Excess compressibility in binary liquid mixtures

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Brillouin scattering experiments have been carried out on some mixtures of molecular liquids. From the measurement of the hypersonic velocities we have evaluated the adiabatic compressibility as a function of the volume fraction. We show how the quadratic form of the excess compressibility dependence on the solute volume fraction can be derived by simple statistical effects and does not imply any interaction among the components of the system other than excluded volume effects. This idea is supported by the comparison of the experimental results with a well-established prototype model, consisting of a binary mixture of hard spheres with a nonadditive interaction potential. This naive model turns out to be able to produce a very wide spectrum of structural and thermodynamic features depending on values of its parameters. An attempt has made to understand what kind of structural information can be gained through the analysis of the volume fraction dependence of the compressibility. © 2007 American Institute of Physics. [DOI: 10.1063/1.2745292]

I. INTRODUCTION

The investigation of the excess thermodynamic properties of different liquid mixtures is a widely adopted approach to gain insight into the nature of intermolecular interactions, phase stability, and concentration dependent structural effects as well as to develop models capable of correlating and predicting their features. In many cases such information is of practical technological relevance in the design of storage and handling facilities for liquid mixtures.

Ultrasonic and hypersonic waves are perfect probes to gain insight on the molecular size and shape and on intermolecular interactions of physical systems. The analysis of the macroscopic acoustic parameters, namely, sound velocity and absorption, provides some details about all thermodynamic processes where density fluctuations are involved. When the density in a binary mixture behaves linearly with density measurements allows us to calculate the concentration behavior of the adiabatic compressibility, which correlates the measured acoustic observables to the structural properties originating from intermolecular interactions. When the density in a binary mixture behaves linearly or almost linearly with the solute volume fraction, a commonly adopted approach starts with the assumption of volume additivity. The volume of an ideal mixture \( V_{id} \) is written as

\[
V_{id} = n_A V_{mA} + n_B V_{mB},
\]

where \( n_A \) and \( n_B \) are the mole numbers of solvent and solute, respectively, and \( V_{mA} \) and \( V_{mB} \) are the corresponding molar volumes. Differentiating the Eq. (1) with respect to the pressure, the ideal value of adiabatic compressibility is obtained as a linear function of the volume fractions, \( \phi_A \) and \( \phi_B \) \((\phi_B = \phi \) and \( \phi_A = 1 - \phi)\),

\[
\beta_{s, id} = -\frac{1}{V_{id}} \left( \frac{\partial V_{id}}{\partial p} \right)_S = \phi_A \beta_A + \phi_B \beta_B = (1 - \phi) \beta_A + \phi \beta_B,
\]

where \( \beta_A \) and \( \beta_B \) are the values of adiabatic compressibility of pure components.

The excess compressibility \( \beta_{ex} \) is usually defined as the difference between the measured adiabatic compressibility and Eq. (2). The observation of deviations from linearity in \( \phi \) is generally reported as a deviation from ideality, and it is commonly related to the interaction between the mixture constituents.

More specifically, a negative (positive) excess compressibility in binary mixtures is related to attractive (repulsive) interactions between unlike species which gives rise to a more (less) rigid local structure. Moreover, more complicated behaviors can be ascribed to the ability of one or both components to develop dynamical networks, whose properties explicitly depend on concentration. Equation (2), although valid in very low density regimes, is often a too rough approximation for ordinary liquid systems.

In general, the Gibbs free energy for a binary mixture is written as

\[
G = x_A G_A^0 + x_B G_B^0 + RT(x_A \ln x_A + x_B \ln x_B) + \Delta G_f,
\]

where \( G_A^0 \) and \( G_B^0 \) are the reference states of A and B \((A \) and \( B \) indicate the two components of the binary mixture), respectively, the third term corresponds to the ideal (random)
mixing, and $\Delta G_f$ is the Gibbs free energy of formation of a binary stoichiometric phase.\(^{16}\) Obviously, the excess term contains both enthalpic and entropic contributions and their disentanglement can be a nontrivial task.

