

Intermolecular and Intramolecular Association of Poly(ethylene glycol) Mediated by Sodium Dodecyl Sulfate in Dilute Solutions

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In mixed solutions of poly(ethylene glycol) and sodium dodecyl sulphate the aggregation of surfactants with polymer chains strengthens the intermolecular or/and intramolecular hydrophobic junctions, resulting in the intermolecular or/and intramolecular association of poly(ethylene glycol) mediated by sodium dodecyl sulphate. If the polymer concentration $c > 0.017$ g/mL different polymer chains associate together through intermolecular hydrophobic junctions. The reduced viscosity of poly(ethylene glycol) increases as the concentration of sodium dodecyl sulphate increases. On the other hand, if $c < 0.017$ g/mL, the poly(ethylene glycol) chains are almost separated and the intramolecular association of poly(ethylene glycol) through intramolecular hydrophobic junctions dominates. Therefore the reduced viscosity of poly(ethylene glycol) decreases considerably as the concentration of sodium dodecyl sulphate increases.

Key Words: Association, Poly(ethylene glycol), Sodium dodecyl sulphate.

INTRODUCTION

The interaction between ionic surfactants and nonionic water-soluble amphiphilic polymers has gained a growing interest¹⁻⁵ because of the various industrial applications of such systems and their inherently interesting properties. It has been well recognized that the interaction takes place when the surfactant concentration is higher than a value termed the critical aggregation concentration (CAC). Then, the surfactants bind onto the polymers in the form of micelle-like aggregates and cause a chain expansion due to electrostatic repulsions between bound micelles. Upon further addition of surfactant, the dimension of polymer chain reaches maximum at the saturation of binding and then decrease due to the screening of electrostatic repulsions by excess counter ions. The most accepted model for the complex formed between a water-soluble polymer and a surfactant was proposed early by cabane to explain typically the interaction between poly(ethylene oxide) (PEO) and sodium dodecyl sulphate (SDS). According to this model, a fraction of the segments of the polymer chain binds to the micellar surface. Stabilization of the interface between the hydrophobic core of the micelles and water is considered to be a major driving force for polymer-micelle interactions⁶.

The system of poly(ethylene glycol) or poly(ethylene oxide) and anionic surfactant sodium dodecyl sulphate has

been well studied in the past two decades using many different techniques, such as surface tension⁷, ITC⁸, neutron scattering⁹, laser light scattering¹⁰, viscosity¹¹, conductivity¹², dialysis equilibrium¹³, NMR¹⁴ and size exclusion chromatography¹⁵. However recent study on conformation of poly(ethylene oxide) (PEO) in poly(ethylene oxide)-sodium dodecyl sulphate aggregates suggested that in the initial regime above the critical aggregation concentration (CAC) polymer-bound micelles are attached to the coils but are noninteracting and in a second regime there is interaction between the attached micelles¹⁶. In the first regime we may expect the polymer-bound micelles attached to chain segments belonged to the same or different polymer chains to form intramolecular or intermolecular association junctions. As a result there is intra- or intermolecular association of polymers mediated by surfactants in solutions.

Of peculiar importance is that the influence of the intra- or intermolecular association of polymers upon the dilute hydrodynamical properties can be significant as presented in this and our previous studies¹⁷ or reported by others^{2,3}.

EXPERIMENTAL

Poly(ethylene glycol) (PEG) sample with nominal molecular weight of 20000 Dalton was obtained from Shanghai Chemical Company. Sodium dodecyl sulphate (SDS) was from Xuzhou Second Chemical Company (purity > 99.9 %) and was used without further purification. The mixtures of polymer

and deionized distilled water were stirred for several minutes until complete dissolution of the polymer occurred. The solutions were allowed to equilibrate for 1 h prior to use. The appropriate amount of surfactant was introduced under the form of a highly concentrated aqueous stock solution.

Detection method: All viscosity measurements were carried out using a conventional Ubbelohde capillary viscometer (inner diameter $\phi = 0.55$ mm) at 30 ± 0.01 °C maintained with a thermostatic water bath. Measurements were initiated after approximately 5-10 min equilibrium time. Each flow time was determined by repeating at least five time measurements and kept long to neglect the kinetic corrections to the observed data. The precision of the measurements was 0.01 s and the reproducibility was 0.1 s. The viscometer was thoroughly cleaned with concentrated chromic acid and deionized distilled water after each experiment.

