8344 *Macromolecules* **1995,** *28,* 8344−8349

Hydrodynamic Properties of Dilute Aqueous Solutions of Poly(*N*-ethylmethacrylamide)

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Received March 10, 1994; Revised Manuscript Received September 5, 1995[⊗]

ABSTRACT: Dilute solution properties of five nonfractionated samples of poly(*N*-ethylmethacrylamide) (PEMAm; $6 \leq M_w \times 10^{-4} \leq 200$), in water at temperatures from 5 to 70 °C were studied by viscometry. The temperature dependence of the intrinsic viscosity was very strong, and the quotients $d \ln[\eta]/dT$ were negative. The exponent a in the Mark−Houwink−Kuhn−Sakurada equation was high and almost constant at temperatures lower than 40 °C whereupon it abruptly decreased to $a = 1/2$ at 70.5 °C. Analysis of the intrinsic viscosity data yields the characteristic ratio of the chain ($C_\infty = 7.2$ at 70.5 °C), the Kuhn statistical segment length ($\lambda^{-1} = 13.6 \times 10^{-8}$ cm), and the polymer−water interaction parameter χ (for temperatures higher than 55 °C). The latter is resolved into its entropic and enthalpic contributions. Both of them are negative. In terms of Franks' nomenclature, the system PEMAm−water can be classified as typically "aqueous". It is shown that the behavior of aqueous solutions of poly(methacrylamide) is rather a "nonaqueous" one.

Introduction

The present study of hydrodynamic properties of dilute solutions of poly(*N*-ethylmethacrylamide) (PEMAm) was initiated by the fact that the polymer is soluble in water at ambient temperature and separates from solution on heating, exhibiting a lower critical solution temperature (LCST).[1−3] Since the theta temperature, θ_L^{PE}, estimated in the study of phase equilibria[3] by extrapolating the LCSTs to infinite chain length is high (67 °C), the solution properties can conveniently be studied over a broad temperature range. Such detailed studies have so far been done only with some polymer−solvent systems displaying upper critical solution temperatures (UCST).

Experimental Section

Samples of poly(*N*-ethylmethacrylamide) were prepared by radical-initiated polymerization in solution and were characterized by light scattering (weight-average molecular weight, $\bar{M}_w$), osmometry (number-average molecular weight, $\bar{M}_n$), and size exclusion chromatography (polymolecularity index, $\bar{M}_w/\bar{M}_n$) (Table 1). Experimental details have been reported.[3]

Viscosity was measured in Ubbelohde capillary viscometers adapted for dilution and equipped with an electronic monitoring of flow times. The kinetic energy correction was negligible. The concentration of solutions c (g/dL) was chosen so that the relative viscosity η_r (ratio of flow times of the solution and solvent) was $1.1 \lesssim \eta_r \lesssim 1.8$. The intrinsic viscosity (Table 2) was evaluated by the Heller method.[4] The temperature was kept constant to ±0.01 °C.

In view of strong hygroscopicity, polymer samples were kept over magnesium perchlorate or phosphorus pentoxide. To prepare a solution, a small amount of polymer was put into a weighed volumetric flask; the system was evacuated and heated to 50 °C for 2 days. After this time the weight was constant. The solvent was added, and the flask was shaken overnight at laboratory temperature.

To reduce accidental errors that might arise because of the hygroscopicity of PEMAm, the intrinsic viscosities were determined in duplicate or triplicate with fresh solution each. Differences in $[\eta]$ were slightly higher than with nonaqueous systems but were mostly within the limits of ±3%.

Table 1. Molecular Characteristics of PEMAm Samples

sample	$\bar{M}_w \times 10^{-6\,a}$	$\bar{M}_w/M_n{}^b$	$\bar{M}_w/\bar{M}_n{}^c$
1	2.04		
2	0.79	3.2	4.5
3	0.20	1.8	1.7
4	0.10	1.5	1.7
5	0.061	1.4	

[a] By light scattering. [b] By combination of $\bar{M}_w$ and $\bar{M}_n$ (osmometry). [c] By GPC.