A very usual approach for modeling the excess quantities makes use of an empirical polynomial expansion (Redlich-Kister polynomials\(^{17}\)) as a function of the component concentrations, $c_A$ and $c_B$, respectively. In the case of the compressibility, we have

$$
\beta_{ex} = c_A c_B \sum_{i=0}^{n} A_i (c_A - c_B)^i,
$$

where $A_i$ are the phenomenological expansion coefficients. Equation (4), adopting the volume fraction as the concentration, can be easily rearranged as

$$
\beta_{ex}(\phi) = \phi(1-\phi) \sum_{i=0}^{n} A_i (1-2\phi)^i.
$$

In this article we will investigate the effective possibilities of extracting information about intermolecular interactions and structural properties from the analysis of the concentration dependence of the compressibility. Within this framework, we will discuss some Brillouin scattering results on binary mixtures exhibiting different kinds of interaction, comparing them with the predictions obtained from a theoretical model.

II. EXPERIMENTAL SECTION AND RESULTS

Binary mixtures of linear alcohols and chloroform in carbon tetrachloride were prepared using CCl$_4$, methanol, ethanol, 1-propanol, 1-butanol, $n$-pentanol, and chloroform from Sigma-Aldrich, reagent grade quality. Each Brillouin scattering measurement was performed in a 90° geometry, using the 532 nm linearly polarized single-mode line of a Coherent DPSS-532-200 laser, operating at a mean power of 100 mW, as the probe. The measurements on the CCl$_4$/CHCl$_3$ mixture were performed by means of a Sandercock-type (3+3)-pass tandem Fabry-Pérot interferometer, working at a free spectral range of 15 GHz with an estimated finesse of 80. All the other spectra were collected by a double pass Fabry-Pérot interferometer made by SO-PRA. This instrument was modified to obtain dynamical self-alignment and high stability over long times and is fully controlled by a PC software.\(^{18}\) The cavity length of the interferometer was set to 10 mm, corresponding to a free spectral range of 15 GHz. The working finesse, determined by the experimental apparent full width at half maximum of the intensity profile from a static scatterer (latex), turned out to be about 50. During the experiment, the samples were thermostated at 20±0.1 °C. The recorded spectra were fitted by the convolution of the experimental resolution function with the following elastic scattering profile:\(^{4}\)

$$
I_{VV}(\omega) = \delta_R + A_B \left[ \frac{\Gamma_B}{\omega - \sqrt{\omega_B^2 - \Gamma_B^2} + i \Gamma_B} \right] + \frac{A_B \Gamma_B}{\sqrt{\omega_B^2 - \Gamma_B^2} \left[ \omega + \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2} - \frac{A_B \Gamma_B}{\sqrt{\omega_B^2 - \Gamma_B^2} \left[ \omega - \sqrt{\omega_B^2 - \Gamma_B^2} \right]^2 + \Gamma_B^2},
$$

where the symbols have the usual meaning.\(^{9,13,14}\)

In Fig. 2 we report, as an example, the experimental Brillouin spectrum obtained for CHCl$_3$/CCl$_4$ mixture at room temperature. It is worth to note that all mixtures are completely miscible and homogeneous at least in the thermodynamic regime investigated in this set of measurements. As a consequence we do not expect in the spectra any signatures of the presence of concentration fluctuations. In addition, an inspection of Fig. 2 clearly shows that no relaxation process resulting in a Mountain mode is detected.

