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Structuring Effects and Hydration Phenomena in Poly(Ethylene Glycol)/Water Mixtures Investigated by Brillouin Scattering

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Aqueous solutions of poly(ethylene glycol) (PEG) of mean molecular mass of 600 g/mol (PEG600) are investigated by Brillouin scattering technique. At high PEG content, a relaxation phenomenon is observed, which is related to a local rearrangement of the polymer structure where the interaction, via hydrogen bonding, with the solvent molecules plays a role. The obtained values of the relaxation times match the literature data very well for a fast relaxation time revealed by dielectric relaxation measurements in very similar mixtures. The calculated concentration behaviors of the excess adiabatic compressibility turns out in good agreement with the previous findings from ultrasonic measurements at 3 MHz. The observed minimum in the adiabatic compressibility is interpreted as the result of the interaction between water and the EO units of the PEG chain, which results in a structure tighter than that typical of bulk water and of pure PEG600. Such a hypothesis is supported by the observation that volume fraction value of about 0.3 coincides with the concentration value at which full hydration of EO units takes place. The observation that at the same concentration, the polymer coils start to overlap each other further supports the idea that the adiabatic compressibility behavior is monitoring the structural evolution of the mixture. However, similar results are obtained for largely different binary mixture which suggests caution in taking this conclusion too literally. In particular, the hypothesis that the occurrence of an extreme in the excess adiabatic compressibility could be simply originated by statistical effects and that further work is required for disentangling entropic contribution from effects of hetero-association and self-aggregation of one or both the components.

1. Introduction

Investigation of the local structure of aqueous polymeric solutions is largely motivated by the technological point of view, due to a number of applications in several fields: cosmetic, detergent, water treatment, oral care, fibers, textiles and paper production, gardening, controlled drug delivery, food product design, oil industry, and many others. The most widespread use of PEG aqueous solutions is in protein crystallization and cell fusion processes.^{1,2} Although the nature of these processes has not been fully recognized yet, it is surely connected with the very high affinity of PEG for water. One commonly accepted explanation of the origin of the attractive force among colloidal particles (proteins, cells, vesicles) in such ternary systems is the depletion phenomenon.^{3–6} Additional mechanisms underlying PEG-water interaction and driving the observed local structure of the mixture could be crucial in further optimization of protein crystallization conditions.

In addition, investigation of the local structure of water in aqueous polymeric solutions is of scientific relevance, motivated by the interest in the role of hydrogen bonding in the peculiar properties of water and its ability to interact with polymer chains giving rise to a large cluster formation or networking. From this point of view, its simple molecular structure, poly(ethylene glycol), represents a perfect model system for the study of water structuring effects in macromolecular solutions.

Very recent Brillouin scattering measurements of solutions of poly(ethylene glycol) of mean molecular mass of 600 g/mol

(PEG600) in nonpolar solvents^{7,8} have revealed that the concentration dependence of the adiabatic compressibility deviates from the ideal behavior. The observed excess compressibility has been interpreted as originating from some kind of hetero-association, driven by excluded volume interaction and stabilized via electrostatic interaction. This process resulting in the establishment of some coordination between other molecules is masked, at high polymer contents, by the self-association process of PEG molecules. The competition between the two mechanisms is a source of distinction between different concentration regimes. In particular, it was proposed that the observed concentration dependence of the hypersonic velocity reflects a general feature of extended hydrogen bonded networks dissolved in a weakly interacting organic solvent.

Following the idea that adiabatic compressibility can furnish information about the structural modifications induced by concentration changes, it becomes natural to extend the investigation to aqueous polymer solutions. Water molecules are able to develop hydrogen bonding both with the EO units of the polymer chain and with the chain ends. In addition, they are able to develop a dynamical hydrogen bonded network also in bulk water. So a comparison of results from PEG/water solutions and PEG/nonpolar solvent mixtures can be a good test to check if the knowledge of the concentration dependence of the hypersonic velocity (or of the adiabatic compressibility) and absorption can be truly useful in monitoring the establishment of local coordination other than that expected by simple statistical arguments. Furthermore, it is of interest to answer the question if hyper-sounds can work as a right probe able to distinguish different intermolecular interactions.

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In this article, we report results of Brillouin scattering measurements of PEG600/water solutions. The experimental findings are compared against the results of previous ultrasonic measurements of the same systems.⁹

In addition, we will try to extract some information about the possible mechanisms underlying the observed concentration dependence of the hydrogen-bonding connectivity, and we will try to draw an almost general point of view.

