

PROPERTIES OF DILUTE SOLUTIONS OF HYDROPHOBICALLY MODIFIED POLY(4-VINYL PYRIDINE) (POLYISOAPS)*

YANG Lijiang (杨立江) and YANG Yajiang (杨亚江)**

(Department of Chemistry, Huazhong University of Science and Technology,
Wuhan, 430074, China)

Abstract Hydrophobically modified poly(4-vinyl pyridines) by alkyl bromides are kinds of polysoap similar to the surfactant. Properties of dilute solutions were studied through the viscosity measurements in pure water and NaCl solutions. In aqueous solutions of polysoaps hydrophobic interaction can be attributed to aggregation of hydrophobic groups of the polysoap main chains. The hydrophobic groups of polysoap can aggregate to form hydrophobic microdomains (micelles) in aqueous solution. This is a compact conformation. The formation of such microdomains is a process of dynamic equilibrium.

Keywords Hydrophobic; Polysoap; Reduced viscosity; Microdomain

INTRODUCTION

For the properties of viscosity, simple substance solution differs much from the polyelectrolyte solution, especially dilute solution. There was much discussion that with decreasing concentration of polyelectrolyte, the viscosity (η_{sp}/C) of solution will increase distinctly^[1]. This phenomenon can be attributed mainly to the coil extending of polyelectrolyte molecule chains when solution was diluted.

Hydrophobically modified poly(4-vinyl pyridines) by alkyl bromides are kinds of polyelectrolytes with both hydrophobic alkyl groups and hydrophilic groups (quaternized pyridine ring). It is so-called polysoap that is similar to surfactants for certain properties^[2]. In aqueous solution of polysoap hydrophobic interactions exist between molecule chains, besides the extension of molecule coil. Long time ago, the hydrophobic interaction was considered as Van der Waals force. Now it is well known that the interaction can be attributed to aggregation of hydrophobic groups on the polysoap main chains^[3].

* The project is financially supported by National Natural Science Foundation of China.

** To whom correspondence should be addressed.

Received October 11, 1996; revised July 20, 1997

EXPERIMENTAL

The 4-vinyl pyridines (4-VP) purified by distillation was polymerized using AIBN as an initiator under N_2 . The polymerization degree of P4-VP was approximately 1375 that was estimated by the measurement of intrinsic viscosity in 92% ethanol^[4].

Quaternarization of poly-4-vinyl pyridines (QPVP) was carried out in DMSO according to the literature reports^[5]. QPVPE is a product quaternized with excessive ethyl bromide at 35°C.

Quaternary degree can be controlled by reaction time. QPVPE-2, QPVPE-8, QPVPE-72 were quaternized for 2, 8, 72h, respectively. Thus, quaternary degree increases with reaction time increasing. QPVPD-5, QPVPD-20, QPVPD-30 are products quaternized with *n*-dodecyl bromide for 72h at 60°C. The feed ratio of *n*-dodecyl bromide is equal to 5%, 20%, 30% of 4-VP(mole). Further quaternization was carried out with excessive ethyl bromide for 72h at 35°C.

The viscosity measurements were carried out with Ubblothe viscometer in water bath at $30 \pm 0.1^\circ\text{C}$ after sample solutions were prepared for 24h.

RESULTS AND DISCUSSION

The effects of quaternary degree on η_{sp}/C

It is well known that mobile counter ions can be dissociated from molecular chains in aqueous solution of polyelectrolytes including polysoaps. When the concentration of polyelectrolyte is higher, the effect of mobile counter ions, for example Br^- on the property of solution is small because of coiling together polymer chains. While the solution of polyelectrolytes is diluted, a pure solvent area appears among molecular chains and mobile counter ions diffuse from polymer solution area to pure solvent area. That can lead to polymer chains carrying surplus positive charges. Polymer chains will extend under the influence of electrostatic repulsion. That leads to the

