

Brillouin Scattering Evidence of Nonideal Mixing in Methanol/CCl₄ Mixtures

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A Brillouin scattering experiment has been performed on the methanol/CCl₄ mixture as a function of the concentration to test the hypothesis, recently suggested by Raman spectroscopy experiments, of some clustering effects. The obtained concentration dependence of the adiabatic compressibility diverges from that expected for an ideal mixture. The observed result is interpreted as due to polarization effects induced by methanol on the (originally) isotropic CCl₄ molecule that induces some coordination with carbon tetrachloride. The occurrence of a maximum in the adiabatic compressibility, near the equimolar concentration, suggests the existence of different regimes in the system and is consistently compared with literature for the solution enthalpy and mixing entropy.

1. Introduction

Hydrogen bond interaction plays a fundamental role in the molecular organization in domains or internally ordered clusters as well as in the architecture of biological molecules. Since the activation energy of the hydrogen bonding is of the order of the thermal energy, at normal ambient condition, the hydrogen-bonded network will experience thermally activated structural relaxation processes.^{1,2} As a consequence, the size distribution of the clusters, determined by the kinetic equilibrium between breaking and reforming processes, will be a function of the temperature.³ Of course, it also will be a function of the system density, since the intercluster interaction plays a role in determining both the average cluster size and the establishment of long-range correlations.^{4–7} The experimental and theoretical investigation of this aspect is of paramount importance in understanding the complex mechanisms underlying the formation of the organized structures usually observed in biological systems or, more generally, the peculiar static and dynamical properties exhibited by every self-assembled material. Of course, water represents the best candidate for this kind of study; however, the interpretation of the experimental data, as well as the theoretical modeling of the hydrogen-bonded network formation, encounters some difficulties as water molecules give rise to two donor configurations. We need to develop a model system that allows us to overcome the above-described difficulties. Keeping these difficulties in mind, methanol represents the simplest organic molecule that is prone to set up a hydrogen bond with only one donor configuration.

Very recently, methanol/CCl₄ mixtures have been studied by means of Raman spectroscopy and molecular dynamics simulations⁸ with the aim of investigating the concentration dependence of the so-called noncoincidence effect (NCE), i.e., the separation in frequency between the isotropic and the anisotropic component of certain vibrational modes, in our case of the C–O⁴ and the O–H^{6,9,10} vibrational modes (see ref 8 and references therein). Such an effect is related to the resonant vibrational

energy transfer between identical vibrational modes of neighboring molecules, which may be established in the presence of a short-range order (see refs 11 and 12 and references therein). The results allowed us to infer concentration-dependent structural changes of the mixture due to the existence of different polymeric (oligomeric?) species. In particular, it was observed that, in a rather wide concentration range, methanol tends to maintain its polymer-like structure consisting of zigzag hydrogen-bonded chains.^{13–18} Consequently, the observed peculiar concentration dependencies of NCE(C–O) and of NCE(O–H) have been interpreted as the result of a locally anisotropic change in the liquid structure that occurs upon dilution, in which intrachain distances do not change very much along the hydrogen bond direction, while the interchain distances increase with dilution.

Some indication that the methanol/CCl₄ mixture could not be a perfect ideal mixture comes from some accurate measurements of density and mixing energy¹⁹ existing in the literature.

Additional evidence has been found in low-frequency dielectric measurements²⁰ and their comparison with the ideal case as described in the framework of Onsager theory.²¹ While homogeneous association of methanol is enough to justify the observed negative excess of the relative dielectric constant, at low methanol contents, heterogeneous association has been proposed to take into account the positive deviations from the ideal behavior that are observed at high concentrations.

The reasonable agreement between simulation and experiment in ref 8, however, should not conceal the fact that, in MD simulations, carbon tetrachloride (a nonpolar, although polarizable, molecule) is considered as a nearly ideal solvent for methanol (i.e., only methanol–CCl₄ interactions which are reflected in the polarizable potential functions^{22,23} are taken into consideration).

Very recent *ab initio* molecular dynamics calculations²⁴ for the acetone/CCl₄ mixture have shown that carbon tetrachloride molecules, surrounded by the electric dipoles of acetone, look as if the chlorine atoms had large positive charges and it was proposed that such an effect could be generated by the atomic quadrupoles of the chlorine themselves.

