

EFFECT OF UREA ON THE BEHAVIOUR OF POLY(2-HYDROXYETHYL METHACRYLATE)-WATER MIXTURES

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Abstract—The effect of urea solutions on the equilibrium swelling of lightly crosslinked poly(2-hydroxyethyl methacrylate) (PHEMA) gels and on the viscometric behaviour of PHEMA, for various concentrations of urea and temperatures, has been studied. Urea raises the degree of swelling of gels and the intrinsic viscosity of PHEMA; the temperature coefficient of both quantities is negative. A thermodynamic analysis of the swelling data shows that a change in entropy is the driving force for the increase in swelling at low temperatures, while at higher temperatures (50–80°) a negative change in enthalpy prevails, both corresponding to the transport of PHEMA from the aqueous medium into urea solutions. The entropy and enthalpy of dilution parameters derived from viscometric measurements have negative values, and their absolute values decrease with increasing urea concentration. It has also been found that the PHEMA molecules in urea solutions under the θ -conditions are much more coiled than in an organic θ -solvent. The results are interpreted in terms of the existence of inter- and intramolecular hydrophobic bonds and by the destruction of hydrophobic clusters caused by urea.

Aqueous urea solutions are known to cause the denaturation of proteins (cf. e.g. [1]). Addition of urea also raises the solubility of a number of polar organic compounds (e.g. amino acids) in water [2]. The effect of urea is explained, on the one hand, by the destruction of the hydrophobic bonds between nonpolar parts of the molecule connected with the structure of water, and on the other, by the attack of urea on the inter- or intramolecular hydrogen bonds. It can be said that the molecules of urea certainly disturb the structure of water, in the first place owing to their different geometry with respect to the water molecules [3].

The effect of urea was also investigated for a number of synthetic hydrophilic polymers, but in most cases these studies (mainly viscometric [4]) were not carried out systematically. The structures of synthetic polymers are often much simpler than those of biopolymers and their investigation could contribute to the elucidation of the mechanism of the effect of urea.

Poly(2-hydroxyethyl methacrylate) is one of the comparatively simple synthetic polymers containing both hydrophobic groups and proton donors and acceptors capable of forming interchain hydrogen bonds and bonds with the water molecules. Since this polymer is widely used in practice (implants, tissue substitutes), an investigation of the effect of urea has also a practical importance. We therefore investigated the effect of urea in concentrated systems—poly(2-hydroxyethyl methacrylate)(PHEMA) gels—by measuring the equilibrium degree of swelling, and also studied viscometrically the solution behaviour in dilute solutions. The phase equilibria in lightly crosslinked PHEMA gels allow, after subtracting the small contribution of the elastic free energy of the network, the

calculation of quantities directly related to the excess thermodynamic functions, which therefore makes possible a characterization of the nature of interaction changes caused by urea. Viscometry supplements these results for the region of infinitely dilute solutions; however, owing to the limited solubility of PHEMA, the viscosity measurements can be carried out only with solutions having a higher concentration of urea. The literature already contains some data about the effects of urea on the swelling of PHEMA gels. Data [5] indicate a dramatic effect of very low urea concentrations: in 0.01 M urea the degree of swelling with respect to water increases more than twice, and decreases again at higher urea concentrations. The existence of such an important effect of low urea concentrations could be proved neither in later [6] nor in our measurements. A more detailed investigation [6] of the effect of 0–1.0 M urea on PHEMA gels seems to suggest that, in the low concentration region under investigation, urea affects rather the hydrogen bonds than the association of nonpolar parts of macromolecules. This conclusion follows mainly from the weak influence of urea on the fluorescence of dye adsorbed in hydrophobic associates. It should be added, however, that the low urea concentrations given above affect the gel properties only slightly, and that it is rather higher concentrations which are interesting.

EXPERIMENTAL

Swelling of gels

Preparation of PHEMA gels. Crosslinked PHEMA gels were obtained by bulk copolymerization of HEMA with 0.32 per cent ethylene dimethacrylate in the form of plates

in a Teflon mould. The mixture of monomers was bubbled with nitrogen and degassed, and the polymerization was initiated with 0.15 per cent diisopropyl percarbonate. The polymerization proceeded at 60°C for 6 hr; the gels were extracted with boiling water and used either swollen or after drying *in vacuo* over P_2O_5 .