The hypersonic frequencies ($f_R=\omega_R/2\pi$) were determined by the fitting procedure with an accuracy of ±1.5%, while the estimated error on the Brillouin half-widths at half maximum (HWHMs) ($\Gamma_R$) was ±5%. The fitting parameters are reported in Fig. 3.
The setup-independent parameters, namely, the hypersonic velocity \( \nu_h \) and of the normalized sound absorption \( \alpha/\nu_h \) were calculated according to the relations

\[
\nu_h = \omega_p/q,
\]

\[
\alpha/\nu_h^2 = 2\pi\Gamma_p/(\nu_h^2\omega_p^2),
\]

where \( q = (4\pi n/\lambda_0)\sin(\theta/2) \) is the amplitude of the exchanged wave vector, \( \lambda_0 \) is the incident wavelength, and \( \theta \) is the scattering angle. The concentration dependence of the hypersonic velocity and absorption is plotted in Fig. 4 for CCl\(_4\)/CH\(_3\)OH mixtures. We found a very good agreement with previously obtained results suggesting that any possible relaxation process takes place far from room temperature.\(^{13,14,19}\) From the knowledge of the hypersonic velocity it is possible to evaluate the adiabatic compressibility through the following expression:

\[
\beta_s = \frac{1}{\rho\nu_h^2}.
\]

The normalized absorption as a function of the volume fraction turns out to be almost independent (within the 5% experimental error) of the kind of linear alcohol investigated and is reported only for the CCl\(_4\)/CH\(_3\)OH mixture in Fig. 4, while the velocities at high alcohol content increase with the alcohol length (see Fig. 5).

### III. DISCUSSION

The observation that both density and refractive indices behave linearly with the volume fraction for each of the studied mixtures makes us confident in describing them as a noninteracting or weakly interacting binary liquid systems.
coefficients are fully analytical up to the third order. To test
the equation of state, namely, the virial expansion whose partial
equation of state is required. We have adopted the simplest
system thermodynamic parameters, an expression for the
value of
withstanding the simplicity of the interaction, by varying the
species minimum distance
for CHCl₃
CCl₄ and 1.49 g/cm³ for CHCl₃
stitution of a chlorine atom with an hydrogen. Even if CHCl₃
light gray area, first order term of Redlich-Kister polynomial; and dotted
Kister polynomial; continuous line first order Redlich-Kister polynomial;
compressibility for this mixture is reported as a function of
is a weakly polar molecule we do not expect that electro-
mations of the ideality condition.
In particular, the carbon tetrachloride/chloroform mixture
can be considered as one of the best experimental approxima-
tions of the ideality condition.
Indeed, carbon tetrachloride and chloroform molecules
have similar molar volumes (96.5 cm³/mole for CCl₄
and 80.0 cm³/mole for CHCl₃) and densities (1.59 g/cm³ for
CCl₄ and 1.49 g/cm³ for CHCl₃) differing just for the sub-
itution of a chlorine atom with an hydrogen. Even if CHCl₃
is a weakly polar molecule we do not expect that electro-
static interactions to be strong enough to produce a local
coordination that is stable in the time scale characteristic (∼10⁻⁹ s) for the present experiment. In Fig. 6 the excess
compressibility for this mixture is reported as a function of
the CHCl₃ volume fraction. The dashed and continuous lines
are the zeroth order and the first order Redlich-Kister polyno-
mials, respectively, while the shadowed area represents the
first order term.
The observation of a positive excess compressibility
suggests that the predominant contributions to the interspe-
cies potential are due to repulsive interactions. In order to
rationalize this result, we introduce the most basic model for
a liquid mixture, i.e., the hard-sphere model. It is character-
ized by two like collision diameters (dₐ, dₐ) and by an inter-
species minimum distance
where the dimensionless parameter Δ accounts for deviations of
unlike excluded volume interactions from additivity.²⁰ Not-
withstanding the simplicity of the interaction, by varying the
value of Δ, the model can provide a surprisingly rich variety
of thermodynamic behaviors. In order to evaluate most of the
system thermodynamic parameters, an expression for the
equation of state is required. We have adopted the simplest
equation of state, namely, the virial expansion whose partial
coefficients are fully analytical up to the third order. To test
the reliability of this choice, we also used some more sophis-
ticated and accurate equations of state obtaining basically the
same final results.²¹,²² In general, the virial equation of state
can be written as

