ARTICLE

Using PVP/SDS Complex as a Probe to Study the Inclusion Complex of β-cyclodextrin with SDS in Aqueous Solution

Xiao-ming Chen, Hai-yang Yang*, Ping-sheng He

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on June 18, 2009; Accepted on September 16, 2009)

PVP/SDS complex was applied as a probe to study the interaction between β-cyclodextrin (β-CD) and sodium dodecyl sulfate (SDS) in aqueous solution. It has been found that a critical concentration, namely c_s, exists in the relative viscosity of solution containing PVP/SDS complex versus β-CD concentration plot. As the β-CD concentration is less than c_s, the relative viscosity of solution decreases sharply by adding β-CD into solution successively. On the other hand, as the β-CD concentration is greater than c_s, the relative viscosity of solution increases gradually by adding β-CD into solution. The decrease of the relative viscosity of solution containing PVP/SDS in the presence of β-CD is just due to the inclusion complex of β-CD with the guest molecule SDS. And, this inclusion interaction takes down SDS from the PVP chains in solution. The ratio of the host molecule β-CD to the guest molecule SDS can be calculated from c_s. In our experiment the inclusion ratio of β-CD to SDS is 1/1. The further experimental results indicate that c_s is associated with SDS but free from PVP in PVP/SDS complex. However, the inclusion ratio of β-CD to SDS has proved to be independent of either SDS or PVP in PVP/SDS complex.

Key words: PVP/SDS complex, β-cyclodextrin, Relative viscosity, Inclusion ratio

I. INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides formed by 6 to 8 glucose units linked by α-1,4 glucosidic bond, and the cyclodextrins with 6, 7 and 8 glucose units are usually called α-, β-, and γ-CD, respectively. Due to being chair conformation for every glucopyranoside unit, the CD molecular structure is a truncated cone shape with a cavity in it. All HO- groups located two and three places in glucose units are in the wider end (secondary or wider rim) of the truncated cone, and all HO− groups located six places in glucose units are in the narrower end (primary or narrow rim) of the truncated cone [1]. CDs interior surface consists of H-atoms located in C3 and C5 and O-atom located in glucosidic bond, thus there exists a hydrophobic environment. On the other hand, the outside of CDs exists hydrophilic due to mass of OH groups as indicated in Fig.1. The amphoteric unique in CDs structure makes it, as being a host, be capable to include guest hydrophobic compound [2,3].

Surfactants with hydrophobic chain and polar end groups are a kind of suitable guest molecules which can form inclusion complex with CDs, the β-CD in particular, because the interior diameter of β-CD is fit for a variety of surfactants with different hydrophobic tails [4]. The physical picture reflecting inclusion between CDs and guest molecules can be studied by measuring the inclusion ratio of host molecular CDs to guest molecules. So far a great number of techniques such as surface tention [5,6], conductivity [7], NMR [8], fluorescence spectroscopy [9], and isothermal titration calorimetry (ITC) [10] have been developed to study the inclusion complexs of CDs with organic guest molecules such as surfactants. The disadvantage of such techniques is that they are time-consuming and need special testing equipments. It is well known that the complex of macromolecules with small organic molecules such as surfactants can be studied effectively and conveniently by the viscosity measurement [11–22]. However, CDs are not the macromolecules and the effect of CDs upon

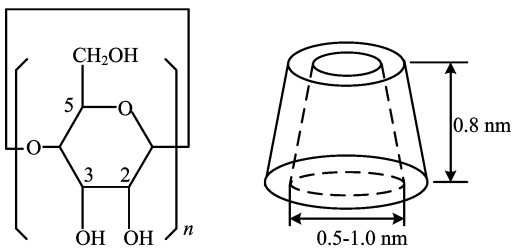

FIG. 1 Structure of cyclodextrin. α-cyclodextrin with n=6, β-cyclodextrin with n=7, and γ-cyclodextrin with n=8.

