Brillouin scattering investigation of ME6N liquid crystal in CCl4

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1. Introduction

The experimental analysis of excess thermodynamic properties of liquid mixtures is a common approach to extract information about the nature of the intermolecular potential [1–7].

Recently, we have shown how concentration dependence of the compressibility behaviour is mainly driven by excluded volume effects [8].

Following such an idea, we successfully have used a very primitive model based on hard-core interactions [9] in order to fit the experimental compressibility of several binary mixtures of molecular liquids [8]. Such a result seems to be a rather general one. In fact, similar conclusions were reached by Vlček and Nezbeda who found that excess properties of a real mixture do not differ significantly from those calculated for a primitive model [10,11].

Although an attempt to apply this theoretical approach to a mixture of a representative room-temperature ionic liquid and a common organic solvent has already been tried [12], its exact generalization to binary mixtures where one of two components is an elongated molecule is still missing. One of the best candidates to this scope seems to be a mixture composed by a liquid crystal immersed in a non-polar solvent. A liquid crystal is a state of the soft condensed matter with properties intermediate to those of liquids and crystals [13]. From a microscopic point of view they are featured by orientational and positional order induced by the long alkyl chain of their molecules. ME6N system has been selected since it has been already investigated through other techniques [14,15] and its average molecular aspect ratio (the ratio between the ellipsoid axes) has been already estimated by means of very recent ab-initio calculations [14].

In this study the experimental compressibility measured by Brillouin scattering is compared with the compressibility dependence on the concentration obtained from the theoretical approach based on a hard-core model.

2. Experimental procedures and results

ME6N has been purchased by Merk KGaA while CCl4 (reagent grade quality, 99.9%) was a Sigma-Aldrich product. ME6N (4-cyanophenyl-4′-hexylbenzoate) is a liquid crystal that exhibits, on heating, the following phase sequence: K–N (46 °C), N–I (47.9 °C), where K, N, and I stand for Crystal Nematic and Isotropic phases, respectively [13]. It is stable in the presence of the ambient oxygen up to approximately 100 °C and above this temperature only under inert atmosphere. It shows a rather high solubility in CCl4 at ambient temperature. ME6N/CCl4 mixtures have been prepared by weight, w, and then the concentration values have been translated into mole fractions, x. Samples have been put into a home-made optical thermostat allowing to control the temperature with an accuracy better than 0.2 °C.

The Brillouin scattering measurements have been carried out by means of a home-made double pass interferometer [16] at T = 60 °C. The cavity length was set to 54.5 mm, corresponding to a free spectral range of 27.5 GHz. The working finesse, estimated by the width of the Rayleigh line from an elastic scatterer (Latex spherules), turned out to be 50, corresponding to an interferometer pass band of 550 MHz. The 532 nm linearly polarized single-mode line of a Coherent Verdi laser, working at a mean power of 100 mW, was used as the probe. The polarized scattered intensity has been collected at different scattering angles (40° ≤ θ ≤ 140°) corresponding to values of the exchanged wave-vector, q, in the range 1.21·107 m−1 ≤ q ≤ 3.33·107 m−1. Density, ρ, and
Refractive index, \( n \), data have been measured, at \( T = 60 \, ^\circ\text{C} \), by means of an Anton Paar DMA 5000 density meter (\( \Delta \rho = \pm 2 \times 10^{-4} \, \text{g/cm}^3 \)) and an Abbe refractometer (\( \Delta n = \pm 0.5\% \)), respectively. The obtained \( x \)-dependencies of density and refractive index are reported in Fig. 1.

In Fig. 2 we report, as few examples, three of the spectra obtained at a scattering angle of 90\(^\circ\), at different sample composition.