Measurement of the equilibrium degree of swelling. The volume degree of swelling was measured dilatometrically with an Abbé comparator (Zeiss, Jena, GDR). Gel strips were fixed in their centre to a Teflon support and placed in a thermostated cell which was fixed to the comparator desk. Two pieces of a platinum wire at the ends of the strip served as marks for measuring the linear dimensions. The time dependences were measured during 1–2 days and the equilibrium value was obtained by extrapolation to infinite time, if necessary. The equilibrium values L/L_0 (L and L_0 are the respective distances between the marks of the swollen and the dry extracted sample) were used for calculating the volume degree of swelling $(L/L_0)^3$ and the volume fraction of the polymer $\varphi_p = (L_0/L)^3$.

Viscometry

The viscometric measurements were performed with two unfractionated samples and six fractions. The

unfractionated samples were prepared from monomer of high purity (with less than 0.01 per cent ethylene dimethacrylate) by radical polymerization in water or ethanol solution with isopropyl percarbonate as initiator. The fractions were prepared by fractional precipitation [7]. The samples were stored in a desiccator over P_2O_5 . They were characterized by their intrinsic viscosity in dimethylformamide (25°C) and the weight average molecular weight \bar{M}_w (determined by light scattering [7]).

The solutions in 6 M and 8 M urea were prepared by shaking overnight an appropriate amount of the polymer with solvent at room temperature. The whole process of sample preparation in 4 M urea was carried out in a refrigerator at $\sim 2^\circ\text{C}$. The samples thus obtained were transparent. Prior to measurements, the solutions were filtered through sintered glass (G2).

The measurements were carried out in Ubbelohde viscometers adapted for direct dilution. The flow times of the solvent were never lower than 100 sec, so that—with respect to the size of the viscometer—no further viscometric correction was necessary. The flow times

Table 1. Equilibrium degree of swelling of PHEMA gels in urea solutions and the interaction parameters

[U]	t	φ_p	χ	h	χ_h	χ_s
0	80	0.549	0.821	200	0.566	0.255
	70	0.563	0.834	120	0.350	0.484
	55	0.568	0.841	0	0	0.841
	40	0.565	0.837	-50	-0.159	0.966
	25	0.553	0.825	-90	-0.301	1.126
1	80	0.536	0.804	15	0.042	0.762
	70	0.537	0.805	10	0.029	0.776
	55	0.538	0.805	-15	-0.046	0.851
	40	0.535	0.801	-50	-0.159	0.960
	25	0.521	0.790	-90	-0.301	1.091
2	80	0.509	0.776	0	0	0.776
	70	0.507	0.775	-25	-0.073	0.848
	55	0.500	0.768	-65	-0.198	0.966
	40	0.489	0.757	-90	-0.287	1.044
	25	0.468	0.740	-110	-0.368	1.108
4	80	0.459	0.732	-35	-0.100	0.832
	70	0.455	0.729	-55	-0.160	0.889
	55	0.443	0.719	-90	-0.274	0.993
	40	0.425	0.704	-100	-0.319	1.023
	25	0.401	0.687	-100	-0.335	1.022
6	80	0.413	0.694	-65	-0.184	0.878
	70	0.405	0.688	-70	-0.204	0.892
	55	0.390	0.678	-85	-0.259	0.937
	40	0.372	0.665	-90	-0.287	0.952
	25	0.349	0.649	-100	-0.335	0.984
8.2	80	0.373	0.665	-105	-0.297	0.962
	70	0.361	0.657	-100	-0.291	0.948
	55	0.340	0.644	-95	-0.290	0.934
	40	0.322	0.631	-90	-0.287	0.918
	25	0.300	0.615	-90	-0.301	0.918

[U] concentration of urea solutions in mol/l at 25°C; t temperature in °C; φ_p volume fraction of the polymer in the swollen gel; χ (± 0.001) the Flory-Huggins interaction parameter; h °K (± 10), χ_h (± 0.04), respectively χ_s are enthalpic, respectively entropic contributions to χ . $\chi = h/T + \chi_s = \chi_h + \chi_s$

were read with an accuracy of ± 0.05 sec; the bath temperature was constant to $\pm 0.02^\circ\text{C}$.

The intrinsic viscosities $[\eta]$ were obtained by extrapolation to zero concentration of data obtained at four or five polymer concentrations chosen so that the specific viscosities lay between 0.15 and 0.8. The determination of the intrinsic viscosity and Huggins constant k_H was made according to Heller [8]. If necessary, the $[\eta]$ values were corrected for changes in the density of urea solutions.

