Solution Thermodynamics of Poly(ethylene glycol)/Water Systems

Cemile Özdemir, Ali Güner

Division of Polymer Chemistry, Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, TR-06532 Ankara, Turkey

ABSTRACT: The unperturbed molecular dimensions of poly(ethylene glycol) (PEG) samples (of different molecular weights) have been evaluated in aqueous solutions from viscosity measurements at 25, 30, 35, and 40°C. The unperturbed dimension, K_θ, has been determined from extrapolation methods, i.e., Kurata–Stockmayer–Fixman (KSF), Inagaki–Suzuki–Kurata (ISK), and Berry equations. The hydrodynamic expansion factor, α_η, as well as the unperturbed root-mean-square end-to-end distance, $\langle r^2 \rangle_0^{1/2}$, found for the system indicated that the polymer coils contract as the temperature is raised from 25 to 40°C. The long-range interaction (excluded volume) parameter, B, was also evaluated and a significant decrease was found for the PEG/water system between 25 and 40°C. The theta temperatures, θ, were obtained from the temperature dependence of $(1/2 - \chi)$ and the second virial coefficient was detected in the temperature interval of 25–40°C for the system and quite a good agreement with the calculated values evaluated via extrapolation and interpolation methods was observed. The thermodynamic interaction parameter χ was evaluated through the sum of the individual values of enthalpy and entropy dilution parameters, χ_H and χ_S, for PEG samples. All the unperturbed molecular dimensions of PEG/water system were calculated and compared according to M_w and M_n values of PEG samples. Calculated values were interpreted mainly on the basis of hydrogen-bond formation between polymer segments and PEG-water molecules in solution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 203–216, 2006

Key words: poly(ethylene glycol); water; solution thermodynamics; extrapolation methods; interpolation methods

INTRODUCTION

The unique properties of poly(ethylene glycol) (PEG), including a wide range of solubility, lack of toxicity, absence of antigenicity and immunogenicity, noninterference with enzymatic activities, and conformations of polypeptides and ease of excretion, make them ideal drug carriers.[1,2] The two-hydroxyl end groups of PEG have been suitably functionalized prior to coupling[3] with ligands of biological relevance, although the hydroxyl groups themselves have been used as well.[4–7] Because the number of terminal groups of PEGs (only two) to attach with drugs limits their drug loading capacity, extensive work has been done to functionalize them by copolymerizing PEGs with various functional monomers.[8] PEG is highly water soluble and has a good structural fit with the water molecules, which assures strong hydrogen bonding between the ether oxygen atom of PEG and hydrogen atoms of the water molecules. The decreased solubility of PEG in water at elevated temperatures is also related to the hydrogen bonding; higher temperatures result in decreased hydrogen bonding and an increase of hydrophobic interactions between the macromolecular chains.[9]

Polymer dissolution in solvents is an important area of interest in polymer science and engineering because of its wide applications in industry, such as microlithography, membrane science, plastics recycling, and drug delivery. Unlike nonpolymeric materials, polymers do not dissolve instantaneously, and the dissolution is controlled by either the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer–solvent interface.[10] The dissolution of a polymer into a solvent involves two transport processes, namely solvent diffusion and chain disentanglement. When an uncrosslinked, amorphous, glassy polymer is in contact with a thermodynamically compatible solvent, the solvent will diffuse into the polymer. Because of plasticization of the polymer by the solvent, a gel-like swollen layer is formed along with two separate interfaces, one between the glassy polymer and gel layer and the solvent. After an induction time has passed, the polymer dissolves. However, there also exist cases where a polymer cracks and no gel layer is formed.[10] The solubility in water and the simple structure make it a good model system for the study of the interaction mechanisms of water with hydrophilic surfaces and

Correspondence to: C. Özdemir (cemileoz@hacettepe.edu.tr or cemile_ozdemir@yahoo.com).

biopolymers (e.g., in water, PEO assumes a helix conformation, as DNA does).[11]

Knowledge of solution thermodynamics is critically important in determining the suitability of a solvent for a molecular weight determination. Once having decided on a suitable solvent, solution thermodynamics provides a basis for determining how an extrapolation to zero concentration is to be carried out. Below the Flory θ-temperature, polymer solutions may phase separate. The higher the molecular weight is, the higher the upper critical solution temperature. At infinite molecular weight, the Flory θ-temperature is reached.

This work has contributed to the solution thermodynamic and in understanding dissolution behavior in PEG/water system by viscometric measurements. The aim of this work was to study the thermodynamic aspect of PEG/water system, to determine the unperturbed dimensions, hydrodynamic expansion, gyration radius, and long-range interaction behavior of the polymer in the employed solvent between 25 and 40°C by intrinsic viscosity measurements. This article describes finally the theta temperature of the polymer found by different ways in water. Besides, in this report, the evaluation of the enthalpy and entropy dilution parameters of the system, employing thermodynamic interaction parameter, were aimed. All of the unperturbed molecular dimensions were calculated according to both $\bar{M}_w$ and $\bar{M}_n$ and compared via extrapolation procedures. Thus, the evaluated results were obtained according to both average molecular weight values.

EXPERIMENTAL

PEG samples used in this study were obtained from Aldrich. The molecular weight characteristics of polymer samples were determined by Aldrich, and the number–average molecular weights of PEG 2000, PEG 4600, PEG 8000, and PEG 10,000 are given as 1289, 3539, 7018, and 5366 g mol^{-1}, respectively. The weight–average molecular weights are given as 1726, 4600, 8000, and 10,636 g mol^{-1}, respectively. The water used as solvent was deionized and bidistilled. Solutions were prepared by mass, using an analytical balance with ±0.1 mg accuracy.

Viscosity measurements were carried out at 25, 30, 35, and 40°C with negligible kinetic energy corrections, with an Ubbelohde type of capillary viscometer. The temperature of thermostat was controlled within a range of ±0.1°C, and the flow times were measured with a digital accuracy of ±0.01 s. The concentration dependence of the viscosity results of dilute polymer solutions (in a 2.5–1.0 g dL^{-1} concentration range) was followed by the well-known Huggins equation. Duplicate measurements, made on fresh portions of the solutions, agreed within 0.1 s. The average elution

TABLE I
Measured Specific Volumes of Aqueous Solutions of PEG's in 1 g/dL and Various Temperatures

T (°C)	PEG 2000	PEG 4600	PEG 8000	PEG 10,000
25	1.0016	1.0006	1.0013	1.0026
30	1.0029	1.0022	1.0023	1.0038
35	1.0046	1.0042	1.0040	1.0047
40	1.0063	1.0065	1.0067	1.0072

times of solutions were determined after several measurements. In the molecular weight range investigated, shear rate effects were assumed to be negligible.

The density measurements were carried out using a 10-cm^3 glass pycnometer. Densities of the polymer solutions were determined in water using a pycnometer at 25, 30, 35, and 40°C. A constant temperature water bath was used to control the temperature at accuracy of ±0.1 K. The reproducibility of density measurements was estimated to be ± 0.02 g cm^{-3}. The concentrations of the solutions were the same as those for viscosity studies. The specific volumes are obtained by calculating reciprocal of densities. The specific volumes of solutions are listed in Table I.

