Solubility Profiles of Poly(ethylene glycol)/Solvent Systems. II. Comparison of Thermodynamic Parameters from Viscosity Measurements

Cemile Özdemir Dinç,[1] Günay Kibarer,[2] Ali Güner[2]

[1]Division of Physical Chemistry, Department of Chemistry, Faculty of Arts and Science, Mustafa Kemal University, TR-31034 Antakya, Türkiye
[2]Division of Polymer Chemistry, Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, TR-06532 Ankara, Türkiye

ABSTRACT: Solution thermodynamics of PEG samples in aqueous and nonaqueous (methanol, chloroform, tetrahydrofuran, and dimethylsulfoxide) solutions have been investigated by viscometric studies at 25, 30, 35, and 40°C. The hydrodynamic expansion factor, a_h, and the unperturbed root mean square end-to-end distance, $\langle r^2 \rangle_\theta^{1/2}$, found for the system indicated that the polymer coils contract as the temperature is raised. The long-range interaction parameter, B, was also evaluated and a significant decrease with increasing temperature was observed. The theta temperatures, θ, obtained from the temperature dependence of $(1/2 - \chi)$ and the second virial coefficient, A_2, are quite good in agreement with the calculated values evaluated via extrapolation and interpolation methods. The thermodynamic interaction parameter, χ, was evaluated through the sum of the individual values of enthalpy and entropy dilution parameters for PEG samples. The restrictions applying to the establishment of concentration regimes, short-range, and long-range interactions are discussed. A parallelism is found between solubility profiles obtained by solution viscometry and solubility parameter approaches for PEG/solvent systems. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1100–1119, 2010

Key words: viscosity; solution properties; thermodynamics

INTRODUCTION

Polymer dissolution is an important area of interest in polymer science and engineering because of its many 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.[1]

Poly(ethylene oxide) (PEO) is one of the most important synthetic polymers from both theoretical and application points of view. The solubility in water and the simple structure of PEO make it a good model system for the study of the interaction mechanisms of water with biopolymers (e.g., PEO assumes a helix conformation in water as DNA does). On the other hand, aggregation behavior of PEO in water, starting from very dilute concentrations and from oligomers up to high M_ws, is both controversial and important.[2] A coil of water molecules around the PEO chain, H-bonded to two sites of ether oxygen, was found. Water spirals are formed in such a way that more water molecules accumulate on the cavities surrounding the oxygen atoms of the PEOs.[3]

An early attempt to explain the solubility of PEO in water was undertaken by Kjellander and Florin.[4] The authors used a structural model for PEO in water in which the system was visualized as a solute surrounded by a water cage. The hexagonal structure of water accommodates PEO molecules, since the distance between the alternate oxygen atoms is 4.7 Å, which is same as the distance between the oxygen atoms in a hexagonally structured water.[5] If the PEO molecule takes a helical formation, the oxygen–oxygen distance in the polymer is 2.88 Å,[4] which compares well with the oxygen–oxygen distance in tetrahedrally associated water, which is 2.85 Å.[5] PEO is known to form a helix in solid state, and there is evidence that, on a local scale, PEO has helical content in water,[6] but is certainly not a stiff global helical structure in water.

PEO is often treated as a simple model protein since it contains both hydrophobic and hydrophilic

segments on the chain. In addition to these segments, PEO, like a protein, also has a secondary structure in solution. The structure shows a reversible transition between a helix and coil between the temperatures of 55 and 60°C.[7]

The helical form of PEG consists of trans-trans-gauche (ttg) sequences. The reported X-ray diffraction (XRD) data[8] show a wide distribution of the C—O torsional angles, suggesting that some C—O bonds are not at the minimum potential energy and implying a distorted helix. Scanning tunneling microscopy of PEO adsorbed on graphite shows single-, double-, and multistranded helices; the average width of the single helix is 7.6 Å. In water, the PEG molecule forms a loose coil.[9] There is some experimental evidence of short-range ttg sequences in PEG molecules in water,[10,11] but simulations show no such helical sequences.[12,13] The overall PEG conformation in water is same that of a coil.

In case of PEG, the alternate structure along the polymer chain of ether oxygen and ethylene units provide different associations with water molecules. The association of ether oxygen units of PEG with water has been observed both by viscometric measurements and thermodynamic studies. Recently, a structural model has been proposed for PEG/water system. PEG in aqueous solution is surrounded by an extended region with enhanced water structure i.e., a hydration sheath.[14,15]

Studies on PEG solution properties are concerned with three subjects. First, PEG exhibits both upper critical solution temperature (UCST) and low critical solution temperature (LCST) phenomena in water.[16] The tendency of PEO to aggregate in solution has also attracted attention. Polik and Burchard[17] reported that PEG chains aggregate significantly in water in a wide temperature range, from 20 to 90°C. Zhou and Brown[18] also reported that the PEG molecules aggregate in methanol at room temperature. However, Kato et al.[19] reported that PEG does not aggregate in water from the measurements of dynamic and static light scattering and viscometry. Kinugasa et al.[20] found that PEG molecules do not aggregate in water, methanol, and acetonitrile at room temperature when the solutions are meticulously prepared.

The theory of solubility, based on the thermodynamics of polymer solutions, is highly developed. In our study, unperturbed molecular dimensions of PEG/water system were calculated according to both $\overline{M}_w$ and $\overline{M}_n$, and it was compared via extrapolation procedures.[21] In this article, $\overline{M}_n$ is used in all of the extrapolation equations (KSF, ISK, and Berry equations) obtained from viscosity data of PEG/solvent system.

This experimental work on PEG/solvent system has been no simpler. Large amount of work has been facilitated in understanding this extremely interesting system. The goal of this work is to understand whether water is a good or weak solvent for PEG. According to a lot of research, PEO is soluble in water, and poly(oxymethylene), poly(oxypropylene), and poly(oxybutylene) are all insoluble in water, even though they are simply homologs of PEO. In this study, behavior of PEG in different solvents is investigated with regard to thermodynamics; thermodynamic equations are used as model systems. In addition, competition between both PEG segments and PEG solvent molecules are considered.

In our former article, solubility parameter approaches for PEG/solvent systems were already compared qualitatively.[22] In this study, it was found that solubility parameters are only half story for constitute of solubility profiles of PEG/solvent systems but usually the most important half. Other half of story about solubility of PEG will be discussed in detail with respect to the solution thermodynamics by viscosity measurements in this article. Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and XRD methods[23] have completed this story. Parallel results to computational calculations and both thermodynamic and spectroscopic data have been obtained.

THEORETICAL BACKGROUND

Flory-Huggins interaction parameter

The Flory-Huggins interaction parameter (χ) is a measure of the interaction between any given solvent and a given polymer. It is a free energy parameter and contains both entropy and enthalpy terms. The interaction parameter is the sum of χ_H and χ_S, which are the excess enthalpy and excess entropy of dilution parameters, respectively. For nonpolar or slightly polar polymer–solvent systems, χ is given by

$$\chi = \chi_S + \chi_H \qquad (1)$$

(no unit), where χ_S is the entropy term and χ_H is the enthalpy term.

The Flory-Huggins theory is useful in considering the thermodynamics of dilute polymer solutions, but it has theoretical limitations. The shortcomings of the Flory interaction parameter include[24,25]: It is not a constant, but depends on polymer concentration and molecular weight as well as temperature. It is not possible to evaluate simply for every polymer–liquid combination. It characterizes a polymer–liquid pair and so is inconvenient for multicomponent systems. It is a composite term influenced by factors such as H-bonding.

Second virial coefficient

The second virial coefficient, A_2, can be evaluated from Flory interaction parameter.

$$A_2 = (1/2 - \chi)\frac{\overline{v}^2}{N_o V_S} \qquad (2)$$

and

$$A_2 = (1/2 - \chi)(\rho_p^2 V_S)^{-1} \qquad (3)$$

where ρ_p, $\overline{v}$, and V_S is density, specific volume of the polymer, and molar volume of solvent, respectively.[26]

A general rule is that

   a. for "good solvents," A_2 is high;
   b. for "poor solvents," A_2 is low; and
   c. at $A_2 = 0$, the polymer precipitates from solution.

The second virial coefficient is dependent on several factors: temperature (A_2 decreases with increasing temperature); polymer–solvent system; molecular weight and molecular weight distribution of the polymer; tacticity of the polymer; and molecular shape of macroions.[25]

Unperturbed dimensions of linear chain macromolecules

The size of macromolecules (dimension) in solution cannot strictly be defined because a single molecular coil alters in shape with time and these conformational changes are due to Brownian motion. The molecular size varies from molecule to molecule of identical mass and structure, and it can only be described in terms of average properties.[25]

Perturbed dimensions are the chain dimensionless in a given solvent, where intermolecular interactions between macromolecules and solvent occur. Unperturbed dimensions are the chain dimensions in a theta solvent or in bulk or vacuum determined solely by bond lengths and angles.

Theta temperature (Flory temperature) and theta solvents

Flory θ−temperature is defined by several different criteria. It is the temperature where A_2 is zero for dilute solutions and $\chi = 0.5$. It is the temperature where the radius of gyration approximates that of the bulk polymer.[26]

In a poor solvent, where both χ_H and χ_S are usually positive, at the theta temperature, $\chi = 0.5$. Flory theta temperatures are associated with both the

upper and lower critical solution temperatures exhibited by all polymer solutions. Theta temperature is the lowest temperature at which a polymer molecule of infinite length would be completely miscible with the liquid. Below the theta temperature, the polymer exists as a ball or tight coil with intramolecular interactions between groups in the same molecule. When the temperature is raised to the theta temperature, these interactions disappear and the polymer behaves as an ideal "statistical" coil; the liquid is called a theta solvent, and the polymer is said to be in the theta condition. At temperatures above θ in poor solvents, there is little change in polymer chain dimensions, but in "good" solvents, the chains tend to uncoil.[25]

Mean square average end-to-end distance

Mean square average end-to-end distance ($\langle r^2 \rangle$) of linear chain molecule is given by

$$\langle r^2 \rangle = \langle r^2 \rangle_o \alpha^2 \qquad (4)$$

(in m² SI), where $\langle r^2 \rangle_o$ is the unperturbed mean square average end-to-end distance and α is the expansion factor.

Square average radius of gyration

Square average radius of gyration ($\langle s^2 \rangle$) is given by

$$\langle s^2 \rangle = \langle s^2 \rangle_o \alpha^2 \qquad (5)$$

where $\langle s^2 \rangle_o$ is the unperturbed square average radius of gyration, α is the expansion factor. For linear polymers,

$$\langle r^2 \rangle = 6\langle s^2 \rangle \qquad (6)$$

Akcasu and Han have shown that the Stokes hydrodynamic radius R_H is not equal to the radius of gyration.[27] The relation between $\langle s^2 \rangle$ and R_H might be expressed as

$$R_H = 0.77\langle s^2 \rangle \qquad (7)$$

where $\langle s^2 \rangle$ is radius of gyration and R_H is Stokes hydrodynamic radius.

The unperturbed dimensions of a linear polymer chain ($\langle r^2 \rangle_o$ or $\langle s^2 \rangle_o$) vary with molecular weight ($\overline{M}_n$). The values of ($\langle r^2 \rangle_o / \overline{M}_n$) or ($\langle s^2 \rangle_o / \overline{M}_n$) depend only on chain structure and not on a solvent or a temperature.