RESULTS AND DISCUSSION

Equilibrium swelling of the PHEMA gels

The results of measurements of the equilibrium degree of swelling in 0.8–2 M urea at 25 – 80°C are summarized in Table 1. The equilibrium degree of swelling increases (the volume fraction of the polymer ϕ_p decreases) with increasing urea concentration at all temperatures, but the temperature dependence of the volume fraction of the polymer changes with increasing urea concentration. The minimum of the degree of swelling which exists in the PHEMA–water systems at 55°C is gradually shifted to higher temperatures with increasing urea concentration and finally disappears, so that at higher urea concentrations the PHEMA gels deswell with increasing temperature over the whole range of temperatures studied.

To obtain more detailed information about the thermodynamics of mixing of PHEMA with urea solutions, we calculated the Flory–Huggins interaction parameter from the swelling data. For simplicity, we assumed that the urea solutions can be regarded as a single-component solvent, implying the same composition of the aqueous urea solution both in the gel and in the liquid phase. Such a “single-liquid” approximation can to a certain degree affect the values of the thermodynamic quantities, but probably will not change the course of their dependence on the temperature and concentration of urea.

The interaction parameter χ is determined by Flory's swelling equation [9]:

$$\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 + \bar{V}_s v^* (\phi_p^3 \langle x^2 \rangle_0 - \phi_p/2) = 0. \quad (1)$$

Here, v^* is the concentration of elastically active chains in the dry gel, \bar{V}_s is the mean molar volume of urea solutions, and the parameter $\langle x^2 \rangle_0$ characterizes the ratio of the mean square end-to-end distance of the network in the dry and reference state. The value of v^* (approximately 0.1 mol/l) was determined from the stress–strain data on swollen gels, and the factor $\langle x^2 \rangle_0$ was taken to be close to unity, since the cross-linking took place in the absence of diluent. The mean molar volume of urea solutions was calculated from

$$\bar{V}_s = 1000/(c_u/\bar{M}_u + (1000\rho - c_u)/\bar{M}_w), \quad (2)$$

where c_u is the urea concentration in g/l, ρ is the specific weight of urea solutions (g/ml), and \bar{M}_u and

\bar{M}_w are molecular weights of urea and water, respectively. Temperature dependence of χ yields the enthalpic (χ_h) and entropic (χ_s) terms

$$\chi = h/T + \chi_s = \chi_h + \chi_s, \quad (3)$$

where $h = [\delta\chi/\delta(1/T)]$. These terms are related to the excess enthalpy and entropy of mixing with respect to an ideal and athermal mixing. It should be noted that the positive value of χ_h means positive heat of mixing (endothermal mixing) and the positive value of χ_s means negative excess entropy of mixing.

It can be seen (Fig. 1) that the maximum value of χ is shifted to higher temperatures and at high urea concentrations the decrease of χ with temperature is almost linear in $1/T$. Table 1 demonstrates that the mixing of PHEMA with water is exothermal at lower temperatures and becomes endothermal at higher temperatures; the change in entropy is less negative. The mixing becomes exothermal for all temperatures with increasing urea concentration, while entropy increases at low temperatures and decreases at higher temperatures.

The thermodynamic behaviour of PHEMA mixtures with water or urea solutions is typical of the so-called “aqueous solutions”, for which it holds that $|\Delta H^E| < T|\Delta S^E|$, i.e. the effect of the entropic contribution prevails in the free enthalpy of mixing [10]. Only in the PHEMA–water system at 80°C , the relationship is a reverse one, which would indicate transition to the behaviour of the so-called “non-aqueous solutions”. High positive χ_s and negative χ_h for

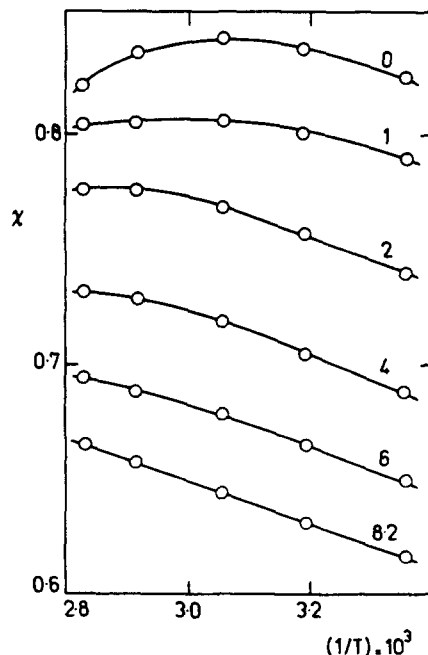


Fig. 1. Dependence of the interaction parameter χ on (absolute temperature) $^{-1}$. Designation of curves corresponds to urea concentration in mol/l in aqueous solution at 25°C .

