

Evidences of Nonideal Mixing in Poly(ethylene Glycol)/Organic Solvent Mixtures by Brillouin Scattering

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The concentration dependence of the hypersonic properties of solutions of poly(ethylene glycol) of mean molecular mass 600 g/mol (PEG600) in benzene and toluene has been investigated by Brillouin scattering. The two solvents are very similar in structure and chemical properties, but while benzene is nonpolar, toluene possess a modest dipole. In both solvents a high-frequency relaxation process has been observed at high concentrations which has been assigned to conformational rearrangements of the polymeric chains, triggered by reorientation of the side groups. In both cases, the concentration dependence of the adiabatic compressibility deviates significantly from linearity, indicating the existence of nonideal mixing phenomena driven by aggregation processes taking place in the systems. However, there is no temperature dependence for solutions of PEG600 in benzene; on the contrary, the results obtained for solutions of PEG600 in toluene are noticeably dependent on the temperature. The comparison of the experimental data with the results of previous experiments on similar systems allows a general picture for weakly interacting mixtures of hydrogen-bonded systems and organic solvents to be developed. In particular, in the presence of a nonpolar solvent molecule the local structure of the mixture is dominated by solute self-association processes and any resulting solute–solvent correlation is barely induced by excluded volume effects. At high enough dilution the self-aggregation of solute molecules produces a variety of new local topologies that cannot be observed in bulk solute, and as a consequence, the concentration evolution of the system is too rich to be described in terms of a linear combination of a few components over the whole concentration range. The situation seems to be simpler for the polar toluene solvent molecules, where a three-component model seems able to fit the experimental concentration dependence of the hypersonic velocity. This result is interpreted to imply that the interaction between the solvent dipoles and the active sites of the solute produces a relatively stable heterocoordination, while the relevance of self-association is partially reduced.

1. Introduction

In the last few decades, the continuing quest for the engineering of new polymeric materials and devices has drawn a growing interest toward the investigation of the structural and dynamical properties of molten polymers and polymer solutions. In particular, poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) are of great industrial and biomedical relevance due to their high solubility in a wide number of organic solvents as well as in water.¹ Their high solubility is a consequence of the structure of the polymer chain, along which hydrophobic monomer units are arranged together with hydrophilic oxygen atoms. This type of structure means that there are a number of active sites available for both inter- and intramolecular hydrogen bonds.² While from the biomedical point of view the main interest is devoted to aqueous solutions, many industrially interesting properties come from the dynamical properties of the chain, responsible both for the transport mechanisms through the polymer network and for the self-aggregation processes among the polymer chains that drive the long-range order of the polymer network. The conformational dynamics of the

polymer chain are known to be solvent sensitive.^{2–11} In the presence of a noninteracting or moderately interacting solvent, any change in the local density of the polymeric component influences the localized fast motions of the polymeric chains.^{12–14} In an attempt to separate the effects of the change in the local density of the hydrogen bonds from those induced by solvent–polymer interaction, we recently performed a Brillouin scattering investigation on solutions of poly(ethylene glycol) with mean molecular mass of 600 g/mol (PEG600) in CCl₄.¹⁵ Carbon tetrachloride is a good candidate for this kind of investigation due to its intrinsically nonpolar nature. A fast relaxation process was detected and assigned to conformational rearrangements of the polymeric chains, triggered by the reorientation of the side groups. The concentration dependence of the hypersonic velocity was interpreted assuming the existence of different concentration regimes, originated by the competition between the self-association process of the polymer chains (dominant at high polymer contents) and the tendency of their active sites to coordinate with the solvent molecules (this becoming relevant in the semidiluted region). Such heteroassociation should be promoted through electrostatic interaction in a fashion very similar to what has been recently observed for methanol/CCl₄ mixtures¹⁶ and theoretically supported by some numerical results from *ab initio* molecular orbital simulations in acetone/CCl₄ clusters.^{17,18}

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With the aim of obtaining further insights on the role played by the interaction between the solvent and the polymer, we present here the results from a new Brillouin scattering experiment on solutions of PEG600 in benzene and toluene. These two solvent molecules are very similar, the main difference being that while benzene is nonpolar a small permanent dipole moment (originating from the presence of the methyl group), characterizes the toluene molecule. Furthermore, the role played by quadrupolar forces on the structure of liquid benzene was pointed out several years ago,^{19,20,21} and this makes benzene a very good candidate for a comparison with our previous results on PEG600/CCl₄ mixtures.¹⁵

The close similarity in the structure and size of the two molecules would suggest that volume effects play almost the same role in both cases. This assumption seems to be supported by the observed close similarity between the results obtained for solutions of PEG600 in benzene and in carbon tetrachloride¹⁵ (whose molar volume is intermediate between benzene and toluene). We propose that the observed concentration dependence of the hypersonic velocity reflects a general feature of an extended hydrogen bonded network dissolved in different organic solvents.

The different behavior observed in PEG600/toluene solutions suggests that, in this case, dipole–dipole interactions could play a nonnegligible role in determining the structural evolution of the system with the concentration.

2. Experimental Section, Data Treatment, and Results

PEG of mean molecular mass 600 g/mol, benzene and toluene were obtained from Fluka Chemie GmbH, BDH Chemicals, Ltd., and POCh Gliwice-Poland, respectively. The solvents were distilled before solution preparation, and PEG was used without any further purification procedure. Solutions of PEG600 in benzene and toluene 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

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

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

The refractive index of each solution was measured with a standard Pulfrich refractometer at four different wavelengths and in the temperature range $288 \leq T \leq 325$ K. The values of refractive index at $\lambda = 532$ nm were obtained by fitting the Cauchy equation to the experimental data.²² The density values in the $288 \leq T \leq 325$ K temperature range were obtained using an Anton Paar DMA38 density meter. The values of the index of refraction and density at higher temperatures were estimated by linear extrapolation of the experimental data. The obtained concentration dependencies of density and refractive index are presented in Figure 1.

