

Studies of the Interaction of Poly(ethylene oxide) with Sodium Dodecyl Sulfate by Gel Filtration

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The interaction between poly(ethylene oxide) (PEO), with a molecular weight of 6000, and sodium dodecyl sulfate (SDS) was studied by the gel-filtration method. The elution curve of the PEO-SDS system showed a tail of the elution volume smaller than that of SDS micelles at a concentration larger than about 4 mmol dm⁻³. This suggests that the PEO-SDS (PS) complex is formed in the system. The dissolution-state diagram in the presence of PEO was then constructed in which the fractions of SDS single ions, SDS micelles, and the PS complex were shown against the SDS concentration. For a constant concentration of PEO, the molecular weight of the PS complex increased with the increase in the concentration of SDS up to the CMC of the PEO-SDS system, beyond which it became constant. The molecular weight of the PS complex was estimated to decrease from 21000 at 0.025 wt% PEO to 15000 at 0.2 wt% PEO.

The interaction of poly(ethylene oxide) (PEO) with sodium dodecyl sulfate (SDS) has been studied by the measurements of: (1) the equilibrium dialysis,¹⁾ (2) the electrical conductance,^{2,3)} (3) the surface tension,^{2,3)} (4) the viscosity,²⁾ and (5) the solubilization.³⁾ (1) is a direct method of detecting the change in molecular size; however, it requires a long time to attain an equilibrium and also needs a supporting electrolyte of a concentration sufficient to suppress the Donnan effect, while from (2) to (5) are indirect methods. The band-gel-filtration method adopted in the present study offers a simple and direct method of measuring PEO-SDS interaction free from any supporting electrolyte. Using this method, two of the present authors have previously reported the interaction between poly(vinyl acetate) and SDS.⁴⁾ The present paper reports the studies of the interaction between PEO and SDS.

Experimental

Materials. Commercial pure-grade SDS previously recrystallized from ethanol was refluxed with charcoal in ethanol, filtered, and recrystallized. The purified sample showed no minimum in the surface tension *vs.* concentration curve. The PEO used was a commercial pure-grade substance with the mean molecular weight of 6000; it was dissolved in methanol, precipitated by the addition of diethyl ether, filtered, and dried. The gel used for packing the column was Sephadex G 100 produced by Pharmacia.

Apparatus and Measurement. Gel-filtration apparatus used is shown in Fig. 1. Gel column used was 30 cm in length and 1.2 cm in inner diameter. For the measurement, sample solution of 30 cm³ was introduced in the gel column, eluted with water and the elution curve was obtained by the conductometry. The flow rate was about 0.5 cm³ min⁻¹. The measurement was made in an air thermostat at 30±0.5 °C.

Results and Discussion

Figure 2 is the elution curve showing the conductance *vs.* elution volume for the SDS solution. In this figure, Curve 1 is the elution curve of the SDS solution below the CMC. The curve shows a single tail, S, and a conductance plateau, κ_s . The elution volume of the tail and the height of plateau, corresponds to the size and the concentration respectively, of SDS single ions. Curve 2 in Fig. 2 is the elution curve of the SDS solution

above the CMC. Here, the elution tail consists of two steps, S' and M, which correspond to the sizes of single ions and micelles, while the heights of the two plateaux, κ_{cmc} and κ_m , correspond to the concentrations of single ions at the CMC and micelles respectively.

Figure 3 shows the elution curve of the PEO-SDS system for constant PEO and various SDS concentrations. Here, Curve 1 indicates the elution curve of the solution containing SDS below 4 mmol dm⁻³. The curve shows a tail of a single step, S, and a corresponding single conductance plateau κ_s . Above 4 mmol dm⁻³ up to a certain concentration which is later identified as the CMC of the PEO-SDS system, the type of elution curve as represented by Curve 2 with tail of two steps, S' and C, and two conductance plateaux,

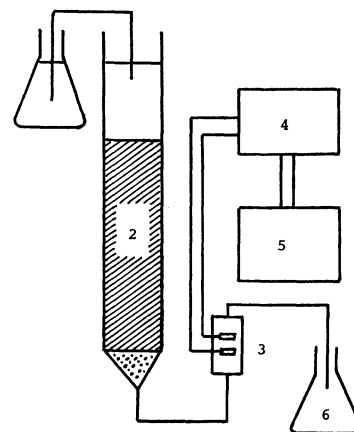


Fig. 1. Gel filtration apparatus.

1; Reservoir, 2; gel column, 3; conductance cell, 4; conductometer, 5; recorder, 6; weighing vessel.