2. Experimental Section

2.1. Handling of Data and Results. PEG600 was purchased from Fluka Chemie GmbH and used without any further purification. Solutions of PEG600 in double distilled and deionized water were prepared as equidistant weight fractions, covering the whole concentration range from pure PEG600 to pure solvent. The concentration scale was then recalculated to monomer molar fraction, x' , defined as follows:

$$x' = \frac{n_{\text{OE}}}{n_{\text{OE}} + n_{\text{solv}}} \quad (1)$$

n_{OE} being the mean number of oxyethylene units of PEG chains in solution, and n_{solv} is the number of solvent molecules.

During the Brillouin scattering experiment, the samples were contained in a quartz cell (Hellma, Germany) and placed in a thermostatic holder, whose temperature was controlled to an accuracy of ± 0.1 K. The linearly polarized line ($\lambda = 532$ nm) of a Coherent DPSS 532 laser, working at a mean power of about 100 mW, was used as the probe. In each measurement the VV component of scattered light was collected in a 90° geometry and analyzed by a Sandercock-type (3 + 3)-pass tandem Fabry–Perot interferometer, working at the free spectral range of 15 GHz with a finesse, estimated by the line-width of the elastic line, of about 80.

The refractive index of each sample was measured by a standard Pulfrich refractometer following the usual procedure.^{7,8} The density values were taken from the literature.⁹

The recorded spectra were fitted with the convolution of the experimental resolution with the usual expression:^{10–12}

$$I_{\text{VV}}(\omega) = \frac{\gamma - 1}{\gamma} \cdot \frac{2D_T q^2}{\omega^2 + (D_T q^2)^2} + \frac{1}{\gamma} \left[\frac{\Gamma q^2}{(\omega - \omega_B)^2 + \Gamma_B^2} + \frac{\Gamma q^2}{(\omega + \omega_B)^2 + \Gamma_B^2} \right] + \frac{1}{\gamma} \left[\Gamma + (\gamma - 1)D_T \right] \frac{q^2}{\omega_B} \left[\frac{\omega + \omega_B}{(\omega - \omega_B)^2 + \Gamma q^2} - \frac{\omega - \omega_B}{(\omega - \omega_B)^2 + \Gamma q^2} \right] \quad (2)$$

The first Lorentzian term, characterized by an intensity $(\gamma - 1)/\gamma$ describes the central Rayleigh line, whose half width at half maximum (HWHM) is expressed as $D_T q^2$, being D_T the thermal diffusion coefficient and $q = (4\pi n/\lambda_0) \sin(\theta/2)$ the amplitude of the exchanged wave-vector (λ_0 is the incident wavelength and θ is the scattering angle). The next two terms describe the symmetric contributions to the Brillouin scattering profile (Γq^2 and ω_B are the HWHM and the shift of the Brillouin line, respectively), whereas the last two terms represent the asymmetric contributions to the Brillouin scattering profile, arising from the first moment preservation selection rule.

The values of the parameters $\Gamma_B = \Gamma q^2$ and ω_B obtained by fitting eq 2 to experimental spectra are displayed in Figure 1 as a function of temperature and at different values of the monomer molar fraction, x' . Then, the values of the hypersonic velocity,

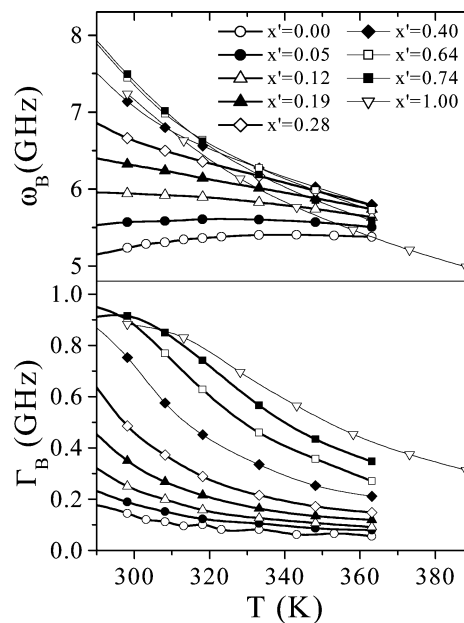


Figure 1. Temperature behavior of Brillouin frequency shift ω_B and half line-width Γ_B for water/PEG600 system. Solid lines are guides for the eye.

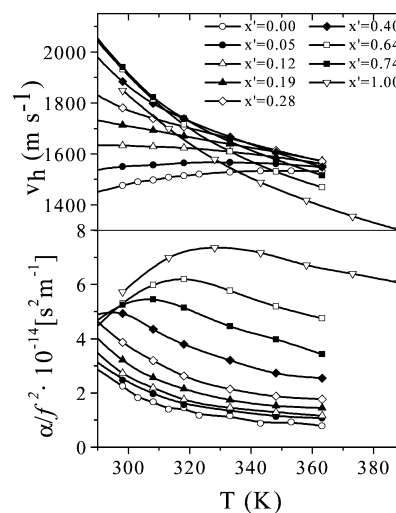


Figure 2. Temperature behaviors of the hyper-sound velocity ν_B , and normalized sound absorption α/f^2 for water/PEG600 system. Solid lines are guides for the eye.

