Evidence of Heterogeneous Aggregation in Methanol/CCl₄ Mixtures: A Brillouin Scattering Investigation

F. Aliotta,*,† M. Musso,‡ R. Ponterio,† F. Saija,† and G. Salvato†

*Istituto per i Processi Chimico-Fisici, Sezione di Messina, Consiglio Nazionale delle Ricerche,
Via La Farina 237, I-98123 Messina, Italy, and Department of Molecular Biology, Division of Physics and
Biophysics, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria*

By means of a Brillouin scattering experiment in methanol/CCl₄ mixtures, deviations of the hyperacoustic parameters from the ideal behavior are studied as a function of concentration and of temperature. The experimental results are compared with the indication from a literature model describing the dependence of hypersonic velocity in weakly interacting liquid mixtures, assuming the system consists of three components, i.e., bulky methanol, bulky CCl₄, and a third unknown component described as by an (hetero-) associated species. The agreement with the model turns out to be qualitatively satisfactory, the observed concentration and temperature dependencies of the hyperacoustic parameters allowing to infer the existence of heteroaggregates, whose nanostructure seems to be more connected with volume effects than with the stoichiometry of the system. The deviations, at low methanol contents, from the three component model prediction are interpreted as being originated by the distribution of oligomeric methanol aggregates, including low-energy configurations, not present in the mixtures for volume fractions of methanol above 0.3.

1. Introduction

During the past few decades, a number of experimental and theoretical works have been devoted to the investigation of the static and dynamical properties of methanol in mixtures with carbon-tetrachloride. The interest is driven by the fact that since methanol on one hand is the simplest organic molecule able to exhibit a self-associative behavior through hydrogen bonding, it is an almost perfect model system for the investigation of clustering effects in H-bonded system. On the other hand, the solvent carbon tetrachloride is in principle an apolar molecule and therefore one is led to assume that it behaves as an inert solvent for methanol. Triggered by self-aggregation phenomena induced by hydrogen bonding in the alcoholic component, a number of deviations from the ideal behavior should be observed in methanol/CCl₄ mixtures. These mixtures are therefore a very well-suited prototype for the study of concentration dependent effects in the local structure of hydrogen-bonded networks.

Accurate measurements of density and enthalpy of mixing[1−3] already indicated, several years ago, that the system is not a perfect ideal mixture. A way to rationalize such deviations from ideality was found in a molecular dynamics experiment on Lennard-Jones and Stockmayer fluids[4,5] (such systems can be considered as the simplest models for polar/apolar fluid mixtures) and its extension to a methanol/CCl₄ mixture,[6] in which the results coming from the adoption of a polarizable CCl₄ model were compared with those obtained when polarizability is not taken into account. In particular, these simulations were able to determine the values of excess energy and free energy of mixing as a function of the system composition, as well as to reproduce the positive asymmetry of the excess energy

experimentally observed at low concentrations of the polar component. The radial distribution functions of like molecules show that they have a tendency to cluster when their concentration is low, this effect being much stronger for polar molecules in a apolar solvent than vice versa. Additionally, in mixtures where the polar component is highly diluted, an alignment phenomenon of the dipolar molecules is observed. In systems that are highly concentrated in the polar component, the distribution function of the Stockmayer fluid particles turns out to be insensitive to the changes in the strengths of the interactions between dipoles, due to frustration effects, i.e., the impossibility to achieve the energetically most favorable orientations when more than two dipoles are in each other's vicinity. Therefore, the local structure of the system remains close to the one observed in the bulk liquid. This frustration effect also provides a molecular explanation for the asymmetry in structural and excess mixing properties, explaining why deviations from random mixing are more pronounced at the lower mole fractions. In the methanol/CCl₄ mixture,[6] the radial distribution functions show a strong tendency of methanol to preserve local order similar to the one in the pure fluid. In fact, throughout the composition range, a majority of the methanol molecules are found to be engaged in two hydrogen bonds leading, as in the simulation of the pure fluid,[7−10] to a pattern of hydrogen bonded chains. Upon dilution, the degree of cross-linking between the chains diminishes whereas the free monomer fraction rises; furthermore, a significant number of cyclic polymers exists due to energetic reasons (see also refs 11 and 12).