An inspection of Figure 1 suggests that in both mixtures the concentration dependence of the density deviates only moderately from the ideal case (the deviations from linearity in the ρ vs volume fraction, ϕ , plots are within 0.5%).

In the Brillouin scattering experiment the samples were contained in square quartz cells (Hellma, Germany) placed in a thermostatic holder, whose temperature was controlled to the precision of ± 0.1 K. The linearly polarized line ($\lambda = 532$ nm) of a Coherent DPSS 532 laser, with a mean power of about 100 mW, was used as the probe. In each measurement the VV

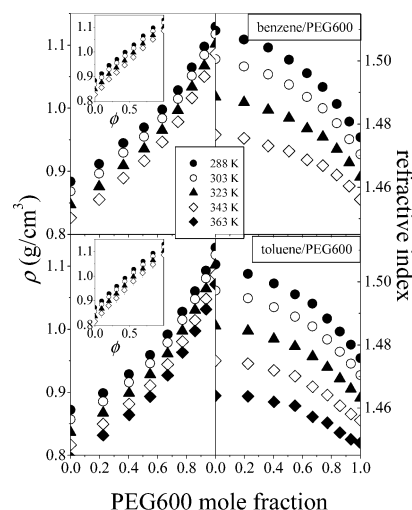


Figure 1. Monomer mole fraction dependencies of density and refractive index for both systems investigated: PEG600/benzene (up) and PEG600/toluene (down). Insets report the volume fraction behaviors of the corresponding densities.

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 free spectral range of 15 GHz with a finesse, estimated by the line-width of the elastic line, of about 80.

In Figure 2, we report some of the Brillouin spectra from the two sets of samples, obtained at $T = 333$ K and at different values of the monomer molar fraction.

The recorded spectra were fitted with the usual expression^{23,24}

$$I_{\text{VV}}(\omega) = \frac{A_{\text{R}}\Gamma_{\text{R}}}{\omega^2 + \Gamma_{\text{R}}^2} + A_{\text{B}} \left[\frac{\Gamma_{\text{B}}}{[\omega - \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}]^2 + \Gamma_{\text{B}}^2} + \frac{\Gamma_{\text{B}}}{[\omega + \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}]^2 + \Gamma_{\text{B}}^2} \right] + \frac{A_{\text{B}}\Gamma_{\text{B}}}{\sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}} \left[\frac{\omega + \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}}{[\omega + \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}]^2 + \Gamma_{\text{B}}^2} - \frac{\omega - \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}}{[\omega - \sqrt{\omega_{\text{B}}^2 - \Gamma_{\text{B}}^2}]^2 + \Gamma_{\text{B}}^2} \right] \quad (2)$$

The first term in the above equation describes the central Rayleigh line, characterized by its half width at half maximum (HWHM), Γ_{R} , and by its intensity, A_{R} . The next two terms describe the symmetric contributions to the Brillouin scattering profile (A_{B} , Γ_{B} , and ω_{B} are the intensity, the HWHM, and shift of the Brillouin line, respectively), whereas the last two terms represent the asymmetric contributions, arising from the first moment preservation selection rule. The values of the parameters Γ_{B} and ω_{B} obtained by fitting eq 2 to experimental spectra are reported in Figure 3 as a function of the temperature and at different values of the monomer molar fraction, x' . For pure solvents, both the Brillouin frequency shift and the line-width change linearly with temperature, suggesting that any possible temperature-dependent relaxation process takes place outside the investigated frequency range.

The obtained values of the fitting parameters, together with the measured refractive indices and densities, were used to calculate the values of the hypersonic velocity, v_{B} , the adiabatic

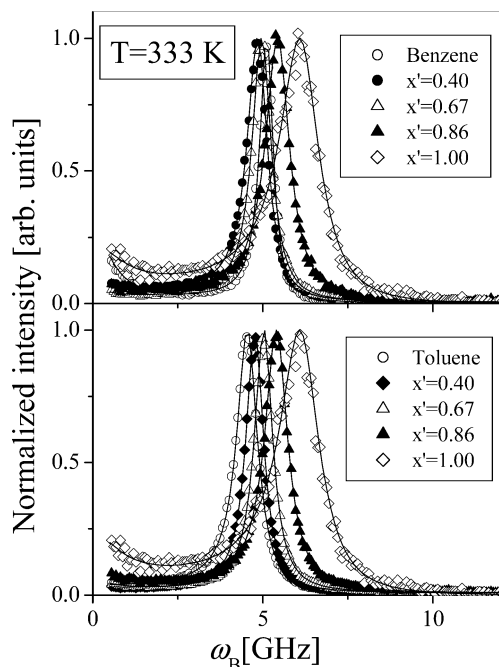


Figure 2. Normalized anti-Stokes side of VV spectra for selected solutions measured at $T = 333$ K for PEG600/benzene (top) and PEG600/toluene (bottom). Solid lines are the results of fitting with eq 2. Concentrations are expressed in monomer molar fraction.

compressibility β_s , and the normalized sound absorption, α/f^2 , according to the relations^{23,24}

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

$$\beta_s = 1/\rho\nu_B^2 \quad (4)$$

$$\alpha/f^2 = 2\pi\Gamma_B/(\nu_B\omega_B^2) \quad (5)$$

where $q = (4\pi n/\lambda_0) \sin(\theta/2)$ is the amplitude of the exchanged wave vector, λ_0 is the incident wavelength, and θ is the scattering angle. The temperature behavior of the calculated ν_B and α/f^2 are presented in Figure 4.

