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THE FORMATION OF PYRENE:CYCLOMALTO-OLIGOSACCHARIDE COMPLEXES IN THE PRESENCE OF NON-IONIC SURFACTANTS

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ABSTRACT

Examination of the interactions of pyrene, cyclomalto-oligosaccharides (cyclodextrins), and selected non-ionic surfactants by measurements of fluorescence life-times indicates that ternary complexes are formed. Studies of surface tensiometry indicate that binary complexes occur between cyclodextrins and non-ionic surfactants.

INTRODUCTION

Cyclomalto-oligosaccharides (cyclodextrins, CDs) have received much attention[1,2] because of their ability to form inclusion complexes with appropriately sized molecules. The photophysical properties of included guest molecules can be affected markedly[3–5].

Fluorescence spectra of aqueous solutions of fluorophores in the presence and absence of CDs can show differences and such spectra have been used extensively to investigate CD systems[6–9]. Changes in the spectral characteristics of a probe molecule such as pyrene allow investigations of the microenvironment of the CD cavity[9]. In addition, the temporal nature of processes which occur in the vicinity of the CD as well as equilibrium concentrations may be measured using data of fluorescence life-times[9,10]. Since the fluorescence life-time of pyrene is extremely sensitive to its microenvironment[11], information about the interaction of the included molecule and the CD can be obtained.

Recently, there has been interest in the interaction of a third component with CD inclusion complexes. Attention has been focused[4,12] on intramolecular and intermolecular formation of excimers in the cavity of CDs. Thus, 1-butanol affects[13] the formation of the pyrene excimer in the cavity of cyclomalto-octaose (γCD). The retardation and enhancement of fluorescence quenching due to the inclusion of a quencher, fluorophore, or both in the cavity of CDs have been investigated[14–16]. Attention has also been given to the effect of alcohols on the interaction

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of CDs with organic solutes[10,17–21]. The fluorescence life-time of pyrene is increased by as much as a factor of three in the presence of CDs and alcohols[19,20]. These increases have been attributed to the formation of ternary complexes[20,21]. Mixed systems of CDs and surfactants also have been shown to have interesting chemical behavior[6,22].

We now report an extension of the investigation of the formation of ternary complexes by examining pyrene:CD:non-ionic surfactant systems. The non-ionic surfactants **1–5** studied had aliphatic and polyethoxy moieties. The aliphatic moieties of **1–5** are similar to those of the alcohols shown to form ternary complexes with pyrene and CDs, such as *tert*-butyl alcohol[20]. The formation constant of a 1:1 surfactant:CD complex is given by

$$K_f = \frac{[\mathrm{S:CD}]}{[\mathrm{CD}][\mathrm{S_f}]}, \tag{1}$$

where [S:CD] and $[\mathrm{S_f}]$ are the concentrations of the complex and the free surfactant, respectively. Assuming that the total concentration $(\mathrm{S_0})$ of surfactant is given by the sum of the complex and free surfactant (which is true only if there are no micellar aggregates), and that CD is present in excess, then equation *1* may be rewritten as

$$\mathrm{S_f} = \frac{\mathrm{S_0}}{K_f\mathrm{CD} + 1}. \tag{2}$$

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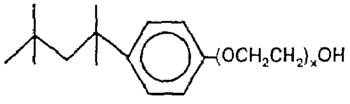

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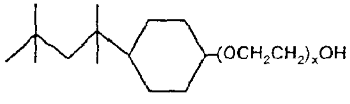

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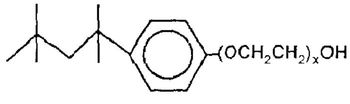

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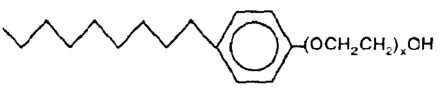

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The concentration of free surfactant can be measured readily by surface tensiometry and provides a measure of the critical micelle concentration (CMC) of a surfactant, since the free surfactant demonstrates surface activity and the micelle shows less surface activity. The change of the CMC on complexation with CD should indicate similar behavior. Therefore, measurements of the surface tension of a solution of surfactant in the presence of CD record the change in free concentration of surfactant produced by complexation with a CD.

