

## ULTRASONIC MEASUREMENTS OF AQUEOUS SOLUTIONS OF $\beta$ -CYCLODEXTRIN WITH ALKYL PYRIDINIUM BROMIDES

Andrzej BALCERZAK

Institute of Fundamental Technological Research  
Polish Academy of Sciences  
Świętokrzyska 21, 00-049 Warszawa, Poland  
e-mail: abalcerz@ippt.gov.pl

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Ultrasonic measurements of the velocity and absorption coefficient,  $\alpha/f^2$ , of aqueous solutions of  $\beta$ -cyclodextrin with alkyl pyridinium bromides  $C_nH_{2n+1}C_5H_4NBr$  ( $n = 8, 10, 12$ ), 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  $\alpha$ -cyclodextrin systems.

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

### 1. Introduction

$\alpha$ -,  $\beta$ - and  $\gamma$ -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,  $\alpha/f^2$ , in aqueous solutions of  $\beta$ -CD (Aldrich) with alkyl pyridinium bromides  $C_nH_{2n+1}C_5H_4NBr$  ( $n = 8, 10, 12$ ) (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):

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

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

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,  $\mu_{mi}$ .  $f$  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 ( $l = 2$  in our case). The relation between  $A_i$  and  $\mu_{mi}$  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  $\beta$ -cyclodextrin with octyl pyridinium bromide.

$f$ [MHz]	temperature [K]			
	288.2	298.2	308.2	318.2
	absorption $\alpha/f^2$ [ $10^{-15} \text{ s}^2\text{m}^{-1}$ ]			
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 [ $\text{kg/m}^3$ ]			
	1001.7	999.6	996.7	992.8

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

$f$ [MHz]	temperature [K]			
	288.2	298.2	308.2	318.2
	absorption $\alpha/f^2$ [ $10^{-15} \text{ s}^2\text{m}^{-1}$ ]			
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 [ $\text{kg}/\text{m}^3$ ]			
	1001.9	999.8	996.9	993.1

The representative plot of the coefficient of sound absorption,  $\alpha/f^2$ , vs. frequency,  $f$ , for the aqueous solution of  $\beta$ -CD and decyl pyridinium bromide at temperature 298.2 K and the plots of the dependence of the excess sound absorption per wavelength,  $\mu$ , 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  $\beta$ -cyclodextrin with dodecyl pyridinium bromide.

$f$ [MHz]	temperature [K]			
	288.2	298.2	308.2	318.2
	absorption $\alpha/f^2$ [ $10^{-15} \text{ s}^2\text{m}^{-1}$ ]			
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 [ $\text{kg/m}^3$ ]			
	1002.4	1000.3	997.3	993.6

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

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

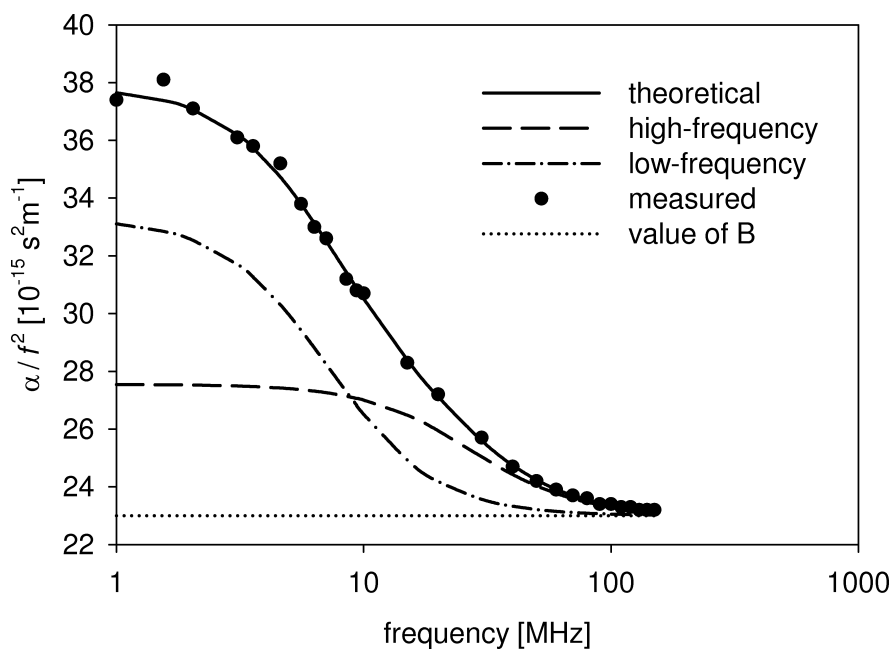


Fig. 1. Plot of the coefficient of sound absorption,  $\alpha/f^2$ , vs. frequency,  $f$ , for the aqueous solution of  $\beta$ -CD and decyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

