SOLUBILIZATION OF POLY (2-HYDROXYETHYL METHACRYLATE) WITH AQUEOUS SALT SOLUTIONS; VISCOMETRIC STUDY OF THE SOLUTIONS

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Reduced specific viscosity values (η_{red}) of 1% solutions of poly(2-hydroxyethyl methacrylate) in aqueous solutions of 20 salts (thiocyanates, iodides, perchlorates, bromides and nitrates) were determined at $20-60°C$. The dependences on salt concentrations and on temperature were expressed by means of simple empirical equations and used to formulate the rules of the solubilization effect of salts. The quotient $d\ln \eta_{red}/dT$ was found to have a linear correlation with η_{red}^{-1}, which was interpreted in terms of the Lumry rule concerning the enthalpy and entropy compensation of some processes occurring in aqueous solutions.

This paper is a continuation of an earlier paper[1] and presents results obtained by the viscometric investigation of uncrosslinked soluble poly(2-hydroxyethyl methacrylate) in aqueous salt solutions. The work was stimulated by the fact that the uncrosslinked polymer does not dissolve in water, but dissolves in aqueous solutions of some salts, if their concentration becomes higher than a certain limit. The work had as its objective an elucidation of the conditions of the solubilization effect of salts and a quantitative, though empirical, analysis of data thus obtained. Quite understandably, numerical results provided by the analysis are related only to the sample used in the work, and would differ quantitatively for a sample of a different molecular weight. Qualitative differences are rather unlikely.

EXPERIMENTAL

An unfractionated sample of poly(2-hydroxyethyl methacrylate) ($\overline{M}_w = 4·5 . 10^5$ by the light scattering method, $[\eta] = 0·752$, dimethylformamide, 25°C) was used; it was prepared by solution, radical initiated polymerization of 2-hydroxyethyl methacrylate (10% solution of monomer in ethanol, dibenzoyl peroxide (0·25%) as initiator) up to 80% conversion at 70°C. The monomer contained c. 0·1% of diester; as a consequence, the polymer was branched. This is also indicated by the fact that the $[\eta]$ values measured in DMF and in a number of variously concentrated aqueous KSCN solutions were lower by $20-25\%$ than those calculated for a linear monodisperse polymer

($\overline{M}_w = 4 \cdot 5 \cdot 10^5$) according to the $[\eta]$–M relationships given in refs[2,3]; consequently, a branching ratio (g') 0·75 was used in the calculations.

The preparation and check of the concentration of salt solutions were performed as described in ref.[1]. Viscosity measurements were carried out with Ubbelohde viscometers at $25-60°C$ maintained with an accuracy of $\pm 0 \cdot 02°C$. Viscometric corrections and differences in the densities of polymer solutions and solvents were negligible. Intrinsic viscosities were determined by the usual extrapolation method.

RESULTS AND DISCUSSION

Preliminary experiments showed that the linear poly(2-hydroxyethyl methacrylate) (further only "polymer") was soluble at $5-60°C$ in aqueous solutions of thiocyanates, iodides and perchlorates of alkali metals and metals of the second group of the periodic system. Of chlorides, the polymer could be dissolved only in zinc chloride; of bromides, lithium and cadmium salts had the same effect, along with nitrates of some bivalent (Mg, Mn, Cu, Co, Ni, Cd) and trivalent (Fe, Cr) metals. To dissolve the polymer, a certain minimum salt concentration is needed, depending on the individual character of the salt. This fact restricts the concentration range on one side; the other boundary is determined by the solubility of salt in water. Because of this, in many cases (*e.g.*, with nitrates) the concentration range within which the solution properties can be studied is very narrow. To characterize the salting-in effect of salts on poly(2-hydroxyethyl methacrylate), we use the reduced specific viscosity values $\eta_{red} \equiv \eta_{sp}/c$ (c being the concentration of the polymer solution) and their dependence on temperature.* The temperature dependence was determined so that a solution of a standard concentration of 1·00 g/dl prepared at 25°C was measured at several temperatures within an interval of $25-60°C$. The η_{red} and C_s (concentration of salt solution) values were corrected for the change in the solvent density (*i.e.* density of the salt solution) with temperature (if the data were available in the literature[4,5]). For the majority of systems the correction was not higher than $2-3\%$. KSCN, with its temperature density quotient d ln ϱ/dT higher by almost one order of magnitude (d ln ϱ/d$T \cdot 10^3 = -0 \cdot 7$ to $+3$ at C_s 1 to 9M), was an exception.

