

SOLUBILIZATION OF POLY(2-HYDROXYETHYL METHACRYLATE) WITH AQUEOUS SALT SOLUTIONS; VISCOMETRY IN SOLUTIONS OF POTASSIUM THIOCYANATE

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The effect of potassium thiocyanate on the viscometric properties of solutions of poly(2-hydroxyethyl methacrylate) at various temperatures (4 to 80°C) and salt concentrations were investigated. It was found that polymer molecules were much more coiled in aqueous solutions of KSCN under the Θ -conditions than in an organic Θ -solvent. The parameters of the entropy and enthalpy of dilution determined from viscosity data are negative and their absolute values decrease with increasing concentration of the salt. The results are interpreted as a consequence of the association of the hydrophobic groups of the polymer in the aqueous system and of its weakening due to salt.

Of the systems examined in an earlier paper¹, the pairs poly(2-hydroxyethyl methacrylate)-aqueous solutions of thiocyanates and iodides, which exhibited maximum on the specific viscosity-salt concentration dependence, appeared to be the most interesting ones. In this paper we discuss the results of detailed viscosity measurements carried out with solutions of several linear fractions (having molecular weights ranging from $0.1 \cdot 10^6$ to $3.7 \cdot 10^6$) in aqueous solutions of potassium thiocyanate (1M to 9M) at 4–80°C. The systems under investigation, *i.e.* a polymer dissolved in an aqueous solution of the dissociated salt, are in fact complicated systems displaying various types of interactions. In spite of this, however, the experimental data are analyzed on the basis of the two-parameter theory of intrinsic viscosity, and the complicated solvent is approximated by the model of a single liquid. Such simplifications, though allowing to analyze the data, provide only a rough idea about the character of the solutions.

EXPERIMENTAL

Viscometry

The measurements were carried out using fractions of the same origin as in ref.². Their molecular weights were determined using the intrinsic viscosity in dimethylformamide (at 25°C) by means of the equation³ $[\eta] = 8.9 \cdot 10^{-5} M^{0.72}$; for two fractions they were verified by employing the Archibald approximation-to-equilibrium method (Table I). Preparation of polymer solutions,

operations carried out with them before measurement, conditions and technique of viscosity measurements and the method of treating the experimental data were the same as in the paper referred to above².

Sedimentation

The sedimentation measurements were performed in an analytical Spinco E-HT ultracentrifuge. The temperature was measured and maintained during the measurement by means of an RTIC regulation and indication system with a maximum deviation of 0.1°C. The course of sedimentation

TABLE I
Viscometric Data of Systems Poly(2-Hydroxyethyl Methacrylate)-Aqueous Solutions of Thiocyanates

T °C	$[\eta]$, dl/g at $M \cdot 10^{-6}$					k_H at $M \cdot 10^{-6}$				
	3.68	0.86 ^a	0.275 ^b	0.116	0.054	3.68	0.86 ^a	0.275 ^b	0.116	0.054
1M-KSCN										
20	0.885	0.370	0.191	0.117	—	0.58	0.66	0.79	0.95	—
25	0.787	0.326	0.180	0.112	—	0.69	0.81	0.88	1.00	—
34	0.580	0.282	0.162	0.104	—	0.97	0.96	0.95	1.05	—
3M-KSCN										
25	1.97	0.702	0.320	—	0.120	0.34	0.39	0.55	—	1.0
5M-KSCN										
4	2.52	0.890	0.412	—	0.156	0.35	0.35	0.60	—	0.75
20	2.20	0.819	0.375	0.219	—	0.33	0.35	0.41	0.33	—
35	2.08	0.755	0.340	0.197	—	—	0.33	0.5	0.9	—
50	1.89	0.680	0.311	0.177	0.113	0.32	0.47	0.54	1.47	—
70	1.56	0.630	0.295	—	0.109	0.49	0.5	0.8	—	1.5
80	1.53	0.600	0.297	—	0.114	0.5	0.51	0.62	—	0.9
7M-KSCN										
25	1.72	0.680	0.319	—	0.132	0.39	0.43	0.53	—	0.71
9M-KSCN										
4	0.752	0.395	0.225	0.140	—	0.66	0.67	0.77	0.85	—
20	0.607	0.333	0.196	0.128	—	0.84	0.88	1.17	1.00	—
25	0.560	0.315	0.185	0.121	—	0.86	1.01	1.24	1.07	—
6M-NH ₄ SCN										
25	2.33	0.800	0.382	—	0.150	0.35	0.46	0.49	—	0.9

