Structural Properties of 1-Octanol/*n*-Octane Mixtures Studied by Brillouin Scattering

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Polarized Rayleigh−Brillouin spectra of 1-octanol/*n*-octane solutions at different mole fractions have been recorded in the temperature range of 5−70 °C by using a 90° scattering configuration. Hypersonic velocities and acoustic attenuations have been calculated by means of a fitting procedure with suitable Lorentzian functions. The relaxation of the liquid structure revealed by viscous and thermal energy losses has been interpreted and discussed in terms of a local H-bond network and conformational modifications. The thermal behavior of macroscopic parameters such as number density and shear viscosity has also been studied in the same temperature range in an effort to better interpret the observed relaxation processes and the distribution of their relaxation times.

1. Introduction

The role played by the strength of H-bonding in the structure and stability of local aggregates of *n*-alcohols has been recognized for a long time.[1−6] It has also been established that the strength of this intermolecular interaction inversely scales with the length of the alkylic chain. More stable aggregates are found in alcohols with a shorter alkylic tail, and the bond forces due to the O−H group interactions prevail over those of the hydrocarbon chain. On the other hand, the length of the chain may in some way govern the shape and size of the self-aggregated species under definite thermodynamic conditions.

Thus, in the bulk of long chain liquid alcohols, the existence of different domains, where ordered and disordered regions are randomly distributed, can be envisaged. Since ordered regions hinder the cooperative effects of adjacent disordered chain segments, it is reasonable to assume that the transport properties of such fluids can be strongly modified by varying the local structure of self-aggregating molecules. These properties are, in fact, very sensitive to the collective motions of the fluid in the hydrodynamic regime. An efficacious and selective variation of the local structure can be carried out with an appropriate chemical dilution. In this respect, a good solvent should have the same, or a very similar, hydrophobic part of the alcohol molecule. In other words, the mixture should be constituted by an alkane/alcohol couple, where the presence of the OH group is the only difference between the two partners. In this way, the dilution of the alcohol with the corresponding alkane lowers the strength of the H-bonding network, leaving the other intermolecular forces unchanged. As a consequence, the scenario of the chain segmental motions is supposed to be the same as that of the pure alcohol, since the local environment of the hydrocarbon tails is unperturbed by the solvent molecules.

In a series of articles mostly from the 1980s,[1−3,5,6] the intermolecular forces of alcoholic liquid systems were explored, to distinguish the effects of hydrogen bonding from those due to the methylenic chain. The changes in molecular structure, linear or branched, were explored,[3] and the effect of the steric hindrance of the hydrogen-bonding network was shown.

In the past few years, we have investigated the structural and transport properties of liquid 1-octanol.[7−10] In this article, we describe the effects of different *n*-octane concentrations on the structural and dynamic behavior of 1-octanol. This system should form phases at different degrees of “rigidity”; that is, the H-bond network can be strongly modified in the solutions with respect to pure 1-octanol. This fact should be indicated by the values of the fluctuating variables in the hydrodynamic regime. Density and viscosity measurements of mixtures at different mole fractions were carried out, and hypersound velocities and acoustic absorption coefficients were detected by Brillouin scattering in the gigahertz (GHz) frequency range.

This work confirms previous literature studies[3,5] performed at room temperature and enhances the knowledge about the behavior of the 1-octanol/*n*-octane system in the temperature range of 5−70 °C and in the GHz domain.

2. Experimental Section

1-Octanol and *n*-octane were spectroscopic grade products from Fluka and were ≥99.5% pure. Mass densities and viscosities of the binary mixtures at the various temperatures were measured with apparatus and methods described elsewhere.[11]

Polarized Rayleigh−Brillouin (R−B) spectra were recorded by using a 90° scattering geometry with a 300 mW, 514.5 nm excitation from an argon ion laser, and the apparatus described in detail elsewhere.[7,11] Accurate frequency calibrations and free spectral range (FSR) evaluations were done through the Brillouin shift position of the carbon tetrachloride. The FSR was varied when the sample was changed in an effort to avoid any overlapping of the adjacent interferometric orders, and the three orders of interferometric R−B signals in the PC-generated oscillographic spectrum; the working finesse was always around 35. The experimental data were deconvoluted by using a Gaussian function having a width equal to that of the instru-

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TABLE 1: Classic and Hypersonic Absorption of *n*-Octane at Different Temperatures

T (°C)	υ_0[5,13,14] (m/s)	$(\alpha/f^2)_{\text{class}}$ ($\times 10^{16}$ s^2/cm)	$(\alpha/f^2)_{\text{hy}}$ ($\times 10^{16}$ s^2/cm)	$(\alpha/f^2)_{\text{hy}}/(\alpha/f^2)_{\text{class}}$
20	1188.6	1.20	4.53	3.77
25	1177.8	1.19	5.15	4.33
30	1150.2	1.22	5.45	4.45