RESULTS AND DISCUSSION

It is commonly known that the unperturbed dimension parameter depends only on the interactions between the polymer segments, but is completely independent of the molecular weight of the polymer, temperature, and solvent. This thermodynamic quantity can be obtained by intrinsic viscosities, [η], according to the extrapolation methods. The unperturbed molecular dimensions of dextran/water,[9] dextran/DMSO,[12] dextran/ethylene glycol,[13] dextran/methoxy ethylene glycol[14] systems, as well as the long-range interaction parameter, were successfully determined previously. A few studies have been achieved on the thermodynamic aspects of the polymer chain in solution.[14,15]

Figure 1 shows the experimental data and the fit curves resulting from linear regression. As shown in Figure 1, solution intrinsic viscosity decreases as temperature increases. The unperturbed dimension parameter, K_θ, is independent of temperature, molecular weight of the polymer, and solvent. It measures only the short-range interactions of the polymer segments, and can be determined by various techniques. One of the basic techniques to receive information on unperturbed dimensions has been found from extrapolation methods starting from viscosity measurements, namely, the Kurata–Stockmayer–Fixman (KSF)[16] equation employed in the present study,

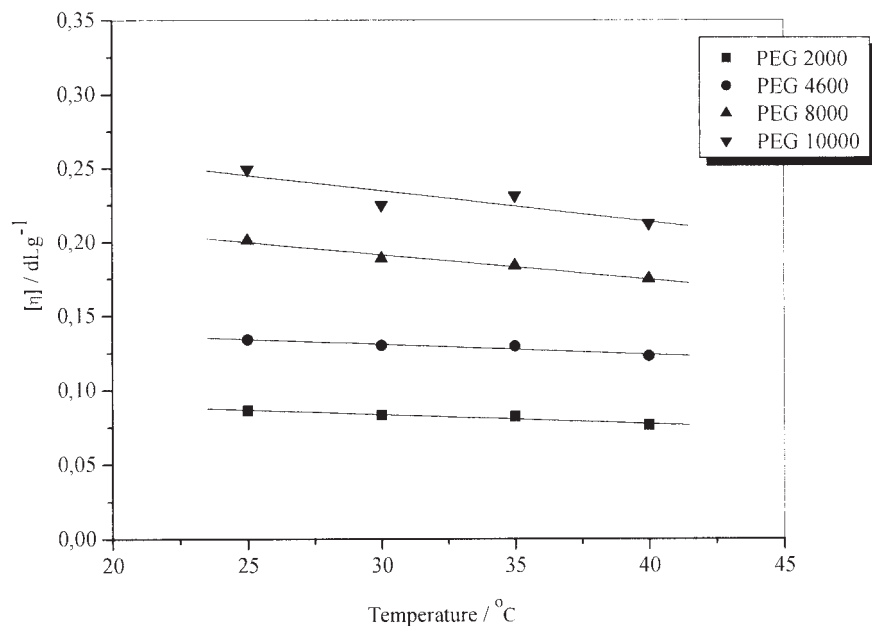$$[\eta]\bar{M}^{-1/2} = K_\theta + 0.51B\phi_0\bar{M}^{1/2} \qquad (1)$$

Figure 1 Dependence of intrinsic viscosity on the temperature for the PEG samples in the water.

and the relationship between K_θ and $\langle r^2 \rangle_0$ is given by

$$K_\theta = [\eta]_\theta \bar{M}^{-1/2} = \phi_0(\langle r^2 \rangle_0 / \bar{M})^{3/2} \qquad (2)$$

where, $[\eta]$ is the intrinsic viscosity, $\bar{M}$ is the average molecular weight of the polymer (separately number–average and weight–average molecular weight; $\bar{M}_n$ and $\bar{M}_w$). K_θ is the conformational parameter related to the unperturbed dimension by eq. (2). B is the parameter for long-range (polymer–solvent) interactions, $[\eta]_\theta$ is the intrinsic viscosity at theta temperature, ϕ_0 is Flory constant (in this study, the value of 2.1×10^{23} was used) and finally, $\langle r^2 \rangle_0^{1/2}$ represents the root-mean-square end-to-end distance of unperturbed polymer chain.

The Berry equation[17]

$$[\eta]^{1/2}\bar{M}^{-1/4} = K_\theta^{1/2} + 0.42 K_\theta^{1/2} B \phi_0 \bar{M}[\eta]^{-1} \qquad (3)$$

and the Inagaki–Suzuki–Kurata (ISK) equation[18]

$$[\eta]^{4/5}\bar{M}^{-2/5} = 0.786 K_\theta^{4/5} + 0.454 K_\theta^{2/5} B^{2/3} \phi_0^{2/3} \bar{M}^{1/3} \qquad (4)$$

have been used for the determination of short- and long-range interaction parameters for the PEG/water system.

By the use of these equations, the plots of $[\eta]\bar{M}^{-1/2}$ against $\bar{M}^{1/2}$, $[\eta]^{1/2}\bar{M}^{-1/4}$ against $\bar{M}[\eta]^{-1}$, and $[\eta]^{4/5}\bar{M}^{-2/5}$ against $\bar{M}^{1/3}$ yielded straight lines with high correlation, the intercept being K_θ and the slope characterizing the polymer–solvent interactions was determined by linear regression analysis as shown in Figures 2-7, respectively. Calculated short- and long-

range interaction parameters are assembled in Tables II and III. These values agree quite well with that determined by Beech and Booth[19] by application of eq. (1) to data obtained for solutions of poly(ethylene oxide) of molecular weight in the range between 5×10^4–10^6 in several poor solvents and acetone.

The K_θ values evaluated from KSF, ISK, and Berry are in high accordance with each other, and an increase at increasing temperature is quite obvious with all these extrapolation techniques as well as the observation for the long-range interaction parameter–temperature behavior. However, the B values are not in conformity with each other. Data in the literature[8,19–23] indicate that K_θ for PEO varies over a wide range, even for θ solvent systems at the same temperature.[21] At this point, it would be better to discuss the interactions between the polymer segments and polymer–solvent molecules. According to the concept of the theta condition, the unperturbed dimension parameter, K_θ, should be independent of the nature of solvent, temperature, and molecular weight of the polymer. However, the K_θ values obtained from extrapolation techniques were in increasing trend with increasing temperature. Considering the structure of PEG, it is strongly expected that hydrogen bonding will form between polymer segments, and obviously these bonds will not break at an increased temperature, which can be related to low critical solution temperature systems.

B is thermodynamic parameter related to the solvent–polymer interaction parameter. Corresponding to the structure of PEG, it is strongly expected that molecular association/interaction will form between
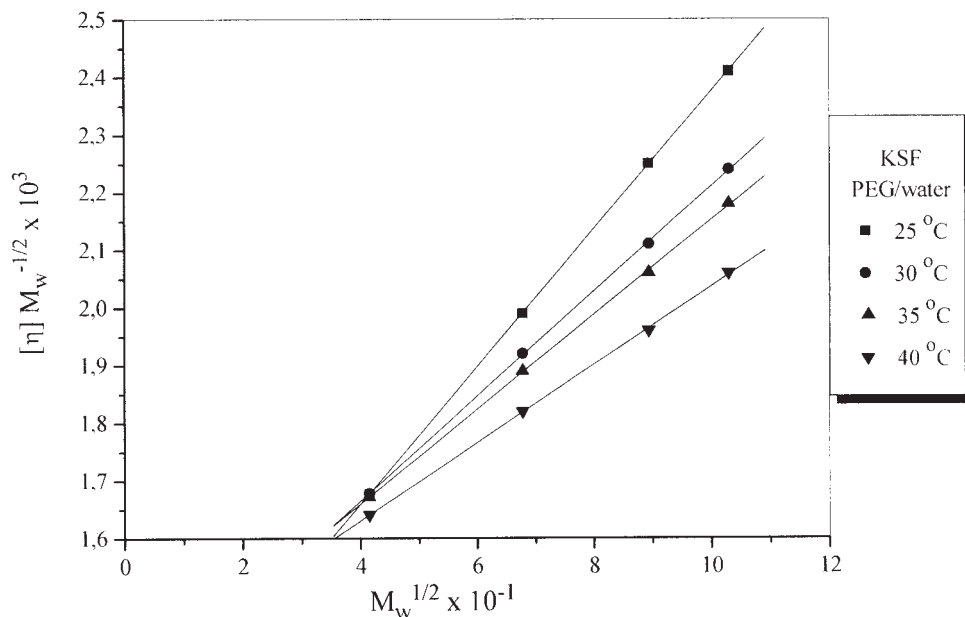
Figure 2 KSF plot for the PEG/water system (calculated according to $\bar{M}_w$).

the polymer segments and solvent molecules through hydrogen bonding. Naturally, increase in K_θ values in terms of temperature increment results in the non-breakage of polymer–solvent association, i.e., hydrogen bonds between polymer and water molecules as well as the strong interactions between the polymer segments.

