

## THE FLOW ACTIVATION ENERGY OF AQUEOUS SOLUTIONS OF POLY(2-HYDROXYETHYL METHACRYLATE) AND POLY(ACRYLAMIDE)

P. BRADNA and O. QUADRAT

*Institute of Macromolecular Chemistry,  
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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Dependences of the difference of the apparent activation energy of solution and solvent,  $\Delta E$ , on the concentration of poly(2-hydroxyethyl methacrylate) and poly(acrylamide) in an aqueous solution of ethanol or in water were found to be qualitatively identical with solutions of polymers of the vinyl type (polystyrene, poly(vinyl acetate), polyisobutene, *etc.*) in nonaqueous solvents. On the other hand, solutions of poly(2-hydroxyethyl methacrylate) in aqueous solutions of urea exhibit a different course of  $\Delta E$ : the dependences have a maximum at low concentrations, and decrease as much as to negative  $\Delta E$  with a further rise in concentration. Basing on the empirical Lyons-Tobolsky equation, which best describes the experimental viscosity-concentration relationship of the above systems, an analysis of the concentration dependences of  $\Delta E$  was made, factors determining these dependences were pointed out, and their quantitative effect was discussed in some cases.

The course of the dependence of the apparent flow activation energies of solution and solvent,  $\Delta E = E - E_s$ , on the concentration of polymers of the vinyl type in nonaqueous solvents is a function of the solvent power<sup>1</sup>. In poor solvents  $\Delta E$  first decreases, the steeper the poorer the solvent. With increasing polymer concentration the dependence becomes reversed and the  $\Delta E$  values increase; the steepness of the curve again depends on the solvent power. In good solvents these dependences increase monotonically over the whole concentration range.

Concentrated aqueous solutions of polymers (with the exception of polyelectrolytes) were not investigated from this standpoint. In this paper, poly(2-hydroxyethyl methacrylate) and poly(acrylamide) were chosen for the investigation. The interesting feature of the former consists in that it dissolves in aqueous solutions of urea exothermally<sup>2</sup>, while in water-ethanol mixtures it dissolves endothermally<sup>3</sup>; the temperature dependences of intrinsic viscosity in such solvents are of an opposite character. The temperature dependence of intrinsic viscosity of the latter polymer in pure water is very small. Owing to such differences it was possible to expect — particularly with respect to temperature — an exceptional rheological behaviour of more concentrated solutions. We therefore concentrated our efforts on a study

of the apparent flow activation energies of these solutions within the broadest possible concentration range.

## EXPERIMENTAL

Poly(2-hydroxyethyl methacrylate) (*I*) was prepared by polymerization in a cosolvent mixture of 60 vol.% ethanol and 40 vol.% water (10 wt.% monomer) with benzoyl peroxide as initiator (80°C, 10 h); the polymer was precipitated from the polymerization mixture with water and dried *in vacuo* after several reprecipitations and washing. The viscosity average molecular weight,  $\bar{M}_\eta = 8 \cdot 10^5$ , was calculated from intrinsic viscosity (6M aqueous solution of urea) at 25°C using the relationship<sup>4</sup>  $[\eta] = 1 \cdot 8 \cdot 10^{-4} M_\eta^{0.563}$ .

Poly(acrylamide) (*II*) was prepared by radical polymerization in an aqueous solution (20 wt.% monomer) with ammonium disulphate and sodium pyrosulphite as initiator (25°C, two days); the polymer was precipitated from the polymerization mixture with methanol. The molecular weight  $M_\eta \approx 6 \cdot 1 \cdot 10^5$  was calculated from intrinsic viscosity (water, 20°C) using the relationship<sup>5</sup>  $[\eta] = 6 \cdot 31 \cdot 10^{-5} M_\eta^{0.80}$ .