TABLE 2: Classic and Hypersonic Absorption of 1-Octanol at Different Temperatures

T (°C)	υ_0[15] (m/s)	$(\alpha/f^2)_{\text{class}}$ ($\times 10^{15}$ s^2/cm)	$(\alpha/f^2)_{\text{hy}}$ ($\times 10^{16}$ s^2/cm)	$(\alpha/f^2)_{\text{hy}}/(\alpha/f^2)_{\text{class}}$
15	1390	1.28	6.35	0.50
20	1365	1.13	7.24	0.64
25	1339	1.00	8.13	0.81
30	1331	0.88	8.24	0.94

mental function measured with a latex nanosphere suspension used as a static scatterer.[12]

The refractive index, $n(T)$, of the mixtures with different compositions was measured at the working temperatures with an Abbe refractometer using a Na light source.

3. Results

Our attention was initially focused on the behavior of the two neat liquids and the results of the Brillouin measurements. The data, reported in Tables 1 and 2, refer to the temperatures at which ultrasonic velocity values are known for both molecular liquids.[5,13−15] The tables show that the ratio $(\alpha/f^2)_{\text{hy}}/(\alpha/f^2)_{\text{class}}$ is very different in the two cases. Here $(\alpha/f^2)_{\text{class}}$ is the acoustic absorption coefficient defined for the vanishing value of the **q** wavevector, whereas $(\alpha/f^2)_{\text{hy}}$ is the analogue defined by the hypersonic quantities from the Brillouin spectra:

$$\left(\frac{\alpha}{f^2}\right)_{\text{class}} = 2\pi^2 \frac{4\eta_s}{3\rho\upsilon_0^{\,3}} \tag{1}$$

$$\left(\frac{\alpha}{f^2}\right)_{\text{hy}} = 2\pi \frac{\Gamma_B}{\upsilon_h \omega_B^{\,2}} \tag{2}$$

where υ_0 and υ_h are the ultrasonic and hypersonic velocities, respectively, ρ is the mass density, η_s is the shear viscosity at zero frequency, and Γ_B and ω_B are the half-width and frequency shift of the Brillouin peak, respectively.

According to the classification of liquids reported in ref 16, the ratio of absorption coefficients in the tables indicates that *n*-octane behaves as a Kneser fluid, while 1-octanol can be considered an associated fluid, at least until 30 °C.

In Figure 1a, the shear viscosity values (η_s) versus temperature are plotted for neat liquids and for three different 1-octanol/*n*-octane mole fractions. It is evident that this macroscopic variable follows the Arrhenius law with an activation energy that is directly correlated with the amount of H-bonded structures. This fact is illustrated in a different way in Figure 1b, where the Arrhenius plots of η_s are shown for the three different solutions and for the pure liquids. As a first approximation, the contribution to the viscous flux due to relaxation processes of the degrees of freedom directly involved in the motion of the hydrocarbon chain can be isolated and assigned to the activation energy value of *n*-octane. By subtraction of this E_a value of ca. 9 kJ/mol from the E_a value of pure 1-octanol, an activation energy of ca. 16 kJ/mol is obtained. This value is close to the H-bond breaking energy value in long chain alcohols.[6]

