

The unperturbed molecular dimensions of poly(ethylene oxide) in aqueous solutions from intrinsic viscosity measurements and the evaluation of the theta temperature

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Intrinsic viscosity measurements were carried out on five well characterized fractions of poly(ethylene oxide) in aqueous solutions at 24.9°, 34.9°, and 45.5°C. The Stockmayer-Fixman extrapolation was applied to the data: it yields the unperturbed dimensions K_θ of the chain. The unperturbed root-mean-square end-to-end distance $\langle \bar{R}^2 \rangle_0^{1/2}$ calculated for the polymer fractions in water indicate that the polymer molecules are expanded in this solvent as the temperature is raised. The temperature coefficient of unperturbed dimension, $d \ln \langle \bar{R}^2 \rangle_0 / dt = 0.024 \text{ K}^{-1}$, calculated for poly(ethylene oxide) in water using the present data is about 100 times higher than the literature values of $0.23 (\pm 0.02) \times 10^{-3} \text{ K}^{-1}$ and $0.2 (\pm 0.2) \times 10^{-3} \text{ K}^{-1}$, respectively, obtained from force-temperature ('thermoelastic') measurements on elongated networks of the polymer in the amorphous state and from viscosity measurements on this polymer in benzene. A value of $\theta = 108.3^\circ\text{C}$ was obtained from the temperature dependence of the interaction parameter B in the Stockmayer-Fixman equation.

Keywords Molecular dimensions; unperturbed; poly(ethylene oxide); intrinsic viscosity measurements; theta temperature; thermoelastic measurements

INTRODUCTION

The unperturbed mean-square radius of gyration $\langle \bar{S}^2 \rangle_0$ is one of the two basic molecular parameters which represents short-range interferences in the chain, and from which valuable information concerning the chain structure is obtained. In addition, in order to estimate the expansion factor as defined by the ratio of the mean-square radius to its unperturbed value, the latter must be determined. Thus, it is often necessary to estimate unperturbed molecular dimensions. This is conveniently done from light-scattering measurements at theta temperatures. However, a number of indirect or extrapolation methods, all based on approximate closed expressions for the expansion factor, have been proposed for estimating unperturbed molecular dimensions.

The intrinsic viscosity may be expressed in the form:

$$[\eta] = [\eta]_\theta \alpha_\eta^3 \quad (1)$$

where the intrinsic viscosity $[\eta]_\theta$ at the theta temperature, or in the unperturbed state, is proportional to the square root of the molecular weight for flexible chains with ordinary molecular weights and without hydrodynamic interactions, that is:

$$[\eta]_\theta = K_\theta M^{1/2} \quad (2)$$

Then,

$$\alpha_\eta^3 = \frac{[\eta]}{K_\theta M^{1/2}} \quad (3)$$

where

$$K_\theta = \varphi_0 A^3 \quad (4)$$

and A is a parameter given by,

$$A^2 = \frac{\langle \bar{R}^2 \rangle_0}{M} \quad (5)$$

The quantity $\langle \bar{R}^2 \rangle_0$ is the mean-square end-to-end distance of a chain in the theta state and is related to $\langle \bar{S}^2 \rangle_0$ through,

$$\langle \bar{S}^2 \rangle_0 = \frac{1}{6} \langle \bar{R}^2 \rangle_0 \quad (6)$$

Equation (2), with (4) and (5), suggests that measurements of intrinsic viscosities at theta temperatures for various molecular weights yield values of K_θ from which the parameter A can be estimated when the value of the viscosity constant φ_0 is given.

Under non-theta conditions, the radius expansion factor α_η for the viscosity is an increasing function of the excluded volume parameter Z which is given by:

$$Z = \left(\frac{3}{2\pi} \right)^{3/2} \left(\frac{B}{A^3} \right) M^{1/2} \quad (7)$$

