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Effects of Nonsolvent on the Thermodynamic Interaction of Nitrocellulose and Butyl Acetate

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Abstract The thermodynamic interaction characteristics of nitrocellulose (NC) with various content of nitrogen and butyl acetate, and effects of nonsolvent on it were ascertained. The chain conformation in nitrocellulose-butyl acetate system was more straightened as nitrogen content decreased, and in the nitrocellulose-butyl acetate-*n*-butanol system with 12% of nitrogen content, the entropy component χ_S of thermodynamic interaction parameter χ was 0.310 and enthalpy component decreased with increase of temperature.

Key words nitrocellulose solution, thermodynamic characteristic, volume expansion coefficient, second viral coefficient

Introduction

The great leader Comrade **Kim Jong Il** said as follows.

"They should intensify their scientific research for the scientific and technical solutions to the problems arising in making the national economy scientifically-based, and thus put the production and management activities of all branches on a new scientific base."

("**KIM JONG IL** SELECTED WORKS" Vol. 10 P. 195)

Nitrocellulose solutions are widely used for various purposes such as protection film or extraction membrane materials of producing electron element [11－14]. In order to prepare various functional membranes by using nitrocellulose solution, the thermodynamic interaction characteristics of nitrocellulose and several solvents must be ascertained.

Now there were many researches on the solubility of nitrocellulose solution [5, 16, 18] but the results of researching the thermodynamic characteristics of nitrocellulose solution with the different content of nitrogen was not appeared.

In this paper, the thermodynamic interaction characteristics of nitrocellulose (NC) with various content of nitrogen and butyl acetate and effects of nonsolvent on that were ascertained.

Experimental Method

Different nitrogen-containing nitrocellulose was solved in butyl acetate individually and its concentrations were determined by evaporation to dryness method, its intrinsic viscocities were determined by using Ubbelohde viscometer. θ-state was made by turbidimetry with adding of the *n*-butanol(99.9%) in butylacetate solution of nitrocellulose and its intrinsic viscosity was determined.

And then volume expansion coefficient α and second virial coefficient A_2, interaction parameter of polymer and solvent χ were estimated.

Relationship between volume expansion coefficient α and intrinsic viscosity is as follows [2−4].

$$\alpha^3 = [\eta]/[\eta]_\theta \quad (1)$$

And relationship between second virial coefficient A_2 and intrinsic viscosity is as follows[6−10].

$$[\eta] - [\eta]_\theta = 5.0 \cdot 10^{-3} A_2 M \quad (2)$$

Relationship between second virial coefficient A_2 and thermodynamic interaction parameter χ is as following[15].

$$A_2 = (0.5 - \chi)/(\rho_2^2 \tilde{V}_1) \quad (3)$$

where ρ_2 is polymer density, which was determined by estimating Van der Waals volume V_w from molecule-nitrogen content relationship and topological index and by considering its crystallinity[17, 19]. Molecular volume $\tilde{V}_1$ was calculated by using density[1, 2].

Results and Discussion

According to different nitrogen content, the determination results of volume percent of nonsolvent $(V)_\theta$ and intrinsic viscosity $[\eta]_\theta$ in θ-state which was necessary to realize the average molecular weight $\overline{M}$ and density, θ-state of nitrocellulose were shown in table 1.

Table 1. Nitrogen content and $\overline{M}$, ρ_2, $[\eta]_\theta$ of nitrocellulose

Nitrogen content/wt%	$\overline{M}/10^4$	$(V)_\theta$	$\rho_2/(g \cdot cm^{-3})$	$[\eta]_\theta/(cm^3 \cdot g^{-1})$
11.4	5.4	0.457	1.718 1	44.1
12.0	4.7	0.433	1.738 1	41.6
12.5	5.1	0.407	1.751 4	44.9

As shown in table 1, volume percent of nonsolvent being need of realizing the θ-state of nitrocellulose has decreased as nitrogen content of that increases. It was due to the decreasing of content of –OH group so that the interaction effects of nonsolvent in the nitrocellulose increase as nitrogen content increases. Because $[\eta]_\theta$ expressing the chain size in the disentanglement state was depending to $\overline{M}$, the tendency according to the nitrogen content was not appeared.

In case of adding the *n*-butanol in nitrocellulose-butyl acetate solution, the change of intrinsic viscosity $[\eta]$ with content of adding *n*-butanol was shown as Fig. 1.