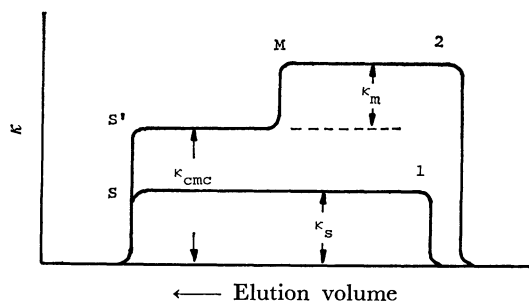


Fig. 2. Elution curve of SDS system.

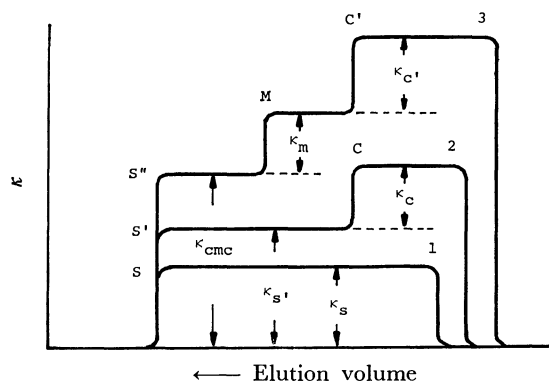
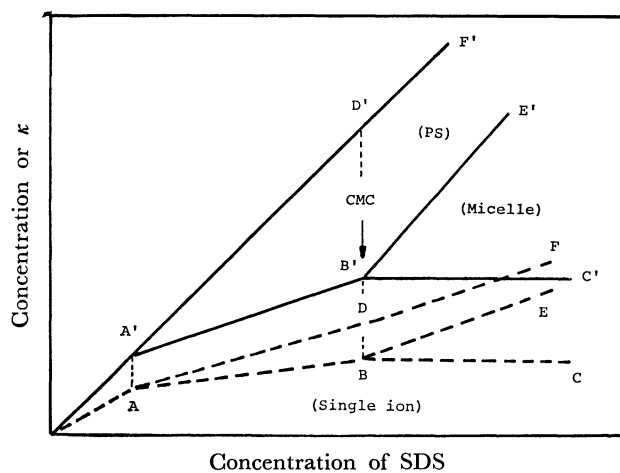


Fig. 3. Elution curve of PEO-SDS system.

Fig. 4. Phase diagram of PEO-SDS system.
—; Concentration, ----; κ .

κ_s , and κ_c , was observed. At a higher concentration of SDS beyond the CMC, Elution Curve 3 was obtained. Here, the elution tail showed three steps, S'' , M , and C' , and three conductance plateaux, κ_{cmc} , κ_m , and $\kappa_{c'}$.

Now, when we compare these three curves, 1, 2, and 3, with Fig. 2, it can be confirmed, that S , S' , and S'' correspond to the tails of SDS single ions, M to the tail of the SDS micelles, and C and C' , to the tails of particles containing SDS and being larger than the SDS micelles. These particles can be regarded as forming the PEO-SDS complex (the PS complex). By plotting the conductances κ_s , κ_m , κ_c , etc., against the total concentration of SDS, the lines in Fig. 4 were obtained. By transforming the conductances into the concentration, the solid lines in Fig. 4 were obtained.

The conductance *vs.* concentration relations for SDS single ions and SDS micelles, as obtained from Fig. 2, were used to convert the conductance values to the concentrations of the single ionic and micellar SDS. The concentration of the PS complex was obtained as the difference between the total concentration of SDS and the sum of the concentration of the SDS single ions and micelles.

The solid lines in Fig. 4 show the range of the regions of the SDS single ions the SDS micelles, and the PS complex; that is, the area below the $OA'B'C'$ line

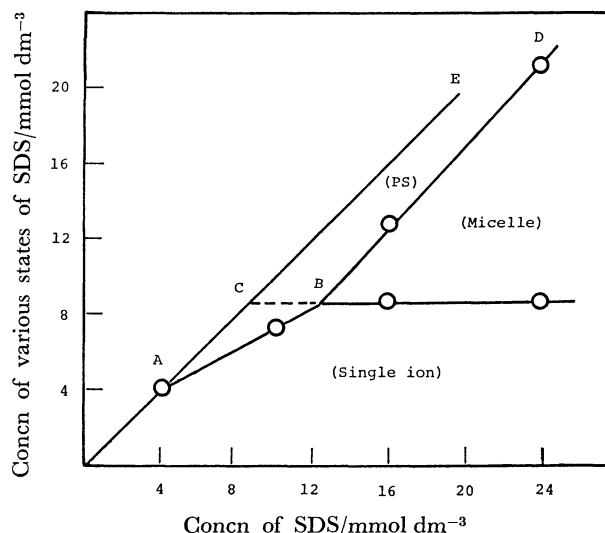


Fig. 5. Phase diagram of PEO-SDS system (0.05wt% PEO).