ν_B , and the normalized sound absorption, α/f^2 , were calculated, according to the following relations:

$$\nu_B = \omega_B/q \quad (3)$$

$$\alpha/f^2 = 2\pi\Gamma_B/(\nu_B\omega_B^2) \quad (4)$$

The temperature behaviors of the calculated ν_B and α/f^2 are presented in Figure 2.

3. Viscoelastic Behavior

The observation, at high polymer contents, of a maximum in the normalized absorption data reported in Figure 2, occurring at the same temperature at which the velocity shows an inflection point, can be related to a relaxation process associated with PEG takes place in the picosecond time scale. This relaxation process had been already observed in pure PEG^{7,8} and was associated with some conformational rearrangement of the polymer chains,

triggered by the reorientation of the side groups. The addition of small amounts of water shifts the relaxation frequency toward lower temperatures. A very similar result has been observed for mixtures of PEG600 in different organic solvents^{7,8} as well as in many other moderately viscous polymers or polymeric solutions.^{13–16}

For pure water, the well-known anomalous behavior of the velocity, with a maximum at 345 K, is observed which is related with the collapse, on heating, of the open 3D structure of the H-bonded network. Such a structural rearrangement results in increasing of density with a simultaneous decrease in compressibility.¹⁷ For pure water, at normal pressure and in the stable liquid phase, any relaxation process proceeds on time scales shorter than those explored in a Brillouin scattering experiment.¹⁸ As a consequence, the values of the hypersonic parameters are the same of those obtained in the low-frequency limit. At low concentrations ($x' < 0.3$), any increase in the polymer content causes just a moderate increase in the overall value of the absorption coefficient. This agrees with the hypothesis that the addition of small PEG amounts does not significantly affect the local structure of water, also in the neighborhood of the polymer molecule.^{19–22} In this regime, the conformation of the POE coil changes in such a way that the distance between adjacent oxygen atoms along the polymer chain almost coincides with the O–O distance in pure water. This structural matching is responsible for the increase in the relative population of gauche conformation around the C–C bond of the POE chain in water²¹ leading to the characteristic helical conformation of the whole polymer chain;^{20,21,23} no similar effect has been observed in organic solutions.²⁴

A comparison of the concentration dependencies of the acoustic parameters obtained from the ultrasonic experiment with the hypersonic values can be useful to estimate the concentration range over which the relaxation process significantly influences the dynamics of the water/PEG600 system.

In many ordinary liquids characterized by low shear viscosity, the shear relaxation proceeds on a time scale much faster than that explored in a typical Brillouin scattering experiment. As a consequence, only bulk relaxations can be observed and the velocity of the longitudinal wave, (v), and its absorption coefficient (α) per wavelength (λ) can be written as follows:^{25,26}

$$v^2 = v_0^2 + \frac{1}{\rho} \left(K'_r(\omega) + \frac{4}{3} G_\infty \right) \quad (5)$$

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho v^3} \left[\eta_b(\omega) + \frac{4}{3} \eta_{s,0} \right] = \left(\frac{\alpha}{f^2} \right)_{\text{bulk}} + \left(\frac{\alpha}{f^2} \right)_{\text{classical}} \quad (6)$$

where v_0 is the low-frequency value of sound velocity, $K'_r(\omega)$ is the relaxing storage part of the compressional modulus, G_∞ is the high-frequency value of the rigidity modulus, η_b is the bulk viscosity (related to structural, chemical, conformational, or other processes) and $\eta_{s,0}$ is the steady-state shear viscosity. In this situation the frequency dependencies of the sound velocity and attenuation coefficient are related only to the bulk properties.

In complex liquids (e.g., aqueous polymer solutions) a significant increase in the shear relaxation time, up to frequencies comparable with those analyzed in a Brillouin scattering experiment, permits the observation of viscoelastic behavior.²⁷ In Figure 3, both the experimental and the classic values of hypersonic attenuation coefficients are shown for comparison.

It can be observed that the measured absorption values, higher than the classical ones at concentrations $x' \leq 0.25$, become lower

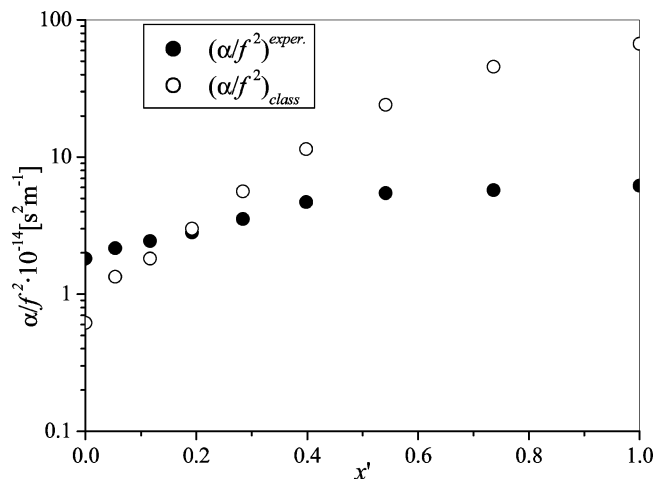


Figure 3. Comparison of experimental and classic values of hypersonic attenuation coefficients.