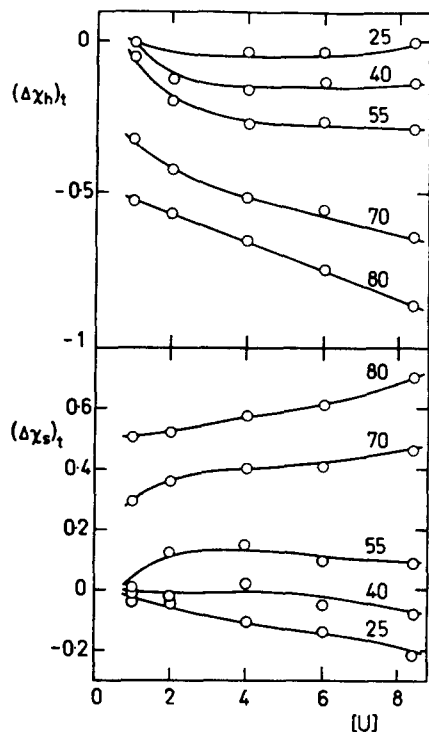


Fig. 2. Dependence of $(\Delta\chi_h)_t$ and $(\Delta\chi_s)_t$ corresponding to the transfer of PHEMA from water into urea solutions. Designation of curves indicates temperature in $^{\circ}\text{C}$.

PHEMA–water systems seem to suggest (as in aqueous solutions of aliphatic alcohols of the corresponding concentration [11]) the existence of hydrophobic associates and formation of new H-bonds. The associates dissociate with increasing temperature and the H-bonds also disappear so that the system becomes more “non-aqueous”. The effect of urea can be studied by using the values of $(\Delta\chi_h)_t$ and $(\Delta\chi_s)_t$ corresponding to the transfer of PHEMA from the aqueous solution into a urea solution (Fig. 2). The low value of $(\Delta\chi_h)_t$ at 25°C , which is little dependent on the urea concentration, suggests that the addition of urea will not cause an essential change in the concentration of the hydrogen bonds in the system, although they certainly undergo rearrangement with the participation of the urea molecules. The driving force of the increase in swelling is the positive entropy change [negative $(\Delta\chi_s)_t$]. At higher temperatures, the strongly negative $(\Delta\chi_h)_t$ values indicate the formation of new hydrogen bonds in systems with urea; this change is compensated for by a large decrease in entropy. Thus, the addition of urea seems to lead to an increase both in order and in the number of hydrogen bonds.

It is interesting that, as in a number of other aqueous systems, compensation exists between h and χ_s corresponding to different temperatures (Fig. 3). All straight lines for different urea concentrations have the same slope of -340°K , but are somewhat shifted.

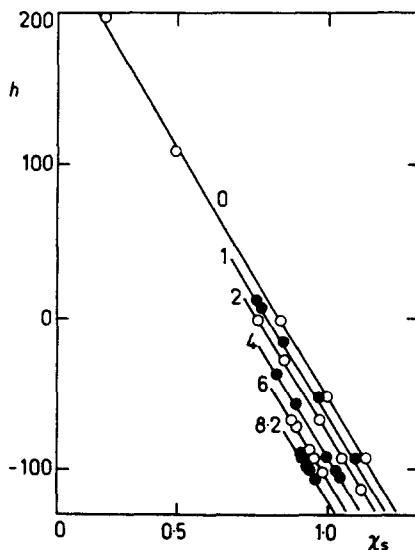


Fig. 3. Compensation of h and χ_s . Designation of curves corresponds to urea concentration in mol/l in aqueous solution at 25°C .

Viscosity measurements

The range of viscosity measurements was determined by the ranges of temperature and of concentration of urea within which it is possible to prepare stable solutions of PHEMA. Preliminary experiments have shown that solutions of PHEMA in 4 M urea allow work at temperatures below 12°C , in 6 M urea below 35°C and in 8 M solutions below 55°C . The viscometric results are summarized in Figs. 4 and 5 and Tables 2, 3 and 4.