Mol. weight determined by the Archibald method ^a 0.76 · 10⁶, ^b 0.265 · 10⁶.

was followed refractometrically by using the Philpot-Svenson optical system. Photographic records of gradient curves on Kodak-metallographic plates were evaluated using a Zeiss two-dimensional reading microscope with an accuracy of reading of at least 0.02 mm in each direction. Measured values $\bar{v} = 0.785 \text{ cm}^3/\text{g}$ and $\rho_0 = 1.041 \text{ g/cm}^3$ were used in the calculations.

RESULTS AND DISCUSSION

The results of viscometric measurements are summarized in Table I. According to the magnitude of the exponent a_η of the Mark-Houwink equation (Table II) in 1M and 9M-KSCN solution, one may assume that at 4–30°C the conditions are near the θ -conditions. Solutions of poly(2-hydroxyethyl methacrylate) (further only "polymer") in 3M, 5M and 7M-KSCN and in 6M-NH₄SCN yield the exponents a_η higher than 0.6. The dependences of intrinsic viscosity on salt concentration (C_s) pass through a maximum (at c. 5M-KSCN). All the temperature coefficients of intrinsic viscosity are negative. The situation observed with 5M solution of KSCN is somewhat unusual, since the exponent a_η increases from 4 to 50°C, while the $[\eta]$ values decrease.

In our analysis of the viscometric data in 1M and 9M-KSCN we employed a procedure, the presumptions and details of which have been examined in ref.². The procedure is based on the equations

$$[\eta] = K_0 M^{1/2} (1 + C_1 B M^{1/2} + \dots), \quad (1)$$

TABLE II
Constants of the Mark-Houwink Equation for Systems Poly(2-Hydroxyethyl Methacrylate)-Aqueous Solutions of Thiocyanates

$T, ^\circ\text{C}$	a_η	$K \cdot 10^4$	a_η	$K \cdot 10^4$	a_η	$K \cdot 10^4$
	1M-KSCN		5M-KSCN		9M-KSCN	
4	—	—	0.64	1.43	0.49	4.76
20	0.58	1.35	0.65	0.99	0.56	6.13
25	0.56	1.59	—	—	0.45	6.64
34	0.50	3.11	0.67 ^a	0.78 ^a	—	—
50	—	—	0.68	0.62	—	—
70	—	—	0.62	1.29	—	—
80	—	—	0.60	1.69	—	—
	3M-KSCN		7M-KSCN		6M-NH ₄ SCN	
25	0.66	0.88	0.61	1.59	0.66	1.07

^a At 35°C.

$$(d \ln [\eta]/dT)_{B=0} = (d \ln K_0/dT)_{B=0} + C_1(dB/dT)_{B=0} M^{1/2}, \quad (2)$$

and consists of the following steps: 1) Construction of the Stockmayer-Fixman plot $[\eta]/M^{1/2}$ vs $M^{1/2}$ for all temperatures and concentrations of salt (Fig. 1*a,b,c,d*), determination of the slope S_{SF} and of the constant K_0 (from an intercept on the y-axis). 2) Plotting the S_{SF} values against $1/T$ (Fig. 2) and interpolation, or extrapolation, of the temperature at which $S_{SF} = 0$ (i.e. $B = 0$) and which is designated by Θ . 3) Determination of the coefficients $(d \ln [\eta]/dT)_{B=0}$ at a temperature at which

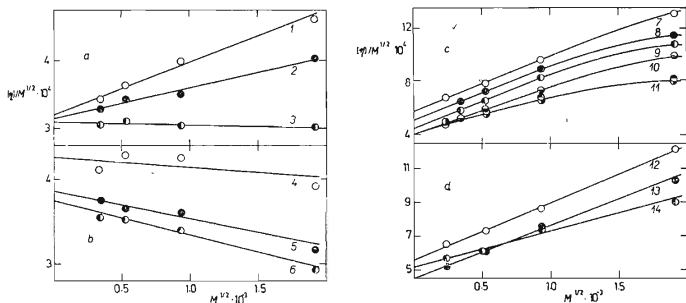


FIG. 1

The Stockmayer-Fixman Plot of Viscometric of Systems Poly(2-Hydroxyethyl Methacrylate)-Aqueous Solutions of Thiocyanates

a) 1M-KSCN at $T(^{\circ}\text{C})$: 1 20 25 3 34; b) 9M-KSCN at $T(^{\circ}\text{C})$: 4 4 5 20 6 25; c) 5M-KSCN at $T(^{\circ}\text{C})$: 7 4 8 20 9 35 10 50 11 70 (●) and 80 (○); d) at 25°C : 12 6M-NH₄SCN, 13 3M-KSCN, 14 7M-KSCN.