The temperature dependence of long-range interaction parameters is given by[24]

$$B = B_0(1 - \theta/T) \qquad (5)$$

where B_0 is a constant (independent of temperature) and θ is the theta temperature of the polymer–solvent pair.

The plots of B obtained from extrapolation methods versus the reciprocal of the temperature according to eq. (5) resulted in straight lines (Figs. 8 and 9), where the slope yielded the theta temperature of the studied system.

Determination of the reliable theta temperature of a studied polymer–solvent system has a great physico-chemical importance for polymer solutions thermody-
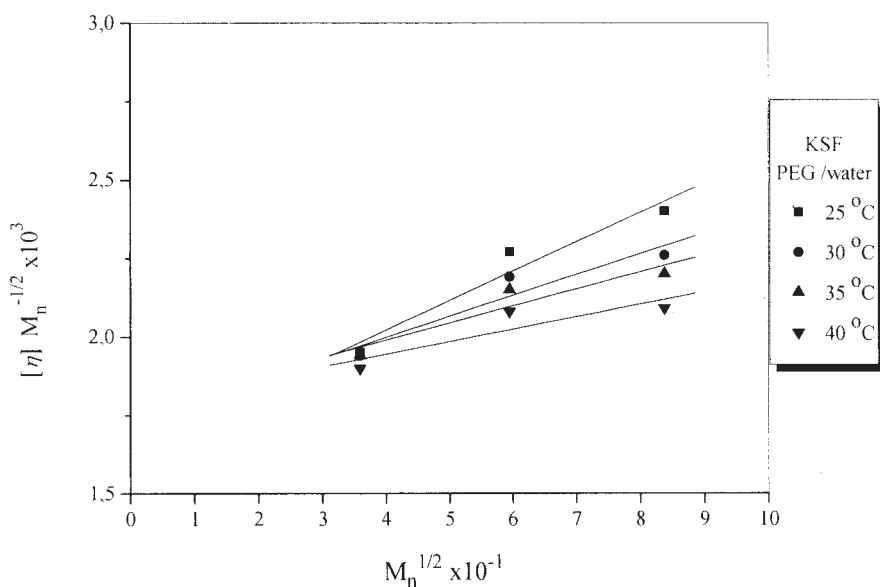

Figure 3 KSF plot for the PEG/water system (calculated according to $\bar{M}_n$).
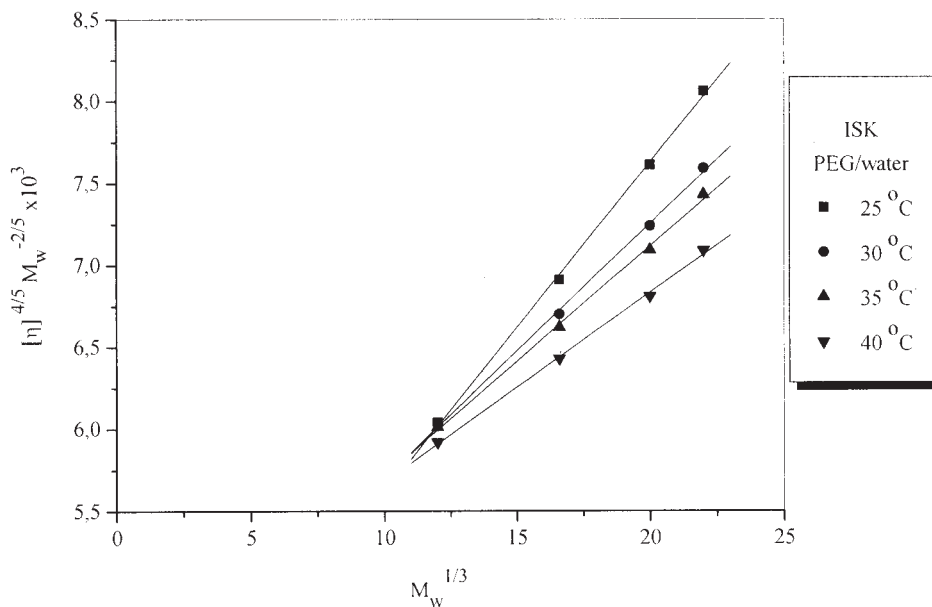
Figure 4 ISK plot for the PEG/water system (calculated according to $\bar{M}_w$).

namically. To obtain more accurate/reliable values of theta temperatures, Flory interaction parameter–temperature and second virial coefficient–temperature relationships were also determined individually for PEG/water system.

It is also possible to follow the effect of temperature on different hydrodynamic magnitudes, such as root-mean-square end-to-end distance of the polymer at unperturbed state according to eq. (2), by determination of the intrinsic viscosity at the theta temperature, and the hydrodynamic expansion factor, α_η, of the polymer is simply given below,

$$\alpha_\eta^3 = [\eta]_T / [\eta]_0 \tag{6}$$

where $[\eta]_T$ is the intrinsic viscosity of the solution at different temperatures.

The magnitudes $[\eta]$, α_η, and $\langle r^2 \rangle_0$ (Tables IV and V) are the measures of the hydrodynamic interactions and the hydrodynamic expansion/contraction of the polymer in solution, respectively. 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, $(1/2 - \chi)$, and θ in eq. (8) are independent of M for high molecular weight polymers of ordinary inter-
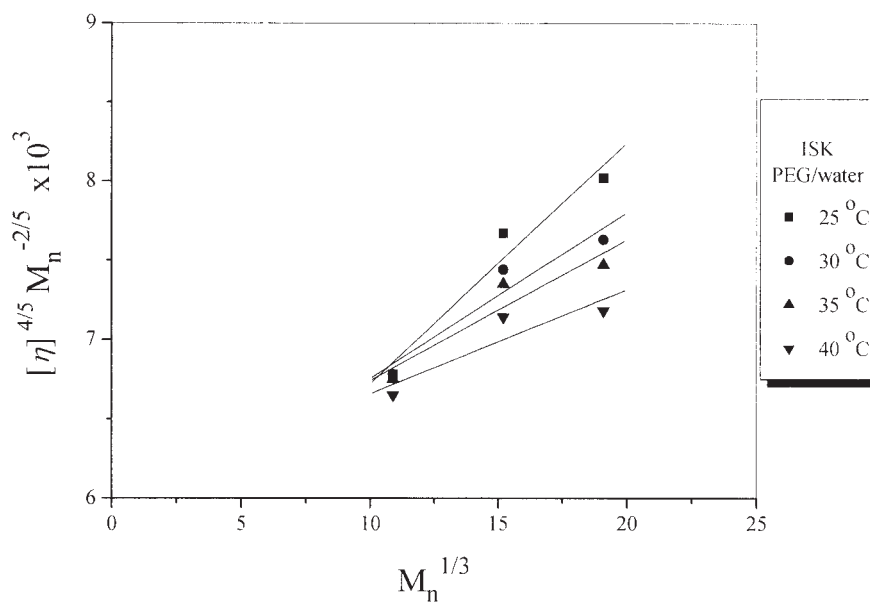

