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ULTRASONIC MEASUREMENTS OF AQUEOUS SOLUTIONS OF β-CYCLODEXTRIN WITH ALKYL PYRIDINIUM BROMIDES

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Ultrasonic measurements of the velocity and absorption coefficient, α/f^2, of aqueous solutions of β-cyclodextrin with alkyl pyridinium bromides $\mathrm{C_nH_{2n+1}C_5H_4NBr}$ ($\mathrm{n} = 8, 10, 12$), were carried out at the following temperatures: 288.2 K, 298.2 K, 308.2 K and 318.2 K, and frequency range from 1 MHz to 150 MHz. Concentration of the both components equaled 0.01 M. The occurrence of two ultrasonic relaxation processes has been reported. Thermodynamic and kinetic parameters related to these processes have been calculated. The obtained results have been compared with data published previously for α-cyclodextrin systems.

Keywords: cyclodextrins, surfactants, ultrasonic spectroscopy, relaxation processes.

1. Introduction

α-, β- and γ-cyclodextrins (CDs) are naturally occurring cyclic oligosaccharides composed of six, seven, and eight D-glucose units, respectively. Because CDs are shaped like a truncated cone with a cavity in center, they accommodate a substrate molecule in their cavities to form an inclusion complex. The hydrophobic cavity forms an ideal harbor in which poorly water-soluble molecules can shelter their most hydrophobic parts. The contact between such a poorly soluble compound and CD in aqueous environment can result in complexation with no covalent bonds. Due to the hydrophilic outside of the CDs, such a complex is a soluble entity on its own. The CDs have been well-known to form inclusion complexes with a variety of molecular species by several kinds of driving forces, where the hydrophobic interaction has been found to play an important role [1–3].

It has been demonstrated that the addition of the CD to an aqueous solution of a surfactant affects dramatically the physicochemical properties of the solution [4–41]. The reason for these changes is the ability of CD to screen the hydrophobic moieties of the surfactant molecules from contact with the surrounding aqueous media by the formation of the inclusion complex in which the hydrophobic chain of the surfactant is inserted into the CD cavity. As a result, surfactants are excellent guests which allow a systematic study of complexation with CDs since both their hydrophobic and hydrophilic moieties can be systematically changed. Indeed, the ability of CDs to modify the physicochemical properties of such aqueous solutions has been used to study their complexation behavior with surfactants, and a variety of experimental techniques have been applied for this purpose. They include calorimetry [6–9], conductivity [10–20, 26, 28], competitive binding using UV-visible and fluorescent probes [16, 21–24, 28], NMR [6, 25–29], surface tension [30, 31], sound velocity [32–34], ultrasound absorption [35, 36] and electrochemical [37–41] methods.

The ultrasonic spectroscopy technique is an important tool for elucidation of basic solution processes and reaction mechanisms occurring in the microsecond to nanosecond range. Despite of the kinetic information, ultrasonic relaxation studies can provide thermodynamic information about the relaxation process [35, 36, 42, 43]. One such area still not well understood is the inclusion of guest molecules by CDs in their cavities.

2. Experimental part

Measurements of the absorption coefficient, α/f^2, in aqueous solutions of β-CD (Aldrich) with alkyl pyridinium bromides $\mathrm{C_nH_{2n+1}C_5H_4NBr}$ (n $= 8, 10, 12$) (Aldrich) were performed in the frequency range from 1 MHz to 150 MHz at the following temperatures: 288.2 K, 298.2 K, 308.2 K and 318.2 K, and at the concentration of 0.01 M of each of the components, i.e. CD and surfactant.

The measurements were made by means of the resonator [44–46] and pulse [43, 47] methods in the frequency range 1–10 MHz and 10–150 MHz, respectively. The measurements errors were about 6% for the former method and below 3% for the latter one.

The additional measurements of the velocity of sound and the density for these solutions were also made. They were needed for further calculations. The velocity of sound was measured applying the resonator method [44–46] at the frequency 1.25 MHz. 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 (1) and (2):

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

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

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 “classical” sound absorption (the effects of viscosity and heat conductivity on sound absorption), B, and the maximum of the excess (i.e. above “classical”) absorption per wavelength, μ_{mi}. f is the measured frequency, α is the ultrasonic absorption, $\mu = (\alpha - Bf^2)\lambda$ is the excess absorption per wavelength λ ($\lambda = c/f$, c is the speed of sound), l is the number of relaxation processes ($l = 2$ in our case). The relation between A_i and μ_{mi} is as follows: $\mu_{mi} = f_{ri}A_i$ $(c/2)$.

3. Experimental results and calculations

The results of the measurements are presented in Tables 1–3.