The indications from these simulations allowed us to rationalize a number of experimental results.

The observed temperature and pressure dependence of the proton chemical shift in mixtures at $x_M \leq 0.2$ ($\phi_M \leq 0.09$), obtained by ¹H NMR spectroscopy,[13] can be accounted for by

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* Corresponding author. E-mail. aliotta@mail.its.me.cnr.it.
† Consiglio Nazionale delle Ricerche.
‡ University of Salzburg.

a model describing the local structure of methanol as determined by the monomer ↔ (cyclic) tetramer kinetic equilibrium. Over the methanol mole fraction range $0 \leq x_M \leq 1$, ^{2}H NMR results[14] revealed the existence of methanol clusters, the different models adopted by the authors agreeing in suggesting that the size of the aggregates increases with concentration up to $x_M \approx 0.2$ ($\phi_M \approx 0.09$), remaining almost constant at higher methanol contents. Analogous measurements of the chemical shifts of hydroxyl and methyl groups in neat methanol at liquid and supercritical densities[15] pointed out a clear change of the hydrogen bonding network with pressure and with temperature, hydrogen bonds still existing also under supercritical conditions (see also the MD simulation in refs 16 and 17). Consistent with the MD simulation results, a model was postulated describing the local structure of neat methanol as consisting of linear hydrogen bonded chains. An increase of the temperature is reflected by a decrease of the average chain length while an increase of the pressure induces opposite effects.

The influence of pressure and of dilution on the methanol structure was also studied through Raman scattering measurements[18−21] and through Monte Carlo[22] and molecular dynamics simulations[21,23] by observing the pressure and the concentration dependence of the separation in frequency between the anisotropic and the isotropic components of the O−H and C−O stretching bands, i.e., of the so-called noncoincidence effect (NCE) (see ref 22 and the references therein). Its peculiar behavior was rationalized, with the help of calculated pair distribution functions of the O−H and of the C−O bonds, in terms of locally anisotropic changes in the methanol structure occurring upon dilution.[21−23]

Additional observations suggest that the observed deviation from the ideal mixture behavior can be partially originated by heteroaggregation between methanol and CCl₄. Indeed, some calorimetric measurements[2,24] showed the existence of a minimum in the mixing entropy that can be interpreted as originating from the competition among different contributions; in particular, the breakage of the chains and mixing effects should be reflected by positive contributions, while negative contributions should be associated with clustering of like molecules and/or with the formation of complexes via interaction between the chlorine of carbon tetrachloride and the hydroxyl oxygen.

This interpretation agrees with very recent low-frequency dielectric measurements,[25,26] performed as a function of the concentration, revealing a behavior that unambiguously deviates from the ideal one;[27] while homogeneous association of the methanol component could be assumed in order to justify the observed negative deviation of the static dielectric constant at methanol volume fractions $\phi_M < 0.6$ (i.e., $x_M < 0.8$), heterogeneous association was invoked as a possible mechanism to take into account the opposite behavior observed at $\phi_M > 0.7$ (i.e., $x_M > 0.85$).

To test the above-mentioned hypothesis of clustering effects in methanol/CCl₄ mixtures, we recently performed a Brillouin scattering experiment[28] at room temperature as a function of the concentration, where we tried to understand the peculiar behavior observed for the adiabatic compressibility, hypothesizing that, at methanol volume fraction ϕ_M higher than 0.2 (i.e., $x_M > 0.35$), the CCl₄ molecules are essentially coordinated with methanol. In this concentration range, any CCl₄ molecule in the mixture is forced to fit into the free volume among methanol chains or is involved in chain ends, as suggested by a simple lattice model for the description of the equilibrium distribution of alcohol clusters in alcohol/CCl₄ binary systems.[26]

A theoretical support of the idea that heteroaggregation could play a role in the structural evolution of methanol/CCl₄ mixtures can be found in the results from ab initio molecular orbital simulations in a acetone/CCl₄ cluster.[29,30] The numerical results suggest that the atomic quadrupolar effect is important for electrostatic interactions around covalently bonded atoms on the third and higher rows in the periodic table; i.e., taking the chlorine atoms as an example, the electron densities in CCl₄ are highly anisotropic, this anisotropy being the electronic structural origin of the large atomic quadrupoles. These ab initio molecular orbital calculations have been very recently extended[31] to estimate the energies of the intermolecular interactions on the 1:1 molecular methanol/CCl₄ cluster, obtaining the information that molecular configuration oriented along the C−Cl...O−H axis is the most stable one, the interaction energy being probably slightly stronger than that between two CCl₄ molecules.