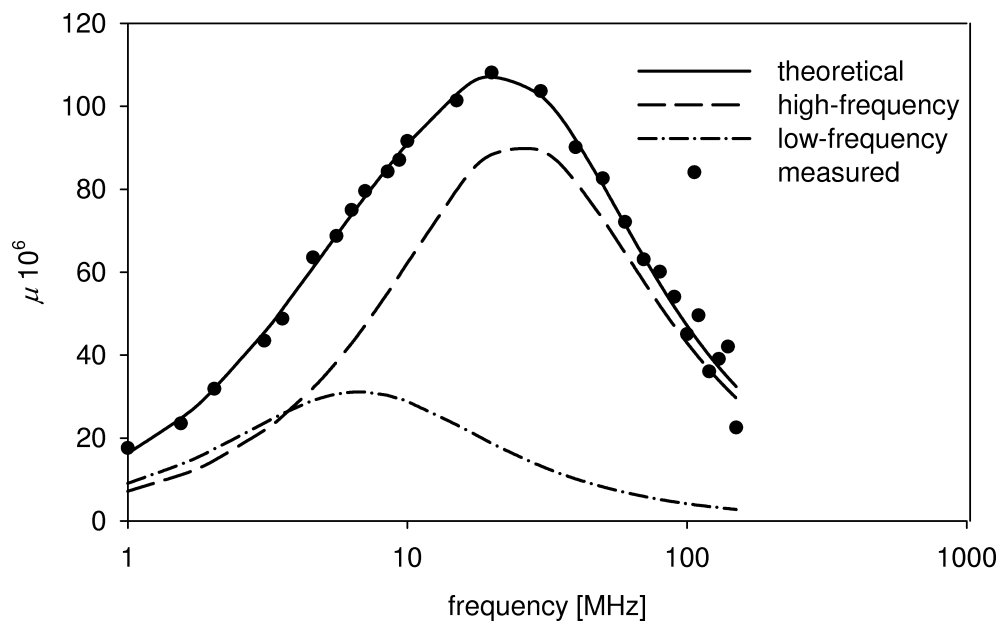


Fig. 2. Plot of the excess sound absorption per wavelength,  $\mu$ , vs. frequency,  $f$ , for the aqueous solution of  $\beta$ -CD and octyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