Table 1. Ultrasound absorption, velocity of sound and density for aqueous solutions of β-cyclodextrin with octyl pyridinium bromide.

	temperature [K]			
	288.2	298.2	308.2	318.2
f [MHz]	absorption α/f^2 [10^{-15} s^{2}m^{-1}]			
1.00	42.8	34.5	27.1	21.4
1.55	40.9	32.9	26.3	21.3
2.04	41.5	33.2	25.6	20.5
3.08	40.3	32.2	25.7	21.3
3.57	40.6	31.9	25.9	20.8
4.60	39.4	32.0	24.8	20.4
5.58	38.8	31.0	24.9	19.8
6.32	38.3	30.7	24.4	19.9
7.06	37.6	30.3	24.1	19.4
8.50	37.1	29.4	23.3	18.9
9.35	36.5	29.0	23.0	18.7
10.00	36.2	28.9	22.8	18.4
15.00	34.6	27.3	21.4	17.1
20.00	33.7	26.4	20.6	16.2
30.00	32.2	25.1	19.3	15.2
40.00	31.4	24.3	18.6	14.5
50.00	30.9	23.9	18.1	14.1
60.00	30.6	23.6	17.9	13.8
70.00	30.4	23.4	17.7	13.6
80.00	30.3	23.3	17.6	13.5
90.00	30.2	23.2	17.5	13.4
100.00	30.1	23.1	17.4	13.3
110.00	30.1	23.1	17.4	13.3
120.00	30.0	23.0	17.3	13.2
130.00	30.0	23.0	17.3	13.2
140.00	30.0	23.0	17.3	13.2
150.00	29.9	22.9	17.2	13.2
	velocity [m/s]			
	1471.3	1501.9	1525.0	1541.6
	density [kg/m^3]			
	1001.7	999.6	996.7	992.8

Table 2. Ultrasound absorption, velocity of sound and density for aqueous solutions of β-cyclodextrin with decyl pyridinium bromide.

	temperature [K]			
	288.2	298.2	308.2	318.2
f [MHz]	absorption α/f^2 [10^{-15} s^2m^{-1}]			
1.00	45.9	37.4	30.6	25.8
1.55	45.9	38.1	29.8	25.8
2.05	45.8	37.1	31.1	25.1
3.08	44.3	36.1	29.7	25.6
3.55	43.7	35.8	29.4	24.8
4.36	42.6	35.2	28.5	24.0
5.61	41.3	33.8	27.9	23.3
6.31	40.5	33.0	27.1	23.0
7.09	39.6	32.6	26.5	22.2
8.50	38.7	31.2	25.6	21.4
9.25	38.1	30.8	24.9	20.8
10.00	37.5	30.7	24.6	20.5
15.00	35.5	28.3	22.4	18.3
20.00	34.1	27.2	21.2	17.2
30.00	32.5	25.7	19.8	15.8
40.00	31.6	24.7	18.9	14.9
50.00	31.1	24.2	18.4	14.4
60.00	30.8	23.9	18.1	14.1
70.00	30.6	23.7	17.9	13.9
80.00	30.4	23.6	17.8	13.8
90.00	30.3	23.4	17.6	13.7
100.00	30.2	23.4	17.6	13.6
110.00	30.2	23.3	17.5	13.5
120.00	30.1	23.3	17.5	13.5
130.00	30.1	23.2	17.4	13.4
140.00	30.1	23.2	17.4	13.4
150.00	30.1	23.2	17.4	13.4
	velocity [m/s]			
	1471.3	1502.2	1525.5	1541.9
	density [kg/m^3]			
	1001.9	999.8	996.9	993.1

The representative plot of the coefficient of sound absorption, α/f^2, vs. frequency, f, for the aqueous solution of β-CD and decyl pyridinium bromide at temperature 298.2 K and the plots of the dependence of the excess sound absorption per wavelength, μ, on frequency, f, for the investigated systems at 298.2 K are shown in Figs. 1–4, respectively.

Table 3. Ultrasound absorption, velocity of sound and density for aqueous solutions of β-cyclodextrin with dodecyl pyridinium bromide.

	temperature [K]			
	288.2	298.2	308.2	318.2
f [MHz]	absorption α/f^2 [10^{-15} s^{2}m^{-1}]			
1.00	49.3	43.3	35.0	28.7
1.55	49.6	40.1	34.2	29.9
2.05	48.2	40.2	34.3	30.2
3.08	47.0	39.6	33.2	28.8
3.55	46.6	39.2	33.4	28.8
4.36	45.5	37.9	32.4	27.9
5.61	43.6	36.7	30.8	26.5
6.31	42.9	35.7	30.4	26.2
7.09	42.1	35.1	29.7	25.4
8.50	40.5	33.9	28.1	24.1
9.25	39.9	33.0	27.7	23.6
10.00	39.2	32.6	27.0	23.1
15.00	36.6	29.5	24.0	20.0
20.00	34.9	27.9	22.3	18.3
30.00	33.0	26.2	20.5	16.4
40.00	32.0	25.1	19.4	15.4
50.00	31.4	24.5	18.9	14.8
60.00	31.0	24.2	18.5	14.4
70.00	30.7	23.9	18.3	14.2
80.00	30.6	23.7	18.1	14.0
90.00	30.4	23.6	17.9	13.9
100.00	30.3	23.5	17.8	13.8
110.00	30.3	23.4	17.8	13.7
120.00	30.2	23.4	17.7	13.6
130.00	30.2	23.4	17.7	13.6
140.00	30.1	23.3	17.6	13.5
150.00	30.1	23.3	17.6	13.5
	velocity [m/s]			
	1471.5	1502.4	1525.5	1542.2
	density [kg/m^3]			
	1002.4	1000.3	997.3	993.6

The values of the parameters of Eqs. (1) and (2) are shown in Table 4.

For β-CD, two relaxation processes occur for the all used alkyl pyridinium bromide surfactants. In case of α-CD there are also two relaxation processes for decyl and dodecyl hydrocarbon chains of the surfactants and single relaxation process for octyl one [48].

