

DILUTE SOLUTION BEHAVIOR OF CHITOSAN IN DIFFERENT ACID SOLVENTS*

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ABSTRACT

Dilute solution behavior of chitosan was studied in formic acid, acetic acid, lactic acid and hydrochloric acid aqueous solution under different pH values. The reduced viscosities, η_{sp}/C , of chitosan solutions were dependent on the properties of acid and pH value of solvents. For a given chitosan concentration, η_{sp}/C decreased with the increase of acid concentration, or decreasing pH of solvent, indicating shielding effect of excessive acid similar to adding salt into solution. The stabilities of dilute chitosan solution in formic acid and lactic acid were better than that in acetic acid and hydrochloric acid.

INTRODUCTION

Chitosan is a cationic polyelectrolyte, it may be used for coagulation of protein, detection of ions and recovery of heavy metals etc, in the form of dilute solution^[1, 2]. In order to obtain a better understanding of the influence of the properties of acid and pH on the characteristics of dilute solution for chitosan, this work involves a study of viscosity and stability of the solution where the formic acid, acetic acid, lactic acid or hydrochloric acid aqueous solution were used as the solvent for chitosan, respectively.

EXPERIMENTAL

Chitosan was obtained from crabshells, the degree of deacetylation (D.D) and molecular weight ($\bar{M}_w$) were 70% (wt%) and 8.37×10^5 by means of the colloid titration and viscosimetric method respectively^[3].

Chitosan solutions in acid solvent with different pH values were prepared by stirring at room temperature until complete dissolution. The solution was allowed to rest for 24h.

The reduced viscosities were determined by using Ubbelohde viscometer at 25°C. No shear correction was made.

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pH values of solvent were measured with DF- 808 Mode pH/ionic Instrument.

RESULTS AND DISCUSSION

The reduced viscosities, η_{sp}/C , of dilute chitosan solution where the concentration is 1×10^{-3} g/ml were measured in four kinds of acids under different pH values, Fig. 1 shows the dependence of the reduced viscosity on pH values of the acid solvent. Obviously, the reduced viscosity is affected by the properties of acid and pH of solvent. If pH is higher than 2, the reduced viscosity is only related to pH, not affected by kind of acid, and increases abruptly with further increase of pH. However, if pH is lower than 2, the reduced viscosity is different for different kinds of acids under the same pH value. The stronger the acidity is, the lower the viscosity. This is believed to be due to the screening effect of anionic group in solution. And the screening effect increases with increasing acidity of acid or decreasing pH value of solvent.

The reduced viscosity of uncharged polymers decreases linearly with decreasing polymer concentration following Huggins equation^[4]. Generally, this is not true for polyelectrolytes. Fig. 2 shows the relationship between the reduced viscosity and polymer concentration with respect to the concentration of acetic acid, i. e. different pH in solution. As it can be seen, the viscosity increases with increasing pH of solvent. When pH of solvent is 3.26, 3.13, 2.78, 2.18 and 1.35, the plot of η_{sp}/C versus C moves from curve 1 to 5. If pH is lower, the relationship between η_{sp}/C and C becomes a straight line gradually. But the viscosity is still greater than that in a solution of 0.1mol/L $\text{CH}_3\text{COOH} + 0.2\text{mol/L NaCl}$. This is why the increase of excessive acid can play a part of screening of electrostatic force, similar to the effect of adding salt, although it is weaker in excessive acid solution than in adding salt solution.

Fig. 3 is the plot of the reduced viscosity versus polymer concentration of chitosan solution under different acid concentrations in HCl aqueous solution. It shows that the reduced viscosity decreases linearly with decreasing polymer concentration. This fits well with the Huggins equation.

$$\eta_{sp}/C = [\eta] + K' [\eta]^2 C \quad (1)$$

The reason is that hydrochloric acid is a strong acid, it will lead to more screening effect in HCl than in CH_3COOH . Table 1 gives the intrinsic viscosity $[\eta]$ and Huggins coefficient K' of dilute solution for chitosan in

HCl and in 0.1 mol/L CH_3COOH + 0.2 mol/L NaCl aqueous solution.

