Solubilization of Aromatic Hydrocarbons in Aqueous β-Cyclodextrin Solutions in the Presence of Bis(4-*tert*-butylphenoxy) Substituted Ammonium Salt

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The solubilization of phenanthrene and fluorene in aqueous β-cyclodextrin (CD) solutions in the presence of 1,4-bis[4-(4-*tert*-butylphenoxy)butyl]-1,4-diazoniabicyclo[2.2.2]octane dibromide (BuDBDiBr) at the constant ratio *n*(CD) : *n*(surfactant) = 2 : 1 is completely suppressed. However, the solubilization of pyrene, acenaphthylene, acenaphthene in these systems remarkably increases. It can be assumed that inclusion complexes of CD with the surfactant containing in the side chains 4-*tert*-butylphenoxy group form associates which are able to solubilize aromatic hydrocarbons of suitable structure with high efficiency. The highest increase of the solubilized amount in the systems CD—BuDBDiBr (the mole ratio 2 : 1) was obtained with pyrene.

Aromatic hydrocarbons form inclusion complexes with cyclodextrins [1—4]. The formation of inclusion complexes of β-cyclodextrin (CD) with fluorene and alcohols or nitriles [5] or those of CD with brominated alcohols and acenaphthene with the amounts of substances ratio 1 : 1 : 1 has been also confirmed [6]. The changes in the absorption and fluorescence spectra of pyrene in systems containing CD and sodium dodecylsulfate (SDS) are explained by *Kasumoto et al.* [7] in terms of complex formation with CD and SDS below the critical micelle concentration (CMC) and the formation of mixed micelles containing CD above it. Due to interactions of β-cyclodextrin with surfactants in aqueous solutions the shift of CMC towards higher concentrations can be observed. This was confirmed by some experimental methods, *e.g.* by measurement of electric conductivity, surface activity, solubilization, or spectrophotometric method using methyl orange [8—16]. In aqueous solutions of CD in the presence of surfactants containing in their molecule one or two 4-*tert*-butylphenoxy groups a pronounced solubilization of the aromatic hydrocarbon pyrene has been observed [14, 15]. This effect was not found with surfactants having n-alkyl or naphthyloxybutyl side chains [12, 13, 16].

The aim of this paper was to investigate the solubilization of some aromatic hydrocarbons in aqueous β-cyclodextrin solutions and its influencing by the presence of diammonium salt 1,4-bis[4-(4-*tert*-butylphenoxy)butyl]-1,4-diazoniabicyclo[2.2.2]octane dibromide (BuDBDiBr) at the constant ratio of the components *n*(CD) : *n*(BuDBDiBr) = 2 : 1.

EXPERIMENTAL

Aromatic hydrocarbons acenaphthylene (BDH), acenaphthene, phenanthrene, fluorene, pyrene (Fluka), and fluoranthene (Schuchard), and β-cyclodextrin (Chinoin, Budapest) were used.

The synthesis of 1,4-bis[4-(4-*tert*-butylphenoxy)-butyl]-1,4-diazoniabicyclo[2.2.2]octane dibromide (BuDBDiBr) is described in Ref. [17].

Solubilization Method

Aqueous CD solutions or CD—BuDBDiBr systems at the constant ratio *n*(CD) : *n*(surfactant) = 2 : 1 were shaken with excess of aromatic hydrocarbon (AH) for 3 h at (20 ± 0.2) °C. The excess of insolubilized AH was then separated by filtration and the solubilized amount of AH in the filtrate was determined spectrophotometrically on a Specord UV—VIS apparatus (Zeiss, Jena) after its dilution (1:1) with ethanol. The investigated concentration range was 0—11.6 mmol dm^{-3} for aqueous CD solutions as well as 0—8 mmol dm^{-3} CD for CD—surfactant systems.

RESULTS AND DISCUSSION

The dependence of AH solubilization on the CD concentration in aqueous solutions gives information about the formation of CD—AH inclusion complexes (Fig. 1). The linear increase of solubilized amount with the increasing CD concentration reflects the formation of water-soluble CD—AH complexes with the amounts of substances ratio 1 : 1, whereas the descending dependence characterizes the formation of complexes with the ratio *n*(CD) : *n*(AH) > 1, less soluble in water. From Fig. 1 it is evident that depending on CD concentration acenaphthylene, acenaphthene, and fluorene can form both the above-mentioned kinds of CD—AH complexes, whereas with phenanthrene and fluoranthene only

