

**ULTRASONIC INVESTIGATIONS OF AQUEOUS SOLUTIONS
OF α -CYCLODEXTRIN AND AMPHIPHIL SUBSTANCES
HAVING DIFFERENT HEADS AND IDENTIC TAILS**

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Velocity and absorption of ultrasonic waves in aqueous solutions of α -cyclodextrin containing amphiphil substances with different “heads” and identic “tails” were carried out. As a result of the mutual interactions between α -cyclodextrin and the amphiphil substance the low frequency ultrasonic relaxation process has been established. Thermodynamic and kinetic parameters related to this process have been calculated. Obtained results have been discussed considering molecular structure of the amphiphil substances.

1. Introduction

α -Cyclodextrin (α CD) (as other cyclodextrins) has a unique spatial configuration forming a torus shaped molecular structure with a hydrophilic exterior and a hydrophobic interior. This macromolecular compound is able to form inclusion complexes without covalent bonds by capturing a number of other compounds into its molecular cavity; among others — amphiphil substances [1–5].

Molecule of the amphiphil substance has two moieties: hydrophobic and hydrophilic. It is known that α CD strongly interacts with the hydrophobic part of the included molecule [4–22]. It would be interesting to investigate an influence of hydrophilic part of that molecule on the complexation process.

2. Experimental part

Measurements of the absorption coefficient, α/f^2 , in aqueous solutions of α -CD (Aldrich) with sodium decanesulfonate $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{SO}_3\text{Na}$ (Aldrich), sodium decyl sulfate $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OSO}_3\text{Na}$ (Aldrich), decyltrimethylammonium bromide $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{N}(\text{CH}_3)_3\text{Br}$ (Fluka), decylpyridinium bromide $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{C}_5\text{H}_4\text{NBr}$

(Fluka) and decyl β -D-glucopyranoside $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OC}_6\text{H}_11\text{O}_5$ (Sigma) 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, e.g. α -CD and amphiphil substance.