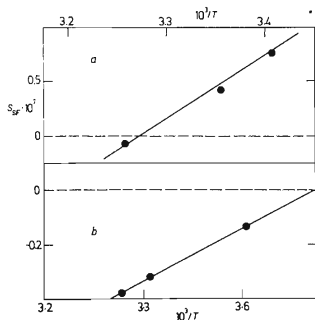


FIG. 2

Dependence of Slopes of the Stockmayer-Fixman Plot (S_{SF}) on Temperature

a) 1M-KSCN, b) 9M-KSCN.

$B = 0$, their plotting against $M^{1/2}$ and determination of the temperature coefficients $d \ln K_0/dT$ and dB/dT . In Eqs (1) and (2) C_1 is a numerical coefficient and B is the parameter of the polymer-solvent interaction.

The results of measurements in 5M-KSCN could not be analyzed employing the same procedure, because judging by the slopes of the Stockmayer-Fixman plots, the temperatures of measurements were too far from the Θ -temperature. We therefore determined the constant K_0 (Fig. 1d) using the Stockmayer-Fixman plot, even if the reliability condition ($[\eta]/K_0M^{1/2} \leq 1.6$) was not fully met⁴, and determined the quotient $d \ln K_0/dT$ from the plot $\ln K_0$ vs T . The parameters B_0 and Θ were determined by means of the equation

$$\alpha_\eta^5 - \alpha_\eta^3 = C \cdot z, \quad (3)$$

in which

$$\alpha_\eta^3 = [\eta]/K_0M^{1/2}, \quad z = B_0(1 - \Theta/T)M^{1/2}. \quad (4)$$

We chose the fraction having the highest molecular weight ($3.68 \cdot 10^6$) in order to reduce to the minimum the effect of the possible error in K_0 and to respect the asymptotic character of Eq. (3). The coefficient C was determined by comparing the coefficient at z in the power series expansion of Eq. (3).

$$\alpha_\eta^3 = 1 + (3/2) Cz + \dots, \quad (5)$$

with the coefficient C_1 of

$$\alpha_\eta^3 = 1 + C_1 z + \dots \quad (6)$$

TABLE III

Constants K_0 and the Quotient $d \ln K_0/dT$ (25°C) of Systems Poly(2-Hydroxyethyl Methacrylate)-Aqueous Solutions of Potassium Thiocyanate

C_s mol/l	$K_0 \cdot 10^4$ for $T, ^\circ\text{C}$							$d \ln K_0/dT \cdot 10^3$
	4	20	25	34	50	70	80	
1	—	3.20	3.15	3.08	—	—	—	-4
3	—	—	4.5	—	—	—	—	—
5	5.7	5.1	—	4.4 ^a	4.1	4.0	4.0	c. -5
6 ^b	—	—	5.6	—	—	—	—	—
7	—	—	5.1	—	—	—	—	—
9	4.25	3.86	3.72	—	—	—	—	-5

^a 35°C. ^b NH_4SCN .

TABLE IV
Interaction Parameters of Systems Poly(2-Hydroxyethyl Methacrylate)-Aqueous Solutions of KSCN

Parameters	1M-KSCN	5M-KSCN	9M-KSCN
$\Theta, ^\circ\text{C}$	33	280	-5
$B_0 \cdot 10^3, 25^\circ\text{C}$	-5.26	-1.47	-0.87
$B_0\Theta/T \cdot 10^3, 25^\circ\text{C}$	-5.35	-2.75	-0.78

derived by the perturbation method for very small z . The most recent theoretical value⁵ (1.06), which appeared to be the most probable one in the experimental check-up⁶, was substituted for C_1 . We plotted the dependence $(\alpha_n^5 - \alpha_n^3)/M^{1/2}$ on $1/T$, determined the slope $S_{SF} = -CB_0\Theta$, and after that determined the parameter B_0 and the temperature Θ by employing the usual procedure. The K_0 , $\ln k_0/dT$, Θ values and the parameters B_0 , $B_0\Theta/T$ thus obtained are summarized in Tables III and IV.