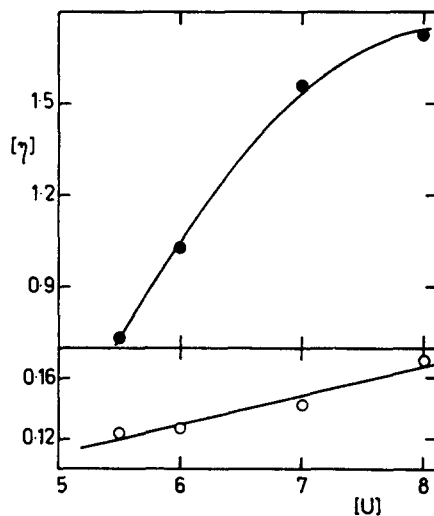


Fig. 4. Dependence of the intrinsic viscosity of PHEMA on urea concentration. Temperature 25°C . Polymers $M \times 10^{-6}$: 0.105 \circ , 5.0 \bullet .

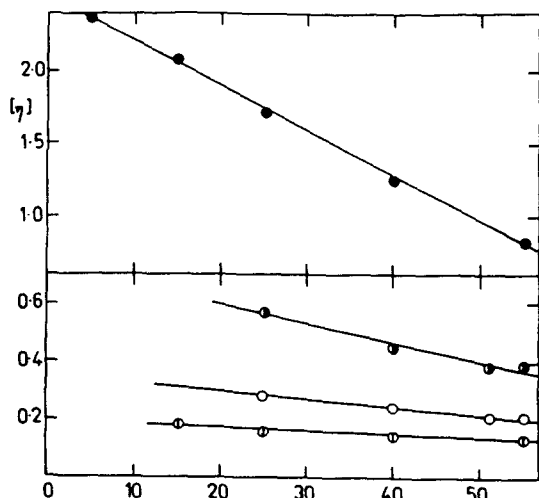


Fig. 5. Dependence of the intrinsic viscosity of PHEMA solutions on temperature. Urea concentration 8 M. Polymers $M \times 10^{-6}$: 0.105 \circ ; 0.275 \circ ; 0.860 \circ ; 5.0 \bullet .

In the following analysis of viscometric data, equations [12, 13]

$$[\eta] = K_0 M^{1/2} (1 + C_1 B M^{1/2} + \dots) \quad (4)$$

and

$$(d \ln [\eta]/dT)_{B=0} = (d \ln K_0/dT)_{B=0} + C_1 (dB/dT)_{B=0} M^{1/2}, \quad (5)$$

are used, where the symbol C_1 denotes the numerical coefficient.

For this relationship, we assume that also for our systems it is possible to separate the effect of interactions of the adjacent chain monomer units (the measure of which is the constant K_0 and its tempera-

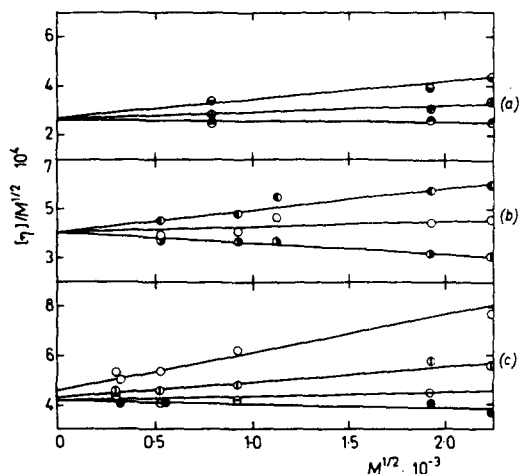


Fig. 6. Determination of the parameter K_0 . (a) $[U] = 4$ M; t ($^{\circ}$ C): 2, 7, 10 (\bullet , \circ , \bullet); (b) $[U] = 6$ M; t ($^{\circ}$ C): 18, 25, 32 (\bullet , \circ , \bullet); (c) $[U] = 8$ M; t ($^{\circ}$ C): 25, 40, 51, 55 (\circ , \circ , \bullet , \bullet).

ture coefficient $d \ln K_0/dT$) from the effect of interactions of remote monomer units and of interactions with solvent (parameter B and dB/dT). When applying Eqn. (4) we have noted the empirical rule [14] that the extrapolation of the plot $[\eta]/M^{1/2}$ vs $M^{1/2}$ to zero molecular weight based on Eqn. (4) is reliable only if $[\eta]/K_0 M^{1/2} \geq 1.6$.