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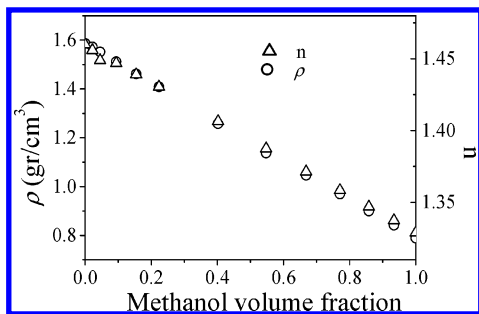


Figure 1. Concentration dependence of density, ρ , and refractive index, n , of the CH₃OH/CCl₄ mixture at 25 °C.

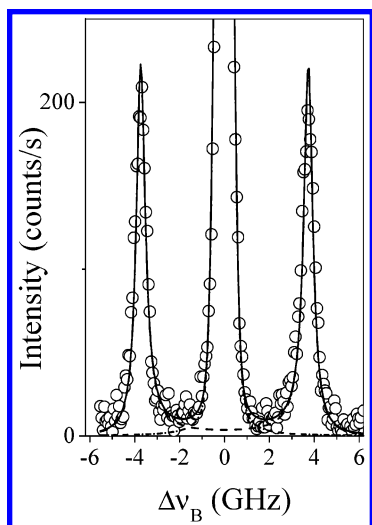


Figure 2. Experimental Brillouin profile for the CH₃OH/CCl₄ mixture at $x_M = 0.93$ (x_M = methanol molar fraction), corresponding to a methanol volume fraction (ϕ) of 0.86.

Similar simulations for the methanol/CCl₄ mixture, including the effect of the atomic quadrupoles of chlorine atoms, soon will be under way. A first hint of the considerable influence of solvation of methanol by CCl₄ comes from the fact that the OH stretch fundamental band is centered around 3641 cm⁻¹,²⁵ which is appreciably red shifted from the gas-phase value around 3680 cm⁻¹²⁶ (see also ref 27 for a theoretical study of hydrogen bond dynamics of methanol in solution).

In this paper, we present the results from a Brillouin scattering experiment performed on CH₃OH/CCl₄ mixtures to test if the structural evolution of the methanol with dilution (hypothesized in refs 8 and 20) is confirmed by the concentration dependence of the hydrodynamic triplet. In addition, from the behavior of the adiabatic compressibility we will try to infer the existence of some kind of interaction between carbon tetrachloride and methanol.

2. Experimental Section: Handling of the Data and Results

Samples have been prepared with CCl₄ and CH₃OH from Sigma-Aldrich (reagent grade quality; 99.9% and 99.8% respectively) without further purification. The mixtures have been obtained by weight and then the concentrations have been translated into mole fractions, x_M . Being the two liquids are fully miscible, the explored concentrations ranged from pure carbon tetrachloride to pure methanol. Complementary measurements of density, ρ , and refractive index, n , have been preliminarily performed, at 25 °C, with use of an Anton Paar DMA 5000 density meter and an Abbe refractometer, respectively. The obtained data are reported in Figure 1.

The Brillouin scattering experiment has been performed, in 90° geometry, by means of a piezoelectrically scanned double pass Fabry–Perot interferometer (SOPRA), working at a free spectral range of 15.5 GHz; this value was determined by the measurement of the Brillouin shift in a known (H₂O) sample. The single-mode single-frequency 532-nm line of a Coherent Verdi laser has been adopted as incident radiation with a mean light power of ~0.5 W. The temperatures of the samples have been set to 25.0 ± 0.1 °C by means of a thermostatic bath. Several spectra (up to 4) have been collected for each sample, using an integration time of 2 s for each scan. In Figure 2 we report, as an example, the experimental Brillouin profile for the CH₃OH/CCl₄ mixture at $x_M = 0.93$, corresponding to a methanol volume fraction (ϕ) of 0.86.

The Brillouin spectra have been fitted with the usual equation:

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

where A_R and A_B are the intensities of the Rayleigh and Brillouin contributions, respectively. In eq 1, the first term describes the quasielastic, resolution-enlarged central line, the next term the symmetrical Brillouin contribution, and the last term the asymmetric contributions.

The fitting procedure furnishes the frequency shift, ω_B , and the HWHM, Γ_B , of the Brillouin lines. In Figure 2, the continuous line represents the result of the fitting with eq 1. The frequency values have been determined with an accuracy of ±2%, while the error estimated on the Brillouin HWHM was ±5%.

