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ORIGINAL ARTICLE

# Study of complex formation between β-cyclodextrin and benzene

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**Abstract** In this work study of complex formation of β-cyclodextrin with benzene was performed both experimentally and theoretically. Interaction of benzene with β-cyclodextrin in aqueous solutions was investigated by means of UV spectroscopy at temperatures in the range 291–303 K. The stoichiometric composition, stability constant, and thermodynamic parameters of "β-cyclodextrin-benzene" supramolecular structures formation were calculated from spectroscopic data. It was proved that 1:1 inclusion complex is mainly formed in aqueous solutions. The calculations of a spatial structure, formation energy, and vibration spectra in IR range for the complex of β-cyclodextrin with benzene were performed by Hartree–Fock–Roothaan method within PM3 semiempirical approximation with quantum chemistry package GAMESS (version 6.4). The calculated energy parameters for "β-cyclodextrin-benzene" inclusion complex are in agreement with experimental data.

**Keywords** Benzene · β-Cyclodextrin · Inclusion complex · UV spectroscopy · Hartree–Fock–Roothaan method

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## Introduction

Separation and removal of trace amounts of chemical compounds with similar properties is an important problem that requires new approaches in the sorption materials design. Aromatics compounds are among the most common pollutants released by chemical, petrochemical, and related industries. Because of the environmental implication of benzene (Benz) and its derivatives, selective separation and removal of aromatics from water by adsorption is a common practice that has been receiving increasing interest during the years [1–5]. An increase in sorption capacity and selectivity of adsorbents could be achieved owing to complicated complex modification of the material surface layer, which could be characterized as active binding sites tailoring on the surface of solid materials. Incorporation of macrocyclic compounds onto solid supports makes possible an efficient removing of organic pollutants from aqueous solutions by means of supramolecular structures formation.

Of great importance is the immobilization of cyclodextrins (CDs) on solid surfaces for creation of selective adsorbents, sensitive sensors, separation and purification of organic compounds, extraction and concentration of impurities of toxic substances, for example benzene and its derivatives [6–13]. Such new materials with incorporated CDs are also well suited for development of promising high effective inorganic membranes for selective separations of aromatics from aqueous solutions [14–16]. CDs are well known macrocyclic oligosaccharides, which form inclusion compounds with organic molecules. For their special hydrophobic cavity structure, they have almost unique ability to form inclusion complexes in solution or in the solid state with different compounds through "host–guest" interactions [17]. Elucidation of the binding

mechanism of aromatics on CD-containing materials is based on the inclusion complex study.

The aim of this study was to investigate a formation of "β-cyclodextrin-benzene" inclusion complex in aqueous solutions by UV spectroscopy. The spectroscopic data are consistent with a binding model that assumes formation of 1:1 inclusion complex. Stability constant for 1:1 inclusion complex at 291–303 K, and thermodynamic parameters of its formation were calculated. In order to understand the mechanism of inclusion complex formation complete, theoretical calculations of a spatial structure, formation energy, and vibration spectra in IR range for the complex of β-cyclodextrin with benzene were performed.

## Experimental

### Determination inclusion complex stoichiometry and formation constant by UV spectroscopy

Benzene (purchased from Macrochim) was of analytical reagent grade and used without additional purification. β-cyclodextrin (Fluka, ≥99%) was used without additional purification too. Doubly distilled water was used throughout.

Complex formation study of Benz with β-CD in aqueous solutions by UV spectrometry was carried out via two experimental procedures. In the first procedure, as called isomolecular series procedure, the concentration of Benz and β-CD was varied from 0.60–0.68 × $10^{-4}$ to 6.0–6.1 × $10^{-3}$ mol $L^{-1}$. In the second, the concentration of benzene was held constant at 2.95–3.10 × $10^{-4}$ mol $L^{-1}$, while β-CD concentration was varied from 3.74 × $10^{-3}$ to 6.46 × $10^{-3}$ mol $L^{-1}$. The initial concentrations of Benz and β-CD aqueous solutions were 6.8 × $10^{-3}$ mol $L^{-1}$. The total volume of binary solutions was 10 mL.