However, the η_{red} values thus corrected are not related to an exactly the same polymer concentration, but to concentrations which gradually decrease with increasing temperature. Recalculation of the reduced specific viscosities to a concentration common at all temperatures (*i.e.* 1·0 g/dl) would call for the knowledge of the values of the Huggins viscometric constant (k_H) in the individual cases. According to detailed measurements involving polymer–KSCN solutions[6], k_H varies within broad limits ($0 \cdot 3 - 1 \cdot 1$) depending on salt concentration and temperature. Assuming that for other systems too the k_H values will lie within the same interval, one can estimate the error committed if the recalculation to the common polymer

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*   Numerical values of η_{red} and dln η_{red}/dT are given in detail in ref.[6].

concentration is left out. It will appear that in a very unfavourable case ($k_H = 1\cdot1$, d ln $\varrho/dT = -2\cdot5 \cdot 10^{-3}$) the error in the reduced specific viscosity will not be higher than 2%, and in d lnη_{red}/dT it will not be higher than 25%. The above example corresponds to the system polymer–8M-NaSCN. For all the other salts (except for KSCN) the error will be much smaller owing to the low d ln ϱ/dT values. Only for solutions in KSCN it may be higher, but for this system we performed detailed measurements allowing us to determine the intrinsic viscosity and the quotient d ln $[\eta]/dT$.
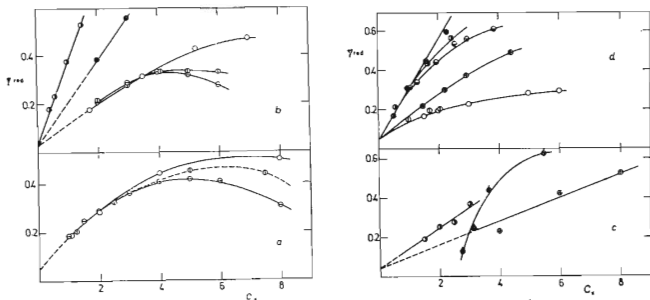

FIG. 1

Dependence of the Reduced Specific Viscosity of Polymer Solutions on Salt Concentration at 25°C
a) Thiocyanates, b) iodides, c) bromides and zinc chloride, d) perchlorates. Polymer concentration (c) 1·00 g/dl. Cations: $\oplus$ Li$^+$, $\circ$ Na$^+$, $\ominus$ K$^+$, $\oplus$NH$_4^+$, $\circ$ Cs$^+$ (with a pip), $\ominus$ Be^{2+}, $\bullet$ Mg^{2+}, $\bullet$ Ca^{2+}, $\ominus$ Ba^{2+}, $\bullet$ Cd^{2+}, $\bullet$ Zn^{2+} (with a pip).
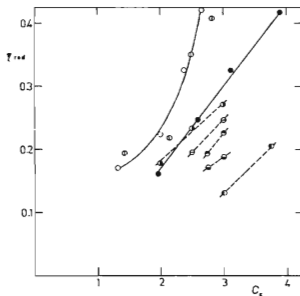

FIG. 2

Dependence of the Reduced Specific Viscosity of Polymer Solutions on the Concentration of Nitrates at 25°C

Polymer concentration c) 1·00 g/dl. Cations: $\bullet$ Mg^{2+}, $\bullet$ Cd^{2+}, $\bullet$ Mn^{2+}, $\bullet$ Cu^{2+}, $\ominus$ Ni^{2+}, $\ominus$ Co^{2+}, $\circ$ Cr^{3+}, $\oplus$ Fe^{3+}.