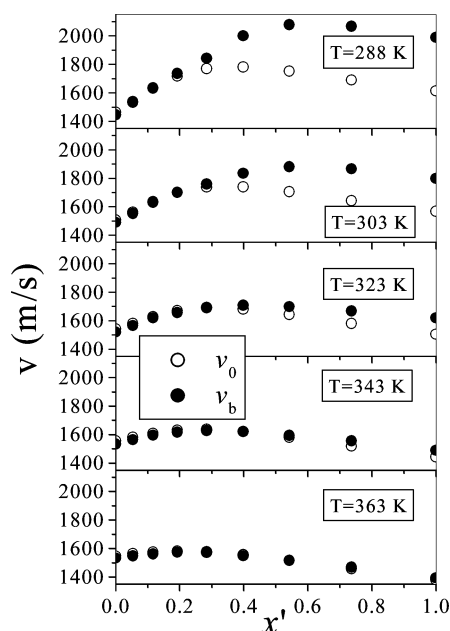


Figure 4. Monomer molar fraction dependence of ultra- (open symbols) and hyper-sound velocities (filled symbols) for different temperatures.

at higher concentrations, indicating that PEG600/H₂O solutions exhibit viscoelastic behavior even in the semidilute region.

Consistent indications follow from Figure 4 showing the monomer molar fraction dependencies for ultra-^{9,28} and hyper-sound velocity at different temperatures. At low concentrations, the low- and high- frequency velocity data coincide, suggesting that, in both cases, the same low-frequency limit sound velocity, v_0 is measured. At high concentrations, however, the hypersonic velocity values are definitely higher than those measured by the ultrasonic probe, with the differences vanishing at $T = 363$ K. It is quite evident that we are observing a relaxation phenomenon from a purely dissipative fluid to an “elastic medium”.

Figure 5 presents the relaxation parameter, defined as $r = v^2/v_0^2$, as a function of the monomer molar fraction. The parameter r is almost equal to 1 irrespective of the solute content at low concentrations. This confirms that any relaxation process observed at $x' > 0.3$ is to be related with a local rearrangement of the polymer structure in which the interaction, via hydrogen bonding, with the solvent molecules plays a role.

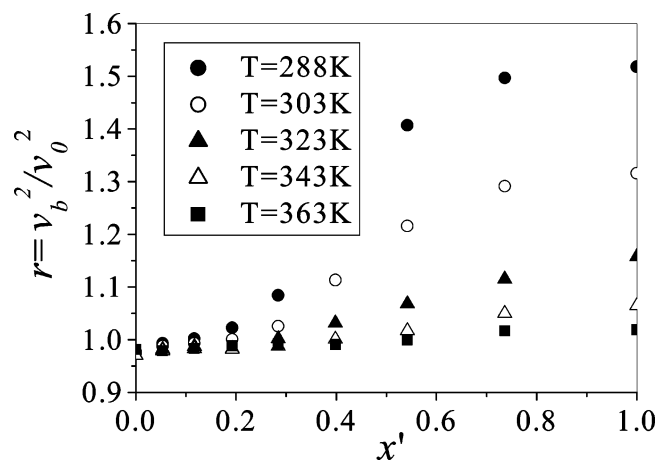


Figure 5. Concentration dependence of the relaxation parameter $r = v_B^2/v_0^2$ for different temperatures.

Following the above considerations, we tried to fit the sound velocity relaxation observed in semidilute and in concentrated solutions with one simple model taking into account a single Debye relaxation process. On this assumption, eqs 8 and 9 can be written as follows:

$$v_B^2(\omega, T) = v_0^2(T) + [v_\infty^2(T) - v_0^2(T)] \frac{\omega^2 \tau^2(T)}{1 + \omega^2 \tau^2(T)}$$

$$\frac{\alpha}{f^2}(\omega, T) = \frac{2\pi^2}{v_B^3(T)} [v_\infty^2(T) - v_0^2(T)] \frac{\tau(T)}{1 + \omega^2 \tau^2(T)} + C \quad (7)$$

where v_∞ represents the high-frequency limit of the sound velocity, τ is the structural relaxation time, and the constant C takes into account for all the nonrelaxing high-frequency contributions. Previous experimental investigations of PEG600 solutions^{7,8} in nonpolar solvents have shown that the assumption of the Vogel–Fulcher–Tamman (VFT) expression (eq 8) for describing the temperature dependence of the structural relaxation time can be a suitable choice to reproduce the experimental data:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (8)$$