In this paper, we extend the Brillouin scattering investigation[28] by adding the study of the temperature dependence of the acoustic parameters in this system. We will show that any observed structural evolution can be rationalized by taking into account only local static structures on which temperature plays a minor role, confirming the existence of weak interaction between methanol and CCl₄. Some of these effects due to methanol−CCl₄ interactions are unambiguously detected, and some indication about the associative constant for the heterostructure is given.

2. Experimental Section and Results

Binary mixtures were prepared using CCl₄ and CH₃OH by Sigma-Aldrich, reagent grade quality (99.9 and 99.8, respectively) without further purification procedure. Different mixtures were obtained by weight and then the concentration values were translated into methanol mole fractions x_M and methanol volume fraction ϕ_M. Samples have been prepared with the following compositions: $x_M = 0, 0.05, 0.07, 0.10, 0.20, 0.30, 0.62, 0.74, 0.89, 0.97, 1$ ($\phi_M = 0, 0.02, 0.03, 0.04, 0.09, 0.15, 0.40, 0.54, 0.77, 0.93, 1$).

The explored temperature range was -8.1 °C $\leq T \leq +30.0$ °C, the temperature of the samples being set and controlled within 0.1 °C by means of a thermostatic bath. Density, ρ, and refractive index, n, data were measured by means of an Anton Paar DMA 5000 density meter ($\Delta\rho = \pm 2 \times 10^{-4}$ g/cm³) and an Abbe refractometer ($\Delta n = \pm 0.5\%$), respectively.

The Brillouin scattering measurements were performed, in a 90° scattering geometry, by means of a piezoelectrically scanned double pass Fabry−Perot interferometer (SOPRA) working at a free spectral range of 15.5(1) GHz, determined by the measurement of the Brillouin shift in a known (H₂O) sample at 25 °C.[32] The single-mode single-frequency line of a Coherent Verdi laser with a vacuum wavelength of $\lambda_0 = 532.2(1)$ nm was adopted as the incident radiation, with a mean light power of ≈ 0.5 W. The working finesse, calculated by the HWHM of the elastic line, turned out to be about 100.

In addition, some samples ($x_M = 0.10, 0.74, 0.89, 0.97,$ and 1, i.e., $\phi_M = 0.04, 0.54, 0.77, 0.93,$ and 1) were explored, at fixed temperature (25 °C), at different scattering angles θ, namely 20, 35, 60, 90, 120, 135, and 145°. With the adopted geometries and the probe wavelength used, the explored range of the exchanged wave vector, $k = (4\pi n/\lambda_0) \sin(\theta/2)$, was 0.5×10^{-12} cm$^{-1} \leq k \leq 3 \times 10^{-12}$ cm^{-1}.

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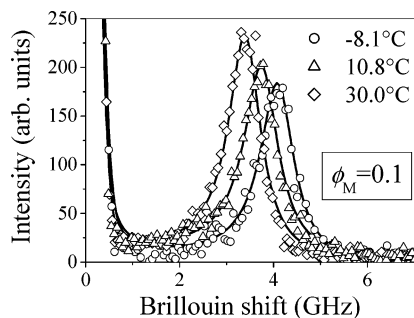
Figure 1. Experimental $I_{VV}(\omega, T)$ spectra at three different temperatures, at a fixed volume fraction ϕ_M of methanol in the methanol/CCl$_4$ mixture. Continuous lines represent the best fit result with eq 1.

