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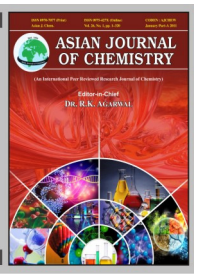

Poly(vinyl pyrrolidone)-Sodium *bis*(2-ethylhexyl)sulfosuccinate Complex as Probe to Study the Inclusion Complex of β-Cyclodextrin with Sodium *bis*(2-ethylhexyl)sulfosuccinate in Aqueous Solution

XIAOMING CHEN[1,2]

[1]Department of Polymer Materials and Engineering, Anhui Jianzhu University, Hefei 230601, P.R. China
[2]School of Chemistry and Chemical Engineering & Anhui Province Key Laboratory of Environment-Friendly Polymer Materials, Anhui University, Hefei 230039, P.R. China

Corresponding author: E-mail: chenxmyn@hotmail.com

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Poly(vinyl pyrrolidone) (PVP)-sodium *bis*(2-ethylhexyl) sulfosuccinate (AOT) complex has been used as a viscosity probe to study the inclusion complexation between β-cyclodextrin (β-CD) and AOT. Viscosity measurements show that the inclusion complexation between β-cyclodextrin and AOT may cause the AOT molecules being stripped off the PVP chains, resulting in the decrease of the solution viscosity due to the decaease of electrostatic repulsion between polymer-bound AOT micelles. The viscosity minimum at $C_{\beta\text{-CD}}/C_{AOT} = 1$ indicate the molecular ratio of host molecule to guest molecule is 1:1 in the β-CD/AOT inclusion complex.

Keywords: Poly(vinyl pyrrolidone), Sodium *bis*(2-ethylhexyl)sulfosuccinate, β-cyclodextrin, Viscosity.

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides of six to eight glucose units linked by α-1,4 linkages, which are called α-, β- and γ-cyclodextrin, respectively. They have a toroidal, truncated, cone shape, with an apolar, hydrophobic interior and two hydrophilic rims, formed by the primary (narrow rim) and secondary (wider rim) OH groups[1]. The commercial utility and scientific interest in cyclodextrins arises because of their ability to form stable inclusion complexes with a wide variety of inorganic and organic guest molecules[2,3].

Surfactants are a kind of suitable guest molecule and their many physical and chemical properties can be changed with the addition of cyclodextrins. Compared with α-cyclodextrin and γ-cyclodextrin, β-cyclodextrin is studied more widely because its interior diameter fits many more guest molecules, such as the hydrocarbon chains of surfactants[4].

To assess the basics of the host-guest inclusion complexes formed by cyclodextrins and guest molecules, determinations of the molecular ratio of host molecule to guest molecule is essential. A set of experimental techniques have been used to study the inclusion complexation such as surface tention[5,6], conductivity[1,7], NMR[8], fluorescence spectroscopy[9] and isothermal titration calorimetry (ITC)[10]. The primary disadvantage of such techniques is that they are time-consuming and need special testing equipments. Comparatively, Ubbelohde viscometer is a type of easily accessible equipment which is commonly used to study the viscosity of either polymer or surfactant solutions. However, the inclusion complexation between cyclodextrins and surfactants may not result in a significant change in the solution viscosity and therefore Ubbelohde viscometer cannot be used to study the host-guest inclusion complexation effectively as presumed.

If surfactants are dissolved in solvent containing a certain concentration of the flexible polymer which interacts strongly with surfactants, the inclusion complexation between cyclodextrins and surfactants in solution will have a great influence on the polymer chain dimention in solution. As a result, the viscosity of solution may have a change enough to be detected by Ubbelohde viscometer. On such an occasion, the polymer-surfactant acts essentially as a sensor by which the inclusion complexation between cyclodextrins and surfactants in solution, including the molecular ratio of host molecule to guest molecule, can be identified with the aid of Ubbelohde viscometer.

In the present study the flow time t_0 of pure water was measured and taken as the reference. The flow time t of β-cyclodextrin in poly(vinyl pyrrolidone)-sodium *bis*(2-ethylhexyl) sulfosuccinate (AOT) mixed solution was measured, respectively by the volume concentrating method. The relative viscosity of β-cyclodextrin in PVP- AOT mixed solution, used for indicating the inclusion complexation between β-cyclodextrin and AOT in solution, was determined by t/t_0, neglecting the kinetic energy correction and fluid density correction as performed in our previous studies.