The values of the hypersonic velocity, v_h , and of the normalized absorption, α/f^2 , have been obtained according to the expressions:

$$v_h = \frac{\alpha_B}{k} \quad (2)$$

$$\frac{\alpha}{f^2} = \frac{2\pi\Gamma_B}{v_h \omega_B^2} \quad (3)$$

with k being the exchanged wave vector. The extracted behavior for the hypersonic velocity and absorption is reported in Figures 3 and 4.

3. Discussion and Conclusions

An inspection of Figure 1 shows that both the density and the refractive index behave linearly (within 1%) with the methanol volume fraction. Such a result suggests that the observed behavior is very similar to that expected for ideal mixing [e.g., $\rho = \rho_1 + (\rho_2 - \rho_1)\phi$] and that interference between the structures does not play a relevant role. In fact, the determination of the mixing volumes for the CH₃OH/CCl₄ mixture, obtained from accurate measurements of the density,¹⁹ shows that the volume changes for the system always remain

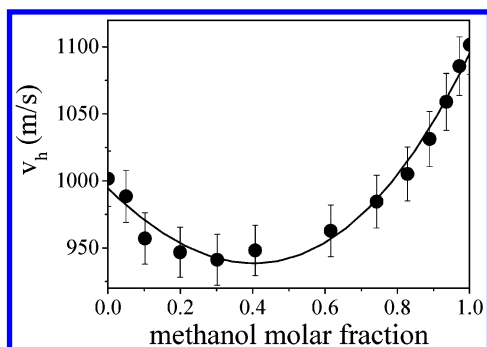


Figure 3. Concentration dependence of the hypersonic velocity in the $\text{CH}_3\text{OH}/\text{CCl}_4$ mixture at 25 °C.

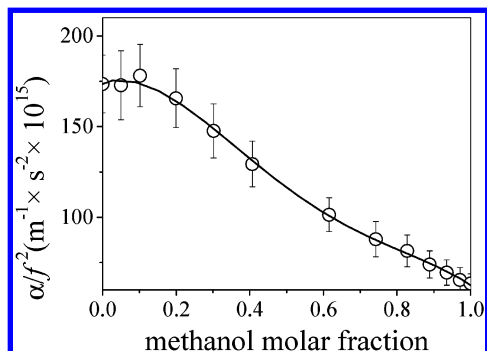


Figure 4. Concentration dependence of the normalized sound absorption α/f^2 in the $\text{CH}_3\text{OH}/\text{CCl}_4$ mixture at 25 °C.

small and in any case limited within 0.1%; a maximum positive molar volume change, ΔV_M , up to $\sim 0.05 \text{ cm}^3/\text{mol}$ is observed at methanol concentrations below $x_M < 0.2$, while the maximum negative excursion ($\Delta V_M \approx 0.08 \text{ cm}^3/\text{mol}$) is observed at around $x_M \approx 0.75$. Such variations are well within the experimental error bars obtained for the hypersonic velocity ($\pm 2.5\%$) and absorption ($\pm 10\%$). As a consequence, the observed dependence of the acoustic parameters, v_h and α/f^2 , on the concentration (see Figures 3 and 4) should be attributed to changes in the local structures, affecting more the compressibility $\beta_s = 1/(\rho v_h^2)$ of the system than the local density. One is led to presume that methanol is mainly responsible for the observed concentration dependence of v_h and α/f^2 , where hydrogen bonding induces the establishment of structures whose extent, local topology, and lifetime depend on the thermodynamic state of the system. In fact, the local structures existing in neat methanol are dynamical objects whose size and polydispersity are determined by the equilibrium between the thermally activated process of the breaking and reforming of hydrogen bonds, by the frequency of collisions between aggregates, and by excluded volume effects.^{13–18,28,29} On the contrary, in the case of neat carbon tetrachloride, due to the nonpolar nature of the molecule, intermolecular interactions essentially originate from induced polarization effects and do not allow the establishment of correlations behind first neighbors.³⁰

The observed minimum of the sound velocity at $x_M = 0.3/0.4$ (see Figure 3) seems to indicate that, in this concentration range, the mixture is characterized by a less “rigid” structure. An analogous behavior of the hypersonic velocity has been recently detected in $\text{CCl}_4/\text{CH}_3\text{CN}$ mixtures,³¹ near the azeotropic concentration, and has been interpreted in terms of the formation of microphase heterogeneities resulting in a maximum of adiabatic compressibility. Our experimental observations are consistent with Raman spectroscopy data,⁸ which have been related to a concentration-dependent (locally anisotropic) change in the nanoscale structure of the mixture, under the hypothesis

