0.04 | 37.2 | 5.72 | 165 | 8.8 | 16.3 | 111 | 14.1 |
| 25 | 0.03 | 32.8 | 5.66 | 140 | 6.0 | 15.2 | 68.9 | 23.8 |
| 25 | 0.02 | 34.0 | 4.26 | 109 | 5.9 | 10.7 | 47.4 | 23.3 |
| 25 | 0.01 | 32.6 | 1.95 | 47.7 | 5.8 | 4.62 | 20.1 | 22.9 |
| dodecylpyridinium bromide | | | | | | | | |
| 15 | 0.04 | 36.2 | 9.28 | 249 | 6.5 | 37.4 | 180 | 30.6 |
| 25 | 0.04 | 38.4 | 7.68 | 223 | 7.4 | 37.9 | 212 | 25.0 |
| 35 | 0.04 | 40.7 | 6.54 | 204 | 8.3 | 35.4 | 225 | 17.7 |
| 45 | 0.04 | 42.8 | 5.33 | 177 | 10.0 | 33.6 | 261 | 14.3 |
| 25 | 0.03 | 38.1 | 5.67 | 163 | 7.7 | 27.4 | 159 | 24.0 |
| 25 | 0.02 | 37.1 | 4.51 | 126 | 7.3 | 17.0 | 93.4 | 23.5 |
| 25 | 0.01 | 37.3 | 2.40 | 67.2 | 7.4 | 7.74 | 43.0 | 23.1 |

fact indicates that above 150 MHz there are no special relaxation processes which could be connected with the presence of $\alpha$-CD and the surfactant in the aqueous solution.

Within the limits of the experimental error ($\cong \pm 5\%$) a linear dependence of $\mu_{mi}$ on concentration $C$ and an independence of $f_{ri}$ of concentration were found.

These features indicate that the origin of the relaxation is a first-order or a pseudo-first-order processes

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} A_2\,, \tag{3}$$

where $A_1$ and $A_2$ denote two stages of the inclusion complex, $k_{12}$ and $k_{21}$ are the rate constants of the direct and opposite reactions, respectively.

**Table 8.** Relaxation parameters for aqueous solutions of α-cyclodextrin with alkyltrimethylammonium bromides at different temperatures and concentrations.

| $t$ [°C] | $C$ [M] | $f_{r1}$ [MHz] | $A_1 \cdot 10^{15}$ [$s^2m^{-1}$] | $\mu_{m1} \cdot 10^6$ | $f_{r2}$ [MHz] | $A_2 \cdot 10^{15}$ [$s^2m^{-1}$] | $\mu_{m2} \cdot 10^6$ | $B \cdot 10^{15}$ [$s^2m^{-1}$] |
|---|---|---|---|---|---|---|---|---|
| octyltrimethylammonium bromide | | | | | | | | |
| 15 | 0.04 | 26.3 | 11.6 | 226 | | | | 29.9 |
| 25 | 0.04 | 27.9 | 9.53 | 201 | | | | 24.1 |
| 35 | 0.04 | 30.1 | 7.81 | 180 | | | | 17.0 |
| 45 | 0.04 | 32.0 | 6.69 | 166 | | | | 13.8 |
| 25 | 0.03 | 27.8 | 7.01 | 147 | | | | 23.9 |
| 25 | 0.02 | 27.2 | 4.02 | 82.2 | | | | 23.0 |
| 25 | 0.01 | 28.5 | 1.88 | 40.3 | | | | 22.9 |
| decyltrimethylammonium bromide | | | | | | | | |
| 15 | 0.04 | 31.8 | 9.43 | 222 | 4.6 | 24.2 | 82.4 | 30.4 |
| 25 | 0.04 | 34.0 | 8.09 | 208 | 5.9 | 20.0 | 89.4 | 24.9 |
| 35 | 0.04 | 35.7 | 6.47 | 177 | 7.3 | 17.5 | 98.0 | 17.3 |
| 45 | 0.04 | 38.4 | 5.51 | 164 | 8.6 | 16.3 | 109 | 13.9 |
| 25 | 0.03 | 32.8 | 5.86 | 145 | 5.7 | 15.2 | 65.3 | 24.0 |
| 25 | 0.02 | 34.4 | 4.29 | 111 | 6.1 | 9.89 | 45.4 | 23.4 |
| 25 | 0.01 | 33.0 | 2.07 | 51.2 | 5.7 | 4.23 | 18.1 | 23.0 |
| dodecyltrimethylammonium bromide | | | | | | | | |
| 15 | 0.04 | 36.5 | 9.09 | 246 | 5.8 | 39.6 | 170 | 31.2 |
| 25 | 0.04 | 39.1 | 7.61 | 225 | 7.0 | 37.4 | 198 | 25.0 |
| 35 | 0.04 | 41.1 | 6.48 | 204 | 8.1 | 36.3 | 225 | 17.9 |
| 45 | 0.04 | 43.3 | 5.30 | 177 | 8.9 | 34.2 | 236 | 14.2 |
| 25 | 0.03 | 38.9 | 5.96 | 175 | 6.6 | 27.5 | 137 | 24.2 |
| 25 | 0.02 | 39.1 | 4.05 | 119 | 6.9 | 18.2 | 94.4 | 23.6 |
| 25 | 0.01 | 40.1 | 2.51 | 75.4 | 6.8 | 9.78 | 49.9 | 23.0 |