where

$$B = \frac{\beta}{M_s} \quad (8)$$

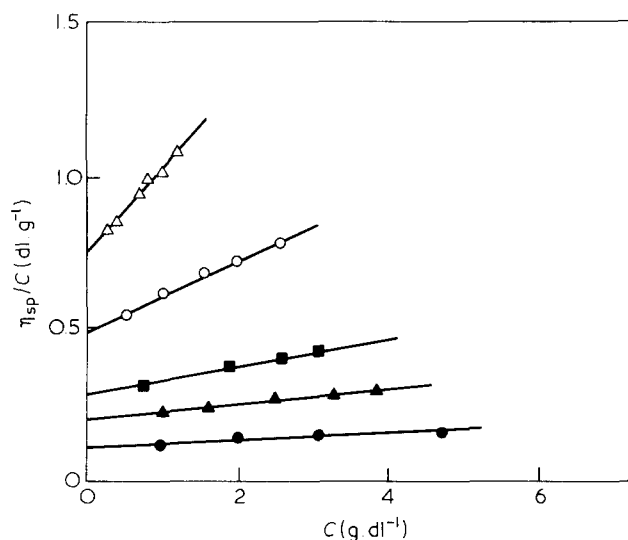


Figure 1 Concentration dependence of the viscosity number for the poly(ethylene oxide) fractions at 24.9°C. PEG 4000, ●; PEG 9000, ▲; PEG 20000, ■; PEG 37000, ○; PEG 100000, △

Here M_s is the molecular weight of the segment and β is called the binary cluster integral. The factor α_η becomes unity as the molecular weight is decreased to zero, since $\alpha_\eta = 1$ at $Z = 0$. In other words, the excluded-volume effect is negligible for short chains. This fact suggests that values of $[\eta]_0$ and K_θ may be obtained by extrapolation to zero molecular weight from intrinsic viscosity data obtained in an ordinary range of molecular weight in good or non-theta solvents. One such extrapolation procedure, which will be used in the present study, is based on the following equation proposed by Stockmayer and Fixman¹:

$$\frac{[\eta]}{M^{1/2}} = K_0 + 0.51\phi_0 \cdot B \cdot M^{1/2} \quad (9)$$

EXPERIMENTAL

Description of samples

The poly(ethylene oxide) fractions, denoted as PEG 4000, PEG 9000, PEG 20000, PEG 37000, and PEG 100000, are the same as those used in a previous study². PEG 4000, PEG 9000, and PEG 20000 are the Dow Chemical Company polyethylene glycol. PEG 37000 is poly(oxyethylene) glycol manufactured by Buckeye Cellulose Corporation, Memphis, Tennessee. PEG 100000 is Union Carbide poly(ethylene oxide), Polyox WSR N-10. PEG 100000 was purified by dialysis using cellophane tubing and water as solvent. The purified material was recovered by freeze drying before use. The other fractions were used as supplied.

Preparation of solutions

Distilled water was used as solvent. All solutions were prepared by weighing. The concentrations of the polymer solutions at 25°C were obtained using the known weights of the solutions and their measured densities. The densities of the solutions at 25°C were measured using a digital precision density-meter (Anton Paar model DMA 60). The same solutions prepared at 25°C were used for the viscosity studies at all other temperatures. Within the temperature interval used in the present study, the

variations in the solution concentrations with temperature have been assumed negligible.

Viscosity measurements

The viscosity measurements were performed at 24.9°, 34.9°, and 45.5°C, using an Ubbelohde type viscometer. Temperatures were controlled to $\pm 0.01^\circ\text{C}$ and efflux times were reproducible to $\pm 0.1\%$. In the molecular weight range investigated, shear rate effects were assumed to be negligible. The intrinsic viscosities $[\eta]$ were obtained from plots of the ratios η_{sp}/C against C and subsequent extrapolations to infinite dilution.

Molecular weight of samples

The number average molecular weights (\bar{M}_n) of PEG 4000, PEG 9000 and PEG 20000 were measured on a Mechrolab model 301 A vapour pressure osmometer at 37°C with water as solvent. All measurements were extrapolated to infinite dilutions.

For the higher fractions (PEG 37000 and PEG 100000) the number average molecular weights were determined in aqueous solutions at 25°C using a block type membrane osmometer provided with organic liquid manometer. Details about the design and functioning of this instrument have been given by Vink³. The organic liquid used as manometer liquid was n-hexane. Acetylated cellophane was used as membrane in the manometer. The preparation and use of such membranes have been described elsewhere⁴.