is the region of single SDS ions, the $E'B'A'F'$ area the region of the PS complex, and the $E'B'C'$, the region of the SDS micelles. Below the point A' , the SDS is exclusively in the state of single ions not combined with PEO. Between A' and B' , free SDS single ions and the SDS complex are in a mutual equilibrium. In the region above the point B' , SDS micelles appear in the solution in addition to the PS complex and free SDS single ions. The concentration of SDS single ions was constant in this region and was equal to the CMC of the pure SDS solution. This suggests that the point B' is the CMC of the PEO-SDS system.

In such a manner, we can construct a diagram of the dissolution state of the SDS. Four such diagrams were obtained for SDS solutions containing 0.025, 0.05, 0.1, and 0.2 wt% of PEO. Figure 5 shows the results obtained for the SDS solution containing 0.05 wt% PEO. The concentration of SDS at point A is 4 mmole dm^{-3} . This concentration was almost independent of the concentration of PEO, except for the lowest concentration of 0.025 wt% PEO, where the point A shifted to 6 mmole dm^{-3} . This tendency is in accord with the results obtained by Jones.²⁾ The amount of SDS bound to PEO, which was estimated as the ordinate between lines AB and AC , increased from point A to B , which may suggest an increase in the size of the PS complex. This is in accord with the decrease in the elution volume from 23.0 cm^3 to 18 cm^3 , for instance, for the 0.1 wt% PEO system. Beyond point B , the size of the PS complex became nearly constant, as judged from the constancies of the elution volume and the ordinate between BD and CE in this region in Fig. 5, although, according to Jones,²⁾ it is uncertain whether or not the size of the complex beyond point B continues to increase by the further binding of SDS.

The maximum amount of SDS bound to PEO can be calculated from the difference in the concentration of SDS between points B and C and the concentration of PEO. The calculated binding ratio de-

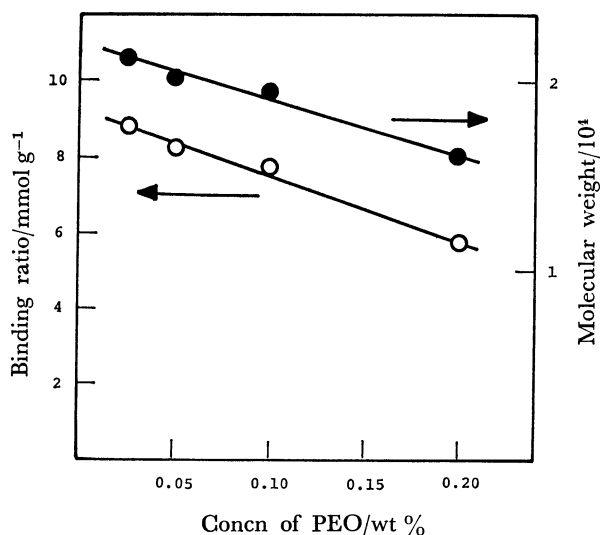


Fig. 6. Binding ratio and molecular weight of PEO-SDS complex.

creased with an increase in the PEO concentration, as is shown by the open circles in Fig. 6. The decrease in the SDS binding ratio agrees with the increase in the elution volume of the PS complex with

the PEO concentration.

In Fig. 6, the maximum binding ratio at 0.1 wt% PEO is 7.7 mmol SDS/g PEO. This is comparable with the value of about 9 mmol SDS/g PEO in the presence of 1 mol dm⁻³ sodium chloride, as estimated from the equilibrium dialysis results obtained by Shirahama.¹⁾

In the present study, the absolute size of the PS complex was not estimated by comparing the elution volume to that of the standard-molecular-weight substances. However, from the known weight ratio of SDS to PEO shown in Fig. 6 and the mean molecular weight 6000 of PEO, the molecular weight of the PS complex at CMC was calculated to be as shown by the solid circles. The molecular weight decreased from about 21000 at 0.025 wt% PEO to 15000 at 0.2 wt% PEO, as may be seen in the figure.

References

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