For this kind of relaxation processes, the following kinetic and thermodynamic formulas can be derived [29–31].

The relaxation frequency, $f_r$, can be expressed as

$$f_r = \frac{1}{2\pi} k_{21}(1+K) = \frac{kT}{2\pi h} \exp\left(\frac{\Delta S_{21}^{\neq}}{R}\right) \exp\left(\frac{-\Delta H_{21}^{\neq}}{RT}\right)(1+K), \tag{4}$$

where $K$ is the equilibrium constant for reaction (3) ($K = k_{12}/k_{21}$), $\Delta S_{21}^{\neq}$ and $\Delta H_{21}^{\neq}$ are the activation entropy and activation enthaply for the opposite reaction, respectively. $T$ is the absolute temperature. $R$, $k$ and $h$ are the gas, Boltzmann and Planck constants, respectively.

The function (4) is a linear one in the $\ln(f_r/T)$ and $(1/T)$ coordinates with the slope

$$a_f = -\frac{\Delta H_{21}^{\neq}}{R} - \frac{K}{1+K}\frac{\Delta H^0}{R} \tag{5}$$

and the intercept

$$b_f = \ln\left(\frac{k}{2\pi h}\right) + \frac{\Delta S_{21}^{\neq}}{R}, \tag{6}$$

when the relationship between the equilibrium constant $K$ and the reaction enthalpy $\Delta H^0$,

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^0}{R}, \tag{7}$$

is applied.

The maximum excess attenuation per wavelength, $\mu_m$, is given by

$$\mu_m = \frac{\pi}{2\beta}\frac{\Delta V_S^2}{RT}\frac{K}{(1+K)^2}C, \tag{8}$$

where $\beta$ is the adiabatic compressibility, $\Delta V_S$ is the isentropic change of volume which accompanies the transition from the state $A_1$ to the state $A_2$, $C$ is the total molar concentration.

In the $\ln(\mu_m \beta T)$ and $(1/T)$ coordinates, the plot of equation (8) is a straight line with the slope

$$a_\mu = \frac{\Delta H^0}{R}\frac{K-1}{K+1} \tag{9}$$

and the intercept

$$b_\mu = \ln\left(\frac{\pi}{2}\frac{\Delta V_S^2}{R}C\right). \tag{10}$$

After combining equations (4), (5) and (9), one can get a formula from that $K$ can be calculated:

$$\frac{f_r}{\frac{kT}{2\pi h}\exp\left(\frac{\Delta S_{21}^{\neq}}{R}\right)} = \exp\left[\frac{1}{T}\left(a_f + \frac{K}{K-1}a_\mu\right)\right](1+K), \tag{11}$$

where the values of $a_f$, $a_\mu$ and $\Delta S_{21}^{\neq}$ can be determined from the ultrasonic measurements.