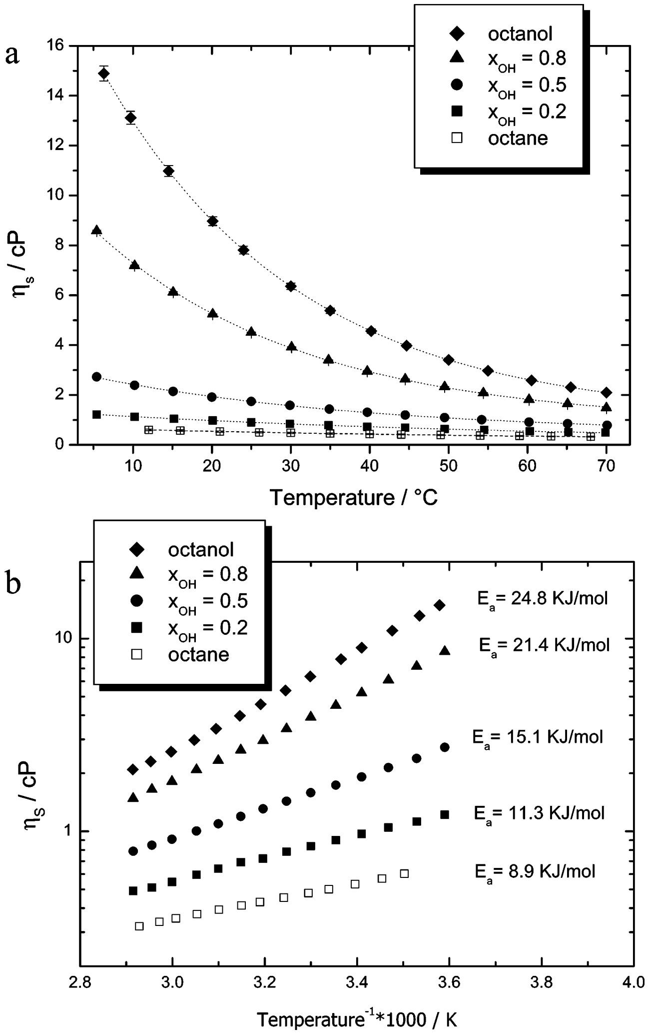

Figure 1. (a) Plot of shear viscosity vs temperature for *n*-octane and 1-octanol neat liquids, and for the three different mixtures. Mole fraction values are indicated in the inset. (b) Arrhenius plot of viscosity values reported in panel a.

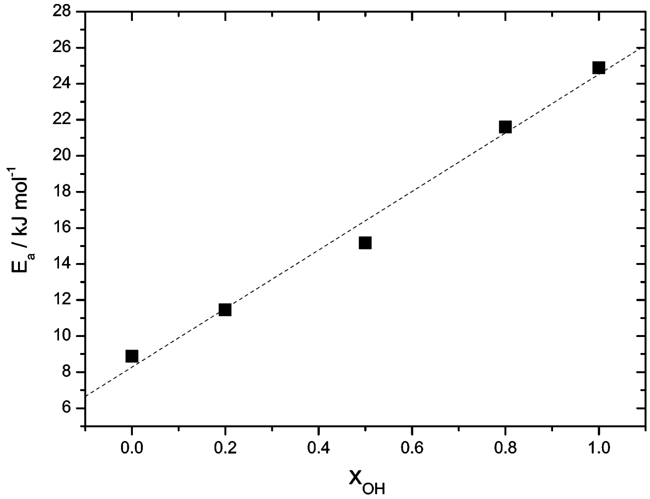

Figure 2. Activation energies of viscous flux vs mole fraction of 1-octanol/*n*-octane mixtures. The maximum of nonideal behavior is shown for an x_{OH} of 0.5.

The activation energy values versus 1-octanol mole fraction x_{OH} are plotted in Figure 2. The linear trend of this correlation shows a small deviation from linearity for the solution when $x_{OH} = 0.5$, indicating a nonideal behavior of the solution. This

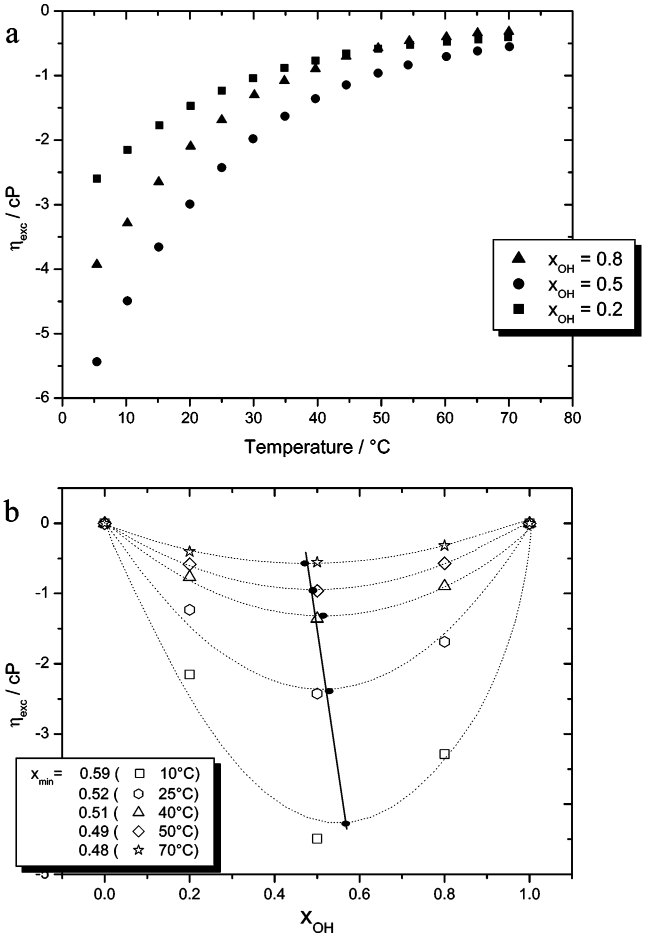

Figure 3. Excess shear viscosity vs (a) temperature for the three different mole fractions and (b) mole fraction at five different temperatures. Solid circles in panel b represent the values of x_{min} at different temperatures.