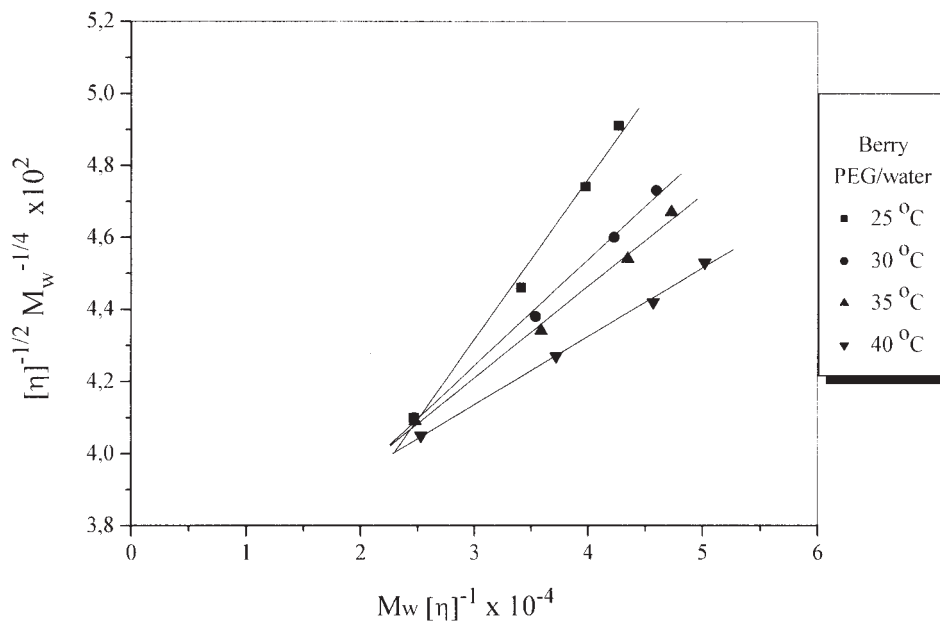**Figure 5** ISK plot for the PEG/water system (calculated according to $\bar{M}_n$).

Figure 6 Berry plot for the PEG/water system (calculated according to $\bar{M}_w$).

est.[24] Therefore, it follows that α_η increases slowly with molecular weight. The decrease of α_η with increasing temperature (Tables IV and V), therefore, indicates that the solvent power of water for PEG decreases as the temperature is raised from 25°C. It is clearly seen that in the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion of the coil are in a decrement trend by temperature increment. Of course, this significant change mainly shows the effect of tempera-

ture on the interactions between the polymer and solvent molecules in solution.

The relation between hydrodynamic linear expansion factor, α, and α_η is given by Kurata and Yamakawa[25]

$$\alpha_\eta^3 = \alpha^{2.43} \tag{7}$$

The thermodynamic linear expansion factor has been related to Flory interaction parameter, χ, through the Flory–Fox[26] equation,
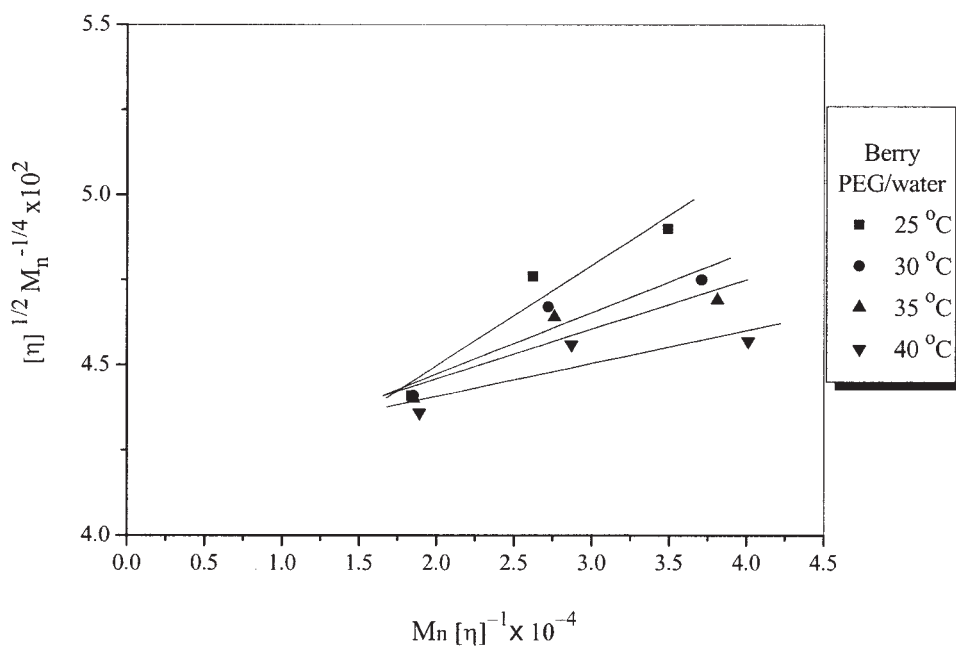

Figure 7 Berry plot for the PEG/water system (calculated according to $\bar{M}_n$).

TABLE II
The Short-K_θ and Long-B Parameters of PEG/Water According to $\bar{M}_w$

Temperature (°C)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)
25	11.9	11.0	11.9	797	8.88	1692
30	13.0	8.46	14.2	487	11.3	992
35	13.3	7.65	14.9	407	11.9	835
40	13.6	6.34	15.8	293	12.7	602

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)\bar{M}^{1/2} \qquad (8)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_s)(1 - \theta/T)\bar{M}^{1/2} \qquad (9)$$

The coefficient C_M is given by,

$$C_M = 27v_2^2\bar{M}^{3/2}/[2NV_t(2\pi\langle r^2\rangle_0)^{3/2}] \qquad (10)$$

where v_2 is the specific volume of the polymer, N is the Avogadro's number, and V_S is the molar volume of the solvent (for water, 18 mL mol^{-1}).

α depends on the factor $((1/2) - \chi_S)(1 - \theta/T)$ in eq. (9), measuring the intensity of the thermodynamic interactions and also representing the power of the solvent. The coefficient C_M seems to be less dependent on temperature, since eq. (10) contains no temperature terms; however, the parameter C_M involves the unperturbed dimension end-to-end distance, $\langle r^2\rangle_0$, which depends on temperature through the effective bond character of the chain. Consequently, C_M is indirectly governed by the temperature through $\langle r^2\rangle_0$ term present in eq. (10). So, the temperature dependence of α is much more governed by this factor, whereas temperature dependence of C_M is not. The decrease of α with increasing temperature, for different molecular weights of sample, therefore indicates that the solvent power of water for PEG decreases as the temperature is raised from 25 to 40°C.