The surface tension (γ) for a surfactant below the CMC can be expressed as

$$\gamma = \gamma_0 - \alpha S_f, \tag{3}$$

where γ_0 is the surface tension of the pure solvent and α is a proportionality constant. Substituting equation *3* into equation *2* gives the expression

$$\gamma = \frac{-\alpha S_0}{K_f CD + 1} + \gamma_0, \tag{4}$$

which can be used to obtain the formation constant of the surfactant:CD complex from surface tension data.

EXPERIMENTAL

Reduced surfactants (**3**, Triton X100R, Triton X114R) were obtained from Sigma and the other surfactants (**1**, **2**, **4**, and **5**) and CDs from Aldrich, and were used without further purification. Measurements of surface tension were made with a Central Scientific Co. Model 70353 CSC-DuNouy Tensiometer. For determinations of CMC in the presence of CDs, samples were prepared by adding surfactant to stock solutions of CD in order to hold [CD] constant. For determination of the formation constant of surfactant:CD complexes, CD was added to stock solutions of surfactant in order to hold [S_0] constant. Measurements of the fluorescence life-times of pyrene:CD complexes in the presence of non-ionic surfactants were made at 24° and the data were analyzed using a non-linear least squares routine[23].

RESULTS AND DISCUSSION

Table I contains the fluorescence life-times of pyrene:CD complexes in the presence of non-ionic surfactants, which demonstrate that many of these large surfactants can produce changes in life-times similar to those observed[19,20] with smaller alcohols. Many of these surfactants have molecular weights that are a magnitude larger than those of the alcohols.

Examination of the first row of Table I shows that the fluorescence life-time of pyrene increases in the presence of CDs. This increase has been attributed[20] to

TABLE I

FLUORESCENCE LIFE-TIMES OF PYRENE IN THE ABSENCE AND PRESENCE OF VARIOUS CDs AND NON-IONIC SURFACTANTS

Surfactant	*Chain*[a]	$\tau_{absence}$[b]	*τγCD*[c]	*τβCD*[d]	*τ2βCD*[e]	*τ3βCD*[f]
None		143	215	339	247	262
1 Brij® 30	4	158	313	382	288	334
Brij® 35	23	208	327	282	290	332
Brij® 58	20	216	322	286	370	272
Brij® 78	20	209	333	251	406	254
Brij® 99	20	190	357	267	319	222
4 Igepal® CA210	2	244	431	336	378	212
Igepal® CA520	5	277	474	442	386	218
Igepal® CA720	12	265	428	478	359	216
Igepal® CO210	2	195	286	307	235	218
Igepal® CO520	5	266	473		375	233
Igepal® CO720	12	264	436	347	306	246
Igepal® CO890	40	234	393	356	321	209
Igepal® CO990	100	233	440	416	370	229
2 Triton® X100	10	258	478	495	392	187
TRiton® X100R	10	236	441	421	403	212
Triton® X114R	8	236	439	454	394	250

[a] The number of -(OCH_2CH_2)- groups in the chain of the surfactant. [b] Life-time of pyrene in the presence of 0.5mM surfactant. [c] Life-time of pyrene in the presence of 0.5mM surfactant and ~2mM γCD. [d] Life-time of pyrene in the presence of 0.5mM surfactant and ~2mM βCD. [e] Life-time of pyrene in the presence of 0.5mM surfactant and ~2mM 2,6-βCD. [f] Life-time of pyrene in the presence of 0.5mM surfactant and ~2mM 2,3,6-βCD.

the formation of pyrene:CD inclusion complexes. When included in the cavity of a CD, the pyrene molecule has decreased interactions with the solvent and such dissolved quenchers as molecular oxygen, and consequently has an increased life-time.