fact had already been observed at room temperature with ultrasonic velocity and sound absorption measurements.[5]

The deviation of the mixtures from ideal behavior was probed by analyzing the excess variables defined in the classic way:[5]

$$A_{exc} = A_{sol} - [A_1x_1 + A_2(1 - x_1)] \tag{3}$$

where A_{exc} is the excess quantity of variable A, x_1 is the molar fraction of component 1, A_{sol} is the measured value of A in solution, and A_1 and A_2 are the values of A in pure components 1 and 2, respectively.

In Figure 3a, the excess shear viscosity at zero frequency, η_{exc}, is plotted as a function of temperature, and in Figure 3b, η_{exc} is plotted as a function of the mole fractions of the solution. Markedly negative values of this excess quantity at all the concentrations can be observed as well as a maximum negative value attained for the 0.5 mole fraction mixture. Moreover, by fitting the experimental data points of Figure 3b at the different temperatures, we see that the mole fraction value at which η_{exc} is minimal (x_{min}; see the inset of Figure 3b) is slightly dependent on temperature. In fact, even if this value is kept around 0.5, it clearly decreases with increasing temperature, and we believe that this is not an artifact due to curve fitting since it is a matter of fact that η values for an $x_{OH} = 0.8$ solution are much lower than those of an $x_{OH} = 0.2$ solution with increasing temperatures.

The variation of the mass densities of pure liquids and solutions with temperature is shown in Figure 4. It can be observed that these trends look quite regular, with the density values of the solutions being distributed between the extreme values of the pure liquids at all the temperatures. In contrast, in reporting the temperature effects on the molar volumes (see Figure 5), one can observe that the behavior is not so regular. The difference between the values of pure liquids slightly increases with temperature: 2.6% at 5 °C and 3.4% at 70 °C. In addition, the observed trends for the solutions are strongly dependent on the composition of the mixtures. The average molar volume of the $x_{OH} = 0.8$ solution tends toward pure 1-octanol values with increasing temperatures while that of the $x_{OH} = 0.2$ solution toward values of *n*-octane. The molar volume behavior of the $x_{OH} = 0.5$ solution tends toward *n*-octane values at lower temperatures and toward those of 1-octanol at higher temperatures. We will try to explain this fact in the Discussion.

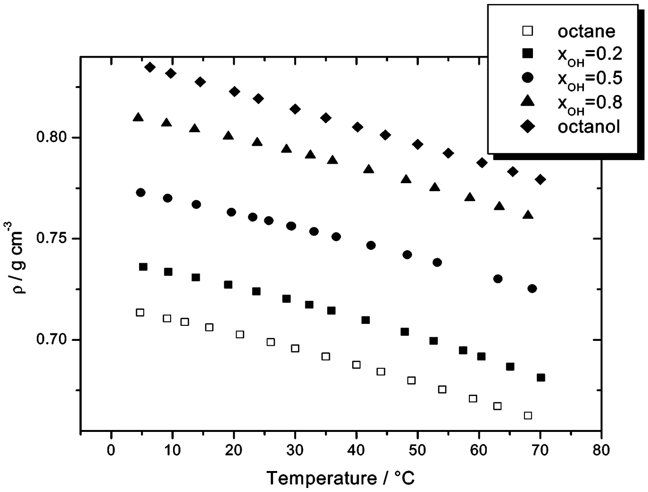

Figure 4. Plot of mass density vs temperature for the neat liquids and 1-octanol/*n*-octane mixtures.

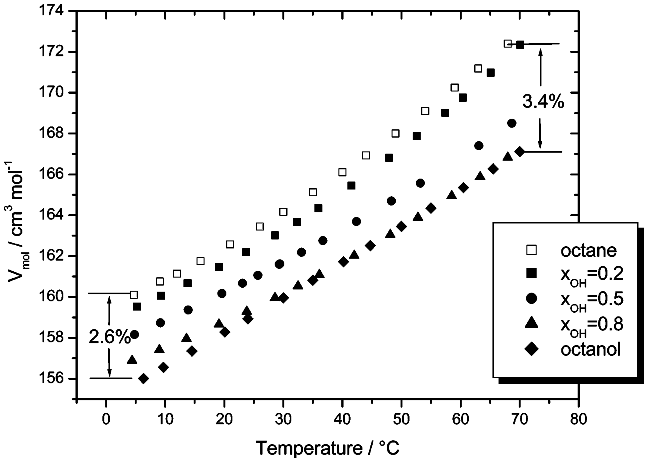

Figure 5. Plot of molar volumes vs temperature for the neat liquids and 1-octanol/*n*-octane mixtures.