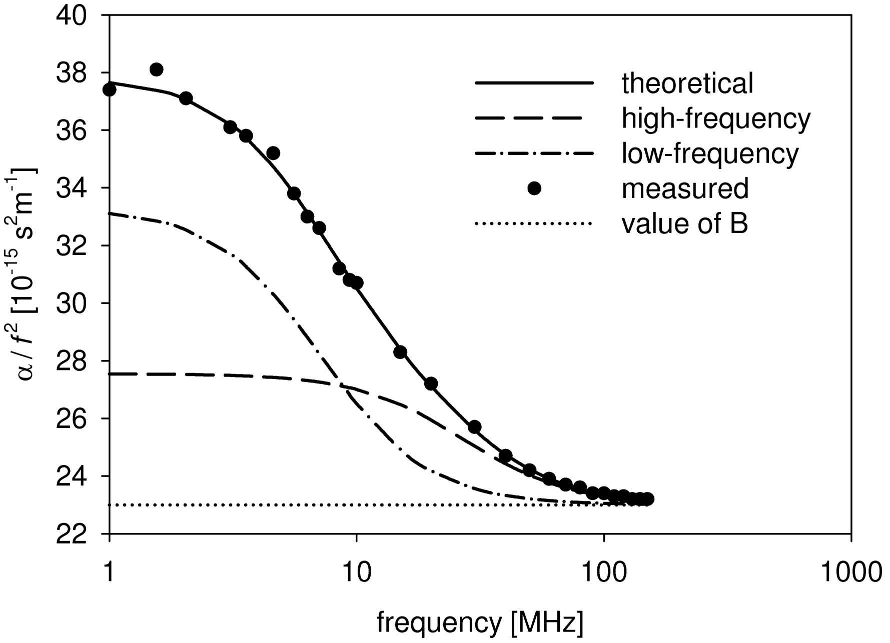

Fig. 1. Plot of the coefficient of sound absorption, α/f^2, vs. frequency, f, for the aqueous solution of β-CD and decyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

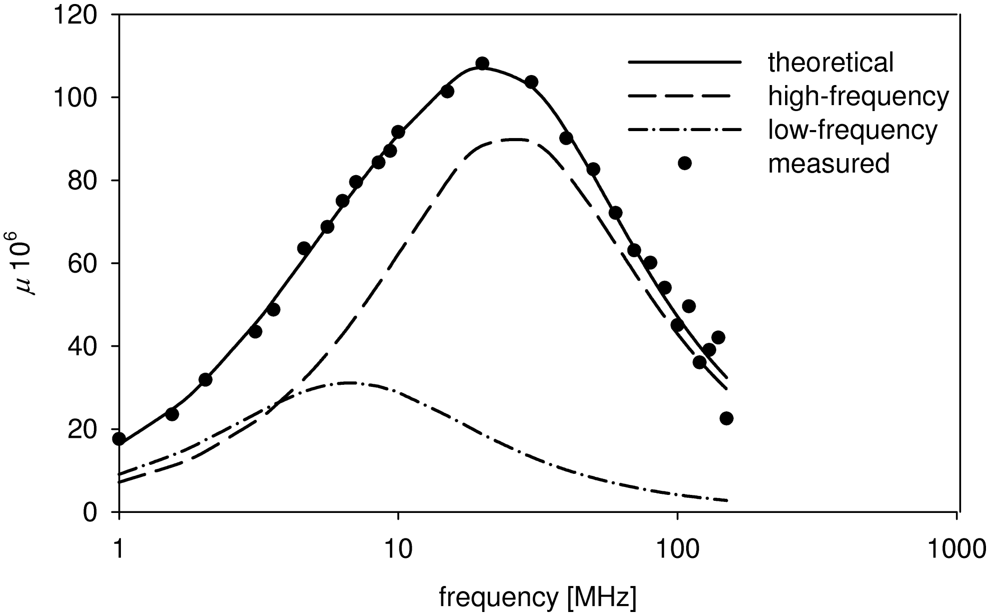

Fig. 2. Plot of the excess sound absorption per wavelength, μ, vs. frequency, f, for the aqueous solution of β-CD and octyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