RESULTS AND DISCUSSION

Figure 1 shows the plot of η_{sp}/C against C for the poly(ethylene oxide) fractions in aqueous solutions at 24.9°C. Similar plots were obtained at 34.9° and 45.5°C. The experimental and calculated data for the poly(ethylene oxide) fractions at 24.9°, 34.9° and 45.5°C are contained in Tables 1, 2 and 3, respectively. The intrinsic viscosity-molecular weight relationships at these three temperatures were determined as:

$$[\eta]_{24.9} C \text{ dl g}^{-1} = 6.04 \times 10^{-5} \bar{M}_n^{0.90} \quad (10)$$

$$[\eta]_{34.9} C \text{ dl g}^{-1} = 8.62 \times 10^{-5} \bar{M}_n^{0.85} \quad (11)$$

$$[\eta]_{45.5} C \text{ dl g}^{-1} = 18.7 \times 10^{-5} \bar{M}_n^{0.78} \quad (12)$$

A survey of the literature^{5,6} shows that the following solvent systems have been cited as theta solvents for poly(ethylene oxide): 0.5 M aqueous MgSO_4 at 25.8°C⁶; 0.45 M aqueous K_2SO_4 at 35°C⁵; and 0.39 M aqueous MgSO_4 at 45°C⁵. Viscosity measurements in these solvent systems gave the following relationships between intrinsic

Table 1 Experimental and calculated data for the poly(ethylene oxide) fractions from intrinsic viscosity measurements at 24.9°C

| Fraction | \bar{M}_n (g mol ⁻¹) | $[\eta]$ (dl g ⁻¹) | $[\eta]_0$ (dl g ⁻¹) | α_η | $(\bar{R}^2)_0^{1/2}$ (Å) |
|------------|---------------------------------------|-----------------------------------|-------------------------------------|---------------|------------------------------|
| PEG 4000 | 4500 | 0.110 | 0.037 | 1.45 | 42.73 |
| PEG 9000 | 7746 | 0.195 | 0.048 | 1.61 | 56.06 |
| PEG 20000 | 13470 | 0.283 | 0.063 | 1.64 | 73.93 |
| PEG 37000 | 22445 | 0.489 | 0.082 | 1.82 | 95.43 |
| PEG 100000 | 37640 | 0.759 | 0.106 | 1.93 | 123.6 |

Table 2 Experimental and calculated data for the poly(ethylene oxide) fractions from intrinsic viscosity measurements at 34.9°C

| Fraction | \bar{M}_n (g mol ⁻¹) | $[\eta]$ (dl g ⁻¹) | $[\eta]_\theta$ (dl g ⁻¹) | α_η | $\langle \bar{R}^2 \rangle_0^{1/2}$ (Å) |
|------------|---------------------------------------|-----------------------------------|--|---------------|--|
| PEG 4000 | 4500 | 0.112 | 0.048 | 1.32 | 46.96 |
| PEG 9000 | 7746 | 0.191 | 0.063 | 1.44 | 61.61 |
| PEG 20000 | 13470 | 0.267 | 0.084 | 1.47 | 81.24 |
| PEG 37000 | 22445 | 0.461 | 0.108 | 1.62 | 104.9 |
| PEG 100000 | 37640 | 0.697 | 0.140 | 1.71 | 135.8 |

Table 3 Experimental and calculated data for the poly(ethylene oxide) fractions from intrinsic viscosity measurements at 45.5°C

| Fraction | \bar{M}_n (g mol ⁻¹) | $[\eta]$ (dl g ⁻¹) | $[\eta]_\theta$ (dl g ⁻¹) | α_η | $\langle \bar{R}^2 \rangle_0^{1/2}$ (Å) |
|------------|---------------------------------------|-----------------------------------|--|---------------|--|
| PEG 4000 | 4500 | 0.130 | 0.077 | 1.19 | 54.74 |
| PEG 9000 | 7746 | 0.202 | 0.100 | 1.26 | 71.82 |
| PEG 20000 | 13470 | 0.284 | 0.132 | 1.29 | 94.70 |
| PEG 37000 | 22445 | 0.463 | 0.171 | 1.39 | 122.3 |
| PEG 100000 | 37640 | 0.680 | 0.221 | 1.45 | 158.3 |

viscosity and molecular weight for the poly(ethylene oxide) fractions used in the present study:

0.5 M MgSO₄,

$$[\eta]_{25.0^\circ\text{C}} \text{ dl g}^{-1} = 48.2 \times 10^{-5} \bar{M}_n^{0.65} \quad (13)$$

0.45 M K₂SO₄,

$$[\eta]_{35.0^\circ\text{C}} \text{ dl g}^{-1} = 70.3 \times 10^{-5} \bar{M}_n^{0.59} \quad (14)$$

0.39 M MgSO₄,

$$[\eta]_{45.0^\circ\text{C}} \text{ dl g}^{-1} = 64.0 \times 10^{-5} \bar{M}_n^{0.61} \quad (15)$$