Figure 6 shows the behavior of the hypersonic velocities as a function of temperature and mole fraction; remarkable differences can be noted. The large differences in the numerical values between the two pure liquids can be easily explained on the basis of the observed values of macroscopic variables discussed above, which strongly affect the hypersound velocity. These differences are due to the contribution of H-bonded structures of alcohol with respect to the *n*-alkane system. In contrast, the behavior of v_h in solutions is not explained by the effect due to the density and viscosity variations that are regularly distributed between the extreme values of pure liquids. It appears that even at the higher 1-octanol mole fraction, the

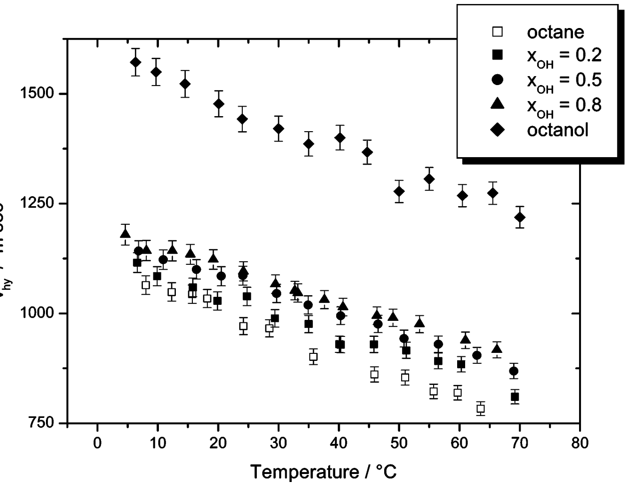

Figure 6. Thermal behavior of hypersonic velocities v_{hy} for neat liquids and solutions.

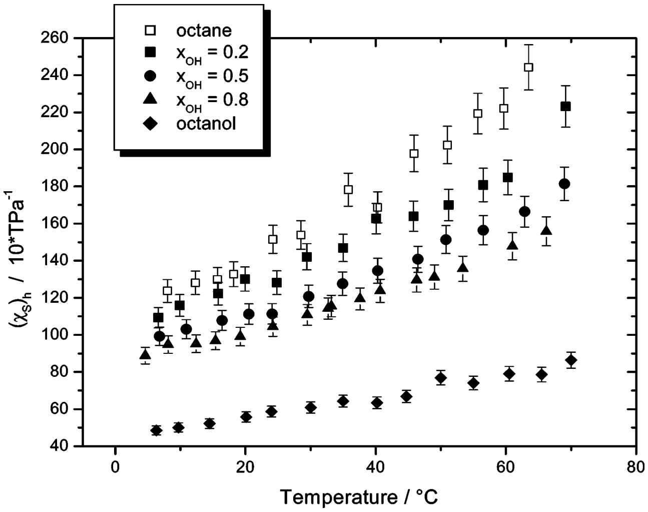

Figure 7. Thermal behavior of the adiabatic compressibility χ_s for neat liquids and solutions.

hypersonic velocities are close to the *n*-octane values at all the temperatures.

In Figure 7, the thermal behavior of the adiabatic compressibility at hypersonic frequencies, $(\chi_S)_h$, at different mole fractions is shown. Even if the distribution of this quantity as a function of x_{OH} seems to be more regular than that of sound velocity, its values are more similar to those of pure alkane. The different trends of v_h and $(\chi_S)_h$ for the five liquid systems are probably due to the balancing contribution coming from the density values, since $(\chi_S)_h$ is defined as

$$(\chi_S)_h = (\rho v_h^{\,2})^{-1} \tag{4}$$

The anomalous behaviors of v_h and $(\chi_S)_h$ cannot be explained on the basis of the associative properties or by considering the cluster formation, especially for the $x_{OH} = 0.8$ mixture. In fact, we observed that even small additions of alkane noticeably reduced the hypersound velocity, thereby increasing the adiabatic compressibility of solutions with respect to pure octanol.

On the other hand, the differences found between the relative $(\chi_S)_h$ values of the two pure liquids are qualitatively in good agreement with the differences observed between the relevant molar volumes; they diverge with a similar trend as the temperature is increased.