UV absorption spectra of Benz in water and β-CD-benzene aqueous solution were recorded on a Specord M-40 spectrophotometer using 2 cm quartz cuvettes. The range of spectra was from 220 to 300 nm. The solutions were prepared just before taking measurements. The registration of Benz and β-CD-benzene aqueous solutions UV spectra was carried out at 291, 298 and 303 K. The initial aqueous solutions of Benz and β-CD for preparing experimental series were kept in a thermostat during 1 h.

### Quantum chemical calculations

Quantum chemical calculations were carried out by the self-consistent field Hartree–Fock method within semiempirical PM3 approximation [18, 19] by means of the GAMESS program package (version 6.4) [20]. The absorption bands shifts of the benzene electron spectra in UV and visible areas in case of complex formation with β-CD are rather small. Therefore the directions and values of absorption bands shifts in theoretical models were estimated on the base of analysis of changes in frontier orbitals energy levels for benzene molecule. Vibrational IR spectra were calculated within the harmonic approximation of rigid rotator at normal condition.

## Results and discussion

### Study of inclusion complex formation of benzene with β-cyclodextrin

Benzene and its derivatives have been largely used as models for investigation of the driving forces contributing to inclusion complex formation. The supramolecular interaction of Benz and β-CD has been studied by different methods, such as microcalorimetry [21], fluorescence spectrophotometry [22], vapour pressure method [23], and others [24]. It was shown that, due to specific geometry, Benz and β-CD in aqueous solution could form inclusion complexes with 1:1, 1:2, and 2:1 stoichiometry. Nevertheless, to the best of our knowledge there is no one UV spectroscopy study of inclusion complex formation between β-CD and Benz.

In this work we have used UV spectroscopy to determine the stability constant and thermodynamic parameters for interaction of Benz with β-CD in aqueous solution.

Given the change of UV spectra absorption parameters of benzene aqueous solutions after adding β-CD an inclusion complex formation was established. It was shown that with addition of β-CD an absorption band intensity at $\lambda = 254$ nm for benzene aqueous solution increased, which suggest the formation of β-CD-Benz inclusion complexes. An absorption band intensity at $\lambda = 254$ nm for binary aqueous solutions with different molar ratio is the highest for 1:1 stoichiometry.

These experimental data could be fitted by considering the formation of a 1:1 "β-CD-Benz" inclusion complex according to the following reaction:

$$\beta\text{-CD} + \text{Benz} \overset{K_s}{\leftrightarrow} \beta\text{-CD} : \text{Benz}.$$

The $K_s$ value was determined by the typical equation [25]:

$$\frac{1}{A - A_0} = \frac{1}{a} + \frac{1}{a \cdot K_S \cdot [\beta\text{-}CD]_0},$$

where $A$ and $A_0$ are absorbance of the benzene aqueous solutions at $\lambda = 254$ nm with and without β-CD, respectively; $a$ is the constant relate to the change in extinction coefficient; $K_s$ is the stability constant of "β-CD-Benz" inclusion complex, and finally $[\beta\text{-CD}]_0$ is the initially concentration of β-CD.