Specific volumes of solutions ν were measured with the Anton-Paar densitometer at four polymer concentrations (weight fraction $0.2 \lesssim w_2 \times 10^2 \lesssim 1$) and five temperatures.[5] Since the plots of $\bar{\nu}$ vs w_2 were linear and the intercepts were in very good agreement with tabulated values of the specific volume ν_1^0 of water, the partial specific volume of polymer at infinite dilution $\bar{\nu}_2^0$ could simply be calculated from the slopes $d\bar{\nu}/dw_2$ of the plots as $\bar{\nu}_2^0 = \nu_1^0 + d\bar{\nu}/dw_2$. The values of $(\bar{\nu}_2^0)^2/V_1$ (where V_1 is the mole volume of solvent) to be used in calculations of the interaction parameters (cf. eq 19) were independent of temperature within ±2.5%, so their arithmetic mean, 3.78×10^{-2} cm^3 g^{-2} mol, was used throughout.

Results and Discussion

Temperature Dependence of the Intrinsic Viscosity. The intrinsic viscosity of aqueous solutions of PEMAm decreases with increasing temperature (Table 2, Figure 1). The plots of $[\eta]$ vs T can be described by the empirical equation

$$\ln[\eta]_T = [\ln[\eta]_r + k_1(T - T_r')]/[1 - k_2(T - T_r')] \quad (1)$$

where $[\eta]_T$ and $[\eta]_r$ are the intrinsic viscosities at a temperature T and a reference temperature T_r', respectively. The parameters k_1 and k_2 are determined from the intercept and slope of the plot of $(\ln[\eta]_T - \ln[\eta]_r)/(T - T_r')$ vs $\ln[\eta]_T$ (Figure 2, Table 3). Though eq 1 fits the dependences for the present system remarkably well (cf. Figure 1), we do not claim that is also works with other polymer−solvent systems.

By differentiating eq 1 with respect to temperature we obtain the formula

$$(d\ln[\eta]/dT)_T = (k_1 + k_2 \ln[\eta]_r)/[1 - k_2(T - T_r')]^2 \quad (2)$$

which facilitates the estimation of the quotient $d \ln[\eta]/dT$ at various temperatures. With PEMAm in water, this quotient is negative, and its absolute values in-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

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Table 2. Intrinsic Viscosities of PEMAm in Water

	$[\eta]$ (dL/g) at temp (°C)										
sample	5	25	30	35	45	55	60	62.5	65	67.5	70
1	4.08	3.60	3.44	3.26	2.75	1.92	1.71	1.50	1.19	0.93_5	0.67_2
2	1.90	1.63	1.59	1.41	1.25	0.86	0.71	0.66	0.56_5		0.38
3	0.61	0.53_5	0.48		0.38_5	0.35	0.28_5		0.24_5	0.22	0.19_5
4	0.33	0.29_5		0.30	0.24	0.21_5	0.18		0.16_5	0.14_5	0.13_5
5	0.23	0.20_5		0.18_5	0.16	0.14_5	0.13		0.12	0.11_5	0.10_5

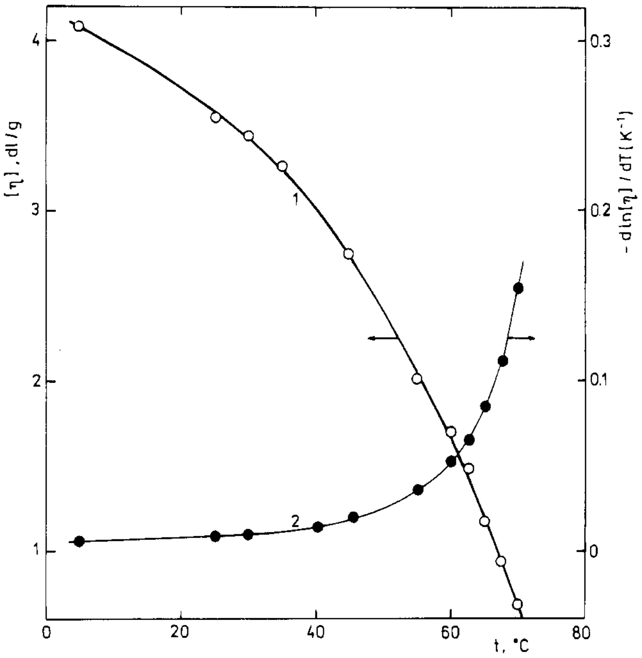

Figure 1. Temperature dependence of the intrinsic viscosity for PEMAm 1 in water. Data points: ○, $[\eta]$; ●, d $\ln[\eta]/\mathrm{d}T$. Curve 1 computed with eq 1 and parameters listed in Table 3. Values of d $\ln[\eta]/\mathrm{d}T$ (curve 2) calculated with eq 2.

