Hydration Study of PEG/Water Mixtures by Quasi Elastic Light Scattering, Acoustic and Rheological Measurements

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To study the hydration effect of poly(ethylene glycol) (PEG) and its dependence on the molecular weight, we report viscosity, compressibility, and quasi elastic light-scattering measurements on aqueous solutions of PEG with different mean molecular weight, M_w, at different concentration and temperature values. In particular, ultrasonic technique allows to evaluate the hydration number for PEG samples at different polymerization degrees. The values deduced by ultrasonic technique are then compared with those deduced from viscosity data following the Linow and Philipp's model. PCS technique allows to obtain information on the hydrodynamic radius and its dependence on the polymer M_w at different temperature values.

1. Introduction

Recently, poly(ethylene glycol) (PEG) has received a growing attention not solely from the applicative point of view. The simpleness of its structure and the unusual solubilty in water,[1,2,3] in fact, make it a precious model system[4] for studying the interaction mechanisms of water with hydrophilic surfaces[5] and macromolecules. The chemical structure, $H-(O-CH_2CH_2)_n-OH$, of this synthetic polymer includes two terminal groups, H and OH, which play an important role in short compounds.[6] The similarity of the ether oxygen spacing (2.88 Å) with that of the oxygens in water (2.85 Å) could explain the polymer solubility in water,[6,7] which persists in all proportions at temperatures lower than the boiling point of water.[3] Above this point it presents a miscibility gap that, by diminishing the polymerization degree, n, shifts toward greater temperatures and vanishes[8] for $n < 48$.

The nature and the extent of hydration of PEG in aqueous solution remains uncertain despite numerous investigation by different experimental methods used, including conductometry,[9,10] neutron scattering,[11] differential scanning calorimetry,[12] nuclear magnetic resonance,[13] Raman spectroscopy,[14] and a molecular dynamics study.[15] The aim of the present work is to study the hydration effects of PEG and its dependence on the molecular weight of the polymer at different temperature values. Therefore, we report on viscosity and compressibility measurements of PEG aqueous solutions at different nominal M_w, concentration, and temperature values. In fact, to gain a better understanding of the hydration properties of aqueous solutions of PEG, a calculation of solvation numbers from the change of solution viscosity with solute concentration can be achieved. The ultrasonic technique represents a good tool for investigating the modifications, induced by the solute in the local structure of the solvent that generates changes in the adiabatic compressibility of the system, and that, in turn, allows to evaluate the hydration number. Finally, photon correlation spectroscopy, PCS, technique allows to obtain information on the hydrodynamic radius and on its dependence on the M_w of the polymer at different temperature values.

2. Experimental Section

We examined high purity samples, purchased from Aldrich-Chemie, of PEG with M_w of 200, 400, 600, 1000, and 2000 Da in aqueous solution at different concentrations.

As far as shear viscosity is concerned, measurements were performed on PEG/water solutions at a temperature of 25 °C by means of standard Ubbhelohde viscometers. The viscometers, mounted in a suitable bath, which stabilizes temperature within ±0.02 °C, were chosen with long flow time to minimize the kinetic energy correction. Before measuring viscosity, the samples were stabilized for sufficient time at the given temperature. Experimental data turn out to be reproducible with an indetermination lower than one part per thousand.

Sound velocity measurements were performed on polymeric aqueous solutions at temperatures of 5, 20, 25, 40, and 70 °C by pulse echoes technique using a homemade thermoregulated (±0.01 °C) acoustic interferometer working at a frequency of 3 MHz, purposely projected to ensure accuracy of the velocity experimental measurements better than ±0.1%. The electronic equipment consisted of a standard Matec Inc. apparatus and the measurements were performed using the echoes overlapping method. We have checked, by performing measurements at some values of concentration and for frequencies from 3 to 20 MHz, that the sound velocity is almost frequency-independent in this range indicating that we are not in the presence of possible relaxation processes. Auxiliary density measurements on polymer/water mixtures, necessary to evaluate the shear viscosity of the solutions from the kinematic one and the compressibility coefficient, were performed using a standard picnometer technique.