The recorded spectra have been fitted with the convolution of the following expression [17] with the experimental elastic scattering profile

\[
I_VV(\omega) = \delta_R + A_B \left( \frac{\Gamma_R}{|\alpha - \sqrt{\omega^2 - \Gamma_R^2}|} + \frac{\Gamma_R}{|\alpha + \sqrt{\omega^2 - \Gamma_R^2}|} \right) + \frac{A_B \Gamma_R}{\sqrt{\omega^2 - \Gamma_R^2}} \left( \frac{\omega - \sqrt{\omega^2 - \Gamma_R^2}}{|\alpha - \sqrt{\omega^2 - \Gamma_R^2}|} + \frac{\omega + \sqrt{\omega^2 - \Gamma_R^2}}{|\alpha + \sqrt{\omega^2 - \Gamma_R^2}|} \right)
\]

where the symbols have the usual meaning [2,8]. From the fitting procedure the hypersonic frequencies (\( f_B = \frac{\omega_B}{2\pi} \)) have been determined with an accuracy of \( \pm 1.5\% \), while the error estimated on the Brillouin HWHMs (\( \Gamma_B \)) was \( \pm 5\% \).

The values of the frequency shifts stay on straight lines which pass through the origin when plotted as a function of the exchanged wave-vector, as it can be noted in Fig. 3. According to this observation, we are allowed to assume that in our systems any relaxation process is occurring on frequencies higher that those explored in our experiment.

The values of the hypersonic velocity, \( v_h \), have been calculated according to the relation:

\[
v_h = \frac{\omega_B}{q}.
\]

In Fig. 4 we report the dependence of the hypersonic velocity on the ME6N mole fraction.

### 3. Handling of data

By measuring the concentration dependence of the hypersonic velocity and density, the adiabatic compressibility, \( \beta_S \), can be calculated as:

\[
\beta_S = \frac{1}{\rho v_h^2}.
\]

The knowledge of the concentration dependence of some thermodynamic quantities can allow an inquiry into the inter-species interaction and into any structuring effect driven by it. In particular, the attention is usually focused on the deviations from some ideal behaviours.

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**Fig. 1.** Density and refractive index of ME6N/CCl\(_4\) mixtures as a function of the liquid crystal mole fraction, measured at 60 °C. Inset: plot of the density vs ME6N volume fraction, estimated following the procedure described in the text.

**Fig. 2.** Experimental Brillouin spectra, obtained at a scattering angle of 90°, at three different sample compositions. Continuous line represents the fitting results with eq. 1.

**Fig. 3.** Plots of the experimental Brillouin shifts vs exchanged wave-vector at three different concentrations. Continuous lines: linear fits of the experimental data.

**Fig. 4.** Hypersonic velocity as a function of the ME6N mole fraction, calculated by eq. 2.
Generally, ideality implies that volumes are additive. In order to test this circumstance we have to translate the mole fraction values into volume fractions, $\phi$.

As a first step we have calculated the apparent molar volumes of the mixtures, $V_M$, as

$$V_M = \frac{M_M}{\rho} = \frac{(1-x)M_{CCl4} + xM_{ME6N}}{\rho}$$  \hspace{1cm} (4)

with $M_M$ being the average molecular weight of the mixture, $\rho$ the density of the mixture and $M_{CCl4}$ and $M_{ME6N}$ the molecular weights of CCl4 and ME6N, respectively. An almost linear $x$-dependence of $V_M$ has been obtained with very small positive excess volumes (see Fig. 5) suggesting for a moderate repulsive interaction between components. We can account for these small deviations from additive behaviour by writing $V_M$ as

$$V_M = (1-x)V_{CCl4} + xV_{app}$$  \hspace{1cm} (5)

with $V_{app}$ being the apparent molar volume of ME6N [12]. It is quite obvious that $V_{app}$ does not correspond to any physical quantity; however, it can be assumed as a hypothetical quantity to which any deviation from ideality can be ascribed.

Once $V_{app}$ is defined, the ME6N volume fraction can be estimated as

$$\phi = \frac{xV_{app}}{(1-x)V_{CCl4} + xV_{app}}.$$  \hspace{1cm} (6)

The linear plot of density as a function of the calculated volume fraction, reported in the inset of Fig. 1, is a clear indication of the suitability of the above approach.