Table 3. Parameters of Eq 1 for PEMAm in Aqueous Solutions[a]

sample	$k_1 \times 10^3$	$k_2 \times 10^{-3}$
1	−127	70
2	−41	29
3	−1.0	35
4	25	35
5	6.0	12

[a] Reference temperature: $T_r^{\prime} = 343$ K for samples 1, 3, 4, 5, and $T_r^{\prime} = 340.5$ K for sample 2.

crease with increasing temperature (Figure 2) and molecular weight.

Molecular Weight Dependence of Intrinsic Viscosity. The intrinsic viscosity of polymolecular polymer samples should be correlated with the viscosity average molecular weight $\bar{M}_\eta$ related to $\bar{M}_w$ by the equation

$$\bar{M}_\eta = \bar{M}_w Q_w^{1/a} \tag{3}$$

where a is the exponent of the Mark–Houwink–Kuhn–Sakurada (MHKS) equation

$$[\eta] = K\bar{M}_\eta^a \tag{4}$$

For the Schulz–Zimm distribution function, which we assume to be applicable to our samples, the correction factor[6] is

$$Q_w^{sz} = \Gamma(b + a + 1)/(b + 1)^a\Gamma(b + 1) \tag{5}$$

where

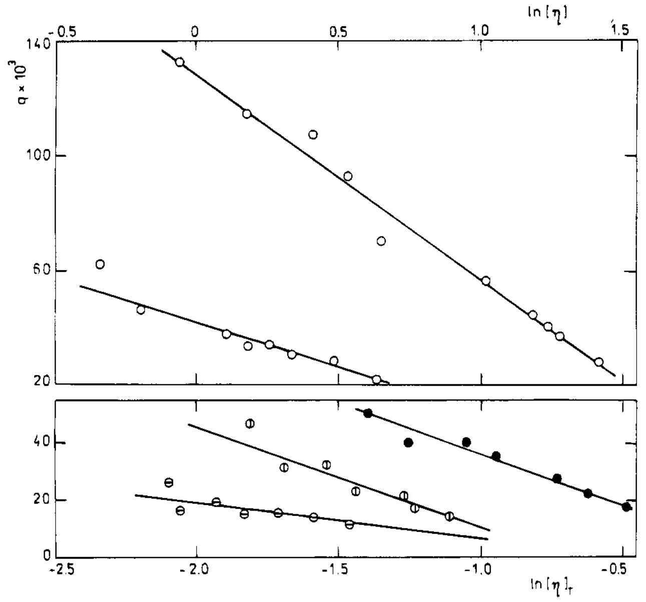

Figure 2. Treatment of the intrinsic viscosity according to eq 1. Data points for PEMAm samples 1–5 (from top to bottom). Reference temperature $T_r^{\prime} = 343$ K (samples 1, 3, 4, and 5) and $T_r^{\prime} = 340.5$ K (sample 2). $q \equiv (\ln[\eta]_T - \ln[\eta]_r)/(T - T_r^{\prime})$.

$$1/b = \bar{M}_w/\bar{M}_n - 1 \tag{6}$$

Before calculating $\bar{M}_\eta$ we plotted logarithmically $[\eta]$ vs $\bar{M}_w$ and estimated approximate values (a') of the exponent a. Then the a' values and the mean values of the polymolecularity index $\bar{M}_w/\bar{M}_n$ were substituted into eqs 5, 6, and 4. With sample 1 the polymolecularity index could not be estimated because the size of a part of the macromolecules was above the exclusion limit of the SEC columns and the number-average molecular weight was too high to be measured by osmometry. When computing the correction factor Q_w^{sz} for this sample we set $\bar{M}_w/\bar{M}_n$ equal to 2. No serious error was probably introduced by this approximation because the correction factors for $\bar{M}_w/\bar{M}_n$, 1.5 and 4, differ by only 2.7% at $a = 0.8$ and by 4.5% at $a = 0.5$.

The parameters of eq 4 were obtained (Table 4) from the logarithmic plots of $[\eta]$ vs $\bar{M}_\eta$ (Figure 3). High values of the exponent at low temperatures, their rapid decrease at higher temperatures, and the concomitant abrupt increase of K are the most remarkable results of this correlation (Figure 4).