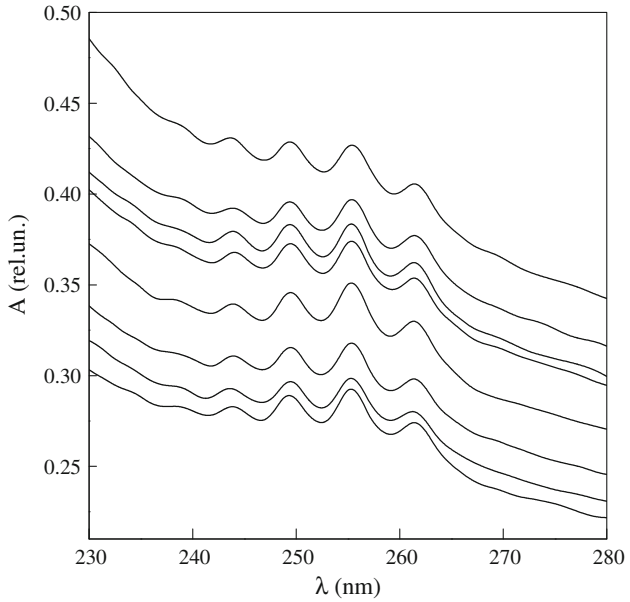


**Fig. 1** UV absorption spectra of benzene aqueous solutions with various concentration of $\beta$-cyclodextrin: from bottom to top, $3.74 \times 10^{-3}$, $4.08 \times 10^{-3}$, $4.42 \times 10^{-3}$, $5.10 \times 10^{-3}$, $5.44 \times 10^{-3}$, $5.78 \times 10^{-3}$, $6.12 \times 10^{-3}$, $6.46 \times 10^{-3}$ mol $L^{-1}$

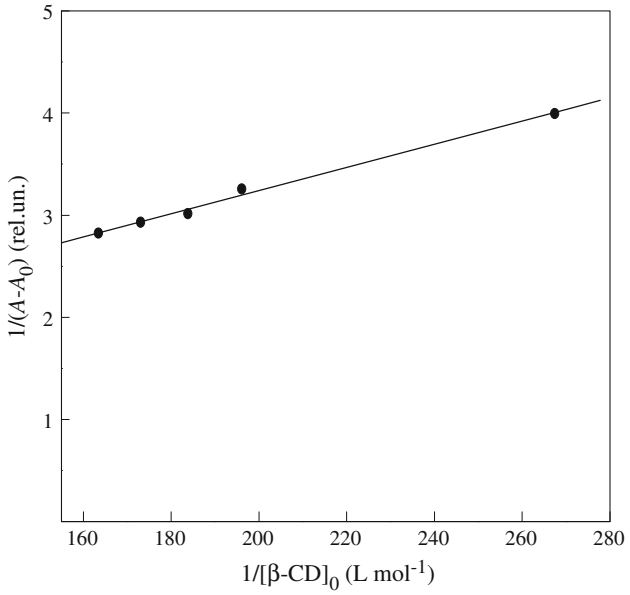


**Fig. 2** Reciprocal plot for 1:1 $\beta$-cyclodextrin-benzene inclusion complex

Figure 1 shows that absorbance of benzene aqueous solutions increases with increasing concentration of $\beta$-CD. The stability constant $K_s$ of inclusion complex can be determined by using above mentioned equation. The $K_s$ was calculated from the slope and intercept of the plot. Good linear correlation ($R^2 = 0.997$) was obtained, confirming the formation of a 1:1 inclusion complex (Fig. 2).

**Table 1** The formation constants of $\beta$-CD-Benz inclusion complex and thermodynamic parameters for the binding of benzene to $\beta$-cyclodextrin

| $T$ (K) | $K_s$ (L $mol^{-1}$) | $\Delta G$ (kJ $mol^{-1}$) | $\Delta H$ (kJ $mol^{-1}$) | $\Delta S$ (J $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| 291 | 116 | −11.5 | | |
| 298 | 86 | −11.0 | −32 | −72 |
| 303 | 68 | −10.6 | | |

The thermodynamic parameters, standard free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes for complexes of Benz with $\beta$-CD were obtained from the Van't Hoff equation: $R\ln K_s = -\Delta H°/T + \Delta S$. The $\Delta H°$ and $\Delta S°$ of the complex formation were calculated from the slope and intercept by plotting $R\ln K$ versus $1/T$ ($R^2 = 0.999$), and $\Delta G°$ was obtained according to the equation $\Delta G° = -RT \ln K_s$. The results are shown in Table 1.

As can be seen from the Table 1, the values of stability constant $K_s$ for 1:1 "$\beta$-CD-Benz" inclusion complex at different temperatures are rather small, and stability constant increases with diminishing of temperature. Therefore, it could be concluded, that there are rather weak interactions between $\beta$-CD and Benz. Such interactions are typical for nonspecific forces or inclusion complexes with volatile compounds [17]. A negative value of $\Delta G°$ indicates that inclusion process proceeded simultaneously. The $\Delta H°$ and $\Delta S°$ are also negative in the experimental temperature range. Hence, the formation of supramolecular structures of $\beta$-CD with Benz is thermodynamically profitable exothermal process, which is accompanied by the decrease of entropy as a result of "guest"-molecule freedom of vibration and rotation restriction in the cavity of $\beta$-CD molecule.