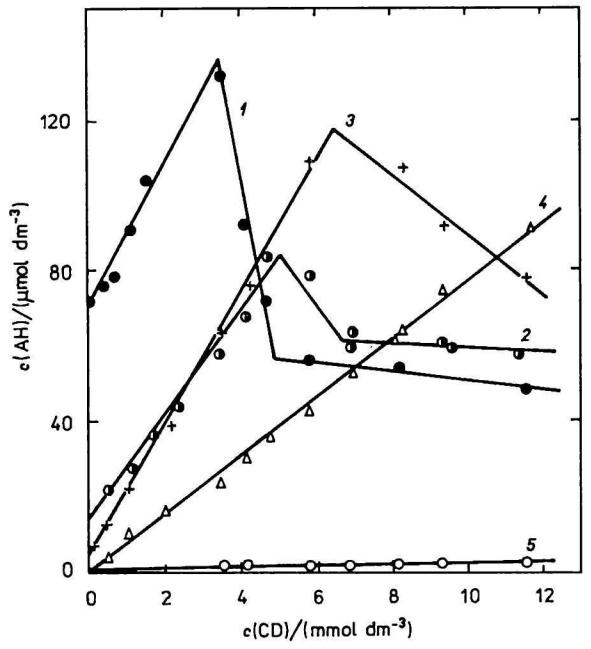

Fig. 1. Solubilization of aromatic hydrocarbons in aqueous β-cyclodextrin solutions at θ = 20 °C. *1*. Acenaphthylene; *2*. acenaphthene; *3*. fluorene; *4*. phenanthrene; *5*. fluoranthene.

the formation of water-soluble 1 : 1 complexes takes place. Parameters evaluated from the solubilization results, which are suitable to characterize the formation of water-soluble complexes as well as of those of limited solubility are shown in Table 1. The apparent association constants (K) for the water-soluble CD complexes were evaluated according to Ref. [18]. Using these parameters it can be concluded that the intensity of water-soluble complex formation decreases in the order fluorene, phenanthrene, acenaphthene, acenaphthylene, fluoranthene, pyrene, whereas the intensity of the formation of complexes with limited solubility (n(CD) : n(AH) > 1) expressed by s_2 decreases in the opposite order – acenaphthylene, acenaphthene, fluorene.

Cationic surfactant BuDBDiBr is an organic diammonium salt with a very low water solubility caused by the rigid structure of 1,4-diazoniabicyclo-[2.2.2]octane part of the molecule which forms a bridge between both side chains containing 4-*tert*-butylphenoxy group. By direct dissolution of BuDBDiBr in water only relatively low concentrations of the surfactant below its CMC can be reached. On the other hand, in the presence of CD at the constant ratio n(CD) : n(BuDBDiBr) = 2 : 1 the solubility of the surfactant due to intense interactions with CD significantly increases. The structure of BuDBDiBr indicates that by the complexation the benzene rings of the surfactant will be inserted in the CD cavities, with protruding 4-*tert*-butyl groups.

Table 1. Parameters Characterizing the Solubilization of Aromatic Hydrocarbons (AH) in Aqueous β-Cyclodextrin (CD) Solutions at θ = 20 °C

AH	K / dm³ mol⁻¹	$c(AH)_{max}$ / μmol dm⁻³	$c(CD)_{min}$ / mmol dm⁻³	$s_2 \cdot 10^3$
Acenaphthylene	265	132.95	3.41	– 51.56
Acenaphthene	1105	83.59	4.96	– 10.16
Phenanthrene	3276	–	–	–
Fluorene	5472	115.58	6.39	– 7.00
Fluoranthene	207	–	–	–
Pyrene	97	–	–	–

K – the apparent association constant of water-soluble complex; $c(CD)_{min}$ – concentration of CD from which starts the formation of AH—CD complex with low water solubility; $c(AH)_{max}$ – the highest concentration of AH reached by solubilization in aqueous CD solutions; s_2 – slope of the descending linear part of the solubilization dependence.

Table 2. The Increase of the Solubilization of AH in the Systems CD—BuDBDiBr with Respect to Their Solubilization in Aqueous CD Solutions at θ = 20 °C

AH	$c_{AH}^{CD\text{-}S}/c_{AH}^{CD}$	
	1 mmol dm⁻³ BuDBDiBr 2 mmol dm⁻³ CD	4 mmol dm⁻³ BuDBDiBr 8 mmol dm⁻³ CD
Acenaphthylene	7.91	61.10
Acenaphthene	15.31	58.31
Fluorene	0.21	0.19
Phenanthrene	0.04	0.09
Fluoranthene	1.06	4.74
Pyrene	47.11	657.00

$c_{AH}^{CD\text{-}S}$ – solubilized amount of AH in the system CD—surfactant; c_{AH}^{CD} – solubilized amount of AH in aqueous CD solution of corresponding concentration.

The solubilization of six AH in aqueous CD solutions and in the systems CD—BuDBDiBr with the constant mole ratio of components 2 : 1 depending on CD concentration is illustrated in Figs. 2*a*—2*f*. In these CD—surfactant systems the solubilized amounts of phenanthrene and fluorene (Figs. 2*d* and 2*e*, curves *2*) have been decreased with respect to AH amounts determined in aqueous CD solutions of corresponding concentrations (Figs. 2*d* and 2*e*, curves *1*) and reached only values of water solubility of these AH. That means, efficient formation of inclusion CD—surfactant complexes took place and the number of free CD and surfactant molecules which are able to solubilize AH has been completely suppressed.