From Figure 5, the temperature θ_L^η at which $a = {}^1/_2$ is estimated to be $\theta_L^\eta = 343.5$ K. It is more accurate than the value reported previously[3] ($\theta_L^\eta = 343$ K) and is higher by 3 K than the θ_L^{PE} temperature evaluated from phase equilibria.[3] The latter difference can be explained by assuming the polymer–solvent interaction parameter to depend on concentration.[7]

At temperatures higher than 50 °C, the a values are in the range usually encountered with flexible chain polymers and their variation with temperature can be

Table 4. Parameters of Eq 2 for PEMAm in Aqueous Solutions

t (°C)	*a′*[a]	*a*[b]	*K* × 10⁴ (dL/g)
5	0.82	0.85	0.18
25	0.82	0.83	0.23
35	0.80	0.81	0.24
45	0.81	0.81	0.21
55	0.72	0.72₅	0.51
60	0.72	0.73	0.41
65	0.64	0.65	0.92
70	0.52	0.52	3.17

[a] Correlation of $[\eta]$ vs $\bar{M}_w$. [b] Correlation of $[\eta]$ vs $\bar{M}_\eta$ (Figure 1).

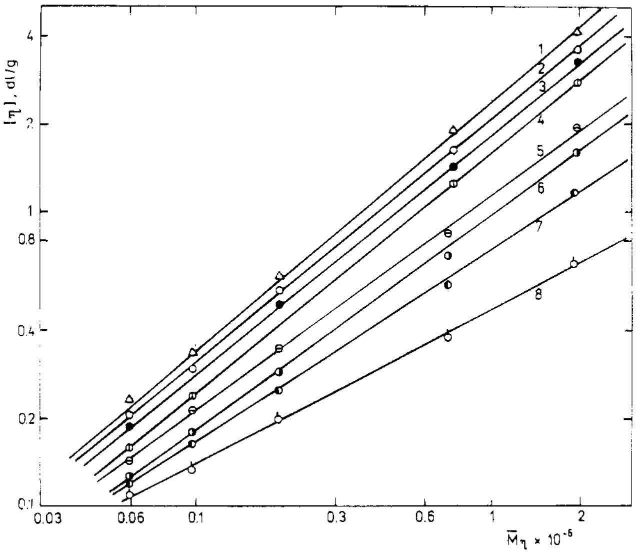

Figure 3. Plot of the intrinsic viscosity $[\eta]$ against the viscosity average molecular weight $\bar{M}_\eta$ for PEMAm in water. Temperatures: 5, 25, 35, 45, 55, 60, 65, and 70 °C (from top to bottom). Lines 1−8 are best-fit lines to experimental data.

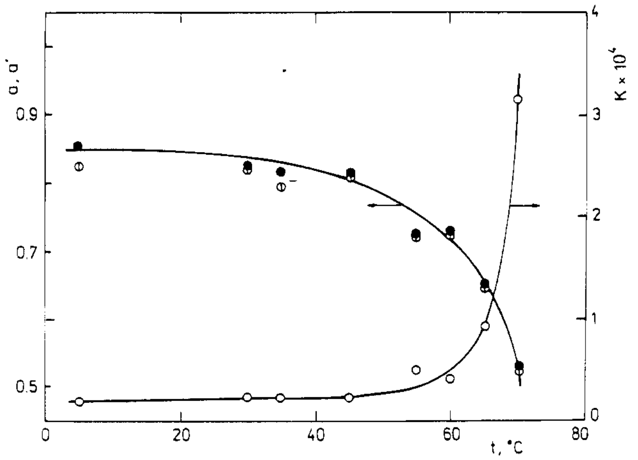

Figure 4. Temperature dependence of the parameters of eq 2. Data points: circle with bar, *a′*; closed circle, *a*; open circle, *K*.

interpreted in terms of the two-parameter theory of polymer solutions.[8,9] On the contrary, the application of the two-parameter scheme to the data for lower temperatures is not legitimate because the *a* values exceed the generally accepted upper limit of the MHKS exponent ($a = 0.8$) for nondraining random coils expanded by the excluded-volume effect.[10,11] They indicate that some factors which are not considered by the two-parameter approach and which are not noticeable with PEMAm at high temperatures are operative at temperatures below 50 °C.