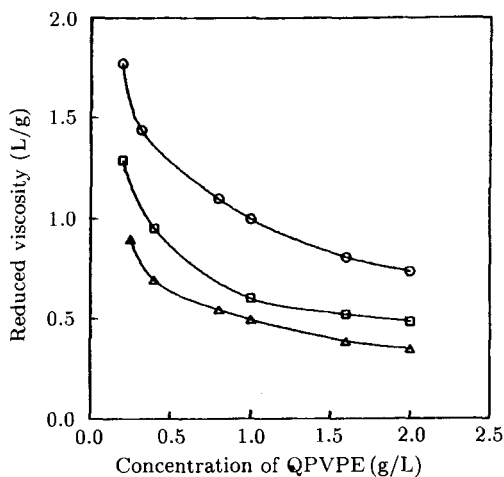


Fig.1 Reduced viscosity of QPVPE in pure water: QPVPE-2 (□); QPVPE-8 (Δ); QPVPE-72 (○)

increas η_{sp}/C of solution. Fig.1 shows that η_{sp}/C of different quaternary degree of QPVPE in aqueous solutions increases along with dilution of solutions.

There are two factors influencing η_{sp}/C of QPVPE aqueous solutions: polymerization degree and quaternary degree of QPVPE. In this paper, the influence of quaternized from P4-VP with same polymerization degree. Fig.1 shows that η_{sp}/C will decrease with increasing quaternary degree when the concentration of QPVPE is constant. It is the main result of the influence of quaternarization on polymers' structures. On the other hand, the higher the quaternary degree, the larger charge density is on the molecular chains. It lead to the increase of electrostatic repulsion among polymer chains and promote extension of molecular chains. Thus, η_{sp}/C increased. In addition, the higher quaternary degree, the larger molecular weight of polymer, it implies that there are fewer molecular chains per unit mass. Thus, η_{sp}/C decreased. Therefore the change of η_{sp}/C is dependant on above two influences.

$[\eta]$ data listed in Table 1 were obtained by viscosity measurements in 0.1mol/L and 0.5mol/L NaCl solutions. It shows that $[\eta]$ decreased along with quaternary degree increased. It can be attributed to shield of electrolyte (NaCl) for the charges on the molecular chains. Thus, the more molecular chains in solution at same concentration per unit mass, the larger $[\eta]$. It is similar to the rule of common polymer solutions.

Table 1 Intrinsic viscosity of quaternized poly-4-vinyl pyridine in 0.1mol/L and 0.5mol/L NaCl solutions

	$[\eta] (\times 100 \text{ L/g})$ in 0.1mol/L NaCl	$[\eta] (\times 100 \text{ L/g})$ in 0.5mol/L NaCl
QPVPE-2	6.98	3.96
QPVPE-8	5.97	3.73
QPVPE-72	5.39	2.98
QPVPD-5	3.44	
QPVPD-20	0.56	0.30
QPVPD-30	0.45	

The effect of ionic strength on η_{sp}/C

It is known that addition of some simple electrolyte in polyelectrolyte solutions will raise ionic strength of system and increase amount of mobile counter ions. That will strengthen interaction between mobile counter ions and polymer chains and shield charges on main chains. Thus, electrostatic repulsion among polymer units becomes weak and η_{sp}/C falls because more compact conformation formed.

Fig.2 is a plot of η_{sp}/C -C that shows η_{sp}/C change with QPVPE in pure water,

0.1mol/L and 0.5mol/L NaCl solutions, respectively. It was found that η_{sp}/C in sodium chloride solutions falls about 2 ~ 3 power series comparing with that in pure water and straight line can be obtained (η_{sp}/C increases linearly along with the concentration increased). Thus, $[\eta]$ can be calculated by extending to $C = 0$ g/L. In addition, the relation between η_{sp}/C and sodium chloride concentration in solutions was also investigated. The results were summarized in Fig.3 which shows η_{sp}/C decreased along with NaCl concentration increased. It indicates that influence of ionic strength on the viscosity is great and larger ionic strength lead to small electrostatic repulsion among polymer units. In this case, more compact conformation was formed.

