Chemistry of Natural Compounds, Vol. 35, No. 6, 1999

PROPERTIES OF SOLUTIONS OF WATER-SOLUBLE MIXED ESTERS OF CELLULOSE

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UDC 661.728.8

The viscosity of solutions of water-soluble mixed esters of cellulose is determined. The dimensions of macromolecular globules and Huggins constants are calculated as functions of the nature of the substituted functional group on the water-soluble acetylcellulose.

The physicochemical and colloidal properties of solutions of high-molecular-weight compounds are known to be functions of the degree of polymerization, the degree of esterification, the nature of the solvent, and the temperature [1, 2].

In the present work, the properties of dilute aqueous solutions of certain mixed esters of cellulose are studied by viscometry. We studied water-soluble acetylcellulose (WSAC) containing 18% bound acetic acid, water-soluble cellulose acetate-phthalate (WAPC) containing 24-25% bound acetic acid and 9-10% phthalyl groups, water-soluble cellulose acetate-ammonium phosphate (WAAPC) containing 20% bound acetic acid and 8% phosphate groups, and water-soluble acetocarboxymethylcellulose (WACMC) in the H- and Na-forms containing 28-30% bound acetic acid and 0.7% carboxymethyl groups. The degree of polymerization of the mixed cellulose esters mentioned above was 190-200. The least-square dimensions of macromolecular globules and Huggins constants were calculated on the basis of the viscosity characteristics. The data are listed in Tables 1 and 2 and Fig. 1.

Table 1 shows that partial substitution of the hydroxyls in WSAC by ionic groups such as phthalyl, carboxymethyl, or phosphate increases the solution viscosity of the resulting mixed acetoesters of cellulose. The solution of H-WACMC has a characteristic viscosity that is comparatively low among the studied samples. The highest viscosity occurs for WAAPC. Thus, WAAPC is a salt, the macromolecule of which easily dissociates to form phosphate anions. The phosphate anions are strongly hydrated. As a result, the solution viscosity increases markedly. The carboxyls of H-WACMC dissociate insignificantly. Therefore, its macromolecules are weakly hydrated. Na-WACMC dissociates readily in solution. Therefore, the solution viscosity increases. The viscosity of the WAPC solution is greater than that of H-WACMC. This can be explained by the fact that the acidity of phthalic acid is greater than that of acetic acid.

Increasing the temperature decreases the viscosity of the studied solutions. This is due to the destruction of the hydration sphere of the macromolecules and the solvent structure.

The nature of the substituted group affects the dimension of the macromolecular globule. This effect was estimated from the least-square distances between their ends (Fig. 1). Figure 1 shows that the dimension of the macromolecular globules of the mixed cellulose esters is greater than that for WSAC and is directly proportional to their solution viscosities because the distance between the macromolecule ends increases as the substituent polarity increases.

As the solution temperature increases, the dimensions of the macromolecular globules of cellulose esters decreases. Apparently increasing the temperature destroys the hydration spheres of the functional groups of macromolecules. As a result, their flexibility increases.

Table 2 shows that the flexibility of Na-WACMC and WAAPC depends little on temperature because they are stronger polyelectrolytes and apparently dissociate readily in solution to form carboxyl anions along the macromolecules. These make the macromolecules rigid.

The Huggins constants K were calculated in order to estimate the equilibrium flexibility of the studied cellulose derivatives. Table 2 lists the results.

Tashkent Chemical Engineering Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 785-788, November-December, 1999. Original article submitted June 7, 1999.

0009-3130/99/3506-0668$22.00

TABLE 1. Characteristic Viscosity of Aqueous Solutions of Cellulose Esters η as a Function of Temperature and Activation Energy of Viscous Flow

Sample	η at temperature, K						E, kJ/mole
	298	303	313	323	333	343	
WSAC	1.50	1.41	1.32	1.24	1.17	1.09	5.14
H-WACMC	1.75	1.68	1.61	1.53	1.46	1.40	5.54
WAPC	1.85	1.76	1.68	1.61	1.53	1.48	7.82
Na-WACMC	2.13	1.95	1.87	1.80	1.73	1.68	7.12
WAAPC	2.21	2.15	2.08	2.01	1.95	1.88	9.48