Changes in fluorescence life-times of pyrene by interactions solely with surfactants are shown in the τ_{absence} column in Table I. The increase in fluorescence life-time of pyrene observed in the presence of each of the surfactants studied can be attributed to the inclusion of pyrene in a surfactant agglomerate or micelle, as has been observed[11] for pyrene and ionic surfactants.

The data in Table I demonstrate that changes in the life-time of pyrene in the presence of non-ionic surfactants can be large. Thus, the fluorescence life-time of pyrene in the presence of γCD and surfactants is greater that of the pyrene:γCD inclusion complex. This observation indicates that pyrene is shielded from interactions which deactivate the excited state to a greater degree when a surfactant molecule interacts with the pyrene:γCD complex. Similar enhancements of the fluorescence life-time of pyrene in the presence of *tert*-butyl alcohol occur by the apparent formation of a ternary CD inclusion complex[19,20].

Whereas enhancements of the fluorescence life-time of pyrene are observed for all of the systems of γCD and surfactants studied, the cyclomaltoheptaose (βCD) systems are somewhat different. Thus, the data in Table I reveal that some of the surfactants produce a decrease in fluorescence life-time of pyrene in the ternary system as compared to the binary pyrene:βCD system.

For the substituted CDs, heptakis(2,6-di-*O*-methyl)-βCD (2,6-βCD) shows results similar to those for γCD. In each of the systems studied, except Igepal CO 210, enhancements of the fluorescence life-time of pyrene are observed with respect to the pyrene:surfactant and pyrene:2,6-βCD systems. However, for heptakis(2,3,6-tri-*O*-methyl)-βCD (2,3,6-βCD), there is a lowering of the fluorescence life-time of pyrene with respect to both pyrene:CD and pyrene:surfactant systems. This finding indicates that pyrene is less protected from excited-state deactivation than either in a surfactant micelle or CD inclusion compound.

Edwards and Thomas[6] observed that, below the CMC, an increase in hydrophobicity in CD-complexed pyrene occurs on the addition of sodium lauryl sulfate (NaLS) and concluded that a ternary complex of NaLS, pyrene, and CD had formed. Hashimoto and Thomas[22] showed similar properties for a variety of ionic surfactants and Kusumoto *et al.*[24] found strong evidence for ternary complexes of NaLS, pyrene, and βCD. By observing changes in the absorbance and fluorescence spectra of the pyrene:CD complex on the addition of NaLS, they concluded that the surfactant participates in the formation of a ternary complex.

The possibility of ternary inclusion complexation in the presence of non-ionic surfactants was examined by observing the interaction of these surfactants with CDs. As suggested for alcohols, third components must complex with CDs before ternary complexes are formed[20]. Surface tensiometry was used to investigate this possibility.

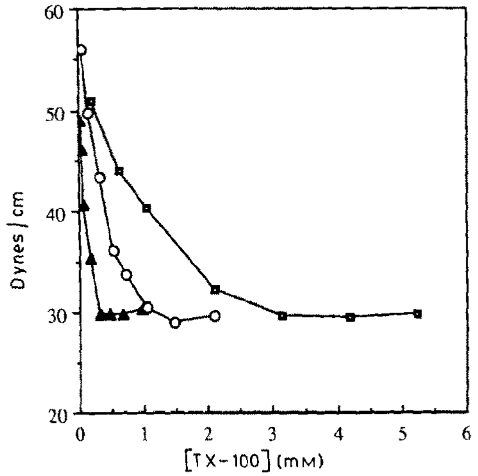

Fig. 1. Plot of surface tension (dynes/cm) *versus* surfactant concentration for Triton® X100R in the absence (—▲—) and presence of concentrations of γCD (—○—, mM; —■—, 3 mM).