Hydrodynamic radius

The hydrodynamic radius, R_H, of the polymer is defined by

$$R_H = \frac{k_B T}{6\pi \eta D_\circ} \qquad (8)$$

where $k_B T$ is the temperature of the solution, η is the viscosity of the solvent, and D_o is the zero concentration translational diffusion coefficient.[27]

The mean size of a polymer molecule is characterized by its radius of gyration, R_G, which is a static property of the polymer measured in static experiments. In a very recent paper, Des Cloizeaux[28] proved the inequality

$$RH > kRG \qquad (9)$$

where k does not depend on N for large N, but it depends on the type of the chain.[27]

The volume of this equivalent hydrodynamic sphere is delimited by the hydrodynamic radius, R_H, the radius of gyration, R_G, or the root mean square end to end distance, $(r^2)^{1/2}$, i.e., the average distance between the two ends of a chain. The relationship between R_H, R_G, and $(r^2)^{1/2}$ is as follows[29]:

$$R_H = 0.665 R_G \qquad (10)$$

$$(r^2)^{1/2} = (6R_G^2)^{1/2} \qquad (11)$$

Rod-like polysaccharides have higher intrinsic viscosities than random-coil polysaccharides of the same molecular weight. Rod-like polymers are dimensionally thicker, i.e., give a shorter $(r^2)^{1/2}$ for the same mass.[29]

Long-range and short-range interactions

Long-range interactions are defined as those between spatially proximate groups that are separated along the chain by many segments. For single chains, both long-range and short-range interactions are intramolecular but the former is intersegmental and the latter intrasegmental.[30]

The dimensions of polymer chains in diluted solutions are determined by short- and long-range interaction.

Short-range interactions

Short-range interactions can be expressed as a characteristic ratio of the square of the actual chain dimensions in the absence of long-range interactions (its unperturbed dimension is given the symbol $\langle r \rangle_o^{1/2}$).

Long-range interactions (expansion factor)

The expansion factor is the ratio of a dimensional characteristic of a macromolecule in a given solvent

at a given temperature to the same dimensional characteristic in θ state at the same temperature. The most frequently used expansion factors are as follows:

expansion factor of the mean-square

$$\text{end-to-end distance, } \alpha_r = \frac{\langle r^2 \rangle^{1/2}}{\langle s^2 \rangle^{1/2}} \qquad (12)$$

expansion factor of the radius of gyration

$$\alpha_s = \frac{\langle s^2 \rangle^{1/2}}{\langle s^2 \rangle_o^{1/2}} \qquad (13)$$

viscosity expansion factor (Flory expansion factor)

$$\alpha_\eta = \frac{[\eta]^{1/3}}{[\eta]_o^{1/3}} \qquad (14)$$

where $[\eta]$ and $[\eta]_o$ are the intrinsic viscosity in a given solvent and in the θ state at the same temperature, respectively. Expansion factors defined by different dimensional characteristics are neither exactly equal nor need they have a constant ratio as a function of relative molecular mass.[24,31]

If the polymer is in a good solvent, the expansion factor (α) is greater than unity; this means that the actual perturbed dimensions exceed the unperturbed dimensions. The expansion factor (α) also increases with molecular weight $(\overline{M}_n)$, because the number of uncompensated interactions between chain segments increases with the number of segments when $T > \theta$.[24]

In a sufficiently poor solvent or at a sufficiently low temperature (since solvent power and α vary with the temperature), it is possible to achieve the condition $\alpha = 1$, where the chain attains its unperturbed dimensions. This special point is called the "Flory temperature" θ; a solvent used at $T = \theta$ is called a θ − solvent.

The parameter α can be evaluated in terms of thermodynamic quantities as follows:

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^{1/2} \qquad (15)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_s)(1 - \theta/T)M^{1/2} \qquad (16)$$

where C_M lumps together numerical and molecular constants. This equation predicts that α increases without limit with increasing molecular weight, since $\langle r_o^2 \rangle$ is proportional to M. It also leads to fact that, at $T = \theta$, $\alpha = 1$ and molecular dimensions are unperturbed by intramolecular interactions. As α

depends on the entropy parameter, χ_S, it is larger in better solvents.[24]

The expansion of the coil in a dilute solution is given by the Flory-Krigbaum equation as follows:

$$\alpha^5 - \alpha^3 = 2C_M \Delta S_m (1 - \theta/T) M^{1/2} \qquad (17)$$

where ΔS_m is the entropy of mixing parameter, θ is the theta temperature, T is the temperature at which expansion of the coil occurs, M is the molecular weight of the polymer, C_M is a quantity defined by

$$C_M = \frac{9}{2^{5/2}\pi^{3/2}} \left(\frac{\overline{v}^2}{N_A V_S}\right) \left(\frac{M}{\langle r^2 \rangle_o}\right)^{3/2} \qquad (18)$$

$\overline{v}$ is the specific volume of a polymer, N_A is the Avogadro number, V_S is the molar volume of solvent, $\langle r^2 \rangle_o$ is the unperturbed mean square end-to-end distance.

The coefficient C_M presented above is also given by,

$$C_M = 27\overline{v}^2 M^{3/2}/[2N V_S (2\pi \langle r^2 \rangle_o)^{3/2}] \qquad (19)$$

where $\overline{v}$ is the specific volume of the polymer, N is the Avogadro's number, and V_S is the molar volume of the solvent.[24]

Excluded volume

The excluded volume is the volume from which a given polymer molecule effectively excludes all others. The excluded volume is a result of the virtual repulsion between polymer molecules arising from their spatial requirements. Each molecule in a very dilute solution in a good solvent will tend to exclude all others from the volume which it occupies.[24]

Intrinsic viscosity (limiting viscosity number)

Intrinsic viscosity ($[\eta]$) is defined as the fractional increase in the viscosity of one unit of solvent due to the addition of 1 g (CGS) or 1 kg (SI) of noninteracting polymer molecules.

To eliminate the influence of intermolecular interactions, intrinsic viscosity is always calculated by extrapolation of the viscosity number (the reduced specific viscosity) or the logarithmic viscosity number (the inherent viscosity) to zero concentration.[24]

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right) = \lim_{c \to 0} \left(\frac{\eta_{rel}}{c}\right) \qquad (20)$$

Methods of determination for the unperturbed chain dimensions from viscosity measurements

The unperturbed chain dimensions of linear polymers can be determined from the following equations:

a. Flory-Fox equation,
b. Extrapolation methods (Kurata-Stockmayer-Fixman, Inagaki-Suzuki-Kurata, and Berry equations), and
c. Interpolation methods ($T - (1/2 - \chi)$ and $T - A_2$ behaviors).

Flory-Fox equation

$$[\eta]\overline{M} = \phi' V_h = \phi'(\langle r^2 \rangle)^{3/2} \qquad (21)$$

where $[\eta]$ is the limiting viscosity number, $\overline{M}$ is the average molecular weight of the polymer, ϕ is a function related to the hydrodynamic behavior of macromolecules in solution-for a narrow fraction and theta condition, $\phi = \phi_o = 2.8 \times 10^{21}$ mol^{-1} ((ϕ is also called the Flory constant), a theoretical value of 3.6×10^{21} dL/mol cm^3 can be calculated from a study of the chain fractional coefficients,[32] V_h is the hydrodynamic volume (i.e., the volume occupied by the macromolecule), and $\langle r^2 \rangle$ is the mean square end-to-end distance.[24]

Replacing $\langle r^2 \rangle$ in eq. (21) by $\langle r^2 \rangle_o \alpha^2$ and isolating the term $\langle r^2 \rangle_o \overline{M}^{-1}$, an equation is obtained that allows calculating the unperturbed chain dimensions ($\langle r^2 \rangle_o$):

$$[\eta] = \phi_o \left(\frac{\langle r^2 \rangle_o}{\overline{M}}\right)^{3/2} \overline{M}^{1/2} \alpha^3 \qquad (22)$$

K_θ is a constant for a given polymer, independent of solvent, temperature, and molecular weight (except in the range of low molecular weight) and is given by

$$K_\theta = \phi_o (\langle r^2 \rangle_o \overline{M}^{-1})^{3/2} \qquad (23)$$

K_θ can be obtained from measurement of the limiting viscosity number at the theta temperature,

$$[\eta]_\theta = K_\theta \overline{M}^{1/2} \qquad (24)$$

The Flory-Fox equation has been replaced by the related semiempirical Mark-Houwink Equation [eq. (25)]. It contains parameters K and a, which are complex functions of the polymer, solvent, co-solutes, and temperature.[33,34]

$$[\eta] = KM^a \tag{25}$$

Extrapolation methods

Unperturbed dimensions were derived via six different extrapolation procedures, namely those of Stockmayer-Fixman,[35] Cowie,[36] Dondos-Benoit,[37] Kurata-Stockmayer,[38] Inagaki-Suzuki-Kurata,[39] and Berry.[40]

In this study, KSF, ISK, and Berry equations have been employed among six methods mentioned above because these equations yield the same B value (parameter of long-range interaction). In extrapolation methods selected, M_n values of PEG samples were used.

Kurata-Stockmayer-Fixman (KSF) equation.

$$[\eta]\overline{M}^{-1/2} = K_\theta + 0.51B\phi_o\overline{M}^{1/2} \tag{26}$$

where K_θ is unperturbed dimension parameter, $[\eta]$ is the intrinsic viscosity, M is the molecular weight of the polymer (number-average molecular weight), B is the parameter for long-range (polymer–solvent) interactions, and ϕ_o is Flory's constant ($2.1 \times 10^{23} \text{ mol}^{-1}$).

$$B = 2\overline{v}^2(1/2 - \chi)/N_A V_S \tag{27}$$

$\overline{v}$ is the specific volume of a polymer, V_S is the molar volume of a solvent, χ is the Flory interaction parameter, and N_A is the Avogadro number.[24]

Inagaki-Suzuki-Kurata (ISK) equation.

$$[\eta]^{4/5}\overline{M}^{-2/5} = 0.786K_\theta^{4/5} + 0.454K_\theta^{2/5}\phi_o^{2/3}B^{2/3}\overline{M}^{1/3} \tag{28}$$

Berry equation.

$$[\eta]^{1/2}\overline{M}^{-1/4} = K_\theta^{1/2} + 0.42K_\theta^{1/2}\phi_o B\overline{M}[\eta]^{-1} \tag{29}$$

Equations (28) and (29) have been used for the determination of short- and long-range interaction parameters for the PEG/solvent systems.

The plot of $[\eta]\overline{M}^{-1/2}$ against $\overline{M}^{1/2}$, $[\eta]^{4/5}\overline{M}^{-2/5}$ against $\overline{M}^{1/3}$, $[\eta]^{1/2}\overline{M}^{-1/4}$ against $\overline{M}[\eta]^{-1}$ yield straight lines. For these all straights slopes yield B value and intercepts yield K_θ value.

