Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 9: 137–143, 1990.

Counterion Binding by Surfactant/β-Cyclodextrin Inclusion Complexes

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(Received: 7 February 1989; in final form: 2 October 1989)

Abstract. Sodium ion activities were determined potentiometrically in sodium dodecylsulfate and sodium dodecanoate solutions containing β-cyclodextrin. Whereas sodium ion did not bind with β-cyclodextrin, its activity decreased noticeably when the 1:1 β-cyclodextrin/surfactant inclusion complex was formed in solution. When the anionic guest was methyl red or methyl orange, no sodium ion binding occurred. When the guest was the cationic dodecylammonium ion in chloride solutions containing β-cyclodextrin, pronounced chloride ion binding to the 1:1 inclusion complex occurred.

Key words. β-Cyclodextrin, surfactant, methyl red, methyl orange, cation binding, anion binding.

1. Introduction

Ions with a considerable hydrophobic component such as monomeric surfactant ions possessing the correct geometry to ensure a snug fit often form strong inclusion complexes within the hydrophobic cavity of cyclodextrin (CD) molecules [1–8]. Even simple anions apparently bind with the uncharged cyclodextrin molecules [4, 9, 10] but the mechanism and presumably the binding site must be different from the binding site for organic ions of considerable hydrophobic nature. For simple ions, the 'snug fit' condition within the CD cavity probably does not hold, so the binding must be of a different type. If, so, there seems to be no *per se* reason why cations cannot also bind with CD molecules but the only discussion of this possibility occurring in water is the recent note of Sanemasa *et al.* [11]. Given the role that cations can play in the structuring of CD complexes in the solid state [12], it is somewhat surprising that this effect has received so little attention in inclusion in solution.

However, conductivity measurements in our laboratory in CD/anionic surfactant systems where Na^+ ion was the only cation appeared to indicate that some Na^+ ion was being effectively removed as charge carriers [6, 8]. Since so little was known of 'inclusion' of simple cations by CD, we decided to investigate Na^+ ion activities in these systems through selective ion electrode studies.

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2. Experimental

Potentiometric and $Na^+_{(aq)}$ activity measurements were performed with an Orion Research microprocessor ion analyzer/901 with 0.1 mV sensitivity at 25.0°C. The sodium selective electrode was an EA-109 Na Metrohm glass electrode and the reference cell was an Orion 90-02 double junction electrode with the outer chamber filled with 5M NH_4NO_3. With this electrochemical cell, the response of the electrode against aqueous NaCl was linear in the concentration range investigated (10^{-2} to 0.5 mmol dm^{-3}) with a slope equal to 57.0 ± 1.0 mV.

β-Cyclodextrin (β-CD) was obtained from Sigma and dried in vacuum before use. The surfactants and dyes were the best available commercially. All solutions were made from nanopure water which was degassed before use.

3. Results and Discussion

Sodium ion activities were determined as a function of β-CD concentration in three pre-micellar sodium dodecylsulfate (SDS) solutions (2.00, 4.00 and 6.00 mmol dm^{-3} SDS), in 0.0100 mmol dm^{-3} SDS solutions which contain SDS micelles (the critical micelle concentration for SDS at 25° is 8 mmol dm^{-3} SDS), in pre-micellar 5.00 mmol dm^{-3} sodium decanoate (SDec) solutions and in methyl red and methyl orange solutions. In each system, 'blank' runs in which the surfactant or dye was omitted but Na^+ ion was present in the form of NaCl(aq) were also examined for sodium ion activity changes as β-CD was added. The results are shown in Figures 1–3. Of the three pre-micellar SDS systems only the 2.00 mmol dm^{-3} SDS system is displayed since all three showed similar effects.

It is clear from the 'blank' runs that Na^+ ion does not interact appreciably with β-CD as there is no detectable change in Na^+ ion activity when β-CD is added to