*Author to whom correspondence should be addressed. E-mail: yhy@ustc.edu.cn

the viscosity of solution is negligible, even if CDs form inclusion complex with the guest molecules.

In this work, we present a new technique by which the inclusion complex of β-CD with the guest molecules can be studied effectively. According to the new technique the macromolecules are selected to form complex with the guest molecules. In case that the guest molecules are taken down from the macromolecules by β-CD, the conformation of macromolecules will change considerably and the viscosity of the investigated solution will decrease significantly. As a result, the inclusion complex of β-CD with the guest molecules can be studied by the viscosity measurement. On such an occasion the complex of macromolecules with the guest molecules acts essentially as a "viscosity probe" which can be applied to detect the inclusion complex of CDs with the guest molecules. With selected poly(vinyl pyrrolidone) (PVP)/sodium dodecyl sulfate (SDS) complex as the probe, the inclusion complex of β-CD with SDS is studied thoroughly as presented in this work.

II. EXPERIMENTS

PVP with average molecular weight of 3.6×10^5 was purchased from Sigma Chemical Company. SDS with the purity greater than 99.9% was obtained from Second Chemical Company (Xuzhou, China). β-cyclodextrin with the purity greater than 99.9% was obtained from Yuanju Biology Technique Company (Shanghai, China). All the samples were used as received without any further purification. De-ionized distilled water was used in all experiments here.

The viscosity measurements were carried out using a conventional Ubbelohde capillary viscometer that was placed in a thermostatically controlled bath with a precision of 0.01 °C. Measurements were initiated after approximately 10 min equilibrium time. The flow times were determined from an average of several readings (more than 5 readings). The relative viscosity η_r was calculated from $\eta_r=t/t_0$ with t and t_0 as the flow time of the solution and the pure water, respectively, neglecting the difference of the density between the solution and the solvent as performed in our previous studies [22–26].

In order to study the inclusion ratio of β-CD to guest molecule SDS, two stock solutions, namely solution A and solution B respectively, were prepared. Both solution A and solution B contain the same concentration of PVP and SDS. The main difference between the two stock solutions is that solution A contains the excess concentration of β-CD whereas solution B contains none of β-CD. By changing the volume ration of solution A and B, the ratio of β-CD to guest molecule SDS varies accordingly. In our experiment, solution B with the volume of 10 mL was put into the viscometer first. Having measuring the flow time of solution B, the solution A with different volumes was added into the viscometer and the flow time of the mixed solution was measured respectively.

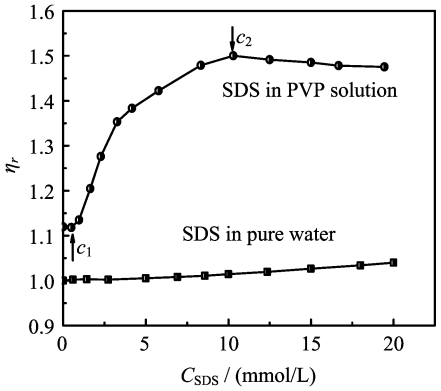

FIG. 2 The relative viscosity η_r of SDS in water and PVP solution at 30°C. The concentration of PVP is 1 g/L.

III. RESULTS AND DISCUSSION

Figure 2 shows the relative viscosity η_r of SDS both in the pure water and in the aqueous PVP solution at 30 °C. It can be seen that two critical concentrations, namely c_1 and c_2, exist for SDS in the presence of PVP. The concentration, known as the critical aggregation concentration (CAC), indicates SDS has bound to PVP chains to form PVP/SDS complex. Obviously, the electric repulsion between polymer-supported micelles will produce the expansion of PVP chains in solution. As a result, the relative viscosity η_r increases with increasing concentration of SDS as shown in Fig.2. The maximum of η_r at c_2 indicates the saturation of bound micelles to polymer chains, and the subsequent decrease of the relative viscosity η_r by further addition of SDS is due to the screening of charge interactions by free micelles of SDS in solution. From Fig.2, it can be seen that, to applying PVP/SDS as the "viscosity probe", the desired concentration of SDS should be less than c_2 whereas greater than c_1. In our experiment, the concentration of SDS is selected as 6 mmol/L.