From the mentioned formulas, the values of $\Delta S_{21}^{\neq}$, $K$, $\Delta H^0$, $\Delta H_{21}^{\neq}$ and $k_{21}$ can be calculated. Subsequently, the values of other kinetic and thermodynamic parameters can be established according to the formulas:

the rate constant of direct reaction

$$k_{12} = K k_{21}, \tag{12}$$

the free enthalpy of activation of the opposite reaction

$$\Delta G_{21}^{\neq} = \Delta H_{21}^{\neq} - T\Delta S_{21}^{\neq}, \tag{13}$$

the free enthalpy of the reaction (3)

$$\Delta G^0 = -RT \ln K, \tag{14}$$

the entropy of this reaction

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}, \tag{15}$$

the enthalpy of activation of the direct reaction

$$\Delta H_{12}^{\neq} = \Delta H^0 + \Delta H_{21}^{\neq}, \tag{16}$$

the entropy of activation of this reaction

$$\Delta S_{12}^{\neq} = \Delta S^0 + \Delta S_{21}^{\neq}, \tag{17}$$

the free enthalpy of activation of the direct reaction

$$\Delta G_{12}^{\neq} = \Delta G^0 + \Delta G_{21}^{\neq}. \tag{18}$$

The modulus of the molar volume change, which accompanies reaction (3), can be calculated from a transformation of equation (8)

$$|\Delta V_S| = \left[\frac{2RT\beta}{\pi} \frac{(1+K)^2}{K} \frac{\mu_m}{C}\right]^{1/2}. \tag{19}$$

The thermodynamic and kinetic parameters of the high- and low-frequency processes are presented in Tables 9–12.

**Table 9.** Kinetic and thermodynamic parameters of the high-frequency relaxation process for aqueous solutions of α-cyclodextrin with alkylpyridinium bromides $C_nH_{2n+1}C_5H_5NBr$ at 25°C.

| $n$ | $a_f$ [$K^{-1}$] | $b_f$ | $a_\mu$ [$K^{-1}$] | $b_\mu$ | $(\mu_m/C)\cdot10^6$ [$m^3$/mole] | $K\cdot10^3$ | $\Delta G^0$ [kJ/mole] | $\Delta H^0$ [kJ/mole] | $\Delta S^0$ [J/(mole·K)] | $k_{12}\cdot10^{-5}$ [$s^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 8 | −309.1 | 12.46 | 901.4 | −27.42 | 4.76 | 5.87 | 12.7 | −7.58 | −68.2 | 9.90 |
| 10 | −256.5 | 12.48 | 922.3 | −27.43 | 5.07 | 3.68 | 13.9 | −7.73 | −72.5 | 7.60 |
| 12 | −211.3 | 12.48 | 951.6 | −27.46 | 5.67 | 3.57 | 14.0 | −7.97 | −73.6 | 8.58 |

| $\Delta G_{12}^{\neq}$ [kJ/mole] | $\Delta H_{12}^{\neq}$ [kJ/mole] | $\Delta S_{12}^{\neq}$ [J/(mole·K)] | $k_{21}\cdot10^{-8}$ [$s^{-1}$] | $\Delta G_{21}^{\neq}$ [kJ/mole] | $\Delta H_{21}^{\neq}$ [kJ/mole] | $\Delta S_{21}^{\neq}$ [J/(mole·K)] | $\lvert\Delta V_S\rvert$ [$cm^3$/mole] |
|---|---|---|---|---|---|---|---|
| 38.8 | −4.97 | −147 | 1.69 | 26.1 | 2.61 | −78.7 | 23.7 |
| 39.4 | −5.59 | −151 | 2.07 | 25.5 | 2.13 | −78.5 | 30.8 |
| 39.2 | −6.18 | −152 | 2.40 | 25.2 | 1.79 | −78.5 | 33.0 |

The high-frequency relaxation process in the liquid systems under test is connected with the exchange of water molecules in the hydratation shell of the α-CD molecule [32, 33], just as for the α-CD + sodium alkyl sulfate aqueous solutions [25]. This conclusion results from the similarity of the ultrasonic, kinetic and thermodynamic parameters of this relaxation process for systems with and without surfactants [34].