For neat PEG600 the occurrence of a maximum in the absorption at the same temperature at which the hypersonic velocity exhibits an inflection point is a clear evidence for a relaxation process taking place in pure polymer, which has been already observed and discussed.¹⁵ The addition of a small amount of solvent (no matter which, benzene or toluene) results in a shift of the relaxation frequency toward lower temperatures, in close analogy to the behavior recently observed for PEG600/ CCl_4 mixtures.¹⁵

3. Discussion

As a first point, we have to discuss the possible contributions to the Brillouin spectra from relaxation processes taking place in the bulk solvents.

Benzene and toluene molecules are chemically very similar. However, toluene is characterized by a nonzero dipole moment arising from the asymmetric methyl group. On this basis, one can expect that electrostatic interactions could drive some differences in the local structure and dynamics of toluene respect to benzene. In addition, we cannot exclude that the differences in shape and in the internal degrees of freedom could play a role too. For the same reasons, different effects of the two solvents on the local arrangement and dynamics of the solute can be hypothesized.

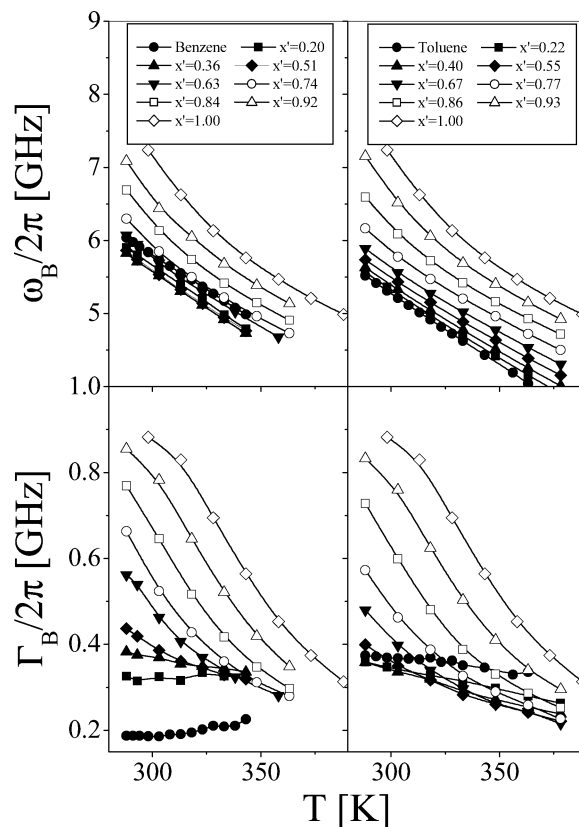


Figure 3. Temperature behavior of Brillouin frequency shift ω_B and half line width Γ_B for PEG600/benzene (left) and PEG600/toluene (right). Solid lines are guides for the eye.

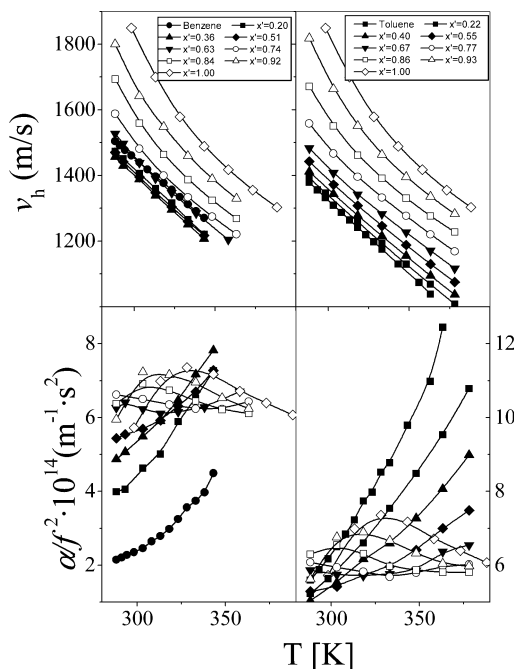


Figure 4. Temperature behavior of hypersonic velocity ν_B and normalized sound absorption α/f^2 for PEG600/benzene (left) and PEG600/toluene (right). Solid lines are guides for eye.

In the case of liquid benzene, both theoretical²⁵ and experimental indications²⁶ for the existence of some local correlations allow to hypothesize some structural relaxation processes, taking place on a time scale comparable with the lifetime of the local cage. This idea agrees with the results from molecular dynamics simulation and depolarized Rayleigh scattering measurements,

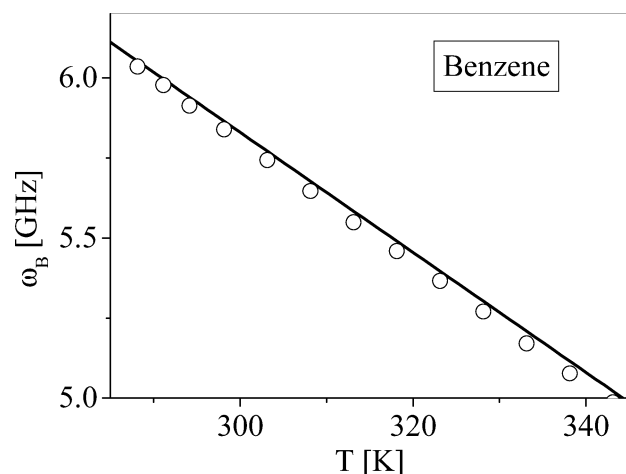


Figure 5. Temperature dependence of the Brillouin shift for benzene. Circles: this work. Continuous line represents the experimental behavior reported in ref 31, scaled taking into account for the difference in the exchanged wave vector.

performed both in benzene and toluene,²⁷ which revealed a double relaxation process taking place on time scales of about 1 and 10 ps. In addition, some vibrational motions (e.g., the breathing motion of the ring or the bending around the C atoms) could relax on time scales not much faster than those explored in a typical Brillouin experiment.²⁵

A few years ago, some experimental results were reported that suggested the presence of a relaxation process or a structural transition involving different local arrangements of the molecules in liquid benzene.^{28–30} In particular, the observation of anomalous temperature behaviors observed both by Brillouin³⁰ and depolarized light scattering³¹ were interpreted on the basis of a competition among different orientational packing arrangements, taking place over a narrow temperature range (27–50 °C).