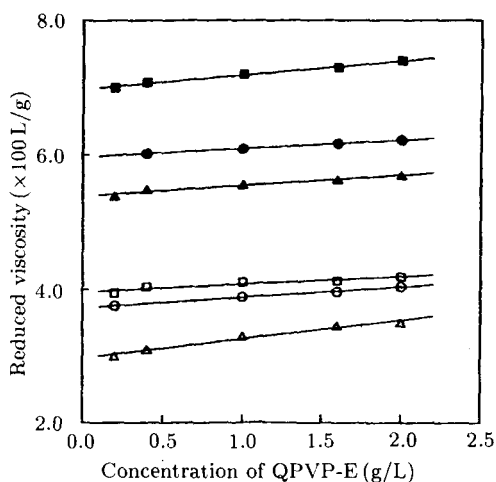


Fig.2 Reduced viscosity of QPVPE in NaCl solutions: QPVPE-2 (0.1mol/L: ■; 0.5mol/L: □); QPVPE-8 (0.1mol/L: ●; 0.5mol/L: ○; QPVPE-72 (0.1mol/L: ▲; 0.5mol/L: △)

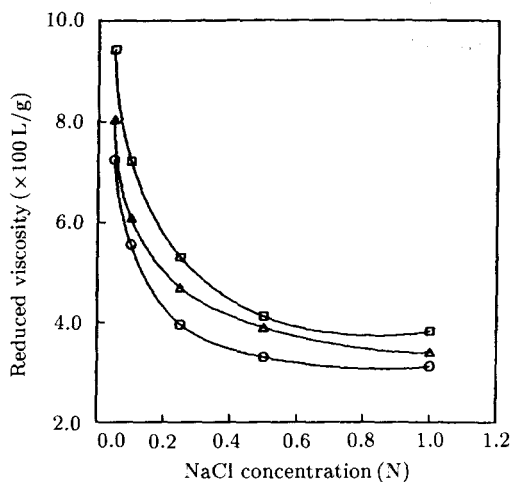
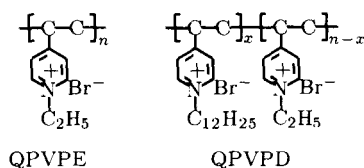


Fig.3 Reduced viscosity of QPVPE in various concentration of NaCl solutions: (□) QPVPE-2; (△) QPVPE-8; (○) QPVPE-72

The influence of hydrophobic groups on η_{sp}/C

QPVPD can be considered as a product which a part of ethyl groups on molecular chains of QPVPE-72 was substituted with *n*-dodecyl groups. The structures of QPVPE and QPVPD were shown in scheme I. Influence of substitute groups on η_{sp}/C can be investigated by comparing both structures.

Fig.4 is plots of η_{sp}/C of QPVPD-20 versus concentration in pure water, 0.1mol/L and 0.5mol/L NaCl solutions respectively. Obviously, comparing Fig.4 with Fig.1, molecular weight of QPVPD-20 is larger than that of QPVPE-72 because of large mass of substitute groups, which leads to decreasing η_{sp}/C in a certain extent. It



Scheme I

was found that η_{sp}/C of QPVPD-20 falls 20 times than that of QPVPE-72 in pure water. It indicates that more compact conformation is formed due to introduction of *n*-dodecyl groups. A distinctive character of polysoap differing from polyelectrolyte is those hydrophobic alkyl groups on main chains can be aggregated together to form hydrophobic microdomains (or so-called micelles) in aqueous solutions similar to surfactants. In such microdomains (micelles), hydrophobic alkyl groups aggregated at interior and hydrophilic groups aggregated at exterior. Thus, hydrophobicity of dodecyl groups is far greater than that of ethyl groups. The difference of hydrophobic conformation caused by hydrophobicity is the main reason for very low η_{sp}/C of QPVPD-20. The relations of *n*-dodecyl groups contents of QPVPD and $[\eta]$ were summarized in Table 1. It indicates that higher content of hydrophobic groups is advantageous to formation of hydrophobic microdomains. It also reveals that this hydrophobic conformation is compact structure.