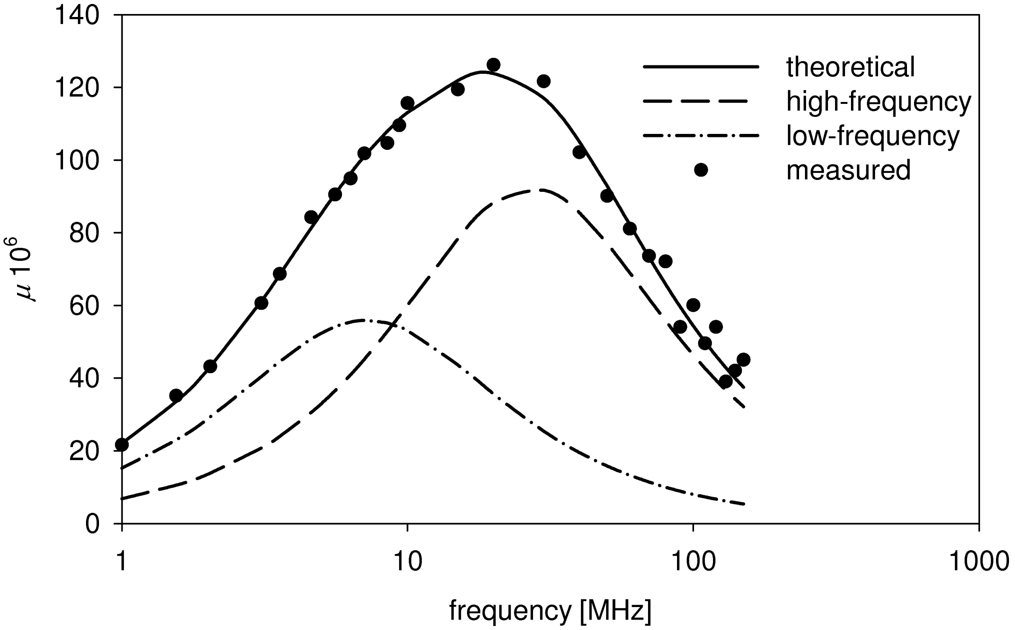

Fig. 3. Plot of the excess sound absorption per wavelength, μ, vs. frequency, f, for the aqueous solution of β-CD and decyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

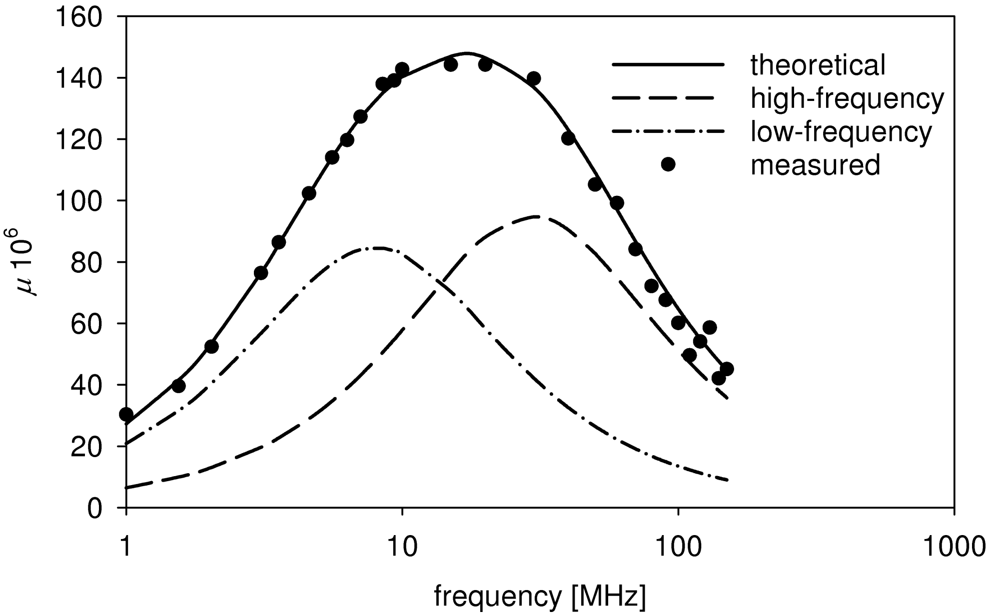

Fig. 4. Plot of the excess sound absorption per wavelength, μ, vs. frequency, f, for the aqueous solution of β-CD and dodecyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

Table 4. Relaxation parameters for aqueous solutions of β-cyclodextrin with alkyl pyridinium bromides at different temperatures.

t [K]	f_{r1} [MHz]	$A_1 \cdot 10^{15}$ [s^{2}m^{-1}]	$\mu_{m1} \cdot 10^6$	f_{r2} [MHz]	$A_2 \cdot 10^{15}$ [s^{2}m^{-1}]	$\mu_{m2} \cdot 10^6$	$B \cdot 10^{15}$ [s^{2}m^{-1}]
octyl pyridinium bromide							
288.2	22.8	5.87	98.4	5.7	6.58	27.6	29.8
298.2	25.2	4.79	90.7	6.7	6.22	31.1	22.8
308.2	27.3	4.01	83.5	8.2	5.44	34.0	17.1
318.2	31.1	3.18	76.3	9.5	5.29	38.7	13.0
decyl pyridinium bromide							
288.2	24.2	5.53	98.5	6.0	11.3	49.9	29.9
298.2	27.0	4.55	92.2	7.2	10.3	55.9	23.0
308.2	30.1	3.59	82.5	8.3	10.2	64.7	17.2
318.2	32.4	3.06	76.4	9.1	9.95	69.8	13.2
dodecyl pyridinium bromide							
288.2	26.8	5.38	106	7.0	14.3	73.7	29.9
298.2	29.4	4.29	94.7	8.0	14.1	84.6	23.1
308.2	32.0	3.51	85.6	9.1	14.2	98.5	17.4
318.2	35.7	2.95	81.1	9.9	14.0	107	13.3

The values of the B parameter are slightly greater then the absorption coefficient α/f^2 for pure water at given temperatures. This can be caused by a higher viscosity of the liquid systems under test than that of water. This fact indicates that above 150 MHz there are no other relaxation processes which could be connected with the presence of β-CD and the surfactant in the aqueous solution.

In the case of β-CD solutions (contrary to α-CD [48, 49], there is lack of the measurements of ultrasonic absorption at different concentrations due to low solubility of β-CD in water) it was assumed that indicate that the origin of the relaxations is a first-order or a pseudo-first-order reactions. Subsequently, this assumption was confirmed by linearity of dependencies ln($f_r/T) = g_1$(1/T) and ln($\mu_m \beta T) = g_2(1/T)$ (g_1 and g_2 denote functions). Thus, for the first-order or a pseudo-first-order reaction is:

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

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.

