ARCHIVES OF ACOUSTICS
18, 3, 447–455 (1993)

ULTRASONIC INVESTIGATIONS OF INCLUSION COMPLEXES OF α-CYCLODEXTRIN WITH AMPHIPHIL SUBSTANCES

A. JUSZKIEWICZ

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

A. BALCERZAK

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

Velocity and attenuation measurements of ultrasonic waves in water solutions of α-cyclodextrin containing different amphiphil substances: sodium octyl sulfate (SOS0), sodium decyl sulfate (SDeS), decylpyridinium bromide (DePyB) and sodium caprinate (SCp) were made. The occurrence of an ultrasonic relaxation process connected with the formation of inclusion complexes of α-cyclodextrin with SDeS, DePyB, SCp was established.

1. Introduction

The inclusion complexes are complexes of different substances with macrocyclic ligands. Both ionic and non-ionic substances, which are fitted to the cavity of a macrocyclic organic compound, may be included. Investigations of the inclusion complex give basic information about non-covalence molecular interactions, which are especially important in biological systems. The inclusion complexes with macrocyclic ligands are used among others as models of enzymes and biocatalysts.

The ultrasonic investigations of the inclusion complexes aim at the study of the mechanism of the complexation through the investigations of kinetics and thermodynamics of this process [1]. It enables to determine selective properties of ions and included molecules as well as the ligands forming those complexes.

In literature, one can find only ultrasonic investigations of inclusion complexes of the crown ethers: 15C5 and 18C6 with the cations: Li^+, Na^+, K^+, NH_4^+, Ag^+, Sr^{++}, Ba^{++}, Pb^{++}, Hg^{++} in different solvents like water, ethanol, dimethylformamide, methanol, dimethoxyethane and others [2–9].

In this article the first results of ultrasonic investigations of the inclusion complexes of α-cyclodextrin (α-CD) with amphiphil substances: sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS), decylpyridinium bromide (DePyB) and sodium caprinate (SCp) are presented.

2. Experimental part

The ultrasonic velocity and the attenuation coefficient α/f^2 measurements in the water solutions of the α-cyclodextrin with the following detergents: sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS), decylpyridinium bromide (DePyB) and sodium caprinate (SCp) were made in the range of frequency 1–150 MHz at temperature 25°C. The concentration of each component of the solutions was equal to 0.04 M. The measurements for 0.04 M solution of cyclodextrin were also made.

The measurements were made by means of the resonator [10–12] and pulse [1, 13] methods in the frequency range 1–10 MHz and 10–150 MHz, respectively. The measurement errors were about 5% for the former method and below 1% for the latter one. The detailed description of equipment used for the resonator method is presented in [11, 12]. For the pulse method we used a sin wave generator combined with a pulse generator and a modulator as a source of the electrical pulse signal. This signal supplied an ultrasonic wide-band probe emitting ultrasonic waves into a tested liquid. The second probe converted received acoustic waves into the electrical signal that was measured on an oscilloscope. The second probe was joined with an arm of cathetometer for accurate measurements of distance between the probes.

Results of the measurements are presented graphically in Figs. 1–10. Theoretical curves are fitted to the experimental results by means of computer calculation programs. These curves present the known theoretical equations as follows:

$$\frac{\alpha}{f^2} = B + \sum_{i=1}^{n} \frac{A_i}{1+(f/fr_i)^2} \tag{1}$$

$$\mu = 2\sum_{i=1}^{n} \mu_{\max_i} \frac{f/fr_i}{1+(f/fr_i)^2} \tag{2}$$

where α is the ultrasonic attenuation, f the measured frequency, fr_i the relaxation frequency, A_i the relaxation amplitude, B the contribution to sound attenuation from any other processes that may be occurring at higher frequencies beyond our frequency range. $\mu = (\alpha - Bf^2)\,\lambda$ represents the excess attenuation per wavelength λ ($\lambda = c/f$, c is the ultrasonic velocity), $\mu_{\max_i}$ the maximum excess attenuation per wavelength. n is the number of relaxation processes.