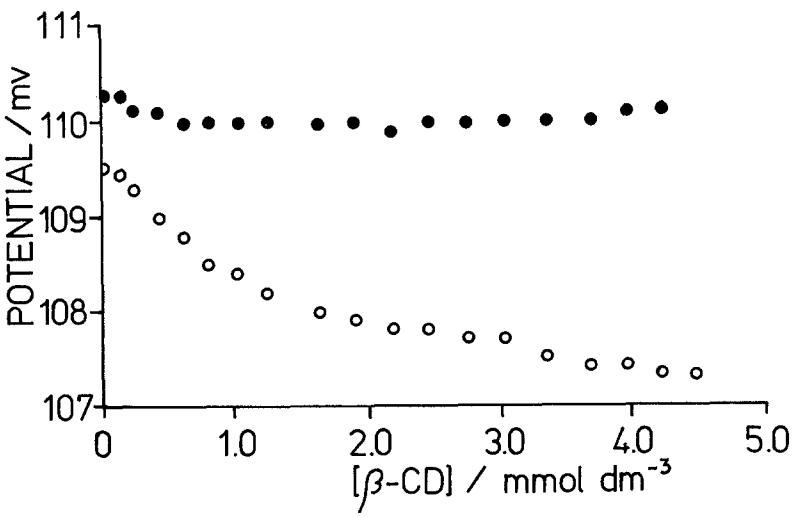

Fig. 1. Sodium ion electrode readings in 2.00 mmol dm^{-3} NaCl (●) and in 2.00 mmol dm^{-3} SDS (○) with added β-CD.

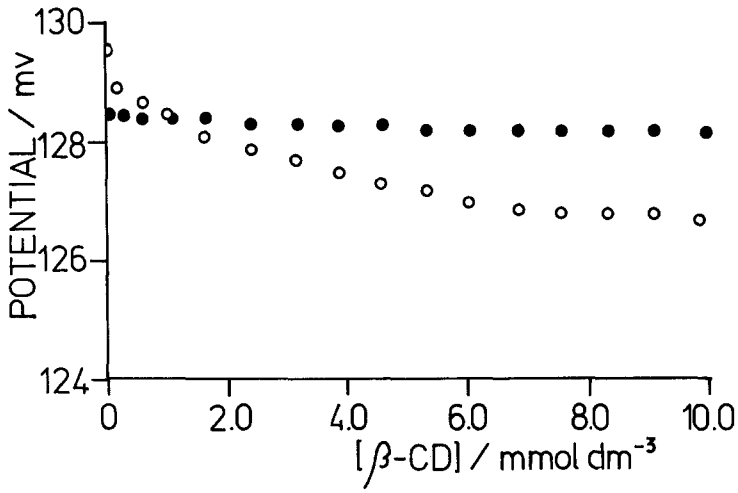

Fig. 2. Sodium ion electrode readings in 5.00 mmol dm^{-3} NaCl (●) and in 5.00 mmol dm^{-3} SDec (○) with added β-CD.

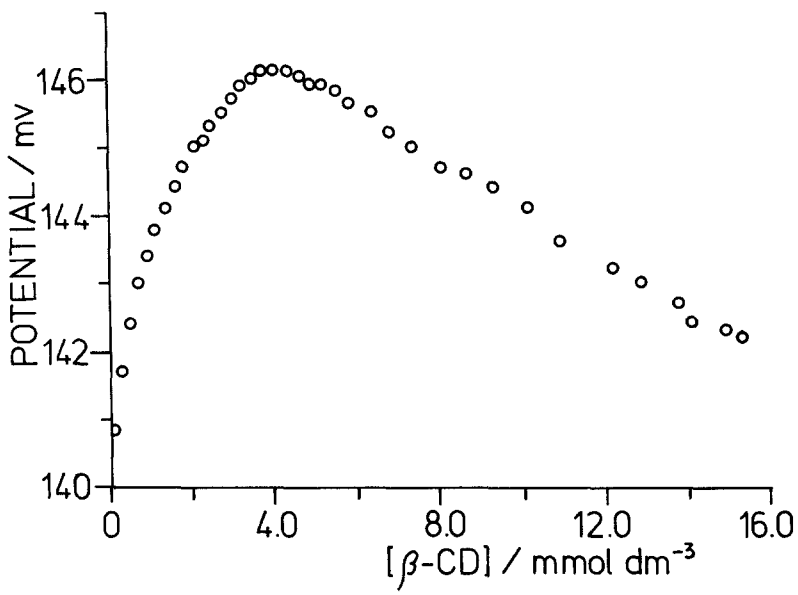

Fig. 3. Sodium ion electrode readings in 0.0100 mol dm^{-3} SDS with added β-CD.

NaCl solutions (Figures 1–3). However, when β-CD was added to aqueous solutions of the surfactants SDS or SDec below their respective critical micelle concentrations, there was a gradual decrease in the Na^+ ion activity to more or less a constant value. It is also significant that the beginning of the plateau in the potential corresponded roughly in β-CD concentration to a 1 : 1 stoichiometry with the surfactant (Figures 1, 2). As with the conductometric results in these systems,

where a similar break was noted at the same ratio [5, 6], the interpretation of this result is that the principal inclusion complex being formed is 1 : 1 β-CD/surfactant. The surfactant sodium perfluorooctanoate also exhibited this behavior in Na^+ ion activity [8].