QELS, quasielastic light scattering, measurements were performed on PEG with M_w, of 400, 600, 1000, 2000, 3400, and 8000 Da in aqueous solutions in the dilute region (weight fraction < 0.03). The measurements were performed by means of PCS technique, using a standard scattering apparatus with a photon-counting optical system and BOOKHAVEN BI-30 correlator to analyze the scattered light.[16,17] As exciting source, the 4880 Å vertically polarized line of an Ar+ laser INNOVA mod.70 working in the power range of 50−400 mW was used. The scattered light, by means of an optical fiber, was detected

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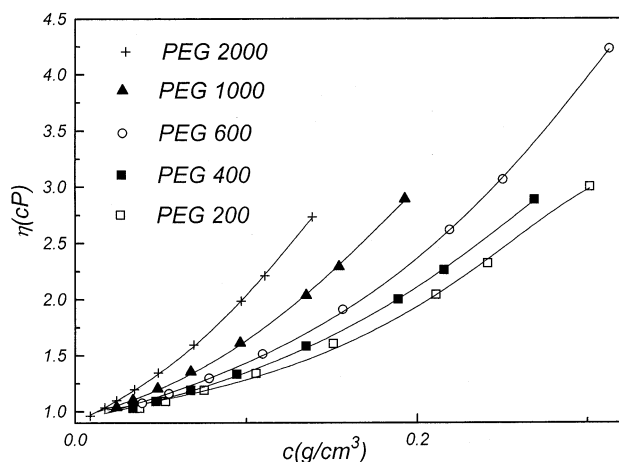
Figure 1. Concentration dependence of viscosity for aqueous solutions of poly(ethylene glycol) at $T = 25$ °C.

Figure 2. Comparison of hydration numbers for poly(ethylene glycol)s of nominal molecular weights: 200, 400, 600, 1000, and 2000 g/mol determined by viscosimetry found in this work and literature values.

in a 90° scattering geometry by a photomultiplier tube connected with the correlator. The scattered intensity was automatically normalized for the incoming beam intensity. Samples were sealed in optical cells and then mounted in an optical thermostat especially built to avoid any unwanted straylight contribution.

The sample high purity, all the systems were carefully subordinate to a filtering procedure in recirculation with an Amicon Millipore filter 0.2 μm of diameter pore size, as well as the optical purity of the sample holder, ensured to collect data with good signal-to-noise ratio and with high reproducibility. Samples were mounted in the thermostat and the investigated temperature range was 20−60 °C with a temperature control better than ±0.02 °C.

3. Results and Discussion

3.1 Viscosity Data. The viscosity data of the PEG/water solutions at different M_w of 200, 400, 600, 1000, and 2000 Da are presented in Figure 1 as a function of concentration, c (grams of solute per cm^3 of solution), at $T = 25$ °C. It can be seen from this figure that the viscosity η of the investigated solutions depends on the average molecular weight of PEG and increases in a nonlinear manner with concentration.

Information on the hydration of solutes can be obtained by a procedure given by Linow and Philipp.[18] Following a relatively simple geometric model based on Einstein's viscosity law,[19] considering the chain molecules as rigid spheres, the relative viscosity, η_r, can be expressed as $\eta_r = \eta/\eta_o = 1 + 2.5\phi$, where η and η_o are the solution and solvent viscosity, respectively, and ϕ is the volume fraction that these spheres occupy. In this way, a calculation of solvation numbers from the change of solution viscosity with solute concentration can be achieved. The specific volume of hydrated solute can be obtained by the following equation:

$$\bar{v}_\eta = \frac{\eta_{sp}}{c}\left(\frac{1}{f + \eta_{sp}}\right) \tag{1}$$

where $\eta_{sp} = (\eta - \eta_0)/\eta_0$ is the specific viscosity, c is the concentration, gram of solute per cm^3 of solution, and $f = 2.5$ is the numerical factor from Einstein equation. As remarked by Linow,[18] the value of specific volume does not depend on the f, which means that for the model used, the shape of the solute particles is not involved in the calculation of the hydration number. On the other hand, from the density of solution, d,
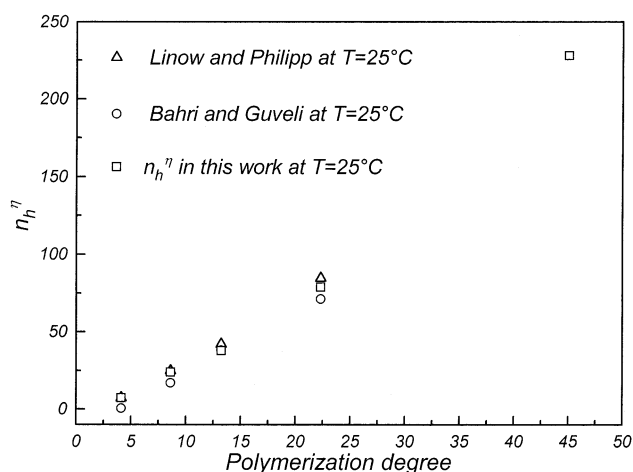
and the density of solvent, $d°$, the apparent specific volume of the solute can be obtained:

