Viscosity properties of aqueous solutions of hydroxyethylcellulose

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In this paper attention is paid to the influence of varying content of the Li^+, K^+, Cu^{2+}, and Mn^{2+} ions bonded to the Cl^- ions and of pH of medium on the change in viscosity properties of the aqueous solutions of hydroxyethylcellulose (HEC) which were subjected to low-temperature degradation in air. The change in properties of HEC solutions was estimated on the basis of the values of limiting viscosity number $[\eta]$, density of statistical coil $\varrho_{[\eta]}$, and Huggins constant k_H under given experimental conditions. It has been found that $[\eta]$ of the·HEC solutions containing univalent metal cations increases with the content of these cations, while it does not change in the presence of the bivalent Mn^{2+} cations. On the other hand, it slightly decreases in the presence of Cu^{2+}. In the course of thermal stress the values of $[\eta]$ usually decrease with increasing temperature in the investigated temperature interval. The influence of the pH value of medium on $[\eta]$ is most significant in strong acid and strong alkaline medium at higher temperatures and at higher time periods of thermal stress. The HEC solutions are most stable below 60 °C in the pH region 6—8.

The calculated values of $\varrho_{[\eta]}$ and k_H change consistently with the value of $[\eta]$ of the HEC solutions.

В работе изучается влияние различного содержания ионов Li^+, K^+, Cu^{2+} и Mn^{2+}, связанных с ионом Cl^- в электролите, и pH среды на изменение вязкостных свойств водных растворов гидроксиэтилцеллюлозы (НЕС), подверженных низкотемпературной деградации на воздухе. Об изменении свойств растворов НЕС делался вывод на основании величин $[\eta]$, $\varrho_{[\eta]}$ и k_H в данных экспериментальных условиях. Обнаружено, что значение $[\eta]$ растворов НЕС с одновалентными катионами металлов возрастает при увеличении их содержания, в то время, как в случае двухвалентных ионов Mn^{2+} ее значение не изменяется, а в случае Cu^{2+} даже несколько снижается. В процессе теплового напряжения в изучаемом интервале температур при повышении температуры значения $[\eta]$, как правило, уменьшаются. Влияние pH среды на значение $[\eta]$ наиболее выражено в сильно кислой и сильно щелочной средах при повышенных температурах и дольшей продолжительности

тепловогo напряжения. Растворы НЕС наиболее стабильны в области pH = 6—8 и температурах до 60 °C.

Адекватно с изменением значений [η] растворов НЕС изменяются и вычисленные значения $\varrho_{[\eta]}$ и k_H.

Hydroxyethylcellulose is widely used in several industrial branches. It is applied as thickening agent, protective colloid or film-forming substance in ceramic, polygraphic and pharmaceutic industry, in polymer chemistry, *etc.*

Though the applications of HEC are rather abundant, the characterization of this substance in solution is not yet satisfactory. The present characterization of this water-soluble derivative of cellulose mainly concerns the influence of solvent and temperature on the hydrodynamic properties of the solutions of HEC [1] while attention has also been given to mixed solvents [2], but only to a lesser extent to solvents containing salts.

The macromolecules with linear chain among which the water-soluble derivatives of cellulose belong are inclined to assume the most probable conformation that is represented by statistical coil [3]. The conformational and configurational properties of macromolecules in solutions are to be appreciated according to their viscosity properties [3, 4] characterized by the limiting viscosity number

$[\eta] = \lim\limits_{c \to 0} (\eta_{sp}/c)$ where η_{sp} is specific viscosity and c is polymer concentration.

[η] is in direct relation with the density of statistical coil $\varrho_{[\eta]}$ according to the Einstein equation

$$\varrho_{[\eta]} = \frac{2.5}{[\eta]}$$

The degree of solvation of macromolecules in solvent is determined by the Huggins constant k_H which depends on thermodynamic properties of solution and chemical character of both components, *i.e.* polymer and solvent.

The influence of thermal stress of polymers on their viscosity properties can be considerable. The effect of heat on cellulosic materials in the solid state has hitherto been studied mostly at temperatures over 200 °C [5, 6]. At low temperatures (under 100 °C) the thermal destruction of cellulose does not usually set in, but many properties and appearance of this substance change, especially if the process proceeds in the presence of oxygen and aromatic rests of lignin. The thermo-oxidizing reactions appear mainly in initial stage of the process and result in a decrease of the degree of polymerization.