From the above, it can be seen that the removal of free Na^+ ion from solution only occurred when both β-CD and surfactant were present in solution. Both SDS and SDec complex strongly with β-CD [5, 6]. Presumably the 'bound' Na^+ ion is held electrostatically by the included surfactant monomeric ion in essentially a trimolecular inclusion complex.

Above the critical micelle concentration, the β-CD concentration dependence of the Na^+ activity for sodium dodecylsulfate rises initially but then decreases as found in pre-micellar surfactant concentrations (Figure 3). The maximum in the curve for 0.0100 mol dm^{-3} SDS is recognized as the β-CD concentration (4.1 mmol dm^{-3} β-CD) required for SDS to have a critical micelle concentration at 0.0100 mol dm^{-3} in the presence of β-CD [5]. In other words, the critical micelle concentration for SDS in the presence of 4.1 mmol dm^{-3} β-CD is 0.0100 mol dm^{-3} SDS. The additions of β-CD first destroy the micelles by sequestering the monomeric surfactant and upsetting the monomer-micelle equilibria. This releases Na^+ counterion from the micelles and the Na^+ ion activity in solution then increases. When sufficient β-CD has been added to destroy all the micelles, there is no further release of Na^+ ion into solution and the potential then peaks because further β-CD addition will simply generate more 1 : 1 β-CD/SDS inclusion complexes with the same Na^+ ion binding as observed in pre-micellar solutions. Presumably the original rise in Na^+ ion activity in Figure 3 is tempered by the binding of some Na^+ ion to the inclusion complex being formed on β-CD titration. The decrease in conductivity that had been previously observed beyond the critical micelle concentration in this system [5] can now be seen to be due not only to surfactant ions being complexed with β-CD but also with some Na^+ ions being bound in some fashion with the resultant complexes.

To test whether Na^+ ion binding to anionic guests was a general phenomenon or specific only to anionic surfactants, Na^+ ion activities were monitored in 1.00 mmol dm^{-3} methyl orange solutions at pH 8 where both dyes are anionic [13]. Both dyes were added as their sodium salts. Both dyes form complexes with β-CD [14]. Methyl orange in anionic form more closely resembles the SDS anion because the 'polar head' is a sulfonate group in the terminal position (para to the diazo link between the benzene groups). Thus, in their inclusion complexes, both SDS and methyl orange should have their negatively charged centres in relatively the same positions *vis à vis* accessibility to Na^+ ion. On the other hand, the location of the carboxylate group, the site of the negative charge, in the structurally similar methyl red molecule is ortho to the diazo link and could conceivably be more protected from Na^+ attack in the β-CD/methyl red complex. However, titration with β-CD led to no changes in Na^+ ion activity in either dye system (Figure 4). Although these two examples can hardly be said to have proved the case, the negative results suggest that the guest must be a surfactant anion or some anion more closely simulating a surfactant monomer than methyl orange resembles a surfactant in order for Na^+ ion binding to occur with the inclusion complex.

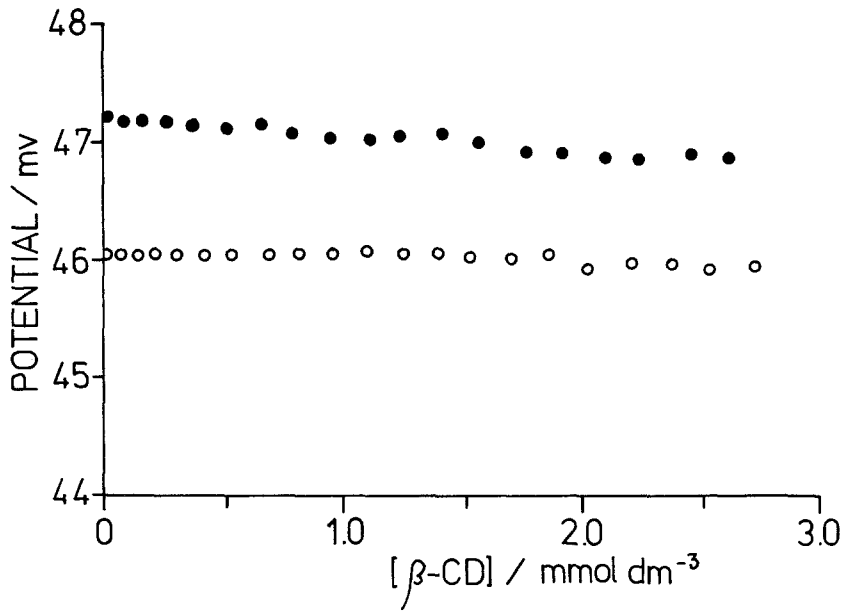

Fig. 4. Sodium ion electrode readings in 1.00 mmol dm^{-3} methyl red (●) and in 1.00 mmol dm^{-3} methyl orange (○) with added β-CD.