EXPERIMENTAL

Poly(vinyl pyrrolidone) sample employed is a commercial product of Sigma Chemical Company. The average molecular weight is 3.6×10^5. Anionic surfactant sodium *bis*(2-ethylhexyl) sulfosuccinate is purchased from Alfa Aesar (96 %), has been purified by the method described in reference[11] and β-cyclodextrin (purity > 99 %) is from Shanghai (China) Yuanju Biology Technique Company. De-ionized distilled water was used in all experiments here.

All viscosity measurements were carried out using a conventional Ubbelohde capillary viscometer(inner diameter φ = 0.55 mm) at 30 ± 0.1 ºC maintained with a thermostatic water bath. Measurements were initiated after 5-10 min equilibrium time. Each flow time was determined by repeating at least three time measurements. The precision of the measurements was 0.01 s and the reproducibility was 0.2 s. The viscometer was thoroughly cleaned with concentrated chromic acid and de-ionized distilled water after each experiment.

The detailed experimental procedures were as follows. Two stock solutions were prepared, both containing the desired concentrations of PVP and AOT. A high concentration of β-cyclodextrin was also included in one of the solutions. Known quantities of the stock solutions were mixed to give any desired concentration of β-cyclodextrin. This procedure was used for all experiments in which it was desired to vary the β-cyclodextrin concentration systematically. In contrast, the method to determine the relative viscosity presented here is somewhat opposite to the volume diluting method. We referred to the technique presented here, therefore, as the volume concentrating method.

RESULTS AND DISCUSSION

Fig. 1 shows the plot of the relative viscosity η_r of AOT in water and in PVP solution at 30 ºC. It is well accepted that surfactant molecules, above a critical aggregation concentration (CAC), interact with polymers and form micelle-like aggregates with them. The CAC is usually considerably lower than the critical micelle concentration (CMC) of the corresponding surfactants in the absence of polymer. A pronounced enhancement of the solution viscosity is one of the consequences of the strong interactions between polymers and surfactants[12]. From Fig. 1 it can be seen that when $C_{AOT} > 1$ mmol/L the relative viscosity of 0.001 g/mL PVP aqueous solution increases sharply with the increase of the concentration of AOT due to the electrostatic repulsive force between the bound AOT micelle-like aggregates on polymer chains. Therefore the critical aggregation concentration (CAC) which indicates the beginning of binding of surfactants to polymer chains is 1 mmol/L here. When $C_{AOT} > 4$ mmol/L the relative viscosity of PVP aqueous solution decreases slightly due to the electrostatic screening introduced by excess AOT ions.

Complexes between PVP and AOT with $C_{AOT} > CAC$ were selected here to determine the inclusion complexation between β-cyclodextrin and AOT to ensure the change of solution viscosity is enough to be detected by Ubbelohde viscometer during the process of β-CD/AOT inclusion complexation.

Fig. 2 shows the plot of the relative viscosity η_r of β-cyclodextrin in PVP (0.001 g/mL)-AOT (2.5 mmol/L) mixed solution, water, PVP (0.001 g/mL) solution and AOT (2.5 mmol/L) solution, respectively. Fig. 2 showed that η_r of β-cyclodextrin in pure water increases slightly with the β-cyclodextrin concentration due to the increase of the β-cyclodextrin fraction in the solution.

