Positron annihilation and speed of sound in the systems containing β-cyclodextrin

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Abstract. Positron annihilation measurements were performed in aqueous solutions of β-cyclodextrin, as well as in solid mixtures of this sugar with a long-chained alcohol, *n*-nonanol. Additionally, acoustic (sound speed, density and compressibility) experiments were done in aqueous β-cyclodextrin and *tert*-butanol systems and in a three-component water-β-cyclodextrin-*tert*-butanol system. The results show that in aqueous solution cyclodextrin does not form inclusive complexes with alcohol, while solid sugar-alcohol mixtures undergo slow changes in time, most probably caused by exchange of guest between interior and exterior of the host molecule.

Key words: sound speed • compressibility • positron annihilation • cyclodextrin • alcohol • inclusion compounds

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Introduction

β-Cyclodextrin molecule, similar to other sugars of this kind, has a unique spatial architecture: a torus shaped with a hydrophilic external part and more hydrophobic interior. So, this macromolecule forms easily adducts to create the so-called inclusion complexes, where no covalent bonds exist, but the molecular cavity captures other molecules: amphiphiles [1], surfactants [5], iodine [13] etc. This phenomenon finds wide application, among others in pharmaceutical and food industries [3].

It is not clear, however, how stable are such adducts in aqueous solutions, because of competition of water molecules forming structured hydrates. Also stability in time of solid inclusion compounds is not investigated so far. Finally, the positron annihilation techniques has been rarely applied to such systems so far. So, the aim of this work is to throw light on these subjects.

In this work, preliminary results of positron annihilation experiment on the systems containing β-cyclodextrin are presented, applied both for liquid aqueous solutions and for solid mixtures of this sugar with *n*-nonanol. Their conclusions for aqueous mixtures are also supported by acoustic investigations.

Experimental

β-Cyclodextrin (puriss., Fluka) was stored in an exsiccator over silica gel to avoid adsorption of water. 1-Nonanol

(*n*-nonanol, *n*-nonyl alcohol, pure, Sojuzchimexport, Russia) and *tert*-butanol (2-methyl-2-propanol, pure, Fluka) were used without additional purification. Fresh-prepared, doubly-distilled water was used as the solvent. All mixtures were prepared by weighting. Solid samples were prepared by mixing weighed components, β-cyclodextrin and *n*-nonanol, in molar proportions 0:1, 1:1, 1:2 and 2:1 (alcohol:cyclodextrin), grinding them in a mortar and storing in a firmly closed glass container. Before annihilation experiment, the powder sample was pressed to pellets, the pressure applied was ca. 2000 kg/cm². It should be noted that such pressure extrudes some amount of alcohol. So, the final proportions of components can be different than the initial ones.

Speed of sound was determined using a computer--steered OPKUD 01/100 (Optel, Wrocław, Poland) apparatus, with an absolute accuracy better than ± 0.2 m·s⁻¹ and the precision of similar order. Measurements are based on the determination of the time an acoustic signal needs to pass through the sample of known length.

The density was measured using a vibrating tube Ecolab MG-2 (Kraków, Poland) apparatus with an accuracy of ca. ± 0.1 kg·m⁻³.

Temperature of the measurements was 25°C ± 0.05, stabilized by a precision MLW UH (Germany) thermostat. Its stability was controlled by a digital thermometer built in the density apparatus, and the absolute value by a precision mercury thermometer.

From the speed of sound and density data, the adiabatic compressibility coefficients, κ_S, were calculated, using the Laplace equation:

$$(1) \qquad \kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{d \cdot u^2}$$

where: V – volume; P – pressure; d – density; u – speed of sound, the index S denotes adiabatic condition.

Positron annihilation experiments were carried out at room temperature (ca. 25°C) using a standard device based on the "fast-slow" coincidence technique described elsewhere [10]. The obtained spectra were resolved into three components, characterized by their lifetimes τ_1, τ_2 and τ_3 and intensities I_1, I_2 and I_3 using POSITRONFIT program, subjected to restriction $I_1 + I_2 + I_3 = 100\%$.