However, later stimulated Brillouin gain spectroscopy³² and depolarized light scattering measurements³³ sound no evidence of this behavior.

Our experimental Brillouin shift values fall on a straight line within the experimental error when plotted as a function of temperature (see Figure 3), and the velocity data do the same (see Figure 4). In addition, our values of the Brillouin frequencies for benzene agree within 1.5% with the results of ref 30, after correction for different values of the exchanged wave vector (see Figure 5). Thus, we also see no indication of the anomalous behavior reported previously.

Looking at toluene, recent Brillouin scattering data³⁴ have been modeled on the basis of the Mountain's theory,³⁵ and the experimental velocity data have been found compatible with a single relaxation process, which is thought to be related to the vibrational relaxation of all but the lowest mode. However, also in this case, our experimental hypersonic velocity data, reported in Figure 6 remain on a straight line when plotted as a function of temperature, suggesting that no relaxation process takes place over the investigated frequency range.

In the same figure, we show, for the sake of comparison, some literature results of hypersonic and ultrasonic velocities.³⁶ In particular, it should be noticed the very good agreement between the different sets of hypersonic data despite a difference of about 18% in the value of the exchanged wave vector, due to the different laser lines used as the probes.

In addition, it appears that the hypersonic velocity value is almost coincident with the low frequency one, with the difference increasing slightly with decreasing *T*. This occurrence

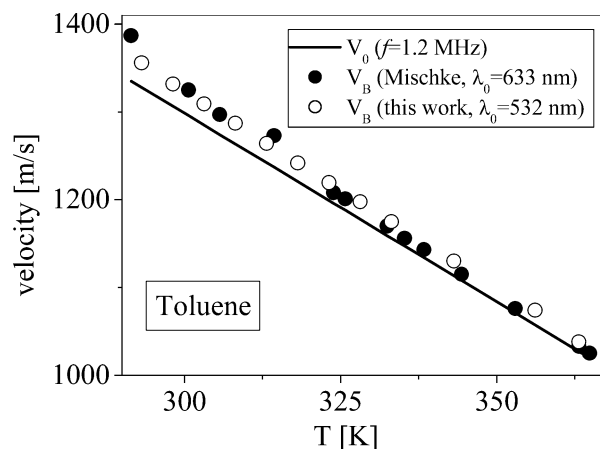


Figure 6. Temperature dependence of the Brillouin shift for toluene. Open circles: this work. Continuous line and solid circles represent the ultrasonic and hypersonic data from ref 34.

would suggest that any relaxation process taking place in liquid toluene occurs on a time scale shorter than that investigated here.

In summary, the results discussed above lead us to conclude that the hypersonic velocities measured in the neat solvents are to be taken as low-frequency data since any relaxation process takes place at higher frequencies. On this basis, we are confident that any relaxation process observed in our mixtures should be connected with a structural relaxation of the solute component or with some change in the local structure of the solvent induced by the interaction with PEG600.

In particular, the maximum in the normalized absorption of the pure PEG600, occurring at the same temperature where v_B exhibits an inflection point, is a common result for many moderately viscous polymers or for polymeric solutions.^{37–40} It is usually assigned to conformational rearrangements of the polymeric chains, triggered by reorientation of the side groups. On dilution, the same relaxation process shifts toward lower temperatures (i.e., toward higher frequencies). The relaxation frequency is experimentally observable down to a PEG600 dilution $x' \approx 0.8$, after which the dynamics become too fast to be investigated by Brillouin scattering. A very similar behavior has been recently observed in PEG600/CCl₄¹⁵ mixtures and has been analyzed with different theoretical models.^{12,38–41} In particular, we have assumed as is the case for many viscous liquids that the relaxation process can be suitably described in terms of a single relaxation time and accordingly we adopted the following expressions for the hypersonic sound velocity and normalized absorption

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

$$\frac{\alpha}{f^2}(\omega, T) = \frac{2\pi^2}{v_B^3(T)} (v_\infty^2(T) - v_0^2(T)) \frac{\tau^2(T)}{1 + \tau^2(T)} + C \quad (6)$$

where v_0 and v_∞ are the low- and high-frequency limit values of the sound velocity, τ is the structural relaxation time, and C is a constant term accounting for all the nonrelaxing high-frequency contributions. Following the same procedure outlined in ref 15, we have fitted our experimental data with two different models for the temperature behavior of the relaxation time, namely, simple Arrhenius, eq 7, or Vogel–Fulcher–Tamman (VFT), eq 8

$$\tau = \tau_0 \exp\left(\frac{E}{R_g T}\right) \quad (7)$$

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

In the first case, E represents the activation energy of the relevant relaxation process and R_g is the universal gas constant. In eq 8, T_0 represents the temperature at which a structural arrest takes place and the relaxation time diverges and D is a coefficient that takes into account both enthalpic and entropic contributions, under the assumption that the structural relaxation time is a function both of the system disorder (configurational entropy) and of the energy barrier that cooperatively rearranging groups have to pass over.^{42,43} In fitting the experimental data with eq 6, the low-frequency velocity data for pure PEG600 have been taken from literature,⁴⁴ the slopes of v_h data have been fixed at the same value of pure PEG600, and the constant term has been taken as an adjustable parameter, following the same procedure described elsewhere.¹⁵ The results of fitting the experimental data with eq 8, under the two different assumptions are summarized in Tables 1 and 2, respectively.