RESULTS AND DISCUSSION

Reduced viscosity of poly(ethylene glycol) solutions as a function of polymer concentration (c) for different surfactant concentrations is shown in Fig. 1. The good linearity allows a successful determination of intrinsic viscosity $[\eta]$ by extrapolation of the reduced viscosity curves to zero polymer concentration. Then Huggins coefficient k_H can be calculated, according to the Huggins equation:

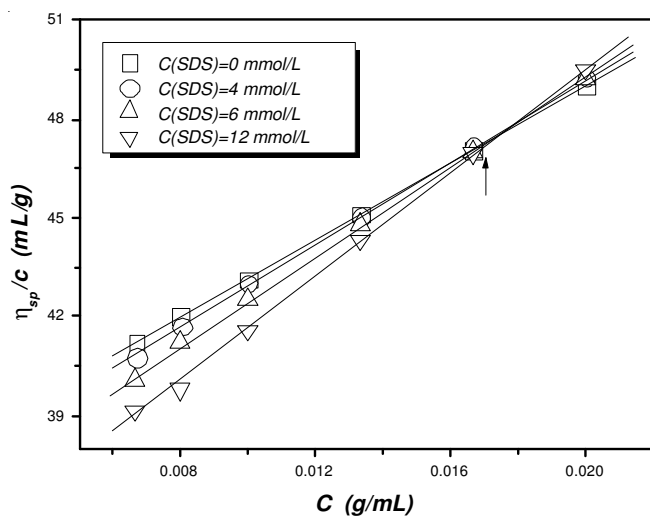


Fig. 1. Reduced viscosity η_{sp}/c versus c for poly(ethylene glycol) at 30 °C

$$\frac{\eta_{sp}}{C} = [\eta] + k_H [\eta]^2 C$$

where η_{sp}/c is the reduced viscosity and Huggins coefficient k_H is a hydrodynamic measure of the intensity of the polymer-polymer interactions. Figs. 2 and 3 show Huggins coefficient and the intrinsic viscosity of poly(ethylene glycol) as a function of surfactant concentration respectively.

It can be seen that if $c < 0.017$ g/mL, the reduced viscosity of poly(ethylene glycol) in sodium dodecyl sulphate aqueous solution is less than that of poly(ethylene glycol) in pure water. In particular, the reduced viscosity of poly(ethylene glycol) decreases considerably as the concentration of sodium dodecyl sulphate increases. On the other hand, if $c > 0.017$ g/mL, the reduced viscosity of poly(ethylene glycol) in sodium dodecyl

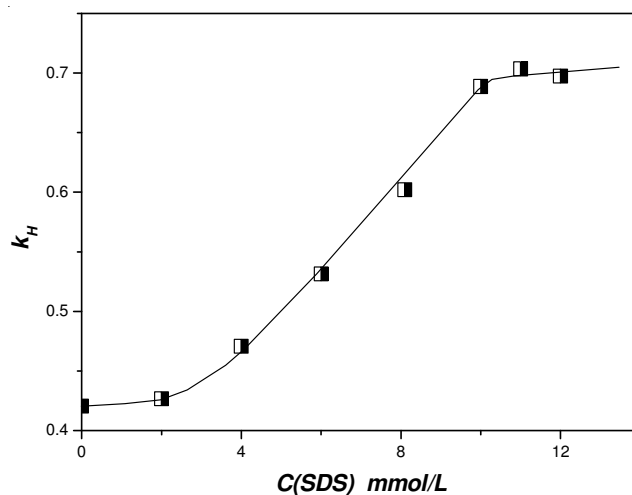


Fig. 2. Huggins coefficient as a function of surfactant concentration for poly(ethylene glycol) solutions

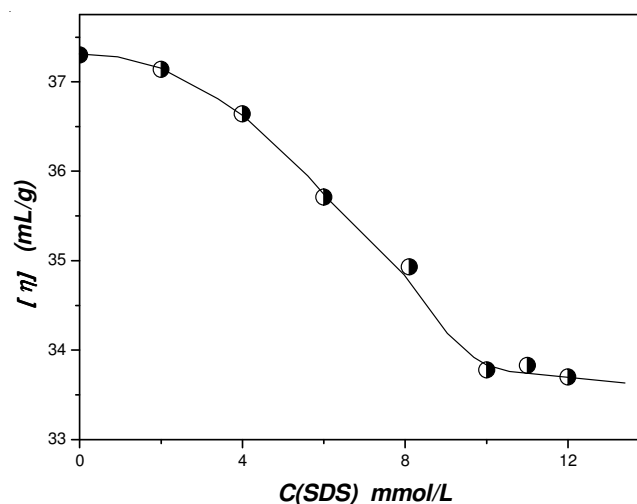


Fig. 3. Intrinsic viscosity as a function of surfactant concentration for poly(ethylene glycol) solutions

sulphate aqueous solution is larger than that of poly(ethylene glycol) in pure water as shown in Fig. 1. The most salient features of Figs. 2 and 3 is the marked increase of the Huggins coefficient and the notable decrease of the intrinsic viscosity of polymer as the concentration of sodium dodecyl sulphate increases from zero to *ca.* 12 mM.