In Fig. 6 the volume fraction dependence of the adiabatic compressibility, calculated in agreement with Eq. (3), is reported (circles). As far as the adiabatic compressibility is concerned, the ideal condition would imply that it behaves linearly as a function of the solute volume fraction. The continuous line in Fig. 6 represents the estimated ideal behaviour of ME6N/CCl4 mixtures, where Eq. (6) has been taken into account to translate $x$-values into $\phi$-ones. While the small excess mixing molar volume, reported in Fig. 5, suggests the presence of repulsive interspecies interactions, the deviations observed for adiabatic compressibility seems to indicate that the expansion of the system corresponds to the establishment of a more rigid local coordination at intermediate concentrations.

In the following pages we will show how these apparently contradictory indications can be rationalized within a unique general framework, where only excluded volume effects are taken into consideration.

4. The model

We consider a binary mixture composed by $N_1$ elongated molecules and $N - N_1$ spherical molecules. We choose to represent the elongated molecules as prolate ellipsoids characterized by a length $l$ and a width $D$ while the diameter of the spherical molecule is $\sigma$. Furthermore, we consider that the molecules interact through a pair-wise additive hardcore potential. Within this scheme the excluded volume effects drive any phase transition. In fact, it has been already shown that a mixture composed of hard convex fluids and hard spheres exhibits a complex and rich phase diagram [18]. In particular, on the basis of a density functional theory, it has been shown that a hard sphere, hard ellipsoid mixture do not undergo phase separation in the isotropic phase. Moreover, the isotropic to nematic phase transition was found to occur at high packing fractions [19].

For sake of clarity we consider the hard ellipsoids as the solute, while the hard spheres are the solvent. For hard convex fluids it is possible to define the virial coefficients in terms of the functionals (volume $V$, surface area $S$ and the (1/4$n$)-multiple of the mean curvature integral, $R$) depending only on the geometric parameters of the ellipsoid (aspect ratio, $\lambda = l/D$) and of the sphere (diameter, $\sigma$) [9]. For the prolate ellipsoids of revolution we have:

$$V_{HE} = \frac{\pi}{6} \lambda D^3;$$
$$S_{HE} = \frac{1}{2} \left( 1 + \frac{\lambda^2 \cos(\lambda^{-1})}{\sqrt{(\lambda^2 - 1)}} \right) \pi D^2$$  \hspace{1cm} (7)
$$R_{HE} = \frac{1}{4} \left( \frac{\ln(\lambda + \sqrt{(\lambda^2 - 1)})}{(\lambda^2 - 1)} \right) D$$

and

$$V_{HS} = \frac{\pi}{6} \sigma^3;$$
$$S_{HS} = \pi \sigma^2$$
$$R_{HS} = \frac{1}{2} \sigma$$  \hspace{1cm} (8)

with $V_{HE}$ and $V_{HS}$, $S_{HE}$ and $S_{HS}$ and $R_{HE}$ and $R_{HS}$ being the volume, surface area and the mean curvature integral of the hard ellipsoid and hard sphere, respectively.

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Fig. 5. Calculated excess volumes of ME6N/CCl4 mixtures as a function of the liquid crystal mole fraction. The error bars are also shown. See text for details.

Fig. 6. Adiabatic compressibility as a function of the volume fraction, calculated in agreement with eq. 3. Circles: experimental results. Continuous line: estimated ideal behaviour (see text for details).
The packing fraction of a hard-core model is defined as:

$$\eta = \frac{\rho}{\beta x_1 V_{HE} + x_2 V_{HS}}$$  \hspace{1cm} (9)$$
where $\rho$ is the number density of the mixture, $x_1$ and $x_2$ are the mole fractions of the two components ($x_1 + x_2 = 1$), respectively.