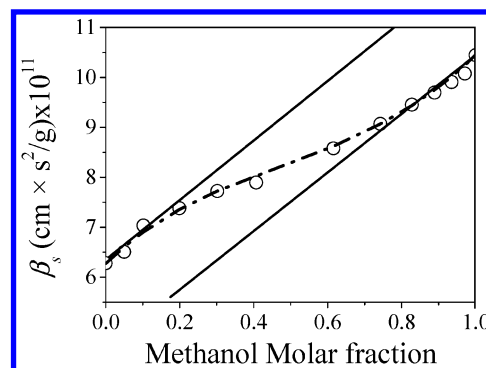


Figure 5. Adiabatic compressibility, β_s , in the $\text{CH}_3\text{OH}/\text{CCl}_4$ mixture at 25 °C as a function of the methanol molar fraction.

that this concentration range marks the transition from a regime in which the arrangement of the methanol molecules preserves its polymer-like structure of branched methanol chains to a new one where the interchain connectivity is lost (see refs 28 and 29 and references therein). At lower methanol concentrations, probably the arrangement of methanol molecules is prevalently a cyclic one (e.g. cyclic tetramers): the nonpolar CCl_4 environment could force the methanol also to be “nonpolar”, for energetic reasons.^{28,29}

The picture is also consistent with the minimum observed in the mixing entropy³² at the same concentration. The behavior of the entropy is determined by the competition among different contributions: the increase of the configurational freedom degrees, due to the breakage of the chains, gives a positive contribution; an additional positive contribution arises from the mixing of different molecular species of different size, complicated by the presence of some clustering effects; an additional, but as above stressed negligible, positive contribution due to mixing volume effects; a negative contribution due to the local order induced by the interaction between the hydroxyl oxygen and the chlorine of the carbon tetrachloride; and a negative contribution due to the clustering of like molecules or to the formation of complexes.

To better clarify this point we report, in the Figure 5, the concentration evolution of the adiabatic compressibility.

Also in this case a flex is observed at $x_M = 0.3/0.4$. An extrapolation of the β_s data obtained at low methanol concentration toward the pure alcohol limit ($x_M = 1$) leads to overestimated values (and vice versa).

Taking into account what was discussed above about the mixing volumes of our mixtures, we can try to calculate the *ideal* adiabatic compressibility, to compare it with the experimental data reported in the Figure 5.

Assuming an (almost) ideal mixing, the volume of the mixture, V_{id} , is given by

$$V_{id} = \frac{n_1 V_{m1} + n_2 V_{m2}}{n_1 + n_2} \quad (4)$$

where n_1 and n_2 are the mole number of CCl_4 and methanol, respectively, and V_{m1} and V_{m2} are the corresponding molar volumes.

The ideal adiabatic compressibility, $\beta_{s,id}$, can be calculated with respect to pressure according to

$$\beta_{s,id} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_s = \frac{\rho_2 n_1 M_1 \beta_1 + \rho_1 n_2 M_2 \beta_2}{\rho_2 n_1 M_1 + \rho_1 n_2 M_2} = \beta_1 + (\beta_2 - \beta_1) \phi \quad (5)$$

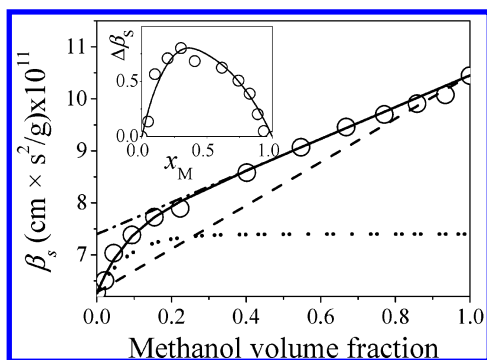


Figure 6. Experimental adiabatic compressibility, β_s (open symbols), and ideal adiabatic compressibility, $\beta_{s,id} = \beta_1 + (\beta_2 - \beta_1)\phi$ (dashed line), in the CH₃OH/CCl₄ mixture at 25 °C as a function of ϕ . The inset represents the excess compressibility, $\beta_s - \beta_{s,id}$, as a function of the mole fraction.

with M_1 , β_1 , ρ_1 and M_2 , β_2 , ρ_2 being the molecular weight, the adiabatic compressibility, and the density of CCl₄ and methanol, respectively.