In eq 8, τ_0 represents the high-temperature limit of the relaxation time and the temperature T_0 marks the transition from the high-temperature regime, where the assumption of a single relaxation process holds, to the low-temperature regime, where additional relaxation processes start becoming relevant. The parameter D takes into account both enthalpic and entropic contributions, on the assumption that the relaxation time measured is a function of both the system disorder and the energy barrier that cooperatively rearranging groups have to overcome.^{29,30} The results of simultaneous fitting of the experimental hypersonic velocities and normalized absorption with eq 7 are given in Figure 6 while the outcomes of the fitting procedure are summarized in Table 1. The relaxation times at 298 K, calculated from eq 7, are given in Figure 7 for each concentration (full circles).

It should be noticed that the relaxation time obtained for pure PEG600 (~30 ps) looks close to the result from recent complex permittivity measurements on liquid oligo(ethylene glycol)s with a degree of oligomerization ranging from 1 to 6.³¹ In that work the dielectric permittivity spectra have been analyzed in terms

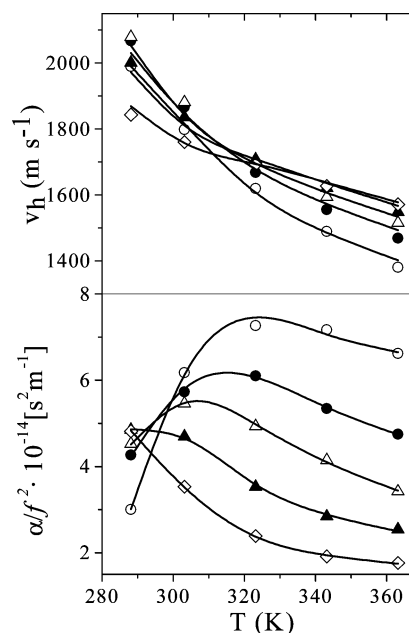


Figure 6. Fitting of experimental data at $x' \geq 0.7$ with eq 7, under assumption of a VFT temperature behavior for the average relaxation time.

TABLE 1: Fitting Parameters Obtained Using Eq 14 Assuming a VFT Temperature Behavior for the Average Relaxation Time^a

x'	τ_0 (ps)	T_0 (K)	D
0.28	0.24	234	1.07
0.40	0.45	227	1.00
0.54	1.06	215	1.02
0.74	1.00	211	1.19
1.00	0.94	219	1.24

^a Estimated uncertainties of T_0 , τ_0 , and D are 15%, 15%, and 5%, respectively.

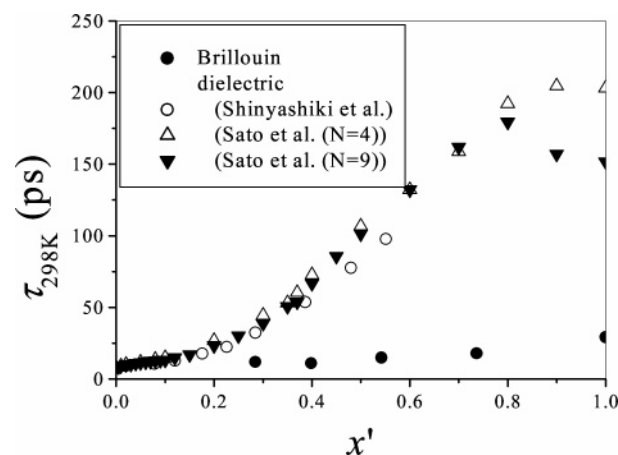


Figure 7. Experimental relaxation times vs monomer mole fraction. Full circles: this work; open circles: dielectric relaxation times from ref 32. Open and filled triangles: water solution of ethylene glycol 200 ($N = 4$) and 400 ($N = 9$) from ref 33.

of the superposition of four distinct Debye processes occurring on different time scales. In particular, one of the four processes, assigned by the authors to the crankshaft motion of free C–O–C groups, relaxes on a time scale of about 20 ps, not too much different from the value measured in our experiment. In addition, one of the other processes, associated with the dynamics of the ether oxygens involved as acceptors in hydrogen bonds, takes

place on a time scale of about 100 ps. This process should be observable in our experiment and the time scale separation should result in the observation of different temperature regimes. In addition, the first process should disappear at concentrations $x' < 0.3$, since at such high water concentrations, no free C—O—C groups should exist. Also, if we are not able to directly observe this second process, its existence can help in rationalizing why the VFT equation turns to fit our data better than the simple Arrhenius law.^{7,8} However, as the authors themselves have pointed out,³¹ the scenario of the four processes should not be taken too literally, since they are not independent of each other.