3. Discussion of results and conclusions

As one can see in Fig. 1 and 2, changes of the attenuation coefficients, α/f^2 and μ, with frequency indicate the occurrence of one relaxation process ($n=1$) with a relaxation frequency of 16.7 MHz in the water solution of α-CD. Especially in Fig. 2,

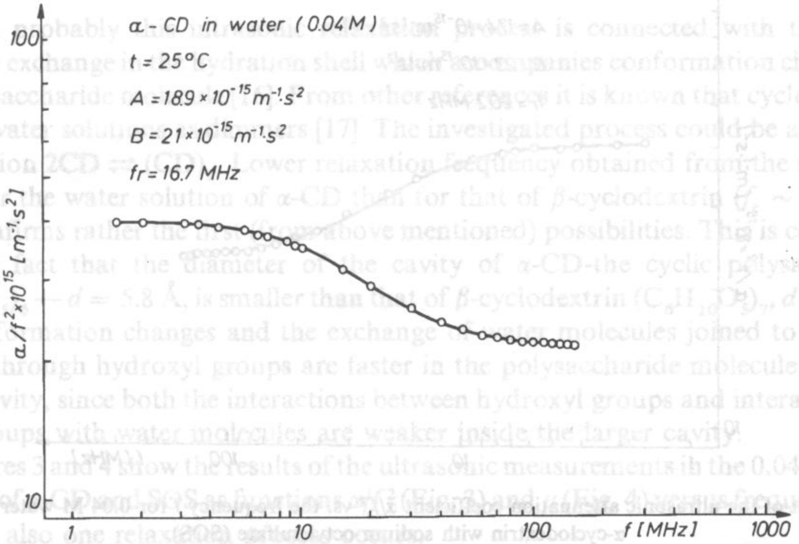

Fig. 1. Plot of the ultrasonic attenuation coefficient α/f^2 vs. the frequency f for 0.04 M water solution of α-cyclodextrin.

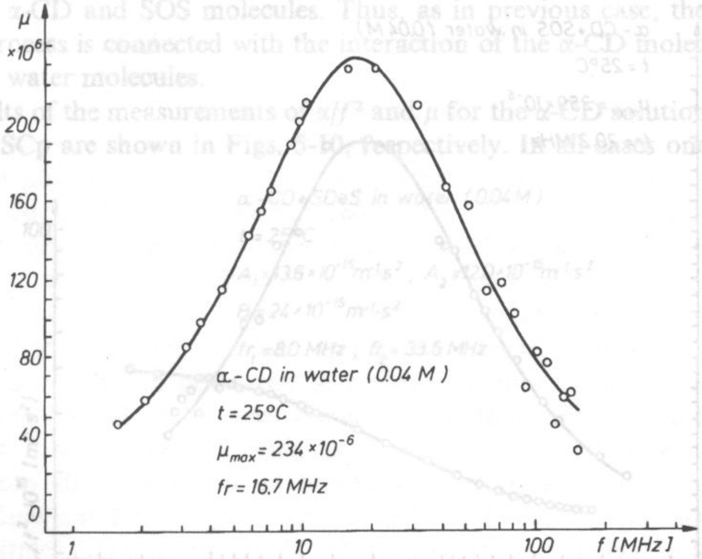

Fig. 2. Plot of the excess ultrasonic attenuation per wavelength μ vs. the frequency f for 0.04 M water solution of α-cyclodextrin.

one can see that because the coefficient μ as a function of frequency f has a regular, gaussian shape typical of single relaxation processes [14, 15]. This result is inconsistent with the data published in ref. [16], in which the occurrence of two relaxation processes was suggested.

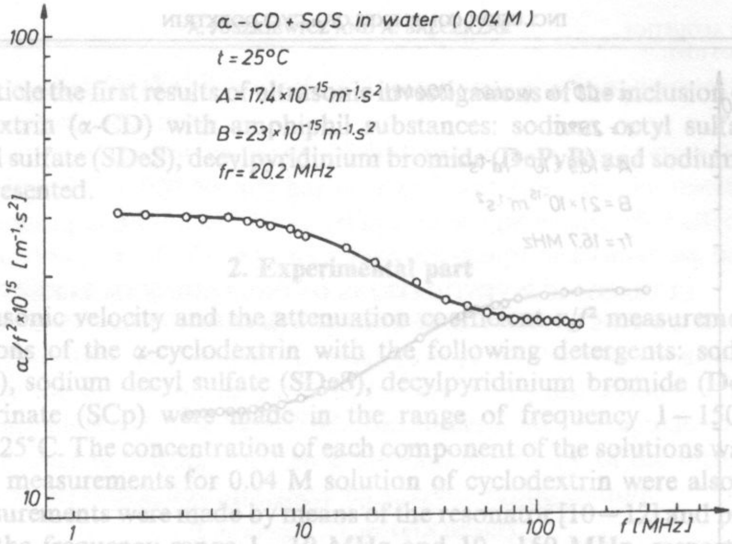

Fig. 3. Plot of the ultrasonic attenuation coefficient α/f^2 vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium octyl sulfate (SOS).