Figure 3 shows the plot of the relative viscosity of β-CD in PVP/SDS solution, PVP solution, SDS solution, and the pure water, at 30 °C respectively. It can be seen that the relative viscosity of β-CD in either PVP or SDS solution increases slightly with increasing the concentration of β-CD. However, our experimental result does not guarantee that there is no interaction between β-CD and PVP (or SDS) in solution. More probably, it is due to that the effect of the interaction between β-CD and PVP (or SDS) upon the viscosity of the solution on such an occasion is negligible. On the other hand, in PVP/SDS solution, the relationship between the relative viscosity and concentration is quite different. From Fig.3, it can be seen that the relative viscosity of β-CD in PVP/SDS solution decreases sharply with increasing β-CD concentration. However, as the concentration of β-CD is greater than c_s, the relative viscosity of β-CD in PVP/SDS solution increases with increasing β-CD con-

DOI:10.1088/1674-0068/22/05/541-544

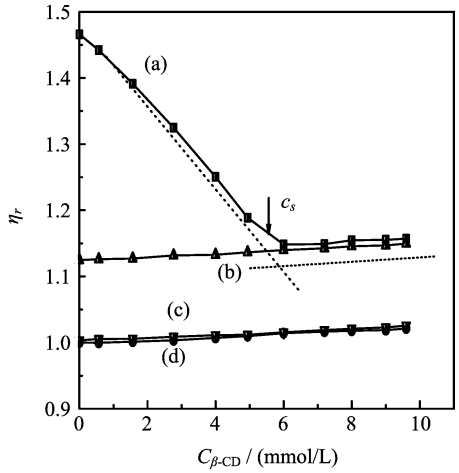

FIG. 3 The relative viscosity η_r of β-CD in PVP/SDS solution (a), in PVP solution (b), in SDS solution (c), and in the pure water (d), respectively at 30 °C.

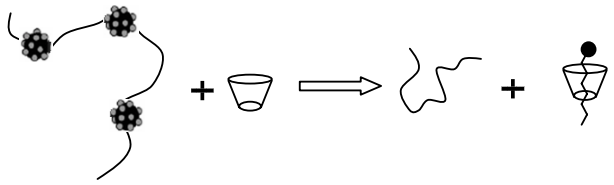

FIG. 4 The schematic interpretation of the effect of inclusion complex of β-CD with SDS upon the conformation of macromolecules in solution.

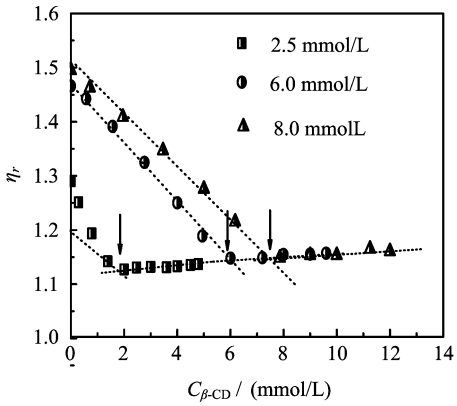

FIG. 5 The relative viscosity η_r of β-CD in PVP/SDS solution at 30 °C. The concentration of PVP is fixed to be 1 g/L. The concentration of SDS is 2.5, 6.0, and 8.0 mmol/L respectively.