The Brillouin spectra were fitted with the usual equation[33]

$$I_{VV}(\omega) = \frac{A_R\Gamma_R}{\omega^2 + \Gamma_R^2} + \left[\frac{A_B\Gamma_B}{[\omega - (\omega_B^2 - \Gamma_B^2)^{1/2}]^2 + \Gamma_B^2} + \right.$$

$$\frac{A_B\Gamma_B}{[\omega + (\omega_B^2 - \Gamma_B^2)^{1/2}]^2 + \Gamma_B^2}\right] +$$

$$\frac{\Gamma_B}{\omega_B^2 - \Gamma_B^2}\left[\frac{\omega - (\omega_B^2 - \Gamma_B^2)^{1/2}}{[\omega - (\omega_B^2 - \Gamma_B^2)^{1/2}]^2 + \Gamma_B^2} + \right.$$

$$\left.\frac{\omega + (\omega_B^2 - \Gamma_B^2)^{1/2}}{[\omega + (\omega_B^2 - \Gamma_B^2)^{1/2}]^2 + \Gamma_B^2}\right] \quad (1)$$

In eq 1, the first term describes the central line of the hydrodynamic triplet, i.e., the quasi-elastic, resolution enlarged Rayleigh contribution with intensity A_R, while the next term describes the symmetrical Brillouin contribution with intensity A_B and the last one the asymmetrical contribution. The fitting procedure furnishes the frequency shift ω_B and the HWHM, Γ_B, of the Brillouin lines. Some of the resulting $I_{VV}(\omega, T)$ spectra are reported, as an example, in Figure 1, together with the fitting results. The frequency values ω_B have been determined with an accuracy of $\pm 1.5\%$, while the error estimated on Γ_B is $\pm 5\%$.

The values of the hypersonic velocity v_h (accuracy $\pm 2\%$) of the normalized absorption α/f^2 (accuracy $\pm 10\%$) have been obtained according to the expressions:

$$v_h = \frac{\omega_B}{k}$$

$$\frac{\alpha}{f^2} = \frac{2\pi\Gamma_B}{v_h\omega_B^2} \quad (2)$$

The extracted behavior for v_h and α/f^2 are reported in Figures 2 and 3, respectively.

Hypersonic velocity v_h and absorption data α/f^2 agree very well with our previous results obtained at 25 °C (Figure 3 in ref 28). In neat methanol, our values for the hypersonic velocity show some discrepancies with literature data,[34,35] but the occurrence of very good agreement of our v_h for pure CCl$_4$ with literature data[36,37] ensures the reliability of the calibration procedure adopted by us.

The hypersonic velocity data reported in Figure 2 show a minimum at a concentration of about $x_M = 0.4$ (corresponding to $\phi_M = 0.22$). As a function of the temperature, we observe an almost linear increase of the velocity with decreasing T, while the position of the minimum does not significantly change (see
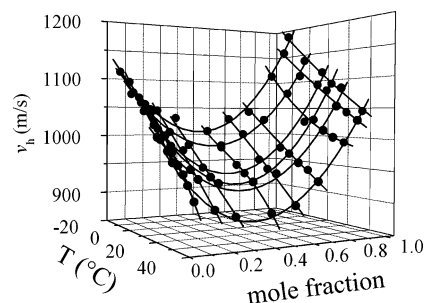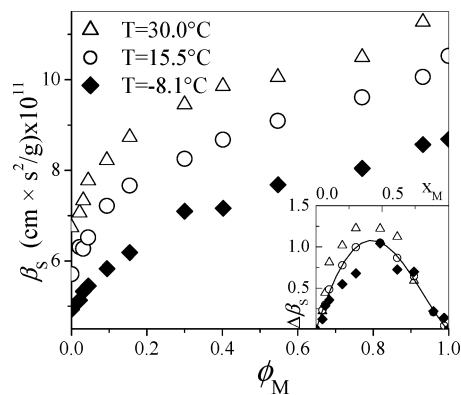