The properties of polysaccharide solutions are also affected by changes in pH of the medium [3, 7]. In acid medium the polysaccharides hydrolyze while in basic medium their hydrolysis is preceded by oxidation, which finally results in degradation of macromolecules and increase in the content of strongly polar carboxyl groups.

The solution properties of polymers may also be influenced by the presence of the electrolytes solved in solvent, the solvation shells of which compete with the envelopes of segments of the polymer chain. In aqueous solutions the cations and anions of low-molecular electrolyte can be physically bound to the oxygen and hydrogen atoms of solvent molecules and to the free --OH groups of the glycose unit of polysaccharide to give ionic complexes. The strength of interactions in solution is dependent on properties of the present ions, their size, charge number, diameter of solvation shell [8] as well as on the content of polar groups (defective or nondefective) in the chain molecule of polymer.

The aim of this study has been to contribute to characterization of the properties of the aqueous solutions of HEC in the presence of low-molecular binary electrolytes and elucidate their influence on low-temperature thermo--oxidation of polymer.

Experimental

The solutions of HEC used for viscosimetric measurements were prepared by dissolving 0.12 g of HEC (product of Hercules, Wilmington, USA, named Natrosol 250 H, degree of substitution 2.5, $[\eta] = 7.8 \times 10^2$ dm^3 kg^{-1}, purity for scientific use) in 0.1 dm^3 of aqueous solution of low-molecular electrolyte (LiCl, KCl, MnCl$_2$, and CuCl$_2$) of 10^{-1}, 10^{-2}, and 10^{-3} mol dm^{-3} concentration or in buffered solutions of pH 2.2, 3, 5, 7, 9, 11, 12 which were prepared by mixing the aqueous solutions of Na$_2$HPO$_4$, C$_6$H$_8$O$_7$, H$_3$BO$_3$, and NaOH in prescribed proportions [9]. The solutions of HEC were homogenized in a shaker for 3 h at laboratory temperature. Other chemicals used were anal. grade reagents (Lachema, Brno).

The solutions were thermally stressed at 60, 80, and 100 °C for 0, 1, 5, and 24 h in an air thermostat where the temperature was held accurate to ± 1 °C.

A capillary Ubbelohde viscosimeter with hanging level was used for measuring the viscosity of the investigated solutions of HEC. The measurements were carried out at the constant temperature of 25 °C which was held by thermostating.

Results and discussion

It is assumed in the theory of polysaccharide solutions that their behaviour is determined by the polymer—solvent interactions. In aqueous solutions these interactions are influenced by the polar character of the water molecule itself [10], while the influence of nonelectrostatic inter- and intramolecular forces must not be neglected. The interactions between polymer and water in solution can be raised or reduced by an addition of low-molecular electrolytes [11].

Besides other factors, the thermal stress, especially in the presence of oxygen,

affects the change in physicochemical properties of the derivatives of cellulose in solution even at temperatures ranging from 50 to 90 °C [5].

The study of viscosity properties of HEC in aqueous solutions has shown that a slight increase in $[\eta]$ appears as early as in the initial stage of annealing, which may be due to the increase in mobility of the hydrated polymer segments, which results in an increased aggregation by the effect of hydrogen bonds and mutual twisting and is accompanied by apparent reduction in density of the statistical polymer coil. A degradation manifesting itself by a decrease in $[\eta]$ sets in with prolonged time of thermal stress and increasing temperature (Fig. 1).
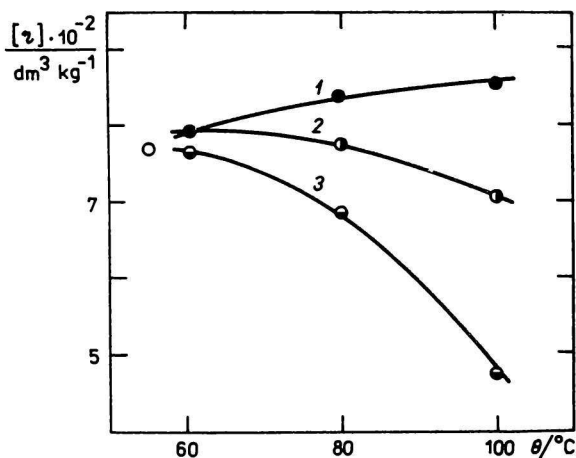

Fig. 1. Dependence of limiting viscosity number $[\eta]$ of the aqueous solution of hydroxyethylcellulose on temperature of thermal stress. Time of thermal stress: 1. 1 h; 2. 5 h; 3. 24 h.