In Figure 6, we report both the experimental adiabatic compressibility (open symbols) and the ideal adiabatic compressibility, $\beta_{s,id} = \beta_1 + (\beta_2 - \beta_1)\phi$ (dashed line), as a function of the methanol volume fraction, $\phi = \rho_1 n_2 M_2 / (\rho_1 n_2 M_2 + \rho_2 n_1 M_1)$.

The compressibility of the mixture is always above the ideal value. The inset, in the same figure, represents the difference $\beta_s - \beta_{s,id}$, reported as a function of the mole fraction. This *excess* compressibility shows a maximum in the same concentration range at which the hypersonic velocity and the excess mixing entropy^{19,32} show a minimum, and the noncoincidence effects of the O–H and C–O bands of methanol start to decrease in magnitude.⁸

As was shown in refs 5 and 22, methanol is supposed to largely preserve its chainlike structure down to $x_M = 0.3/0.4$. This seems to be supported by the fact that the adiabatic compressibility of the mixture behaves linearly with ϕ down to $\phi \approx 0.3$, although exceeding the ideal behavior given by $\beta_{s,id}$.

The result could be consistent with the idea that the addition of carbon tetrachloride locally gives rise to a structure in which the CCl₄ molecules interact with the methanol molecules involved in the polymer-like chains (heterogeneous association). The formation of such kinds of complexes goes on until the equimolar concentration is reached, after that regions of bulky CCl₄ become highly probable. Such an idea can be supported by a recent *ab initio* molecular orbital calculation for the acetone–(CCl₄)₄ cluster,²⁴ where the interaction between acetone and carbon tetrachloride has been related to the apparent electric field around a CCl₄ molecule: a similar effect could take place in methanol–CCl₄ mixtures driving the electrostatic interaction between the chlorine atom and the oxygen of the methanol molecule.

The situation appears as if the system could be described in terms of the ideal mixture of bulk methanol plus another (unknown) system, characterized by a compressibility value intermediate between methanol and carbon tetrachloride.

We have tried to extract the concentration dependence of the adiabatic compressibility associated with such heteroaggregates, under the assumption that the measured compressibility can be described as the linear combination between the pure methanol value and that (concentration dependent) of the heteroaggregates, i.e., $\beta_s = \beta_{het} + (\beta_2 - \beta_{het})\phi$. The resulting β_{het} is reported in Figure 6 as a dotted line. The continuous line in the same figure corresponds to the linear combination (weighted by the volume

fraction) between pure methanol and the values represented by the dotted line. The dashed–dotted line in Figure 5 has been obtained analogously, while the continuous line in the inset in Figure 6 has been obtained by subtraction between the calculated compressibility and the ideal compressibility (dashed line in Figure 6).

We are led to recognize the existence of some heterostructures, in which carbon tetrachloride molecules are coordinated with methanol. Such a situation would imply that no bulky CCl₄ is present in the system at methanol concentration as low as $\phi \approx 0.3$. In this range of concentration any carbon tetrachloride molecule added to the system is forced to fit into the free volume among the methanol chains (or to be involved in chain ends³³). Such a local structural arrangement could justify both the excess in the adiabatic compressibility and the observed minimum in the mixing entropy.³⁰

These local clusters become more and more improbable as the methanol content falls to a critical value, due to two different concomitant effects: on one hand, the very low methanol content would imply the existence of finite volumes containing bulk CCl₄; and on the other hand, the high methanol dilution is reflected in a decrease of the average length of the methanol polymer-like chains (probably with formation of some cyclic structures).

At infinite dilution, carbon tetrachloride acts as an inert solvent for methanol that is now almost completely dissociated; as a consequence, by dilution the asymptotic trend of the adiabatic compressibility toward the value of pure CCl₄ is retrieved.

In summary, the local structure of the bulk methanol turns out to be highly stable against any change in the density of the system. Only at a high enough dilution, where not negligible volumes of bulky CCl₄ are present, does the polymer-like structure of methanol begin to be destroyed. In particular, the observation that the excess compressibility reaches a maximum at the same concentration where the NCE associated with the O–H stretching band starts decreasing, due to the increasing weight of the end group contribution,⁸ agrees with a picture in which that concentration marks the percolation threshold for methanol.

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