The influence of the time on the formation of hydrophobic microdomains

Simple substance solution can immediately attain equilibrium by diffusion when it was dilute while the solution of polyelectrolyte must overcome the difficulty of conformation adjustment. Moreover disintegration and reformation of hydrophobic microdomains exist when diluting polysoap solution. A typical experimental result was presented in Fig.5 for QPVPD-30. It showed a tendency of changing the η_{sp}/C with time. η_{sp}/C of a dilute polysoap solution that has been freshly prepared by dilution of more concentrated solution decreased for a considerable time. Hydrophobic conformation in polysoap solution was destroyed after the solution was diluted. Thus, η_{sp}/C attains maximum value at $t = 0$ min. Then, polysoap molecular chains adjust its hydrophobic conformation along with equilibrium undergoing. Generally, the equilibrium process takes about 24h after dilution. The process of η_{sp}/C falling with time is a process of forming compact hydrophobic conformation. It can be considered that formation of hydrophobic microdomains was a dynamic equilibrium process. The results also prove existence of aggregate of hydrophobic alkyl side chains in polysoap solutions.

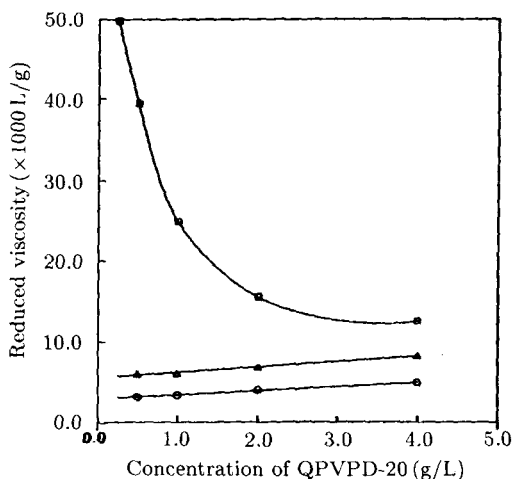


Fig.4 Reduced viscosity of QPVPD-20 in pure water, 0.1mol/L and 0.5mol/L NaCl solutions: in pure water (□); 0.1mol/L NaCl (Δ); 0.5mol/L NaCl (○)

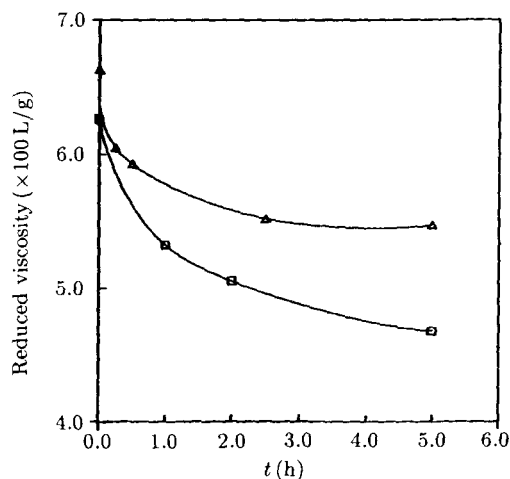


Fig.5 The stability of reduced viscosity of QPVPD-30 along with the time after dilution using various concentrations of NaCl solutions: 0.02mol/L NaCl (Δ); 0.1mol/L NaCl (□)

CONCLUSION

There are something in common for the viscosity properties between hydrophobically modified poly(4-vinyl pyridine) (polysoap) and normal polyelectrolyte. η_{sp}/C of polysoap aqueous solution will decrease along with the concentration increased. The viscosity will also decrease in the presence of electrolyte (NaCl). The hydrophobic groups of polysoap can aggregate to form hydrophobic microdomains (micelles) in aqueous solution of polysoaps. This is a compact conformation that leads to low viscosity of polysoap in aqueous solutions. The formation of microdomains is a process of dynamic's equilibrium in aqueous solution of polysoaps.

REFERENCES

- [1] Polymer Physics Laboratory, Science and Technology University of China, "The Structure and Properties of Polymers (Chinese Version)", Science Press, Beijing, 1981, p.423
- [2] Strauss, U.P., Gershfeld, N.L., *J. Phys. Chem.*, **1954**, 58, 747
- [3] Strauss, U.P., Williams, B.L., *J. Polym. Sci.*, **1965**, 1390
- [4] Boyes, A.G., *J. Polymer Sci.*, **1956**, 22, 463
- [5] Strauss, U.P., Gershfeld, N.L., Crook, E.H., *J. Phys. Chem.*, **1956**, 60, 577