The basic solutions of polymers for viscosity measurements in dilute solutions were prepared by shaking the polymer with the solvent in volumetric flasks. As shaking could not be used for solutions having a higher concentration because of their considerable viscosity, these were prepared in wide-neck conic flasks by stirring the polymer with the solvent using steel balls sealed in glass (c. 15 mm in size) and rotating the flasks on an inclined plane (in some cases perfect dissolution of the polymer required as much as several weeks). Before measurement, the solutions were filtered through glass fritted discs S2; concentrated solutions had to be filtered under elevated pressure. The viscosities of diluted and concentrated solutions were measured in dilution viscometers of the Ubbelohde type (shear stress c.  $10 \text{ dyn/cm}^{-2}$ ), the temperature was maintained constant with an accuracy of  $\pm 0.05^\circ\text{C}$ , the flow time time was measured with an accuracy of  $\pm 0.1\%$ . Intrinsic viscosity was determined by Heller's plot<sup>6</sup>.

## RESULTS AND DISCUSSION

Polymer *I* can be dissolved in aqueous solutions of urea within the concentration range from 5.5M to c. 9M; lower concentration is not suitable because of the poor solubility of the polymer under normal conditions (25°C), while the maximum concentration is given by the solubility of urea at the given temperature. With respect to the experimental equipment, which provides the highest accuracy of measurements within a temperature interval of c. 10–50°C, and owing to the properties of the system described above, the measurements were carried out in solutions of 6M and 8M urea. In the cosolvent mixture water–ethanol, polymer *I* is soluble within an interval of the volume fraction of water  $\varphi_1 = 0.1–0.7$  with a maximum<sup>3</sup> corresponding to  $\varphi_1 0.4$ . The mixtures used had  $\varphi_1 0.675$ ;  $0.576$  and  $0.400$ .

The preparation of solutions was based on the requirement that the measurements should be carried out within the broadest possible polymer concentration range. The maximum concentrations were restricted by the possibility of preparing a homogeneous mixture at a finite time of dissolution, by using a capillary viscometer (al-

lowing a high experimental accuracy at precisely adjusted temperatures), and by a limited quantity of the material. The highest concentrations suitable from this point of view were determined by preliminary experiments; for solutions of polymers *I* and *II* the respective concentrations were c. 18 g/dl and 7.5 g/dl of solution.

The temperature intervals of measurements start in the vicinity of the critical solution temperature of the individual systems. For the system polymer *I*-6M urea the lower critical solution temperature is 27.9°C, but for the polymer used in this work even at 30°C phase separation still did not set in. The lower critical solution temperature of the system *I*-8M urea is 52.2°C; 50°C was chosen to be the highest experimental temperature. The upper critical solution temperature of the systems *I*-ethanol-water and *II*-water is not known; we therefore performed the measurements at the lowest temperature at which the polymer did not precipitate from solution.

In the system *I*-ethanol-water the course of the concentration dependence of the difference of the apparent flow activation energy of solution and solvent,  $\Delta E$ , is similar in all three cases, irrespective of the volume fraction of water in the solvent, and thus of the solvent power (Fig. 1a); it resembles the  $\Delta E$  vs  $c$  dependence of the vinyl polymers in nonaqueous thermodynamically poor solvents. In the low concentration region  $\Delta E$  decreases; with increasing polymer concentration there is an in-

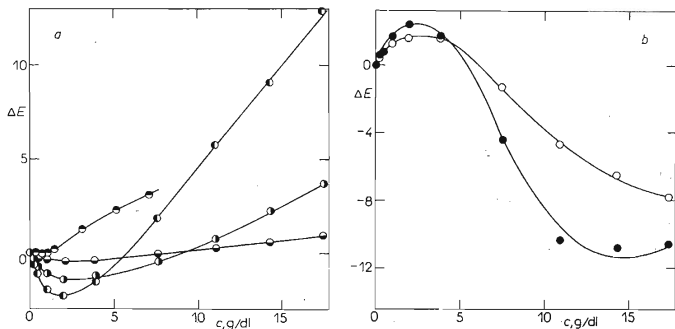


FIG. 1

Dependence of the Difference of the Apparent Flow Activation Energy of Solution and Solvent,  $\Delta E$  (kcal), on Polymer Concentration at 25°C