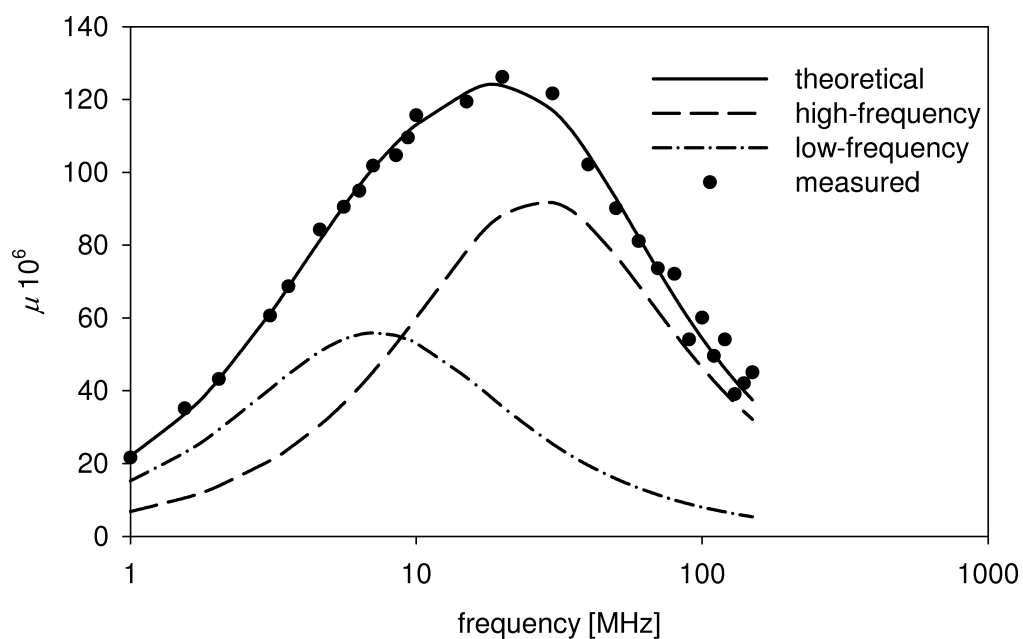


Fig. 3. Plot of the excess sound absorption per wavelength,  $\mu$ , vs. frequency,  $f$ , for the aqueous solution of  $\beta$ -CD and decyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

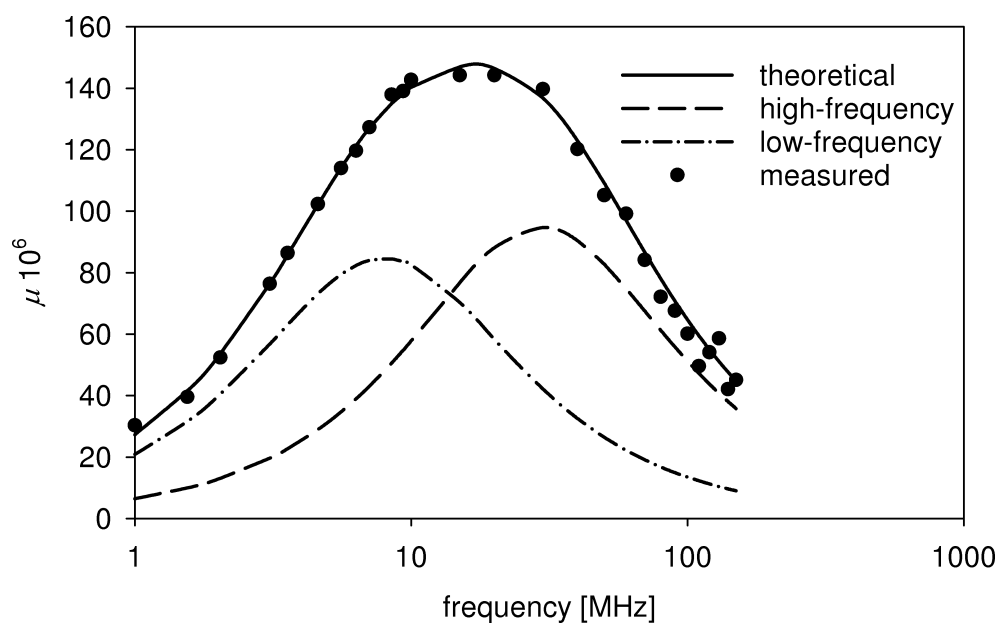


Fig. 4. Plot of the excess sound absorption per wavelength,  $\mu$ , vs. frequency,  $f$ , for the aqueous solution of  $\beta$ -CD and dodecyl pyridinium bromide. Temperature 298.2 K, concentration 0.01 M.

**Table 4.** Relaxation parameters for aqueous solutions of  $\beta$ -cyclodextrin with alkyl pyridinium bromides at different temperatures.

$t$ [K]	$f_{r1}$ [MHz]	$A_1 \cdot 10^{15}$ [s <sup>2</sup> m <sup>-1</sup> ]	$\mu_{m1} \cdot 10^6$	$f_{r2}$ [MHz]	$A_2 \cdot 10^{15}$ [s <sup>2</sup> m <sup>-1</sup> ]	$\mu_{m2} \cdot 10^6$	$B \cdot 10^{15}$ [s <sup>2</sup> m <sup>-1</sup> ]
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 than the absorption coefficient  $\alpha/f^2$  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  $\beta$ -CD and the surfactant in the aqueous solution.