Figure 2. Temperature and concentration dependence of the hypersonic velocity v_h in methanol/CCl$_4$ mixtures. Continuous lines are guide for eye.
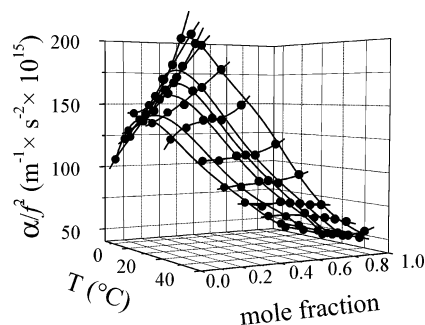
Figure 3. Temperature and concentration dependence of the hypersonic normalized absorption in methanol/CCl$_4$ mixtures. Continuous lines are guide for eye.
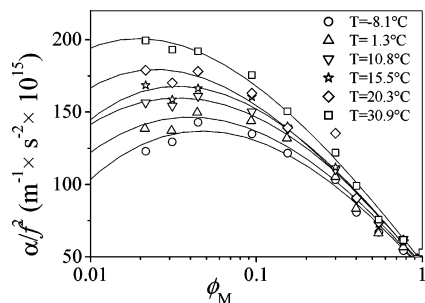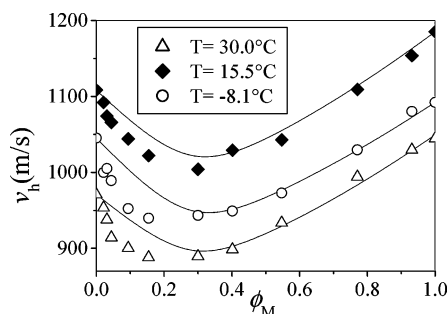

Figure 4. Hypersonic normalized absorption, at different temperatures, reported as a function of the methanol volume fraction ϕ_M. The continuous lines are guides for eye. A logaritmic scale has been adopted for ϕ_M in order to better point out the position of the maximum.

Figure 5. Adiabatic compressibility data, reported as a function of the volume fraction ϕ_M of methanol in the methanol/CCl$_4$ mixtures at three different temperatures. In the inset, the differences between the experimental data and the expected results from an ideal model are reported, as a function of the mole fraction x_M (see ref 28 for details).

also Figure 6, where the concentration dependence of the hypersonic velocity is reported for three different temperatures including the lowest and the highest explored ones).

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Figure 6. Concentration dependence of the hypersonic velocity v_h in methanol/CCl$_4$ mixtures at three different temperatures. The continuous lines represent the fit with eq 4.

Our hypersonic normalized absorption data α/f^2 at $x_M = 1.0$ are in reasonable agreement with those observed for neat methanol in ref 34. The α/f^2 value increases with temperature with a slope increasing from neat methanol (almost flat) to neat CCl$_4$. As a function of the concentration, α/f^2 shows a maximum at $x_M = 0.1$ (corresponding to a volume fraction $\phi_M = 0.04$). The maximum position slightly shifts to lower concentration values when the temperature increases, as is shown in Figure 4, where α/f^2 is reported in a semilog plot as a function of the methanol volume fraction ϕ_M.

Concerning the samples explored as a function of k at 25 °C, the obtained v_h values turned out to be independent of k within their uncertainty, suggesting that any possible relaxation process has to take place outside the explored temperature and frequency range. In fact, the Brillouin data for neat methanol from ref 34 suggest that a relaxation process appears to take place below −23 °C, the hypersonic velocity approaching the ultrasonic value at about 20 °C.

In addition, a simple inspection of the data in Figures 2 and 3 ensures that we are far from any possible temperature-dependent relaxation process, since we do not observe either an absorption maximum or a flex of the hypersonic velocity as a function of the temperature.

As a consequence, we can be confident that any variation of the acoustic parameters observed in our data has to be related just to the temperature dependence of the densities and/or to concentration effects on the static local structure.

3. Discussion

The above results well agree with the indications from recent literature data[29−31] suggesting that steric hindrance (entropic) effects favor via electrostatic interactions the formation of heteroaggregates, already hypothesized in our previous Brillouin experiment.[28] As a consequence, we can describe our mixtures as weakly interacting ones, the same indication coming from the concentration dependence of their density and refractive indices.[1,28]

Very recently, a model of calculating association constants in mixtures of two weakly interacting liquids was proposed[38,39] in order to interpret the experimental results of sound velocity measurements in these mixtures, assuming the system consists of three components, i.e., in our case bulky methanol, bulky carbon tetrachloride, and a third unknown component consisting of an (hetero-) associated species. Starting from acoustic data, one may be able to furnish a value of the (conditional) association constant K_{As}, conditional meaning that K_{As} may depend on the side processes competing association.