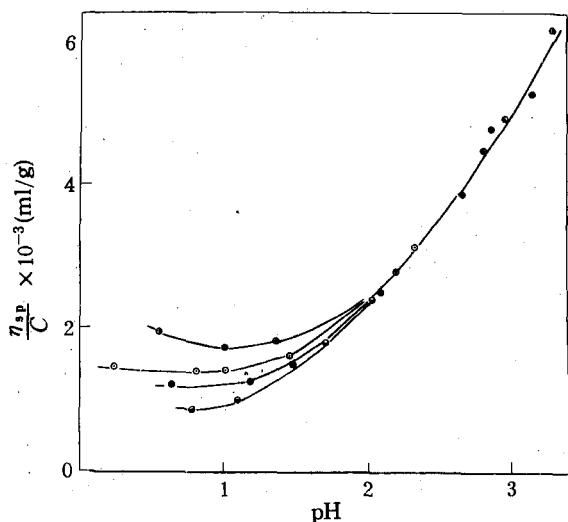


Fig. 1 Effect of pH value of solvent on reduced viscosity of dilute chitosan solution (1×10^{-3} g/ml) in different acids

⊗ Acetic acid; ○ Lactic acid;
● Formic acid; ◐ Hydrochloric acid

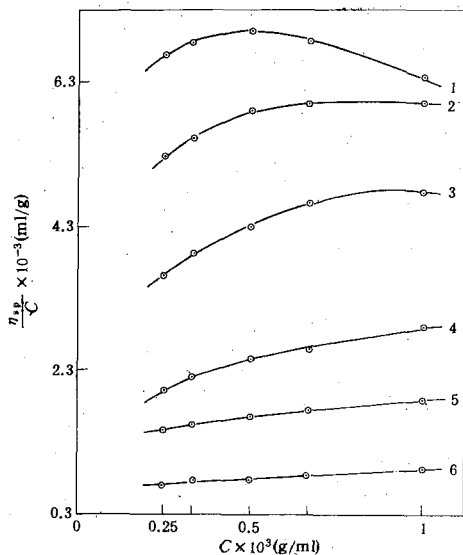


Fig. 2 Plot of reduced viscosity versus concentration of chitosan solution in acetic acid

1—0.1% , 2—0.25% , 3—1%
4—10% , 5—50% ,
6—0.1mol/L CH_3COOH
+ 0.2mol/L NaCl

Table 1 The intrinsic viscosity and Huggins coefficient K' of dilute chitosan solution

Solvent	0.01mol/L HCl	0.02mol/L HCl	0.1mol/L HCl	0.1mol/L CH_3COOH + 0.2mol/L NaCl
$[\eta]$ (ml/g)	1397	1155	740	659
K'	1.07	0.65	0.27	0.25

It is clear that intrinsic viscosity decreases with the increase of the screening effect. So does Huggins coefficient K' , which indicates the interaction between the polyelectrolyte and counterions in solution.

The stabilities of dilute chitosan solution in four kinds of acid were studied. Fig. 4 shows the dependence of the decrease in percent of reduced viscosity, $\Delta(\eta_{sp}/C)$, on the properties of acid and the pH value of solvent. It can also be seen that the stability of chitosan solution in HCOOH or $\text{CH}_3\text{CHOHCOOH}$ is better than in CH_3COOH or HCl aqueous solution. And

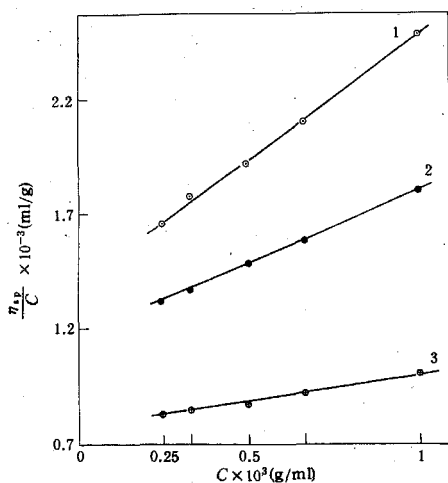


Fig. 3 Plot of reduced viscosity versus concentration of dilute chitosan solution (1×10^{-3} g/ml) in hydrochloric acid

⊙ 0.01mol/L; ● 0.02mol/L;
⊗ 0.1mol/L

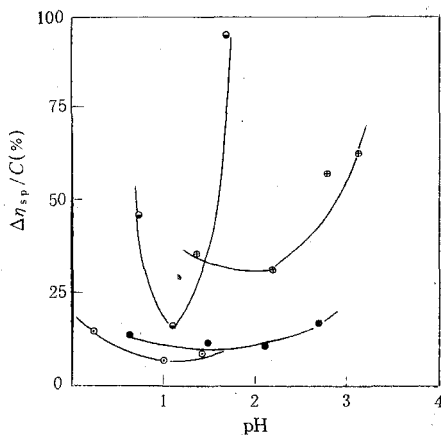


Fig. 4 Decrease in percent of reduced viscosity of dilute solution of chitosan after 30 days.

⊕ Acetic acid; ⊙ Lactic acid;
● Formic acid;
◐ Hydrochloric acid

in the range of pH from 1 to 2, the decrease in percent of the reduced viscosity is the least after 30 days. From this point of view, HCOOH or $\text{CH}_3\text{CHOHCOOH}$ aqueous solution with pH from 1 to 2 should be used as solvent in the application of chitosan.

Keywords:

Chitosan; Dilute solution properties; Dependence of solvent with different pH values

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