The polymer–solvent interaction parameter, χ, introduced by Flory was only intended to account for the enthalpic contributions during mixing. Through ex-perimentation, however, Flory discovered that χ is the sum of χ_H and χ_S, which are the excess enthalpy and excess entropy of dilution parameters. Thus, the χ parameter characterizes the overall interaction of a polymer segment with solvent molecules. Presently, it is common practice to express χ as the sum of an enthalpic and an entropic contribution:

$$\chi = \chi_S + (\chi_H/T) \qquad (11)$$

χ_h and χ_s are considered as constants that depend on the polymer and solvent but are independent of the fluid temperature, T, and polymer average molecular weight, M. Recent findings have shown that χ_s is correlated with χ_h and the polymer–solvent theta temperature, θ.[27]

$$\chi_s = (1/2) - (\chi_H/\theta) \qquad (12)$$

Thus, the experience of χ on the temperature can be expressed as the sum of enthalpic, χ_H/T, and entropic, $\chi_S = (1/2) - (\chi_H/\theta)$, contributions:

$$\chi = 1/2 - \chi_H[(1/\theta) - (1/T)] \qquad (13)$$

On the basis of Flory's work, Stockmayer and Fixman[28] developed an intrinsic viscosity relationship for high molecular weight flexible-chain polymers, neglecting solvent draining effects:

$$[\eta] = K_\theta\sqrt{\bar{M}} + \frac{0.51\phi_\theta\bar{M}}{N_AV_s\rho_p^2}(1 - 2\chi) \qquad (14)$$

TABLE III
The Short-K_θ and Long-B Parameters of PEG/Water According to $\bar{M}_n$

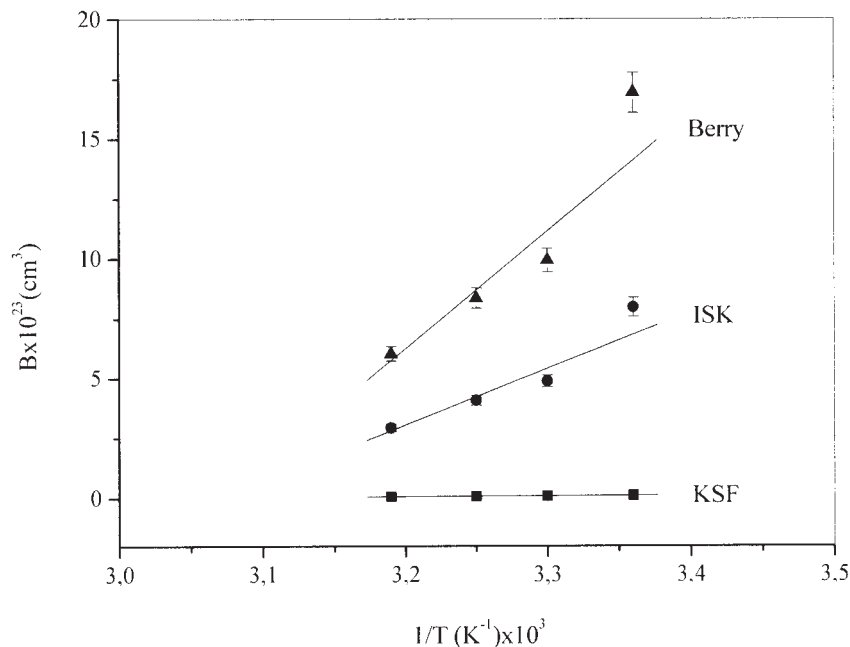| Temperature (°C)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)	$K_\theta \times 10^4$ (dL g^{-1})	$B \times 10^{25}$ (cm^3)
25	16.5	8.75	18.9	398	15.3	854
30	17.3	6.22	21.2	211	16.9	498
35	17.7	5.05	21.9	162	17.4	395
40	17.9	3.69	22.6	101	17.8	260

Figure 8 Plot of the interaction parameter B (KSF, ISK, and Berry) as a function of the reciprocal of the absolute temperature, according to $\bar{M}_w$.

In eq. (14), K_θ is the Mark–Houwink–Sakurada K value at the theta temperature, $\bar{M}$ is the weight–average polymer molecular weight, χ is the polymer–solvent interaction parameter, V_s is the solvent molar volume, ρ_p is the polymer density, ϕ_θ is the Flory constant 2.8 $\times$ 10^{23}, and N_A is Avogadro's number.

Use of the expression for χ in eq. (14) gives

$$[\eta] = K_\theta \sqrt{\bar{M}} + \frac{1.02\phi_\theta \bar{M}\chi_h}{N_A V_s \rho_p^2}\left(\frac{1}{\theta} - \frac{1}{T}\right) \qquad (15)$$

The first term on the right side of eq. (15) is the intrinsic viscosity at the theta condition. At the theta condition, the polymer's coil volume or intrinsic viscosity is at minimum because, at this condition, the polymer coil is not swollen by the presence of a solvent. At the theta condition, the polymer coil volume is only due to molecular conformational constraints and $[\eta] = [\eta]_0 = K_\theta \bar{M}^{1/2}$.

The second term on the right side of eq. (15) is the partial change in the intrinsic viscosity associated with
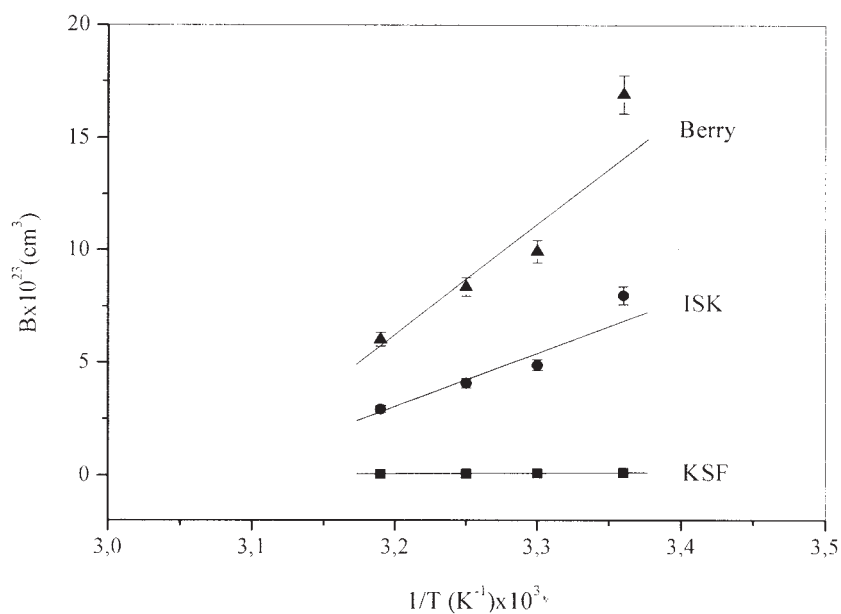

Figure 9 Plot of the interaction parameter B (KSF, ISK, and Berry) as a function of the reciprocal of the absolute temperature, according to $\bar{M}_n$.

TABLE IV
Calculated Data for PEG/Water Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to M_w Values

	$[\eta]_T \times 10^2$ (dL g^{-1})	$[\eta]_\theta \times 10^2$ (dL g^{-1})	α_η	$\langle r^2 \rangle_0^{1/2}$ (Å)	$\langle S^2 \rangle \times 10^6$ (Å)
$T = 25°C$					
PEG 2,000	6.99	4.90	1.13	74.0	1.21
PEG 4,600	13.5	8.00	1.19	121.0	3.70
PEG 8,000	20.1	10.6	1.24	159.0	7.11
PEG 10,000	24.9	13.4	1.27	183.0	10.0
$T = 30°C$					
PEG 2,000	6.98	5.40	1.09	76.0	1.20
PEG 4,600	13.0	8.82	1.14	125.0	3.56
PEG 8,000	18.9	11.6	1.18	164.0	6.70
PEG 10,000	23.1	13.4	1.20	189.0	9.35
$T = 35°C$					
PEG 2,000	6.95	5.53	1.08	77.0	1.19
PEG 4,600	12.8	9.02	1.12	125.0	3.50
PEG 8,000	18.4	11.9	1.16	165.0	6.54
PEG 10,000	22.5	13.7	1.18	191.0	9.12
$T = 40°C$					
PEG 2,000	6.82	5.65	1.06	77.0	1.17
PEG 4,600	12.4	9.22	1.10	126.0	3.39
PEG 8,000	17.5	12.2	1.13	167.0	6.25
PEG 10,000	21.2	14.0	1.15	192.0	8.65

a change in system entropy. This term accounts for changes in the system order because of polymer–solvent interaction and is proportional to the ratio of χ_h to θ.