In contrast to the above-mentioned two AH the solubilization of further four studied AH in aqueous CD solutions has been significantly increased in the presence of BuDBDiBr (Figs. 2*a*—2*c* and 2*f*, curves *2*). This synergetic effect concerning AH solubilization was smaller at lower concentrations of the components in the system (c(CD) < 6 mol

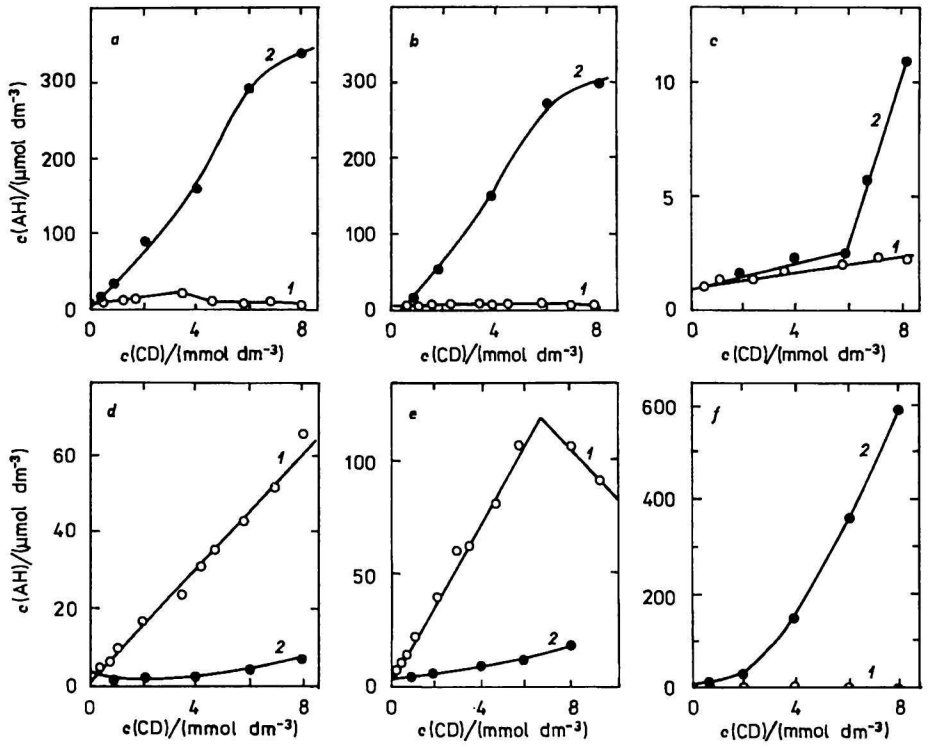

Fig. 2. Solubilization of aromatic hydrocarbons in aqueous β-cyclodextrin solutions (*1*) and in the systems CD—BuDBDiBr with the constant mole ratio 2 : 1 (*2*) at θ = 20 °C. *a*) Acenaphthylene; *b*) acenaphthene; *c*) fluoranthene; *d*) phenanthrene; *e*) fluorene; *f*) pyrene.

dm^{-3} for fluoranthene, < 2 mol dm^{-3} for pyrene and < 1 mmol dm^{-3} for acenaphthylene or acenaphthene) and showed a pronounced increase with the further increasing of the concentrations of components.

The results of the AH solubilization increase in aqueous CD solutions by the presence of surfactant for c(CD) = 2 and 8 mmol dm^{-3}, respectively, are summarized in Table 2. The synergetic solubilization effect in the systems CD—BuDBDiBr decreases in the following order: pyrene, acenaphthene, acenaphthylene, fluoranthene. The most pronounced synergetic effect in the whole investigated concentration range was reached with pyrene.

As mentioned above, the complete suppression of phenanthrene or fluorene solubilization in CD—BuDBDiBr (2 : 1) systems indicates efficient formation of CD—surfactant complexes in aqueous solutions. The increased solubilization of further four studied AH (acenaphthylene, acenaphthene, fluoranthene, and pyrene) in the same CD—BuDBDiBr system can be probably explained as follows: the CD—surfactant complexes associate in aqueous solutions *via* interaction of bulky 4-*tert*-butyl groups protruding from the cavity of CD and in this manner a certain nonpolar space (cavity), limited by 4-*tert*-butyl groups is formed which shows ability to solubilize some AH with high efficiency. The significant increase of AH solubilization is possible only at suitable sterical structure of AH allowing the best space-filling of this nonpolar cavity formed by CD—surfactant associates. Phenanthrene and fluorene do not accommodate to this condition, whereas the highly symmetrical molecule of pyrene is obviously the most suitable, which is reflected in the largest synergetic effect with respect to AH solubilization. These findings are in good accordance with the results obtained by pyrene solubilization in aqueous solutions of some mono- and diammonium salts containing 4-*tert*-butylphenoxy group in the presence of CD [14, 15]. In good agreement with the presented results are also those obtained by solubilization of the studied AH in *N*,*N*′-bis[4-(4-*tert*-butylphenoxy)butyl]-*N*,*N*′-dimethyl-1,6-hexanediammonium dibromide—CD systems [19].

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