The second virial coefficient of the system polymer-1M-KSCN at 33° was determined by using the Archibald method (Fig. 3). The values of A_2 thus obtained for two fractions, namely, $-0.6 \cdot 10^{-5}$ and $-3.5 \cdot 10^{-5} \text{ g}^{-2} \text{ cm}^3 \text{ mol}$, suggest that the system is very close to the Θ -conditions. It should be added that the latter A_2 value is larger mainly because of the value of $1/M_{app}$ measured at the lowest concentration at which the accuracy of the measurement is the lowest.

The value of the Θ -temperature obtained for 1M-KSCN is more accurate, since it was determined by interpolating S_{SF} against $1/T$. In 9M-KSCN we were restricted

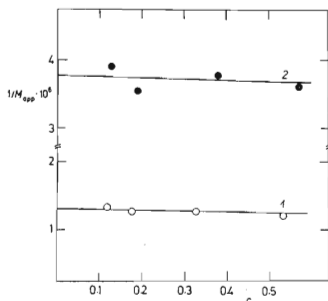


FIG. 3

Determination of Molecular Weight of the Polymer According to Archibald (1M-KSCN, 33°C)

$$M_n: 1.085 \cdot 10^6, 2.0275 \cdot 10^6.$$

by experimental possibilities to temperatures higher than 4°C, so that the determination of the θ -temperature was possible by extrapolation only.

Of the K_0 values, the ones related to 34°C in 1M-KSCN and to 4°C in 9M-KSCN are regarded as the most reliable ones, because the Stockmayer-Fixman plots had very low slopes (slightly negative). As for 5M-KSCN, the K_0 values at 70° and 80°C obtained by extrapolation with a comparatively low slope seem to be the most reliable ones.

The parameter B_0 could not be determined in 1M and 9M-KSCN with the same accuracy. In the case of 9M-KSCN the measurements could not be carried out directly in the surroundings of the θ -temperature, but at a temperature higher by 9°C, so that the procedure used is justified only assuming that the dependence $[\eta]-T$ is linear for all fractions even at $\theta < T < \theta + 9^\circ\text{C}$. According to the statistical thermodynamical theory, the parameter B_0 is proportional to the Flory parameter of the entropy of dilution, ψ , and the parameter $B_0\theta/T$ is proportional to the parameter of the enthalpy of dilution, κ . The solutions of poly(2-hydroxyethyl methacrylate) in KSCN solutions behave as exothermal systems. This is quantitatively illustrated by line 2 in Fig. 4, which describes the dependence of the parameter $B_0\theta/T$ on the thiocyanate concentration at 25°C. The enthalpy of dilution is negative within the whole concentration range, and thus favourable to dissolving the polymer. The parameter of the entropy of dilution is also negative within the whole scale of salt concentration, but owing to the salt effect it becomes less negative and more favourable

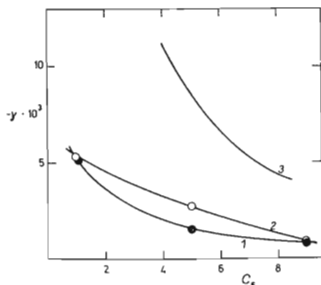


FIG. 4

Dependence of the Interaction Parameters of Poly(2-Hydroxyethyl Methacrylate) on the Concentration of KSCN

γ : 1 B_0 , 2 $B_0\theta/T$, 3 $B_0 \theta/T$ for polymer-aqueous solutions of urea (schematically).