The procedure and results of analysis can be summarized as follows: (1) Stockmayer-Fixman's plots $[\eta]/M^{1/2}$ vs $M^{1/2}$ (Fig. 6) meet the above condition of a reliable extrapolation for solutions in 4 M and 6 M urea at all temperatures and in 8 M urea at temperatures 40–55 $^{\circ}$ C. The constants K_0 increase with increasing urea concentration, probably to a limit (Table 5). (2) We determined the slopes (S_{SF}) of the straight lines in Fig. 6; from their dependence on $1/T$ (Fig. 7) we

Table 2. Viscometric data of the system PHEMA—4 M urea solution

$M \times 10^{-6}$ t ($^{\circ}$ C):	$[\eta]$ (dl/g)				k_H			
	2.0	4.0	7.0	10.0	2.0	4.0	7.0	10.0
0.620	0.265	0.245	0.225	0.195	1.07	1.17	1.43	1.97
3.68	0.760	0.695	0.600	0.500	0.75	0.85	0.05	1.38
5.00	1.00	0.900	0.760	0.570	0.70	0.81	1.03	1.65

Table 3. Viscometric data of the system PHEMA—6 M urea solution

$M \times 10^{-6}$ t ($^{\circ}$ C):	$[\eta]$ (dl/g)			k_H		
	18.0	25.0	32.0	18.0	25.0	32.0
0.105	—	0.127	—	—	0.97	—
0.275	0.238	0.206	0.204	0.69	1.06	0.77
0.860	0.444	0.378	0.342	0.54	0.70	0.74
1.25	0.618	0.519	0.407	0.48	0.59	0.88
3.68	1.10	0.851	0.605	0.48	0.65	1.0
5.00	1.34	1.03	0.695	—	—	—

Table 4. Viscometric data of the system PHEMA—8 M urea solution

$M \times 10^{-6}$ $t(^{\circ}\text{C})$:	$[\eta]$ (dl/g)										k_H
	5	15	25	40	51	55	5	15	25	40	55
0.090	—	—	0.160	0.144	0.134	0.140	—	—	0.62	0.69	0.63
0.105	—	—	0.162	0.143†	—	0.131	—	—	—	—	—
0.275	—	0.184*	0.283	0.240	0.213	0.214	—	—	0.55	0.64	0.73
0.860	—	—	0.574	0.450	0.390	0.390	—	—	0.46	0.57	0.67
3.68	—	—	—	1.11	0.866	0.781	—	—	—	0.67	0.73
5.00	2.37	2.09	1.72	1.26	—	0.824‡	0.31	0.34	0.42	0.57	0.90‡

* $t = 18^{\circ}\text{C}$; † $t = 42^{\circ}\text{C}$; ‡ $t = 54^{\circ}\text{C}$.

determined by interpolation those temperatures at which $B = 0$. They increase with increasing urea concentration; linear extrapolation gives us an estimate of this temperature for pure water (ca. 240°K) (Fig. 9, Table 5). (3) At these temperatures we determined the coefficients $(d \ln [\eta]/dT)_{B=0}$, plotted them against $M^{1/2}$ (Fig. 8) and obtained the coefficients $d \ln K_0/dT$ and $(dB/dT)_{B=0}$ (ca. -5×10^{-3}).

Table 5. Characteristics of the systems PHEMA-aqueous urea solutions

[U]: θ (°C)	4 M	6 M	8 M
$K_0 \times 10^4$	2.5*	4.0*	4.25*
$C_1 B_0 \times 10^3$	-12.4†	-7.0†	-4.1†
	-10.5‡	-6.9‡	-3.9‡
$S_\theta \times 10^6$	-37§	-23§	-12§
$(\theta/T)C_1 B_0 \times 10^3$	-11.8	-7.0	-4.6

* At the respective θ -temperature. † Determined from Fig. 7. ‡ Determined from Fig. 8. § Slope of straight lines in Fig. 8. $(d \ln K_0/dT = -5 \times 10^{-3})$. || For $T = 298^\circ\text{K}$.

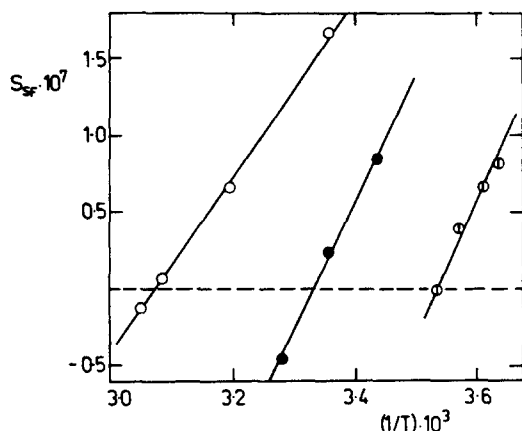


Fig. 7. Temperature dependence of slopes S_{SF} . $S_{SF} (\equiv C_1 B K_0)$ slope of straight lines in Fig. 6. [U] = 4 M ○, 6 M ○, 8 M ●.