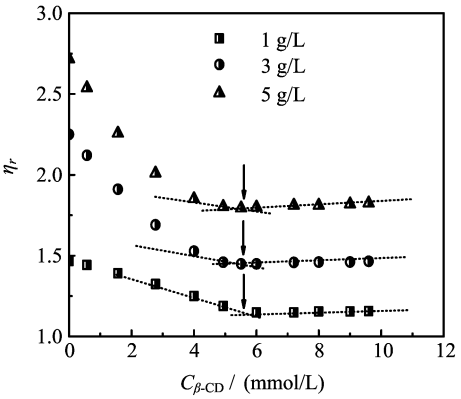

FIG. 6 The relative viscosity η_r of β-CD in PVP/SDS solution at 30°C. The concentration of SDS is fixed to be 6.0 mmol/L. The concentration of PVP is 1, 3, and 5 g/L respectively.

centration, the same as in PVP solution. The reasonable interpretation is that, due to the inclusion complex of β-CD with the guest molecules, SDS is taken down from PVP chains as indicated in Fig.4. As a result, the PVP chains will change back to the conformation in the solution free from SDS. At the critical concentration c_s, the relative viscosity of β-CD in PVP/SDS solution is almost the same as in PVP solution. This suggests that SDS has been almost completely taken down from the PVP chains due to the inclusion complex of β-CD with SDS. We can therefore calculate the ratio of β-CD to the guest molecules SDS from the critical concentration c_s as shown in Fig.3. Our experimental result indicates that the molecular ratio of the host molecule β-CD to the guest molecule SDS is 1/1 approximately.

If the ratio of the host molecule β-CD to the guest molecule SDS is fixed and free from the concentration of either PVP or SDS, the critical concentration c_s will change with the ratio of PVP to SDS accordingly. Figure 5 shows the relative viscosity of β-CD in PVP/SDS solution at 30 °C. In Fig.5 the concentration of PVP is fixed to be 1 g/L, just the same as indicated in Fig.3. On the other hand, the concentration of SDS is selected to be 2.5, 6.0, and 8.0 mmol/L, respectively. From Fig.5, it can be seen that, with the decrease of SDS in PVP/SDS complex, the critical concentration c_s decreases accordingly. However, the ratio of the host molecule β-CD to the guest molecule SDS at the critical concentration c_s keeps the same as expected. Figure 6 also shows the relative viscosity of β-CD in PVP/SDS solution at 30 °C. In Fig.6 the concentration of SDS is fixed to be 6.0 mmol/L but the concentrations of PVP are selected to be 1, 3, and 5 g/L, respectively. Considering that the ratio of the host molecule β-CD to the guest molecule SDS is free from PVP, c_s should independent of the PVP concentration. The experimental results, as shown in Fig.6, verify our assumption completely.

IV. CONCLUSION

We have shown that PVP/SDS complex can be applied as a probe to study the interaction between β-CD and SDS in aqueous solution. Our technique is based on the design that the inclusion complex of β-CD with the guest molecule SDS will take down SDS from the poly-

DOI:10.1088/1674-0068/22/05/541-544

mer chains and change the conformation of the polymer chains accordingly. On such an occasion, the viscosity of solution containing PVP/SDS complex will change significantly. As a result, the interaction between β-CD and SDS in aqueous solution can be detected by the viscosity measurement. PVP/SDS complex, as presented in our new technique, acts essentially as a "viscosity probe" by which the inclusion complex of β-CD with the guest polymer can be studied effectively and conveniently. Our experimental results indicate that a critical concentration, namely c_s, exists in the relative viscosity versus β-CD concentration plot. As the β-CD concentration is less than c_s, the relative viscosity of solution containing PVP/SDS complex decreases sharply by adding β-CD into solution successively. On the other hand, as the β-CD concentration is greater than c_s, the relative viscosity of solution containing PVP/SDS complex increases gradually by adding β-CD into solution. The decrease of the relative viscosity of solution containing PVP/SDS in the presence of β-CD is just due to the inclusion complex of β-CD with the guest molecule SDS. The ratio of the host molecule β-CD to the guest molecule SDS can be calculated from c_s. In our experiment the inclusion ratio of β-CD to SDS is 1/1 approximately. The critical concentration c_s has found to be associated with SDS but free from PVP in PVP/SDS complex. However, the inclusion ratio of β-CD to SDS is independent of either SDS or PVP in PVP/SDS complex.