\[
\frac{p}{k_B T} = \sum_{i=1}^{\infty} b_i \rho^i,
\]

where \( p \) is the pressure, \( T \) is the absolute temperature, \( k_B \) is
the Boltzmann constant, \( \rho = \rho_A + \rho_B \) is the total number
density (\( \rho_A \) and \( \rho_B \) being the number densities of the species
\( A \) and \( B \), respectively), and \( b_i \) are the virial coefficients
(\( b_1 = 1 \)).
For a binary hard-sphere mixture \( b_2 \) and \( b_3 \) are given by
simple analytical expressions and depend explicitly on the
molar fractions of the two species and on the collision
B20 diameters. The isothermal susceptibility \( \chi_T \) is defined by
the following expression:

\[
\chi_T^{-1} = \frac{1}{k_B T} \left( \frac{\partial p}{\partial T} \right)_T = \sum_{i=2}^{\infty} (i-1) b_{i-1} \rho^{i-2},
\]

where the number density depends on the packing fraction \( \eta \)
through the following relation:

\[
\rho = \frac{6}{\pi [xd_A + (1-x)d_B]} \eta,
\]

with \( x \) and \( (1-x) \) being the mole fractions of the two components.
The adiabatic compressibility \( \beta_s \) is related to isothermal
compressibility \( \beta_T \) through the expression

\[
\beta_s = \beta_T \frac{c_v}{c_p} = \rho k_B T \frac{c_v}{c_p} \chi_T,
\]

where \( c_p \) and \( c_v \) are the specific heats at constant pressure
and volume, respectively. It is easy to show that for a hard-
sphere mixture,²⁰

\[
c_v = \frac{3}{2} Nk_B
\]

and

\[
\frac{c_p}{Nk_B} = \frac{3}{2} Nk_B + \rho k_B T \beta_T \left[ \frac{p}{k_B T} \right]^2,
\]

where \( N \) is the number of particles. In Fig. 6 the dotted line
represents the best fitting of excess compressibility with Eq.
(13). In the procedure, four fitting parameters should be in-
volved, namely, \( d_A, d_B, \eta, \) and \( \Delta \). However, we will assume
that the values of \( \eta \) are low enough to ensure a complete
random mixing of the two components. Under this condition
\( \eta \) only affects the absolute value of the calculated compres-
sibility, while it has no influence on the shape of its concen-
tration dependence. In addition, we note that the shape of the
calculated curves markedly depends only on the diameter
ratio.
The best fitting reported in Fig. 6 has been obtained for
\( d_B/d_A = 0.79 \) and \( \Delta = 0 \) (additive mixture), which are realistic
values for chloroform/carbon tetrachloride mixtures (in our
fitting procedure the value of the \( \eta \) parameter has been set to
0.2 and a prefactor has been inserted in order to fit the am-
plitude of the compressibility).
It appears quite evident that a purely additive hard-
sphere potential is able to model a positive excess value of

![Graph](image-url)
the compressibility. Figure 6 shows that the curve obtained from this simple model is almost indistinguishable from the first order Redlich-Kister polynomial. This is not surprising since the zeroth order term of the polynomial expansion [Eq. (5)] is a quadratic term \( \propto \phi(1 - \phi) \), i.e., it is proportional to the probability that two unlike molecules come into close contact.

It can be easily verified that both the zeroth order polynomial and the hard-sphere mixture give the same results in the \textit{almost} equal diameter case \((d_B/d_A \simeq 1)\). Taking into account for different sizes of the mixing species, the hard-sphere model leads to deviations from the symmetric quadratic form. Similarly, the first order expansion of Eq. (5) leads to the appearance of the same asymmetry.