These results confirm that cyclodextrins are promising candidates for producing CD-containing materials for efficient benzene removal from aqueous solutions.

## Theoretical simulation of the inclusion complex

The theoretical study aimed at giving further information about the interaction between $\beta$-cyclodextrin and benzene with formation 1:1 "$\beta$-CD-Benz" inclusion complex. Calculated energy characteristics of $\beta$-CD, Benz, and their inclusion complex are given in Table 2. It follows from these data that the calculated energy of interaction between Benz and $\beta$-CD is relatively small (−59 kJ $mol^{-1}$) and semiquantitatively agrees with that found in the experiment (−32 kJ $mol^{-1}$). The frontier orbitals energy levels of benzene molecule included into cyclodextrin cavity practically coincide with those of free molecule. Thus, the UV absorption maximum in both cases is the same.

**Table 2** Calculated energy characteristics of $\beta$-cyclodextrin, benzene, and their inclusion complex

| Structure | Heat of formation (kJ mol$^{-1}$) | Energy of frontier orbitals (eV) | | Energy gap (eV) |
|---|---|---|---|---|
| | | LUMO | HOMO | |
| $\beta$-CD | −6033 | 1.44 | −11.00 | 12.44 |
| Benz | +98 | 0.40 | −9.75 | 10.15 |
| $\beta$-CD-Benz | −5994 | 0.40 | −9.75 | 10.15 |

**Table 3** Calculated IR spectra of benzene and its inclusion complex with $\beta$-CD (strong bands)

| Benzene | | Complex $\beta$-CD-Benz | |
|---|---|---|---|
| Wave number (cm$^{-1}$) | Relative intensity | Wave number (cm$^{-1}$) | Relative intensity |
| 3080 | 0.053 | 3081 | 0.030 |
| 3071 | 0.023 | | |
| 3064 | 0.035 | | |
| 3053 | 0.023 | 3052 | 0.030 |
| 3043 | 0.003 | 3045 | 0.080 |
| 1548(2) | 1.281(2) | 1564 | 1.384 |
| | | 1557 | 1.384 |
| 1226 | 0.002 | 1228 | 0.194 |
| 1149 | 0.001 | 1148 | 0.962 |
| 1147 | 0.004 | 1146 | 0.148 |
| 1069(2) | 2.248(2) | 1068 | 0.244 |
| 719 | 2.363 | 706 | 1.734 |

Inclusion complex formation may be also proved by IR spectroscopy because bands resulting from the included guest molecule are generally shifted or their intensities are altered. Theoretical vibrational spectra of both free and included benzene molecule are shown in Table 3. Analysis of calculated IR spectra gives us an opportunity to make definite conclusions on the peculiarities of intermolecular interaction. Thus, an attention should be paid to changes in relative intensities of individual absorption bands. Moreover, absorption bands at 3064 and 3071 cm$^{-1}$ practically disappears due to the complex formation that could be caused by decreasing position symmetry when benzene molecule enter into $\beta$-cyclodextrin cavity.

## Conclusions

In this work it was used UV spectroscopy to prove that $\beta$-cyclodextrin and benzene could form 1:1 "host–guest" inclusion complex in aqueous solution. The stability constant of "$\beta$-cyclodextrin-benzene" supramolecular structures formation was calculated from spectroscopic data in the range 291–303 K. Thermodynamic values showed that the complex formation is the spontaneous and thermodynamically favoured process. Formation of 1:1 "$\beta$-cyclodextrin-benzene" inclusion complex is thermodynamically profitable exothermal process, which is accompanied by the release of high-enthalpy water molecules and the decrease of entropy as a result of "guest"-molecule restriction in the cavity of $\beta$-CD molecule. The results of calculations on spatial structure, energy characteristics, and parameters of optical spectra of the inclusion complex between $\beta$-cyclodextrin and benzene give us an opportunity to estimate the interaction energy and degree of mutual complexation effects on spectral characteristics.

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