The change in $[\eta]$ of the solutions of HEC produced by the effect of pH of medium and thermal stress can be seen in Fig. 2a, b. In agreement with literature [12] the value of $[\eta]$ increases with the increasing pH value of solution. A slight increase in $[\eta]$ can also be achieved by the effect of thermal stress at lower temperatures and shorter time of duration. After a longer annealing at 100 °C and at boundary values of pH a rapid decrease in viscosity of the solutions of HEC sets in by the effect of an increased content of the H_3O^+ and OH^- ions producing acid and alkaline hydrolysis of the polymer chain owing to which the macromolecular coils curl up to a smaller volume. We may state that the aqueous solutions of HEC subjected to low-temperature thermo-oxidizing degradation are most stable in slightly alkaline solution.

The influence of ions on viscosity properties of polymer solutions is in relation to charge number, hydrodynamic radius of electrolyte ions, electronegativity of ions, and ionic strength of solutions.

The variations of $[\eta]$ of the aqueous solutions of HEC in the presence of LiCl

Fig. 2. Dependence of limiting viscosity number $[\eta]$ of the aqueous solutions of hydroxyethylcellulose on pH after their thermal stress
a) at 60 °C; *b*) at 100 °C.
Time of thermal stress: *1.* 0 h; *2.* 1 h; *3.* 5 h; *4.* 24 h.
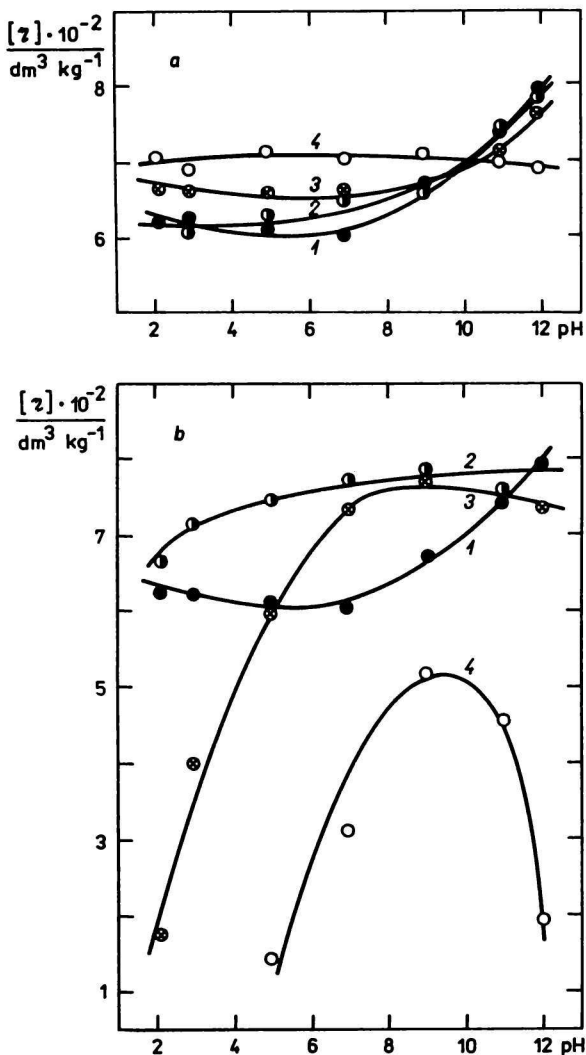
of different concentrations at three investigated temperatures are represented in Fig. 3*a*, *b*, *c* for individual times of thermal stress. As obvious, the values of $[\eta]$ increase with increasing concentration of LiCl in the solution, but an increase in temperature and time of thermal stress brings about a decrease in $[\eta]$ of the solutions of HEC. The changes in absolute values are smaller at higher concentrations of LiCl when compared with aqueous solutions of HEC.

Analogous influence on $[\eta]$ of the solutions of HEC was also observed for additions of KCl. The measured values of $[\eta]$ are listed in Table 1.

Table 1

Values of $[\eta]$, $\varrho_{[\eta]}$, and k_H of the aqueous solutions of HEC after thermal degradation in the presence of low-molecular electrolytes