The knowledge of the analytical expressions of the geometric parameters allows obtaining the exact expression of the second virial coefficient of the mixture:

$$B = x_1^2 B_{11} + 2 x_1 x_2 B_{12} + x_2^2 B_{22}.$$  \hspace{1cm} (10)$$

The partial virial coefficients ($B_{11}$, $B_{12}$, $B_{22}$) can be expressed as:

$$B_{11} = V_{HE} + R_{HE} S_{HE}$$
$$B_{12} = V_{HS} + R_{HE} S_{HS}$$
$$B_{22} = \frac{1}{2} (V_{HE} + V_{HS} + S_{HE} R_{HS} + S_{HS} R_{HE}).$$  \hspace{1cm} (11)$$

In the last decades, many equations of state have been proposed for hard-bodies mixtures and the predictions of some of these are in excellent agreement with the estimates of numerical simulation [9,19–21]. However, the aim of our approach is to show as even the most simple equation of state, is able to obtain reliable agreement with the experimental results.

The virial equation of state truncated after the second term is:

$$\beta P = \rho + B(x) \rho^2$$  \hspace{1cm} (12)$$
where $\beta$ is the inverse of the temperature in terms of the Boltzmann constant $k_B$. For the third virial coefficient only the analytical lower and upper limits are known [9]. However, the effect of higher coefficients may be taken into account indirectly by resummation theories such as the $y$-expansion theory of Barboy and Gelbart [21]. Within this approach the equation of state is written as a series of terms depending on a new variable, $y = 1/(1 - \rho V_0)$, ($V_0 = V_{HE} + V_{HS}$ is the total volume of the model):

$$\beta P = y + C(x) y^2$$  \hspace{1cm} (13)$$
where:

$$C(x) = B(x) - V_0.$$  \hspace{1cm} (14)$$

The isotherm susceptibility is defined by the following expression:

$$\chi_I^{-1} = \beta \left( \frac{\partial P}{\partial \rho} \right)$$  \hspace{1cm} (15)$$
while the adiabatic susceptibility is related to the isotherm susceptibility through the specific heat capacity (at constant volume and pressure):

$$\chi_S = \frac{C_V}{C_P} \chi_I$$  \hspace{1cm} (16)$$

For a hard core fluid [22]:

$$C_P = C_V + \chi_I \left( \frac{\beta P}{\rho} \right)^2.$$  \hspace{1cm} (17)$$

Hence, it is trivial to infer that in the analytical expression of the adiabatic compressibility the geometric parameters $L$ and $D$ explicitly enter.

5. Results

The experimental adiabatic compressibility has been compared with the estimates obtained using the non-additive hard-sphere model and the hard-sphere/hard ellipsoids model.

5.1. Hard-sphere model

As first attempt we used as a model a non-additive hard-sphere mixture. This system is characterized by two collision diameters ($\sigma_1, \sigma_2$) and by an interspecies minimum distance $\sigma_{12} = 1/2(\sigma_2 + \sigma_1)(1 + \Delta)$ where the dimensionless parameter $\Delta$ accounts for inter-specie interactions besides the purely additive hard sphere interactions (see Ref. [8] for details). This choice is due to the negative value of the experimental adiabatic compressibility. In fact, it appears quite evident that a purely additive ($\Delta = 0$) hard-sphere potential should be able to model only a positive excess value of the compressibility. Within this scheme, the ME6N molecule is very roughly approximated by a sphere with an effective radius $\sigma_2$ [8,11]. We have used as equation of state the virial expansion arrested to the third virial coefficient which for hard spheres is given by a simple analytical expression (see Ref. [8] for details). The fitting procedure requires the determination of the ratio between the effective diameters of ME6N and CCl4 (represented as a sphere of diameter $\sigma_1$). As a first step, the calculated experimental number

![Fig. 7. Number density as a function of ME6N mole fraction. Circles: data calculated through the experimental data. Continuous line: fitting result with the hard sphere model.](image1)