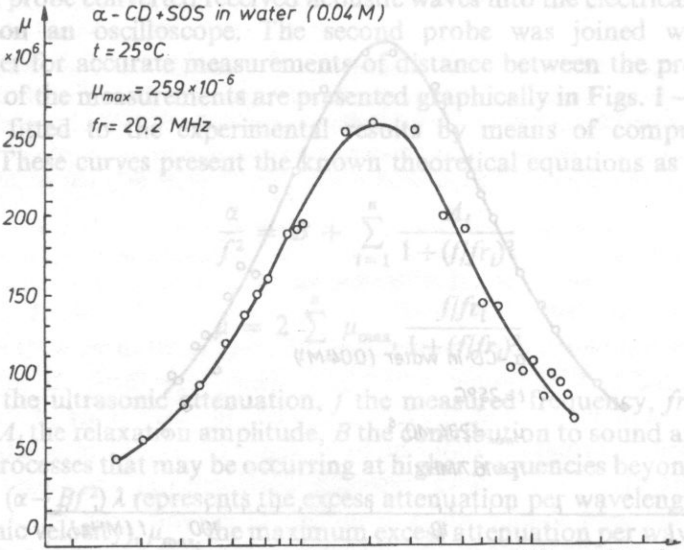

Fig. 4. Plot of the excess ultrasonic attenuation per wavelength μ vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium octyl sulfate (SOS).

Most probably this ultrasonic relaxation process is connected with the water molecule exchange in the hydration shell which accompanies conformation changes of the polysaccharide molecule [16]. From other references it is known that cyclodextrins exist in water solutions as dimmers [17]. The investigated process could be a result of the reaction $2CD \rightleftharpoons (CD)_2$. Lower relaxation frequency obtained from the measurements for the water solution of α-CD than for that of β-cyclodextrin ($f_r \sim 20$ MHz [18]), confirms rather the first (from above mentioned) possibilities. This is connected with the fact that the diameter of the cavity of α-CD-the cyclic polysaccharide $(C_6H_{10}O_5)_6$—$d = 5.8$ Å, is smaller than that of β-cyclodextrin $(C_6H_{10}O_5)_7$, $d = 7.8$ Å. The conformation changes and the exchange of water molecules joined to polysaccharide through hydroxyl groups are faster in the polysaccharide molecule with the grater cavity, since both the interactions between hydroxyl groups and interactions of these groups with water molecules are weaker inside the larger cavity.

Figures 3 and 4 show the results of the ultrasonic measurements in the 0.04 M water solution of α-CD and SOS as functions α/f^2 (Fig. 3) and μ (Fig. 4) versus frequency f. In this case also one relaxation process occurs.

The numerical values of α/f^2, μ, f_r and A for this solution are approximately equal to those for the α-CD solution. Thus the addition of SOS to the α-CD solution does not cause an essential change in the ultrasonic attenuation and, this suggests no interaction between the α-CD and SOS molecules. Thus, as in previous case, the investigated relaxation process is connected with the interaction of the α-CD molecules with the surrounding water molecules.