Electrolyte	c / mol dm^{-3}	θ / °C	$[\eta] \cdot 10^{-2}$/(dm^3 kg^{-1})				$\bar{\varrho}_{[\eta]} \cdot 10^4$/(kg dm^{-3})				k_H			
							Time of thermal stress/h							
			0	1	5	24	0	1	5	24	0	1	5	24
LiCl	10^{-1}	60	9.42	8.97	8.32	7.67	26.5	27.8	30.0	32.9	0.83	1.02	1.31	1.54
	10^{-2}		9.00	8.85	8.00	7.10	27.7	28.2	31.3	35.2	0.96	1.07	1.22	1.75
	10^{-3}		8.57	8.59	7.61	6.45	29.2	29.0	32.8	38.7	1.16	1.13	1.19	2.09
	10^{-1}	80		9.54	8.87	8.70		26.2	28.1	27.5		0.75	0.76	0.44
	10^{-2}			9.28	8.62	7.95		26.9	29.0	31.5		0.89	0.89	0.65
	10^{-3}			9.07	8.82	6.81		41.2	28.3	36.6		0.87	0.75	0.82
	10^{-1}	100		9.57	7.84	7.28		26.1	31.9	34.4		0.68	0.73	0.42
	10^{-2}			8.98	7.23	4.68		28.8	34.6	53.5		0.80	0.77	0.49
	10^{-3}			8.66	6.43	4.26		28.9	38.9	58.7		0.70	0.40	0.12
KCl	10^{-1}	60	9.35	9.31	9.20	9.08	26.7	26.9	27.2	27.5	0.87	0.89	0.86	0.79
	10^{-2}		9.40	9.33	9.02	8.74	26.6	26.8	27.7	28.6	0.90	0.89	0.88	0.86
	10^{-3}		9.10	8.98	8.73	8.64	27.5	27.8	28.6	28.9	0.93	0.95	0.94	0.69
	10^{-1}	80		9.20	8.98	7.94		27.2	27.8	31.5		0.79	0.78	0.74
	10^{-2}			9.51	8.99	7.66		26.3	27.8	32.6		0.78	0.75	0.76
	10^{-3}			9.02	9.03	6.75		27.7	27.7	37.0		0.89	0.60	0.67
	10^{-1}	100		9.02	7.75	7.31		26.1	32.3	34.2		0.86	0.82	0.43
	10^{-2}			8.57	7.51	5.19		29.2	33.3	38.2		0.96	0.62	0.43
	10^{-3}			8.60	7.57	5.36		29.1	33.0	46.6		0.51	0.66	0.43
CuCl$_2$	10^{-1}	60	9.50	9.40	8.75	7.38	26.3	26.5	28.5	33.8	0.87	0.79	1.02	0.87
	10^{-2}		9.52	9.51	8.87	7.60	26.2	26.3	28.2	32.9	0.87	0.87	1.03	
	10^{-3}		9.50	9.52	9.23	8.60	26.3	26.3	27.0	29.1	0.84	0.86	0.80	1.01
	10^{-1}	80		8.75	8.55	6.55		28.6	29.2	38.2		0.98	0.78	0.59
	10^{-2}			8.92	9.21	7.60		28.0	27.1	32.8		1.00	0.76	0.70
	10^{-3}			8.94	8.76	8.34		28.0	28.5	30.0		0.97	0.88	0.71

Table 1 (Continued)