$$v_\phi = \frac{1000(d° - d)}{mdd°M_W} + \frac{1}{d} \tag{2}$$

where m is the molality and M_w is the molecular weight of solute. From eq 1 and eq 2, we can evaluate the volume of solvent bound per gram of solute, $v_\eta - v_\phi$, related to the viscosity solute−solvent interaction strength parameter, also called Magazù parameter, $\mathcal{M}$, by the following equation:

$$\mathcal{M} = \frac{\rho(\bar{v}_\eta - \bar{v}_\phi)M_W}{M_{wo}} \tag{3}$$

where M_{wo} is the solvent molecular weight. Thus, all volume changes connected with the hydration process are included. From the extrapolation at infinite dilution of eq 3, the hydration number, n^η_h, that is, the number of moles of bonded water molecules in the inner hydration sphere per mole of solute, can be calculated:

$$n^\eta_h = \lim_{c \to 0} \mathcal{M} \tag{4}$$

The behavior of hydration number for different polymerization degrees is shown in Figure 2. n^η_h increases with the average molecular weight of the solute; the same behavior has been also observed by other authors.[10,20] In the same figure, data from literature are reported for comparison. Hydration numbers evaluated in this work are in good agreement with those reported by Linow[18] and Bahri.[20]

In Figure 3, the number of moles of bonded water per monomer unit of polymer is shown together with the values reported from Linow[18] and Bahri.[20] There is not a full agreement with Bahri's data.[20] However, we consider his data not reliable because the basic hydration of PEG is not satisfied until two water molecules have been added to each −CH$_2$CH$_2$O− group[2].

3.2 Acoustic Data. To get information on the solute−solvent interaction, strength, density, and ultrasonic velocity measurements were performed on polymeric aqueous solutions as a function of concentration at 5, 20, 25, 40, and 70 °C. Through the evaluation of the adiabatic compressibility coefficient by the Lorentz relationship $\beta = 1/\rho v^2$, we are able to get information on the polymeric hydration number. We assume,
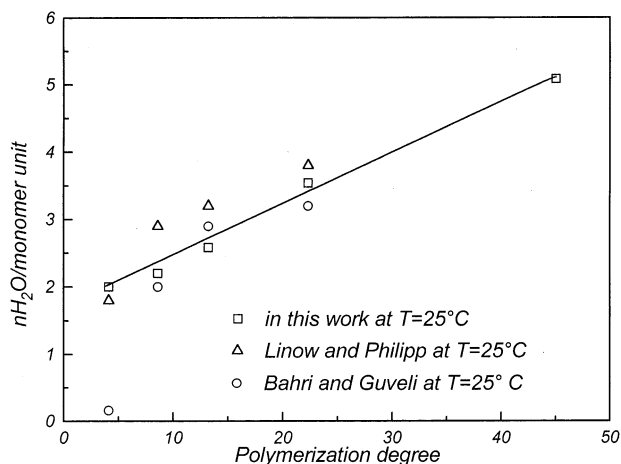
Figure 3. Comparison of average numbers of moles of water bound per mole of monomeric unit of poly(ethylene glycol)s of nominal molecular weights: 200, 400, 600, 1000, and 2000 g/mol detemined by viscometry found in this work and literature values.

following a molecular model,[21] that the volume of the solution V can be partitioned into two contributions: the hydration volume, V_H, where significant interactions between the polymer and water occur, and the bulk water volume, V_w. Following this model, the volume of the solution can be written as $V = n_p V_H + (n_w - n_p n^\beta_H)V_w$, where n_p and n_w are the mole numbers of polymer and of water, respectively. Taking the derivative with respect to pressure at constant entropy, we find:

$$V\beta = - n_p \frac{\partial V_H}{\partial P} + (n_w - np n^\beta_H)V_w\beta_w \tag{5}$$

where $V = ((n_w M_w + n_P M_p)/\rho)$ and ρ is the solution density. Under the hypothesis of negligible compressibility for hydrated units, $(\partial V_H/\partial P) = 0$, we obtain for the hydration number the formula:

$$n^\beta_H = \lim_{n_p \to 0} \frac{n_w V_w\beta_w - V\beta}{n_p V_w\beta_w} \tag{6}$$

where β and β_w are the adiabatic compressibility of the solution and of the water, respectively. It is well known that the main drawback in calculating hydration numbers from ultrasonic measurements is the assumption that the compressibility of polymer together with its closely associated water molecules is negligible.[21] Inherent in this model is the further assumption that the compressibility of water molecules near but not inside the primary hydration shells is the same as that of pure water. Therefore, in general, the hydration number derived in this way can be different from those derived by means of local probes such as neutron scattering[22] or EXAFS, and also because different models are used with the various approaches and critical assumptions underlying these models.

As an example, in Figure 4 and Figure 5 we report density and ultrasonic velocity measurements for PEG 600 aqueous solutions as a function of concentration, c, at different temperatures. Density and sound velocity data of the other PEG samples show similar behavior. In Figure 6, we report the values of the number of bonded water molecules as a function of the polymerization degree at the investigated temperatures. The data can be fitted by straight lines with a slope that corresponds to the number of water molecules bonded with each oxirane group The obtained <abv>n^β_H values at two investigated temperatures
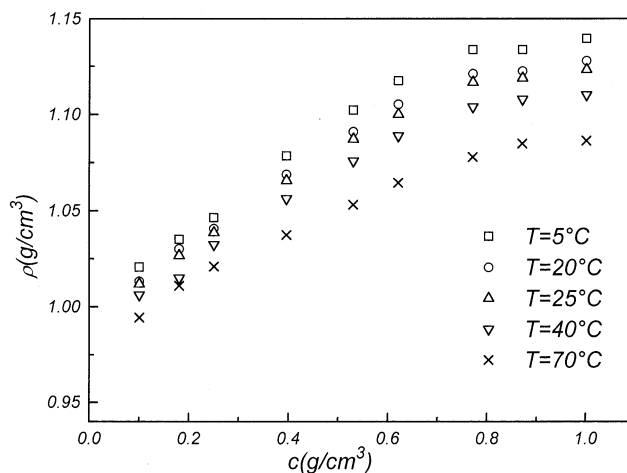

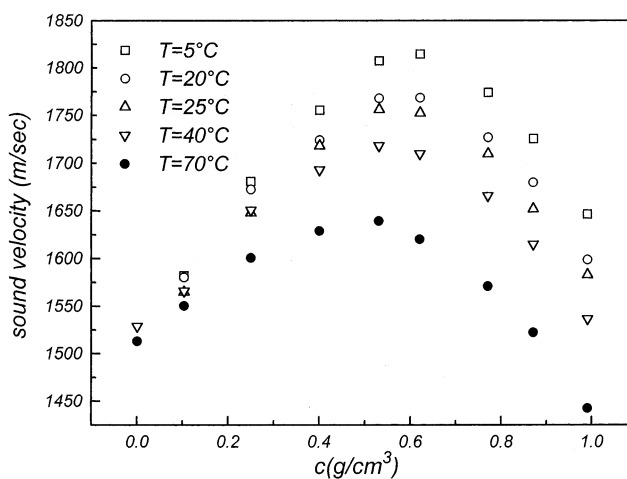**Figure 4.** Density measurements performed in polymeric aqueous solutions of PEG 600 at different temperatures.

Figure 5. Ultrasonic velocity measurements performed in PEG 600 aqueous solutions at different temperatures.
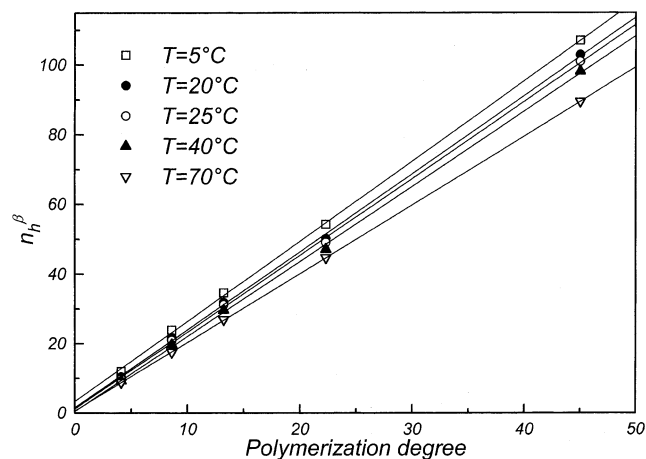

Figure 6. Hydration numbers for poly(ethylene glycol)s aqueous solutions at different temperatures deduced by acoustic data.

are reported in Table 1 together with those obtained from viscosity measurements.