1/T−B behavior. The theta temperature dependence of the long-range interaction parameter, B is given by Flory[32] [eq. (30)]:

$$B = B_o\left(1 - \frac{\theta}{T}\right) \tag{30}$$

where B_o is a constant (independent of temperature) and θ is the theta temperature of the polymer–sol-

TABLE I
The Molecular Weight Characteristics of PEGs[a]

Molecular weight	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	HI
PEG 2000	1880	2030	2666	1.080
PEG 4600	3940	4040	4099	1.025
PEG 8000	7330	7550	7659	1.030
PEG 10000	10,850	10,950	11,069	1.009

[a] GPC-RALS study conditions (solvent: NaH$_2$PO$_4$, NaCl; column set: 2xG2500PWXL aqueous column; triple detector: refractive index, right angle light scattering, viscometer; detector temperature: 35°C).

vent pair. $1/T−B$ graphics intercept at the same B_o point with KSF, ISK, and Berry straights.

Interpolation methods

T − (1/2 − χ) behavior. The plot of $(1/2 - \chi)$ against temperature yields straight lines. θ-temperature is determined by interpolation.

T − A$_2$ behavior. The plot of A_2 versus temperature also yields straight lines. θ-temperature is determined by interpolation.

EXPERIMENTAL

Four different molecular weights of PEG samples (PEG 2000, 4600, 8000, and 10000) used in this study were supplied from Aldrich (St. Louis, MO). The molecular weight characteristics where $\overline{M}_n$ is the number-average molecular weight, $\overline{M}_w$ is the weight-average molecular weight, and $\overline{M}_w/\overline{M}_n$ is the polydispersity index of polymer samples are determined by the manufacturer and are given in Table I.

All the polymer samples were dried and stored *in vacuo* at least for 24 h at 25°C just before preparation of the solution and were used without further purification. All the solutions were prepared by standing in the dark without shaking at room temperature for 24 h to minimize degradation of the polymer samples. Solvents used for PEG are chloroform, THF, DMSO, methanol, and water.

Viscosity measurements

The viscometric measurements were carried out at 25, 30, 35, and 40°C, using 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 2.5–0.2 gdL^{-1} concentration range) was followed by the well-known Huggins equation. For intrinsic viscosity studies, a stock solution were prepared from which dilutions were made such that the maximum

concentration was approximately $1/5[\eta]$, where $[\eta]$ is in gdL^{-1}.[36] Duplicate measurements are made on fresh portions of the solutions, agreed within 0.1 s. The average elution times of solutions were determined after several measurements.

Gennes et al.[41] determined a regime as shown below for the formulation of concentration regimes in a good solvent,

$1 < c[\eta] < 10$ in semidilute (coil overlap)
$c[\eta] \geq 10$ in concentrated (entanglement)

This regime appears in this work as follows:

$$0.2 < c[\eta] < 0.6$$

Thus, neither coil overlap nor entanglements will be observed.

Kinetic energy correction

For kinetic energy control of the Ubbelohde-type capillary viscometer used in this study, Poiseuille equation was used, which is given as follows:

$$\eta = \frac{\pi(h\rho_S g)R^4}{8v\ell}t - \frac{mv\rho_S}{8\pi\ell}\frac{1}{t} \qquad (31)$$

where η is the absolute viscosity, h is the height of solvent in capillary, ρ_S is the liquid density, g is the gravitational acceleration, R is the radius of capillary tube, v is the viscometer bulb volume, ℓ is the length of capillary tube, t is the efflux time, and m is a number that characterizes the kinetic energy contribution.

Kinematic viscosity (v) is given by the equation as below:

$$v = \frac{\eta}{\rho_S} \qquad (32)$$

According to this, the above equation is rearranged as:

$$v = \underbrace{\frac{\pi hgR^4}{8v\ell}}_{A}t - \underbrace{\frac{mv}{8\pi\ell}}_{B}\frac{1}{t} \qquad (33)$$

and simplifying it more, v maybe simply written as $v = At - B(1/t)$. By neglecting of the term $B(1/t)$, $v = At$ equation is obtained. Because of the numerical closeness of $\frac{t_A}{t_B} = \frac{v_A}{v_B}$ ratios of efflux time for two different solvents (A and B), one can decide whether a kinetic energy correction is required. If the ratios were distinct from each other, the neglecting of term $B(1/t)$ cannot be done.

The kinetic energy control of the Ubbelohde-type capillary viscometer has been achieved in two differ-

ent solvents (benzene and toluene) and at two different temperatures (25 and 30°C).

Statistical analysis

Statistical analysis has been applied to linear behaviors such as $y = a + bx$ (KSF, ISK, Berry equations and long-range interactions parameter, B versus $1/T$) and $y = a - bx$ [$(1/2-\chi)$ versus T and A_2 versus T]; subsequently, the results have been evaluated employing Origin 7.5 computer program. The evaluation of intercept and slope values together with their standard error values have been followed by the calculation of t-values.[42]

Determination of density and specific volume

The densities of PEG solutions with molecular weights of 2000, 4600, 8000, and 10000 gmol^{-1} were measured. The density measurements were carried out using a 10 mL glass pycnometer. Densities of the polymer samples were determined in water, THF, DMSO, chloroform, and methanol using a pycnometer at 25, 30, 35, and 40°C. A constant temperature water bath was used to control the temperature at accuracy of $\pm$ 0.1 K. The reproducibility of density measurements was estimated to be $\pm$ 0.02 gcm^{-3}.

The volume of the pycnometer was calibrated as a function of temperature using double distilled water. The densities of water at 25, 30, 35, and 40°C were taken from Perry's Chemical Engineering Handbook.[43,44] For measurement of density, the pycnometer was filled with the solution and immersed in the water bath. After thermal equilibrium was achieved, the pycnometer was weighed quickly. Densities were determined from measurements of the mass of the samples and the pycnometer volume. Specific volume was determined from the reciprocal of density.

RESULTS AND DISCUSSION

Results of kinetic energy control for ubbelohde viscometer

The ratio of kinematic viscosities and ratio of efflux times of benzene (B) and toluene (T) at 25 and 30°C were determined.

At 25°C, $v_B/v_T = 1.0766$; $\bar{t}_B/\bar{t}_T = 1.0770$

At 30°C, $v_B/v_T = 0.0600$; $\bar{t}_B/\bar{t}_T = 0.0603$

The ratio values calculated for each temperature have been found to be very close to each other, thus, no requirement is needed for kinetic energy correction (in both solvents, kinematical viscosity values have been taken from International Critical Tables.[45]

TABLE II
Calculated Thermodynamic Parameters for PEG/Water Solution

	KSF		ISK		Berry	
t (°C)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)
25	16.0	0.573	19.3	6.84	15.4	0.492
30	15.7	0.492	19.0	5.88	15.0	0.435
35	15.5	0.410	19.3	4.26	15.2	0.324
40	14.5	0.408	17.7	4.73	14.1	0.284

TABLE IV
Calculated Thermodynamic Parameters for PEG/DMSO Solution

	KSF		ISK		Berry	
t (°C)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)
25	16.4	0.603	19.5	7.64	15.6	0.539
30	16.2	0.525	19.6	6.13	15.5	0.458
35	14.4	0.492	17.4	6.01	13.9	0.417
40	14.2	0.408	17.3	4.80	13.7	0.341

Statistical analysis

Four different molecular weights (PEG 2000, 4600, 8000, and 10000) and four different temperatures (25, 30, 35, and 40°C) are employed to be substituted in the equation used. Degrees of freedom have been taken as; $n - 1 = 4 - 1 = 3$. At this degree of freedom, the probability of right hand side values have been obtained from the t-table as $t_{0.05} = 2.3534$ for $P = 0.05$.[42] This value indicates the reliability of these equations up to 95%. The calculated t-values being larger than 2.3534 strongly exhibit the validity of the employed model (equations in this study). Another criteria is that, near is the Prob $> |t|$ to zero, much more valid will be employed model be assumed. In the equations we use, the high correlation coefficient ($r^2 > 0.96$), low standard deviation, t value > 2.3534, and Prob $> |t|$ values being closer to zero have been considered, and thus the reliability of the parameters obtained from the intercept and slope values has been determined while those values not complying with these criteria are quitted.

METHODS USED TO RECEIVE INFORMATION ON UNPERTURBED DIMENSION PARAMETERS CALCULATED RESPECTIVELY FOR PEG/SOLVENT SYSTEMS

Extrapolation methods

KSF equation (from $\overline{M}^{1/2}$–$[\eta]\overline{M}^{-1/2}$ graph)

– Intercept: K_θ (short-range interaction parameter)

- Other parameters calculated respectively, from K_θ
- $[\eta]_\theta$ (dLg^{-1}) (intrinsic viscosity at the theta temperature)
- $\langle r^2 \rangle_\circ^{1/2}$ (Å) (mean square average end-to-end distance)
- $\langle r^2 \rangle^{1/2}$ [Å; mean square average end-to-end distance]
- $\langle s^2 \rangle^{1/2}$ [Å] (radius of gyration)]
- α_η (viscosity expansion factor)
- α (expansion factor)
- C_M (coefficient lumps together numerical and molecular constants)
- χ (thermodynamic interaction parameter)
- χ_S (entropy term of thermodynamic interaction parameter)
- χ_H (enthalpy term of thermodynamic interaction parameter)
- A_2(mol cm^{3}g^{-2}) (second virial coefficient)
- a (Mark-Houwink exponential)
– slope: B (cm^3) (long-range interaction parameter) (excluded volume parameter)
  - from $1/T - B$ graph $\rightarrow$ slope: θ – temperature $\rightarrow$ intercept: $B_\circ$ (constant independent of temperature)

ISK equation (from $\overline{M}^{1/3}$–$[\eta]^{4/5}\overline{M}^{-2/5}$ graph)
All of parameters calculated from KSF equation are calculated also from ISK equation.

TABLE III
Calculated Thermodynamic Parameters for PEG/Methanol Solution

	KSF		ISK		Berry	
t (°C)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)
25	12.5	0.625	14.4	9.88	11.6	0.621
30	11.6	0.582	13.1	10.0	10.5	0.605
35	11.4	0.523	13.3	8.39	10.6	0.514
40	11.4	0.430	13.5	6.44	10.8	0.391

TABLE V
Calculated Thermodynamic Parameters for PEG/chloroform Solution

	KSF		ISK		Berry	
t (°C)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)
25	17.1	1.21	18.2	21.0	14.6	1.47
30	14.2	1.05	15.0	20.1	11.8	1.35
35	14.2	0.95	15.3	17.0	12.3	1.10
40	14.0	0.88	15.4	15.2	12.3	1.00

TABLE VI
Calculated Thermodynamic Parameters for PEG/THF Solution

	KSF		ISK		Berry	
t ($^\circ$C)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)	K_θ ($\times 10^4$ dLg^{-1})	B ($\times 10^{28}$ cm^3)
25	12.8	0.592	14.9	9.01	11.9	0.580
30	12.8	0.544	15.0	7.93	12.0	0.517
35	12.7	0.514	14.9	7.46	11.9	0.482
40	11.4	0.438	13.4	6.58	10.8	0.399

Berry equation (from $\overline{M}[\eta]^{-1}$–$[\eta]^{1/2}\overline{M}^{-1/4}$ graph)
All of parameters calculated from KSF equation are calculated also from Berry equation.

Interpolation methods

1. $T - (1/2 - \chi)$ graph $\xrightarrow{\text{interpolation}}$ θ – temperature
2. $T - A_2$ graph $\xrightarrow{\text{interpolation}}$ θ – temperature

Calculation of short-range and long-range parameters from extrapolation methods (KSF, ISK, and Berry)

K_θ is short-range interactions of the polymer segments. One of the basic techniques to receive information on unperturbed dimensions has been found from extrapolation methods starting from viscosity measurements, namely, the KSF equation [eqs. (23) and (26)] employed in the present study, and the relationship between K_θ and $\langle r^2 \rangle_o$ is given by,

Figure 1 Plot of the B, interaction parameter obtained from the KSF, ISK, and Berry equations as a function of the reciprocal of the temperature for the PEG/water system.