Indicating with c_C, and c_M the initial molar concentration of carbon tetrachloride and of methanol, and with c_{As} the molar concentration of the hypothetical (hetero-) associated species,

respectively, according to this model the molar equilibrium association constant K_{As} can be defined as

$$K_{As} = \frac{c_{As}}{(c_C - c_{As})(c_M - c_{As})} \tag{3}$$

As fitting equation for the sound velocity v_h in the mixture, we adopted the model[36] assuming the additivity of the time of transmission of the acoustic signal with the volume fractions ϕ_M, ϕ_C, and ϕ_{As} of the components[40]

$$v_h = \frac{v_M v_C v_{As}}{\phi_M v_C v_{As} + \phi_C v_M v_{As} + \phi_{As} v_C v_M} \tag{4}$$

where v_M, v_C, and v_{As} are the sound velocities in neat methanol, in carbon tetrachloride, and in the heteroassociated species, respectively. In adopting eqs 3 and 4, we need to gain the knowledge about the densities of the three systems. While the densities ρ_C and ρ_M of the pure components are known, some assumptions have to be made for the density ρ_{As} of the heteroassociated system. Fortunately, the outcome of the model seems to be only slightly influenced by this last value (we assumed for ρ_{As} the average value of the pure compounds ρ_C and ρ_M, as in ref 39).

We first tried to reproduce our experimental data with eq 4 by a two parameters (v_{As} and K_{As}) fit procedure. However, such a procedure was not able to furnish a unique solution, probably because eq 4 turned out to be unsuitable to fit data at very low methanol content, as will be shown in the following. We tried to establish a working procedure in order to avoid the occurrence of large random errors of the parameters (although some systematic errors cannot be avoided). With this aim, we made a further assumption: following the indication given by the concentration dependence of the adiabatic compressibility from our previous experiment,[28] systems at high methanol content ($0.25 \leq \phi_M \leq 1$ i.e., $0.44 \leq x_M \leq 1$) can be described as a linear combination of bulk methanol and the heteroaggregates. Such a picture has the following implications: (i) there is no significant structural change of the methanol over this high concentration range; (ii) no volume of bulk CCl$_4$ exists in the same concentration range. Both implications are supported by the fact that the noncoincidence effects of the CO and of the OH stretching vibrations in methanol do not appreciably change with dilution in the range $0.15 \leq \phi_M \leq 1$ ($0.3 \leq x_M \leq 1$).[21] In other words, the structure of the liquid mixture is not greatly modified in that concentration range, as evidenced by the MD simulation results for the pair distribution function of the CO and of the OH bonds also given in ref 21.

Following the same procedure adopted in ref 28, we calculated the adiabatic compressibility β_S values as well as the excess contributions, $\Delta\beta_S$, with respect to the ideality; the results are reported in Figure 5.

From the extrapolation of the adiabatic compressibility behavior in methanol rich systems to $\phi_M = 0$, we obtained an estimate of the adiabatic compressibility values for the associated species; then, adopting the above-mentioned assumption for the density ρ_{As}, we obtained the estimated values of the hypersonic velocity v_{As} in the associated systems. Such a procedure indicates an average value of 900 m/s.

In such a way, the fitting procedure involves the determination of only one parameter, K_{As}. We obtain a satisfactory fit in the methanol concentration region $0.4 \leq \phi_M \leq 1$ ($0.61 \leq x_M \leq 1$) using a K_{As} value of about 0.5, while the fit underestimates the values in the methanol concentration region $\phi_M < 0.4$ ($x_M \leq$

0.61) by up to 5% (see Figure 6). This error is well above the experimental uncertainty of the sound velocity v_h (well within $\pm 2\%$).

Qualitatively, such a discrepancy should be not surprising since we have to take into account that, under dilution at $\phi_M <$ 0.4 ($x_M \leq 0.61$), the relative populations of the different species (dimers, trimers, n-mers) existing in the system change,[11–12,26] since dilution implies a change of the kinetic equilibrium between breaking and re-forming processes of the methanol chains. Consistently, we have to expect a change in the density of the hydrogen bonds of methanol and therefore a change of its adiabatic compressibility.