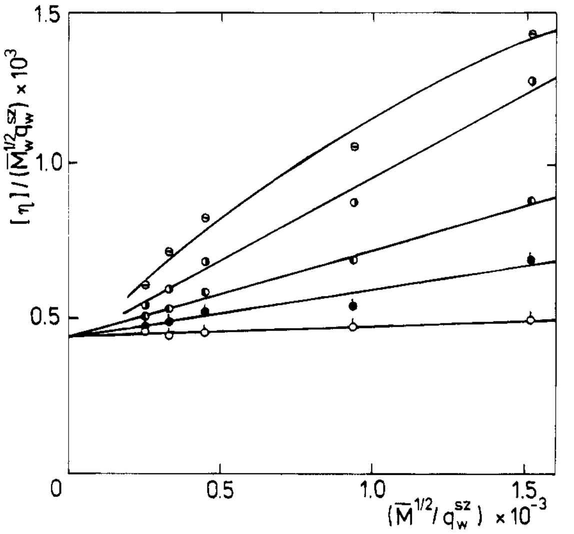

Figure 5. The Burchard−Stockmayer−Fixman plot. PEMAm in water at temperatures 55, 60, 65, 67.5, and 70 °C (from top to bottom).

With respect to these facts, the discussion is divided into two parts. In the former, the intrinsic viscosity data measured at temperatures from 55 °C to $\theta = 70.5$ °C are analyzed in terms of the two-parameter theory. The latter part is a qualitative discussion of the factors that may be responsible for high values of the MHKS exponent at low temperatures.

Analysis of the Intrinsic Viscosity Data. According to the two-parameter theory, the intrinsic viscosity expansion factor α_η^3 (in the nondraining regime) is a universal function of the excluded-volume variable z.[8,9] These quantities are defined by the equations

$$\alpha_\eta^3 = [\eta]/K_0M^{1/2} \tag{7}$$

$$K_0 = \Phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2} \tag{8}$$

$$z = (3/2\pi)^{3/2}(\langle R^2\rangle_0/M)_\infty^{-3/2}BM^{1/2} \tag{9}$$

where $(\langle R^2\rangle_0/M)_\infty$ is the ratio of the unperturbed mean-square end-to-end distance and the molecular weight (in the random coil limit), $\Phi_{0,\infty}$ is the Flory viscosity constant[8] (2.5×10^{21} g^{-1} if $[\eta]$ is expressed in dL/g), and B is the polymer−solvent interaction parameter.

The Burchard−Stockmayer−Fixman method[12,13] (plot of $[\eta]/M^{1/2}$ vs $M^{1/2}$) is based on the equations[8]

$$\alpha_\eta^3 = 1 + C_\eta z \quad \text{for} \quad \alpha_\eta^3 \lesssim 1.6 \tag{10}$$

where $C_\eta = 1.14$, or

$$\alpha_\eta^3 \simeq 1.05 + 0.87z \quad \text{for} \quad \alpha_\eta^3 \lesssim 2.5 \tag{11}$$

To account for the effect of polymolecularity consistently with these equations,[6] we plot $[\eta]/(\bar{M}_w^{1/2}q_w^{sz})$ vs $\bar{M}_w^{1/2}/q_w^{sz}$ (Figure 5) where q_w^{sz} is the correction factor for the Schulz-Zimm distribution function. It differs slightly from the Q_w^{sz} factor used above.

The plots for temperatures from 60 to 70 °C are linear and suitable for the estimation of K_0 and B (from the slope) (Table 5). This is not the case with low temperatures where the values of $[\eta]/(\bar{M}_w^{1/2}q_w^{sz})$ exceed many

Table 5. Interaction Parameters of PEMAm and Water[a]

temp (°C)	$B \times 10^{27}$	$\beta \times 10^{24}$ (cm^3)	χ
60	0.65	8.2	0.493
65	0.40	5.0	0.496
67.5	0.19	2.5	0.498
70	0.04	0.5	0.499

[a] The values of B were estimated from the slopes of plots in Figure 5.