Figure 2 Plot of the theta temperature obtained from $T - (1/2 - \chi)$ behavior for PEG/water system.

$$K_\theta = [\eta]_\theta M^{-1/2} = \phi_o(\langle r^2 \rangle_o \overline{M}^{-1})^{3/2} \tag{34}$$

where $[\eta]_\theta$ is the intrinsic viscosity at theta temperature, and finally, $\langle r^2 \rangle_o^{1/2}$ represents the root mean square end-to-end distance of unperturbed polymer chain.

By the use of eqs. (26), (28), and (29), the plots of $[\eta]\overline{M}_n^{-1/2}$ against $\overline{M}_n^{1/2}$, $[\eta]^{1/2}\overline{Mn}^{-1/4}$ against $\overline{M}_n[\eta]^{-1}$, and $[\eta]^{4/5}\overline{M}_n^{-2/5}$ against $\overline{M}_n^{1/3}$ 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 for five different solvents according to KSF, ISK, and finally Berry, respectively. θ good or marginal solvents used for PEG are H-donor solvent (chloroform), H-acceptor solvents (THF and DMSO), and both H-acceptor and H-donor solvents (methanol and water).

Figure 3 Plot of the theta temperature obtained from $T - A_2$ behavior.

TABLE VII
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/Water System

Methods	From KSF equation T (K)	From ISK equation T (K)	From Berry equation T (K)
From (1/T) − B behavior	336	326	329
Average		330 ± 5	
From T − (1/2 − χ) behavior			
PEG 2000	332	286[a]	331
PEG 4600	333	303	331
PEG 8000	332	313	331
PEG 10000	332	317	330
Average	332 ± 1	311 ± 7	331 ± 1
From T − A₂ behavior			
PEG 2000	332	287[a]	331
PEG 4600	334	303	332
PEG 8000	333	313	331
PEG 10000	332	317	331
Average	333 ± 2	311 ± 7	331 ± 1

[a] Has been ignored with regard to the statistical analysis results.

TABLE IX
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/DMSO System

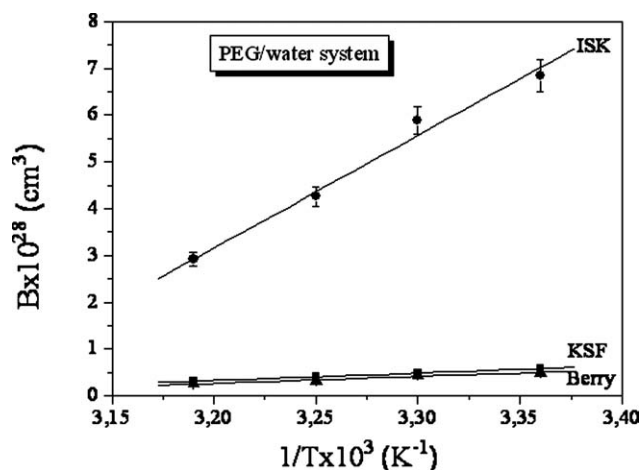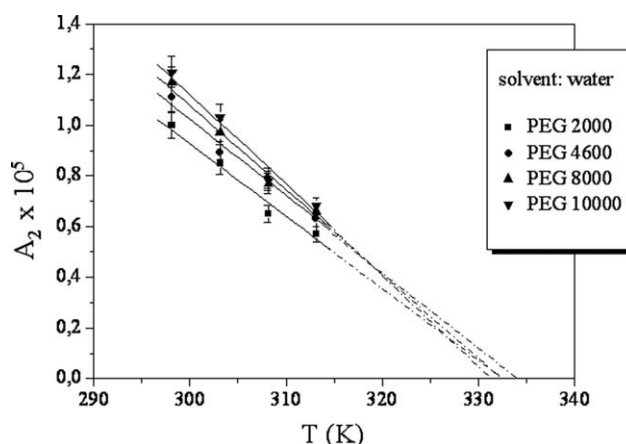| Methods	From KSF equation T (K)	From ISK equation T (K)	From Berry equation T (K)
From (1/T) − B behavior	352[a]	347	345
Average		346 ± 1	
From T − (1/2 − χ) behavior			
PEG 2000	342	291[a]	339
PEG 4600	338	310	336
PEG 8000	337	316	335
PEG 10000	340	322	338
Average	339 ± 3	316 ± 6	337 ± 2
From T − A₂ behavior			
PEG 2000	345	291[a]	341
PEG 4600	340	310	337
PEG 8000	338	316	337
PEG 10000	342	322	340
Average	341 ± 4	316 ± 6	339 ± 2

[a] Has been ignored with regard to the statistical analysis results.

The unperturbed dimension parameters (K_θ) and long-range interaction parameters (B) calculated from extrapolation methods are given in Tables II–VI for PEG/water, PEG/methanol, PEG/DMSO, PEG/chloroform, PEG/THF, respectively.

The unperturbed dimension parameters evaluated from KSF and Berry are in high accordance with each other, and a decrease in K_θ values at increasing temperatures is quite obvious with all these extrapolation techniques as well as the observation for the

long-range interaction parameter—temperature behavior. At this point, it would be better to discuss the interactions between the polymer segments and polymer solvent molecules. Corresponding of the structure of PEG, it is strongly expected that molecular association/interaction will form between the polymer segments and solvent molecules through H-bonding. Of course, this decrement in terms of temperature increment results in the break of polymer–solvent associations, i.e., H-bonds between

TABLE VIII
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/Methanol System

Methods	From KSF equation T (K)	From ISK equation T (K)	From Berry equation T (K)
From (1/T) − B behavior	347[a]	334	334
Average		334	
From T − (1/2 − χ) behavior			
PEG 2000	333	313	328
PEG 4600	336	319	330
PEG 8000	331	320	328
PEG 10000	331	322	328
Average	333 ± 3	319 ± 5	329 ± 1
From T − A₂ behavior			
PEG 2000	336	313	329
PEG 4600	337	318	331
PEG 8000	333	320	329
PEG 10000	332	322	328
Average	335 ± 2	318 ± 5	329 ± 2

[a] Has been ignored with regard to the statistical analysis results.

TABLE X
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/Chloroform System

Methods	From KSF equation T (K)	From ISK equation T (K)	From Berry equation T (K)
From (1/T) − B behavior	365[a]	357	349
Average		353 ± 4	
From T − (1/2 − χ) behavior			
PEG 2000	350	329	338
PEG 4600	347	332	338
PEG 8000	342	331	335
PEG 10000	345	334	337
Average	346 ± 4	332 ± 3	337 ± 2
From T − A₂ behavior			
PEG 2000	356	330	341
PEG 4600	351	334	340
PEG 8000	346	334	338
PEG 10000	350	337	341
Average	351 ± 5	334 ± 4	340 ± 2

[a] Has been ignored with regard to the statistical analysis results.

TABLE XI
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/THF System

Methods	From KSF equation T (K)	From ISK equation T (K)	From Berry equation T (K)
From $(1/T) -$ B behavior	371[a]	358	356
Average		357 ± 1	
From $T - (1/2 - \chi)$ behavior			
PEG 2000	345	312[a]	340
PEG 4600	347	325	342
PEG 8000	349	334	344
PEG 10000	342	331	339
Average	346 ± 4	330 ± 5	341 ± 2
From $T - A_2$ behavior			
PEG 2000	349	312[a]	343
PEG 4600	352	326	345
PEG 8000	354	336	347
PEG 10000	346	333	342
Average	350 ± 4	332 ± 5	344 ± 3

[a] Has been ignored with regard to the statistical analysis results.

polymer and solvent molecules as well as in rupture of the interactions between the polymer segments.

Calculation of theta temperatures from extrapolation and interpolation methods

The plots of the B values obtained from extrapolation methods (KSF, ISK, and Berry) against the reciprocal of the temperature according to eq. (30), resulted in straight lines, where the slope yielded the theta temperature of each studied polymer/solvent system. As an example to $1/T-B$ behavior, plot of PEG/water system is given in Figure 1. The graph of $1/T-B$ is also plotted for other PEG/solvent systems but is not given because article will be too long.

To check the validity of the determined theta temperature or obtain more reliable values of theta temperatures, $(1/2 - \chi)$ and A_2 versus temperature rela-

tionship were also investigated individually. Theta temperatures of PEG/solvent systems are determined as the interpolation values at $y = 0$ respect to $T - (1/2 - \chi)$ behavior for each extrapolation method (KSF, ISK, and Berry) and each solvent (THF, DMSO, water, chloroform, and methanol) and each molecular weight (2000, 4600, 8000, and 10,000). A typical $T - (1/2 - \chi)$ behavior is given for PEG/water system in Figure 2. In this figure, $1/2 - \chi$ values are calculated by using of K_θ values obtained from KSF equation for each one of the temperature (25, 30, 35, and 40°C). The reason for using the KSF equation (Berry equation can also be used) instead of ISK equation is that the unperturbed dimension parameters evaluated from KSF and Berry are in high accordance with each other.

Interpolation graphics with respect to $T - A_2$ behavior by using of A_2 values calculated for K_θ value obtained from each extrapolation method (KSF, ISK, and Berry) and for each solvent (THF, DMSO, water, chloroform, and methanol) and each molecular weight (2000, 4600, 8000, and 10,000) are plotted. A typical $T - A_2$ behavior plot of PEG/water system is given in Figure 3. This graph is also plotted for other PEG/solvent systems, but it is not given here because article will be too long. A_2 values in Figure 3 are calculated by using of K_θ values obtained from KSF equation for each one temperature (25, 30, 35, and 40°C).

The Gibbs free energy of mixing for relation of χ and A_2 is given by Wakker[46] [eq. (3)].

As quite well known, at θ temperature, Flory interaction parameter takes the value of 0.5; whereas the second virial coefficient is zero. Subsequently, the interpolated values at which $\chi = 0.5$ or $1/2 - \chi = 0$ and A_2 is zero may be readily obtained. These values characterize the theta temperature for that system and have been successfully applied to Dextran/solvent systems.[47,48] The theta temperatures of studied systems determined by these two interpolation methods with respect to $T - (1/2 - \chi)$ and $T - A_2$ behaviors have been given in Tables VII–XI for each polymer/solvent pair.

