Properties of pseudo Polyelectrolytes Self-assembled from PVP/SDS Complex Determined by Viscosity Measurement

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Abstract: Reduced viscosity of the complex self-assembled by polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) was determined by Ubbelohde viscosity meter. Flow time of 2 g/L PVP aqueous solutions and PVP/SDS complex solutions at 30 °C were separately measured. The results showed that the higher the SDS concentration, keeping PVP at 2 g/L, the lower the viscosity of the system, presenting a similar characteristic with polyelectrolytes. All of the results showed that the PVP/SDS complex system presented a supermolecular structure and was a pseudo polyelectrolyte.

Keywords: pseudo polyelectrolyte; reduced viscosity; PVP; SDS

Introduction

The interaction of surfactants with nonionic water-soluble polymers has been the subject of active research for the past decades. Polymer/surfactant complex system has been widely applied in life science, medicine, food, tertiary oil recovery, daily chemicals, nanometer material preparation, and other fields. Study of interaction between surfactant and polymer appears to be of great theoretical and practical significance. Early studies mainly concerned with the effects of anionic surfactant on natural proteins, began in the 1940s[1,2]. Present researches most focused on the phenomenon of double critical concentration of surfactant, called critical aggregation concentration(CAC) and polymer saturation point (PSP)[3,4], the interaction parts between them and their specific applications[5-7]. However, the understanding of the nature of the interaction of polymer/surfactant system is still inadequate, limited in qualitative research. Quantitative research and related deeper mechanism need further exploration.

Previous report[8] showed that polymer/surfactant system presented some properties of polyelectrolyte. It was thus assumed to form a special super-molecular structure, called pseudo polyelectrolyte. It provides a new and significant perspective, using the general methods of studying polyelectrolyte to demonstrate the mechanism of interaction between nonionic polymer and surfactant, as well as the nature of its complex structure. But there was no systematic study about its quasi-polyelectrolyte properties reported up to now.

In this paper, polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) were chose as the samples of nonionic polymer and surfactant. Viscosity properties were
investigated by measuring the flow time of PVP/SDS complex solutions at different concentrations on an Ubbelohde viscosity meter.

Experimental Section

Materials.
SDS was supplied by Acros organics with a purity of 99% and was used without further purified. PVP-k30 was obtained as a pure polymer from ISP. Sodium polyacrylate (PAANa) was purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). Ultrapure water, with the resistivity of 18.2 MΩ·cm, was twice distilled and filtered.

Viscosity Measurements.
Viscosity Measurements were performed on an Ubbelohde viscosity meter 0.45 mm in diameter. The temperature was controlled by a water bath and maintained at 30.0±0.05 °C. Complex solution with different concentrations of PVP/SDS was prepared in 100 mL volumetric flask, filtered by No. 2 sand core funnel before measuring. The same step was pure PVP solution and PAANa aqueous solution.

Results and Discussion

Early in the 1940s, Fuoss and co-workers proposed an empirical relationship for the viscosity of polyelectrolyte solutions from a series of experiments[^9]:

$$\eta_{rs} = \frac{a}{1 + bC^{1/2}} + d$$

Where $\eta_{rs}$ is the reduced specific viscosity (defined as $\eta_{rs} = (\eta - \eta_0)/(\eta_0 C)$, where $\eta$ and $\eta_0$ are the viscosity of solution and solvent, respectively), $C$ is the polyelectrolyte concentration, and $a$, $b$, and $d$ are system-related constants. The value of $b$ is dependent on the polyelectrolyte-solvent interaction, and $a + d$ can be regarded as the intrinsic viscosity in the limit of $C$ approaching zero. This relationship has been verified to be accurate in the semi-dilute regime in which $\eta_{rs}$ increases monotonically to $a+d$ with decreasing $C$. And it is the specific viscosity of polyelectrolyte other than neutral polymer.

In this study, $\eta$ is the viscosity of PVP/SDS complex solutions at different SDS concentrations with fixed 2 g/L PVP solution. And $\eta_0$ is the viscosity of 2 g/L PVP. $\eta_{rs}$ were calculated through the equation $\eta_{rs} = (t - t_0)/(t_0C_{SDS})$ ($t$ and $t_0$ are the flow time of PVP/SDS complex solution and 2 g/L PVP solution through the viscosity meter, respectively). Keep PVP solution at 2 g/L, $\eta_{rs}$ increases with SDS concentration ranging from 0.4 mM to 1.6 mM, and also 4.0 mM to 18.0 mM (Fig. 1a). However, it appears that
the higher SDS concentration, the lower the reduced viscosity of the system when SDS comes to the field of 1.6 mM to 4.0 mM, presenting the same characteristics with polyelectrolytes. Reduced viscosity of nonionic polymer PVP and polyelectrolyte PAANa were also investigated as the contrasted samples (Fig. 1b and 1c). It supposes that PVP/SDS presents different characteristics with pure PVP solution, but the same performance with PAANa in a certain SDS concentration range. The complex system begins to self-assemble a super-molecular structure when SDS concentration reaches 1.6 mM, forming a pseudo polyelectrolyte. It outreaches the region of electric viscosity performance when SDS concentration is above 4 g/L.

![Graphs showing reduced viscosity vs. SDS and PAANa concentrations.](image)

Fig. 1  Reduced viscosity of (a) PVP/SDS complex, (b) PVP and (c) PAANa solution at 30 °C . In (a), PVP was kept at 2 g/L.

Conclusions
During certain SDS concentrations range, with SDS concentration decreasing, the reduced viscosity of PVP/SDS complex increases. The system presents the same characteristic with polyelectrolyte solution. A supermolecular structure was self-assembled by the PVP/SDS complex system, forming a pseudo polyelectrolyte.
References