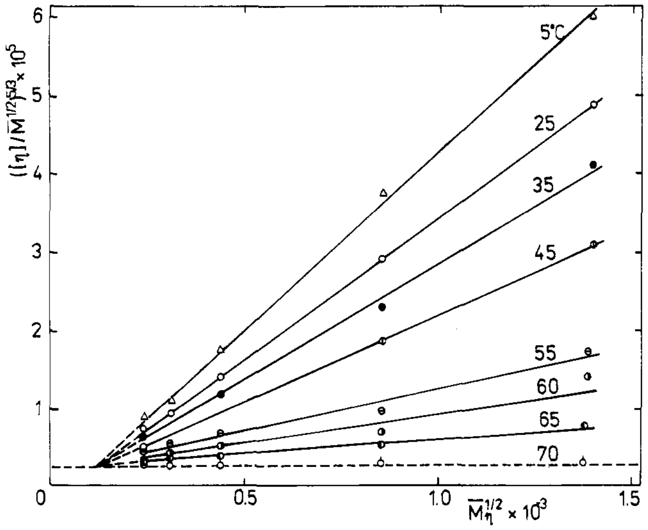

Figure 6. The Tanaka plot. PEMAm in water at temperatures (°C) as noted. Dashed line for θ_L^η, 70.5 °C.

times the value of 2.5 K_0 (cf. eq 11) and the plots (not shown in Figure 5) are curved.

A few years ago, Tanaka[12] derived the equations

$$\alpha_\eta^5 = 1 + C'_\eta z \tag{12}$$

and

$$([\eta]/M^{1/2})^{5/3} = K_0^{5/3} + 0.627\Phi_{0,\infty}^{5/3}(\langle R^2\rangle_0/M)_\infty BM^{1/2} \tag{13}$$

with $C'_\eta = 1.90$ and showed that they fitted the viscosity data for systems where the viscosity expansion factors α_η^3 were high.

In Figure 6, data for PEMAm in water are plotted as $([\eta]/\bar{M}_\eta^{1/2})^{5/3}$ vs $\bar{M}_\eta^{1/2}$. The viscosity average molecular weight $\bar{M}_\eta$ is used to correct data for the effect of polymolecularity. This correction is not fully consistent with eq 13, still, it is sufficiently accurate for the present purpose. The plots are linear at all temperatures. However, contrary to expectation, the straight lines for low temperatures cross the horizontal line corresponding to Θ conditions at a finite molecular weight ($\sim 10^4$), and the intercepts of some of them are close to zero or even negative. This finding indicates that the effect of factors, which are responsible for high values of the MHKS exponent found at these temperatures, is strong especially at low molecular weights. Among them may be the strength of hydrodynamic interaction and chain stiffness.

The hydrodynamic behavior of PEMAm under Θ conditions is similar to that of other flexible chain polymers with no indication of partial draining of solvent. This may, however, be due to rather high molecular weights of samples ($M > 60 \times 10^3$) and does not preclude the possibility that weaker hydrodynamic interaction exists at low molecular weights. Moreover, since the intramolecular distances of chain units are increased as the chains are expanded in good solvents, the hydrodynamic interaction may become weaker than under Θ conditions.[15] Therefore, the intrinsic viscosity may be decreased below the value corresponding to the nondraining limit and this effect may persist to higher molecular weights than in Θ solvent.

The stiffness of polymer chains is known to affect the onset of the excluded-volume effect on chain dimensions. This problem has theoretically been investigated by Yamakawa and Stockmayer[16] and Yamakawa and Shimada.[17,18] These authors have found that the numerical factor $K(n_K)$ in the equation relating the expansion factor of the mean-square end-to-end distance α_R^2 to the parameter z

$$\alpha_R^2 \equiv \langle R^2\rangle/\langle R^2\rangle_0 = 1 + K(n_K)z + ... \tag{14}$$

is a function of the number n_K of the Kuhn statistical segments. It is zero at $n_K \rightarrow 1$ and approaches the limit ($K(\infty) = 4/3$) at rather high n_K. It is probable that the coefficients C_η and C'_η is eqs 10 and 12 depend on the chain length in a similar manner. Then, the intrinsic viscosity at low molecular weights is close to the value for Θ conditions.

These factors may combine to raise the MHKS exponent. Taking these effects into account, Yamakawa et al.[16-19] devised methods to treat the experimental data of $[\eta]$. However, to resolve these effects, more experimental results are needed, such as the intrinsic viscosities in the low molecular weight range, radii of gyration, and second virial coefficients. Unfortunately, none of them could be obtained with PEMAm in water with a precision which is necessary for this purpose.