For this kind of relaxation processes, the following kinetic and thermodynamic formulas can be derived [50–52].

The relaxation frequency, f_r, can be expressed as

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

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 enthalpy 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 ($1/T$) co-ordinates 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 ΔH^0,

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

is applied.

The maximum excess attenuation per wavelength, μ_m, is given by

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

where β is the adiabatic compressibility, ΔV_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 ($1/T$) system of co-ordinates, the plot of Eq. (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 Eqs. (4), (5), (9), one can get a formula from that K can be calculated:

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

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

Thus, from the Eqs.: (6), (11), (9), (5) and (4), the values of $\Delta S^{\neq}_{21}$, K, ΔH^0, $\Delta H^{\neq}_{21}$ and k_{21} can be calculated. Subsequently, the values of other kinetic and thermodynamic parameters can be determined 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

$$\Delta G^{\neq}_{21} = \Delta H^{\neq}_{21} - T \Delta S^{\neq}_{21}, \tag{13}$$

- the free enthalpy of the reaction (3)

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

- the entropy of the reaction (3)

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

- the enthalpy of activation of the direct reaction

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

- the entropy of activation of the direct reaction

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

- the free enthalpy of activation of the direct reaction

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

The thermodynamic and kinetic parameters of the high- and low-frequency processes are presented in Tables 5 and 6.

The high-frequency relaxation process in the liquid systems, which were subjects of testing, is connected with the exchange of water molecules in the hydratation shell of the CD molecule [53, 54]. This conclusion results from the similarity of the ultrasonic, kinetic and thermodynamic parameters of this relaxation process for systems with or without surfactants, and this process is similar to described one [54, 55]. Thus, penetration of the surfactant into CD cavity only slightly modifies the exchange of water molecules. However, one can notice the decrease of the equilibrium constant, K, (Table 5), when the length of the surfactant alkyl chain increases (n becomes larger). This means that a longer alkyl chain of the surfactant makes more difficult the exchange of water molecules.

The obtained results suggest that the origin of the low-frequency relaxation process is the penetration of the hydrophobic alkyl chain of the surfactant into the cavity of CD. The rate constant k_{12} and the equilibrium constant K (Table 6) 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 CD. As it was mentioned in [48], for the short octyl chain in the case of α-CD (this

Table 5. Kinetic and thermodynamic parameters of the high-frequency relaxation process for aqueous solutions of β-cyclodextrin with alkyl pyridinium bromides $\mathrm{C_nH_{2n+1}C_5H_5NBr}$ at 298.2 K.

n	a_f [$\mathrm{K^{-1}}$]	b_f	a_μ [$\mathrm{K^{-1}}$]	b_μ	$K \cdot 10^3$	ΔG^o [kJ/mol]	ΔH^o [kJ/mol]	ΔS^o [J/(mol·K)]	$k_{12} \cdot 10^{-5}$ [$\mathrm{s^{-1}}$]	$\Delta G^{\neq}_{12}$ [kJ/mol]	$\Delta H^{\neq}_{12}$ [kJ/mol]	$\Delta S^{\neq}_{12}$ [J/(mol·K)]	$k_{21} \cdot 10^{-8}$ [$\mathrm{s^{-1}}$]	$\Delta G^{\neq}_{21}$ [kJ/mol]	$\Delta H^{\neq}_{21}$ [kJ/mol]	$\Delta S^{\neq}_{21}$ [J/(mol·K)]
8	−620.6	13.43	724.4	−27.58	4.31	13.5	−6.08	−65.7	6.80	39.7	−0.89	−136	1.58	26.2	5.19	−70.6
10	−588.7	13.39	761.0	−27.70	2.71	14.7	−6.36	−70.5	4.59	40.7	−1.44	−141	1.69	26.1	4.92	−70.9
12	−566.8	13.40	782.9	−27.72	1.54	16.1	−6.53	−75.7	2.84	41.9	−1.81	−147	1.84	25.8	4.72	−70.8

Table 6. Kinetic and thermodynamic parameters of the low-frequency relaxation process for aqueous solutions of β-cyclodextrin with alkyl pyridinium bromides $\mathrm{C_nH_{2n+1}C_5H_5NBr}$ at 298.2 K.

n	a_f [$\mathrm{K^{-1}}$]	b_f	a_μ [$\mathrm{K^{-1}}$]	b_μ	$K \cdot 10^3$	ΔG^o [kJ/mol]	ΔH^o [kJ/mol]	ΔS^o [J/(mol·K)]	$k_{12} \cdot 10^{-5}$ [$\mathrm{s^{-1}}$]	$\Delta G^{\neq}_{12}$ [kJ/mol]	$\Delta H^{\neq}_{12}$ [kJ/mol]	$\Delta S^{\neq}_{12}$ [J/(mol·K)]	$k_{21} \cdot 10^{-8}$ [$\mathrm{s^{-1}}$]	$\Delta G^{\neq}_{21}$ [kJ/mol]	$\Delta H^{\neq}_{21}$ [kJ/mol]	$\Delta S^{\neq}_{21}$ [J/(mol·K)]
8	−1312	14.43	−1052	22.69	36.2	−8.90	−9.24	−1.16	4.10	29.6	10.7	−63.4	11.3	38.5	19.9	−62.3
10	−984.5	13.38	−1101	−21.92	43.3	−9.34	−9.59	−0.83	4.42	29.4	7.97	−71.8	10.2	38.7	17.6	−71.0
12	−809.8	12.91	−1220	−21.12	63.0	−10.3	−10.5	−0.67	4.95	29.1	6.57	−75.6	7.85	39.4	17.0	−74.9

chain has 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. For β-CD solutions two relaxation processes have been established for all used surfactant i.e. with octyl, decyl and dodecyl chains., This difference behavior of the α-CD and β-CD solutions can be connected with the dimensions of the cavity, which are greater for β-CD than for α-CD. This means less steric hindrances when the alkyl chain penetrates the β-CD's cavity than the α-CD's one. It seems that the stability of the inclusion complexes depends mainly on a geometric factor i.e. similarity between the cavity dimensions and the penetrating moiety, as it was stated in [49, 56].