In addition, some dielectric relaxation measurements on an aqueous solution of PEG with an average molecular weight of 1450³³ and of two oligo(ethylene glycol)s, with molecular weights of 200 and 400,³² revealed a slow process whose relaxation time markedly depends on the monomer concentration (see Figure 7). The existence of two relaxation processes in liquid polymers at high temperatures (above T_g) is an almost general result. Usually the fast process is assigned to some rotation of side-groups while the slow process is attributed to the intermolecular interaction of several monomers (micro-Brownian motion). However, only part of the chains are involved in this type of motion, which can explain why it appears almost independent of the PEG chain length. Within this frame it can be assumed that the effect of decreasing concentration is the same as that of increasing temperature.

Under dilution, the interaction among different chains disappears and only the rotation of the side groups (both free and interacting with water molecules) is observed. Consequently, the value of the parameter T_0 obtained by the VFT model can be related with the crossover temperature (the temperature above which the splitting from the single process behavior to the double relaxation is observed). The values of this parameter increase under dilution, consistent with the above considerations.

The quite weak dipole moment fluctuation connected with the crankshaft motion of the C—O—C group would be responsible for a relatively low value of the dielectric relaxation strength for this process; this observation can help in rationalizing why this fast process is not revealed in dielectric measurements.

4. Excess Compressibility

The observed increase in the hypersonic velocity with the concentration at $x' < 0.2$ corresponds to a decrease in the adiabatic compressibility, $\beta_s = 1/\rho v^2$, in the same concentration range. At higher polymer concentration the sound velocity reaches a maximum (and the compressibility a minimum). A similar result has already been observed in a number of ultrasonic experiments performed in alike systems^{9,28,34–36} and was found to be typical of amphiphile/water mixtures.^{37,38}

It could be interesting to describe the concentration dependence of the adiabatic compressibility in terms of its excess value, $\Delta\beta_s$. In the case of ideal mixing, when we do not take into account for any mixing volume, the adiabatic compressibility of the mixture can be written as follows:

$$\beta_{s,\text{id}} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s = \beta_w + (\beta_p - \beta_w)\phi \quad (9)$$

where β_p and β_w are the values of adiabatic compressibility for pure polymer and water; ϕ is the polymer volume fraction. However, in the present case, the observation of a nonnegligible mixing volume introduces some difficulties in deriving the true values of ϕ . Nevertheless, an attempt can be made to estimate

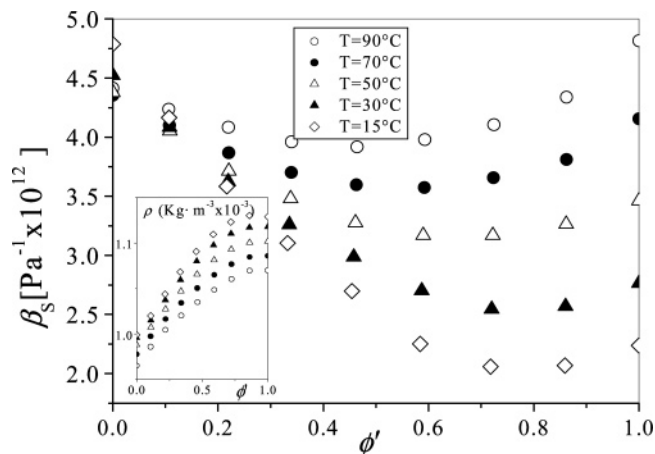


Figure 8. Plot of the adiabatic compressibility as a function of the EO volume fraction, ϕ' , at different temperatures. Inset: ϕ' dependence of the density, at different temperatures.

the corrected values of the monomer unit volume fractions by the values of the solution molar volume, V_M .^{39,40}

$$V_M = \frac{M_M}{\rho} = (1 - x')V_W^0 + x'V_{\text{app}} \quad (10)$$

where x' is the monomer mole fraction, $M_M = (1 - x')M_W + x'M_S$ is the solution molar mass, being M_W and M_S the molar masses of water and EO monomer respectively, V_W^0 is the molar volume of pure water and V_{app} is the apparent molar volume of the effective solute. This quantity does not correspond to a real solute properties, however, in the lack of a suitable thermodynamic model it can be taken as a quantity accounting for all the excess properties of our mixtures.