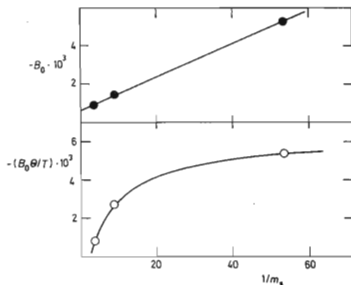


FIG. 5

Dependence of the Interaction Parameters of Poly(2-Hydroxyethyl Methacrylate) on the Mole Fraction of KSCN (m_s).

to dissolving. At salt concentrations 1M and 9M at 25°C, $|B_0| > |B_0\theta/T|$; this results in a limited solubility in salt solutions of these concentrations. As documented by Fig. 4, the difference $(B_0 - B_0\theta/T)$ is highest at c. 4M salt concentration and decreases towards lower and higher concentrations. As a consequence, there is a maximum on the dependences $\alpha_n^3 - C_s$ and $[\eta] - C_s$. (Similar maxima were also observed with other thiocyanates and iodides of univalent cations. We believe that these maxima could be explained in a similar manner).

The dependence $B_0\theta/T$ vs C_s is apparently linear and may misleadingly suggest an extrapolation to $C_s = 0$, i.e. an estimate of $B_0\theta/T$ for the polymer in pure water. As demonstrated by the comparison with a similar dependence for the polymer in aqueous urea solutions (Fig. 4), linear extrapolation is not justified. In the range in which viscosity measurements cannot be performed (at $C_s < 1M$) the dependence $B_0\theta/T - C_s$ probably becomes steeply curved downwards.

Plotting the interaction parameters against $1/m_s$, where m_s is the mole fraction of the salt (Fig. 5), proved to be useful for providing an idea of the interaction of the polymer with pure thiocyanate. While the dependence B_0 vs $1/m_s$ is roughly linear and at $m_s = 1$ leads to $B_0 \approx -0.6 \cdot 10^{-3}$, the dependence $B_0\theta/T$ vs $1/m_s$ is curved and directed towards positive values. It seems, therefore, that an interaction of the polymer with thiocyanate alone would be endothermic and moreover entropically disadvantageous.

Owing to an unfavourable change in the entropy accompanying the formation of contacts of water with the aliphatic, hydrophobic parts of polymer molecules, poly(2-hydroxyethyl methacrylate) showed a tendency towards the association of these parts (hydrophobic bonding). According to Silberberg⁸, this association leads to an effective shortening of the chain, and thus also to a lower K_0 . With increasing salt concentration, the absolute negative entropy of mixing decreases, the number of intramolecular associations diminishes, and the constant K_0 increases. However, its increase has a maximum, after which, at the highest attainable salt concentrations, K_0 almost returns to its value at 1M salt concentration. This suggests that here again we have an association of the nonpolar parts of the polymer molecule. A change in the structure of aqueous salt solutions at high C_s may also be operative here⁷.

Very high values of the Huggins viscometric constant k_H (Table I) (e.g., $k_H = 1$ in 1M-KSCN under the θ -conditions) also indicate a strong interaction between parts of the polymer chain (intermolecular in this case); its decrease due to the salt means weakening of these interactions.

In the preceding paper² the solubilizing effect of urea on poly(2-hydroxyethyl methacrylate) has been ascribed for a great part to its effect on the supermolecular structure of liquid water. In the case of KSCN (and salts in general) the effect is essentially more involved: sorption measurements carried out with gels of the cross-

linked polymer⁷ have shown that at low concentrations thiocyanates (and similarly iodides and perchlorates) are preferentially sorbed by the gel. Electrophoretic studies⁹ of solutions of the polymer in 0.5M magnesium perchlorate have proved the bonding of the anion to the polymer chain. These factors also contribute to the salting-in of the polymer.

REFERENCES

1. Vošický V., Bohdanecký M., Dušek K.: *This Journal* **42**, 1615 (1977).
2. Dušek K., Bohdanecký M., Machovská E.: *Eur. Polym. J.* **10**, 239 (1974).
3. Bohdanecký M., Tuzar Z., Štol M., Chromeček R.: *This Journal* **33**, 4140 (1968).
4. Berry G. C.: *J. Chem. Phys.* **46**, 1338 (1967).
5. Yamakawa H., Tanaka G.: *J. Chem. Phys.* **55**, 3188 (1971).
6. Bohdanecký M., Petrus V.: *Eur. Polym. J.* **8**, 893 (1972).
7. Dušek K., Bohdanecký M., Vošický V.; *This Journal* **42**, 1599 (1977).
8. Silberberg A.: *ACS Polymer Preprints* **9**, 578 (1968).
9. Machovská E., Bohdanecký M.: *This Journal* **38**, 1502 (1973).

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