In the case of  $\beta$ -CD solutions (contrary to  $\alpha$ -CD [48, 49], there is lack of the measurements of ultrasonic absorption at different concentrations due to low solubility of  $\beta$ -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:



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

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

where  $K$  is the equilibrium constant for reaction (3) ( $K = k_{12}/k_{21}$ ),  $\Delta S_{21}^\ddagger$  and  $\Delta H_{21}^\ddagger$  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

$$a_f = -\frac{\Delta H_{21}^\ddagger}{R} - \frac{K}{1+K} \frac{\Delta H^0}{R} \quad (5)$$

and the intercept

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

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

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

is applied.

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

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

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  $(1/T)$  system of co-ordinates, the plot of Eq. (8) is a straight line with the slope

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

and the intercept

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

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

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

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

Thus, from the Eqs.: (6), (11), (9), (5) and (4), the values of  $\Delta S_{21}^\ddagger$ ,  $K$ ,  $\Delta H^0$ ,  $\Delta H_{21}^\ddagger$  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

$$k_{12} = Kk_{21}, \quad (12)$$

- the free enthalpy of activation of the opposite reaction

$$\Delta G_{21}^\ddagger = \Delta H_{21}^\ddagger - T\Delta S_{21}^\ddagger, \quad (13)$$

- the free enthalpy of the reaction (3)

$$\Delta G^0 = -RT \ln K, \quad (14)$$

- the entropy of the reaction (3)

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

- the enthalpy of activation of the direct reaction

$$\Delta H_{12}^\ddagger = \Delta H^0 + \Delta H_{21}^\ddagger, \quad (16)$$

- the entropy of activation of the direct reaction

$$\Delta S_{12}^\ddagger = \Delta S^0 + \Delta S_{21}^\ddagger, \quad (17)$$

- the free enthalpy of activation of the direct reaction

$$\Delta G_{12}^\ddagger = \Delta G^0 + \Delta G_{21}^\ddagger. \quad (18)$$

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 hydration 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  $\alpha$ -CD (this

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

$n$	$a_f$ [K <sup>-1</sup> ]	$b_f$	$a_\mu$ [K <sup>-1</sup> ]	$b_\mu$	$K \cdot 10^3$	$\Delta G^\circ$ [kJ/mol]	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [J/(mol·K)]	$k_{12} \cdot 10^{-5}$ [s <sup>-1</sup> ]	$\Delta G_{12}^\ddagger$ [kJ/mol]	$\Delta H_{12}^\ddagger$ [kJ/mol]	$\Delta S_{12}^\ddagger$ [J/(mol·K)]	$k_{21} \cdot 10^{-8}$ [s <sup>-1</sup> ]	$\Delta G_{21}^\ddagger$ [kJ/mol]	$\Delta H_{21}^\ddagger$ [kJ/mol]	$\Delta S_{21}^\ddagger$ [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  $\beta$ -cyclodextrin with alkyl pyridinium bromides  $C_nH_{2n+1}C_5H_5NBr$  at 298.2 K.

$n$	$a_f$ [K <sup>-1</sup> ]	$b_f$	$a_\mu$ [K <sup>-1</sup> ]	$b_\mu$	$K \cdot 10^3$	$\Delta G^\circ$ [kJ/mol]	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [J/(mol·K)]	$k_{12} \cdot 10^{-5}$ [s <sup>-1</sup> ]	$\Delta G_{12}^\ddagger$ [kJ/mol]	$\Delta H_{12}^\ddagger$ [kJ/mol]	$\Delta S_{12}^\ddagger$ [J/(mol·K)]	$k_{21} \cdot 10^{-8}$ [s <sup>-1</sup> ]	$\Delta G_{21}^\ddagger$ [kJ/mol]	$\Delta H_{21}^\ddagger$ [kJ/mol]	$\Delta S_{21}^\ddagger$ [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  $\alpha$ -CD. For  $\beta$ -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  $\alpha$ -CD and  $\beta$ -CD solutions can be connected with the dimensions of the cavity, which are greater for  $\beta$ -CD than for  $\alpha$ -CD. This means less steric hindrances when the alkyl chain penetrates the  $\beta$ -CD's cavity than the  $\alpha$ -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,  $\alpha/f^2$ , of aqueous solutions of  $\beta$ -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  $\alpha$ -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 hydration 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  $\alpha$ -CD and  $\beta$ -CD solutions with alkyl pyridinium bromides can be connected with the dimensions of their cavities.

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