Dependence of the η_{red} Values on Salt Concentration

The reduced specific viscosity of salt solutions of poly(2-hydroxyethyl methacrylate) depends on the concentration and type of salt and on temperature. For bromides, nitrates, perchlorates, iodides of bivalent cations it increases monotonically with salt concentration, while for thiocyanates and iodides of univalent cations the dependence $\eta_{sp}/c-C_s$ passes through a maximum (Figs 1, 2). For sodium, potassium and ammonium thiocyanates (Fig. 1a) the dependence is almost identical up to $C_s = 3M$, similarly as for iodides of alkali metals and ammonium (Fig. 1b). At higher concentrations, however, the dependences become differentiated according to the height and position of the maximum and to the course beyond the maximum. The decrease is largest with the potassium salts, smaller with the ammonium salts and smallest with the sodium salts. Thus, while the anions play the decisive role in the ascending part, the effect of the character of the univalent cation being only very insignificant, the descending part strongly depends on the cation. For perchlorates too (Fig. 1d) no marked difference between the cations Na^+ and NH_4^+ can be observed, but for lithium perchlorate the η_{sp}/c values are higher.

The quantitative analysis of results is based on the fact that the dependences η_{sp}/c *vs* C_s are very adequately described by a simple empirical relationship

$$\eta_{sp}/c = a_0 + a_1 C_s + a_2 C_s^2 . \tag{1}$$

The absolute term a_0 should not depend on the character of the salt. Its values at various temperatures were determined by extrapolation of the η_{sp}/c *vs* C_s dependences (to $C_s = 0$) for zinc perchlorate, linear at all temperatures within the whole broad concentration range. The fact that with a_0 values thus estimated, linear plots $(\eta_{sp}/c - a_0) C_s^{-1}$ *vs* C_s were obtained at all temperatures also for other salts (Fig. 3), justifies the confidence in the correctness of these values. Such procedure could not be
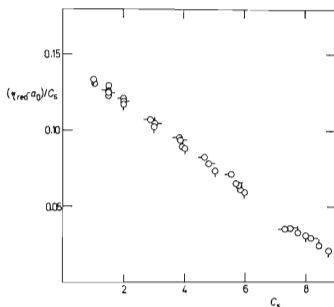

Fig. 3

Determination of the Parameters of Eq. (1) for the System Polymer–Aqueous Solution of KSCN

Temperatures (distinguished by pips): 25°C (downwards), 35°C (upwards), 45°C (right), 55°C (left).

employed for nitrates, where the dependence η_{sp}/c vs C_s was convex or where the concentration range was too narrow. In these cases a quantitative analysis was given up.

The cases when the η_{red} vs C_s dependences possess a maximum can also be described very adequately and within the whole concentration range by Eq. (1). The coordinates of the maximum are given by

$$(C_s)_{max} = \left| a_1/2a_2 \right|, \tag{2}$$

$$(\eta_{red})_{max} = a_0 + \left| a_1^2/4a_2 \right|. \tag{3}$$

The position of the maximum obviously depends on the ratio of the absolute values of the parameters $\left| a_1/2a \right|_2$, and thus on the type of the salt and on temperature. If the ratio is lower than the solubility of salt in water, the maximum can be found experimentally (thiocyanates, iodides). If it is higher, no maximum will appear.

It would be easy to regard the term a_0 as a reduced specific viscosity exhibited by a 1% polymer solution in pure water. The solubility of the polymer in water is very small, however (perhaps with the exception of polymers of a very low molecular weight), so that verification of such assumption would be beyond what is experimentally feasible. Nevertheless, the parameter a_0 and its temperature coefficient da_0/dT can be regarded as empirical characteristics of the interaction of the polymer with water.