We notice that equally acceptable fits can be obtained with a relatively large range of values of the fitting parameters varying within relatively large intervals. However, the values of the parameters (E and τ° under the adoption of eq 7, D , and τ° under the adoption of eq 8) are not statistically independent, and we find that the resulting value of the relaxation time in fact varies within a comparatively narrower interval ($\Delta\tau$ turns out to be less than 7% under the adoption of the Arrhenius law and 5% under adoption of VFT equation).

This means that $\tau(T)$ is well estimated by the actual fitting function, despite the apparently poor sensitivity performance of the procedure with respect to each of the fitting parameters taken singularly.

In Figure 7, the results from the two fitting procedures are compared, both for PEG600/benzene and PEG600/toluene mixtures. It appears that while both models fit the experimental velocity data well in the high-temperature regimes (above the relaxation frequency) the simple Arrhenius model proves less adequate at lower temperatures. A similar result has been obtained for CCl₄/PEG600 mixtures,¹⁵ where the observed relaxation process has been assigned to the conformational rearrangement of the polymeric chains, already observed in pure PEG,^{12,37,45} that becomes faster on dilution. Keeping in mind that the structure of molten PEG is dominated by hydrogen-bonding interactions among neighboring chains, the assumption of a single relaxation time is probably too crude approximation. Thus, the obtained values for τ should be interpreted just as the average values of (narrow) distributions of relaxation times, corresponding to distributions of different local topologies originated by the kinetic equilibrium between the breaking and reforming mechanisms of the hydrogen bonding. Such a picture implies that, under a temperature change, any variation of the above-described kinetic equilibrium will be reflected in a variation of both the width and the average value of the distribution of relaxation times. For these reasons the VFT equation turns out to be a better approximation.

At enough high PEG concentration, the hydrogen-bonded network tends to preserve its connectivity. The main effect of adding small quantities of solvent (either benzene or toluene) to bulk PEG is to force the polymer network to reorganize into less compact configurations in order to make room for the

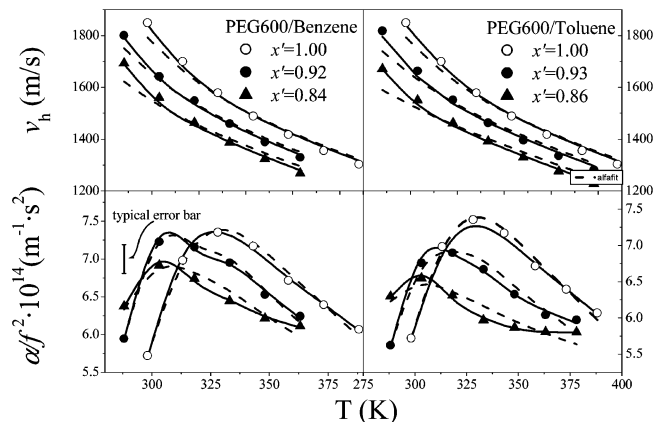


Figure 7. Comparison between the results of fitting the experimental data with eq 6, under the assumption of a simple Arrhenius behavior (dashed lines) or a VFT law (continuous line) for the relaxation time (the experimental error bars for v_h data are smaller than symbol size).

TABLE 1: Fitting Parameters Obtained Using Eq 6, under the Assumption of a Simple Arrhenius Temperature Behavior for the Average Relaxation Time (Estimated Uncertainties on the Obtained Values of τ° and E Are 50 and 15%, Respectively)

	x	τ° (ps)	E (kJ/mol)
neat PEG600	1.00	0.02	16
benzene/PEG600	0.92	0.02	16
	0.84	0.04	14
toluene/PEG600	0.93	0.03	15
	0.86	0.05	12

TABLE 2: Fitting Parameters Obtained Using Eq 6, under the Assumption of a VFT Temperature Behavior for the Average Relaxation Time (Estimated Uncertainties on the Obtained Values of T_0 , τ° , and D Are 15, 15, and 5%, Respectively)

	x	T_0 (K)	τ° (ps)	D
neat PEG600	1.00	208	1.2	1.24
benzene/PEG600	0.92	218	2.3	0.74
	0.84	245	3.3	0.34
toluene/PEG600	0.93	224	2.0	0.71
	0.86	241	2.8	0.38

solvent molecules. This leads to an acceleration of the conformational rearrangements of PEG chains (as an example, the adoption of eq 8, with parameter values taken from Table 2, furnishes τ values, at $T = 290$, ranging from about 25 ps at $\phi = 1$ –20 ps at $\phi = 0.7$).

In Figure 8, we report the adiabatic compressibilities as a function of the volume fraction for PEG600 solutions in benzene and toluene together with our previous results for PEG/CCl₄ mixtures.¹⁵ As the volume is an extensive quantity, a linear behavior should be observed for the adiabatic compressibility under ideal mixing. An inspection of Figure 8 suggests that interferences between the structure of the polymer network and the solvent must be taken into account.

The occurrence of almost the same linear behavior at high concentrations, in all three solvents, supports the idea that in this region the system is almost completely dominated by the polymeric component. Of course, there will be some regions in the sample where the original polymer connectivity will be partially lost. One can expect that the volume fraction of these low connectivity regions scales linearly with dilution, at least until the polymer network can be considered a statistically percolated structure, stabilized via hydrogen bonding. Under such conditions, the two structures coexist in an almost ideal mixing. Only after further dilution does the behavior of the

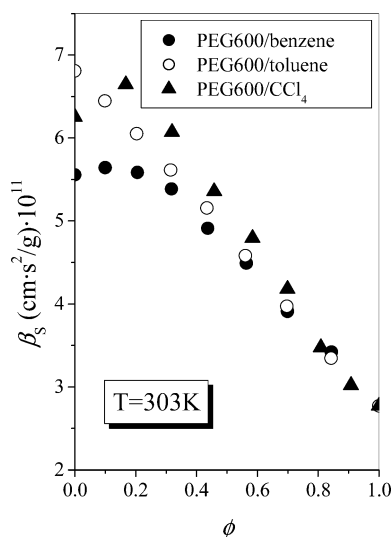


Figure 8. Comparison of the adiabatic compressibilities of PEG solutions in benzene, toluene and CCl₄ at $T = 303$ K.