Then, the volume fractions of the monomer EO units, ϕ' can be calculated as the following:

$$\phi' = \frac{x'V_{\text{app}}}{(1 - x')V_W^0 + x'V_{\text{app}}} \quad (11)$$

In Figure 8 we report the obtained dependence of the adiabatic compressibility by ϕ' , while the inset in the same figure presents the ϕ' dependence of the solution densities. The concentration behavior of the excess adiabatic compressibility at different temperatures explored is illustrated in Figure 9. The results are in good agreement with the previous findings from ultrasonic measurements at 3 MHz,²⁵ despite a difference between the sound frequencies larger than three decades. This suggests that the concentration dependence of β_s (or $\Delta\beta_s$) obtained is only moderately affected by the relaxation process observed in concentrated samples. The main feature observed in the concentration dependence of $\Delta\beta_s$ is a pronounced minimum centered at about $\phi' = 0.6$ at $T = 15^\circ\text{C}$ that moves toward the value $\phi' = 0.5$ as the temperature increases.

This value is very close to that observed in ultrasonic experiment⁹ and interpreted as the indication of the building up of local coordination between water molecules and the two lone pairs of each oxygen atom. Such kind of an interaction results in a structure tighter than that typical of bulk water or pure PEG600.

It is not surprising that the minimum is near the concentration corresponding to the complete hydration of the oxygen atoms in the monomer units. The value of the monomer volume fraction at which the minimum is observed corresponds to a monomer molar fraction of about 0.3, that means about 2.3 water

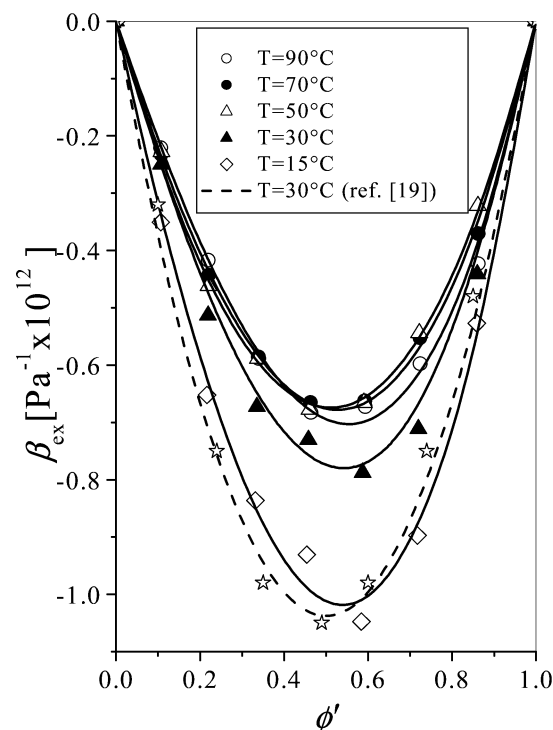


Figure 9. Excess adiabatic compressibility as a function of monomer volume fraction. Solid lines are the fits with Redlich–Kister equation.

molecules per each EO unit, which is very close to the value expected taking into account that two water molecules can hydrate to the oxygen atom of each oxirane group of the polymeric chain. Moreover, an additional effect can play a role in determining some significant change in the structure and dynamics of the system at about the same concentration.

Using the literature density values⁹ and taking for the gyration radius of the polymer coil the value $R_g = 8.1 \text{ \AA}$ from refs 20 and 41, the value of the overlap molar concentration, c^* , can be estimated from the following relation:⁴²

$$c^* = \frac{M_W}{\frac{4}{3}N_A\pi R_g^3} \quad (12)$$

where M_W denotes the molecular weight of the polymer and N_A is the Avogadro's number. We estimated a value of c^* of about 0.5, to which a monomer molar fraction $\phi' \approx 0.28$ corresponds, very close to the value at which the minimum in the excess compressibility is observed. In summary, we observe that almost the same concentration corresponds to the situation where adjacent polymeric chains start to overlap and where full hydration of the PEG chain occurs. The hypothesis of a local structure very close to the one typical of gels or cross-linked polymers has been already advanced to interpret intra-diffusion⁴³ and volumetric⁴⁴ results for concentrated water/PEG solutions.

The study of the process of network formation can be of paramount relevance in understanding the mechanisms of protein crystallization, one of the more common utilizations of PEG.^{1,2} The most popular technique for particle aggregation makes use of aqueous PEG solutions. It is observed that the polymer concentration required to drive proteins from the solution decreases when the PEG chain length increases,⁶ which is not surprising when one assumes that the best aggregation conditions are met near the overlap concentration for the polymer coils or when the polymeric chain is fully hydrated. It is probable that the two conditions take place simultaneously, and this would

mean that particle aggregation becomes more efficient in the presence of an extended hydrogen bonded network.

This indicates that optimization of protein crystallization conditions could require, besides depletion interactions, consideration of the networking effects.

4. An alternative Interpretation of Excess Compressibility

An extreme in the concentration dependence of the excess compressibility has been already observed in solutions of PEG-600 in non interacting or weakly interacting solvents^{7,8} and has been related with the formation of statistical local hetero-correlations between the solute and the solvent. On this basis, the concentration dependence of the sound velocity was analyzed under the assumption of existence of three average local environments: pure solvent, pure solute, and local volumes where solvent and solute molecules coexist.^{45,46} This appealing picture proved capable of qualitative reproduction of a number of situations.