TABLE XII
The θ Temperatures Obtained from KSF, ISK, and Berry Equations of PEG/Solvent Systems

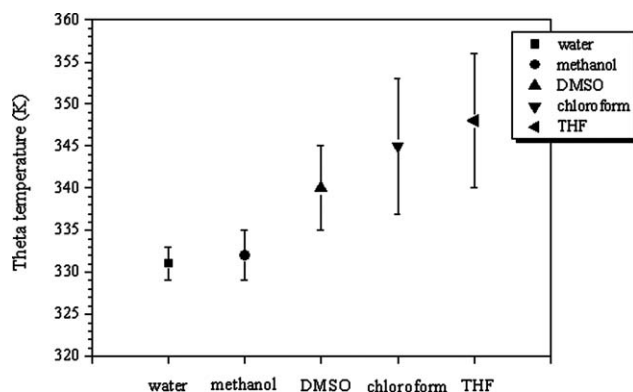| Solvent	From $(1/T) -$ B behavior KSF+ ISK+ Berry	From $T - (1/2 - \chi)$ behavior KSF	Berry	From $T - A_2$ behavior KSF	Berry	Average
Water	330 ± 5	332 ± 1	331 ± 1	333 ± 2	331 ± 1	331 ± 2
Methanol	334	333 ± 3	329 ± 1	335 ± 2	329 ± 2	332 ± 3
DMSO	346 ± 1	339 ± 4	337 ± 2	341 ± 4	339 ± 2	340 ± 5
Chloroform	353 ± 4	346 ± 4	337 ± 2	351 ± 5	340 ± 2	345 ± 8
THF	357± 1	346 ± 4	341 ± 2	350 ± 4	344 ± 3	348 ± 8

Figure 4 Theta temperatures are given versus each solvent in terms of statistical bars.

When these tables are examined, it is observed that θ temperatures are quite scattered for $T - (1/2 - \chi)$ and $T - A_2$ behaviors with the use of ISK equation, and the θ temperatures thus obtained by these two interpolation methods display rather low values for each five distinct solvent.

The theta temperatures determined for PEG/solvent systems are collectively presented in Table XII (except for ISK). Besides, for a better overview, the θ temperatures are given versus each solvent in terms of statistical bars in Figure 4.

In this work, three different extrapolation and two distinct interpolation methods have been employed for the determination of θ corresponding to 331 ± 2 K for PEG in water. θ temperature of PEG/methanol system has been subsequently found as 332 ± 3 K, closer to that of PEG/water. θ temperatures of PEG/DMSO, PEG/chloroform, and PEG/THF systems all display an increasing trend. Solvent that has lower theta temperature is the weakest solvent. According

to the results in Table XII, solvency power of solvents for PEG decreases in the below order, which is compatible with the algorithmic calculations:

THF > Chloroform > DMSO > Methanol > Water

Among the systems studied, the θ temperatures of PEG/chloroform and PEG/THF solutions have been found to be higher (THF somewhat higher). In a good solvent, the polymer coil is expected to expand. In other words, long-range interactions are greater than short-range interactions. Consequently, polymer–solvent interactions are much more dominant with regard to those of polymer molecule segments; the determination of θ temperature for those solutions seems to be more probable at high temperatures.

Among five different solvents employed in this study, only for PEG (or PEO)/solvent system theta temperatures are available in literature. The determined theta temperatures are scattered between an extremely wide ranges of temperature such as 280–390 K. Although Chew and Couper[49] are faced with a θ temperature around 280 K for a molecular weight of 1000–6000, Boucher and Hines[50] and Ataman[14] have obtained a high theta temperature like 369 ± 3 K for PEO with a molecular weight of 20,000. On the other hand, Napper[51] has found a theta temperature corresponding to 390 ± 20 K. In the studies of Saeki group,[52] the θ temperature of PEG/water system has been reported as 371 K. Polik and Burchard[17] have estimated the theta temperature of PEO to be 375 K.

The θ temperatures determined for water/K_2SO_4 and water/$MgSO_4$ systems vary in the range of 308–318 K.[53] Barton has reported the θ temperature of

TABLE XIII
Mark-Houwink Exponent for PEG and PEO in Water

t (°C)	MW range	Method	a	Reference
20	60–11,000	End group titration[a]	0.76	54
25	2000	Stokes radius-[η]– molecular weight relationship	0.67	55
25	630–1470	Capillary viscometry and GPC	0.50	56
25	190–1000	End group titration[b]	0.50	54
35	400–4000	End group titration[c]	0.82	54
25	4000–100,000	Vapor pressure osmometer and viscosity	0.90	57
35	4000–100,000	Vapor pressure osmometer and viscosity	0.85	57
45	4000–100,000	Vapor pressure osmometer and viscosity	0.78	58,59
30	35,000	Limiting viscosity and light scattering	0.78	60
30	20,000–5,000,000	Light scattering, sedimentation, and diffusion[d]	0.78	54
30	36,900–1,020,000	Light scattering and sedimentation-diffusion	0.78	61
35	30,000–7,000,000	Limiting viscosity number–molecular weight relationship[d]	0.82	54
45	30,000–7,000,000	Limiting viscosity number–molecular weight relationship[d]	0.81	54
72	111,000–633,000	Light scattering, viscosity	0.58	62

[a] Narrow MWD polymers or well-fractioned polymers, HI ≤ 1.25.
[b] Narrow MWD polymers or well-fractioned polymers, HI ≤ 1.25 and limited to low MW polymers.
[c] Poorly fractioned polymers or most probable MWD polymers 1.8 ≤ HI < 2.4 and limited to low MW polymers.
[d] Poorly fractioned polymers or most probable MWD polymers 1.8 ≤ HI < 2.4.

TABLE XIV
Mark-Houwink Exponent for PEG and PEO in Chloroform, Methanol, and THF

Solvent	t (°C)	MW range	Method	a	Reference
Chloroform	25	200–1500	End group titration	0.5	54
Methanol	20	60–19,000	End group titration	0.72	54
Methanol	25	–	Light scattering and sedimentation-diffusion	0.57	54
THF	25	68000–914000	–	0.42	63
THF	30	85,000–860,000	Viscosity	0.76	64
THF	72	111,000–633,000	Light scattering, viscosity	0.60	62

PEO as 323 K in a series of solvents (methylisobutyl ketone, diethylene glycol, and diethyl ether).

Theta temperature (ideal temperature) is the temperature at which, for a given polymer-solvent pair, the polymer exists in its unperturbed dimensions. Under these conditions, the long-range forces between polymer molecule segments that cause contraction are just balanced by the polymer–solvent interactions causing the polymer molecular coil to expand. Theta temperature is defined as the temperature at which long-range and short-range interactions balance each other. On the other hand, cloud point is expressed as the temperature at which short-range interactions are more dominant, in other words, short-range interactions are more effective when compared with long-range interactions. In the systems displaying LCST, cloud point (phase separation temperature) is found as the temperature above θ temperature. The "closed loop" phase separation behavior of PEO in water has been confirmed[52] for $M_W < 2000$, and for $M_W = 10^6$, LCST = 372 K.[53]

Determination of θ temperature by the use of cloud point temperatures have also been achieved via different extrapolation methods by Flory.[32] However, θ temperature values obtained from cloud point studies are rather high when compared with those obtained by scatterings occurring in extrapolation methods.

Calculation of Mark-Houwink Exponent "a" for PEG

Mark-Houwink exponents of PEG and PEO in water are being given in Table XIII. As can be seen from the table "a" exponent is scattered among a quite

wide range. Only for PEG, this exponent is observed to be between 0.5 and 0.82.

Practically, Mark-Houwink exponent is a magnitude that characterizes the expansion of the selected polymer in a certain solvent. This exponent exhibits the value of zero in spherical form of the polymer coil whereas its numerical value is 0.5 at θ temperature. In a partly extended polymer chain, $0.5 < a < 1$, and $a = 1.0$ in the extended chain. In a semiflexible and/or rod-like structure, $1.0 < a < 2.0$, and finally, $a = 2.0$ in rod-like structures. Worm-like polymer chains exhibit a value that range from 0.764 to 2.0. High values are encountered with rigid chains of low molar mass. High molar mass, flexible chains have lower a values.[26,30]

Mark-Houwink exponents of PEG and PEO in different solvents are presented in Table XIV. In literature, no such value exists as reported by Mark-Houwink exponent related with PEG/DMSO system. When the exponents in Table XV are examined, even in the same solvent, different Mark-Houwink exponents are being displayed. Mark-Houwink exponent "a" for PEG/solvent systems according to both $\overline{M}_n$ and $\overline{M}_w$ values are given in Tables XV and XVI.

When these tables are examined, Mark-Houwink exponents determined for water have been found to be somewhat closer to or a little higher than 0.60. The values determined for methanol and DMSO have also been obtained again somewhat higher than the "a" value encountered in water; when the other two solvents (THF and chloroform) are considered, the highest Mark-Houwink exponent has been found in chloroform. According to polymer geometry definition of Sperling[26] and Elias,[30] since the

TABLE XV
Mark-Houwink Exponent "a" for PEG /Solvent Systems According to $\overline{M}_n$

t (°C)	Water	Methanol	DMSO	Chloroform	THF
25	0.60	0.62	0.61	0.67	0.64
30	0.59	0.62	0.59	0.67	0.63
35	0.58	0.61	0.60	0.66	0.62
40	0.58	0.60	0.59	0.66	0.62

TABLE XVI
Mark-Houwink Exponent "a" for PEG /Solvent Systems According to $\overline{M}_w$

t (°C)	Water	Methanol	DMSO	Chloroform	THF
25	0.62	0.64	0.62	0.69	0.66
30	0.61	0.64	0.61	0.70	0.65
35	0.60	0.63	0.62	0.68	0.64
40	0.60	0.62	0.61	0.68	0.64

TABLE XVII
Calculated Data for PEG/Water Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to KSF, ISK, and Berry Equations

	$[\eta]_\theta$ (dLg^{-1})			α_η			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle$ ($\times 10^6$ Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
$T = 25°C$															
PEG 2000	0.07	0.08	0.07	1.05	0.99	1.07	1.07	0.99	1.08	85	91	84	1.38	1.34	1.38
PEG 4600	0.10	0.12	0.10	1.08	1.01	1.09	1.09	1.01	1.11	123	131	122	3.04	2.95	3.06
PEG 8000	0.14	0.17	0.13	1.10	1.03	1.11	1.12	1.04	1.14	168	179	166	5.98	5.80	6.01
PEG 10000	0.17	0.20	0.16	1.12	1.05	1.13	1.15	1.06	1.16	205	218	202	9.19	8.93	9.25
$T = 30°C$															
PEG 2000	0.07	0.08	0.07	1.05	0.98	1.06	1.06	0.98	1.08	85	90	83	1.34	1.30	1.35
PEG 4600	0.10	0.12	0.09	1.06	1.00	1.08	1.08	1.00	1.10	123	131	121	2.93	2.84	2.95
PEG 8000	0.13	0.16	0.13	1.09	1.02	1.10	1.11	1.03	1.13	167	178	165	5.75	5.58	5.79
PEG 10000	0.16	0.20	0.16	1.11	1.04	1.12	1.13	1.05	1.15	204	217	201	8.86	8.60	8.92
$T = 35°C$															
PEG 2000	0.07	0.08	0.07	1.04	0.97	1.05	1.05	0.96	1.06	84	91	84	1.30	1.26	1.31
PEG 4600	0.10	0.12	0.10	1.06	0.99	1.07	1.07	0.98	1.08	122	131	121	2.88	2.78	2.88
PEG 8000	0.13	0.17	0.13	1.07	1.00	1.08	1.09	1.00	1.10	167	179	166	5.54	5.35	5.56
PEG 10000	0.16	0.20	0.16	1.09	1.01	1.10	1.11	1.01	1.12	203	218	201	8.44	8.16	8.47
$T = 40°C$															
PEG 2000	0.06	0.08	0.06	1.04	0.97	1.04	1.04	0.96	1.06	83	88	82	1.25	1.20	1.24
PEG 4600	0.09	0.11	0.09	1.05	0.98	1.06	1.06	0.98	1.08	120	128	118	2.76	2.61	2.71
PEG 8000	0.12	0.15	0.12	1.07	1.00	1.08	1.09	1.00	1.10	163	174	162	5.35	5.07	5.25
PEG 10000	0.15	0.19	0.15	1.08	1.01	1.09	1.10	1.02	1.12	198	212	197	8.19	7.74	8.02

value is about 0.60, its corresponding geometry is called as partly extended.