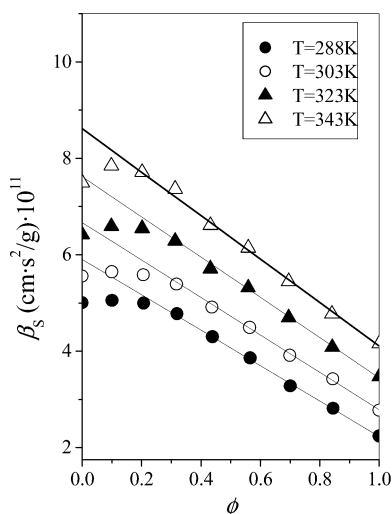


Figure 9. Adiabatic compressibility for PEG solutions in benzene at different temperatures.

adiabatic compressibility deviate from linearity and approach the value characteristic of the bulk solvent. In the above picture, the low connectivity regions represent volumes where solvent molecules are entrapped within a vacancy in the hydrogen-bonded network. In our experiment they are seen as regions where the properties of the system are driven by the interaction between PEG network and solvent molecules so, following the same nomenclature previously adopted, we will refer them as “heterostructures”. However, it should be clear that just excluded volume interactions are sufficient for their existence.

The hypothesis that the local structure of concentrated solutions is dominated by geometric effects (site percolation) connected with the polymeric component can be supported (at least when the solvents are CCl₄ or benzene) by the observation that adiabatic compressibility behaves linearly in the same concentration range (from about $\phi = 0.3$ –1) regardless of the solvent and the temperature, as shown for PEG/benzene mixtures in Figure 9.

On the contrary, the adiabatic compressibility of the PEG/toluene mixtures, reported in Figure 10, shows a clear dependence on temperature, with the concentration threshold for the linear behavior moving to higher values when T increases.

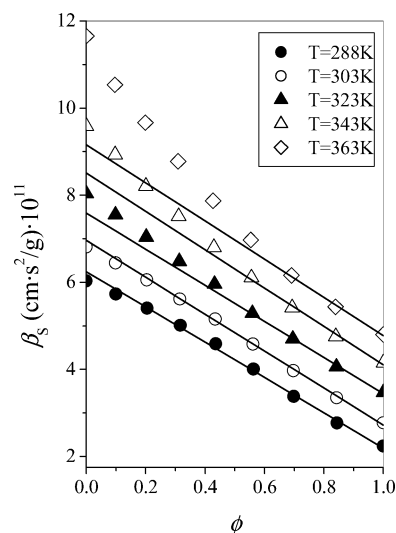


Figure 10. Adiabatic compressibility for PEG solutions in toluene at different temperatures.

This would suggest that additional mechanisms contribute to the interaction potential between polar solvent molecules and the polymer network.

However, the extrapolations to infinite dilution of the linear trends observed for the adiabatic compressibilities in the polymer-rich phases look almost independent of the solvent (see Figures 9 and 10). This observation ensures us that the same microscopic processes are driving the system evolution at high polymer content and that any differences become significant only at intermediate concentrations (in our picture, the $\phi = 0$ values of the linear extrapolations reported in Figures 9 and 10 represent the values of the adiabatic compressibility of the above-defined “heterostructures”). We can imagine that our mixtures consist of three components: pure solvent, neat PEG600, and heterostructure. The almost linear volume fraction dependence of the solution densities (see insets in Figure 1) suggests a very weak interaction between solvent and PEG, so one would expect that, at any system composition, heterostructures represent only very small sample volume fractions.

On this basis, we have adopted the model proposed by Glinski,^{46,47} which was also used to analyze the concentration dependence of the hypersonic velocity in PEG/CCl₄ mixtures.¹⁵ The model defines an association constant K_{As} in terms of the molar concentration, c_{As} , of the associated species through the relation

$$K_{As} = \frac{c_{As}}{(c_S - c_{As})(c_{PEG} - c_{As})} \quad (9)$$

where c_S and c_{PEG} are the initial molar concentrations of solvent and PEG, respectively.

Under the assumption of additivity of the time of transmission of acoustic signal with the volume fractions ϕ_s , ϕ_{PEG} , and ϕ_{As} of the mixture components, we can write

$$v_B = \frac{v_{PEG} v_s v_{As}}{\phi_{PEG} v_s v_{As} + \phi_s v_{PEG} v_{As} + \phi_{As} v_{PEG} v_s} \quad (10)$$

where v_s , v_{PEG} , and v_{As} are the sound velocities in pure solvent, pure PEG, and their associate, respectively.

In fitting our experimental data with eq 10 we adopted a two-step procedure: first we estimated the values of v_{As} through the extrapolation to $\phi = 0$ of the adiabatic compressibility reported in Figures 9 and 10 (the density of the associated

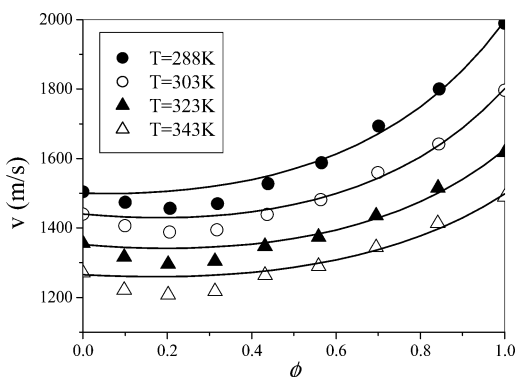


Figure 11. Volume fraction dependence of the hypersound velocity of PEG600/benzene solutions at different temperatures. Continuous lines represent the results of fitting with eq 10.