As we have observed for viscosity measurements, also in this case, the hydration number increases with the increasing of polymerization degree. This result can be rationalized by assuming that at low M_w only tightly bound water is associated with the PEG chain. Furthermore, the number of bonded water molecules falls with temperature: in PEG 600, for example,

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TABLE 1: Hydration Numbers Deduced by Acoustic and Viscosity Data

molecular weight	n^{β}_h (5 °C)	n^{β}_h (25 °C)	n^{η}_h (25 °C)
200	12.0	7.4	9.9
400	23.9	21.0	24.0
600	34.6	31.2	38.0
1000	54.3	49.1	78.9
2000	107.0	101.0	228.0

n^{β}_H decreases from 34.6 at $T = 5$ °C to 31.2 at $T = 25$ °C. Considering that PEG 600 is composed of 13 monomeric units, the n values indicate that, at low temperature, more than two water molecules per each oxygen of the oxirane group contribute to hydration. This evidence is due to those water molecules bonded to the terminal OH groups and supports the indication of a partial second hydration shell, dynamical in character. The temperature increase lowers the polymer interaction strength giving rise to the loss of the water molecules not tightly bonded to the polymer. However, even at the highest temperature (70 °C), the two water molecules bonded to the oxygen of the oxirane groups still remain. As we can see from Table 1, this is a general behavior independent from M_w. In fact at low temperatures, it is reasonable to hypothesize that the interaction strength allows water to bond not only to the polymer backbone oxygens but also to the terminal groups or allows water to form a second coordination shell. As the temperature increases, the water molecules weakly bonded to the polymer (such as second water shell) break their bonds.[23]

From the comparison of viscosity and acoustic data, see Table 1, it emerges that hydration numbers determined by viscometry are larger than those determined by acoustic measurements. In particular, the n^{η}_h results are higher than n^{β}_H for the investigated samples; this occurrence could be justified by the different spatial sensitivity of the probe. The ultrasonic probe is more local in respect to viscosity technique, and for the same reason, the obtained values of hydration number result are different from that obtained by other probes, like neutron.[24]

3.3 PCS Data. As far as the light-scattering measurements, we used the photon correlation spectroscopy technique.[25,26] It allows the measure of the time correlation function of the scattered intensity $I_S(Q,t)$:

$$G_2(Q,t) = <I_S(Q,0)I_S(Q,t)> \qquad (7)$$

In particle motion independence, the Siegert's relationship can be applied:

$$G_2(Q,t) = <I(Q)>^2[1+\alpha|G_1(Q,t)|^2] \qquad (8)$$

where α is a constant which depends on the experimental setup, and $G_1(Q,t)$ is the field autocorrelation function.

In the time domain typical for a light-scattering experiment ($\geq 10^{-6}$ s), that is for times between the characteristic viscous flow relaxation and the diffusive relaxation over a scale as great as particle dimension, hydrodynamic interactions can be considered as instantaneous and direct interactions do not affect particle configuration.[27,28] Under these conditions and for diffusing monodisperse spherical scatterers, intensity correlation function decays exponentially, according to

$$G_2(t) = <I(Q)>^2[1+\alpha\exp(-2D_cQ^2t)] \qquad (9)$$

In the limit $Q \rightarrow 0$, the effective diffusion coefficient is identified with the collective-diffusion coefficient, defined by the generalized Stokes−Einstein relation $D_c = (\partial\Pi/\partial c)_T$-
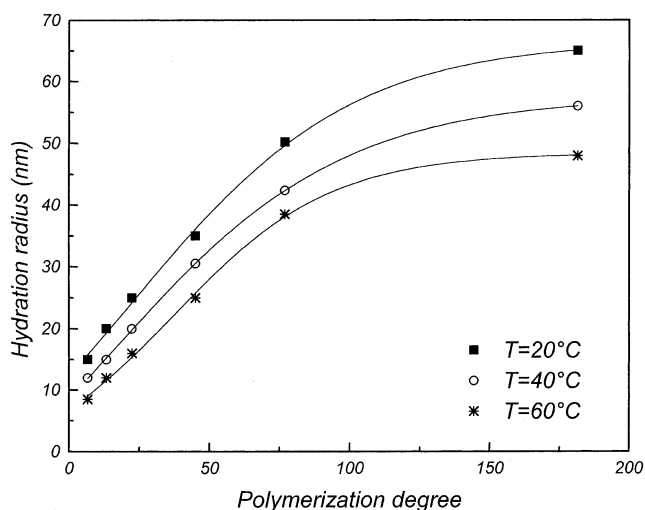