If we look for the explanation of results in point (1), it seems advisable to compare them with K_0 determined under the θ -conditions in an organic solvent [15] (isopropanol, $\theta = 37^\circ\text{C}$, $K_0 = 6.0 \times 10^{-4}$). The values found in aqueous urea solutions amount only to 42–70 per cent of the above value and mean that the radius of an equivalent hydrodynamic sphere has been reduced to 77–89 per cent of the radius in isopropanol.

According to the theory [12] of the intrinsic viscosity of polymers with a flexible chain, the changes in the constant K_0 due to solvent (less than 10–20 per cent in most cases) are explained by the changes in the so-called characteristic ratio; the decrease in both quantities indicates less hindered rotation in the main chain and more frequent participation of conformations with smaller steric requirements (without change

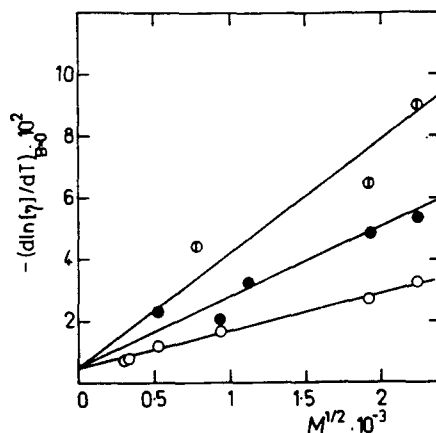


Fig. 8. Determination of parameters $d \ln K_0/dT$ and $(dB/dT)_{B=0}$. [U] = 4 M ○, 6 M ○, 8 M ●.

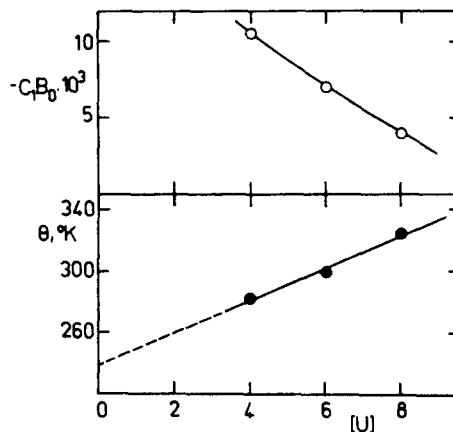


Fig. 9. Dependence of parameters θ and $C_1 B_0$ on urea concentration.

in the Gaussian character of the chain). A question arises if the dramatic reduction of the K_0 values found by us is compatible with the view that the only process that occurred here was a release of the barriers of rotation, or that there were some other causes involved. We favour the latter alternative.

In the part devoted to the swelling of crosslinked PHEMA gels, we concluded that in the PHEMA networks the nonpolar parts of the chains become associated inside the network. It is easy to imagine that the same type of interaction is operative also between close monomer repeat units inside the coils of linear molecules, which is reflected in low values of K_0 . Intramolecular associations decrease in number with increasing urea concentration, so that the dimensions of molecules (in the absence of the excluded volume effect) and the constant K_0 increase. However, uncoiling does not attain such a degree as in an organic θ -solvent, where the hydrophobic interactions are not operative. The abrupt slope of the K_0 -[U] dependence

which appears if one proceeds to low urea concentrations indicates that at $[U] < 4$ M (if solutions could be prepared under such conditions) the PHEMA molecules would be strongly coiled and very compact. One can see here a certain resemblance to proteins.

As can be seen from Fig. 7 (plot $S_{SF} = C_1 B K_0$ vs $1/T$), the dependence of the parameter B on temperature in the surroundings of the temperature at which $B = 0$ can be described by the equation

$$B = B_0 (1 - \theta/T), \quad (6)$$

the parameters of which (B_0 , θ) are given in Table 5. Practically, the same B_0 values are obtained from plots in Fig. 8, the slope of which according to Eqns. (5) and (6) is $S_\theta = C_1 B_0/\theta$.

According to the statistical-thermodynamic theory [16] of polymer solutions, the empirical parameters B and B_0 are directly related to the Flory parameters of the heat of dilution (κ) and entropy of dilution (ψ). It can be said on the basis of viscometric measurements that the systems PHEMA-aqueous urea solutions are exothermal (that they become less exothermal with increasing urea concentration) that the parameter of the entropy of dilution is negative and that its absolute value decreases (Table 5). For the dissolution of the polymer, the former fact is unfavourable and the latter favourable. In the concentration and temperature range in which the viscometric measurements could be carried out, the above conclusion is in a qualitative agreement with that derived from swelling.