Conformational Parameters of PEMAm. The characteristic ratio C_∞ and the Kuhn segment length λ^{-1} are the fundamental conformational characteristics of polymer chains. The former is defined[20] as the ratio of the mean-square end-to-end distance of the real chain and the freely jointed one (in the random coil limit). The values of C_∞ and λ^{-1} are calculated by means of the equations

$$C_\infty = (\langle R^2\rangle_0/M)_\infty M_0/(2l^2) \tag{15}$$

$$\lambda^{-1} = (\langle R^2\rangle_0/M)_\infty M_L \tag{16}$$

$$M_L = M_0/l_m \tag{17}$$

where M_0 is the molecular weight of the monomeric unit ($M_0 = 113$), l is the length of the backbone C−C bond ($l = 1.53 \times 10^{-8}$ cm),[20] M_L is the molecular weight per unit contour length of a fully extended chain in an all-trans conformation, and l_m is the length of the projection of the monomeric unit on the contour length ($l_m = 2.5 \times 10^{-8}$ cm).[20]

The following values of the conformational parameters are obtained at 70.5 °C: $K_0 = 0.43 \times 10^{-3}$ (dL/g), $(\langle R^2\rangle_0/M)_\infty = 0.30 \times 10^{-16}$ cm, $C_\infty = 7.2$, and $\lambda^{-1} = 13.6 \times 10^{-8}$ cm. The characteristic ratio for poly(methacrylamide) ($C_\infty = 6.0$)[21] is lower whereas the value for poly(N-butylmethacrylamide)[22] is distinctly higher ($C_\infty = 9.9$).

Interaction Parameters of PEMAm and Water. The interaction of polymers with solvents can be characterized[8] by the parameter B in eq 9, by the binary cluster integral β defined by

$$\beta = BM_0^2 \tag{18}$$

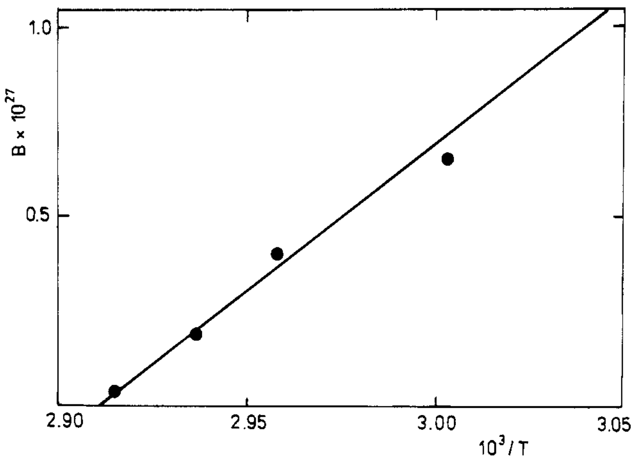

Figure 7. Interaction parameter B plotted against $1/T$. Data points estimated from the slopes of plots in Figure 7 (●) and from the intercepts of plots in Figure 5.

or by the Flory–Huggins interaction χ parameter related to B by the equation

$$B = (2/N_A)[(\bar{v}_2^0)^2/V_1]\left(\frac{1}{2} - \chi\right) \qquad (19)$$

The χ parameter can be resolved into the entropy of dilution and enthalpy of dilution parameters, ψ and κ, respectively,

$$\frac{1}{2} - \chi = \psi - \kappa \qquad (20)$$

The ψ parameter is a sum of the combinatorial term ($^1/_2$) and a noncombinatorial contribution referred to as the reduced residual partial molar entropy.[23]

The B values (Table 5) for PEMAm in water were computed from the slopes of plots in Figure 7 (at 60–70 °C) by means of eq 10. They were converted to χ by means of eq 19. The temperature dependence of $(\langle R^2\rangle_0/M)_\infty$ was not taken into account.

The binary cluster integral β can be thought of as an effective covolume for a pair of chain units immersed into the solvent.[8] Reported β values for nonpolar polymer systems do not exceed 40×10^{-24} cm^3. The values for PEMAm in water are of this order of magnitude at temperatures above 60 °C. At lower temperatures, they are probably higher and illustrate the surprisingly strong solvent power of water for this polymer.