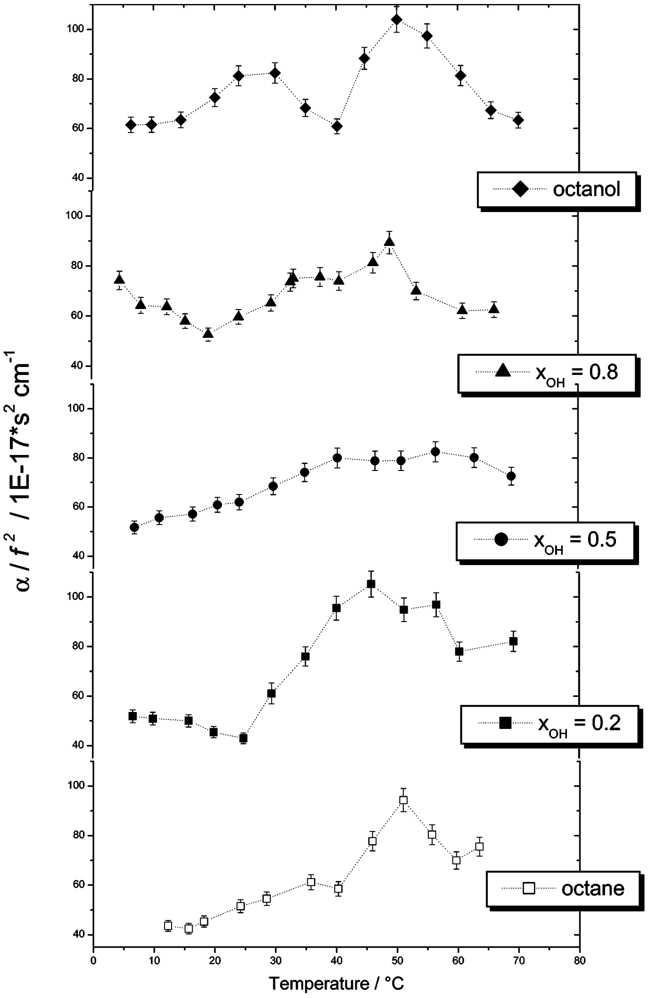

Figure 8. Thermal behavior of the sound absorption coefficient α/f^2 for neat liquids and solutions.

A second important quantity extracted from the analysis of the hydrodynamic triplet band shape is the acoustic absorption coefficient α/f^2. As given in eq 2, such a quantity depends on the half-width of the Brillouin signal. The maxima found in the frequency or temperature dispersion curves of α/f^2 suggest that relaxation processes occur in which the translational energy is coupled with internal motions.[9] The study of the wavevector dependence of relaxation times can provide important information about the dynamics of these liquids and will be done in the future.

Figure 8 shows α/f^2 as a function of temperature for the three solutions and for the pure liquids. In pure alcohol, two maxima are present around 30 and 50 °C, while only one maximum is found in pure *n*-octane. Both the amplitude and position of the second maximum in 1-octanol correspond to the values found in *n*-octane. The behavior of solutions is intermediate between that of the pure liquids and depends on the composition. In the $x_{OH} = 0.8$ solution, the evidence of a maximum at a lower temperature is found, as well as for pure octanol.

4. Discussion

In a crude approximation of the liquid phases, as well as highly disordered lattices, we can correlate the static ($\omega = 0$) shear viscosity values with the frictional forces that reduce particle mobility in adjacent planes. This approximation encompasses all the molecular relaxation processes, even those caused by the internal rotations of the hydrocarbon chains. We can interpret the curves in Figure 1 by assuming that when the system goes from pure alkane to pure alcohol there is a monotonic increase in the number of species involved in the formation of the H-bond network which can strongly reduce the fluid mobility. The systematic decrease in the viscous flux activation energy, going from pure alcohol to pure *n*-octane, is attributed to an increase in the molecular mobility of fluid particles when the H-bond interactions are weakened by the cooperative action of temperature and dilution. After examination of the viscosity data, it appears that an increase in either temperature or solvent concentration influences the motion that mainly involves the polar heads of alcohol molecules. In contrast, the chain seemed to be affected little by temperature variations. In pure alcohol and all the solutions, the limiting viscosity values at the highest temperatures were close to those of pure alkane (see Figure 1a).