In algorithmic calculations of PEG/solvent systems,[22] THF was a better solvent when compared with chloroform, and sometimes they both exhibited a similar behavior during the evaluation of 2D and 3D diagrams. If Mark-Houwink exponents are considered, chloroform seems as the best solvent among

TABLE XVIII
Calculated Data for PEG/Methanol Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to KSF, ISK, and Berry Equations

	$[\eta]_\theta$ (dLg^{-1})			α_η			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle$ ($\times 10^6$ Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
$T = 25°C$															
PEG 2000	0.05	0.06	0.05	1.07	1.02	1.10	1.09	1.03	1.12	79	82	77	1.22	1.19	1.23
PEG 4600	0.08	0.09	0.07	1.11	1.05	1.13	1.13	1.07	1.17	114	119	111	2.76	2.70	2.80
PEG 8000	0.11	0.12	0.10	1.13	1.08	1.16	1.17	1.10	1.21	155	163	151	5.47	5.35	5.54
PEG 10000	0.13	0.15	0.12	1.16	1.10	1.19	1.20	1.13	1.24	189	198	184	8.53	8.34	8.63
$T = 30°C$															
PEG 2000	0.05	0.06	0.05	1.07	1.03	1.11	1.09	1.04	1.13	77	80	74	1.16	1.14	1.18
PEG 4600	0.07	0.08	0.07	1.10	1.06	1.14	1.13	1.07	1.17	111	116	107	2.61	2.56	2.65
PEG 8000	0.10	0.11	0.09	1.13	1.08	1.17	1.16	1.11	1.21	151	158	147	5.16	5.06	5.23
PEG 10000	0.12	0.14	0.11	1.16	1.12	1.20	1.21	1.15	1.25	184	192	178	8.21	8.05	8.33
$T = 35°C$															
PEG 2000	0.05	0.06	0.05	1.07	1.02	1.09	1.08	1.02	1.12	76	80	74	1.14	1.11	1.15
PEG 4600	0.07	0.08	0.07	1.09	1.04	1.12	1.12	1.05	1.15	110	116	108	2.53	2.47	2.56
PEG 8000	0.09	0.11	0.09	1.12	1.07	1.15	1.16	1.09	1.19	151	158	147	5.05	4.93	5.10
PEG 10000	0.12	0.14	0.11	1.15	1.09	1.18	1.19	1.11	1.22	183	193	179	7.86	7.68	7.95
$T = 40°C$															
PEG 2000	0.05	0.06	0.05	1.05	1.00	1.07	1.07	1.00	1.09	76	81	75	1.10	1.08	1.11
PEG 4600	0.07	0.08	0.07	1.08	1.02	1.10	1.10	1.03	1.12	110	117	108	2.46	2.40	2.48
PEG 8000	0.09	0.12	0.09	1.10	1.04	1.12	1.12	1.05	1.15	151	159	148	4.78	4.65	4.82
PEG 10000	0.12	0.14	0.11	1.13	1.07	1.15	1.16	1.08	1.18	183	194	180	7.50	7.31	7.56

TABLE XIX
Calculated Data for PEG/DMSO Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to KSF, ISK, and Berry Equations

	$[\eta]_\theta$ (dLg^{-1})			α_η			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle$ ($\times 10^6$ Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
$T = 25°C$															
PEG 2000	0.07	0.08	0.07	1.05	0.99	1.07	1.07	0.99	1.09	86	91	85	1.40	1.36	1.21
PEG 4600	0.10	0.12	0.10	1.08	1.02	1.10	1.10	1.02	1.12	124	132	123	3.11	3.03	2.54
PEG 8000	0.14	0.17	0.13	1.10	1.04	1.12	1.13	1.05	1.15	170	180	167	6.09	5.93	4.72
PEG 10000	0.17	0.20	0.16	1.12	1.06	1.14	1.15	1.07	1.18	207	219	203	9.45	9.20	6.99
$T = 30°C$															
PEG 2000	0.07	0.09	0.07	1.05	0.98	1.06	1.06	0.98	1.08	86	91	84	1.38	1.34	1.20
PEG 4600	0.10	0.12	0.10	1.07	1.00	1.08	1.08	1.00	1.10	124	132	122	3.02	2.93	2.51
PEG 8000	0.14	0.17	0.13	1.09	1.02	1.10	1.11	1.03	1.13	169	180	167	5.88	5.71	4.67
PEG 10000	0.17	0.21	0.16	1.11	1.04	1.13	1.14	1.05	1.16	206	219	203	9.14	8.87	6.92
$T = 35°C$															
PEG 2000	0.06	0.08	0.06	1.05	0.99	1.06	1.06	0.98	1.08	82	88	81	1.28	1.24	1.13
PEG 4600	0.09	0.11	0.09	1.07	1.01	1.08	1.09	1.01	1.10	119	127	118	2.81	2.72	2.37
PEG 8000	0.12	0.15	0.12	1.09	1.02	1.10	1.11	1.03	1.13	163	173	161	5.47	5.30	4.40
PEG 10000	0.15	0.18	0.15	1.12	1.05	1.13	1.14	1.06	1.16	198	211	195	8.54	8.29	6.51
$T = 40°C$															
PEG 2000	0.06	0.08	0.06	1.04	0.98	1.05	1.05	0.97	1.07	82	88	81	1.24	1.20	1.07
PEG 4600	0.09	0.11	0.09	1.06	0.99	1.07	1.07	0.99	1.09	119	127	117	2.71	2.63	2.24
PEG 8000	0.12	0.15	0.12	1.08	1.01	1.09	1.10	1.01	1.11	162	173	160	5.25	5.09	4.18
PEG 10000	0.15	0.18	0.14	1.10	1.03	1.11	1.12	1.04	1.14	197	210	195	8.15	7.91	6.18

the selected five other solvents. On the other hand, water strongly supports our algorithmic results with its lowest Mark-Houwink exponent.

Calculation of unperturbed dimensions of PEG

Calculated $[\eta]_\theta$, α_η, $\langle r^2 \rangle_o^{1/2}$, and $\langle s^2 \rangle$ values according to KSF, ISK, and Berry equations are presented in

TABLE XX
Calculated Data for PEG/Chloroform Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to KSF, ISK, and Berry Equations

	$[\eta]_\theta$ (dLg^{-1})			α_η			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle$ ($\times 10^6$ Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
$T = 25°C$															
PEG 2000	0.07	0.08	0.06	1.09	1.07	1.15	1.11	1.09	1.19	87	89	83	1.58	1.56	1.62
PEG 4600	0.11	0.11	0.09	1.15	1.13	1.21	1.19	1.16	1.27	126	129	120	3.75	3.71	3.84
PEG 8000	0.15	0.16	0.13	1.18	1.16	1.25	1.23	1.20	1.32	172	176	163	7.53	7.45	7.72
PEG 10000	0.18	0.19	0.15	1.21	1.18	1.27	1.26	1.23	1.35	210	214	199	11.6	11.5	11.9
$T = 30°C$															
PEG 2000	0.06	0.07	0.05	1.10	1.08	1.17	1.12	1.10	1.21	82	83	77	1.41	1.40	1.45
PEG 4600	0.09	0.09	0.07	1.15	1.13	1.23	1.19	1.17	1.29	119	121	112	3.34	3.32	3.44
PEG 8000	0.12	0.13	0.10	1.19	1.17	1.27	1.24	1.22	1.34	162	165	152	6.74	6.69	6.94
PEG 10000	0.15	0.16	0.12	1.22	1.19	1.29	1.27	1.25	1.37	197	200	185	10.5	10.4	10.8
$T = 35°C$															
PEG 2000	0.06	0.07	0.05	1.09	1.06	1.14	1.11	1.07	1.17	82	84	78	1.38	1.36	1.41
PEG 4600	0.09	0.10	0.08	1.14	1.11	1.20	1.18	1.14	1.25	119	122	113	3.27	3.22	3.34
PEG 8000	0.12	0.13	0.11	1.18	1.14	1.23	1.22	1.18	1.29	162	166	154	6.50	6.42	6.64
PEG 10000	0.15	0.16	0.13	1.20	1.17	1.25	1.25	1.21	1.32	197	202	188	10.1	9.94	10.3
$T = 40°C$															
PEG 2000	0.06	0.07	0.05	1.08	1.05	1.13	1.10	1.06	1.17	82	84	78	1.35	1.33	1.38
PEG 4600	0.09	0.10	0.08	1.13	1.10	1.18	1.17	1.12	1.23	118	122	113	3.17	3.12	3.24
PEG 8000	0.12	0.13	0.11	1.16	1.13	1.22	1.21	1.16	1.27	161	166	154	6.30	6.20	6.43
PEG 10000	0.15	0.16	0.13	1.19	1.15	1.24	1.24	1.19	1.31	196	202	188	9.82	9.67	10.0

TABLE XXI
Calculated Data for PEG/THF Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–40°C According to KSF, ISK, and Berry Equations

	$[\eta]_\theta$ (dLg^{-1})			α_η			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle$ ($\times 10^6$ Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
$T = 25°C$															
PEG 2000	0.06	0.07	0.05	1.07	1.02	1.09	1.08	1.02	1.12	79	83	77	1.23	1.20	1.13
PEG 4600	0.08	0.09	0.08	1.09	1.04	1.12	1.12	1.05	1.15	115	121	112	2.73	2.67	2.87
PEG 8000	0.11	0.13	0.10	1.13	1.07	1.16	1.16	1.09	1.19	157	165	153	5.48	5.35	5.75
PEG 10000	0.13	0.16	0.12	1.15	1.09	1.18	1.19	1.11	1.22	190	200	186	8.49	8.29	8.92
$T = 30°C$															
PEG 2000	0.06	0.07	0.05	1.06	1.01	1.09	1.08	1.01	1.11	79	84	78	1.21	1.18	1.13
PEG 4600	0.08	0.09	0.08	1.09	1.03	1.11	1.11	1.04	1.14	115	121	112	2.69	2.62	2.80
PEG 8000	0.11	0.13	0.10	1.12	1.06	1.14	1.15	1.07	1.18	156	165	153	5.37	5.23	5.59
PEG 10000	0.13	0.16	0.13	1.14	1.08	1.16	1.17	1.10	1.20	190	201	186	8.29	8.08	8.63
$T = 35°C$															
PEG 2000	0.06	0.07	0.05	1.06	1.00	1.08	1.07	1.00	1.10	79	83	77	1.20	1.17	1.11
PEG 4600	0.08	0.09	0.08	1.08	1.03	1.10	1.10	1.03	1.13	114	121	112	2.65	2.58	2.72
PEG 8000	0.11	0.13	0.10	1.11	1.05	1.14	1.14	1.07	1.17	156	165	153	5.29	5.15	5.42
PEG 10000	0.13	0.16	0.12	1.13	1.07	1.15	1.16	1.09	1.19	190	200	186	8.12	7.92	8.33
$T = 40°C$															
PEG 2000	0.05	0.06	0.05	1.06	1.00	1.07	1.07	1.00	1.09	76	80	75	1.10	1.08	1.03
PEG 4600	0.07	0.08	0.07	1.08	1.02	1.10	1.10	1.03	1.12	110	116	108	2.44	2.38	2.48
PEG 8000	0.10	0.12	0.09	1.11	1.05	1.13	1.14	1.06	1.16	150	159	148	4.87	4.75	4.94
PEG 10000	0.12	0.14	0.11	1.12	1.06	1.14	1.16	1.08	1.18	183	193	180	7.44	7.25	7.55

Tables XVII–XXI for PEG/solvent systems. The magnitudes, $[\eta]_\theta$, α_η, $\langle r^2 \rangle_o^{1/2}$, and $\langle s^2 \rangle$ are the measures of the hydrodynamic volume, intensity of the thermodynamic interactions, and the hydrodynamic expansion and contraction of the polymer in solution, respectively.