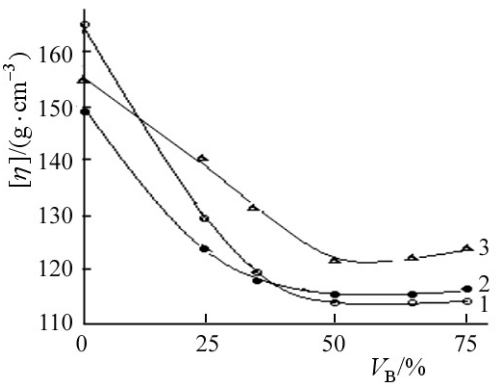

Fig. 1. The change of $[\eta]$ according to the content of *n*-butanol in the different nitrogen-containing nitrocellulose
1−3 are nitrogen content of 11.4, 12.0 and 12.5%

As shown in Fig. 1, intrinsic viscosity decreased rapidly as content of *n*-butanol increased to *V*=50% and at more than that of the content of *n*-butanol, intrinsic viscosity increased a little.

The change of volume expansion coefficient calculating by formula (1) was shown as table 2.

α is the value to express the degree of straightening the macro chains in solution. The conformation of chains in solution straightened as the thermodynamic interaction between polymer and solvent was strong. The facts in table 2 was shown that *n*-butanol itself was a bad solvent for nitrocellulose but effect of one on chain conformation is good at the comfortable solvent mixture. The smaller the nitrogen content of nitrocellulose was, the better chain swelled.

The changes of thermodynamic interaction parameter between nitrocellulose, butyl acetate and solvent mixture χ and second virial coefficient A_2 were shown as table 3.

Table 2. Change of the volume expansion coefficient according to the content of *n*-butanol in the different nitrogen-containing nitrocellulose

Nitrogen content/%	V_B/%				
	0	25	50	65	75
11.4	1.555	1.434	1.370	1.371	1.372
12.0	1.531	1.443	1.407	1.409	1.413
12.5	1.509	1.460	1.395	1.401	1.406

Table 3. Change of A_2 and χ according to the content of nitrogen and nonsolvent.

V_B/%	Nitrogen content/wt %					
	11.4		12.0		12.5	
	A_2	χ	A_2	χ	A_2	χ
0	0.450	0.482	0.459	0.482	0.429	0.483
25	0.321	0.489	0.354	0.487	0.372	0.486
50	0.257	0.492	0.316	0.490	0.302	0.490
65	0.258	0.492	0.320	0.490	0.310	0.490
75	0.259	0.492	0.323	0.490	0.314	0.490

As shown in table 3, χ value in nitrocellulose-butyl acetate increased a little as nitrogen content of nitrocellulose increased. That is, affinity between the nitrocellulose with big substitution degree and butyl acetate was bad.

When the content of nitrogen in the most of solvent component was 12%, A_2 was big. A_2 is the value of deviate degree from ideal behavior and at the 12% of nitrogen content conformation state has differed most far from unperturbed state. But χ value in the nitrocellulose-butyl acetate-*n*-butanol system decreased as nitrogen content increased. It was shown that the more nitrogen content was, the better the effect of *n*-butanol in solution on the thermodynamic interaction between the macro chain and solvent was.

At the 12.0% of nitrogen content and 25% of V_B, χ value according to the temperature was estimated and entropy component χ_s of χ was etimated as 0.310 by $\chi - 1/T$ relationship(Fig. 2).

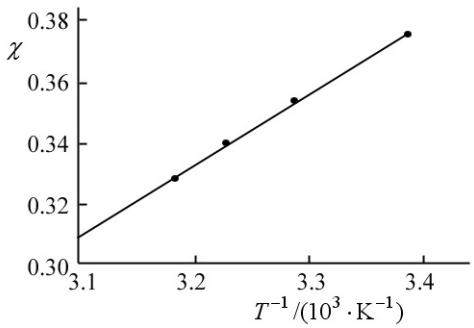

Fig. 2. $\chi - 1/T$ relationship

The change of thermal function component χ_h according to temperature was as table 4.

Table 4. Change of χ_h according to temperature

T/K	298	303	308	313
χ_h	0.083	0.061	0.044	0.037

As shown in table 4, thermal function component χ_h value in nitrocellulose-butyl acetate-*n*-butanol system decreased as temperature increased.

Conclusion

The chain conformation in nitrocellulose-butyl acetate system was more straightened as nitrogen content decreased.

The effect of *n*-butanol on the interaction between nitrocellulose and butyl acetate was negative and became less with increase of nitrogen content.

In nitrocellulose-butyl acetate-*n*-butanol system with 12% of nitrogen content, the entropy component χ_s of thermodynamic interaction parameter χ was 0.310 and enthalpy component decreased with increase of temperature.

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