Therefore, the first order Redlich-Kister polynomial and the additive hard-sphere potential are able to fit positive excess compressibility with comparable accuracy. In order to investigate the role played by aggregative phenomena in one of the components, due to hydrogen-bondlike interactions, we have considered a more complicated class of liquid mixtures represented by linear alcohols solutions in carbon tetrachloride.

Some calorimetric measurements\(^5,23\) in methanol/CCl\(_4\) mixtures revealed a minimum in the mixing entropy which was interpreted as a result of the competition among different contributions. In previous works on the same solutions\(^13,14\) the concentration dependence of the hypersonic velocity was interpreted on the basis of the formation of a weak local heterocoordination, theoretically predicted\(^24\) and experimentally supported by noncoincidence Raman scattering results\(^25\) and dielectric relaxation measurements.\(^26,27\) In particular, the positive deviation of the adiabatic compressibility from the ideal behavior [Eq. (2)] was ascribed to a local coordination between alcohol and carbon tetrachloride molecules.

A similar positive deviation of the adiabatic compressibility has been observed for the whole set of linear alcohols/CCl\(_4\) mixtures, as it is shown in Fig. 7. We note an increase of the compressibility with increasing alcohol length. This behavior can be interpreted as a consequence of a linear decrease of the pure alcohol compressibility as a function of molar volume, which is documented in the inset of Fig. 7. This would suggest that the main contribution to the concentration dependence of the compressibility in these mixtures is due to the density of hydrogen bonds involved in the local structure. In fact, a longer alcohol chain implies a higher density of intrachain covalent bonds with respect to the density of the intermolecular hydrogen bonds. Figure 8, where the density dependence on the molecular weights is plotted for the pure linear alcohols, seems to support this hypothesis.

In particular, in Fig. 7 the almost linear dependence of the mixture compressibility, observed for \( \phi \approx 0.3 \), can be associated\(^13,14\) with the tendency of the alcohols to maintain their bulk structure under dilution. It is only low enough concentrations that the hydrogen bond connectivity is lost and the compressibility falls down towards the value of the bulk CCl\(_4\) (see Fig. 7). At intermediate concentrations, one could assume the establishment of nontrivially random coordinations between the solvent and the alcohol, driven by electrostatic interaction beyond excluded volume effects.\(^24,25\)

In Fig. 9 we plot the excess compressibility of the mixtures, calculated as the differences between the \( \beta_s \) values reported in Fig. 7 and Eq. (2). A positive excess compressibility can be observed with a maximum located at about \( \phi = 0.3 \), independently of the alcohol under consideration. Unfortunately, the absolute values of each set of data can be affected by different systematic errors, whose effects are enhanced after the subtraction of the ideal behavior. As a consequence, the difference between the absolute values of \( \beta_{ex} \) from mixtures involving different alcohols is intrinsically affected by errors and we will not further discuss this point.

![FIG. 7. Adiabatic compressibility for mixtures of linear alcohols in CCl\(_4\) as a function of the alcohol volume fraction. Inset: dependence of the adiabatic compressibility on the molar volume of pure alcohols. The error bars are systematically smaller than the size of the markers.](image)

![FIG. 8. Density of pure linear alcohols as a function of the molecular weight. The error bars are systematically smaller than the size of the markers.](image)
mental excess compressibility for aqueous solutions of poly-
compressibility is observed, we show in Fig. 10 the experi-
information about the occurrence of concentration dependent
result as the negative nonadditive parameter.
structure. The second order term in the Redlich-Kister ex-
ure, the dashed and continuous lines represent the fitting of
nificant OH free group density dependence. In the same fig-
order and a first order Redlich-Kister polynomial; dark gray area, second order term of Redlich-Kister poly-
and dotted line, best fitting with Eq. (13). Typical errors are reported
only for the methanol set of data.

