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Use of liquid crystals for imaging different inclusion abilities of α-cyclodextrin and β-cyclodextrin toward cetyltrimethyl ammonium bromide

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ABSTRACT

We herein report a method for the imaging of different inclusion abilities of α-cyclodextrin (α-CD) and β-cyclodextrin (β-CD) toward cetyltrimethyl ammonium bromide (CTAB) using liquid crystals (LCs). The optical transition from the dark to the bright state was caused by the inclusion interaction between CTAB and CDs. It was confirmed that α-CD formed more stable CTAB complexes than β-CD, leading to different optical responses of the LCs from the α-CD/CTAB and β-CD/CTAB systems. This method could be used to provide a visual method for selection of the correct CD molecules for interaction with surfactant molecules in recognition systems.

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, or eight glucose units, which are known as α-, β- and γ-CD, respectively [1]. The CDs are bound together in α-(1–4) linkages to form doughnut-shaped rings with hydrophilic outer walls and hydrophobic inner cavities [2]. The CD cavity can therefore provide a hydrophobic space in which certain guest molecules can reside, giving a water-soluble inclusion complex [3]. As the different CDs (α-, β- and γ-CD) have different sized cavities, selection of the most suitable cyclodextrin for complexation with a given guest is influenced significantly by the size of the cavity [1–4].

CDs are known to form inclusion complexes with surfactants in which the hydrophobic chain of the surfactant resides inside the hydrophobic environment of the CD cavity [5–9]. Such inclusion complexes between surfactants and CDs are particularly useful in a number of areas, such as catalysis [10,11], materials science [12], medicine and pharmaceutical sciences [13,14]. These complexes have been studied by a range of analytical techniques, including UV–vis and fluorescence spectroscopy [14,15], surface tension [16], potentiometry [17], conductivity [18,19], NMR spectroscopy [19,20] and microcalorimetry [21].

Liquid crystals (LCs), anisotropic fluids which exhibit long-range orientational order, have received increasing attention due to fundamental and technological interest [22–24]. The orientation of a LC is extremely sensitive to changes in the surface with which they are in contact. This phenomenon, combined with their optical birefringence properties, provides a practical tool for probing and amplifying chemical and biological events at the interface into optical signals that are visible to the naked eye under a crossed polarizer [25–27]. Compared to conventional analytical methods, LC-based techniques have several advantages, such as no requirement for the use of labeled analytes, complex instruments, or laborious techniques [22–27].

Previous studies have demonstrated that the self-assembly of surfactant monolayers with linear tails can trigger an orientational transition of LCs from planar to the homeotropic state, leading to a change in optical response from bright to dark [28–33]. In contrast, surfactant monolayers can be disrupted by the hydrophobic CD cavities due to the formation of inclusion complexes [6,14,34]. In addition, we previously reported that LCs can be used as an optical probe to investigate inclusion interactions between β-CD and sodium dodecyl sulfate (SDS) or cetyltrimethyl ammonium bromide (CTAB) [33]. Driven by our interest regarding the effects of different cavity sizes on the inclusion phenomena of CTAB and CDs, we used LCs for determining which CD system (*i.e.* α-CD or β-CD) formed stronger complexes with CTAB.

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2. Experimental

2.1. Materials

4-Cyano-4′-pentylbiphenyl (5CB), cyclodextrins (α-CD and β-CD), and cetyltrimethyl ammonium bromide (CTAB) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Glass microscopy slides and Copper TEM (transmission electron microscope) grids (100 mesh, 18 μm thickness, 285 μm grid spacing, 55 μm bar width) were obtained from Beijing Zhongjingkeyi Technology Co., Ltd. All aqueous solutions were prepared using deionized water.

2.2. Preparation of LC optical cells

The LC optical cells were prepared following the procedures reported in the previous studies [28,33]. Briefly, glass slides were cleaned by sonication in ethanol for 15 min and then dried in a 100 °C oven for 30 min. Next, a silicon plate support with holes 5 mm in diameter and 0.5 mm depth was placed onto the slide and the bubbles between the slide and the silicon plate was removed through pressure. Subsequently, the silicon plate was secured on the slide *via* adhesion. Meanwhile, TEM copper grids (100 mesh, 18 μm thickness, 285 μm grid spacing, and 55 μm bar width) were first cleaned in methanol, ethanol, and acetone (sonication for 10 min in each solvent), then heated overnight at 45 °C to evaporate residual solvents. The copper grid was then impregnated with about 0.5 μL of 5CB using a capillary tube. Excess of 5CB was removed by contacting the LCs with the other end of the capillary tube. The grids containing LCs were then put on the wells of the plate containing samples of interest. This optical cell was then ready for examination under cross-polarized lighting.