[1] A. A. Rafatia, A. Bagheria, H. Iloukhania, and M. Zarinehzad, J. Mol. Liq. **116**, 37 (2005).
[2] M. E. Brewster and T. Loftsson, J. Pharm. Sci. **85**, 1017 (1996).
[3] Y. Yin, J. Xie, and G. Diao, Chemistry **72**, 320 (2009).
[4] R. Guo, X. J. Zhu, and X. Guo, Colloid Polym. Sci. **281**, 876 (2003).
[5] U. R. Dharmawardana, S. D. Christian, E. E. Tucker, R. W. Taylor, and J. F. Scamehorn, Langmuir **9**, 2258 (1993).
[6] R. Lu, J. Hao, H. Wang, and L. Tong, J. Colloid Interface Sci. **192**, 37 (1997).
[7] R. Palepu, J. E. Richardson, and V. C. Reinsborough, Langmuir **5**, 218 (1989).
[8] N. Funasaki, H. Yamaguchi, S. Ishikawa, and S. Neya, J. Phys. Chem. B **105**, 760 (2001).
[9] J. W. Park and H. J. Song, J. Phys. Chem. **93**, 6454 (1989).
[10] W. Eli, W. Chen, and Q. Xue, J. Chem. Thermodyn. **31**, 1283 (1999).
[11] N. Jain, S. Trabelsi, S. Guillot, and D. Mcloughlin, D. Langevin, P. Letellier, and M. Turmine, Langmuir **20**, 8496 (2004).
[12] P. C. Griffiths, N. Hirst, A. Paul, S. M. King, R. K. Heenan, and R. Farley, Langmuir **20**, 6904 (2004).
[13] N. Plucktaveesak, A. J. Konop, and R. H. Colby, J. Phys. Chem. B **107**, 8166 (2003).
[14] S. Guillot, M. Delsanti, S. Désert, and D. Langevin, Langmuir **19**, 230 (2003).
[15] D. Zanette, V. Soldi, A. P. Romani, and M. H. Gehlen, J. Colloid Interface Sci. **246**, 387 (2002).
[16] X. Zheng and W. Cao, Eur. Polym. J. **37**, 2259 (2001).
[17] E. Hoff, B. Nyström, and B. Lindman, Langmuir **17**, 28 (2001).
[18] K. Y. Mya, A. M. Jamieson, and A. Sirivat, Langmuir **16**, 6131 (2000).
[19] S. Panmai, R. K. Prudhomme, and D. G. Peiffer, Colloids Surf. A. **147**, 3 (1999).
[20] T. Aubry, M. Moan, J. F. Argillier, and A. Audibert, Macromolecules **31**, 9072 (1998).
[21] J. Fundin, P. Hansson, W. Brown, and I. Lidegran, Macromolecules **30**, 1118 (1997).
[22] J. Li, H. Li, H. Yang, P. Zhu, and P. He, Chin. J. Polym. Sci. **26**, 31 (2008).
[23] Y. F. Yan, H. Z. Li, H. Y. Yang, J. S. Qian, P. P. Zhu, and P. S. He, Chin. J. Chem. Phys. **21**, 169 (2008).
[24] X. Chen, H. Yang, X. You, P. Zhu, and P. He, Chin. J. Polym. Sci. **24**, 437 (2006).
[25] H. Yang, Y. Yan, P. Zhu, H. Li, Q. Zhu, and C. Fan, Eur. Polym. J. **41**, 329 (2005).
[26] H. Yang, S. Zhang, H. Liu, X. Xu, J. Zhang, and P. He, J. Mater. Sci. Lett. **40**, 4645 (2005).

DOI:10.1088/1674-0068/22/05/541-544