The concentration at which excess compressibility ex-
hits its maximum value should depend on the free OH
group density (i.e., on the length of the alcohol). On the
 contrary, the curves reported in Fig. 9 do not show any sig-
ificant OH free group density dependence. In the same fig-
ure, the dashed and continuous lines represent the fitting of
the experimental excess compressibility (averaged over the
different alcohols) with the zeroth order and the second order
Redlich-Kister polynomials, respectively, while the light
gray and dark gray areas are the first order and second order
terms, respectively.

The hard-sphere model can be successfully applied also
to these binary mixtures. In fact, in Fig. 9 the dotted line
represents the best fitting of the excess compressibility ob-
tained with Eq. (13) for $d_B/d_A=0.81$ and $\Delta = -0.1$. A nonzero
$\Delta$ value implies some interaction between the unlike compo-
nents. Hence, the nonadditive parameter takes into account
the extra contribution to the interspecies potential that could
affect the local coordination in a concentration dependent
way. In particular, with the value of $\eta$ being fixed and, as a
consequence, the values of $\rho_i$, $\Delta < 0$ models a less rigid
structure. The second order term in the Redlich-Kister ex-
pansion (dark shadowed area in Fig. 9) produces the same
result as the negative nonadditive parameter.

Summing up, a positive excess compressibility carries
information about the occurrence of concentration dependent
aggregative phenomena. In order to test if the hard-sphere
model can be extended to cases where a negative excess
compressibility is observed, we show in Fig. 10 the experi-
mental excess compressibility for aqueous solutions of poly-
(ethylene glycol). The dashed and the continuous lines in
Fig. 10 are the fits of the experimental data with a zeroth
order and a first order Redlich-Kister polynomial, respec-
tively, while the shadowed area represents the first order
term.

The dotted line in Fig. 10 represents the fitting of the
experimental data with Eq. (13), obtained for $d_B/d_A=1.04$
and $\Delta = 5 \times 10^{-4}$. In this case, a positive $\Delta$ value models a
more rigid structure which is consistent with the existence of
heteroaggregation via hydrogen bonding. The very low value
of the $\Delta$ parameter also agrees with the experimental evi-
dence that volumes are nearly additive.

IV. CONCLUDING REMARKS

In this paper we have reported some results from Bril-
louin scattering experiments carried out on several binary
liquid mixtures. We have noted positive or negative excess
contributions in the adiabatic compressibility depending on
the nature of the intermolecular interactions underlying in
the different investigated mixtures. The behavior of the ex-
cess compressibility can be adequately modeled by the sim-
plest reference system for liquids, namely, the hard-sphere
model. The introduction of the nonadditive parameter in such
a system allows us to tune the interactions between unlike
molecules maintaining the basic repulsive features.

Consistent results have been recently obtained by Vlček
and Nezbeda who performed simulations on water-methanol
mixtures. In their approach they used interaction potentials
based on the concept of primitive models, i.e., models that
descend directly from the considered realistic parent models
and that reproduce the structure of the parent fluids
semiquantitatively. By considering only the pseudohard
body fluids underlying the primitive models (i.e., by
switching off the attractive interactions) and incorporating a
nonadditive hard-sphere repulsion, they found that excess
properties do not differ significantly from those calculated
for the full primitive model (i.e., with also attractive interac-
tions).

Both results lead to conclude that the nonideality of liq-
uid mixtures depends mainly on the excluded volume effects,
particularly on their nonadditive nature. This also agrees
with the indication coming from the well-known Prigogine-
Flory-Patterson theory, suggesting that geometrical ef-
fects play the major role in determining both the sign and the amplitude of excess properties in liquid mixtures.

In addition, we have shown how an excess compressibility can also be observed in systems for which the ideal condition given by Eq. (2) is rigorously fulfilled (fixing the value of the $\eta$ parameter in the hard-sphere model implies that volumes are additive). On this perspective, our result agrees with the statement of Flory according to which the choice of the null volume state as the ideal one is rather arbitrary since it does not imply, a priori, that all the other thermodynamic quantities should follow the same linear behavior as a function of the concentration.

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