Equations (13), (14) and (15) show that equation (2) is not satisfied for poly(ethylene oxide) in these solvent systems and at the stated temperatures. As far as the present author is concerned these solvent systems cannot be regarded as theta solvents for poly(ethylene oxide) at the quoted temperatures. The 'theta' solvent 0.5 M aqueous MgSO₄ has been arrived at through osmotic-pressure measurements⁶ and in the words of the authors⁶ the measurements were of limited success. The other two 'theta' solvents, 0.45 M aqueous K₂SO₄ and 0.39 M aqueous MgSO₄, have been deduced using unfractionated samples⁵ in the molecular weight range 10⁴–10⁷. Since Union Carbide Polyox resins used in these measurements⁵ are characterized by a very broad molecular weight distribution⁷, sometimes of the order of 15–20, caution must be exercised in the use of the above solvent systems as theta solvents for well defined poly(ethylene oxide) fractions. In the present study, the viscosity radius expansion factor α_η will therefore be calculated (equation (1)) using measured values of $[\eta]$ for the poly(ethylene oxide) fractions at the various temperatures and the corresponding $[\eta]_\theta$ obtained through the Stockmayer–Fixman equation.

According to theory⁸,

$$\alpha_\eta^5 - \alpha_\eta^3 = 2C_M \psi_1 \left(1 - \frac{\theta}{T}\right) M^{1/2} \quad (16)$$

$$\psi_1 \left(1 - \frac{\theta}{T}\right) = \frac{1}{2} - \chi_1 \quad (17)$$

where ψ_1 is the entropy parameter, θ is the parameter called the theta temperature, and χ_1 is the thermodynamic interaction parameter for a given polymer–solvent pair. The parameter C_M is given by:

$$C_M = \left(\frac{27}{2^{5/2} \pi^{3/2}}\right) \left(\frac{\bar{v}^2}{N_A^2 V_0}\right) \left(\frac{\langle \bar{R}^2 \rangle_0}{M}\right)^{-3/2} \quad (18)$$

Here N_A is Avogadro's number, \bar{v} is the polymer partial specific volume, and V_0 is the molar volume of the solvent.

The quantity $(\alpha_\eta^5 - \alpha_\eta^3)$ is proportional to the square root of the polymer molecular weight M except at $T = \theta$, since C_M , ψ_1 and θ are independent of M for high-molecular-weight polymers of ordinary interest⁹. Therefore it follows that α_η increases slowly with molecular weight (assuming that $\psi_1 \left(1 - \frac{\theta}{T}\right) > 0$) and without limit even when the molecular weight becomes very large. This conclusion is borne out by the data for α_η in Tables 1–3.

α_η depends on the factor $\psi_1 \left(1 - \frac{\theta}{T}\right)$ which represents the intensity of the thermodynamic interaction. This factor therefore represents the solvent power or the 'goodness' of the solvent; the larger this factor, the better the solvent. Therefore, the better the solvent, the greater the value of α_η for a given polymer molecular weight. The parameter C_M defined by equation (18) involves the unperturbed dimension $\langle \bar{R}^2 \rangle_0$ which depends on temperature through the effective bond length of the chain. In most cases, however, C_M is less dependent on the temperature than the factor $\psi_1 \left(1 - \frac{\theta}{T}\right)$ so that the temperature dependence of α_η is governed mainly by this factor. The decrease of α_η with increasing temperature (Tables 1–3) therefore indicates that the solvent power of water for poly(ethylene oxide) decreases as the temperature is raised from 25°C.

The calculated values of $\langle \bar{R}^2 \rangle_0^{1/2}$ are contained in the last columns of Tables 1–3. $\langle \bar{R}^2 \rangle_0^{1/2}$ is seen to increase with increasing temperature. From the data at the three temperatures, the temperature coefficient of unperturbed dimension $d \ln \langle \bar{R}^2 \rangle_0 / dT$ was calculated for each polymer fraction. Its average value gave $d \ln \langle \bar{R}^2 \rangle_0 / dT = 0.024 \text{ K}^{-1}$. This value is about 100 times higher than the literature values of $0.23 (\pm 0.02) \times 10^{-3} \text{ K}^{-1}$ and $0.2 (\pm 0.2) \times 10^{-3} \text{ K}^{-1}$ obtained respectively from force-temperature ('thermoelastic') measurements on elongated networks of poly(ethylene oxide) in the amorphous state¹⁰ and from viscosity measurements on the polymer in the thermodynamically good solvent, benzene¹¹. The value for $d \ln \langle \bar{R}^2 \rangle_0 / dT$ obtained in the present study differs in both magnitude and sign from those reported for low molecular weight poly(ethylene oxide) in the solvents acetone and dioxane¹². Poly(ethylene oxide) molecules in aqueous solutions exhibit an unusual solvation effect⁷.

