BRILLOUIN SCATTERING IN THE LIQUID MIXTURE CARBON DISULFIDE + CARBON TETRACHLORIDE

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Abstract: For the mixture carbon disulfide + carbon tetrachloride hypersound, ultrasound speed, and ultrasound damping were measured at 293.15 K.From the experimental data the energy vibrational relaxation time was determined.

For the mixture carbon disulfide + carbon tetrachloride Brillouin spectra were measured at 293.15 K and 1 bar. The spectrometer was a Fabry-Perot interferometer with a free spectral range of 15.38 GHz and a finesse of 38 [1]. In addition the speed of sound and sound absorption have been measured, at 293.15 K and at ca. 5, 15, 26 and 36 MHz. Using molar heat capacitites at constant pressure (by flow calorimetry) and molar volumes (by vibrating tube densimetry) from the literature [2], the molar heat capacity at constant volume and the isothermal compressibility have been evaluated.

All these date were necessary to extract the energy vibrational relaxation time from the experimental Brillouin spectra. This was done by fitting the experimental Brillouin spectra to theoretical ones, using Mountain`s theory[3] with consideration of the instrumental function of the spectrometer.

Figure 1 shows subadditive composition dependences for both, the ultrasound speed and the hypersonic speed, respectively. The sound dispersion is about 95 m/s for pure CS_2, and 115 m/s for pure CCl_4 .

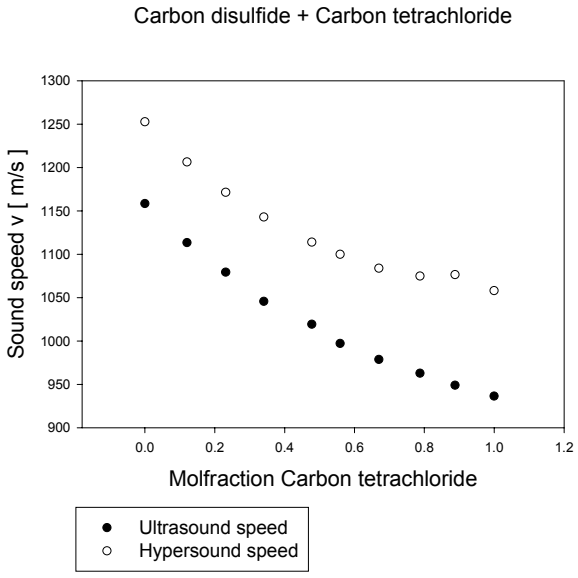

Figure1

In Figure 2 the experimental sound absorption is plotted as a function of composition

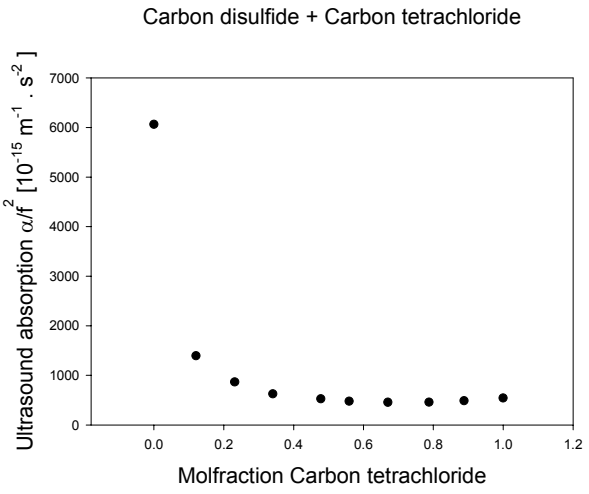

Figure 2

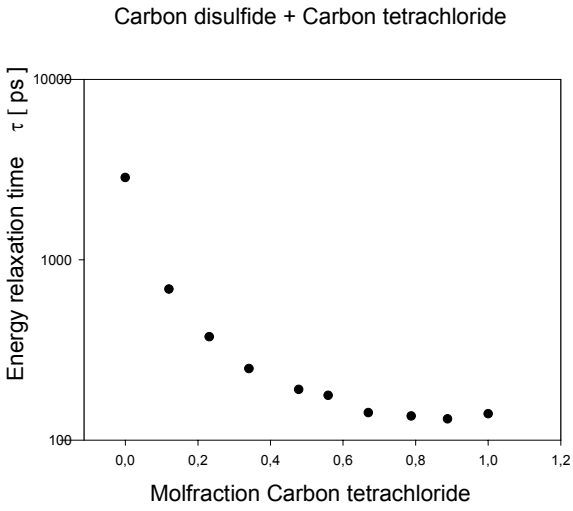

Figure 3

For pure carbon disulfide and mixtures rich in this component, ultrasound absorption varies strongly with mole fraction. We note that particular care must be exercised to obtain the low frequency (thermodynamic) sound speed of these systems because of the unusually low relaxation frequency , i. e. 78 MHz for pure CS_2: dispersion of ultrasonic speed even at such small frequency used by us (5MHz) must not be neglected.
Figure 3 shows the composition dependence of the energy relaxation time t, which is obtained from the experimental accessible relaxation time t_v (Brillouin spectra, see above) according to $t = t_v / (1 - C_i / C_v)$. Here, C_v denotes the heat capacity at constant volume, and C_i is the relaxing heat capacity.

One has to be very prudent in interpreting the results of frequency dependent sound speed and sound absorption data. Sound speed dispersion data are correlated to t_v, whereas ultrasonic absorption data are correlated to t_p, where $t = t_p / (1 - C_i / C_p)$ and C_p denotes the heat capacity at constant pressure. Neglecting these relationships a comparison of classical literature data on ultrasonic and Brillouin measurements can lead to misinterpretation, (see for example table I of a review on vibrational energy relaxation by Chesnoy and Gale [4]).
When Carbon tetrachloride is added to carbon disulfide, t decreases strongly. Appropriate theories (V V´- energy transfer, V T –energy transfer) have been advanced and will be considered briefly [5].

Finally, a preliminary discussion in terms of the Isolated Binary Collision model (IBC) is presented.

References:

1. Asenbaum, C. Theisen, G. Moser, M. Musso, E. Wilhelm. Proceedings of the XVIIIth International Conference on Raman Spectroscopy, 25 – 30 August 2002, Budapest, Hungary. Edited by J. Mink, 2002, John Wiley & Sons, Chicester.
2. E. Wilhelm, A. Asenbaum and J.-P. Grolier, to be published.
A preliminary version will be presented at the EMLG meeting in Sheffield, UK, 3-7 September (2004).
3. R. D. Mountain, J. Res. Natl. Bur. Stand. **70A**, 207 (1966).
4. J.Chesnoy and G. M. Gale, Ann. Phys. Fr. **9**, 893 (1984).
5. K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, 1959, Academic Press, New York.