*a* Poly(hydroxyethyl methacrylate)-ethanol-water,  $\varphi_1$ : ● 0.675, ● 0.576, ○ 0.400; poly-(acrylamide)-water: ●. *b* Poly(2-hydroxyethyl methacrylate)-urea-water, concentration of the aqueous urea solution: ● 6M, ○ 8M.

version of the course at concentrations of 2–3 g/dl and  $\Delta E$  monotonically increases, the increase being almost linear at higher concentrations. The improvement of the solvent power<sup>3</sup> is reflected in a decrease in the absolute value of the initial slope and in a slower increase in  $\Delta E$  in the higher concentration range of the polymer.

Contrariwise, the character of the  $\Delta E$  vs  $c$  dependence for the system *I*–urea–water is completely different and particularly interesting (Fig. 1*b*). In the region of dilute solutions  $\Delta E$  increases with the polymer concentration; the dependence becomes reversed at  $c$ . 3 g/dl, after which  $\Delta E$  decreases to considerably negative values. In the range of high polymer concentrations the course is a different one; in 8M urea the decrease in  $\Delta E$  is slightly slowed down, stopping completely in 6M urea and eventually increasing slowly once again. Since, however, there are not sufficient experimental values available, and also in view of experimental errors it cannot be decided whether such indication of a minimum is not only an apparent one. A comparison of the  $\Delta E$  vs  $c$  courses in 8M and 6M urea shows that the initial (positive) slope of this plot is much higher in the poorer solvent (6M urea).

A practically zero initial slope of the  $\Delta E$  vs  $c$  plot was found for a solution of polymer *II* in water. A further increase in the polymer concentration makes  $\Delta E$  increase monotonically, similarly to the system *I*–ethanol–water, with the slope of the dependence decreasing (Fig. 1*a*).

To be able to interpret the course of such dependence, we must know above all how to express analytically the dependence of viscosity on polymer concentration. Unfortunately, a theoretical derivation of such function is very difficult already for slightly concentrated solutions, and has not been accomplished yet. Of empirical equations, the three-parameter Lyons–Tobolsky equation<sup>7</sup> proved to be suitable for this purpose:

$$\eta_{sp}/[\eta]c = \exp [k_L[\eta]c/(1 - bc)], \quad (1)$$

where  $[\eta]$  is intrinsic viscosity. The equation parameters  $k_L$  and  $b$  were determined by numerical calculation using a WANG desk computer and an optimization procedure which proved useful in an earlier work<sup>8</sup> for solutions of polystyrene and cellulose nitrate. The values were determined as usual from the experimental results obtained with dilute solutions.

The apparent flow activation energy of a polymer solution is given by

$$E = \partial \ln \eta / \partial (1/RT), \quad (2)$$

where  $T$  is absolute temperature and  $R$  is the universal gas constant. For the difference of the apparent flow activation energy of solution and solvent it can be written

$$\Delta E = -RT^2(\partial \ln \eta_i / \partial T). \quad (3)$$

By rearranging the Lyons–Tobolsky equation to become

$$\ln \eta_r = \ln [1 + [\eta] c \exp (k_L[\eta] c / (1 - bc))], \quad (4)$$

differentiating with respect to temperature and substituting into Eq. (3) we obtain

$$\begin{aligned} \Delta E = & -RT^2(c[\eta] \exp [k_L[\eta] c / (1 - bc)] / \{1 + [\eta] c \exp [k_L[\eta] c / (1 - bc)]\}) \cdot \\ & \cdot (\partial \ln [\eta] / \partial T + \partial \ln \varrho / \partial T + [k_L[\eta] c / (1 - bc)] \cdot \{\partial \ln [\eta] / \partial T + \\ & \partial \ln k_L / \partial T + \partial \ln \varrho / \partial T + [bc / (1 - bc)] [\partial \ln b / \partial T + \partial \ln \varrho / \partial T]\}), \quad (5) \end{aligned}$$

where  $\varrho$  is the solution density.