As can be seen in Table I, the coefficients a_1, a_2 depend on the nature of the salt and on temperature. The former one (always positive) is a measure of the salting-in capacity of the salt. It obeys rules similar to those found in analyzing the results of swelling[1]: 1) For salts of ammonium and alkali metals (except Li^+) it is almost independent of the cation, but depends strongly on the anion. In the case of a common cation it decreases in the order $SCN' > I' > ClO_4' > Br'$. 2) For lithium perchlorate it is higher by c. 20% than for the sodium and ammonium salt. 3) In accord with the decreasing a_1, the cations are arranged as follows: $Be^{2+} > Mg^{2+} > Ba^{2+} \simeq Cd^{2+} > Zn^{2+} > Ca^{2+} > Li^+ > Na \simeq NH_4^+$ for perchlorates, and $Cd^{2+} > Mg^{2+} > NH_4^+ \simeq K^+ \simeq Na^+$ for iodides. 4) The a_1 values of salts of bivalent cations are $1.5 - 3$ times higher than those of salts of alkali metal cations. That may be partly due to the fact that at the same molar concentration the anion concentration is twice as high in solutions of the former salts. 5) The cations Cd^{2+}, Zn^{2+} occupy a special position, particularly if combined with halide anions. Of bromides, it is only the cadmium(II) salt that dissolves the polymer (besides LiBr). The coefficient a_1 of cadmium bromide can be compared with the value for iodides or perchlorates of alkali metals. For CdJ_2 it is the highest of all the values measured. While for perchlorates the order of cations is $Mg^{2+} \simeq Cd^{2+} > Na^+$, for iodides there is an inversion between Cd^{2+} and Mg^{2+}: $Cd^{2+} > Mg^{2+} > Na^+$.

The coefficient a_2 is always negative (or zero) and may be regarded as an expression of the salting-out effect of salts. From the fact that in Eq. (1) it is related to the square of salt concentration one may infer that it follows from the mutual interaction of ions and from changes in the structure of solutions due to such interaction[7]. Thus, what is observed here is not a salting-out effect in the sense of electrostatic theories[8], which depends on the first power of salt concentration.

The parameter a_2 varies within much broader limits than a_1. The order of cations (for a common anion) according to decreasing a_2 is completely different from the order set up with respect to a_1. It is of importance that the order is considerably different also for salts of alkali cations whose a_1 values are close or identical. This gives rise to differences between the coordinates of the maxima on the η_{sp}/c vs C_s curves and between the steepnesses of these curves beyond the maxima (Fig. 1). However, it is not possible to explain the above differences on the basis of the structure of concentrated salt solutions at the present-day state of knowledge.

Dependence of Reduced Viscosity on Temperature

As follows from Eq. (1) differentiated with respect to temperature at a constant salt concentration

$$(d\eta_{red}/dT)_{C_s} = (da_0/dT) + C_s(da_1/dT)_{C_s} + C_s^2(da_2/dT)_{C_s}, \qquad (4)$$

the temperature coefficients da_0/dT, da_1/dT and da_2/dT contribute to the temperature coefficient of reduced viscosity. The first of them is negative $(-1\cdot8 \cdot 10^{-3})$ and can be interpreted so that with increasing temperature (at $T < 60°C$) the dissolving power of water for the linear poly(2-hydroxyethyl methacrylate) decreases. This is in accord with the results obtained by measurements of the swelling of gels based on poly(2-hydroxyethyl methacrylate)[9]. The $d\eta_{red}/dT$ values of many systems are negative at lower salt concentrations, the order of magnitude being 10^{-3}, and numerically close to da_0/dT. This means that in such cases the contribution of the first term is important or even decisive. The values of the quotient da_1/dT lie within 10^{-4} to 10^{-3} order of magnitude, are positive for all perchlorates and for CdI_2 and negative for the other iodides and for thiocyanates (Table I). In the former case the salting-in power of the salt increases with increasing temperature, while in the latter it decreases. The sign of the quotient da_2/dT is always opposite to that of da_1/dT. This demonstrates the opposite effect of temperature on the salting-in efficiency of salts (coefficient a_1) and on their salting-out efficiency at higher concentrations (coefficient a_2). Hence, and from Eq. (4) it follows that the temperature coefficient of reduced viscosity should exhibit an extremum at salt concentration

$$(C_s)_{ex} = -\frac{da_1/dT}{2(da_2/dT)}. \qquad (5)$$

The temperature coefficients of reduced viscosity $(d\eta_{red}/dT)$ are predominantly negative and their absolute value decreases at increasing salt concentration. At the highest concentrations, zero or even slightly positive values are found with some systems, especially with perchlorates.