The third term on the right side of eq. (15) is the partial change in the intrinsic viscosity associated with a change in the system enthalpy. This term accounts for changes in the system heat because of polymer–solvent interaction and is proportional to the ratio of χ_h to T.

Examination of eq. (15) reveals that four possible solution conditions may exist with respect to fluid temperature changes. Intrinsic viscosity variations due to fluid temperature changes depend upon the sign of χ_h and the fluid temperature, T, relative to the theta temperature, θ. A negative value of χ_h indicates that mixing of the polymer with the solvent is exothermic and mixing is improved at lower temperatures, that is, χ becomes less at lower temperatures. As shown by eq. (14), the value of χ depends upon the solution temperature, T, in relation to the theta temperature. Two possibilities existing are $T > \theta$ or $T < \theta$, giving the remaining two dilute solution conditions. At these two conditions, the intrinsic viscosity decreases as the fluid temperature increases. In contrast, a positive value of χ_h indicates that mixing of the polymer with the solvent is endothermic and mixing is improved at higher temperatures, that is, χ becomes less at higher temperatures.[29]

Calculated Flory interaction parameters, excess enthalpy and excess entropy of dilution parameters, and second virial coefficient for the PEG/water system are

given in Tables VI and VII, and it must be equal to 0.5 at the theta temperature. As χ values begin to exceed 0.5, extremely high molecular weight polymer molecules will phase separate from the solution. As χ values become less than 0.5, the polymer coils expand and the intrinsic viscosity increases. With increase in temperature, water is less capable of expanding the polymer coils and the coils contract in volume, as reflected by both a larger χ value and a smaller intrinsic viscosity at 40°C compared to 25°C. The χ value changes less with the polymer molecular weight and the parameters K_θ, V_s, and ρ_p are not highly dependent on the temperature.

Hydration, hydrogen bonding/molecular association between polymer segments and water molecules, are not destroyed with an increment of temperature for the system. It is observed that a strong interaction between polymer segments and solvent molecules through hydrogen bonding will form for the PEG/water system. Therefore, χ_H must be negative. Experimental χ values seem to be equal to 0.5 and χ_S values are the only dominant driving force in setting χ numerically to 0.5, which is believed to be the ideal condition of polymer solutions.

$$\chi = \chi_H + \chi_s \qquad (16)$$

This stipulation is formed as, $(1/2 - \chi) < 1.0 \times 10^{-4}$ for the PEG/water system. Enthalpically, solubility/solvation of polymer in the aqueous solution is preferred; however, entropically it is not, because of the surrounding of the polymer chain with regular solvent

TABLE V
Calculated Data for PEG/Water Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to $\bar{M}_n$ Values

	$[\eta]_T \times 10^2$ (dL g^{-1})	$[\eta]_\theta \times 10^2$ (dL g^{-1})	α_η	$\langle r^2 \rangle_0^{1/2}$ (Å)	$\langle S^2 \rangle \times 10^6$ (Å)
$T = 25°C$					
PEG 2,000	6.99	0.0592	1.06	71.0	0.973
PEG 4,600	13.5	0.0982	1.11	118.0	3.03
PEG 8,000	20.1	0.138	1.13	167.0	6.29
PEG 10,000	24.9	0.121	1.27	146.0	6.41
$T = 30°C$					
PEG 2,000	6.98	0.0621	1.04	73.0	0.965
PEG 4,600	13.0	0.1029	1.08	120.0	2.92
PEG 8,000	18.9	0.145	1.09	169.0	5.94
PEG 10,000	23.1	0.127	1.22	148.0	5.98
$T = 35°C$					
PEG 2,000	6.95	0.0635	1.03	73.0	0.958
PEG 4,600	12.8	0.1053	1.07	121.0	2.87
PEG 8,000	18.4	0.148	1.07	170.0	5.79
PEG 10,000	22.5	0.130	1.20	149.0	5.83
$T = 40°C$					
PEG 2,000	6.82	0.0643	1.02	73.0	0.941
PEG 4,600	12.4	0.1065	1.05	122.0	2.78
PEG 8,000	17.5	0.150	1.05	171.0	5.54
PEG 10,000	21.2	0.131	1.17	150.0	5.54

TABLE VI
Thermodynamic Parameters for the PEG/Water System According to $\bar{M}_w$

	α	C_M	χ_S	χ_H	χ	$A_2 \times 10^5$
$T = 298$ K						
PEG 2,000	1.25	14.090	0.5045	$-4.918.10^{-3}$	0.49957	2.40
PEG 4,600	1.24	14.063	0.5058	$-6.299.10^{-3}$	0.49948	2.89
PEG 8,000	1.30	14.080	0.5071	$-7.674.10^{-3}$	0.49940	3.32
PEG 10,000	1.34	14.117	0.5077	$-8.397.10^{-3}$	0.49935	3.62
$T = 303$ K						
PEG 2,000	1.19	12.789	0.5039	$-4.185.10^{-3}$	0.49970	1.69
PEG 4,600	1.17	12.765	0.5049	$-5.210.10^{-3}$	0.49965	1.95
PEG 8,000	1.22	12.780	0.5059	$-6.267.10^{-3}$	0.49961	2.18
PEG 10,000	1.25	12.814	0.5063	$-6.756.10^{-3}$	0.49958	2.34
$T = 308$ K						
PEG 2,000	1.18	12.575	0.5043	$-4.611.10^{-3}$	0.49974	1.48
PEG 4,600	1.15	12.566	0.5055	$-5.799.10^{-3}$	0.49970	1.69
PEG 8,000	1.20	12.562	0.5067	$-7.002.10^{-3}$	0.49967	1.84
PEG 10,000	1.23	12.578	0.5073	$-7.689.10^{-3}$	0.49964	2.00
$T = 313$ K						
PEG 2,000	1.132	12.340	0.5047	$-4.915.10^{-3}$	0.49979	1.16
PEG 4,600	1.128	12.344	0.5137	$-1.395.10^{-2}$	0.49977	1.30
PEG 8,000	1.16	12.349	0.5184	$-1.861.10^{-2}$	0.49975	1.39
PEG 10,000	1.19	12.361	0.5203	$-2.061.10^{-2}$	0.49974	1.49

molecules, which is not preferred at all. Solvation/association between polymer segments and water molecules are not disturbed with an increment of temperature for polymer/polar solvent systems. According to determined dynamic and thermodynamic magnitudes, it is observed that the strong interactions between polymer and solvent molecules through hydrogen bonding will occur for the PEG/water system. It is obvious that χ_H must be negative. Calculated χ values seem to be lower than 0.5, as shown in Tables VI and VII and χ_S is the only indicated force in setting χ numerically equal to 0.5.