4. Conclusions

Ultrasonic measurements of the velocity and absorption coefficient, α/f^2, of aqueous solutions of β-CD with alkyl pyridinium bromides $C_nH_{2n+1}C_5H_4NBr$ (n = 8, 10, 12), were carried by means of ultrasonic spectroscopy. For all of them two relaxation processes have been established. Thermodynamic and kinetic parameters of these processes have been calculated. The obtained results have been compared with data published previously for aqueous solutions of α-CD with the same surfactants.

It seems, that the origin of the high-frequency relaxation process is connected with the exchange of water molecules in the hydratation shell of CD. The low-frequency process results from the penetration of the alkyl chain of the surfactants into the CD cavity. The occurrence or not of the low-frequency process in the α-CD and β-CD solutions with alkyl pyridinium bromides can be connected with the dimensions of their cavities.

References

[1] BENDER M.L., *et al.*, *Cyclodextrin Chemistry*, Springer Verlag, Berlin 1978.

[2] SZEJTLI J., *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest 1982.

[3] TANFORD C., *The Hydrophobic Effect. Formation of Micelles and Biological Membranes*, John Wiley & Sons, New York 1980.

[4] DE LISI R., LAZZARA G., MILIOTO S., MURATORE N., *Characterization of the cyclodextrin-surfactant interactions by volume and enthalpy*, J. Phys. Chem. B, **107**, 47, 13150–13157 (2003).

[5] FUNASAKI N., YODO H., NEYA S., *Stoichiometries and equilibrium constants of cyclodextrin-surfactant complexations*, Bull. Chem. Soc. Jpn., **65**, 5, 1323–1330 (1992).

[6] QU X.K., ZHU L.Y., LI L., WEI X.L., LIU F., SUN D.Z., *Host-guest complexation of β-, γ-cyclodextrin with alkyl trimethyl ammonium bromides in aqueous solution*, J Solution Chem., **36**, 5, 643–650 (2007).

[7] SUN D.Z., WANG S.B., SONG M.Z., WEI X.L., YIN B.L., *A microcalorimetric study of host-guest complexes of α-cyclodextrin with alkyl trimethyl ammonium bromides in aqueous solutions*, J. Solution Chem., **34**, 6, 701–712 (2005).

[8] ELI W.J., CHEN W.H., XUE Q.J., *The association of anionic surfactants with β-cyclodextrin. An isothermal titration calorimeter study*, J. Chem. Thermodyn., **31**, 10, 1283–1296 (1999).

[9] LIVERI V.T., CAVALLARO G., GIAMMONA G., PITARRESI G., PUGLISI G., VENTURA C., *Calorimetric investigation of the complex formation between surfactants and α-, β- and γ-cyclodextrins*, Thermochim. Acta, **199**, 1, 125–132 (1992).

[10] SEHGAL P., SHARMA M., LARSEN K.L., WIMMER R., DOE H., OLTZEN D.E., *Interactions of γ-cyclodextrin with the mixed micelles of anionic surfactants and their inclusion complexes formation*, J. Disper. Sci. Technol., **29**, 6, 885–890 (2008).

[11] RAFATI A.A., BAGHERI A., ILOUKHANI H., ZARINEHZAD M., *Study of inclusion complex formation between a homologous series of n-alkyltrimethylammonium bromides and β-cyclodextrin, using conductometric technique*, J. Mol. Liq., **116**, 1, 37–41 (2005).

[12] JUNQUERA E., PENA L., AICART E., *Micellar behavior of the aqueous solutions of dodecylethyldimethylammonium bromide. A characterization study in the presence and absence of hydroxypropyl-β-cyclodextrin*, Langmuir, **13**, 2, 219–224 (1997)

[13] JUNQUERA E., PENA L., AICART E., *Conductivity studies of the molecular encapsulation of sodium perfluoroctanoate by β-cyclodextrin derivatives*, J. Inclus. Phenom. Mol., **24**, 3, 233–239 (1996).

[14] AMAN E.S., SERVE D., *A conductimetric study of the association between cyclodextrins and surfactants – application to the electrochemical study of a mixed aqueous system: substrate, cyclodextrin, surfactant*, J. Colloid. Interface Sci., **138**, 2, 365–375 (1990).

[15] PALEPU R., RICHARDSON J.E., REINSBOROUGH V.C., *Binding constans of β-cyclodextrin/surfactant inclusion by conductivity measurements*, Langmuir, **5**, 1, 218–221 (1989).

[16] JOBE D.J., VERRAL R.E., PALEPU R., REINSBOROUGH V.C., *Fluorescene and conductometric studies of potassium 2-(p-toluidinyl)naphthalene-6-sulfonate/cyclodextrin/surfactant systems*, J. Phys. Chem., **92**, 12, 3582–3586 (1988).