Correlation of the $d \ln \eta_{red}/dT$ *vs* $1/\eta_{red}$ *Values*

If plotted against salt concentrations, the $d \ln \eta_{red}/dT$ values of poly(2-hydroxyethyl methacrylate) in salt solutions offer a rather vague picture. The plot $d \ln \eta_{red}/dT$ *vs*

TABLE I

Parameters of Eq. (1)

$a_0 . 10^2$ values (at given temperatures): 5·5; 3·0; 1·5; 0.

Cation	$a_1 . 10^1$ at T, °C				$a_2 . 10^2$ at T, °C				da_1/dT $. 10^3$	da_2/dT $. 10^3$	C_s range mol/l
	25	35	45	55	25	35	45	55			
					Thiocyanates						
Na$^+$	1·45	1·46	1·40	1·30	1·1	1·2	1·0	0·9	−0·55	1·0	1—8
K$^+$	1·45	1·44	1·46	1·47	1·4	1·4	1·45	1·4	0	0	1—8·8
NH$_4^+$	1·36	1·37	1·40	1·37	1·1	1·1	1·1	1·0	+0·1	0	1·25—10
					Iodides						
Na$^+$	0·80	0·80	0·70	0·64	0·25	0·3	0·15	0·1	−0·6	0·065	1·75—7
K$^+$	1·06	0·98	1·00	0·86	1·1	0·9	1·1	0·9	−0·38	0	2—6
NH$_4^+$	1·06	1·01	0·98	0·95	1·0	0·95	0·85	0·8	−0·36	0·07	2—6
Cs$^+$	1·24	1·00	—	—	1·4	0·7	—	—	—	—	2—3
Mg^{2+}	1·65	1·60	1·61	1·48	0	0	0	0	c. −0·35	0	2—3
Cd^{2+}	3·20	3·40	3·85	3·85	1·1	2·0	4·2	4·0	2·9	−1·2	0·4—2
					Bromides						
Li$^+$	0·61	0·62	0·56	0·54	—	—	—	—	c. −0·3	—	4—8
Cd^{2+}	0·96	0·95	0·97	1·03	0	—	—	—	c. 0	—	1·5—3
					Perchlorates						
Li$^+$	1·17	1·32	—	1·40	0·35	0·5	—	0·4	c. 0·8	c. 0	1·5—4·4
Na$^+$,											
NH$_4^+$	0·95	1·00	1·00	—	1·2	1·2	1·2	—	c. 0·25	c. 0	1·5—6
Be^{2+}	3·00	3·30	3·80	3·90	3·0	3·6	4·6	4·8	3·5	−0·65	0·5—4·2
Mg^{2+}	2·55	2·90^a	—	3·25^b	0·8	2·0^a	—	2·8^b	2·0	−0·80	0·5—3·3
Ca^{2+}	1·60	1·68	1·68	1·68	0·6	0·5	0·5	0·5	0·22	c. 0	2—5
Ba^{2+}	2·52	2·70	3·05	3·00	2·9	3·0	4·0	3·7	1·6	−0·3	1·3—3·8
Zn^{2+}	2·23	2·35	2·35	2·48	0·55	0·65	—	0·7	0·75	c. 0	0·8—2·5
Cd^{2+}	2·55	2·75	3·00	3·35	1·8	2·5	3·3	3·8	2·6	−0·7	0·5—3·3

^{a} 40°C; ^{b} 60°C.