For the initial slope of the  $\Delta E$  vs  $c$  dependence defined by

$$S = (\partial \Delta E / \partial c)_{c=0}. \quad (6)$$

Eq. (5) assumes the limiting form

$$S = -RT^2[\eta] (\partial \ln [\eta] / \partial T + \partial \ln \varrho_s / \partial T) \quad (7)$$

( $\varrho_s$  being the solvent density), identical with an expression derived earlier<sup>1</sup> by means of Kraemer's equation. As the intrinsic viscosity is always positive, the sign of the

TABLE I

Temperature Dependence of the Parameters of the Lyons–Tobolsky Equations for Systems with Poly(2-Hydroxyethyl Methacrylate) (*I*) and Poly(Acrylamide) (*II*)

System	$10^3 \cdot \partial \ln [\eta] / \partial T$	$10^3 \cdot \ln k_L / \partial T$	$10^3 \cdot \ln b / \partial T$	$10^3 \cdot \partial \ln \varrho / \partial T$
<i>I</i> -6M urea	-23	34	-37	-0.32
<i>I</i> -8M urea	-17	29	-30	-0.45
<i>I</i> -ethanol-water ( $\varphi_1 = 0.675$ )	16	-3.9	-24	-0.54
<i>I</i> -ethanol-water ( $\varphi_1 = 0.578$ )	82	-6.9	23	-0.65
<i>I</i> -ethanol-water ( $\varphi_1 = 0.400$ )	2.8	-2.5	18	-0.75
<i>II</i> -water	3.6	-8.2	-5.0	-0.21

initial slope is determined by the sum of the temperature dependences of intrinsic viscosity and of the solvent density.  $\partial \ln [\eta]/\partial T$ , is the decisive term in this sum, because in such systems it is at least ten times higher than  $\partial \ln \rho_s/\partial T$  (Table I). Accordingly, the positive initial slope of the  $\Delta E$  vs  $c$  dependence of a solution of polymer *I* in 6M and 8M urea is a result of the negative temperature dependence of intrinsic viscosity (Fig. 2a), while the negative initial slope of the systems *I*-ethanol-water and *II*-water corresponds to a positive  $\partial \ln [\eta]/\partial T$ .

With increasing polymer concentration further terms become operative in Eq. (5), which involve the effect of intermolecular interactions, and the sign and magnitude of their temperature dependence assumes a decisive influence on the form of the

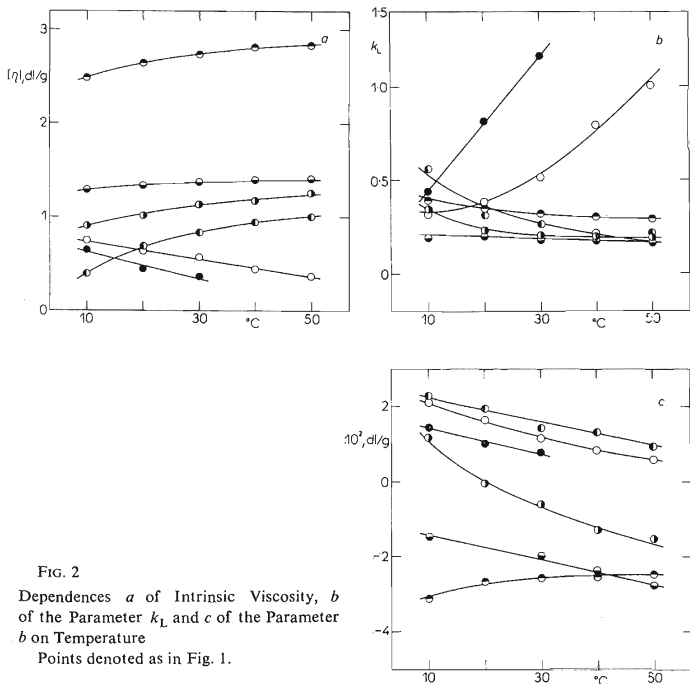


FIG. 2

Dependences *a* of Intrinsic Viscosity, *b* of the Parameter  $k_L$  and *c* of the Parameter  $b$  on Temperature