![Fig. 8. Excess adiabatic compressibility of ME6N/CCl4 as a function of mole fraction. Open circles: experimental results; Dotted line: Virial equation of state arrested to the third order of a non-additive hard-sphere model; Continuous line: Barboy-Gelbart equation of state for a hard sphere, hard ellipsoid model; Dashed line: Virial equation of state arrested to the second order for hard sphere, hard ellipsoid model.](image2)
density (proportional to $1/V_M$, open circles in Fig. 7) is fitted with the theoretical expression for the hard-sphere model. The best fitting procedure converges when the value of this ratio $(\sigma_2/\sigma_1)$ reaches the value of 1.202.

Turning back to fit the experimental adiabatic compressibility, the only free parameter remains the non-additive term. A best fit is obtained for $\Delta = 0.00712$ (dotted line in Fig. 8). The value of the packing factor, $\eta_i$, is fixed to 0.2. A positive value of the $\Delta$ parameter agrees with the idea that, due to the non-spherical shape of one of the components, the mixture can exhibit a more dense local structure than that would be allowed by a purely additive (i.e., $\Delta = 0$) hard-sphere system.

5.2. Hard sphere, hard ellipsoid model

A more natural system to model the real liquid crystal is a binary hard sphere, hard ellipsoid mixture. In this case we do not need to add the non-additive parameter. This condition agrees with some density functional theory results showing that the isotropic phase of the hard-convex mixture does not demix and in a sense, the fluid is additive. The calculated number density of the hard sphere, hard ellipsoid mixture perfectly fits the corresponding experimental quantity, when the ratio between the ellipsoid axes (the aspect ratio $L/D$) is set to 3.8 (consistently with ab initio calculation results [14]) and the ratio between the smaller size of the ellipsoid and the diameter of the sphere is set to 0.778 (see Fig. 9). The fitting result is indistinguishable from that obtained through the hard-sphere model reported above in Fig. 6. However, it is worth to remark that in this case the model does not need accounting for a non-additive term. In Fig 8, we also compared the excess contribution of the adiabatic compressibility of the hard-sphere, hard ellipsoids mixture, obtained using the virial and the more sophisticated Barboy-Gelbart equation of state, with the estimate obtained by the hard-sphere model, forcing to represent the shape of the liquid crystal molecule as an effective sphere. We found that the only way to obtain a fit comparable with the experimental data was to impose a non-additive condition to the hard-sphere mixture. Vice versa, adopting the hard sphere/hard ellipsoid model, we can avoid to insert the non-additivity effects. This result is also in agreement with a previous density functional study on a hard sphere/ hard ellipsoid mixture where it was demonstrated that the isotropic phase is additive [19].

Among the different adopted equations of state, the Barboy-Gelbart one seems more adequate than the simple virial equation (truncated to the second order), since it allows reproduction of the experimental data with a realistic value of the packing fraction. This result supports our assumption that excess compressibility is mainly originated by excluded volume (hard-core) effects and that is additive in nature, in agreement with the experimentally observed additivity of volumes, also when mixtures of non-spherical particles are taken into account.

6. Concluding remarks

In this paper we report some Brillouin scattering measurements carried out on a mixture of the ME6N liquid crystal immersed in CCl₄ liquid. The experimental results have been rationalized modelling the system as composed by a mixture of hard convex bodies.

We have used two different hard-core models to fit the adiabatic compressibility of the mixture. In the first case, we roughly used a hard-sphere mixture forcing to represent the shape of the liquid crystal molecule as an effective sphere. We found that the only way to obtain a fit comparable with the experimental data was to impose a non-additive condition to the hard-sphere mixture. Vice versa, adopting the hard sphere/hard ellipsoid model, we can avoid to insert the non-additivity effects. This result is also in agreement with a previous density functional study on a hard sphere/hard ellipsoid mixture where it was demonstrated that the isotropic phase is additive [19].

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