The results of the measurements of α/f^2 and μ for the α-CD solutions with SDeS, DePyB and SCp are shown in Figs. 5-10, respectively. In all cases one can observe

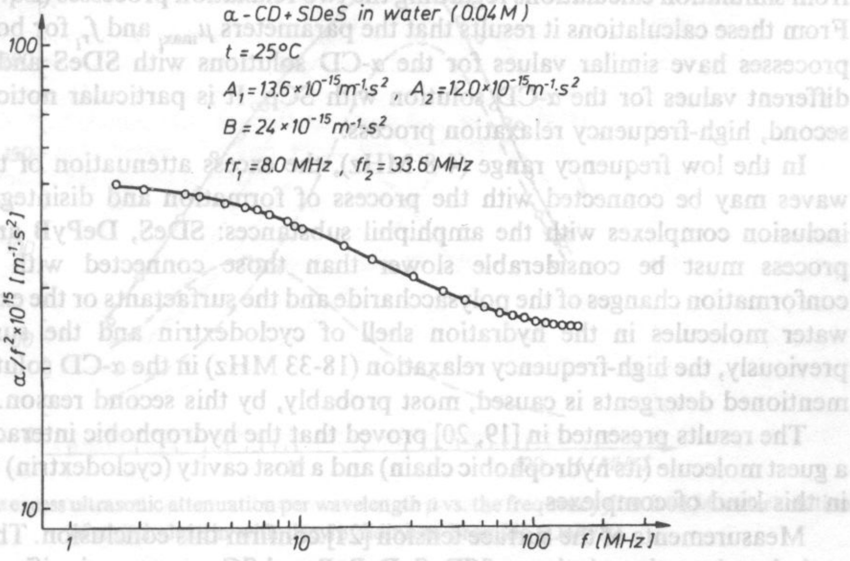

Fig. 5. Plot of the ultrasonic attenuation coefficient α/f^2 vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium decyl sulfate (SDeS).

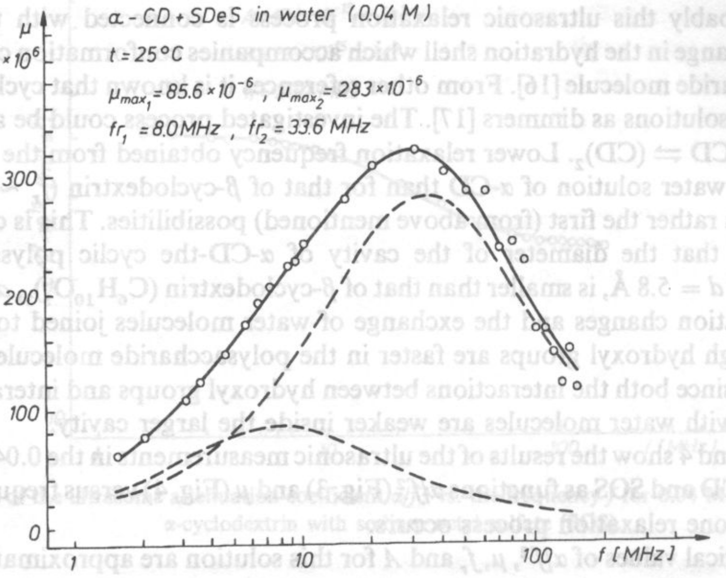

Fig. 6. Plot of the excess ultrasonic attenuation per wavelength μ vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium decyl sulfate (SDeS).

a considerable increase of the attenuation coefficients, α/f^2 and μ, and the widened region of the dependence of μ on frequency in comparison to the α-CD and α-CD+SOS solutions. These differences indicate at least two relaxation processes ($n=2$). In Figs. 6, 8 and 10 dashed lines mark the function μ versus frequency obtained from simulation calculations regarding the two relaxation processes (Eq. (2) for $n=2$). From these calculations it results that the parameters $\mu_{\max_i}$ and f_{r_i} for both relaxation processes have similar values for the α-CD solutions with SDeS and DePyB and different values for the α-CD solution with SCp. It is particular noticeable for the second, high-frequency relaxation process.

In the low frequency range (4-8 MHz), the excess attenuation of the ultrasonic waves may be connected with the process of formation and disintegration of the inclusion complexes with the amphiphil substances: SDeS, DePyB and SCp. This process must be considerable slower than those connected with the possible conformation changes of the polysaccharide and the surfactants or the exchange of the water molecules in the hydration shell of cyclodextrin and the surfactants. As previously, the high-frequency relaxation (18-33 MHz) in the α-CD solutions with the mentioned detergents is caused, most probably, by this second reason.

The results presented in [19, 20] proved that the hydrophobic interaction between a guest molecule (its hydrophobic chain) and a host cavity (cyclodextrin) are dominant in this kind of complexes.