In this work, the observation of similar result in a totally different situation would suggest to reconsider the basic assumptions of the model. In other words, since similar concentration effects are observed both in weakly interacting mixtures and in solutions where hydrogen bonding interactions dominates, we are faced with the problem of finding an answer to the question if the observation of an extreme in an excess quantity can be safely interpreted as the indication of some structuring effect or it is more simply to be related with the dependence of the mixing entropy by the concentration.

A possible answer can be that eq 9 is too crude an approximation for modeling very simple binary mixtures. The problem is that eq 9 describes the mixture as a volume average of the two components. Also, in the presence of noninteracting systems, we can imagine that a microscopic volume in which molecules of the two components come in close contact can be characterized by local properties that cannot be simply related to the average properties of the constituents. It is not hard to imagine that, also in an almost ideal binary mixture, the difference between the energetic content of a local configuration where like molecules occupy contiguous sites and the one in which other molecules are in close contact can be small but finite. If the mixture is randomly distributed, in condition of equilibrium (maximum of the configurational entropy) the probability, C , of finding two molecules of different species in close contact will be given by the product of their respective volume fractions

$$C = \phi \cdot (1 - \phi) \quad (10)$$

As a consequence, the concentration dependence of adiabatic compressibility should make allowance for a third-term taking into account the local compressibility corresponding to the above-described local configuration, whose weight will be given by the probability C . This should be an almost general result. Different situations are expected only in the presence of deviations from random mixing, i.e., in the presence of a self-association process of one (or both) of the two components resulting in a lower equilibrium configuration entropy (micro-phase separation).

Of course, hetero-aggregation would play a role too, mainly in determining the sign of the excess compressibility. In the present case, the building up of an extended hydrogen bonded network in which both water and PEG molecules are involved, seems to be the main process responsible for the observed increase of the system rigidity, resulting in a negative excess adiabatic compressibility.

5. Concluding Remarks

Our experimental results suggest that the current ideas that the concentration dependence of the excess compressibility in binary systems can be taken as an indication of some structural rearrangement should be, at least partially, revised. In particular, it has been proposed that, in the absence of any hetero-association, an excess compressibility has to be observed, due to local coordination simply originated by statistical effects. On this basis, it is not clear if the study of the shape of excess compressibility can distinguish between statistical correlation, hetero-association, and self-association.

The adequacy of this idea is supported by an inspection of the ultrasonic data (stars) presented in Figure 9 together with the result of the fitting with eq 10 (weighted by an appropriate multiplicative parameter). Also the high-frequency data at temperatures higher than 50 °C are well-reproduced by the same equation. In contrast, the hypersonic data at lower temperatures clearly show some deviation from the proposed behavior on the high PEG concentration side. Also, in such a situation, it is possible to fit the experimental data assuming that the contribution, β_h , to adiabatic compressibility originated from sample volumes containing PEG units interacting with water molecules could be concentration dependent. This contribution should be weighted by the probability C . Under such an assumption, the excess adiabatic compressibility is as follows:

$$\Delta\beta_s = \beta_h(\phi') \cdot C(\phi') \quad (11)$$

It should be noticed that the above equation becomes equivalent to the Redlich–Kister equation

$$\Delta\beta_s(\phi) = \phi_1\phi_2 \sum_n B_n(\phi_1 - \phi_2)^n = \phi'(1 - \phi') \sum_n B_n(1 - 2\phi')^n \quad (12)$$

if we assume that the quantity $\beta_h(\phi')$ can be approximated in terms of a power series of the quantity $(\phi_1 - \phi_2)$, ϕ_1 and ϕ_2 being the volume fractions of the two components (that in our case, reduce to the quantities ϕ' and $1 - \phi'$ respectively). The continuous line in Figure 9 represents the results of fitting the experimental data with the first-order polynomials eq 12.

In our case, the observed deviation from the simpler expression given by eq 11 should not be imagined as originating from some dependence of the local structure on concentration, but is simply related to the fact that, on the polymer rich side, a relaxation process takes place which affects the high concentration behavior of the excess compressibility. This process moves toward lower temperatures upon dilution. With increasing temperature, the relaxation moves toward higher frequencies and the same concentration dependence observed in the ultrasonic experiment is retrieved. However, the fact that, at temperatures higher than 50 °C, the excess compressibility (obtained both from ultra- and hyper-sonic measurements) perfectly fits with eq 11 does not imply that in this temperature regime self-association does not take place. It could be that its effect is masked by that of hetero-association. Further work is required to compare this result with those obtained for weakly interacting binary mixtures in order to find a way to disentangle self-association and hetero-association contributions.

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