Figure 7. Hydration radius evaluated as a function of the polymerization degree at different temperatures. The continuous lines are guides for the eye.

$(1/\zeta(c))(1 - Vc)$, with $((\partial c/\partial\Pi))_T \propto [S(0)]^{-1}$ osmotic compressibility, ζ is the frictional coefficient, V is molecule partial specific volume, and c is the concentration. The concentration dependence of D_c gives information about intermolecular interactions; in the dilute regime, in fact, the first-order virial expansion can be applied:

$$D_c = D_0(1 + k_Dc) \qquad (10)$$

Sign and magnitude of the slope, k_D, are related, neglecting the contribution of the volume V, to frictional and osmotic compressibility virial coefficients, and hence, to the character of direct and frictional interactions:[29]

$$k_D = 2A_2M - B_\zeta \qquad (11)$$

with A_2 and B_ζ as the second virial coefficient of direct and frictional interactions. In the very diluted limit, the theory of Brownian motion relates the measured D to the self-diffusion coefficient D_0, which is connected to the center of mass motion of the isolated coil and allows to evaluate the hydrodynamic radius, R_H, of the particles by the Einstein−Stokes relation:

$$D_0 = \frac{K_BT}{6\pi\eta R_H} \qquad (12)$$

where η is the viscosity coefficient of the continuous medium.

Now specifically, the hydrodynamic radius extracted by means of the Stokes−Einstein law refers to the diffusive entity which is constituted by the polymeric coil plus the water molecules hydrogen bonded to the polymer chain, molecules which constitute its hydration shell. As we can see in Figure 7, the hydrodynamic radius increases with the increasing of polymerization degree. This result is in good agreement with the hydration number behavior as a function of polymerization degree, evaluated by viscosity measurements.

The hydrodynamic radius evolution can be interpreted by considering that temperature affects the solvent quality: when temperature is raised, the intramolecular interactions increase. Because R_H gives a measure of the diffusing entities dimension together with their solvation shell, its decrease at higher temperature can be enhanced by the thermal motions leading to lower residence times of the solvent molecules in the hydration shell of the polymer; as a consequence, the average

number of the solvent molecules moving together with the polymer will be lower.

4. Concluding Remarks

A calculation of the hydration numbers from the change of solution viscosity with solute concentration and from ultrasonic measurements is presented. The evaluated hydration numbers both from viscosity and acoustic data increase remarkably with the increase of polymerization degree. Furthermore, from acoustic data, we observe that the temperature increase lowers the polymer−water interaction strength; this process gives rise to the loss of the water molecules not tightly bonded to the polymer. From a comparison of the hydration numbers evaluated from acoustic and viscosity data, differences have been evidenced. The apparent discrepancy in experimental determination of hydration number deduced by viscosity and acoustic measurements is intriguing and points toward different definitions of the hydration number. Moreover, attempts are in progress to clarify the probe dependence of this relevant physical parameter that plays an important role in H-bonded system. Finally, concerning light-scattering data, it is well known that from the limit value of the diffusion coefficient at infinite dilution, evaluated by PCS, the hydrodynamic radius of the polymer can be easily calculated through the Stokes−Einstein relationship. These PCS data confirm the behavior of hydration number of the polymer as a function of temperature and polymerization degree, evaluated by acoustic and viscosity measurements, respectively.

The hypothesis that the friction reducer properties of PEO are due to an interfacial layer of PEO between the water flow and the tube would be supported by evidence of aggregation. For this, aggregation behavior of PEO in water, starting from very dilute concentrations and from low up to high M_w's, is both controversial and important. All the presented experimental evidences show that at low concentration water is a good solvent for PEO which behaves like a typical swollen random coil with no evidence aggregation. It clearly emerges that the unaggregate state provides the starting reference point for clarifying many of the friction properties of such systems.

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