Measurements of the surface tension [21] confirm this conclusion. The addition of cyclodextrin to the solutions of SDeS, DePyB and SCp causes a significant increase of the surface tension. That must be connected with blocking of the hydrophobic chains

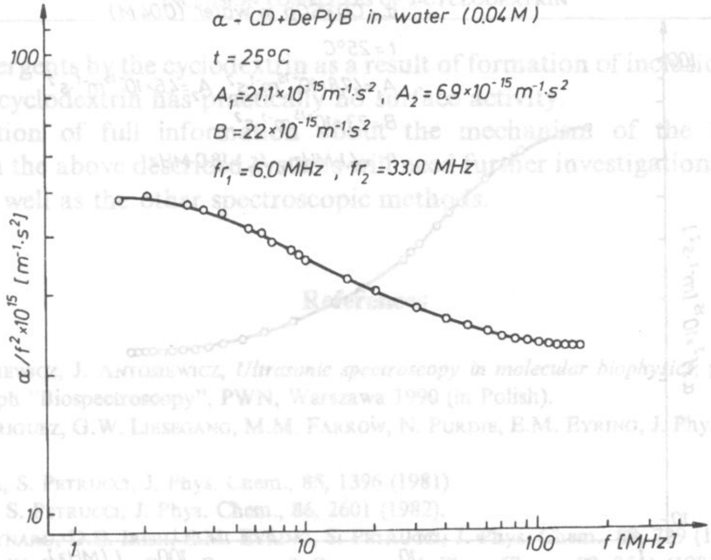

Fig. 7. Plot of the ultrasonic attenuation coefficient α/f^2 vs. the frequency f for 0.04 M water solution of α-cyclodextrin with decylpyridinium bromide (DePyB).

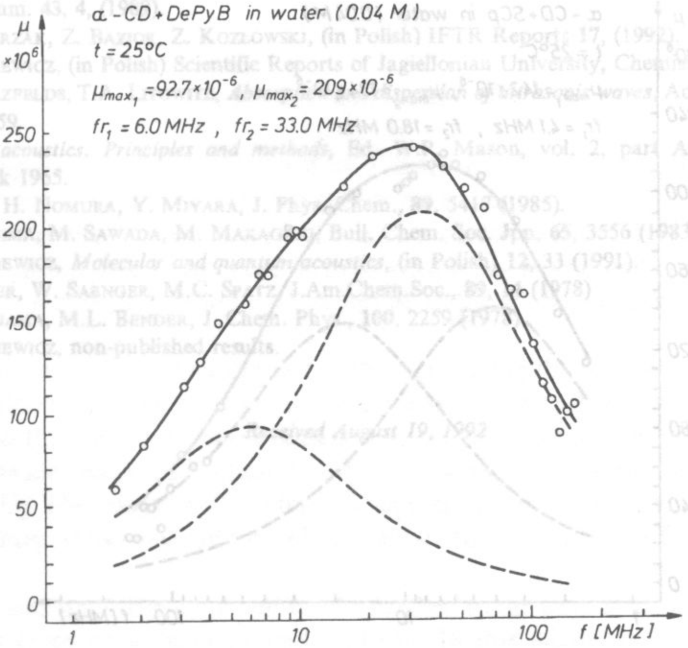

Fig. 8. Plot of the excess ultrasonic attenuation per wavelength μ vs. the frequency f for 0.04 M water solution of α-cyclodextrin with decylpyridinium bromide (DePyB).

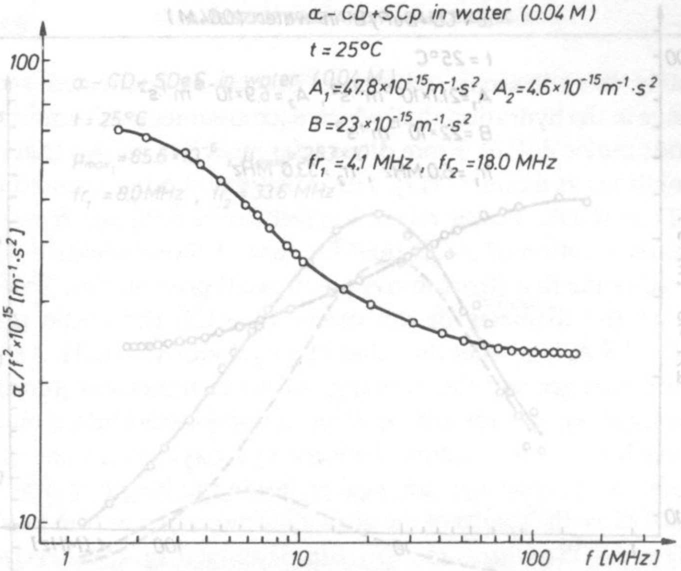

Fig. 9. Plot of the ultrasonic attenuation coefficient α/f^2 vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium caprinate (SCp).