2.3. Preparation of the mixed solutions of CTAB and CDs

The mixed solutions of CTAB and α-CD (α-CD:CTAB) were prepared by mixing CTAB with α-CD, and the α-CD:CTAB mixed solutions were incubated in an Electro-Thermostatic Water Bath at a temperature of 40 °C for a set time period of 12 h. The β-CD:CTAB mixed solutions were prepared following the preparation of α-CD:CTAB mixed solutions. The mixed solutions were used to characterize the optical response of 5CB, surface tension.

2.4. Characterizations

The optical texture of the 5CB films filled in the pores of the copper grids was examined by using plane-polarized light in transmission mode on an UOP UB200i microscope with crossed polarizer. All optical microscopy images were taken at room temperature (approximately 25 °C) with a digital camera (DPIXEL DP330C CCD Camera) mounted on the polarizing optical microscope. Arthroscopic examinations were performed with the source light intensity set to 50% of full illumination and the aperture set to 10% so as to collimate the incident light.

The surface tension of the CD:CTAB mixed solutions were measured at room temperature with the use of a Powereach tensiometer (JK99C, Powereach, China).

An isothermal calorimeter (ITC) (MicroCal ITC200, GE Healthcare Life Sciences, USA) was used for determining a single titration curve of the enthalpy of interaction between CTAB and the CDs, and where appropriate, the inclusion constant corresponding to the formation of a complex between those species. The reaction cell and reference cell of the calorimeter were initially loaded with CTAB solution (300 μL, 0.2 mM) and pure water (300 μL). The titrant solution was injected into the stirred sample vessel in 20 aliquots of 2 μL using a Hamilton syringe controlled by a 612 Lund Pump (Thermometric, USA). The concentrations of α-CD and β-CD titrants used were 5.0 mM. The interval between the two injections was 40 min, which was sufficient time for the signal to return to the baseline. The system was stirred at 30 rpm with a gold propeller. All experiments were performed at 298.15 ± 0.01 K and were commenced following baseline stabilization. The dilution heat of each CTAB and CD solution was measured by a titration experiment, where each CD solution was titrated into the solvent (pure water), and the solvent into the CTAB solution. All dilution heats were found to be negligible. The binding enthalpies and inclusion constants were obtained by non-linear fitting (Wiseman isotherm) incorporated into the software, which assumes a single set of identical binding sites [35].

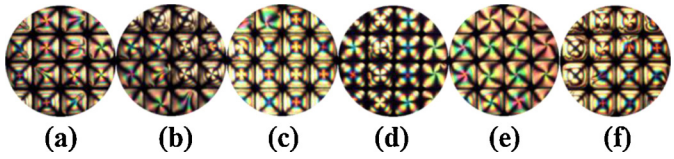

Figure 1. Optical images of 5CB (confined within a copper grid) after exposure to aqueous solutions of: β-CD (a) 0.5 mM, (b) 1 mM and (c) 2 mM; and α-CD (d) 0.5 mM, (e) 1 mM and (f) 2 mM.

3. Results and discussion

3.1. Effect of CDs on the orientation of LC

We initially chose to monitor the optical responses of 4-cyano-4′-pentylbiphenyl (5CB) to aqueous solutions of α- and β-CD, monitoring at the LC-aqueous interface. We previously demonstrated that the interaction between β-CD and 5CB is extremely weak, to the extent that β-CD could not induce significant changes in the optical appearance of 5CB at the LC-aqueous interface [33] (Figure 1a–c). In accordance with the previous study [33], it was found that α-CD did not affect the orientation of 5CB to the same extent as β-CD (Figure 1d–f).

3.2. Optical responses of LC to CTAB

We then examined the optical responses of 5CB at different time intervals after contact with water (Figure 2a) and aqueous solutions of CTAB (Figure 2b–e). The increasingly dark images observed with increasing time intervals could be associated with the orientational transition of 5CB from the planar to the homeotropic alignment, and could be observed in both 3 μM and 5 μM solutions of CTAB (Figure 2b and c, respectively). In addition, it could be seen that at higher CTAB concentrations, the time taken to achieve orientational transition of 5CB was shorter. No orientational transitions of 5CB were observed at concentrations greater than 10 μM after 0.5 min (Figure 2d and 2e), indicating that the interaction between CTAB and 5CB is both time-dependent and concentration-dependent. These results are consistent with previous studies [31–33] where it was reported that hydrophobic interactions between the LC molecules and the surfactant tails played a crucial role in determining the homeotropic orientation of the LCs.

3.3. Imaging the different inclusion ability between α-CD and β-CD toward CTAB

In order to successfully image the inclusion phenomena of CTAB by CD cavities of varying size using LCs, copper grids filled with 5CB were placed onto a 10 μM aqueous solution of CTAB for 10 min. The 5CB films were then removed and placed on an aqueous solution of either α-CD or β-CD. It was found that the optical appearance of