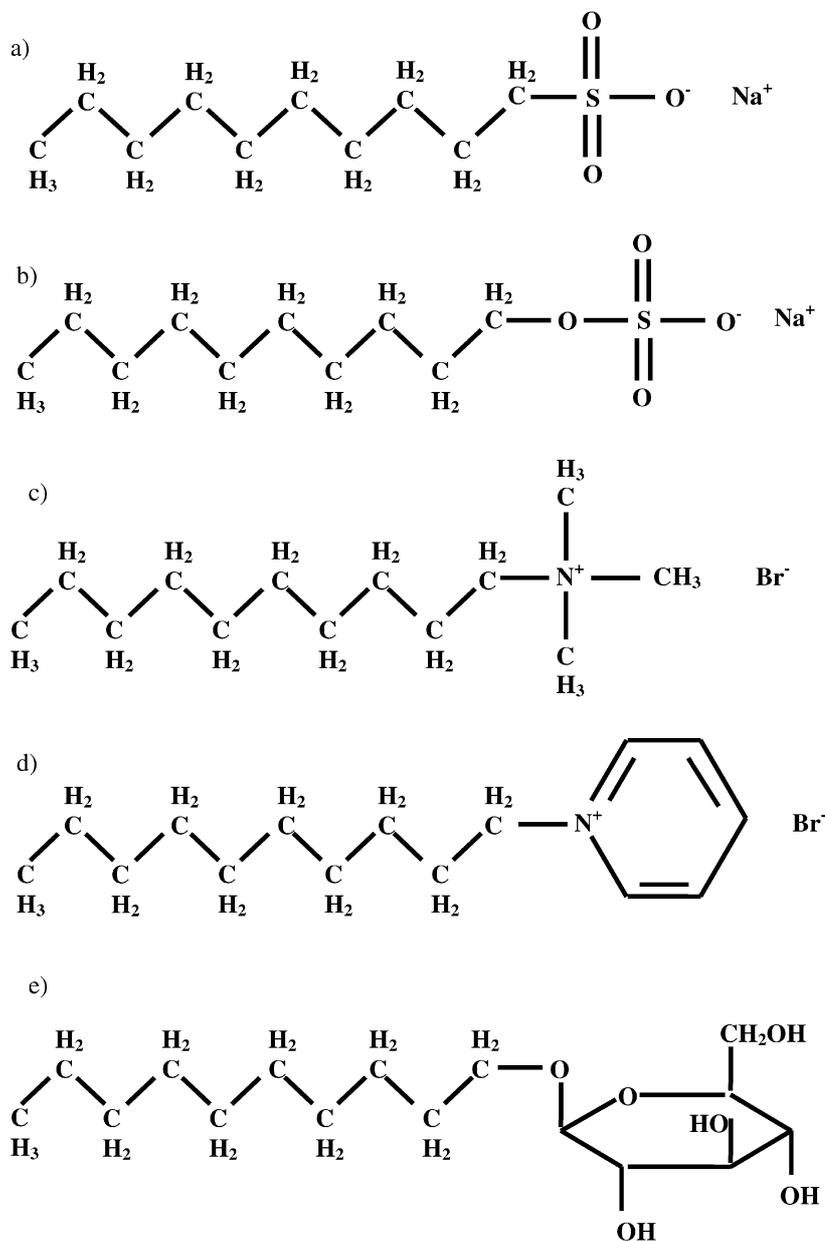


Fig. 1. Schemes of the molecules of investigated amphiphil substances: a) sodium decanesulfonate, b) sodium decyl sulfate, c) decyltrimethylammonium bromide, d) decylpyridinium bromide, e) decyl β -D-glucopyranoside.

At 25°C the measurements were also made for 0.01, 0.02 and 0.03 M equimolar aqueous solutions of both components. For all used amphiphil substances the hydrophobic moieties are identical i.e. decyl hydrocarbon chain. In aqueous solution the molecules of these substances have anionic (sulfonate and sulfate), cationic (trimethylammonium and pyridinium) and neutral (glucopyranoside) "heads". The schemes of these molecules are presented in Fig. 1.

The measurements were made by means of the resonator [23–25] and pulse [26, 27] methods in the frequency range 1–10 MHz and 10–150 MHz, respectively. The measurements errors were about 5% for the former method and below 1% for the latter one.

The additional measurements of the speed of sound and the density for these solutions were also made. They are needed for further calculations. The speed of sound was measured applying the resonator method [23–25] 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 [28]

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

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

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 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, 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 ($l = 1$ or 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

Representative plots of the dependence of the excess sound absorption per wavelength, μ , on frequency, f , for all investigated systems at 25°C are shown in Figs. 2–6.

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

The values of the B parameter are slightly greater than 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 special relaxation processes which could be connected with the presence of α -CD and the amphiphil substance in the aqueous solution.

For these solutions, a linear dependence of μ_{mi} on concentration C as well as an independence of f_{ri} with the concentration were found within the limits of the experimental error ($\cong \pm 5\%$).

Table 1. Relaxation parameters for aqueous solution of α -cyclodextrin with amphiphil substances at different temperatures and concentrations.

t [°C]	C [M]	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]
sodium decanesulfonate								
15	0.04	23.5	16.8	293	3.0	25.1	55.8	31.5
25	0.04	25.3	13.5	258	3.9	21.4	63.2	24.7
35	0.04	26.7	11.4	233	5.0	15.7	66.2	18.0
45	0.04	28.4	9.40	207	6.0	15.6	72.4	14.4
25	0.03	26.1	9.45	186	4.1	14.1	43.5	24.2
25	0.02	24.9	4.86	91.0	3.8	12.1	34.5	23.4
25	0.01	25.0	3.59	67.3	3.9	6.15	18.0	23.1
sodium decyl sulfate								
15	0.04	24.7	16.0	293	5.4	19.6	78.3	31.7
25	0.04	25.8	13.5	263	6.3	18.0	85.6	24.6
35	0.04	28.1	11.2	240	8.8	14.4	96.8	18.1
45	0.04	29.9	8.85	205	9.9	13.8	106	14.3
25	0.03	25.7	10.6	206	5.9	16.1	71.5	24.0
25	0.02	24.8	6.45	120	6.1	8.39	38.4	23.3
25	0.01	24.5	3.85	70.7	6.0	4.32	20.1	23.2
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
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
decyl β -D-glucopyranoside								
15	0.04	26.8	12.0	238	2.9	25.2	54.2	31.4
25	0.04	28.2	9.85	210	3.7	20.8	58.2	24.4
35	0.04	29.8	8.15	186	4.6	17.7	62.5	17.9
45	0.04	31.7	6.92	170	5.9	15.2	69.7	14.2
25	0.03	28.5	6.93	149	3.6	14.7	39.9	23.9
25	0.02	28.1	5.20	110	3.8	9.38	26.8	23.5
25	0.01	29.2	2.27	49.7	3.8	5.47	15.6	22.9