**Table 10.** Kinetic and thermodynamic parameters of the high-frequency relaxation process for aqueous solutions of $\alpha$-cyclodextrin with alkyltrimethylammonium bromides $C_nH_{2n+1}(CH_3)_3NBr$ at 25°C.

| $n$ | $a_f$ [$K^{-1}$] | $b_f$ | $a_\mu$ [$K^{-1}$] | $b_\mu$ | $(\mu_m/C)\cdot10^6$ [$m^3$/mole] | $K\cdot10^3$ | $\Delta G^0$ [kJ/mole] | $\Delta H^0$ [kJ/mole] | $\Delta S^0$ [J/(mole·K)] | $k_{12}\cdot10^{-5}$ [$s^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 8 | −311.5 | 12.50 | 891.7 | −27.35 | 4.83 | 5.56 | 12.9 | −7.50 | −68.3 | 9.69 |
| 10 | −265.1 | 12.54 | 907.5 | −27.41 | 5.13 | 4.40 | 13.5 | −7.61 | −70.6 | 9.36 |
| 12 | −212.3 | 12.50 | 932.1 | −27.39 | 5.80 | 3.00 | 14.4 | −7.80 | −74.4 | 7.35 |

| $\Delta G_{12}^{\neq}$ [kJ/mole] | $\Delta H_{12}^{\neq}$ [kJ/mole] | $\Delta S_{12}^{\neq}$ [J/(mole·K)] | $k_{21}\cdot10^{-8}$ [$s^{-1}$] | $\Delta G_{21}^{\neq}$ [kJ/mole] | $\Delta H_{21}^{\neq}$ [kJ/mole] | $\Delta S_{21}^{\neq}$ [J/(mole·K)] | $\lvert\Delta V_S\rvert$ [$cm^3$/mole] |
|---|---|---|---|---|---|---|---|
| 38.9 | −4.87 | −147 | 1.74 | 26.0 | 2.63 | −78.3 | 24.6 |
| 38.9 | −5.38 | −149 | 2.13 | 25.5 | 2.24 | −78.0 | 28.4 |
| 39.5 | −6.01 | −153 | 2.45 | 25.1 | 1.79 | −78.3 | 36.4 |

**Table 11.** Kinetic and thermodynamic parameters of the low-frequency relaxation process for aqueous solutions of $\alpha$-cyclodextrin with alkylpyridinium bromides $C_nH_{2n+1}C_5H_5NBr$ at 25°C.

| $n$ | $a_f$ [$K^{-1}$] | $b_f$ | $a_\mu$ [$K^{-1}$] | $b_\mu$ | $(\mu_m/C)\cdot10^6$ [$m^3$/mole] | $K$ | $\Delta G^0$ [kJ/mole] | $\Delta H^0$ [kJ/mole] | $\Delta S^0$ [J/(mole·K)] | $k_{12}\cdot10^{-7}$ [$s^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 10 | −1617 | 15.33 | −924.7 | −22.04 | 2.31 | 24.4 | −7.92 | −8.35 | −1.43 | 3.62 |
| 12 | −1004 | 13.49 | −1136 | −20.53 | 5.18 | 47.7 | −9.58 | −9.85 | −0.90 | 4.55 |

| $\Delta G_{12}^{\neq}$ [kJ/mole] | $\Delta H_{12}^{\neq}$ [kJ/mole] | $\Delta S_{12}^{\neq}$ [J/(mole·K)] | $k_{21}\cdot10^{-5}$ [$s^{-1}$] | $\Delta G_{21}^{\neq}$ [kJ/mole] | $\Delta H_{21}^{\neq}$ [kJ/mole] | $\Delta S_{21}^{\neq}$ [J/(mole·K)] | $\lvert\Delta V_S\rvert$ [$cm^3$/mole] |
|---|---|---|---|---|---|---|---|
| 29.9 | 13.1 | −56.2 | 14.8 | 37.8 | 21.5 | −54.8 | 6.5 |
| 29.3 | 8.15 | −71.0 | 9.55 | 38.9 | 18.0 | −70.1 | 13.3 |