It should be pointed out, in conclusion to the above analysis of the viscometric results, that the Huggins constant k_H has extremely high values, exceeding by 50–300 per cent those found by us for PHEMA in isopropanol [15] under comparable conditions. The high k_H values indicate strong intermolecular inter-

actions and their decrease with increasing urea concentration means also weakening of these interactions.

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Résumé—On a étudié l'effet de solutions d'urée sur l'équilibre de gonflement de gels légèrement réticulés de poly(hydroxyéthyl-2-méthacrylate) (PHEMA) et sur le comportement viscosimétrique du PHEMA pour diverses concentrations d'urée et diverses températures. Le taux de gonflement des gels et la viscosité intrinsèque du PHEMA augmente avec la concentration d'urée; leurs coefficients de températures sont tous deux négatifs. L'analyse thermodynamique des données de gonflement montre qu'aux basses températures l'augmentation de gonflement est régie par le changement dans l'entropie tandis qu'aux températures plus élevées (50–80°) domine le changement négatif dans l'enthalpie; dans les deux cas ceci correspond au transport de PHEMA du milieu aqueux dans les solutions d'urée. L'entropie et l'enthalpie des paramètres de dilutions, calculés à partir des mesures viscosimétriques, sont négatives et leurs valeurs absolues diminuent lorsque la concentration d'urée augmente. On a également trouvé que dans des solutions d'urée aux conditions θ les molécules de PHEMA sont beaucoup plus enroulées que dans un solvant θ organique. Les résultats sont interprétés par l'existence de liaisons hydrophobes inter- et intra-moléculaires et par la destruction d'aggrégats hydrophobes provoqués par l'urée.

Sommario—Si è studiato l'effetto che soluzioni di urea presentano sul rigonfiamento d'equilibrio di geli di poli(2-idrossietilmetacrilato) (PHEMA) e sul comportamento viscometrico del PHEMA, con varie temperature e concentrazioni di urea. L'urea aumenta il grado di rigonfiamento dei geli e la viscosità intrinseca del PHEMA; il coefficiente di temperatura di entrambe le quantità è negativo. L'analisi termodinamica dei dati di rigonfiamento mostra che il cambiamento di entropia è la forza motrice per l'aumento del rigonfiamento a basse temperature, mentre a temperature più elevate (50–80°) prevale un cambiamento negativo dell'entalpia; in entrambi i casi si ha il trasporto di PHEMA dal mezzo acquoso alla soluzione d'urea. L'entropia e l'entalpia dei parametri di diluizione ricavati da misurazioni viscometriche posseggono valori negativi e i loro valori assoluti diminuiscono con l'aumentare della concentrazione dell'urea. Si è pure trovato che le molecole di PHEMA in soluzioni di urea in condizioni θ sono molto più avvolte a spirale di quanto lo sarebbero in un solvente organico θ . Si spiegano i risultati con l'esistenza di legami idrofobi inter- e intramolecolari e con la distruzione dei gruppi idrofobi da parte dell'urea.

Zusammenfassung—Untersucht wurde der Einfluß von Harnstofflösungen auf die Gleichgewichtsquellung von nur schwach vernetzten Poly-(2-hydroxiäthyl)-methacrylat (PHEMA)-Gelen und auf das viskosimetrische Verhalten von PHEMA bei verschiedenen Harnstoffkonzentrationen und Temperaturen. Harnstoff erhöht den Grad der Quellung der Gele und der Viskosität von PHEMA; für beide Größen ist der Temperaturkoeffizient negativ. Eine thermodynamische Analyse der Quellungsdaten zeigt, daß eine Änderung der Entropie die treibende Kraft für die Zunahme der Quellung bei tiefen Temperaturen ist, während bei höheren Temperaturen (50–80°) eine negative Änderung in der Enthalpie überwiegt; beides hängt von dem Transport von PHEMA von dem wässrigen Medium in die Harnstofflösung ab. Die Verdünnungsentropie- und -enthalpieparameter, abgeleitet aus Viskositätsmessungen, haben negative Werte, deren absolute Werte mit zunehmender Harnstoffkonzentration abnehmen. Es wurde ferner gefunden, daß die PHEMA-Moleküle in Harnstofflösung unter θ -Bedingungen mehr geknäuelte sind als in organischen θ -Lösungsmitteln. Die daraus erhaltenen Ergebnisse werden unter Berücksichtigung von inter- und intramolekularen hydrophoben Bindungen interpretiert: Harnstoff zerstört die hydrophoben Kluster.