α_η and α values calculated according to ISK equation use to fall below 1 for PEG 2000 and PEG 4600 in water and DMSO. However, in all solvent systems, lower values with respect to those obtained from KSF and Berry equations have been encountered. Among the three different extrapolation methods,

TABLE XXII
Thermodynamic Parameters for the PEG/Water System

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
$T = 298$ K									
PEG 2000	0.5016	−0.0018	0.49982	0.5009	−0.0009	0.50004	0.5021	−0.0023	0.49977
PEG 4600	0.5017	−0.0019	0.49980	0.5015	−0.0015	0.49997	0.5021	−0.0024	0.49976
PEG 8000	0.5018	−0.0020	0.49979	0.5012	−0.0013	0.49994	0.5023	−0.0025	0.49975
PEG 10000	0.5019	−0.0022	0.49978	0.5013	−0.0014	0.49992	0.5023	−0.0026	0.49975
$T = 303$ K									
PEG 2000	0.5016	−0.0017	0.49985	0.5010	−0.0009	0.50005	0.5023	−0.0025	0.49979
PEG 4600	0.5016	−0.0018	0.49984	0.5004	−0.0004	0.50000	0.5022	−0.0024	0.49980
PEG 8000	0.5018	−0.0020	0.49983	0.5011	−0.0012	0.49996	0.5023	−0.0025	0.49979
PEG 10000	0.5020	−0.0021	0.49982	0.5013	−0.0014	0.49994	0.5024	−0.0027	0.49978
$T = 308$ K									
PEG 2000	0.5015	−0.0016	0.49988	0.5014	−0.0013	0.50010	0.5019	−0.0021	0.49986
PEG 4600	0.5017	−0.0019	0.49986	0.5019	−0.0018	0.50003	0.5021	−0.0023	0.49984
PEG 8000	0.5017	−0.0019	0.49986	0.5000	−0.00001	0.50000	0.5021	−0.0023	0.49985
PEG 10000	0.5018	−0.0020	0.49986	0.5006	−0.0006	0.49998	0.5022	−0.0023	0.49985
$T = 313$ K									
PEG 2000	0.5017	−0.0018	0.49990	0.5010	−0.0009	0.50008	0.5023	−0.0024	0.49987
PEG 4600	0.5017	−0.0018	0.49989	0.5010	−0.0010	0.50003	0.5023	−0.0024	0.49987
PEG 8000	0.5019	−0.0020	0.49988	0.5007	−0.0008	0.50000	0.5024	−0.0026	0.49986
PEG 10000	0.5021	−0.0022	0.49988	0.5013	−0.0013	0.49998	0.5025	−0.0027	0.49986

TABLE XXIII
Thermodynamic Parameters for the PEG/Methanol System

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
$T = 298$ K									
PEG 2000	0.5025	−0.0028	0.49970	0.5017	−0.0018	0.49992	0.5043	−0.0048	0.49957
PEG 4600	0.5028	−0.0032	0.49965	0.5025	−0.0026	0.49983	0.5044	−0.0049	0.49953
PEG 8000	0.5033	−0.0036	0.49963	0.5029	−0.0031	0.49979	0.5047	−0.0052	0.49953
PEG 10000	0.5035	−0.0039	0.49962	0.5030	−0.0032	0.49976	0.5048	−0.0053	0.49952
$T = 303$ K									
PEG 2000	0.5031	−0.0033	0.49972	0.5034	−0.0035	0.49989	0.5053	−0.0058	0.49957
PEG 4600	0.5029	−0.0032	0.49969	0.5033	−0.0034	0.49983	0.5050	−0.0055	0.49956
PEG 8000	0.5034	−0.0038	0.49968	0.5036	−0.0038	0.49980	0.5053	−0.0058	0.49957
PEG 10000	0.5041	−0.0044	0.49963	0.5040	−0.0043	0.49975	0.5059	−0.0064	0.49952
$T = 308$ K									
PEG 2000	0.5035	−0.0038	0.49975	0.5036	−0.0036	0.49995	0.5056	−0.0060	0.49964
PEG 4600	0.5035	−0.0038	0.49974	0.5031	−0.0032	0.49989	0.5051	−0.0054	0.49965
PEG 8000	0.5043	−0.0046	0.49971	0.5040	−0.0042	0.49985	0.5059	−0.0062	0.49963
PEG 10000	0.5050	−0.0054	0.49969	0.5040	−0.0042	0.49982	0.5060	−0.0064	0.49962
$T = 313$ K									
PEG 2000	0.5030	−0.0032	0.49981	0.5046	−0.0045	0.50001	0.5055	−0.0058	0.49974
PEG 4600	0.5049	−0.0051	0.49978	0.5096	−0.0097	0.49994	0.5089	−0.0091	0.49973
PEG 8000	0.5063	−0.0065	0.49979	0.5099	−0.0099	0.49992	0.5101	−0.0103	0.49974
PEG 10000	0.5067	−0.0070	0.49976	0.5084	−0.0085	0.49988	0.5102	−0.0105	0.49972

KSF and Berry equations have yielded much more expressive results.

It is clearly seen in Tables XVII–XXI that in the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion of the coil are in a decrement trend by temperature on the interactions between the polymer and solvent molecules in solution. The point which we strongly wish to emphasize is that at each selected temperature and molecular weight, being related to the solvent nature, the variations in thermodynamic magnitudes such as hydrodynamic volume and hydrodynamic expansion/contraction of polymer may be followed.

When the hydrodynamic magnitudes of PEG in the selected solvents are regarded, highest values of

TABLE XXIV
Thermodynamic Parameters for the PEG/DMSO System

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
$T = 298$ K									
PEG 2000	0.5061	−0.0070	0.49909	0.5035	−0.0034	0.5001	0.5090	−0.0102	0.4988
PEG 4600	0.5077	−0.0087	0.49898	0.5054	−0.0056	0.4998	0.5101	−0.0114	0.4987
PEG 8000	0.5080	−0.0091	0.49895	0.5061	−0.0065	0.4996	0.5101	−0.0114	0.4987
PEG 10000	0.5082	−0.0093	0.49886	0.5064	−0.0069	0.4995	0.5101	−0.0114	0.4987
$T = 303$ K									
PEG 2000	0.5061	−0.0069	0.49921	0.5060	−0.0057	0.5002	0.5091	−0.0101	0.4989
PEG 4600	0.5072	−0.0080	0.49918	0.5009	−0.0009	0.5000	0.5097	−0.0107	0.4990
PEG 8000	0.5077	−0.0085	0.49914	0.5043	−0.0045	0.4998	0.5098	−0.0108	0.4990
PEG 10000	0.5079	−0.0089	0.49904	0.5053	−0.0056	0.4997	0.5099	−0.0110	0.4989
$T = 308$ K									
PEG 2000	0.5068	−0.0076	0.49924	0.5031	−0.0029	0.5002	0.5096	−0.0106	0.4990
PEG 4600	0.5081	−0.0089	0.49922	0.5069	−0.0070	0.5000	0.5104	−0.0113	0.4991
PEG 8000	0.5085	−0.0092	0.49921	0.5070	−0.0072	0.4998	0.5104	−0.0113	0.4991
PEG 10000	0.5088	−0.0097	0.49909	0.5075	−0.0078	0.4997	0.5107	−0.0117	0.4990
$T = 313$ K									
PEG 2000	0.5063	−0.0069	0.49942	0.5042	−0.0039	0.5003	0.5093	−0.0101	0.4992
PEG 4600	0.5131	−0.0137	0.49939	0.4754	0.0247	0.5001	0.5177	−0.0185	0.4993
PEG 8000	0.5138	−0.0144	0.49938	0.5367	−0.0368	0.4999	0.5178	−0.0185	0.4993
PEG 10000	0.5134	−0.0141	0.49929	0.5183	−0.0185	0.4998	0.5170	−0.0178	0.4992

TABLE XXV
Thermodynamic Parameters for the PEG/Chloroform System

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
$T = 298$ K									
PEG 2000	0.521	−0.025	0.4964	0.527	−0.030	0.4972	0.552	−0.059	0.4931
PEG 4600	0.532	−0.037	0.4948	0.538	−0.042	0.4956	0.563	−0.071	0.4917
PEG 8000	0.537	−0.043	0.4945	0.542	−0.047	0.4953	0.567	−0.075	0.4917
PEG 10000	0.534	−0.040	0.4945	0.539	−0.044	0.4952	0.561	−0.069	0.4919
$T = 303$ K									
PEG 2000	0.522	−0.025	0.4966	0.531	−0.034	0.4973	0.556	−0.063	0.4936
PEG 4600	0.532	−0.037	0.4954	0.541	−0.045	0.4961	0.566	−0.074	0.4924
PEG 8000	0.539	−0.043	0.4951	0.546	−0.050	0.4957	0.571	−0.079	0.4924
PEG 10000	0.536	−0.041	0.4950	0.542	−0.047	0.4956	0.566	−0.073	0.4925
$T = 308$ K									
PEG 2000	0.521	−0.024	0.4971	0.528	−0.030	0.4981	0.551	−0.056	0.4951
PEG 4600	0.533	−0.037	0.4959	0.539	−0.042	0.4969	0.563	−0.069	0.4940
PEG 8000	0.538	−0.042	0.4959	0.543	−0.046	0.4967	0.566	−0.072	0.4942
PEG 10000	0.534	−0.039	0.4958	0.539	−0.043	0.4966	0.560	−0.066	0.4942
$T = 313$ K									
PEG 2000	0.522	−0.025	0.4974	0.530	−0.031	0.4985	0.556	−0.061	0.4956
PEG 4600	0.548	−0.052	0.4964	0.571	−0.073	0.4975	0.606	−0.111	0.4947
PEG 8000	0.560	−0.063	0.4964	0.581	−0.083	0.4973	0.617	−0.122	0.4949
PEG 10000	0.553	−0.057	0.4962	0.570	−0.073	0.4971	0.604	−0.109	0.4948

α, α_η, $\langle r \rangle_o^{1/2}$, and $\langle s^2 \rangle_o$ appear in chloroform. However, occasionally these values seem to be somewhat alike both in chloroform and THF. Although sometimes displacements may take place between THF and DMSO, generally, the values found for THF are higher than those found for DMSO. A net change is not being observed related to the type of solvent when the magnitudes α, α_η, $\langle r \rangle_o^{1/2}$, and $\langle s^2 \rangle_o$ are compared.