Results and discussion

Acoustic experiment

The sound speed and related compressibility coefficient are parameters very well related to the microscopic structure of liquid, in particular, any specific interactions occurring between the components of liquid mixture should reflect in them [4, 6]. In this work, this method was applied in the following way.

First, the dependence of sound velocity, density and resulting adiabatic compressibility coefficient on concentration was measured for two-component mixtures of β-cyclodextrin in water up to the molar fraction of the former equal to ca. 0.00027, close to the saturation. The same was done for *tert*-butyl alcohol. Both these dependences are linear, but differ meaningly in their slopes. This is easy to understand because the solutes differ strongly in size and the number of functional
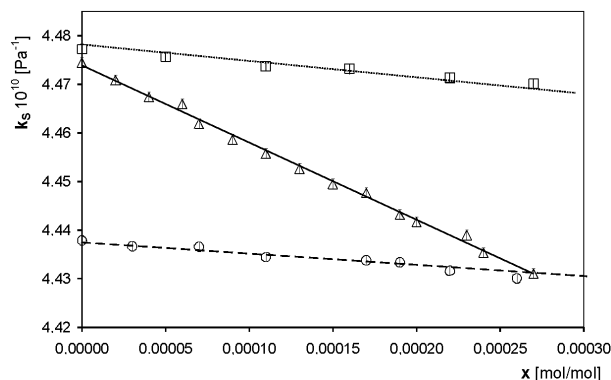

Fig. 1. Adiabatic compressibility coefficient vs. concentration of solutes. Squares – *tert*-butanol in water; triangles – β-cyclodextrin in water; circles – *tert*-butanol in aqueous cyclodextrine solutions ($x_{CD} = 0.00025$).

groups, and consequently in their hydration numbers – the parameter related to the slope of compressibility vs. concentration κ_S [2, 7]. Finally, the third experiment was done, in which the solution of cyclodextrin containing ca. 0.00025 mole fraction of the sugar was used as the solvent and *tert*-butanol was added to it gradually. The results – limited to adiabatic compressibility only – are shown in Fig. 1.

The slopes of dependences corresponding to addition of *tert*-butanol to pure water or to water almost saturated by β-cyclodextrin are identical, at least in the limits of experimental error. This means that *tert*-butanol does not incorporate in the voids of cyclodextrin molecule. The reason is undoubtedly the competition of hydration water: before being inserted in the void the alcohol molecule has to remove its hydration water, the same concerns partially water hydrating sugar in the part close to the void. This is energetically unfavorable, even if it leads to a local increase of entropy (the number of unbounded water molecules increases).

It should be also noted that the solution of β-cyclodextrin in water behaves typically. From the slope in Fig. 1 (triangles), one can calculate the hydration number of this sugar using the Pasynski formula [12]:

$$(2) \qquad n_h = \frac{n_1}{n_2} \cdot \left(1 - \frac{\kappa_S}{\kappa_S^0}\right)$$

where: n_1 and n_2 are the numbers of moles of water and solute in solution, respectively, κ_S is adiabatic compressibility coefficient of the solution and κ_S^0 is that of pure solvent). This quantity for the cyclodextrin under investigation is close to 38.

Positron annihilation experiment

Aqueous solutions of β-cyclodextrin

In Fig. 2 the results for the shortest and the longest components of the annihilation spectrum are plotted vs. composition of liquid mixture.