Quantitatively, the too large value obtained for the association constant K_{As} (about 0.5, while a systematic investigation of different systems indicates typical values on the order of 0.01[39]) probably represents a nonphysical result. In addition to the above-mentioned consideration, the value of K_{As} may be largely overestimated as a consequence of the assumptions made to estimate the sound velocity v_{As} in the associated structure. First of all, we have to take into account that, probably, also in the methanol-rich phase a change of the methanol content is reflected by a redistribution of the various existing polymeric species. As a consequence, the idea itself of an average heteroaggregate could be ambiguous at higher methanol content due to the occurrence of a higher density of branching points.[11] In addition, the assumption of the absence of any bulky CCl_4 at $\phi_M \geq 0.25$ ($x_M \geq 0.44$) is probably a too severe approximation (this assumption directly implies an overestimation of the association constant K_{As}). Despite these evident limitations, the obtained behaviors seem to be reasonable, at least from a qualitative point of view. In particular, the fits suggest that the association process reaches its maximum efficiency at about $\phi_M = 0.2$–0.3 (i.e. $x_M = 0.4$–0.5). Such an indication appears to be consistent with the observed behavior of the adiabatic compressibility β_S and with the observation of a maximum in its excess value $\Delta\beta_S$ with respect to the ideal one, reported in Figure 5.

The minimum in the hypersonic velocity observed at a concentration comparable to the azeotropic one for our mixture ($x_M = 0.54$, $\phi_M = 0.33$, at 57.5 °C[41]) is analogous to a similar result, recently obtained from Brillouin scattering measurements in CH_3CN/CCl_4 mixtures near their azeotropic concentration, performed as a function of the temperature in a 90° scattering geometry.[42] It is generally accepted that, at the azeotropic concentration, a positive deviation from the Raoult's law is to be related to the existence of a repulsive interaction between unlike molecules or to a preferred self-organization of one of the two existing species.[43] In ref 42, the authors assumed that, at the azeotropic concentration, the repulsive potential between the polar and apolar liquid should reach a maximum inducing the formation of microphase heterogeneities, which results in a maximum of the adiabatic compressibility. In our case, a repulsive interaction cannot be hypothesized, but the hydrogen bonding between methanol molecules could be the source of the observed positive deviation of β_S from ideality.

4. Concluding Remarks

In summary, our Brillouin scattering results confirm the idea that, contrary to what could be expected, CCl_4 is far from behaving as an inert solvent for methanol.

The divergences from ideality are originated both by the tendency of methanol molecules to self-aggregate via hydrogen bonding and, additionally, by some nonnegligible electrostatic interactions between chorine atoms and free O−H chain ends.

In particular, when the mixtures are investigated as a function of the concentration, the nonideal behavior is reflected by the appearance of distinct regimes.

At high methanol contents the system behavior seems to be dominated by the structure of methanol. The only effect of dilution seems to be that of locally breaking some of the branching points, making room to the chlorine atoms giving rise to local heteroaggregation via electrostatic interaction. In this respect, the maximum observed in the normalized absorption around $x_M = 0.1$ (i.e., $\phi_M = 0.05$) could mark the transition from a regime in which an extended hydrogen bonded network still exists to a new one where the dilution promotes the formation of a number of different local geometries for the methanol aggregates, while carbon tetrachloride tends to assume its bulky properties. The existence of distinct regimes is also suggested by the result of the fitting of our velocity data with the model for weakly interacting liquid mixtures proposed in ref 39. The agreement between our data and the model at concentrations above $\phi_M \sim 0.3$ ($x_M \sim 0.3$) supports the idea that the mixtures can be described in terms of three component (bulky methanol, bulky carbon tetrachloride, and hetero-aggregates) systems.

At lower concentration the situation turns out to be more complicated due to the existence of a distribution of local configurations.[11–12,26] However, the adoption of a suitable model for the description of the aggregates size distribution function at these lower concentrations could be adequate to remove the quantitative discrepancies between the results of the model[39] and the experimental data: in this regime, the three component model should be replaced by a new model in which the bulky methanol is substituted by a distribution of contributions.

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