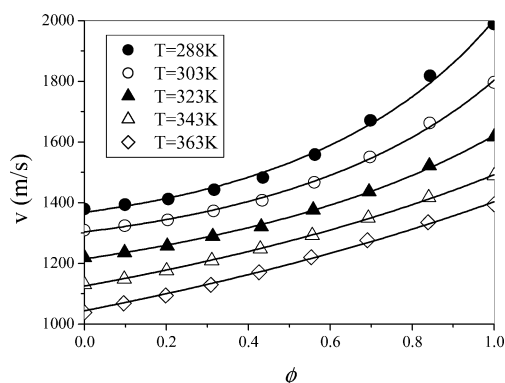


Figure 12. Volume fraction dependence of the hypersound velocity of PEG600/toluene solutions at different temperatures. Continuous lines represent the results of fitting with eq 10.

TABLE 3: Outcome Values of K_{As} Obtained by Fitting the Experimental Hypersonic velocity with Eq 10, with Fixed Values of the Velocities v_{As} ^a

T (K)	v_{As} (m/s)		K_{As}	
	benzene/PEG600	benzene/PEG600	toluene/PEG600	toluene/PEG600
288	1033	0.05	1097	0.05
303	953	0.05	1033	0.04
323	931	0.05	1063	0.03
343	917	0.05	1044	0.01
363			1005	3×10^{-7}

^a The hypersonic velocities in the hypothetical heterostructures, v_{As} , are calculated from the extrapolation to $\phi = 0$ of the adiabatic compressibility dependence in the high polymer concentration range. The density of heterostructure ρ_{As} was assumed to be the average density of pure components.

species has been taken as the averaged value of the pure components), then we tried to reproduce our experimental data with eq 10 by a simple one-parameter fitting procedure. The results of the fitting are reported in Figures 11 and 12 as continuous lines while the estimated values of the involved parameters are reported in Table 3. For benzene/PEG solutions the fitting procedure furnished $K_{As} \approx 0.05$ almost independently of the temperature, while for toluene the value of K_{As} turned out to range from about 0.05, at $T = 288$ K, to 0, at $T = 363$ K.

While the three-component model seems to reproduce well the concentration dependence of the hypersonic velocity in PEG/toluene systems, the fit is considerably worse for PEG/benzene mixtures. In particular, the model does not give a suitable approximation of the system evolution at volume fractions lower than about 0.4. A similar result has been obtained in our previous work on CCl_4 /PEG mixtures,¹⁵ where the failure of the Glinski

model at intermediate and low concentrations was interpreted in terms of a large structural evolution of the polymer network, when driven below its percolation threshold. This evolution makes the system markedly different from the bulk polymer and induces a large polydispersity in cluster sizes. The three-component model becomes inadequate because the structural properties of one of the components change with the concentration. The comparison with the results from our previous experiment on methanol/ CCl_4 mixtures¹⁶ suggests a general behavior for any system consisting of a hydrogen-bonded network dissolved in an inert solvent. In that case, both theoretical^{17,18} and low-frequency dielectric measurements^{48,49} suggested the idea of a non-negligible role played by electrostatic interactions in promoting some coordination between carbon tetrachloride molecules and methanol chain ends.

The same point of view has been recently adopted in interpreting the Brillouin scattering results from PEG/ CCl_4 mixtures,¹⁵ taking into account the more complicated situation due to the existence of a number of possible active sites, not simply localized at the chain ends.

In the case of toluene/PEG systems, we are led to hypothesize that the differences observed in the concentration and temperature behavior of the adiabatic compressibility (see Figure 10) have to be connected with the polar nature of the solvent molecule. In this case, the same excluded volume mechanisms will be present as for a nonpolar solvent, but some electrostatic interactions (most probably dipole–dipole interactions) between toluene and the polar groups of the PEG chain are now playing a non-negligible role. However, we cannot further speculate about the meaning of the temperature dependence of K_{As} or about the specific values we obtained, since the Glinski model does not account for the possible self-association of solute molecules. In our case, PEG chains interact giving rise to extended structures. Moreover, we are supposing that this mechanism is largely responsible for the structural evolution of the system and that it plays a role in establishing correlations between free active sites in the polymer network and solvent molecules. So, the values we obtained for K_{As} are largely affected by PEG self-association. The fact that the Glinski model seems to be more adequate for the PEG/toluene systems can be taken as a clue of an interaction (beyond mere volume effects) between solvent and PEG. On one hand, the polymeric network loses its connectivity under dilution faster than in benzene/PEG solutions, and on the other hand the interaction between the solvent molecules and the active sites of the polymer chains largely reduce the huge cluster size fluctuation characterizing PEG/benzene solutions at intermediate concentrations.

The hypothesis that the structural behavior in solutions of PEG in benzene and CCl_4 is driven by excluded volume interactions is supported by the observed temperature independence of the lowest concentration ($\phi \approx 0.3$) at which the adiabatic compressibility behaves linearly: if the local structure were related to the number density of interchain hydrogen bonds, we would expect temperature to play a role. This suggests that $\phi \approx 0.3$ should correspond to the overlap concentration, c^* , defined as the polymer concentration at which neighboring polymer coils start to overlap. The radius of gyration, R_g , of the polymer coil can be related to the overlap concentration through the expression⁵⁰

$$c^* = \frac{M_w}{\frac{4}{3}N_A\pi R_g^3} \quad (11)$$

where M_w denotes the molecular weight of the polymer and

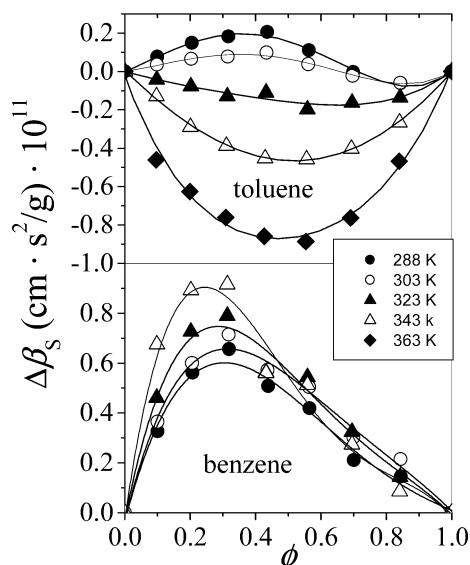


Figure 13. Excess adiabatic compressibility for PEG600/toluene and PEG600/benzene solutions, reported as a function of the solute volume fraction at different temperatures.