Points denoted as in Fig. 1.

further course of the concentration dependence of  $\Delta E$ . To simplify the discussion of these factors, we defined

$$A = \{[\eta] c \exp [k_L[\eta] c/(1 - bc)]\} / \{1 + [\eta] c \exp [k_L[\eta] c/(1 - bc)]\} \quad (8)$$

$$B = (\partial \ln [\eta] / \partial T) + (\partial \ln \varrho / \partial T), \quad (9)$$

$$D = (\partial \ln [\eta] / \partial T) + (\partial \ln \varrho / \partial T) + (\partial \ln k_L / \partial T) \quad (10)$$

$$G = (\partial \ln b / \partial T) + (\partial \ln \varrho / \partial T). \quad (11)$$

The values of the terms  $B$ ,  $D$ , and  $G$  follow from the derivatives of the dependences  $\ln [\eta]-T$ ,  $\ln k_L-T$ ,  $\ln b-T$  and  $\ln \varrho-T$  at  $25^\circ\text{C}$  (Fig. 2*b,c*), given in Table I. On substitution, Eq. (5) becomes

$$\Delta E = -RT^2 A \{B + D[k_L[\eta] c/(1 - bc)] + G[k_L b[\eta] c^2/(1 - bc)^2]\}. \quad (12)$$

The term  $A$  is in all systems a monotonic function of concentration and increases from zero to a limit equal to unity. Consequently, the product  $-RT^2 A$  decreases with concentration from zero to a limit equal to  $-RT^2$ . Thus, the course of the  $\Delta E$  vs  $c$  dependence is determined by the second part of the right-hand side of Eq. (12), i.e. by the sum of three terms containing the parameters  $B$ ,  $D$ , and  $G$ . The meaning of contributions of the individual terms is shown by their concentration dependence as plotted in Fig. 3. The values obtained for solutions of polymer *I* in 8*M* urea and in the mixture ethanol-water ( $\varphi_1 = 0.675$ ), and for a solution of polymer *II* in water

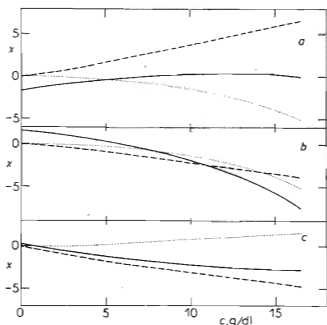


FIG. 3

Dependence of Terms from Eq. (12) on Polymer Concentration

*a* Poly(2-hydroxyethyl methacrylate)-8*M* urea, *b* poly(2-hydroxyethyl methacrylate)-ethanol-water,  $\varphi_1 = 0.675$ , *c* poly(acrylamide)-water; - - - -  $x = D[k_L[\eta] c / (1 - bc)]$ , .....  $x = G[k_L b[\eta] c^2 / (1 - bc)^2]$ , ———  $x = B + D[k_L[\eta] c / (1 - bc)] + G[k_L b[\eta] c^2 / (1 - bc)^2]$ .

are given as an example. In order that the  $\Delta E$  vs curve could have an extreme at a real concentration, the dependence of the sum of three terms on concentration must intersect the  $y$ -axis in a non-zero point. This is fulfilled according to Figs 3a and 3b. In the former case a) the system involved is poly(2-hydroxyethyl methacrylate) – 8M urea, for which a maximum was found experimentally on the  $\Delta E$  vs  $c$  curve; in the latter case b) the system is poly(2-hydroxyethyl methacrylate)–ethanol–water, and the extreme is a minimum. In the case of the system poly(acrylamide)–water (Fig. 3c) the intersection point of the curve is very close to zero, which corresponds to the indication of a minimum (but rather to a zero initial slope) on the experimental curve  $\Delta E$  vs  $c$ .

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