Fluorescence Enhancement of α-Naphthyloxyacetic Acid in the Cavity of γ-Cyclodextrin, assisted by a Space-regulating Molecule

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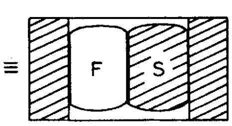
Summary The fluorescence intensity of α-naphthyloxyacetic acid in aqueous solution is slightly enhanced by addition of γ-cyclodextrin (γ-CD), but markedly enhanced in the presence of both γ-CD and cyclohexanol, showing the role of cyclohexanol as a space-regulator which narrows the cavity of γ-CD to allow the inclusion of the fluorophore.

Cyclodextrins (CDs) have a lipophilic cavity with inner diameters of 4·5, 7·0, and 8·5 Å for α-, β-, and γ-CD, respectively, and form host–guest complexes with many kinds of molecules.[1] The stoicheiometry of complex formation with α-CD and β-CD is usually 1:1, but there are exceptions.[2–4] On the other hand, the cavity of γ-CD seems to be too large to include one molecule of a benzene or naphthalene derivative, and examination of molecular models suggests that it is suitable for accommodating two guest molecules. We have shown[5] that the enhanced excimer fluorescence of sodium α-naphthylacetate in the presence of γ-CD provided evidence for inclusion of two guest molecules into γ-CD. In this particular case, the two guest molecules included in the γ-CD cavity were the same. The present study deals with another three-component complex, composed of γ-CD, a fluorophore (α-naphthyloxyacetic acid), and a space-regulator (cyclohexanol), and the formation of a complex is shown by the increased fluorescence of the fluorophore.

Fluorescence spectroscopy has been shown to be a useful method for the investigation of the complexation behaviour of CDs.[4–7] In the presence of β-CD, sodium 8-anilinonaphthalene-1-sulphonate exhibits enhanced fluorescence which may be caused by a change in environment from the polar aqueous media to the lipophilic cavity on forming a 1:1 complex.[7] We have observed similar fluorescence behaviour for α-naphthyloxyacetic acid in the presence of β-CD. However, the fluorescence enhancement of the fluorophore was slight with γ-CD, probably because of the unsuitable size of the CD cavity for the guest.† Nevertheless, a marked enhancement in its fluorescence intensity at *ca.* 360 nm was observed when cyclohexanol was added. The effect of cyclohexanol addition is opposite in the case of β-CD, the fluorescence enhancement being suppressed because of the replacement of the fluorophore by cyclohexanol in the β-CD cavity. We suggest, therefore, that cyclohexanol acts as a space-regulator which narrows the cavity of γ-CD to allow the inclusion of the fluorophore (equation 1), where F is the fluorophore and S is the space-

$$\gamma\text{-CD:F} + \text{S} \rightleftharpoons \gamma\text{-CD:(F·S)} \rightleftharpoons \gamma\text{-CD:S} + \text{F} \quad (1)$$

γ-CD:(F•S) ≡ 

regulator. In this three-component complex, the fluorophore is sandwiched between the hydrophobic wall of γ-CD and cyclohexanol, the lipophilic environment around the fluorophore being similar to that in β-CD. This result is consistent with the enhanced circular dichroism reported

† In contrast with sodium α-naphthylacetate (ref. 5), α-naphthyloxyacetic acid exhibits no excimer fluorescence either in the presence or absence of γ-CD.

by Tabushi *et al.* for *p*-nitrophenol included in γ-CD together with another guest molecule.[8]

This property of γ-CD enables us to make use of γ-CD as a reaction medium in which two different kinds of molecules such as a catalyst and a substrate can be brought together effectively.

(*Received*, 24*th November* 1980; *Com.* 1252.)

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