Electrolyte	c / mol dm^{-3}	θ /°C	$[\eta] \cdot 10^{-2}$/(dm^3 kg^{-1})				$\bar{\varrho}_{[\eta]} \cdot 10^4$/(kg dm^{-3})				k_{H}			
			Time of thermal stress/h										
			0	1	5	24	0	1	5	24	0	1	5	24
CuCl$_2$	10^{-1}	100		8.86	4.71	1.27		28.0	53.1	96.1		0.97	0.41	0.01
	10^{-2}			8.84	7.47	3.82		28.3	33.5	65.4		0.96	0.66	0.76
	10^{-3}			9.40	8.35	6.09		26.6	30.0	41.1		0.76	0.62	0.44
MnCl$_2$	10^{-1}	60	9.45	8.85	8.66	7.90	26.5	28.0	28.9	31.6	0.88		1.18	0.72
	10^{-2}		9.30	8.75	8.68	8.50	26.9	28.3	28.8	29.4	1.13		0.89	0.80
	10^{-3}		9.15	8.86	9.06	8.50	27.3	28.6	27.6	29.4	0.92	1.02	0.92	0.73
	10^{-1}	80		9.05	8.93	8.78		28.2	28.0	28.5		0.87	0.77	0.68
	10^{-2}			9.11	8.90	8.47		27.6	30.3	29.5		0.89	1.06	0.81
	10^{-3}			9.32	9.20	8.91		27.5	27.0	28.1		0.86	0.47	0.75
	10^{-1}	100		9.26	9.04	8.13		26.8	27.6	30.8		0.85	0.60	0.59
	10^{-2}			9.12	8.95	8.52		27.0	27.9	29.3		0.89	0.73	0.64
	10^{-3}			8.95	8.50	7.84		27.4	29.4	31.9		0.92	0.79	0.62
								27.9						
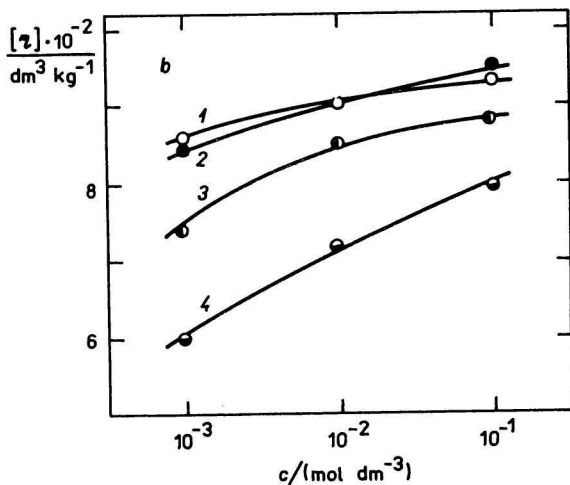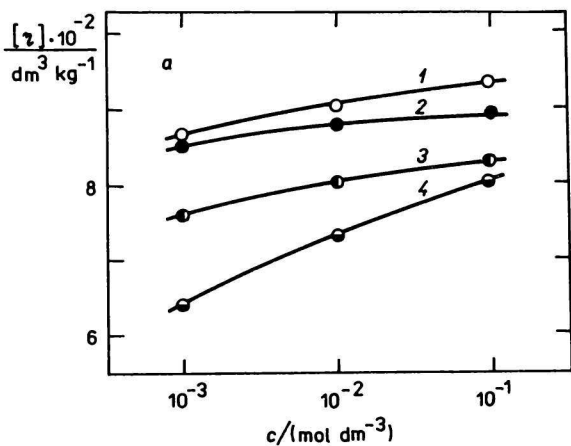
The influence of the bivalent Cu^{2+} ions on $[\eta]$ of the aqueous solutions of HEC is illustrated in Fig. 4a, b, c. The increasing content of $CuCl_2$ in aqueous solution of HEC does not affect the values of $[\eta]$ at shorter times of thermal stress, while a considerable decrease can be observed at increased temperature and longer times of thermal stress. For instance, for 24 h thermal degradation at 100 °C the value of $[\eta]$ falls from 400 dm^3 kg^{-1} observed for aqueous solution of HEC to 100 dm^3 kg^{-1} observed at the highest investigated concentration of $CuCl_2$ (10^{-1} mol dm^{-3}).

The presence of $MnCl_2$ only slightly affects the viscosity properties of the

Fig. 3. Limiting viscosity number $[\eta]$ of the aqueous solutions of hydroxyethylcellulose as a function of the added LiCl after thermal stress *a*) at 60 °C; *b*) at 80 °C; *c*) at 100 °C. Time of thermal stress: *1.* 0 h; *2.* 1 h; *3.* 5 h; *4.* 24 h.
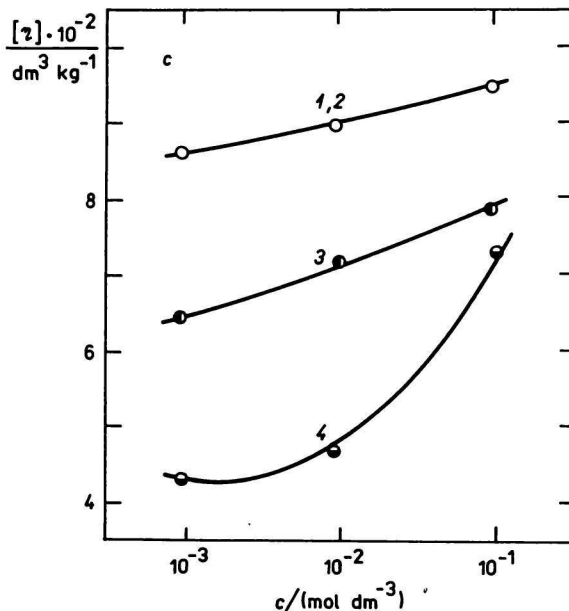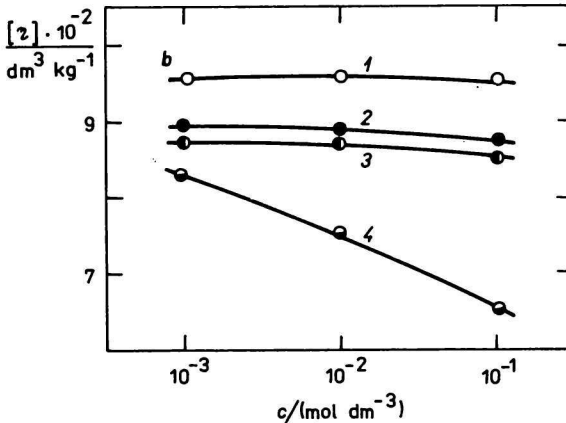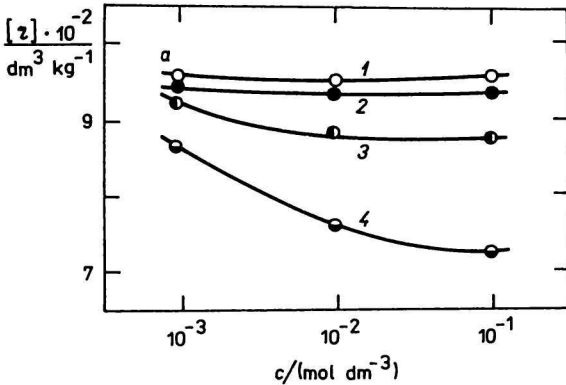
aqueous solutions of HEC at the investigated temperatures and times of thermal stress (Table 1).