For flexible polymer in good solvents the Huggins coefficient usually takes values of *ca.* 0.3-0.5¹⁸. In this study k_H is 0.42 for poly(ethylene glycol) in pure water. High values of k_H are observed in poor solvents or in the case of enhanced coil-coil interactions. For amphiphilic polymers the high values of k_H usually indicates the hydrophobic associations³. In poly(ethylene glycol)-sodium dodecyl sulphate mixed solutions the aggregation of surfactants with polymer chains strengthens the inter- or/and intramolecular hydrophobic junctions. This suggests that poly(ethylene glycol) chains may associate together mediated by sodium dodecyl sulphate, resulting in the increase of Huggins coefficient. If the polymer concentration $c > 0.017$ g/mL different polymer chains associate together through intermolecular hydrophobic junctions. The reduced viscosity of poly(ethylene glycol) increases as the concentration of sodium dodecyl sulphate increases. On

the other hand, if $c < 0.017$ g/mL, the poly(ethylene glycol) chains are almost separated and the intramolecular association of poly(ethylene glycol) through intramolecular hydrophobic junctions dominates. As a result, polymer chains shrink in size, resulting in the decrease of the intrinsic viscosity. Therefore the reduced viscosity of poly(ethylene glycol) decreases considerably as the concentration of sodium dodecyl sulphate increases.

To gain further insight into the effect of polymer concentration on the viscosity properties of poly(ethylene glycol)-sodium dodecyl sulphate mixed solutions, the relative viscosity is plotted *versus* surfactant concentration for various polymer concentrations (Fig. 4). As expected, when the polymer concentration $c = 0.02$ g/mL the relative viscosity of sodium dodecyl sulphate solutions are larger than that in pure water due to intermolecular association of poly(ethylene glycol) chains. However, in the cases of the polymer concentration $c = 0.013$ g/mL and $c = 0.01$ g/mL intramolecular association of poly(ethylene glycol) chains mediated by sodium dodecyl sulphate becomes apparent. The relative viscosities of sodium dodecyl sulphate solutions, therefore, are less than that in pure water.

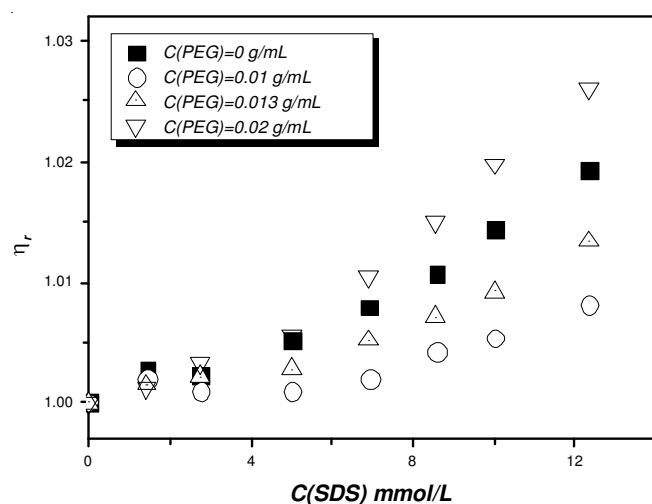


Fig. 4. Relative viscosity η_r versus c for sodium dodecyl sulphate at 30 °C

Conclusion

The viscosity study of mixed solutions of poly(ethylene glycol) and sodium dodecyl sulphate show that the aggregation

of surfactants with polymer chains strengthens the inter- or/ and intramolecular hydrophobic junctions, resulting in the inter- or/and intramolecular association of poly(ethylene glycol) mediated by sodium dodecyl sulphate. If the polymer concentration $c > 0.017$ g/mL different polymer chains associate together through intermolecular hydrophobic junctions. On the other hand, if $c < 0.017$ g/mL, the poly(ethylene glycol) chains are almost separated and the intramolecular association of poly(ethylene glycol) through intramolecular hydrophobic junctions dominates.

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