$1/\eta_{red}$ provides considerable simplification and clarity (Fig. 4). The following argument should elucidate this fact. It is based on the two-parameter theory of polymer solutions and on the approximation of the mixed solvent by means of a simple liquid. This is undoubtedly a great simplification of the involved system, but at the present-day state of the theory of polymer solutions it cannot be avoided.

For many phenomena occurring in aqueous solutions of low- and high-molecular weight compounds a linear correlation was observed between enthalpy, $H(x)$, and entropy, $S(x)$, if some variable (x) determining the conditions of the phenomenon[10-12], e.g. composition of a mixed solvent, was systematically varied:

$$\Delta H(x) = \Delta H_0 + T_c \, \Delta S(x) \, . \tag{6}$$

The symbol T_c denotes the so-called compensation temperature, and for the majority of aqueous systems lies within a comparatively narrow interval of $270-300$ K regardless of the nature of the process and of the chemical structure of the compounds involved. This finding has been explained by Lumry and Rajender[10] as a consequence of the fact that the decisive role in such processes is played by the supermolecular structure of liquid water. For this reason, the determination of the compensation temperature is regarded as an appropriate diagnostic test of the participation of water in these processes[10-12], also suitable for revealing unusual effects.
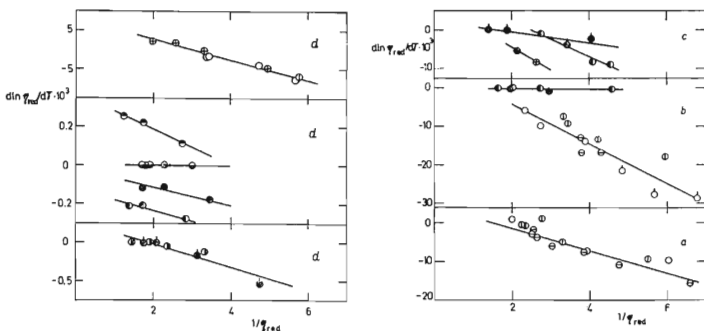

Fig. 4

Correlation of dln η_{red}/dT vs $1/\eta_{red}$ Values at 40°C

a) Thiocyanates, b) iodides, c) bromides and zinc chlorides, d) perchlorates (Symbols as in Fig. 1).

Let us assume that the linear correlation holds for the entropy $\Delta \bar{S}_1$ and enthalpy $\Delta \bar{H}_1$ of dilution, resp. and thus also for the Flory interaction parameters $\psi_1, \varkappa_1$ defined by[13]

$$\varkappa_1 = \Delta \bar{H}_1 / RTv_2^2 \,, \tag{7}$$

$$\psi_1 = \Delta \bar{S}_1 / Rv_2^2 \,, \tag{8}$$

in which v_2 is the volume fraction of the polymer in solution.
Then

$$\varkappa_1 = \varkappa_0 + T^* \psi_1 \,, \tag{9}$$

where $T^* = Tc/T$. For the interaction parameter χ_1, related to the parameters $\psi_1, \varkappa_1$ by

$$\tfrac{1}{2} - \chi_1 = \psi_1 - \varkappa_1 \tag{10}$$

we obtain

$$\tfrac{1}{2} - \chi_1 = A'\varkappa_1 + A'' \,, \tag{11}$$

where

$$A' = (1/T) - 1, \quad A'' = -(\varkappa_0/T^*) \,. \tag{12, 13}$$

Since the parameter χ_1 can be calculated from intrinsic viscosity and the parameter $\varkappa_1$ can be determined from the temperature coefficient of intrinsic viscosity, $\mathrm{d} \ln [\eta]/\mathrm{d}T$, Eq. (11) indicates the possibility of correlating both viscometric quantities.