N_A is Avogadro's number. By use of the experimental density values reported in Figure 1, we find that $\phi \approx 0.3$ corresponds to $c^* \approx 0.35$ from which $R_g \approx 9.7 \text{ \AA}$ is deduced. This value is very close to the value $\approx 10 \text{ \AA}$ obtained by a molecular dynamics simulation on a solution of poly(oxyethylene) (POE) (15 chain units instead of the 13 units of our polymer) in benzene.⁴ If we assume that the substitution of PEG with PEO should not be relevant near the overlap threshold, then the close correspondence between the two values can be taken as an indication of the validity of the proposed picture. The fact that the adiabatic compressibility behaves linearly with concentration, down to a methanol volume fraction of about 0.3, in methanol/ CCl_4 solutions as well¹⁶ suggests that this could be a general picture for solutions of hydrogen-bonded networks in nonpolar solvents. Of course, in this last case, the meaning of the overlap concentration is not immediately obvious. However, one can imagine that, at a volume fraction $\phi \approx 0.3$, the kinetic equilibrium between breaking and reforming of the hydrogen bonds among methanol molecules, plus excluded volume effects, induce the formation of polymerlike methanol clusters of suitable shape and size to be considered just at the percolation threshold. This should not be surprising since the value $\phi \approx 0.3$ is quite near the percolation threshold for 3D mixtures of near spherical or ellipsoidal particles of different sizes.⁵¹

In Figure 13, we report the volume fraction dependences of the excess values of the adiabatic compressibility for benzene/PEG and toluene/PEG mixtures at different temperatures. An inspection of this figure gives further support to the proposed working hypothesis. It is quite evident that, for benzene/PEG solutions, the value of $\Delta\beta_s$ is almost independent of the temperature (at least for $\phi \geq 0.4$). No changes are observed other than a moderate increase in the excess compressibility with temperature at lower concentrations and that can be simply explained by the usual thermal expansion. In these mixtures, any apparent heterostructure (which gives rise to the observed excess compressibility) simply originates from local coordinations driven through steric hindrance effects, which are only weakly dependent on temperature. The situation looks completely different in the case of toluene/PEG (see top of Figure 13). In particular, the excess value of the adiabatic compressibility, which is moderately positive at $T = 288$ and 303 K , becomes negative when the temperature increases. In looking

for an explanation of this behavior one should take into account that the interaction between the polar solvent and the active sites of the polymeric component produces a large change in the polymeric network. In particular, one can imagine that the interaction between toluene and the polar groups of PEG produces local correlations surviving for times comparable with those characteristic of the hydrogen bonding kinetics. In this way, the interaction between toluene and a free active site of PEG shields the site from further interactions. This shielding produces a variation of the kinetic equilibrium on which the dynamical connectivity of the hydrogen-bonded network depends and, as a consequence, disturbs the local topology of the system. Probably, as for nonpolar solvent, the local breakage of the polymer network connectivity produces a more compressible structure, but the establishment of an electrostatic interaction between the broken sites and the solvent acts in the opposite direction. So the excess adiabatic compressibility is positive or negative depending on which of the two effects dominates. To observe any interactions between toluene and PEG, the local breakage of some points of the network is required. This breakage becomes more probable at higher temperatures, and for this reason the excess adiabatic compressibility becomes more negative as the temperature increases.

The above arguments fit well with the conclusions we have drawn from the application of the Glinski model to the hypersonic velocities in the different systems. In PEG/benzene, PEG/ CCl_4 , or methanol/ CCl_4 , the inadequacies of the model in fitting the experimental data is ascribed to the high level of self-aggregation exhibiting by the solute molecules. The model does not take explicitly into account the self-aggregation and, in addition, is not able to account for the changes of the self-aggregation efficiency on dilution. As a consequence, the model is able to produce a suitable fit of the experimental data at concentrations high enough to maintain the original network connectivity, but it fails when dilution destroys the original network and gives rise to different topologies. In other words, the model fails since it is not possible to describe the system structure in terms of a linear combination of only three local structures (or at least the same three local structures) over the whole concentration range.

In the toluene/PEG systems, the interaction between the solute and the solvent reduces the effects of self-aggregation, and this could explain why the Glinski model turns out to be adequate enough.

4. Concluding Remarks

Very recently, J. Glinski made an attempt to improve the model, by taking into account the dimerization of solute molecules.⁵² This model has been successfully used to reproduce the concentration dependence of sound velocity in hydrocarbon/normal alcohol solutions. However, difficulties were reported in obtaining unambiguous values for both the fitting parameters (namely, the dimerization constant and the difference between the sound velocities in the nondimerized and dimerized forms of the solute). In addition the values of the parameters influence the calculated velocities very weakly: as a consequence, Glinski expressed doubts about the sensitivity of the sound velocity to structural phenomena in liquids.

However, we feel that such doubts might be removed, if one considers that any structural change has to be reflected in a change in the compressibility of the system. The large deviations of the adiabatic compressibility from the ideal mixing that we detected (also in absence of significant mixing volumes) lend support to this idea, and for further attempts to obtain a

theoretical description of the self-association processes producing clustering effects on very large volumes.

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