**Table 12.** Kinetic and thermodynamic parameters of the low-frequency relaxation process for aqueous solutions of $\alpha$-cyclodextrin with alkyltrimethylammonium bromides $C_nH_{2n+1}(CH_3)_3NBr$ at 25°C.

| $n$ | $a_f$ [$K^{-1}$] | $b_f$ | $a_\mu$ [$K^{-1}$] | $b_\mu$ | $(\mu_m/C)\cdot10^6$ [$m^3$/mole] | $K$ | $\Delta G^0$ [kJ/mole] | $\Delta H^0$ [kJ/mole] | $\Delta S^0$ [J/(mole·K)] | $k_{12}\cdot10^{-7}$ [$s^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 10 | −1626 | 15.33 | −913.7 | −22.10 | 2.21 | 23.8 | −7.86 | −8.62 | −1.36 | 3.56 |
| 12 | −1022 | 13.47 | −1096 | −20.72 | 4.81 | 42.9 | −9.32 | −9.55 | −0.77 | 4.30 |

| $\Delta G_{12}^{\neq}$ [kJ/mole] | $\Delta H_{12}^{\neq}$ [kJ/mole] | $\Delta S_{12}^{\neq}$ [J/(mole·K)] | $k_{21}\cdot10^{-5}$ [$s^{-1}$] | $\Delta G_{21}^{\neq}$ [kJ/mole] | $\Delta H_{21}^{\neq}$ [kJ/mole] | $\Delta S_{21}^{\neq}$ [J/(mole·K)] | $\lvert\Delta V_S\rvert$ [$cm^3$/mole] |
|---|---|---|---|---|---|---|---|
| 29.9 | 13.2 | −56.1 | 15.0 | 37.8 | 21.4 | −54.8 | 6.3 |
| 29.5 | 8.28 | −71.0 | 10.0 | 38.8 | 17.8 | −70.3 | 12.1 |

The origin of the low-frequency relaxation process is the penetration of the hydrophobic alkyl chain of the surfactant into the cavity of $\alpha$-CD [26]. The rate constant $k_{12}$ and the equilibrium constant $K$ increase when the alkyl chain becomes longer (i.e. when $n$

increases). These facts reflect a deeper penetration of the longer (and more hydrophobic) hydrocarbon chain into the hydrophobic cavity of α-CD. For the short octyl chains (having rather weak hydrophobicity), this kind of penetration does not take place, thus there is no low-frequency relaxation process in the aqueous solutions of α-CD with octylpyridinium bromide or octyltrimethylammonium bromide. These conclusions are similar to those for sodium alkyl sulfates [26].

Taking into account the results for sodium alkyl sulfates, and presented in this work, for alkylpyridinium bromides and alkyltrimethylammonium bromides, one can notice that the occurrence of the low-frequency relaxation process does not depend on the structure of the polar head of the surfactant and on its electric character (cationic or anionic). This can be the evidence of a diminutive influence of interactions between the polar head of the surfactant with the α-CD molecule on above described penetration. Nevertheless, this influence exists since ultrasonic, kinetic and thermodynamic parameters have slightly different values for those three groups of the surfactants.

## References


[1] M.L. BENDER and M. KOMIYAMA, *Cyclodextrin chemistry*, Springer-Verlag, Berlin 1978.

[2] J. SZEJTLI, *Cyclodextrins and their inclusion complexes*, Akademiai Kiado, Budapest 1982.

[3] M.KOMIYAMA and M.L. BENDER, J. Am. Chem. Soc., **100**, 2259 (1978).

[4] W. SAENGER, Angew. Chem., **19**, 344 (1980).

[5] W. SAENGER, *Inclusion compounds*, Vol. 2, Academic Press, London 1984.

[6] C. TANFORD, *The hydrophobic effect. Formation of micelles and biological membranes*, 2-nd ed., John Wiley and Sons, New York 1980.