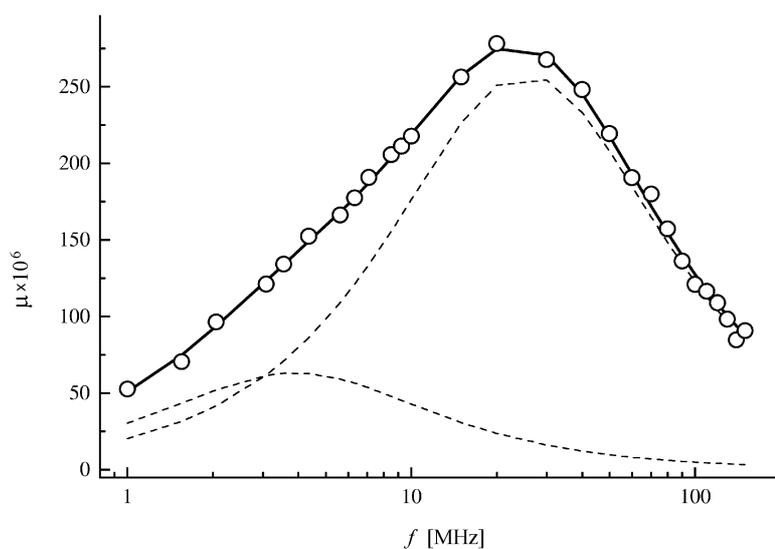


Fig. 2. Plot of the excess sound absorption per wavelength, μ , vs. frequency, f , for the aqueous solution of α -CD and sodium decanesulfonate. Temperature 25°C, concentration 0.04 M. Circles — experimental values, dashed lines — μ_1 and μ_2 , solid line — μ .

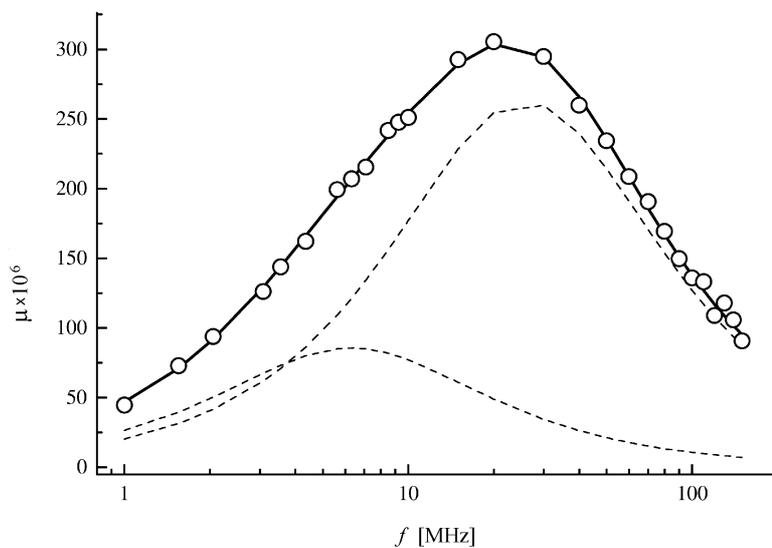


Fig. 3. Plot of the excess sound absorption per wavelength, μ , vs. frequency, f , for the aqueous solution of α -CD and sodium decyl sulfate. Temperature 25°C, concentration 0.04 M. Circles — experimental values, dashed lines — μ_1 and μ_2 , solid line — μ .

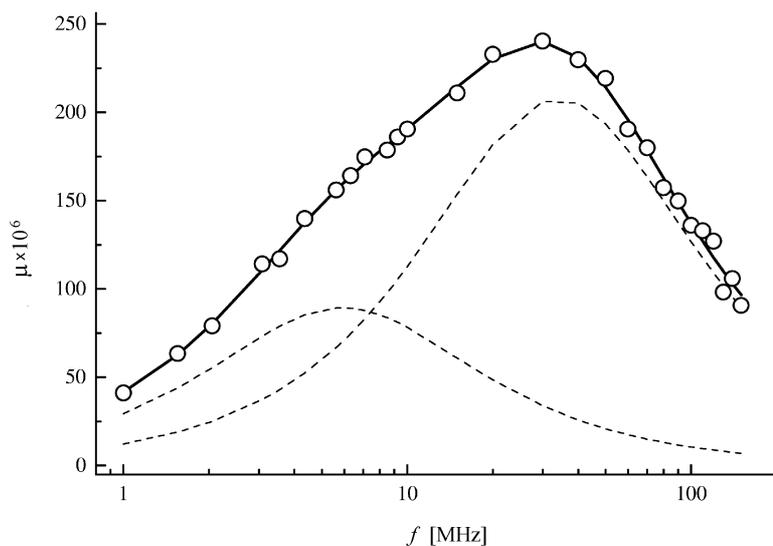


Fig. 4. Plot of the excess sound absorption per wavelength, μ , vs. frequency, f , for the aqueous solution of α -CD and decyltrimethylammonium bromide. Temperature 25°C, concentration 0.04 M. Circles — experimental values, dashed lines — μ_1 and μ_2 , solid line — μ .