TABLE 2. Huggins Constants *K* as Functions of Temperature

Sample	K at temperature, K					
	298	303	313	323	333	343
WSAC	0.40	0.41	0.43	0.44	0.45	0.47
H-WACMC	0.38	0.39	0.41	0.42	0.43	0.44
WAPC	0.34	0.34	0.35	0.36	0.37	0.37
Na-WACMC	0.30	0.30	0.32	0.32	0.33	0.33
WAAPC	0.26	0.26	0.27	0.27	0.28	0.28

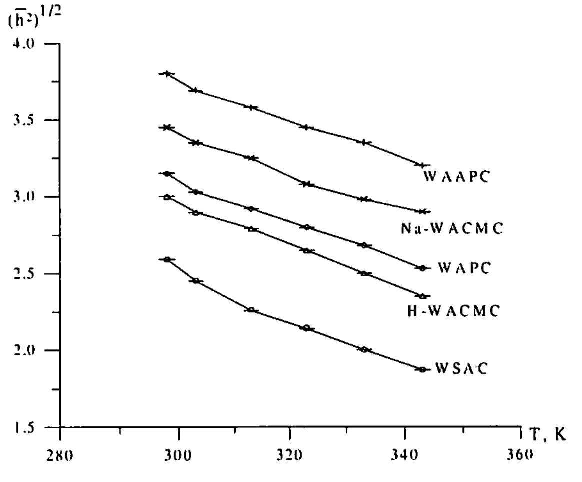

Fig. 1. Least-square dimension of macromolecular globule of cellulose esters $(\bar{h}^2)^{1/2}$ as a function of temperature in aqueous solution.

The Huggins constants are known to be directly proportional to the flexibility of polymeric macromolecules, i.e., the lower *K*, the less flexible the macromolecule [1]. For example, the *K* value decreases from 0.40 to 0.38 if carboxymethyl groups are introduced into WSAC; to 0.34, for phthalate groups. The most rigid macromolecule is WAAPC. The Huggins constant for it at 298°K is 0.26.

Thus, WAPC and Na-WACMC have intermediate flexibilities among the mixed cellulose esters.

In all instances the Huggins constants increase slightly with increasing temperature. This is consistent with an increased equilibrium flexibility for the macromolecules. The *K* values calculated according to the literature [2] agree well with the values calculated using $(\bar{h}^2)^{1/2}$ (Fig. 1).

Intermolecular interactions in solution were estimated by calculating the viscosity temperature coefficient. This coefficient can then be used to calculate the apparent activation energy of viscous flow ΔE using the equation

$$d\ln[\eta] / d(1/T) = \Delta E/R.$$

The ΔE value is also easily determined graphically from a plot of $\ln[\eta] = f(1/T)$ (Table 1).

These data show that the solution viscosity decreases with increasing temperature, i.e., the viscosity temperature coefficient is positive (Table 1). The activation energies of viscous flow for the solutions of cellulose esters also depend on the nature of the substituted functional group. The higher the polarity of the substituted functional group, the greater the activation energy.

Thus, the viscosity of solutions of water-soluble mixed cellulose esters and the conformation and flexibility of their macromolecules depend on the nature of the substituents. The cellulose esters can be placed in the following order according to solution viscosity and macromolecule rigidity: WSAC < H-WACMC < WAPC < Na-WACMC < WAAPC. Hence it can be concluded that WSAC is not an electrolyte and that the polyelectrolyte properties of these mixed cellulose esters increase from left to right.

EXPERIMENTAL

Viscosity of aqueous solutions was determined using an Ubbelohde viscometer and the literature method [3] in the presence of 1% KCl. The degree of polymerization of the cellulose esters was of the order of 200.

Dimensions of macromolecular globules was calculated using the literature formula [2] that relates the characteristic viscosity $[\eta]$ of the solution to the least-square distance between the macromolecule ends $(\overline{h^2})^{1/2}$ and the average polymer molecular mass M:

$$[\eta] = (\overline{h^2})^{3/2}\ \Phi/M,$$

where Φ is the Flory constant ($2.84 \cdot 10^{21}$) if $[\eta]$ is measured in units of dl/g.

Huggins constants (K) were calculated using the formula

$$K = (\eta_{re} - [\eta]) / c[\eta]^2,$$

where c is the solution concentration and η_{re} is the reduced viscosity.

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