[17] PALEPU R., REINSBOROUGH V.C., *Surfactant-cyclodextrin interactions by conductance measurements*, Can. J. Chem., **66**, 2, 325–328 (1988).

[18] SATAKE I., IKENOUE T., IAKESHITA T., HAYAKAWA K., MAEDA T., *Conductometric and potentiometric studies of the association of α-cyclodextrin with ionic surfactants and their homologs*, Bull. Chem. Soc. Jpn., **58**, 10, 2746–2750 (1985).

[19] SATAKE I., YOSHIDA S., HAYAKAWA K., MAEDA T., KOSUMOTO Y., *Conductometric determination of the association constants of β-cyclodextrin with amphiphilic ions*, Bull. Chem. Soc. Jpn., **59**, 12, 3991–3993 (1986).

[20] OKUBO T., KITANO H., ISE N., *Conductometric studies on association of cyclodextrin with colloidal electrolytes*, J. Phys. Chem., **80**, 24, 2661–2664 (1976).

[21] HERSEY A., ROBINSON B.H., KELLY H.C., *Mechanism of inclusion-compound formation for binding of organic dyes, ions and surfactants to α-cyclodextrin studied by kinetic methods based on competition experiments*, J. Chem. Soc. Faraday Trans. 1, **82**, 1271–1287 (1986).

[22] PARK J.W., SONG H.J., *Association of anionic surfactants with β-cyclodexrin. Fluorescene-probed studies no the 1:1 and 1:2 compexation*, J. Phys. Chem., **93**, 17, 6454–6458 (1989).

[23] PARK J.W., PARK K.H., *Inclusion of (aminostyryl)-1-methylpyridinium dyes by β-cyclodextrin and its use for fluorescent-probe studies on association of cationic and neutral molecules with β-cyclodextrin*, J. Inclusion Phenom. Mol. Recognit. Chem., **17**, 3, 277–290 (1994).

[24] JIANG Y.B., WANG X.J., *Direct evidence for β-cyclodextrin-induced aggregation of ionic surfactant below critical micelle concentration*, Appl. Spectrosc., **48**, 11, 1428–1431 (1994).

[25] XING H., LIN S.S., YAN P., XIAO J.X., CHEN Y.M., *NMR studies on selectivity of β-cyclodextrin to fluorinated/hydrogenated surfactant mixtures*, J. Phys. Chem. B, **111**, 28, 8089–8095 (2007).

[26] CABALEIRO–LAGO C., NILSSON M., VALENTE A.J.M., BONINI M., SODERMAN O., *NMR diffusometry and conductometry study of the host-guest association between β-cyclodextrin and dodecane 1,12-bis(trimethylammonium bromide)*, J. Colloid. Interf. Sci., **300**, 2, 782–787 (2006).

[27] GUO W., FUNG B.M., CHRISTIAN S.D., *NMR study of cyclodextrin inclusion of fluorocarbon surfactants in solution*, Langmuir, **8**, 2, 446–451 (1992).

[28] MEHTA S.K., BHASIN K.K., MAMA S., SINGLA M.L., *Micellar behavior of aqueous solutions of dodecyldimethylethylammonium bromide, dodecyltrimethylammonium chloride and tetradecyltrimethylammonium chloride in the presence of α-, β-, HP β-, and γ-cyclodextrins*, J. Colloid. Interf. Sci., **321**, 2, 442–451 (2008).

[29] FUNASAKI N., ISHIKAWA S., NEYA S., *1:1 and 1:2 complexes between long-chain surfactant and α-cyclodextrin studied by NMR*, J. Phys. Chem. B, **108**, 28, 9593–9598 (2004).

[30] GOKTURK S., MAHRAMANLIOGLU M., TUNCAY M., *Surface tension studies of lauryl sulfobetaine – β-cyclodextrin and dodecyltrimethylammonium bromide – β-cyclodextrin inclusion complexes in aqueous solution*, Can. J. Chem., **77**, 7, 1208–1213 (1999).

[31] DHARMAWARDANA U.R., CHRISTIAN S.D., TUCKER E.E., TAYLOR R.W., SCAMEHORN J.F., *A surface tension method for determining binding constants for cyclodextrin inclusion complexes of ionic surfactants*, Langmuir, **9**, 9, 2258–2263 (1993).

[32] GONZALEZ–GAITANO G., CRESPO A., TARDAJOS G., *Thermodynamic investigation (volume and compressibility) of the systems β-cyclodextrin plus n-alkyltrimethylammonium bromides plus water*, J. Phys. Chem. B, **104**, 8, 1869–1879 (2000).

[33] JUNQUERA E., TARDAJOS G., AICART E., *Effect of the presence of β-cyclodextrin on the micellization process of sodium dodecyl sulfate or sodium perfluorooctanoate in water*, Langmuir, **9**, 5, 1213–1219 (1993).

[34] PENA L., JUNQUERA E., AICART E., *Ultrasonic study of the molecular encapsulation and the micellization processes of dodecylethyldimethylammonium bromide-water solutions in the presence of β-cyclodextrin or 2,6-di-o-methyl- β -cyclodextrin*, J. Solution Chem., **24**, 10, 1075–1091 (1995).

[35] JOBE D.J., VERRAL R.E., JUNQUERA E., AICART E., *Effects of β-cyclodextrin/surfactant complex formation on the surfactant monomer-micelle exchange rate in aqueous solutions of sodium perfluorooctanoate and β-cyclodextrin*, J.Phys.Chem., **98**, 42, 10814–10818 (1994).