Sodium-23 NMR studies were conducted on these systems with a Varian XL-100 instrument in the hope that the exchange between bound Na^+ and free Na^+ would be slow enough to give rise to two peaks in the spectrum or, if only one peak did appear, it would be modified sufficiently in width or in frequency so as to yield more information about the site and relative importance of bound Na^+. However, within instrumental accuracy, no change in peak characteristics could be discerned in the systems previously investigated potentiometrically. This expectation of a change in spectrum was probably unrealistic since the proportion of bound Na^+ to free Na^+ must be quite small. After all, the decreases in potential that had occurred on Na^+ binding in the pre-micellar SDS and SDec systems had been only of the order of 1–2%.

To examine whether this phenomenon had its counterpart in electrolytic anions binding to inclusion complexes of β-CD with cationic surfactants, potential measurements were undertaken with a chloride selective electrode in pre-micellar 5.00 mmol dm^{-3} dodecylammonium chloride (DDAC) solutions to which β-CD had been added. DDAC forms a strong 1 : 1 complex with β-CD additions up to 0.01 mol dm^{-3} β-CD [5]. The resulting pH-type curve (Figure 5) showed an inflection at 5 mmol dm^{-3} β-CD or at a stoichiometric ratio of 1 : 1 β-CD to DDAC. The chloride ion activity is in the opposite sense to the measured potential so that on the formation of the 1 : 1 complex the concentration of Cl^- ion in solution is seen to decrease markedly to a plateau value. Chloride ion does bind weakly with cyclodextrins with an association constant of about 2 [9], but this hardly accounts for the 50% drop in Cl^- ion concentration that had been observed.

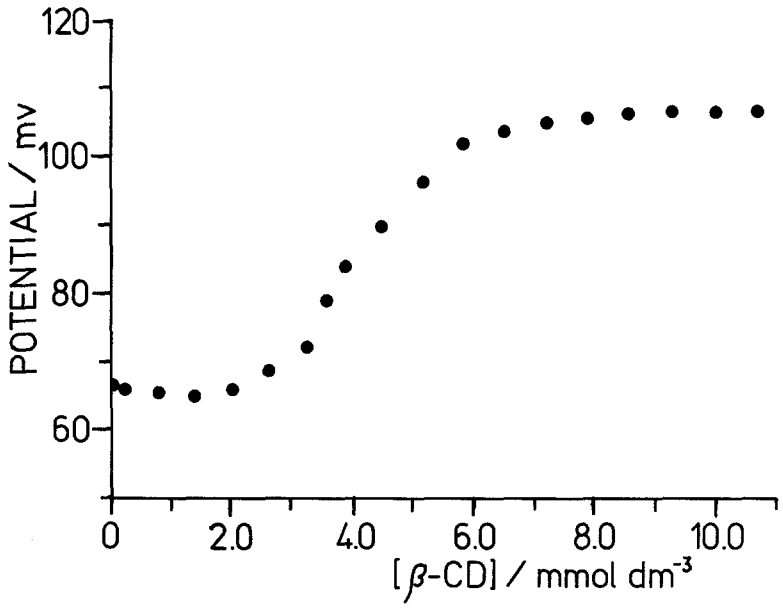

Fig. 5. Chloride ion electrode readings in 5.00 mmol dm^{-3} DDAC solutions with added β-CD.

In fact, when potential measurements were made in 5 mmol dm^{-3} NaCl solutions and only β-CD was added, no change in Cl^- ion activity was detected. As with the Na^+ ion binding situation, Cl^- ion binding in the presence of DDAC/β-CD may be due to the formation of a trimolecular inclusion complex involving the simple ion, the surfactant ion and the cyclodextrin molecule. The much more dramatic changes observed in Cl^- ion activity suggest that indeed simple anions may be more easily induced into this *ménage à trois* than are simple cations. Studies with various specific ion electrodes are now underway to determine the extent of complicity of different cations and anions in this interaction with inclusion complexes.

Acknowledgements

We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support and for Summer Research Scholarships to Y.E.M.

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