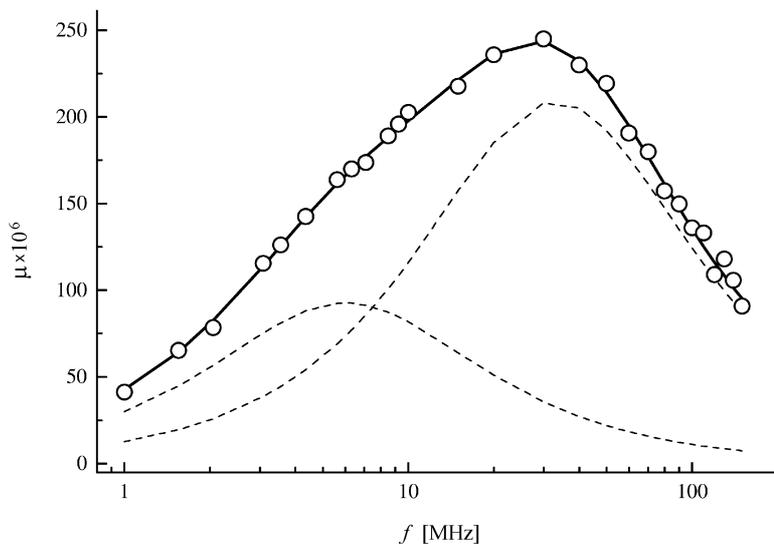


Fig. 5. Plot of the excess sound absorption per wavelength, μ , vs. frequency, f , for the aqueous solution of α -CD and decylpyridinium bromide. Temperature 25°C, concentration 0.04 M. Circles — experimental values, dashed lines — μ_1 and μ_2 , solid line — μ .

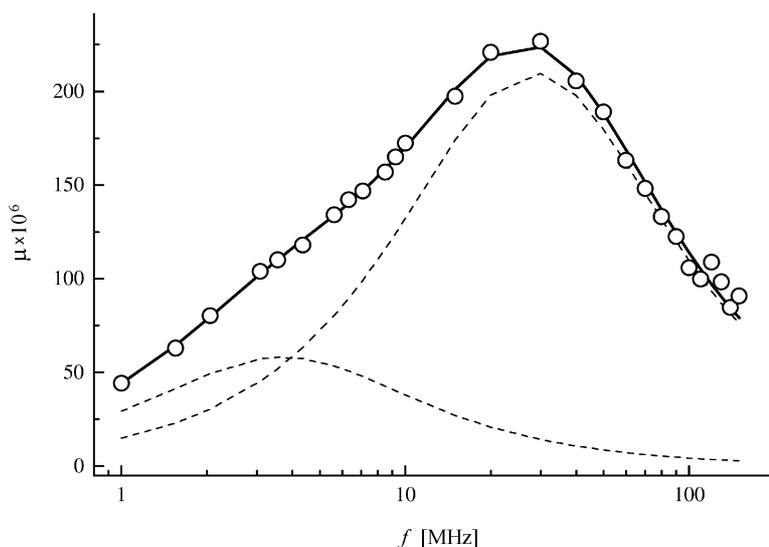


Fig. 6. Plot of the excess sound absorption per wavelength, μ , vs. frequency, f , for the aqueous solution of α -CD and decyl β -D-glucopyranoside. Temperature 25°C, concentration 0.04 M. Circles — experimental values, dashed lines — μ_1 and μ_2 , solid line — μ .

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



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 [28–30].

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) ($K = k_{12}/k_{21}$), ΔS_{21}^\ddagger and ΔH_{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 ΔH^0 ,

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

is applied.

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

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

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 equation (8) is a straight line with the slope

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

and the intercept

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

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

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

where the values of a_f , a_μ and ΔS_{21}^\ddagger can be determined from the ultrasonic measurements.