According to the Flory-Fox theory[13], intrinsic viscosity is related to the interaction parameter χ_1 by

$$\tfrac{1}{2} - \chi_1 = (\alpha^5 - \alpha^3)/X \,, \tag{14}$$

$$\alpha^3 = [\eta]/[\eta]_\Theta \,, \tag{15}$$

$$X = C(\bar{v}^2/V_1)(\overline{R_0^2}/M)^{-3/2} M^{1/2} \tag{16}$$

C is the numerical constant (whose value is of no importance for our purposes), $\bar{v}$ is the partial specific volume of the polymer, V_1 is the molar volume of the solvent, $(\overline{R_0^2})^{1/2}$ is the mean square end-to-end distance of a polymer chain unperturbed by the effect of the excluded volume, M is molecular weight of the polymer and $[\eta]_\Theta$ is the intrinsic viscosity under Θ-conditions. For the temperature coefficient of intrinsic viscosity $\mathrm{d} \ln [\eta]/\mathrm{d}T$ this theory gives the relationship[14]

$$\mathrm{d} \ln [\eta]/\mathrm{d}T = (1/P) \, \mathrm{d} \ln \overline{R_0^2}/\mathrm{d}T + (Q/P) \left[\mathrm{d} \ln (\bar{v}^2/V_1) / \mathrm{d}T + \mathrm{d} \ln (\tfrac{1}{2} - \chi_1)/\mathrm{d}T \right] \,, \tag{17}$$

where

$$(1/P) = 3\alpha^2/(5\alpha^2 - 3) \,, \tag{18}$$

$$(Q/P) = 3(\alpha^2 - 1)/(5\alpha^2 - 3) . \tag{19}$$

If Eq. (10) holds, we have with respect to Eq. (7)

$$d \ln \left(\tfrac{1}{2} - \chi_1\right)/dT = (\varkappa_1/T)/(\tfrac{1}{2} - \chi_1) . \tag{20}$$

On rearrangement, we obtain from Eqs (11) and (14)

$$\varkappa_1 = (2/A') \left[(\alpha^5 - \alpha^3) X^{-1} + A''\right] , \tag{21}$$

so that according to Eq. (20)

$$d \ln \left(\tfrac{1}{2} - \chi_1\right)/dT = (1/A'T)\left(1 - \frac{A''X}{\alpha^5 - \alpha^3}\right) . \tag{22}$$

After substitution into Eq. (17) and rearrangement we have

$$\alpha^3 \, d \ln [\eta]/dT = \alpha^3\{(1/P)\,(d \ln \overline{R_0^2}/dT) + (Q/P)\,[d \ln (\bar{v}^2/V_1)/dT + 1/A'T]\} - \\ - (3A''X/A'T)/(5\alpha^2 - 3) . \tag{23}$$

From Eq. (23) it follows that the intercept of the plot $\alpha^3 \, d \ln [\eta]/dT \, vs \, 1/\alpha^3$ should be

$$u = (3/2) \left[d \ln \overline{R_0^2}/dT - A''X/A'T\right] \tag{24}$$

and that the slope of the dependence at $(1/\alpha^3) = 1$ is

$$s_1 = (3/2)\,d \ln \overline{R_0^2}/dT - d \ln (\bar{v}^2/V_1)/dT - (1/A'T) - (4A''X/A'T) . \tag{25}$$
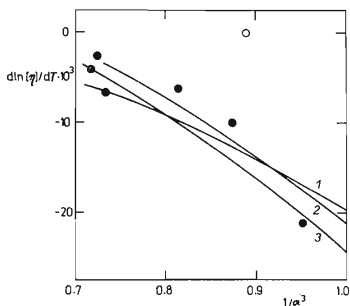
Fig. 5

Correlation of $d \ln [\eta]/dT \, vs \, 1/\alpha^3$ Values

● (○) Exper. data for the polymer in aqueous solutions of KSCN (40°C) before (beyond) the maximum of the $[\eta]$–C_s dependence. Calculated dependences for $(T^*; A''X/A'T)$: 1 (0·86; 10 . 10^{-3}), 2 (0·92; 13 . 10^{-3}), 3 (0·92; 11 . 10^{-3}).

By combining Eqs (24) and (25), it is possible to determine the parameters α_0 and T^*. As is shown by the results of model calculations, in practice we meet with difficulties in determining the intercept u and particularly the initial slope s_1.