TABLE II

CMC VALUES FOR TRITON® X-100R IN THE PRESENCE OF CDs

CD	*[CD] (mM)*	*CMC (mM)*	*CMC/[CD]*
Nonew		0.164	
βCD	1.03	0.210	0.204
βCD	3.10	0.620	0.200
γCD	1.01	0.646	0.640
γCD	3.03	1.873	0.624

The CMC for non-ionic surfactants increases in the presence of CDs, and Fig. 1 demonstrates the effect using Triton X100R. As γCD increases, the break point moves to higher values. This effect has been observed also through conductance measurements of ionic surfactant and CD systems[26]. These results imply that the CD forms an inclusion complex with the surfactant, with lowered surface activity for non-ionic surfactants or lowered conductance for ionic surfactants.

The CMC values for the data in Fig. 1, as well as corresponding data for βCD, are reported in Table II. These values again demonstrate that the CMC increases in the presence of CD. Whereas the CMC values increase with increase of [CD], the ratio of CMC to [CD] remains essentially constant for a given CD, which points to the formation of surfactant:CD complexes. This ratio is the surfactant:[CD] at which micelles begin to form.

Representative surface tensiometry *versus* CD concentration data that were fitted to equation *4* are shown in Fig. 2. As noted from the data and the curve fit, equation *4* is a good model of the surfactant:CD system and suggests that com-

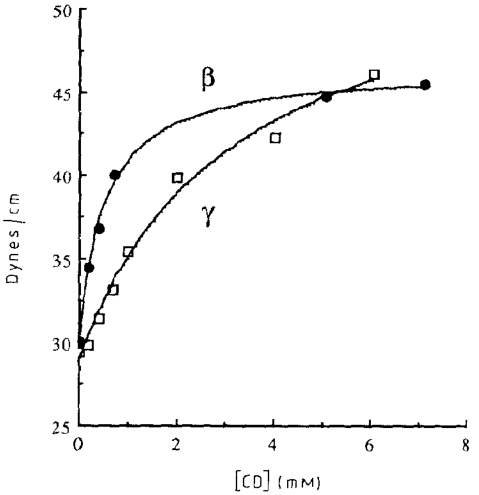

Fig. 2. Plot of surface tension (dynes/cm) *versus* [CD] for βCD, γCD, and Igepal® CA520. Non-linear fits of the data to equation *4* are shown by solid lines.

TABLE III

FORMATION CONSTANTS FOR VARIOUS SURFACTANT:CD SYSTEMS[a]

Surfactant	K_f^{β} (M^{-1})	K_f^{γ} (M^{-1})
Triton® X100R	145	760
Igepal® CA520	1850	320
Igepal® CO520	1460	250

[a] Calculated by fitting surface tensiometry data to equation *4*.

plexes between surfactants and CDs are indeed formed. A summary of the formation constants for the data presented in Fig. 2 and other selected surfactant:CD systems is presented in Table III. These formation constants were obtained by a fit of surface tension *versus* [CD] data to equation *4*, using a non-linear least squares program. Formation constants for all the surfactant:CD systems reported in Table I were not measured. However, the data presented in Fig. 2 and Table III demonstrate that non-ionic surfactants complex with CDs. In addition, the relative magnitudes for the Triton X100R:CD formation constants are in agreement with the CMC/[CD] ratios presented in Table II. The formation constant for Triton X100R:γCD is the largest, as is the CMC/[γCD] ratio. These results agree well with observations[26,27] for CD:ionic surfactant systems.

The observation of non-ionic surfactant:CD complexes, coupled with the data on fluorescence life-times in Table I, indicate that ternary associations of pyrene, CDs, and non-ionic surfactants are likely. The entire surfactant molecule cannot be included in the CD cavity. Each of the surfactants studied contains a polyethoxy chain; yet, the data vary with the type of surfactant employed, suggesting that it is the aliphatic moiety that is included in the CD. These moieties have a size similar to that of the smaller alcohols and therefore it is reasonable to expect the observed effects on fluorescence life-times of the included pyrene.

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