Thus, from the Eqs.: (6), (11), (9), (5) and (4), the values of ΔS_{21}^\ddagger , K , ΔH^0 , ΔH_{21}^\ddagger and k_{21} can be calculated. Subsequently, the values of other kinetic and thermodynamic parameters can be established according to the formulas:

a_f [K ⁻¹]	b_f	a_μ [K ⁻¹]	b_μ	$(\mu_m/C) \cdot 10^6$ [m ³ /mol]	K	ΔG^0 [kJ/mol]	ΔH^0 [kJ/mol]	ΔS^0 [J/(mol·K)]	
sodium decanesulfonate									
-1874	15.75	-825.8	-22.78	1.57	18.0	-7.17	-7.67	-1.70	
sodium decyl sulfate									
-1706	15.73	-1007	-21.83	2.18	30.2	-8.45	-8.95	-1.68	
decyltrimethylenammonium bromide									
-1626	15.33	-913.7	-22.10	2.21	23.8	-7.86	-8.62	-1.36	
decylpyridinium bromide									
-1617	15.33	-924.7	-22.04	2.31	24.4	-7.92	-8.35	-1.43	
n-decyl-β-d-glucopyranoside									
-1840	15.60	-812.4	-22.87	1.41	17.0	-7.02	-7.60	-1.93	

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

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

Table 2. Kinetic and thermodynamic parameters of the low-frequency relaxation process for aqueous solutions α -cyclodextrin with amphiphil substances at 25°C.

$k_{12} \cdot 10^{-7}$ [s ⁻¹]	ΔG_{12}^\ddagger [kJ/mol]	ΔH_{12}^\ddagger [kJ/mol]	ΔS_{12}^\ddagger [J/(mol·K)]	$k_{21} \cdot 10^{-5}$ [s ⁻¹]	ΔG_{21}^\ddagger [kJ/mol]	ΔH_{21}^\ddagger [kJ/mol]	ΔS_{21}^\ddagger [J/(mol·K)]	$ \Delta V_S $ [cm ³ /mol]
sodium decanesulfonate								
2.32	30.5	15.2	-53.0	12.9	38.1	22.9	-51.3	4.6
sodium decyl sulfate								
3.83	29.8	13.8	-53.2	12.7	38.2	22.8	-51.5	6.9
decyltrimethylenammonium bromide								
3.56	29.9	13.2	-56.1	15.0	37.8	21.4	-54.8	6.3
decylpyridinium bromide								
3.62	29.9	13.1	-56.2	14.8	37.8	21.5	-54.8	6.5
n-decyl- β -d-glucopyranoside								
2.20	31.1	14.9	-54.5	12.9	38.1	22.5	-52.5	4.3

The thermodynamic and kinetic parameters of the low-frequency processes are presented in Table 2.

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 [31–33] and was described in details previously [34].

As formerly [34] the low-frequency relaxation process is caused by the penetration of the hydrophobic alkyl chain of the amphiphil substance into the cavity of α -CD.

One can notice that most values of the kinetic and thermodynamic parameters presented in Table 2 are similar for different amphiphil substances. This observation leads to general conclusion that influence of the “head” of the amphiphil substance on the process of the penetration of the alkyl chain into the cyclodextrin cavity is diminutive. As we noticed in [34–36] the values of the kinetic and thermodynamic parameters of this process mainly depend on the length of alkyl chain.

However, in the case of sodium decyl sulfate values of the equilibrium constant K , the rate constant k_{12} and modulus of the molar volume change $|\Delta V_S|$ are the largest ones. On the other hand, the rate constants of the opposite reaction k_{21} is the lowest one. These facts mean deeper penetration of alkyl chain into cyclodextrin cavity and more stable inclusion complex, which are caused by bigger hydrophobicity of the alkyl chain joined with an oxygen atom from the sulfate group than for the chain without that atom [4].

For the system with decyl β -D-glucopyranoside values of the equilibrium constant K , the rate constant k_{12} and modulus of the molar volume change $|\Delta V_S|$ are the lowest ones. These observations reflect shallower penetration of the alkyl chain into the cyclodextrin cavity caused by substantial steric hindrances produced by the biggest “head” from these ones which have been investigated.

4. Conclusions

The aqueous solutions of α -CD with sodium decanesulfonate, sodium decyl sulfate, decyltrimethylammonium bromide, decylpyridinium bromide and decyl β -D-glucopyranoside were investigated by means of the modulus of the molar volume change by ultrasonic spectroscopy. For all of them the high-frequency ultrasonic relaxation process has been found out. Its origin is connected with the exchange of water molecules in the hydration shell of CD.

The low frequency relaxation process has been established. This process results from the penetration of decyl hydrocarbon chains into the CD cavity.

Thermodynamic and kinetic parameters for the low relaxation processes have been calculated. Obtained results have been discussed in consideration of molecular structures of investigated amphiphil substances.

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