While some investigators¹³ assume a non-free draining coil model for the poly(ethylene oxide) molecules in aqueous solutions, others^{14–16} contend that in water the polymer molecules exist in the helix form. Based on the results from studies of heats of solution and dilution for

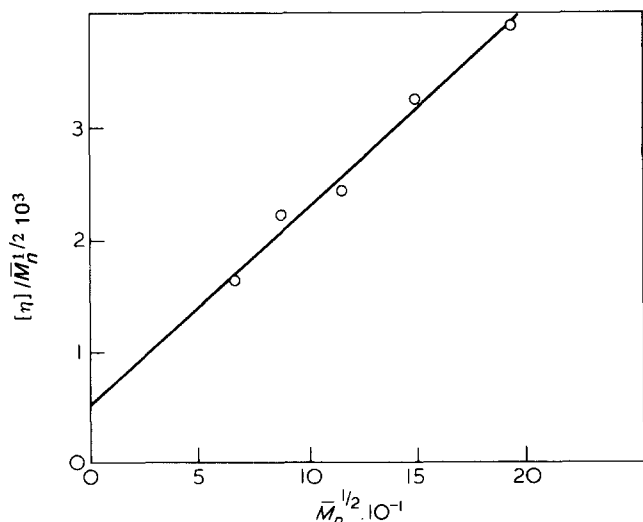


Figure 2 Stockmayer-Fixman plot for the poly(ethylene oxide) fractions at 24.9°C

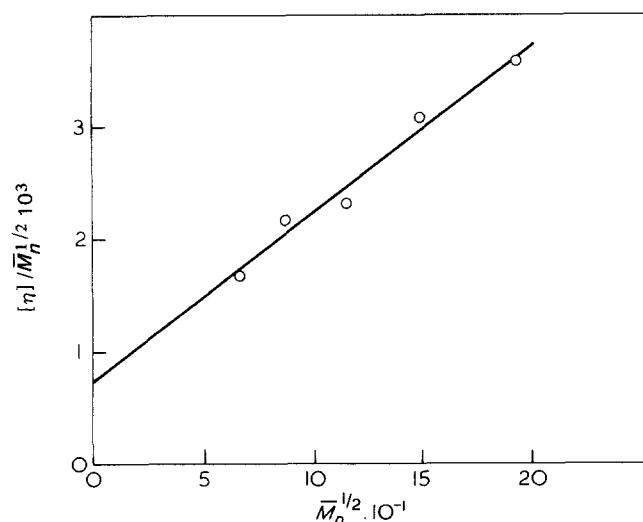


Figure 3 Stockmayer-Fixman plot for the poly(ethylene oxide) fractions at 34.9°C

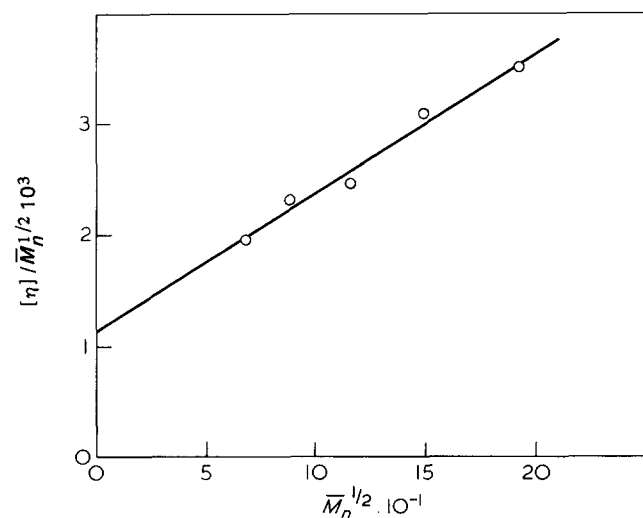


Figure 4 Stockmayer-Fixman plot for the poly(ethylene oxide) fractions at 45.5°C

poly(ethylene oxide) in several solvents¹⁶, it has been suggested that the formation of this helix in aqueous solutions involves the evolution of 39.3 cal per gram of polymer which accounts for the difference in the thermal behaviour of this polymer in water as compared with organic solvents. The presence of the helix form is known to persist up to at least 80°C¹⁶.