The influence of ionic strength of the investigated uni-univalent electrolytes on viscosity properties of the aqueous solutions of HEC is analogous. An increase in temperature of the investigated system has significant influence not only on the change in mobility of ions and diameter of their hydration shell, but also on physicochemical changes in polymer coil, which manifests itself in a decrease in $[\eta]$, especially at lower concentrations of the added LiCl.

The influence of the Cu^{2+} and Mn^{2+} ions on $[\eta]$ of HEC solutions is different for equal ionic strength and equal experimental conditions. The Cu^{2+} ions to a great extent change the conformation of HEC macromolecules. The abrupt drop of $[\eta]$ due to thermal stress may be attributed not only to the increase in density of the statistical coil, but also to the positive catalytic effect of the present Cu^{2+} ions on the thermo-oxidizing process which proceeds probably *via* formation of complexes with oxygen on the C-2 carbons and C-2—C-3, C-3—C-4 bonds of the glucose unit of macromolecule. An addition of Mn^{2+} into solution has a stabilizing effect on HEC macromolecules in the investigated concentration and temperature interval, which shows itself in the course of thermal stress of the aqueous solutions of HEC.

The efficacy of intermolecular interactions in polymer solutions can be estimated according to the change in value of the Huggins constant k_H which is

to be regarded as a criterion of expansibility of the macromolecular coil in the investigated solvent. The values of k_H of the solutions of HEC in distilled water in the presence of the investigated electrolytes after thermal stress at different temperatures are given in Table 2.

The changes in the values of k_H obtained for shorter times of thermal stress (1 and 5 h) are insignificant. Greater changes were observed after 24 h thermal stress in the main at 100 °C.

The decreasing values of k_H indicate impairment of the polymer—solvent interactions by the effect of increased temperature and prolonged degradation [13, 14].

Other value proper for characterizing the volume of macromolecule in solution is the density of statistical coil $\varrho_{[\eta]}$ calculated from the Einstein equation. The density of coil depends on the kind and molar mass of polymer, the solvent

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Fig. 4. Limiting viscosity number $[\eta]$ of the aqueous solutions of hydroxyethylcellulose as a function of the added $CuCl_2$ after thermal stress *a*) at 60 °C; *b*) at 80 °C; *c*) at 100 °C.