In Figure 7, the values of B at 60–70 °C are plotted against $1/T$. The plot is fitted by a straight line. That indicates that the well-known equation

$$\frac{1}{2} - \chi = \psi(1 - \theta_L^\eta/T) \qquad (21)$$

with constant ψ provides a good approximation to the $\chi(T)$ dependence in this temperature range.

The ψ parameter ($\psi = -0.235$) is estimated from the slope of the plot in Figure 7 and the κ values are calculated as

$$\kappa = \psi\theta_L^\eta/T \qquad (22)$$

Both parameters are negative. Negative ψ implies strongly negative reduced residual partial molar entropy, showing that dilution is associated with a decrease in entropy opposing dilution. On the contrary, negative κ promotes dilution. As the temperature is increased, κ decreases and becomes equal to ψ at θ_L^η. At higher temperatures, the entropy term would prevail and induce coiling of polymer chains into compact particles and phase separation.

Comparison of Interaction Parameters for PEMAm and PMAm. It seems worthwhile comparing the interaction parameters for PEMAm with those for aqueous solutions of poly(methacrylamide) (PMAm):

(i) There is contradictory information on the solubility of PMAm in water. Some authors reported on insolubility[24] or limited solubility.[25] Silberberg et al.[26] estimated the θ temperature (UCST type) to be $\theta_u = 279$ K from the temperature dependence of the second virial coefficient of a sample with $M_w = 320 \times 10^3$. However, a negative value of A_2 was found later by Eliassaf[27] at 303 K, i.e., 24 K above the Silberberg θ_u value, for $M_w = 78 \times 10^3$. Solubility experiments carried out by Titkova et al.[21] indicated θ_u to be higher than 100 °C.

(ii) The second virial coefficient as well as the intrinsic viscosity were found to increase with increasing temperature. The κ parameter was positive though low ($\kappa T = 1.62$ K) and so was the ψ parameter ($\psi = 0.58 \times 10^{-2}$).[26]

(iii) In a more recent paper,[21] the χ, ψ, and κ values were assessed by extrapolation to pure water of the data for solutions in aqueous solutions of urea or magnesium perchlorate at 25 °C. While the extrapolation was fair with χ and κ, leading to $\chi > {}^1/_2$ and $\kappa > 0$, it was very uncertain with ψ, yielding a value close to zero.

In spite of being in poor quantitative correspondence, the results of these papers consistently show that the system PMAm–water has an UCST and is slightly endothermic. In terms of Rowlinson's and Franks' nomenclature,[28] it is a "nonaqueous" system. On the contrary, the behavior of PEMAm in water is typically "aqueous" ($\kappa < 0$, $\psi < 0$, LCST).

The latter type of behavior is currently ascribed to the "hydrophobic interaction" of water and solute, involving association of hydrophobic groups in contact with water and a concomitant enhancement of the supramolecular structure of water in the vicinity of these groups.[28] Though the hydrophobic interaction is a relevant contribution to the overall interaction in the present system because ethyl groups render PEMAm more hydrophobic than PMAm, other types of interaction cannot be neglected because they also may depend on the structure of the solute. Some of them which exist already in pure state of both components (e.g., hydrogen bonding between the amide groups of the polymer and between water molecules in pure water) are destroyed by mixing. The corresponding contributions to enthalpy and entropy of dilution will be positive. In mixtures, hydrogen bonds form between water molecules and CONH groups. The corresponding contribution to κ will be negative, and the accompanying orientation of water molecules will bring about a decrease in entropy.

The interaction parameters estimated from solution properties are sums of contributions due to different types of interaction. It is actually impossible to assess the weight of the individual types.

Concluding Remarks. Poly(*N*-ethylmethacrylamide) appears to be an attractive substance for studying the interaction of water with polymers containing hydrophilic and hydrophobic groups. A study along similar lines of other *N*-alkyl derivatives of poly(methacrylamide) is in progress in this laboratory. We are aware that the analysis of the intrinsic viscosity cannot provide more than global information. Anyway, it may initiate further investigation by other methods that are more appropriate for the elucidation of the details of this interaction.

Acknowledgment. The authors thank Dr. A. Sikora for making available his unpublished volumetric results and acknowledge with gratitude the technical cooperation of Mrs. J. Škochová, D. Švábová, and L. Žižková.

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MA946405J