Naturally, determination of the correct theta temperature of a chosen polymer/solvent system has a great physicochemical importance for polymer solutions thermodynamically. To check the previously determined theta temperature or to obtain more reliable values of theta temperature, $(1/2 - \chi)$ and second virial coefficient A_2 versus temperature relationships were investigated individually. These interpolation

TABLE VII
Thermodynamic Parameters for the PEG/Water System According to $\bar{M}_n$

|	α	C_M	χ_S	χ_H	χ	$A_2 \times 10^5$
$T = 298$ K						
PEG 2,000	1.28	10.0761	0.5026	$-2.816.10^{-3}$	0.49975	1.37
PEG 4,600	1.26	10.0570	0.5041	$-4.487.10^{-3}$	0.49963	2.06
PEG 8,000	1.29	10.0692	0.5040	$-4.356.10^{-3}$	0.49966	1.89
PEG 10,000	1.49	10.0959	0.5160	$-1.733.10^{-2}$	0.49866	7.47
$T = 303$ K						
PEG 2,000	1.23	9.63452	0.5022	$-2.320.10^{-3}$	0.49983	0.94
PEG 4,600	1.20	9.62180	0.5034	$-3.666.10^{-3}$	0.49975	1.37
PEG 8,000	1.22	9.62279	0.5032	$-3.364.10^{-3}$	0.49979	1.17
PEG 10,000	1.40	9.65258	0.5144	$-1.532.10^{-2}$	0.49905	5.29
$T = 308$ K						
PEG 2,000	1.19	9.44874	0.5021	$-2.199.10^{-3}$	0.49987	0.70
PEG 4,600	1.16	9.44244	0.5036	$-3.796.10^{-3}$	0.49980	1.10
PEG 8,000	1.17	9.43899	0.5033	$-3.412.10^{-3}$	0.49984	0.90
PEG 10,000	1.35	9.45142	0.5168	$-1.763.10^{-2}$	0.49918	4.58
$T = 313$ K						
PEG 2,000	1.20	9.37537	0.5018	$-1.910.10^{-3}$	0.49992	0.45
PEG 4,600	1.19	9.37878	0.5098	$-9.911.10^{-3}$	0.49986	0.78
PEG 8,000	1.19	9.38277	0.5104	$-1.053.10^{-2}$	0.49990	0.59
PEG 10,000	1.36	9.39190	0.5420	$-4.262.10^{-2}$	0.49936	3.59
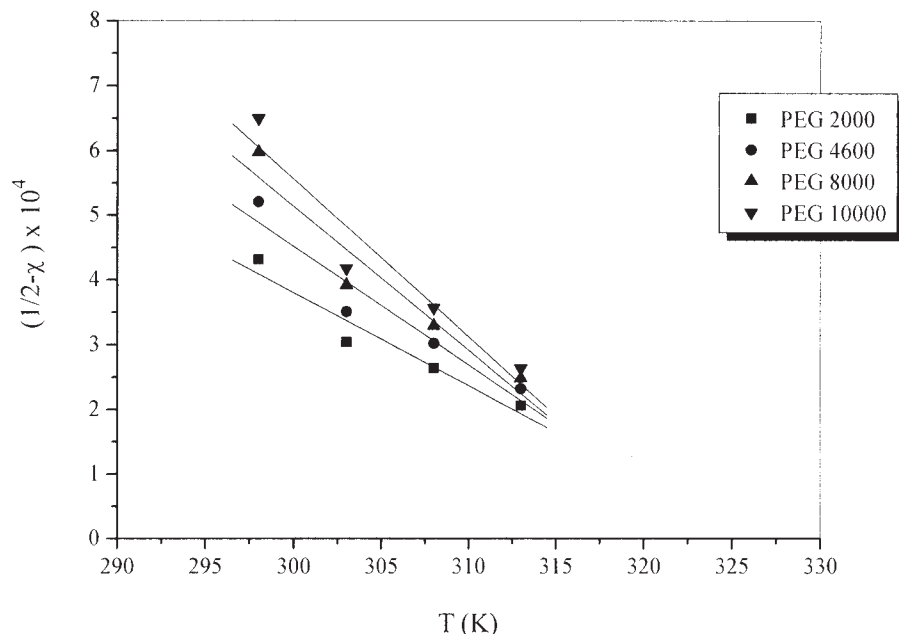
Figure 10 Dependence of $(1/2 - \chi) = 0$ on the temperature for the PEG samples in the water solutions, according to $\bar{M}_w$.

methods seem to be previously used in recent report successfully for the dextran/solvent systems.[14,15] It is quite well-known that the A_2 can also be evaluated from osmometry and light scattering measurements, which consequently exhibits temperature dependence, finally yielding the theta temperature for the system under study. However, the evaluation of A_2 from Zimm plot is really a time consuming and difficult task, although quite reliable. The Gibbs free energy of mixing for the relation of χ and A_2 is given by Wakker,[30] and is predicted as

$$A_2 = (1/2 - \chi)(\rho_p^2 V_s)^{-1} \tag{17}$$

where ρ_p is the density of the polymer and V_S is the molar volume of the solvent. The dependence of $(1/2 - \chi)$ on the temperature is shown in Figures 10 and 11. The theta temperatures for PEG samples are given in Table VIII as the interpolation values at $(1/2 - \chi) = 0$ (correlation: 0.93 ± 0.01 according to $\bar{M}_w$ and 0.96 ± 0.02 according to $\bar{M}_n$).

The dependence of A_2 on the temperature is displayed in Figures 12 and 13. A_2 of PEG aqueous solution is increased linearly with a decrease in temperature. Generally a positive value of A_2 implies that a solvent is good for dissolving a polymer, and consequently intermolecular forces between the polymer chain and the solvent are stronger than those between solvent and solvent or polymer and polymer. The size of a polymer coil in a solution is related to the excluded volume, which in turn is proportional to A_2, solvent quality, which in turn is dependent on tem-

perature, concentration, and molecular architecture of the polymer molecule. The plot of A_2 versus temperature also yielded a straight line (correlation coefficients being 0.93 ± 0.01 according to $\bar{M}_w$ and 0.96 ± 0.02 according to $\bar{M}_n$) from which interpolated values were determined and presented in Table VIII. The results indicate that A_2 decreases with a rise in temperature and an increase with molecular weight.

The values of θ determined in this work were determined to be 324 ± 3 K according to $\bar{M}_w$ and 323 ± 4 K according to $\bar{M}_n$ in water. The θ temperature in the literature is obtained as (390 ± 20 K) by Napper,[31] (369 ± 3 K) by Boucher,[32] and also (369 ± 2) by Ataman.[33]

The high correlation between the evaluated theta temperatures for four different molecular weights of PEG samples implied that theta temperature is rather independent of molecular weight of the polymer. The thermodynamic interaction parameter, χ, is an important and reliable tool, which can be directly employed in the evaluation of theta temperature. Three different theta temperatures obtained from viscometric studies (KSF, ISK, Berry) and χ or A_2 temperature relation by extrapolation and interpolation methods have all resulted in almost similar values which are in quite good agreement with each other.