Figures 2, 3 and 4 show plots of $[\eta]/\bar{M}_n^{1/2}$ against $\bar{M}_n^{1/2}$ for the poly(ethylene oxide) fractions. The parameters K_θ and B calculated for the poly(ethylene oxide) fractions at the three temperatures are contained in Table 4. The numerical value of the universal constant ϕ_0 in equation (9) was taken as $2.1 \times 10^{23} \text{ mol}^{-1}$. Table 4 shows that $10^3 K_\theta$ increases from 0.52 dl g⁻¹ at 298.1 K to 1.13 dl g⁻¹ at 318.7 K. Data in the literature^{5,6,11,17,18} indicate that K_θ for poly(ethylene oxide) varies over a wide range, even for θ solvent systems at the same temperature⁶. The temperature dependence of B , as suggested originally by Flory⁹, is given by:

$$B = B_0 \left(1 - \frac{\theta}{T} \right) \quad (19)$$

where B_0 is a constant, independent of temperature, which can be determined from the temperature dependence of the second virial coefficient near the theta temperature.

The plot of B against $\frac{1}{T}$ according to equation (19) is shown in Figure 5. The straight line through the three experimental points in Figure 5 is given by the following equation:

$$B = -65.7 \times 10^{-27} \left[1 - \frac{381.5}{T} \right] \quad (20)$$

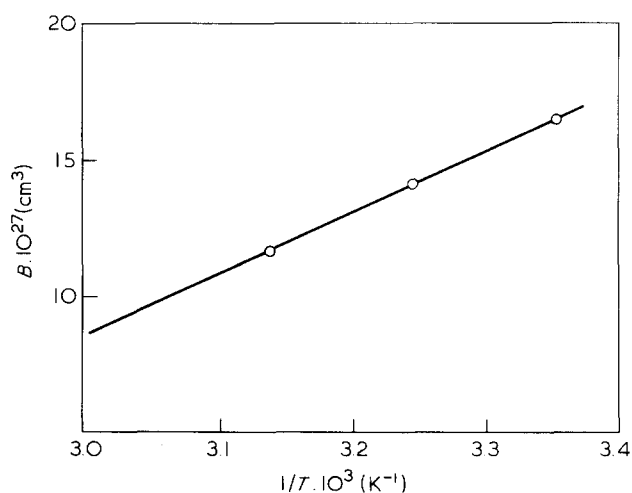


Figure 5 Plot of the interaction parameter B as a function of the reciprocal of the absolute temperature

Table 4 Summary of calculated parameters for the poly(ethylene oxide) fractions at the various temperatures using equation (9)

| T (K) | 298.1 | 308.1 | 318.7 |
|---|-------|-------|-------|
| $1/T \cdot 10^3$ (K ⁻¹) | 3.355 | 3.246 | 3.138 |
| $K_\theta \cdot 10^3$ (dl g ⁻¹) | 0.52 | 0.72 | 1.13 |
| $B \cdot 10^{27}$ (cm ³) | 16.47 | 14.01 | 11.60 |

Comparing equations (19) and (20) yields $\theta = 108.3^\circ\text{C}$ for the poly(ethylene oxide) molecules in aqueous solution. It is interesting to note that this value of θ compares approximately to the lower critical solution temperature (LCST) for poly(ethylene oxide) in aqueous solution^{5,19}. A plot of the exponents of \bar{M}_n in equations (10), (11) and (12), against $\frac{1}{T}$ is approximately linear. The straight line through the points is given by the following equation:

$$a = \frac{552.8}{T} - 0.95 \quad (21)$$

where a is the exponent in the Mark-Houwink equation, $[\eta] = KM^a$. Substitution of $T = 381.5$ in equation (21) gives $a = 0.5$. The value of $\theta = 108.3^\circ\text{C}$, obtained through equation (19) therefore appears reasonable. An equation having the form of equation (20) corresponds to a negative heat of dilution causing the polymer to deswell upon heating; it also yields a negative value of Flory's entropy parameter ψ_1 ²⁰ which may be related to orientation effects involving solvent molecules around polymer segments. The existence of a lower consolute temperature in aqueous solutions of poly(ethylene oxide) tends to confirm the view that negative entropies of dilution control the solution properties of this polymer in aqueous solution.

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