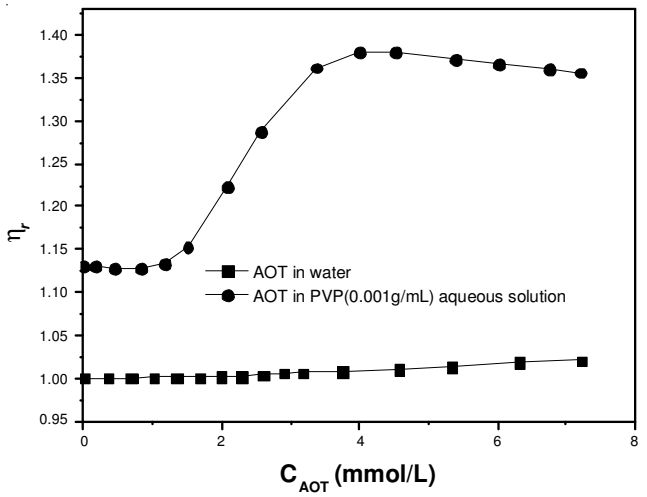

Fig. 1. Relative viscosity η_r of AOT in both water and PVP solution at 30 ºC

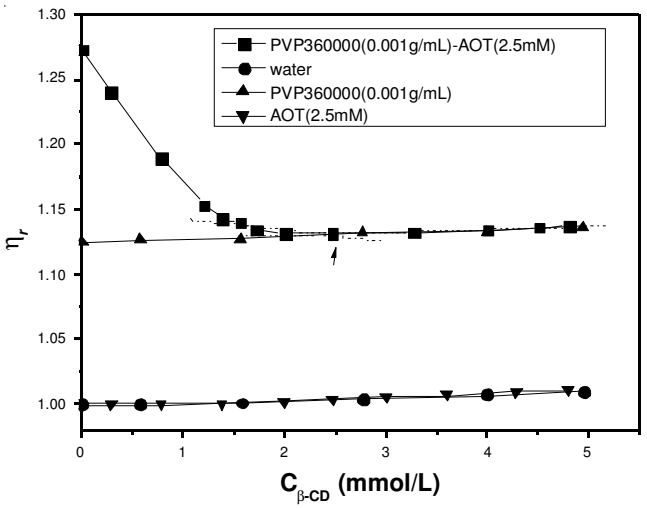

Fig. 2. Relative viscosity η_r of β-cyclodextrin in PVP (0.001 g/mL)-AOT (2.5 mmol/L) mixed solution, water, PVP (0.001 g/mL) solution and AOT (2.5 mmol/L) solution, respectively at 30 ºC

The relative viscosity corresponding to β-cyclodextrin in PVP (0.001 g/mL) solution is almost parallel to the one which is corresponding to β-cyclodextrin in pure water. That means the slight increase of the relative viscosity β-cyclodextrin in PVP (0.001 g/mL) solution is also due to the the increase of the β-cyclodextrin fraction in the solution. As a result the viscometry does not provide support for the complexation between PVP and β-cyclodextrin coincided with the conclusion reported by Horski[13] in the PVP/(2-hydroxypropyl)-β-cyclodextrin system.

The relative viscosity corresponding to β-cyclodextrin in AOT (2.5 mmol/L) solution is almost negligible in the whole concentration range, indicating that the inclusion complexation of β-cyclodextrin and AOT cannot be detected.

Of peculiar interest is that the relative viscosity corresponding to β-cyclodextrin in PVP (0.001 g/mL)-AOT (2.5

mmol/L) mixed solution decreases sharply with the β-cyclodextrin concentration and reaches the minimum approximately at $C_{β\text{-}CD}$ = 2.5 mmol/L = C_{AOT} as can be seen from Fig. 2. This experimental result indicates clearly that the inclusion complexation of β-cyclodextrin and AOT has a great influence on the conformation of PVP chain in solution as presumed.

To gain a better understanding of the origin of relative viscosity minimum at $C_{β\text{-}CD}$ = 2.5 mmol/L = C_{AOT}, we have to interpret why η_r of β-cyclodextrin in PVP (0.001 g/mL)- AOT (2.5 mmol/L) mixed solution decreases sharply with the increase of $C_{β\text{-}CD}$ (Fig. 2). The electrostatic repulsion introduced by bound AOT micelles on PVP chains produce a chain expansion as indicated in Fig. 3. With the addition of β-cyclodextrin to PVP/AOT mixed solutions the inclusion complexation between β-cyclodextrin and AOT occurs. The hydrophobic association between surfactants or surfactants and polymer chains decreases immediately. As a result the bound AOT molecules is continually being stripped off the polymer chains until the polymer becomes free of bound surfactant. The PVP chains, therefore, shrink sharply until the PVP chain reaches the AOT-free chain conformation as indicated in the decrease of the viscosity shown in Fig. 2. The viscosity minimum at $C_{β\text{-}CD}/C_{AOT}$ = 1 indicate the molecular ratio of host molecule (β-cyclodextrin) to guest molecule (AOT) is 1:1 in the β-CD/AOT inclusion complex.

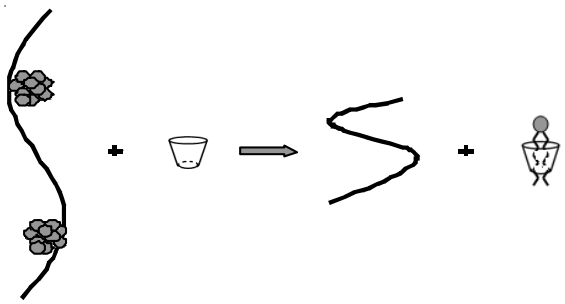

Fig. 3. Schematic interpretation of the inclusion complexation of β-cyclodextrin and AOT in PVP solution