Fig. 5 shows a plot d $\ln[\eta]/\mathrm{d}T$ vs $1/\alpha^3$ constructed for the system poly(2-hydroxyethyl methacrylate)–aqueous solutions of KSCN. The expansion factors α^3 were calculated from the $[\eta]$ values (Table II) using the K_0 values, determined[3] for the polymer in KSCN solutions of various concentration, after an approximate correction for the branching of our polymer (branching ratio, $g' = 0.75$):

$$\alpha^3 \simeq [\eta]/K_{0,1}M^{1/2}g' . \tag{26}$$

The figure also contains dependences calculated using the values d $\ln \overline{R_0^2}/\mathrm{d}T = -3$. $. 10^{-3}$ and d $\ln(\bar{v}^2/V_1)/\mathrm{d}T = -1 . 10^{-3}$. The exact value of the quotient d $\ln(\bar{v}^2/V_1)/\mathrm{d}T$ is not important for the calculation; the value given here is probably the highest of those which may appear for such system. Before comparing the calculated and experimental dependences, one must stress the approximate character of correction for branching, considerable errors in the d $\ln[\eta]/\mathrm{d}T$ values and the fact that the quotient d $\ln \overline{R_0^2}/\mathrm{d}T$ was determined using fractions of the linear polymer. Data for solutions having salt concentration higher than $(C_s)_{\max}$ deviate from the correlation in Fig. 6. Comparison shows that experimental data at 308 K are best satisfied by $T^* \simeq 0.90$, that is, $T_c \simeq 280$ K, in other words by a value lying inside the interval mentioned above.

With other systems, only reduced specific viscosities at c 1 g/dl and their temperature coefficients can be correlated. The discussion is therefore only qualitative;

TABLE II

Viscometric data of the System Poly(2-Hydroxyethyl Methacrylate)–Aqueous Solutions of KSCN (35°C)

C_s mol/l	$[\eta]^a$ dl/g	$\dfrac{\mathrm{d}\ln[\eta]}{\mathrm{d}T} . 10^3$ K^{-1}	C_s mol/l	$[\eta]^a$ dl/g	$\dfrac{\mathrm{d}\ln[\eta]}{\mathrm{d}T} . 10^3$ K^{-1}
1.0	0.138	-21	5.0	0.341	-2.4
1.5	0.175	-10	6.0	0.331	—
2.0	0.226	-6.2	8.0	0.255	$+0.3$
3.0	0.289	-6.7	8.8	0.211	—
4.0	0.327	-4.0			

^{a} For 35°C.

in Fig. 4 we have a common dependence for sodium, potassium and ammonium thiocyanates at $C_s < (C_s)_{max}$, so that the conclusion reached for the potassium salt approximately holds also for the other salts. The dependences for perchlorates and iodides of univalent cations are shifted in the vertical direction, but resemble those for thiocyanates. On the other hand, for salts of bivalent cations the $d \ln \eta_{red}/dT$ values are mostly very close to zero and only slightly dependent on $1/\eta_{red}$. Eqs. (24) and (25) show that for $s_1 = 0$ and $u = 0$ to be simultaneously valid, the condition

$$(1/A'T)_{s=0, u=0} = -\left(\tfrac{5}{2} \, d \ln \overline{R_0^2}/dT + d \ln (\bar{v}^2/V_1)/dT\right). \tag{27}$$

must be fulfilled. If the same values $d \ln \overline{R_0^2}/dT$ and $d \ln (\bar{v}^2/V_1)/dT$ as for thiocyanates were also valid for the above salts, at least approximately, $1/A'T$ would be approximately $+8.5 \cdot 10^{-3}$ and $T_c \approx 230$ K. Apparently, the causes of solubilization of poly(2-hydroxyethyl methacrylate) with salts of bivalent cations are more complicated than those of salts of univalent cations. For instance, the ability of bivalent cations to coordinate the hydroxylic groups of alcohols[1] (hydroxylic groups of the polymer) may play a role here.

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