[36] JOBE D.J., VERRALL R.E., JUNQUERA E., AICART E., *Ultrasonic absorption studies of aqueous solutions of cetyltrimethylammonium bromide and 2,6-O-dimethyl-β-cyclodextrin*, J. Colloid. Interf. Sci., **189**, 2, 294–298 (1997).

[37] WAN JUNUS W.M.Z., TAYLOR J., BLOOR D.M., HALL D.G., WYN-JONES E.J., *Electrochemical measurements on the binding of sodium dodecyl sulfate and dodecyltrimethylammonium bromide with α- and β-cyclodextrins*, J. Phys. Chem., **96**, 22, 8979–8982 (1992).

[38] PATIL S.R., TURMINE M., PEYRE V., DURAND G., PUCCI B., *Study of β-cyclodextrin/fluorinated trimethyl ammonium bromide surfactant inclusion complex by fluorinated surfactant ion selective electrode*, Talanta, **74**, 1, 72–77 (2007).

[39] RAFATI A.A., BAGHERI A., *Electrochemical and thermodynamic studies of inclusion complex formation between tetradecyltrimethylammonium bromide (TTAB) and β-cyclodextrin (β-CD),* Bull. Chem. Soc. Jpn., **77**, 3, 485–490 (2004).

[40] GHARIBI H., JALILI S., RAJABI T., *Electrochemical studies of interaction between cetyltrimethylammonium bromide and α-, β-cyclodextrins at various temperature*, Colloid. Surface A, **175**, 3, 361–369 (2000).

[41] TOMINAGA T., HACHITSU D., KAMADO M., *Interactions between the tetradecyltrimethylammonium ion and α-, β- and γ-cyclodextrin in water as studied by a surfactant-selective electrode*, Langmuir, **10**, 12, 4676–4680 (1994).

[42] BERNASCONI C.F., *Relaxation Kinetics*, Academic Press, New York 1976.

[43] JUSZKIEWICZ A., ANTOSIEWICZ A., *Ultrasonic Spectroscopy in Molecular Biophysics* (in monograph: Biospectroscopy) [in Polish], PWN, Warszawa 1990.

[44] EGGERS F., FUNCK TH., *Ultrasonic measurements with milliliter liquid samples in the 0.5–100 MHz range*, Rev. Sci. Instrum., **44**, 8, 969–977 (1973).

[45] GALIŃSKI G., KOZŁOWSKI Z., *Ultrasonic spectroscopy equipment for the 0.5–15 MHz frequency range*, Sci. Instrum., **4,** 1, 43–50 (1989).

[46] BALCERZAK A., BAZIOR Z., KOZŁOWSKI Z., *Automatized set-up for ultrasonic measurements in liquids by resonator (Eggers) method* [in Polish], IFTR Reports, **17**, 1–14 (1992).

[47] BALCERZAK A., PŁOWIEC R., *Characteristic and construction of IFTR's set-up for ultrasonic investigation of relaxation phenomena in liquids in 10–150 MHz frequency range* [in Polish], IFTR Reports, **21**, 1–16 (1994).

[48] BALCERZAK A., PŁOWIEC R., JUSZKIEWICZ A., *Absorption of ultrasonic waves in aqueous solutions of α-cyclodextrin with alkylpyridinium or alkyltrimethylammonium bromides*, Arch. Acoust., **23**, 3, 411–428 (1998).

[49] BALCERZAK A., PŁOWIEC R., JUSZKIEWICZ A., *Investigations of ultrasonic velocity and absorption in aqueous solutions of α- and β-cyclodextrin with sodium alkyl sulfates*, Arch. Acoust., **26**, 1, 37–63 (2001).

[50] LAMB J., *Physical Acoustics*, W.P. MASON [Ed.], Vol. II, Part A, Ch. 4, Academic Press, New York 1965.

[51] CHEN C.C., PETRUCCI S., *Mechanism of complexation of 18-crown-6 with alkali metal ions in methanol*, J. Phys. Chem., **86**, 14, 2601–2605 (1982).

[52] RODRIGUEZ L.J., EYRING E.M., PETRUCCI S., *Isomeric relaxation kinetics of the macrocycles 18-crown-6, diaza-18-crown-6, and cryptand 222 in acetonitrile and methanol*, J. Phys. Chem., **93**, 17, 6357–6363 (1989).

[53] JOBE D.J., VERRALL R.F., JUNQUERAE., AICART E., *Effects of surfactant/β-cyclodextrin complex formation on the surfactant monomer-micelle exchange rate in aqueous solution of decyltrimethylammonium bromide*, J. Phys. Chem., **97**, 6, 1243–1248 (1993).

[54] KATO S., NOMURA H., MIYAHARA Y., *Ultrasonic relaxation study of aqueous solutions of cyclodextrins*, J. Phys. Chem., **89**, 25, 5417–5421 (1985).

[55] RAUH S., KNOCHE W., *Ultrasonic attenuation in aqueous solutions of α-, β-, and γ-cyclodextrins*, J. Chem. Soc. Faraday Trans., **81**, 1, 2551–2559 (1985).

[56] BALCERZAK A., *Ultrasonic investigations of inclusion complexes of cyclodextrins with amphiphilic substances – further results and conclusions*, Arch. Acoust., **29**, 3, 461–466 (2004).