It seems clear that for aqueous solutions no significant changes of annihilation parameters (lifetimes τ and intensities I of the short- and long-lived components of the annihilation spectrum) were observed. This is easy to explain because the maximum concentration of the organic component is very low, too low to affect the

electron density of the system. On the other hand, the exterior of cyclodextrin molecule is hydrophilic and does not influence the spatial structure of the solvent. This interpretation confirms well the acoustic measurements: the sound speed, density, as well as the adiabatic
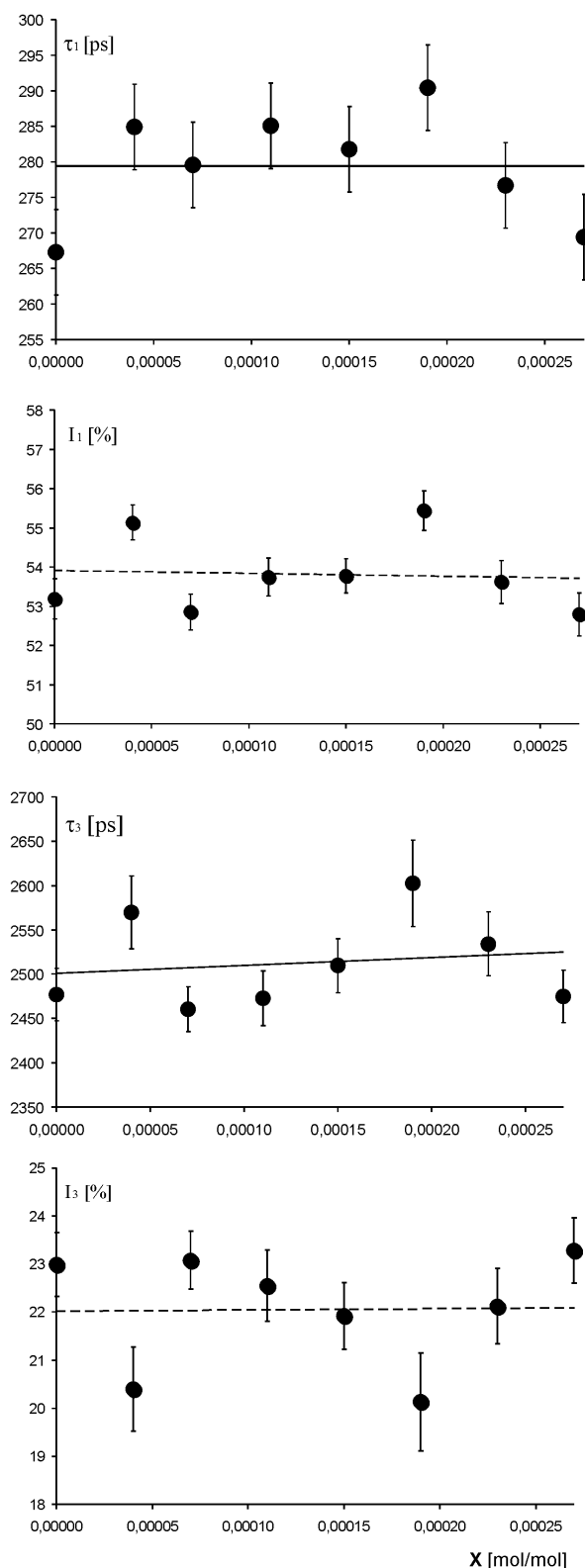

Fig. 2. Positron annihilation parameters vs. concentration of β-cyclodextrin in water (expressed in mole fractions). τ_1, τ_3, I_1, I_3 – lifetimes (the shortest and the longest) and corresponding intensities of the components of annihilation spectrum, respectively.

compressibility changes are linear with sugar content in solution, in the manner suggesting that only the hydration of hydrophilic exterior governs them. Moreover, very low content of cyclodextrin makes it impossible observation of the effect of positronium formed in the hydrophobic cage inside the cyclodextrin ring, which is supposed to be long-living. It should be noted, however, that Hsu *et al.* [8] investigated, in aqueous solutions, formation of complexes of cyclodextrins (α, β and γ) with *m*-nitrophenol and *p*-nitrophenol and found there measurable changes of annihilation parameters, which even allowed to determine the equilibrium constants of formation of these complexes. Our results are not contradicting these of Hsu *et al.*, but the changes are of the range of experimental error and thus cannot be interpreted. Note also that, unfortunately, β-cyclodextrin is that of the lowest solubility in the family, what makes experiments even more difficult.