Calculation of thermodynamic parameters of PEG solutions

Calculated Flory interaction parameters are given in Tables XXII–XXVI for PEG/solvent pairs and it must be equal to 0.5 at the theta temperatures. This stipulation is almost formed as $0.5 \approx 0.499$ for the PEG–solvent systems.

Calculated excess enthalpy and entropy of dilution parameters and Flory interaction parameters for

TABLE XXVI
Thermodynamic Parameters for the PEG/THF System

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
$T = 298$ K									
PEG 2000	0.5046	−0.0053	0.49927	0.5033	−0.0034	0.49984	0.5076	−0.0086	0.49894
PEG 4600	0.5046	−0.0054	0.49924	0.5032	−0.0035	0.49970	0.5070	−0.0080	0.49898
PEG 8000	0.5051	−0.0060	0.49913	0.5038	−0.0043	0.49954	0.5072	−0.0084	0.49889
PEG 10000	0.5061	−0.0070	0.49910	0.5046	−0.0052	0.49948	0.5082	−0.0093	0.49888
$T = 303$ K									
PEG 2000	0.5046	−0.0053	0.49936	0.5020	−0.0021	0.49994	0.5075	−0.0084	0.49909
PEG 4600	0.5047	−0.0054	0.49932	0.5029	−0.0031	0.49979	0.5070	−0.0079	0.49910
PEG 8000	0.5051	−0.0059	0.49923	0.5035	−0.0039	0.49964	0.5072	−0.0081	0.49904
PEG 10000	0.5062	−0.0070	0.49921	0.5044	−0.0048	0.49959	0.5082	−0.0092	0.49903
$T = 308$ K									
PEG 2000	0.5049	−0.0055	0.49941	0.5022	−0.0023	0.49997	0.5081	−0.0090	0.49916
PEG 4600	0.5049	−0.0056	0.49937	0.5031	−0.0033	0.49982	0.5075	−0.0083	0.49918
PEG 8000	0.5054	−0.0061	0.49928	0.5038	−0.0041	0.49968	0.5077	−0.0086	0.49911
PEG 10000	0.5065	−0.0072	0.49928	0.5048	−0.0051	0.49964	0.5088	−0.0096	0.49912
$T = 313$ K									
PEG 2000	0.5048	−0.0052	0.49951	0.5023	−0.0022	0.50001	0.5078	−0.0085	0.49933
PEG 4600	0.5048	−0.0053	0.49948	0.5032	−0.0033	0.49987	0.5072	−0.0079	0.49934
PEG 8000	0.5053	−0.0059	0.49939	0.5039	−0.0041	0.49974	0.5075	−0.0082	0.49927
PEG 10000	0.5063	−0.0069	0.49941	0.5047	−0.0050	0.49972	0.5085	−0.0092	0.49930

PEG/solvent systems are also presented in Tables XXII–XXVI. Enthalpically, solubility or solvation of polymer in solution is preferred; whereas entropically it is not, due to the surrounding of the polymer chain with regular solvent molecules.

Solvation/association between polymer segments and solvent molecules are 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 H-bonding will occur for the PEG/solvent systems. It is obvious that χ_H must be negative. Calculated χ values seem to be a little bit smaller than 0.5, as shown in Tables XXII–XXVI, and χ_S is the only indicated force in setting χ numerically to 0.5, which is believed to be the ideal condition for polymer solutions.

CONCLUSIONS

In this study, solution thermodynamics of the polymer and the type of similarities/agreements displayed on the basis of various thermodynamic magnitudes to interpret the solvent power in PEG/solvent systems have been employed on the basis of the algorithmic (arithmetical) methods based on the computational application of the principle, "like dissolves like."

When the hydrodynamic and thermodynamic magnitudes of the polymer in selected solvents are compared, THF and chloroform display similar behaviors. According to the calculated thermodynamic parameters, solvency power of solvents for PEG decreases below order. This order is compatible with algorithmic calculations: THF > chloroform > DMSO > methanol > water.

The theta temperature of PEG/THF system has been found to be somewhat higher than that of PEG/chloroform system but still Mark-Houwink exponent of PEG/chloroform two-component system appears to be a little bit higher compared with that of PEG/THF system.

In this article, a comparison is made between the calculated solubility parameters and thermodynamic magnitudes for PEG and different solvents. Solubility profiles of PEG/solvent systems clarified by comparison of thermodynamic parameters from viscosity measurements. Similar agreements also have been observed from XRD, FTIR, and Raman spectroscopic results from the detections in the solid state.[23] Consequently, it was again faced with the unchanging fact that water still displays its nature as the weakest solvent.

References

1. Miller-Chau, B. A.; Koening, J. L. Prog Polym Sci 2003, 28, 1223.
2. Magazù, S.; Maisano, G. J Mol Liquids 2001, 93, 7.
3. Aray, Y.; Marquez, M.; Rodriguez, J.; Coll, S.; Simon-Manso, Y.; Gonzalez, C.; Weitz, D. A. J Phys Chem B 2003, 107, 8946.
4. Kjellander, R.; Florin, E. J Chem Soc Faraday Trans 1981, 1, 2053.
5. Blandamer, M. J.; Fox, M. F.; Powell, E.; Stafford, J. W. Macromol Chem 1969, 124, 222.
6. Borodin, O.; Douglos, R.; Smith, G. A.; Trouw, F.; Petrucci, S. J Phys Chem 2003, 6, 107, 6813.
7. Alessi, M. L. Coil-to-Helix Transition of Poly(ethylene oxide) in Solution, PhD thesis, University of Maryland: College Park, 2004.
8. Takahashi, Y.; Tadokoro, H. Macromolecules 1973, 6, 672.
9. Vennaman, N.; Lechner, M. D.; Oberthuer, R. C. Polymer 1987, 28, 1738.
10. Oesterhelt, F.; Rief, M.; Gaub, H. E. New J Phys 1999, 1, 6.1.
11. Begun, R.; Matsuura, H. J Chem Soc Faraday Trans 1997, 93, 3839.
12. Smith, G. D.; Bedrov, D.; Borodin, O. J Am Chem Soc 2000, 122, 9548.
13. Bedrov, D.; Smith, G. D. J Chem Phys 2003, 118, 6656.
14. Ataman, M. J Macromol Sci Chem A 1987a, 24:967.
15. Kawaguchi, S.; Imai, G.; Suzuki, J.; Miyahara, A.; Kitano, T.; Ito, K. Polymer 1997, 38, 2885.
16. Friberg, S. E.; Lindman, B. Organized Solutions: Surfactants in Science and Technology, Surfactant Science Series, 44, Marcel Dekker: New York, 1992.
17. Polik, W. F.; Burchard, W. Macromolecules 1983, 16, 978.
18. Zhou, P.; Brown, W. Macromolecules 1990, 23, 1131.
19. Kato, T.; Nakamura, K.; Kawaguchi, M.; Takahashi, A. Polym J 1981, 13, 1037.
20. Kinugasa, S.; Nakahara, H.; Fudagawa, N.; Koga, Y. Macromolecules 1994, 27, 6889.
21. Özdemir, C.; Güner, A. J Appl Polym Sci 2006, 101, 203.
22. Özdemir, C.; Güner, A. Eur Polym J 2007, 43, 3068.
23. Özdemir Dinç, C.; Güner A. Polym J, to appear.
24. Rabek, J. F. Experimental Methods in Polymer Chemistry; Wiley-Interscience: New York, 1980.
25. Barton, A. F. M. CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters; CRC Press: Boca Raton, 1990
26. Sperling, L. H. Introduction to Physical Polymer Science; 3rd ed.; Wiley: New York, 2001.
27. Akcasu, A. Z.; Han, C. C. Macromolecules 1979, 12(2):276–280.
28. Des Cloizeoux, J.; Jannink, G. Polymers in Solution Their Modelling and Structure; Clarendon Press: Oxford, United Kingdom, 1990.
29. Walter, R. H. Polysaccharide Association Structures in Food; Marcel Dekker: New York, 1998.
30. Elias, H. G. An Introduction to Polymer Science; VCH: Weinheim, 1997.
31. IUPAC. Compendium of Macromolecular Nomenclature; Blackwell Scientific Publications: Oxford, 1991.
32. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, New York, 1953.
33. Keary, C. M. Carbohyd Polym 2001, 45, 293.
34. Carraher, C. E. Polymer Chemistry: An Introduction; Marcel Dekker: New York, 1996.
35. Stockmayer, W. H.; Fixman, M. J Polym Sci Part C: Polym Symp 1963, 1, 137.
36. Cowie, J. M. G. Polymer 1966, 7, 487.
37. Dondos, A.; Benoit, H. Polymer 1978, 19, 523.
38. Kurata, M.; Stockmayer, W. H. Fortschr Hochpolym Forsch 1963, 3, 196.
39. Inagaki, H.; Suzuki, H.; Kurata, M. J Polym Sci Part C: Polym Symp 1966, 15, 409.
40. Berry, G. C. J Chem Phys 1967, 46, 1338.
41. Gennes, P. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, New York, 1979.

42. Fleming, M. C.; Nellis, J. N. Principles of Applied Statistics; Routledge & Kegan Paul: London, 1994.
43. Perry, H. R.; Green, W. D. Perry's Chemical Engineering Handbook, 7th ed.; McGraw-Hill: New York, 1997.
44. Perry, H. R.; Green, W. D. Water: Density at Atmospheric Pressure and Temperatures from 0 to 100 °C. Tables of Standard Handbook Data; Standartov: Moscow, 1978.
45. Washburn, E. W. International Critical Tables of Numerical Data, Physics, Chemistry and Technology; 1st Electronic ed.; Knovel: Norwich, New York, 2003.
46. Wakker, A. Polymer 1991, 32, 279.
47. Güner, A.; Kibarer, G. Eur Polym J 2001, 37, 619.
48. Güner A.; Çatiker, E. J Appl Polym Sci 2001, 82, 948–953.
49. Chew, B.; Couper, A. J Chem Soc-Faraday Transactions I 1976, (72), 382.
50. Boucher, E. A.; Hines, P. M. J Polym Sci Par B: Polym Phys 1976, 14, 2241.
51. Napper, D. H. J Colloid and Interf Sci 1970, 33, 384.
52. Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. Polymer 1976, 17, 685.
53. Barton, A. F. M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters; CRC Press: Boca Raton, Florida, 1991.
54. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989.
55. Wang, K. Y.; Matsuura, T.; Chung, T. S.; Guo, W. F. J Membrane Sci 2004, 240, 67.
56. Desilets, C. P.; Pinkerton, T. C. Appl Radiat Isotopes 1987, 38, 107.
57. Amu, T. C. Polymer 1982, 23, 1775.
58. Boucher, E. A.; Hines, P. M. J Polym Sci Part B: Polym Phys 1978, 16, 501.
59. Bailey, F. E.; Callard, R. W. J Appl Polym Sci 1959, 1, 56.
60. Quesada, M. A. Curr Opin Biotech 1997, 8, 82.
61. Bailey, F. E.; Kucera, J. L.; Imhof, L. G. J Polym Sci 1958, 32(125):517–518.
62. Park, H.; Kim, M. J. Macromolecules 1997, 30, 3849.
63. Sung, J.H. and Lee, D.C. Polymer 2001, 42, 5771.
64. Berek, D.; Tarbajovska, J. J Chromatog A 2002, 976, 27.