The data in Figure 2 show that the E_a values for the viscous flux in the $x_{OH} = 0.5$ solution deviate slightly from linearity. This fact has been interpreted by assuming that repulsive interactions between molecules of two components reach the maximum value at this dilution. The behavior of the quantity η_{exc} shown in Figure 3 substantially supports this view, confirming what had already been observed in ultrasonic dispersion data at room temperature.[5]

In addition, the nonideal behavior of the solution is clearly indicated by the average molar volume values, especially when these data are compared with the density values as a function of temperature (see Figures 4 and 5). In particular, the data of Figure 5 were obtained by evaluating the average molar volume with the following formula:

$$V_{mol} = \frac{x_{OH}M_{octanol} + (1 - x_{OH})M_{octane}}{\rho} \qquad (5)$$

where x_{OH} is the octanol mole fraction, M is the molecular weight, and ρ is the density value of the sample. In Figure 5, it appears that the behavior of the $x_{OH} = 0.5$ solution is quite peculiar, even though the densities of the solutions are regularly distributed between the extreme values of the two liquids at all the temperatures. In fact, at higher temperatures, the average molar volume of the solution is close to that of pure alcohol; the opposite situation is verified at lower temperatures. The alkane molecules occupy the void volumes of the alcohol structure much less efficiently when $x_{OH} = 0.5$. This happens because of a larger contribution of repulsive interactions that leads to a higher dgree of molecular segregation. This nonideal behavior is expected for the liquid mixture that is being studied because of the drastic differences in polarity and in interaction forces between A- and B-type molecules.

Even the molecular size of the two components is not what one would expect. In fact, what is really surprising is that both V_{mol} and $(\chi_S)_h$ values of the two pure liquids diverge with a similar trend at higher temperatures. We had expected 1-octanol to become more octane-like with increased temperatures, because of the dwindling H-bond effects. A possible explanation for the observed behavior can be achieved considering the results of Brillouin measurements.

The data shown in Figure 6 suggest that even small quantities of *n*-octane strongly influence the propagation of sound waves. The $x_{OH} = 0.8$ solution has sound velocity values closer to those of *n*-octane than to those of 1-octanol. This fact seems to indicate that the translational motion is more affected by dilution than by temperature in the range of 5−70 °C.

The experimental trends observed for octanol/octane solutions definitely confirm the hypersonic relaxation processes previously observed in pure octanol.[9] An analysis of Figure 8 clearly shows that a maximum of acoustic absorption, and then a relaxation process, occurs around 50 °C in all samples. Another maximum around 30 °C increases with increased octanol content in octane solutions. On the basis of both relaxation time and activation energy values, we have attributed these relaxation processes to the energy exchanges between the translations and internal rotational modes of the chain.[9] In particular, we think that the low-temperature maximum in pure 1-octanol, which is also quite evident in the $x_{OH} = 0.8$ solution, is due to the relaxation that mainly involves the internal rotation around the C−O bond of clustered molecules. These assignments are supported by recent MD simulation studies performed in our laboratory.[17]

The high temperature maximum observed in all samples is also associated with a conformational rearrangement of the alkyl chain. It is obviously very difficult to exactly define where the internal rotation is localized along the chain. As a consequence, we agree with previous assignments of ultrasonic and shear impedance spectrometry relaxations observed for *n*-alkanes and *n*-alcohols. Beherends et al.[15] assigned a high-frequency relaxation to the transition from an all-trans chain conformation to one in which a certain number of C−C−C−C bonds has a gauche conformation. This rearrangement is cooperative in the sense that it is not the simple sum of independent rotations around single C−C bonds, and it also has a relevant contribution from the overall molecular reorientation.

In light of this experimental evidence of conformational rearrangement, we can now propose a new reading of our molar volume and compressibility data, especially for the two pure liquids.

It is clear that the formation of gauche conformers along the chain produces a stronger effect on the structural modifications in liquid alkane than in liquid alcohol.

In fact, in the latter sample, the liquid structure is mainly governed by the H-bond interactions since, even at 70 °C, more than 90% of 1-octanol molecules are involved in H-bonding.[18] In contrast, for the hydrocarbon molecules, the structural characteristics are essentially due to the conformational rearrangements of the chains. Thus, the loss of an all-trans conformation and the weaker packing capability over 50 °C justify the noticeable increase in molar volume and adiabatic compressibility observed for *n*-octane, as well as the divergent behavior of the two pure liquids at higher temperatures.

We can even suggest that the properties of the octanol solutions depend on two main factors: the H-bond interaction and the steric hindrance of the alkyl chain. These two factors prevail on each other depending on the relative amounts of alcohol and alkane in solution, and on the temperature. We will indicate these two factors as H-structure and volume-structure effects.

According to this simple picture, we can say that the shear viscosity is largely dependent on the extent of H-bonding (H-structure) while the molar volume depends on the hindrance of molecules (volume-structure); the compressibility of the liquid is the result of the balance of these two factors.

The excess compressibility χ_{exc} for the three solutions as a function of temperature is reported in Figure 9. These data can be discussed in terms of intermolecular interactions and relative packing between solute and solvent molecules. We will see that these two factors produce opposite effects on the temperature trend of compressibility.