Solid systems β-cyclodextrin + n-nonanol

The second series of experiments was performed for solid (microcrystalline) β-cyclodextrin, pure and mixed with a long-chained alcohol, namely *n*-nonyl alcohol. This alcohol was chosen for this series of experiment because of its big molar mass and also because of a very long hydrophobic hydrocarbon tail, which is supposed to be easily incorporated into the internal cavity of the sugar molecule. Because of the size of the tail, it could be assumed that *n*-nonanol is captured in the cavities of the host cyclodextrin molecule in the maximum molar ratio close to 1:1. The tested contents of the "guest" were 0, 1 and 2 mole ratio (nonanol to sugar). It was expected that the results of annihilation measurements will be sensitive to the degree of filling of the intramolecular cavities, following the work and development of Hsu, Jang and Jang [9]. The results are collected in Table 1.

Also this part of experiment was successful proving that the positron annihilation method is a useful tool for investigating local, molecular in scale non--homogeneities. Firstly, addition of the long-chained alcohol causes an increase of the lifetime of short--living component. It could be generated in the film of nonanol formed during pressing, but more possible is that it is caused by increased average electron density of the system when alcohol molecules fill empty spaces of the structure. More important is, in our opinion, the rapid decrease of the intensity of the long-living component I_3, which is evidently caused by blocking the empty spaces of the cyclodextrin interior by nonanol, as described above. Such blocking leads to a decrease of empties available for formation of electron-positron pairs and, consequently, to the slight but measurable decrease of I_3 parameter. Similar effect was observed by us for aqueous solutions of non-electrolytes, where the empties were those of the water network structure, influenced by the addition of solutes [11].

There is, however, another behaviour which was observed by us and has been not already reported in literature. We did not limit to positron annihilation experiment just after pressing the pellets, but repeated it in two-day intervals. The results clearly show that after ca. 6 days a rapid transformation occurs, causing

Table 1. The results of positron annihilation experiments for solid samples. Note that the errors (statistical) are approx. as follows: for τ_1 – 3 ps, for τ_2 – 40 ps, for τ_3 – 80 ps, for I_1 – 0.6%, for I_2 – 1%, for I_3 – 1.3%

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	I_3 (%)
Pure β-cyclodextrin (CD)	263	936	2193	59.0	25.0	16.0
CD + *n*-nonanol 1:1	273	1070	2445	61.5	25.8	12.7
CD + *n*-nonanol 1:2	293	1070	2314	59.1	26.6	14.3
For CD + *n*-nonanol 1:1 only:						
after 2 days	277	1112	2445	62.0	26.9	11.1
after 4 days	276	1156	2505	62.2	27.5	10.3
after 6 days	260	967	2139	59.6	23.4	17.1
after 10 days	275	1064	2252	61.2	24.8	14.0
after 12 days	260	971	2125	59.8	23.8	16.5
after 14 days	270	1036	2218	60.7	24.1	15.2

in particular an increase of I_3, and after this the system becomes stable. Of course this observation needs confirmation and repeated tests, and here is mentioned only as a preliminary communication.

Conclusions

1. In aqueous solution of β-cyclodextrin no significant structural changes occur. Addition of *tert*-butanol to such solution does not lead to the inclusion of alcohol into empties of sugar molecule.
2. For solid mixtures of β-cyclodextrin and *n*-nonanol, the positron annihilation exhibits a meaningful decrease of the intensity of long-living component I_3, accompanied by an increase of the lifetime of the short-living one τ_1, due to decreased number of empties mentioned above and a subsequent increase of the total electron density of the system.
3. It was observed, but not already confirmed, that positron annihilation spectra are changing in time for the solid system containing equimolar contents of β-cyclodextrin and *n*-nonanol. These transformations end after ca. 6 days. This phenomenon needs further investigations and analysis.

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