Time of thermal stress: *1.* 0 h; *2.* 1 h; *3.* 5 h; *4.* 24 h.
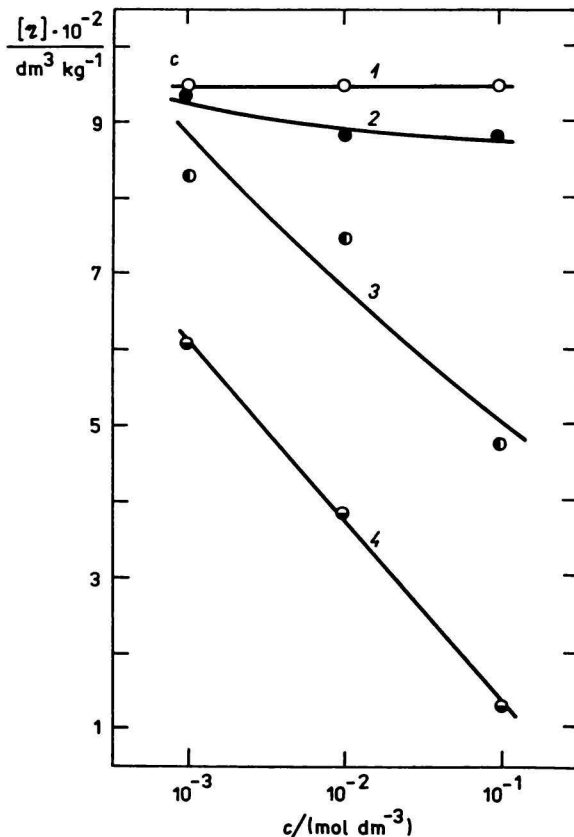
and the temperature of solution [3]. The values of $\varrho_{[\eta]}$ obtained for the aqueous solutions of HEC at varying pH after thermal stress and in the presence of individual electrolytes at different temperatures are given in Tables 1 and 2.

As obvious, individual ions affect the density of coil in different way. While the univalent ions reduce the density of coil with their increasing content in solution, the bivalent ions raise the density of coil. For the highest investigated content of $CuCl_2$ the increase in the value of $\varrho_{[\eta]}$ is approximately 5-fold after 24 h thermal stress at 100 °C. This fact may be in relation to association. The increase in charge number of cation influences the conformation of macromolecule so that the statistical coil turns into almost compact globule, which manifests itself by an increase in $\varrho_{[\eta]}$ [15]. An increase in $\varrho_{[\eta]}$ (at 25 °C) also comes into existence by the effect of the increased temperature in the process of thermal degradation of HEC solutions, especially in the temperature interval 80—100 °C.

Table 2

Values of $[\eta]$, $\varrho_{[\eta]}$, and k_H of the aqueous solutions of HEC after thermal degradation at different pH values

θ	Time	pH						
°C	h	2.2	3.0	5.0	7.0	9.0	11.0	12.0
60	0	6.22	6.24	6.10	6.00	6.74	7.40	7.92
$[\eta] \cdot 10^{-2}$	1	6.19	6.03	6.25	6.49	6.60	7.44	7.85
$\mathrm{dm^3\,kg^{-1}}$	5	6.75	6.70	6.64	6.70	6.65	7.20	7.70
	24	7.09	6.90	7.10	7.01	7.10	7.03	6.92
	0	40.2	40.0	41.0	41.7	37.1	33.8	31.6
$\varrho_{[\eta]} \cdot 10^4$	1	40.4	41.5	40.0	38.5	37.9	33.5	33.6
$\mathrm{kg\,m^{-3}}$	5	37.0	37.3	37.7	37.3	37.6	34.8	34.7
	24	35.3	36.2	35.2	35.7	35.2	34.8	35.6
	0	4.04	3.09	2.94	3.10	2.39	1.48	1.23
k_H	1	3.63	3.46	2.59	2.42	2.67	1.03	1.46
	5	1.96	2.61	2.14	1.94	2.47	0.89	1.46
	24	0.88	1.91	1.55	1.49	1.74	0.63	1.10
80	1	7.16	7.13	7.50	7.85	7.62	7.90	7.85
$[\eta] \cdot 10^{-2}$	5	6.64	6.72	7.05	7.50	7.80	7.61	7.76
$\mathrm{dm^3\,kg^{-1}}$	24	3.20	4.41	5.83	7.29	7.66	6.17	5.18
	1	34.9	35.1	33.3	31.9	32.8	31.6	32.0
$\varrho_{[\eta]} \cdot 10^4$	5	37.7	37.2	35.5	33.3	32.1	32.9	32.5
$\mathrm{kg\,m^{-3}}$	24	78.1	56.7	42.9	34.3	32.6	40.5	48.2
	1	1.70	1.83	1.57	1.57	1.61	1.22	1.15
k_H	5	0.64	1.40	1.62	1.45	1.06	0.71	0.72
	24	0.45	1.15	1.48	0.97	0.51	0.42	0.43
100	1	6.65	7.15	7.44	7.73	7.86	7.62	7.94
$[\eta] \cdot 10^{-2}$	5	1.70	3.97	5.95	7.33	7.70	7.62	7.36
$\mathrm{dm^3\,kg^{-1}}$	24	—	—	1.45	3.09	5.17	4.57	1.97
	1	37.6	35.0	33.6	32.3	31.8	32.8	31.5
$\varrho_{[\eta]} \cdot 10^4$	5	147.1	63.0	42.0	34.1	32.5	32.8	34.0
$\mathrm{kg\,m^{-3}}$	24	—	—	172.4	80.9	48.4	54.7	126.9
	1	0.60	2.55	1.28	1.35	1.31	1.32	1.06
k_H	5	1.15	0.77	0.19	0.62	0.69	0.91	0.35
	24	—	—	0.29	0.24	0.56	0.86	—