Positive adiabatic excess compressibility values indicate less rigidity in real solutions with respect to the properties of pure

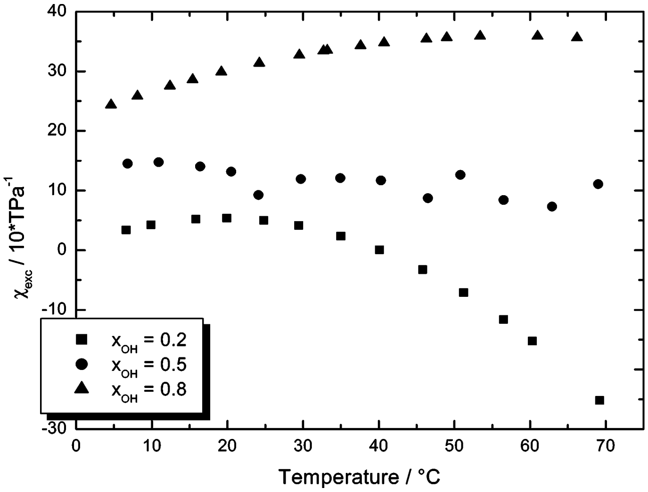

Figure 9. Thermal behavior of the excess adiabatic compressibility χ_{exc} for the three solutions.

liquids. Higher fluidity in the solutions is indicated by the negative excess viscosity values of the mixtures.

With regard to the η_{exc} data, we believe that the temperature and composition trends observed in the octanol/octane mixtures are essentially due to a reduced degree of self-association of solutions with respect to pure alcohol. The viscosity values mainly depend on the number of H-bonds present in the liquid.[6]

In our opinion, the reduced degree of self-association also causes the positive χ_{exc} values, since the rigidity of this kind of sample is strictly connected with the existence of aggregate structures.

The great difference between viscosity and compressibility is that the η_s and η_{exc} data are only sensitive to H-structure, while the dilution and temperature behavior of χ_{exc} reflects the effects of both volume- and H-structure. We know from the V_{mol} trends that the differences in the mole size of the two components increase with increasing temperatures. This could suggest that the mixing of the solute and solvent is not perfectly homogeneous, and that locally octanol- and octane-rich regions can be recognized. The micro-inhomogeneity of the solutions that depends on the volume-structure reduces the compressibility of the liquid since it is in someway connected to its rigidity through the concept of local order. Consequently, we can say that we have an H-structure effect that produces positive χ_{exc} values, and a volume-structure effect by which the value of excess compressibility decreases as the temperature increases.

In this scenario, we can understand why the slope of a plot of χ_{exc} versus T in an $x_{OH} = 0.8$ solution decreases when $T >$ 30 °C, and tends toward zero at 70 °C. This explains why the slope in an $x_{OH} = 0.2$ solution even becomes negative. The octane content in this mixture is high, and then the effects of its hydrophobic character with respect to a hydrophilic one prevail.

With regard to the $x_{OH} = 0.5$ solution, in Figure 9 we can see that the χ_{exc} values are always positive, and this is probably due to the effects of the reduced degree of self-association. Moreover, the limited dependence of the excess quantity on temperature for this composition suggests that the hydrophobic and hydrophilic characteristics are almost perfectly counterbalanced along the entire temperature range. The composition, in fact, is close to that of a maximum of repulsive forces, and thus a maximum of nonideality. In this situation, a micro-inhomogeneity of the solution is always present even at low temperatures. Therefore, at low temperatures as well as at higher ones, the effects of molecular packing are as strong as those of H-bond interactions.

5. Conclusions

The results of this study on octanol/octane solutions provide further experimental evidence of the dynamics and structural dependence of *n*-alcohols on the correlation between H-bonding interactions, and the flexibility of the hydrocarbon chain.

A large variety of dynamic characteristics of pure liquids and solutions have been probed by light scattering techniques,[7−9,19−21] and the results show that structural relaxations in the bulk liquid develop in the time domain of tens to hundreds of picoseconds.

Although Rayleigh−Brillouin light scattering is a spectroscopic technique that is sensitive to collective motions that produce density fluctuations, there is a strong correlation between microscopic local properties and hydrodynamic modes. As well as it was observed in other molecular liquids,[22] this correlation allows the effects of single-molecule reorientation and conformational rearrangement to be followed, thus suggesting the microscopic origin for the temperature behavior of macroscopic quantities (viscosity, density, etc.) in pure liquids.

A comparison of the data from octanol, octane, and octanol/octane solutions is crucial for understanding the structural properties of the liquid alcohol. The compressibility data, in fact, provide the key for interpreting the anphiphility of 1-octanol; it shows the effects associated with the interactions of the polar heads, and the mobility of the hydrophobic tail, as a function of temperature and the composition of the alcohol/alkane mixture.

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