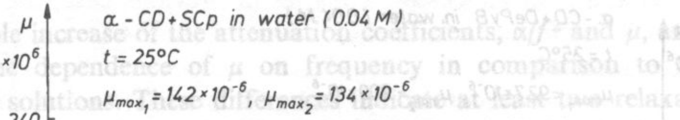

Fig. 10. Plot of the excess ultrasonic attenuation per wavelength μ vs. the frequency f for 0.04 M water solution of α-cyclodextrin with sodium caprinate (SCp).

of these detergents by the cyclodextrin as a result of formation of inclusion complexes, since mere cyclodextrin has practically no surface activity.

Acquisition of full information about the mechanism of the complexation processes in the above described systems will need further investigations by mens the acoustic as well as the other spectroscopic methods.

References

[1] A. Juszkiewicz, J. Antosiewicz, *Ultrasonic spectroscopy in molecular biophysics*, part II, vol. 5 in monograph "Biospectroscopy", PWN, Warszawa 1990 (in Polish).

[2] L.J. Rodriguez, G.W. Liesegang, M.M. Farrow, N. Purdie, E.M. Eyring, J. Phys. Chem., **82**, 647 (1978).

[3] H. Faber, S. Petrucci, J. Phys. Chem., **85**, 1396 (1981)

[4] C. Chen, S. Petrucci, J. Phys. Chem., **86**, 2601 (1982).

[5] K.J. Maynard, D.E. Irish, E.M. Eyring, S. Petrucci, J. Phys. Chem., **88**, 729 (1984).

[6] C. Chen, W. Wallace, E.M. Eyring, S. Petrucci, J. Phys. Chem., **88**, 2541 (1984).

[7] C. Chen, W. Wallace, E.M. Eyring, S. Petrucci, J. Phys. Chem., **88**, 5445 (1984).

[8] W. Wallace, E.M. Eyring, S. Petrucci, J. Phys. Chem., **88**, 6353 (1984).

[9] H. Farber, S. Petrucci, J. Phys. Chem., **85**, 2987 (1981).

[10] F. Eggers, F. Funck, K.H. Richmann, H. Schneider, E.M. Eyring, J. Phys. Chem., **91**, 1961 (1987).

[11] G. Galiński, Z. Kozłowski, *Ultrasonic spectroscopy equipment for the 0.5 – 15 MHz frequency ragne*, Sci. Instrum. **43**, 4, (1989).

[12] A. Balcerzak, Z. Bazior, Z. Kozłowski, (in Polish) IFTR Reports **17**, (1992).

[13] A. Juszkiewicz, (in Polish) Scientific Reports of Jagiellonian University, Chemistry, **19**, 109 (1974).

[14] K.F. Herzfelds, T.A. Litowitz, *Absorption and dispersion of ultrasonic waves*, Academic Press, New York, 1959.

[15] *Physical acoustics. Principles and methods*, Ed. W.P. Mason, vol. 2, part A. Academic Press, New York 1965.

[16] S. Kato, H. Nomura, Y. Miyara, J. Phys. Chem., **89**, 5417 (1985).

[17] K. Miyajima, M. Sawada, M. Makagaki, Bull. Chem. Soc. Jpn, **65**, 3556 (1983).

[18] A. Juszkiewicz, *Molecular and quantum acoustics*, (in Polish) **12**, 33 (1991).

[19] F. Cramer, W. Saenger, M.C. Spatz, J.Am.Chem.Soc., **89**, 14 (1978)

[20] M. Komijama, M.L. Bender, J. Chem. Phys., **100**, 2259 (1978).

[21] A. Juszkiewicz, non-published results.

Received August 19, 1992