It should be considered that whether the concentration of AOT or PVP in the viscosity probe (the PVP- AOT complex) would influence the inclusion complexation between β-cyclodextrin and AOT or not. Figs. 4 and 5 show the plots of the relative viscosity η_r of β-cyclodextrin in PVP- AOT mixed solution with different AOT concentration and PVP concentration, respectively. It can be seen that with different AOT concentration (1.7, 2.5 and 3 mmol/L) the addition of β-cyclodextrin produces the viscosity minimum at $C_{β\text{-}CD}$ = 1.7, 2.5 and 3 mmol/L, respectively, which is equal to C_{AOT} accurately. Furthermore results of Fig. 5 show that the inclusion complexation of β-cyclodextrin and AOT would not be influenced by polymer concentration. In each experiment the viscosity minimum at $C_{β\text{-}CD}/C_{AOT}$ = 1 indicate the molecular ratio of host molecule (β-cyclodextrin) to guest molecule (AOT) is 1:1 in the β-CD/AOT inclusion complex. Results from our experiments presented in this study indicate convincingly that the molecular ratio of host molecule to guest molecule in the host-guest inclusion complexes formed by β-cyclodextrin and surfactants can be determined by viscosity measurement.

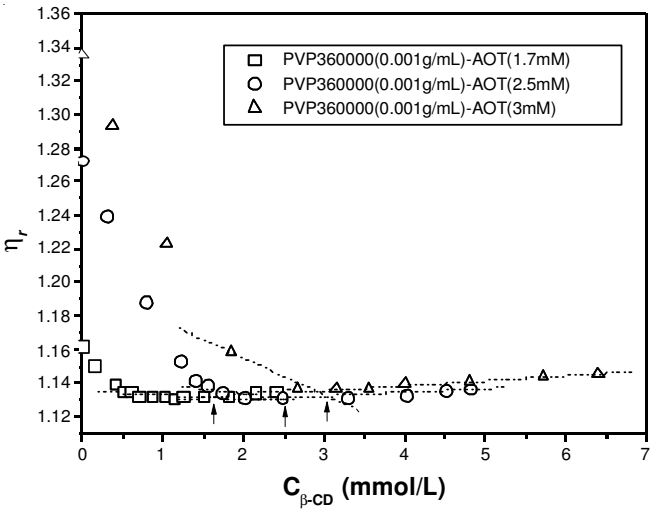

Fig. 4. Relative viscosity η_r of β-cyclodextrin in PVP (0.001 g/mL)-AOT mixed solution with different AOT concentration at 30 ºC

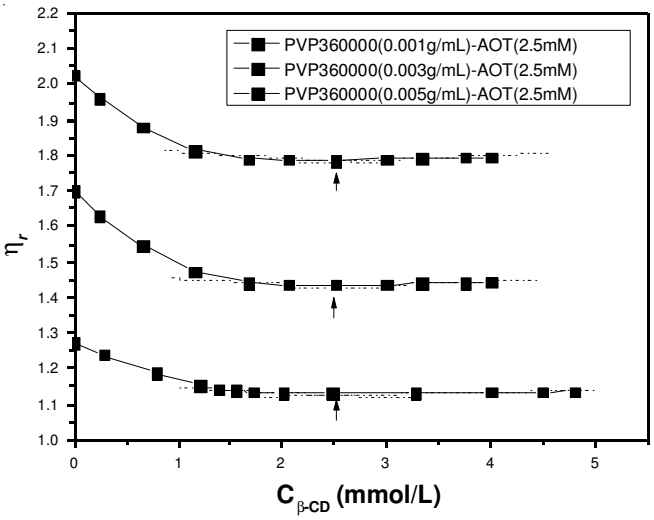

Fig. 5. Relative viscosity γ_r of β-cyclodextrin in PVP- AOT (2.5 mmol/L) mixed solution with different PVP concentration at 30 ºC

Conclusion

The results presented in this study indicate convincingly that the molecular ratio of host molecule to guest molecule in the host-guest inclusion complexes formed by β-cyclodextrin and surfactants can be determined by viscosity measurement. PVP-AOT complex has been used as a viscosity probe to study the inclusion complexation between β-cyclodextrin and AOT. Viscosity measurements show that the inclusion complexation between β-cyclodextrin and AOT may cause the AOT molecules being stripped off the PVP chains, resulting in the decrease of the solution viscosity due to the decaease of electrostatic repulsion between polymer-bound AOT micelles. The viscosity minimum at $C_{β\text{-}CD}/C_{AOT}$ = 1 indicate the molecular ratio of host molecule to guest molecule is 1:1 in the β-CD/AOT inclusion complex.

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