[7] N. FUNASAKI, H. YODO and S. NEYA, Bull. Chem. Soc. Jpn., **65**, 1323 (1992).

[8] V.T. LIVERI, G. CAVALLARO, G. GIAMMONA, G. PITTARRESI, G. PUGLISI and C. VENTUNA, Thermochim. Acta, **199**, 125 (1992).

[9] D.J. JOBE, R.E. VERRAL, R. PALEPU and V.C. REINSBOROUGH, J. Phys. Chem., **92**, 3582 (1988).

[10] R. PALEPU and V.C. REINSBOROUGH, Can. J. Chem., **67**, 1550 (1989).

[11] R. PALEPU, J.E. RICHARDSON and V.C. REINSBOROUGH, Langmuir, **5**, 218 (1989).

[12] J.W. PARK and K.H. PARK, J. Inclusion Phenom. Mol. Recognit. Chem., **17**, 277 (1994).

[13] T. TOMINAGA, D. HACHITSU and M. KAMADO, Langmuir, **10**, 4676 (1994).

[14] E. JUNQUERA, J.G. BENITO, L. PENA and E. AIRCART, J. Colloid. Interface Sci., **163**, 355 (1994).

[15] E. JUNQUERA, G. TARDAJOS and E. AIRCART, Langmuir, **9**, 1213 (1993).

[16] D.J. JOBE, R.E. VERRAL, E. JUNQUERA and E. AIRCART, J. Phys. Chem., **98**, 10814 (1994).

[17] K.J. SASAKI, S.D. CHRISTIAN and E.E. TUCKER, J. Colloid. Interface Sci., **134**, 412 (1990).

[18] W.M.Z. WAN JUNUS, J. TAYLOR, D.M. BLOOR, D.G. HALL and E.J. WYN-JONES, J. Phys. Chem., **96**, 899 (1992).

[19] Y.-B. JIANG and X.-J. WANG, Appl. Spectrosc., **48**, 1428 (1994).

[20] U.R. DHARMAWARDANA, S.D. CHRISTIAN, E.E. TUCKER, R.W. TAYLOR and J.F. SCAMEHORN, Langmuir, **9**, 2258 (1993).

[21] D. JEZEQUEL, A. MAYAFFRE and P. LETELLIERA, Can. J. Chem., **69**, 1865 (1991).

[22] A. HERSEY, B.H. ROBINSON and H.C. KELLY, J. Chem. Soc. Faraday Trans., **182**, 1271 (1986).

[23] B.M. FUNG, W. GUO and S.D. CHRISTIAN, Langmuir, **8**, 446 (1992).

[24] E.S. AMAN, D. SERVE, J. Colloid. Interface Sci., **183**, 365 (1990).

[25] A. JUSZKIEWICZ and A. BALCERZAK, Archives of Acoustics, **21**, 431 (1996).

[26] F. EGGERS and T. FUNCK, Rev. Sci. Instrum., **44**, 969 (1973).

[27] F. EGGERS, T. FUNCK and K.H. RICHMANN, Rev. Sci. Instrum., **47**, 361 (1976).

[28] A. LABHARDT and G. SCHWARZ, Berichte der Bunsen-Gesellschaft, **80**, 83 (1976).

[29] J. LAMB, *Physical acoustics*, W.P. MASON [Ed.], Academic Press, New York 1965, Vol. II, Part A, Chapter 4.

[30] C.C. CHEN and S. PETRUCCI, J. Phys. Chem., **86**, 2601 (1982).

[31] L.J. RODRIGUEZ, E.M. EYRING and S. PETRUCCI, J. Phys. Chem., **93**, 6356 (1989).

[32] D.J. JOBE, R.E. VERRALL, E. JUNQUERA and E. AIRCART, J. Phys. Chem., **97**, 1243 (1993).

[33] S. KATO, H. NOMURA and Y. MIYARA, J. Phys. Chem., **89**, 5417 (1985).

[34] A. JUSZKIEWICZ and A. BALCERZAK, Archives of Acoustics, **18**, 447 (1993).