The mechanism of the thermodegradation process of HEC in the presence of low-molecular electrolytes is most frequently explained by formation of complexes of the effective ions with oxygen or hydrogen of the —OH group on the C-2 carbon or C-2—C-3 and C-3—C-4 bonds of the β-D-glucose unit of poly-

mer molecule the subsequent decay of which may result in breaking of the chain [16—19].

The changes in $\varrho_{[\eta]}$ due to pH of solution are small at 60 °C or at shorter times of thermal stress at higher temperatures. The greatest changes in $\varrho_{[\eta]}$ were observed as late as after 5 and especially 24 h thermal stress at 100 °C. The dependence of $\varrho_{[\eta]}$ on pH exhibits a minimum at about pH 9.

The changes in viscosity properties of the polymer solutions of HEC and corresponding characteristic quantities k_H and $\varrho_{[\eta]}$ are influenced not only by temperature and time of thermal stress, but also by chemical character of the added ions, their amount, size of their hydration shell and pH of solution. These factors affect the conformation of macromolecules and the diffusion of solvent into polymer coil. The influence of individual factors cannot be separated from each other and all observed effects are an integral resultant of these factors.

References

1. Brown, W., Henley, D., and Öhman, J., *Makromol. Chem.* 64, 49 (1963).
2. Brown, W., Friedberg, F., Henley, D., and Öhman, J., *Makromol. Chem.* 66, 168 (1963).
3. Vollmert, B., *Základy makromolekulárni chemie.* (Fundamentals of Macromolecular Chemistry.) Academia, Prague, 1970.
4. Amis Eric, J., *Am. Chem. Soc., Polym., Prepr.* 27, 269 (1986).
5. Madorskii, S., *Termicheskoe razlozhenie organicheskikh polimerov.* Mir, Moscow, 1967.
6. Pugachevskii, G., *Iznashivanie tsellyuloznykh tkanei pri vozdeistvii razlichnykh faktorov.* Legkaya industriya, Moscow, 1977.
7. Mackowiak, A. and Góreckij, M., *Acta Pol. Pharm.* 42, 159 (1985).
8. Erdey-Grúz, T., *Transport Phenomena in Aqueous Solutions.* Akadémiai Kiadó, Budapest, 1974.
9. Sýkora, V. and Zátka, V., *Příručni tabulky pro chemiky.* (Manual Tables for Chemists.) P. 63, 67. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1956.
10. Mandel, M., *Angew. Makromol. Chem.* No. 123/124, 63 (1984).
11. Lazár, M. and Mikulášová, D., *Syntéza a vlastnosti makromolekulových látok.* (Synthesis and Properties of Macromolecular Substances.) Alfa Publishers, Bratislava, 1976.
12. Bikales, N. and Segal, I., *Tsellyuloza i ee proizvodnye.* Mir, Moscow, 1974.
13. Sakal, T., *J. Polym. Sci.,* A-2 6, 1535 (1968).
14. Bohdanecký, M., *Collect. Czechoslov. Chem. Commun.* 35, 1972 (1970).
15. Klooster, N. Th. M., Touw, F., and Mandel, M., *Macromolecules* 17, 2078 (1984).
16. Samal, R. K., Satrusallya, S. C., Sahoo, P. K., Ray, S. S., and Nayak, S. N., *Colloid Polym. Sci.* 262, 939 (1984).
17. McCormick, Ch. L., Callais, P. A., and Hutchinson, B. H. J., *Macromolecules* 18, 2394 (1985).
18. Pogrebnyak, V. G., Naumchuk, N. V., Tverdokhleb, S. V., and Ivanyuta, Yu. F., *6. Resp. konf. po fizikokhimii, tekhnol. poluch. i primeneniya promyvoch. zhidkostei, dispers. sistem i tamponazh. rastvorov.* P. 177—178. Ivano Frankovsk, Oct.—Nov., 1985. Part 2. Kiev, 1985.
19. Bekturov, E. A., Kudaibergenov, S. E., Zhaimina, G. M., Saltykov, Y. P., and Pelmenstein, B. Ya., *Makromol. Chem., Rapid Commun.* 7, 339 (1986).

Translated by R. Domanský