At theta conditions, the excess chemical potential of mixing is zero and the coil volume is minimum. If the heat of polymer–solvent mixing is endothermic (requires heat), an increase in the solution temperature will increase the polymer coil hydrodynamic volume. If the heat of polymer–solvent mixing is exothermic (releases heat), an increase in solution temperature
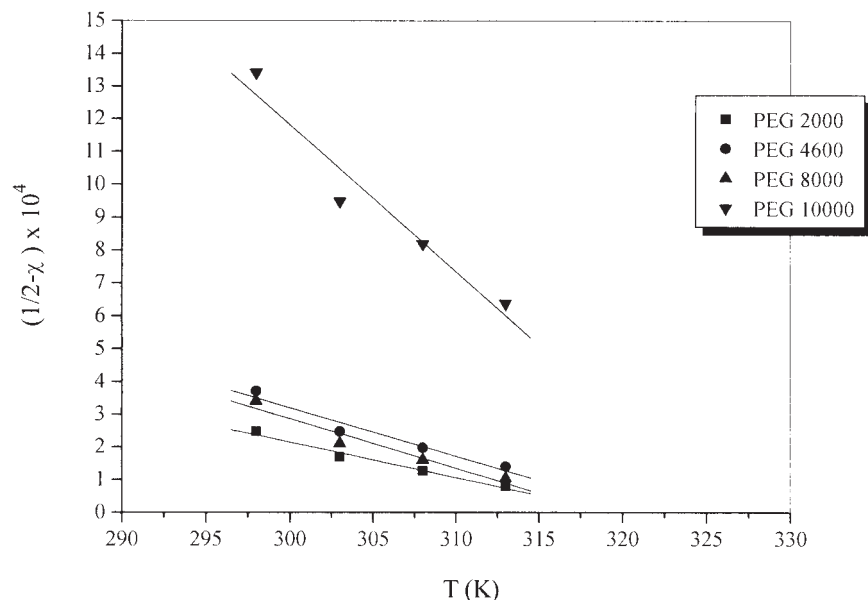
Figure 11 Dependence of $(1/2 - \chi) = 0$ on the temperature for the PEG samples in the water solutions, according to $\bar{M}_n$.

will decrease the polymer coil hydrodynamic volume. A polymer coil hydrodynamic volume depends upon the polymer molecular weight and its thermodynamic interaction with the solvent. As the polymer molecular weight increases, the coil volume becomes greater. Polymer–solvent thermodynamic interactions depend upon the polymer molecular structure and concentra-

TABLE VIII
Theta Temperatures of PEG/Water Solution

Methods	T (K)	
	Calculated from $\bar{M}_w$	Calculated from $\bar{M}_n$
From $B - (1/T)$ behaviour according to KSF equation	337.9[a]	325.5
From $B - (1/T)$ behavior according to ISK equation	322.4	317.9
From $B - (1/T)$ behavior according to Berry equation	321.8	319.8
From $(1/2 - \chi) - T$ behavior		
PEG 2,000	326.5	319.8
PEG 4,600	324.7	321.6
PEG 8,000	323.1	318.9
PEG 10,000	322.8	326.4
From $A_2 - T$ behavior		
PEG 2,000	326.9	319.9
PEG 4,600	325.0	321.7
PEG 8,000	323.3	319.1
PEG 10,000	323.1	326.7
Average	324 ± 3	323 ± 4

[a] Exception.

tion, the solvent molecular structure, and the solution temperature.[28]

A high correlation was observed between the thermodynamic magnitudes and solubility parameters of dextran with the algorithmic calculations of solution dynamics in a previous report.[34] In our ongoing work, investigation solution dynamism of the PEG/chloroform, PEG/DMSO, PEG/methanol, PEG/THF system by viscometric measurements is being studied in detail. Following the algorithmic calculation of the polymer solvent solubility parameters, for PEG and different solvent mentioned earlier, a comparison will be made between the calculated solubility parameters and thermodynamic magnitudes.

CONCLUSIONS

A complete characterization of thermodynamic and hydrodynamic solution properties of PEG has been performed. Despite keen interest in the solution properties of PEG, few investigations have been reported, involving the solution aspects of polymer solution as far as known. In this respect, this study reports unperturbed dimensions, hydrodynamic expansions, the short-range interactions, and the thermodynamic aspects of the PEG/water system in dilute solution between 25 and 40°C, extensively.

Referring to hydrodynamic magnitudes, it has been pointed out that interaction between both polymer segments and polymer–solvent molecules are in competition with each other and with increasing temperature, and it is most probable that both types of interaction may be suppressed.
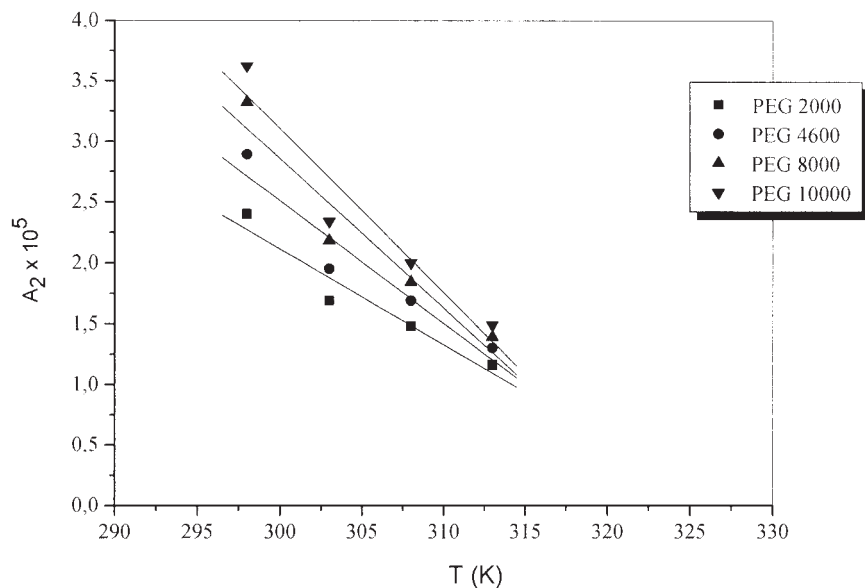
Figure 12 Dependence of $A_2 = 0$ on the temperature for the PEG samples in the water solutions, according to $\bar{M}_w$.

The important role of Flory interaction parameter in the determination of theta temperature of polymer/solvent systems were also pointed out in the present study. Three theta temperature sets obtained from different methods have all resulted in almost similar values, which are in quite good agreement with each other (except in the theta temperature, the B values obtained from KSF equation). θ, K_θ, and χ_H describe the polymer coil size at unperturbed conditions and the polymer coil expansion capabilities of water as a function of the fluid temperature.

The θ temperature detected in this study are lower than those in the previous works.[31–33] The methods used in those studies have been achieved in the presence of inorganic salts by cloud point measurements. The essence of these works mainly involve the destroy chain of the hydrogen bond dynamism of water by those salts in many as well interact with the polymer segments, thus significantly affecting the thermodynamics magnitudes of the polymer chain.
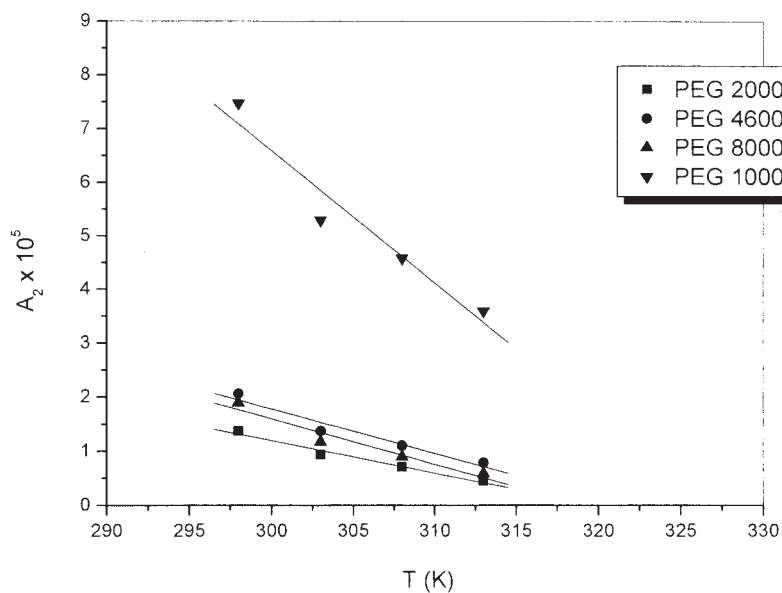
Figure 13 Dependence of $A_2 = 0$ on the temperature for the PEG samples in the water solutions according to $\bar{M}_n$.

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