

Fig. 6. Light scattering rotational relaxation time for chloroform versus pressure.

Parkhurst et al. [23] have determined the effect of pressure on the proton spin lattice relaxation time of toluene- d_3 . They found a significant increase in the rotational relaxation time with pressure. The rotational relaxation time for toluene, as measured using NMR, reflects both spinning and tumbling of the molecular axis, and we feel detailed comparisons of the NMR data to our depolarized Rayleigh data are not justified.

B. Chloroform

Our high pressure light scattering results for pure chloroform in Fig. 10 show τ_{LS} to be a linear function of viscosity at constant temperature. Also shown in Fig. 10 are data of Campbell and Jonas [8] for rotational relaxation times at high pressures measured using both Raman scattering and NMR.

The light scattering rotational relaxation time for chloroform has been shown by Alms et al. [7] to be strongly concentration dependent, suggesting pair correlations are affecting the light scattering data at high concentrations. They report values for fN and gN of 1.0 ± 0.1 and 0.0 ± 0.1 , respectively, for the pure liquid.

Both Raman and NMR measure rotations perpendicular to the symmetry axis and in the absence of complicating effects, should yield the same value of τ_1 under the same conditions. It is readily seen from Fig. 10 that this is not the case, except at atmospheric pressure. Campbell and Jonas suggested the differ-

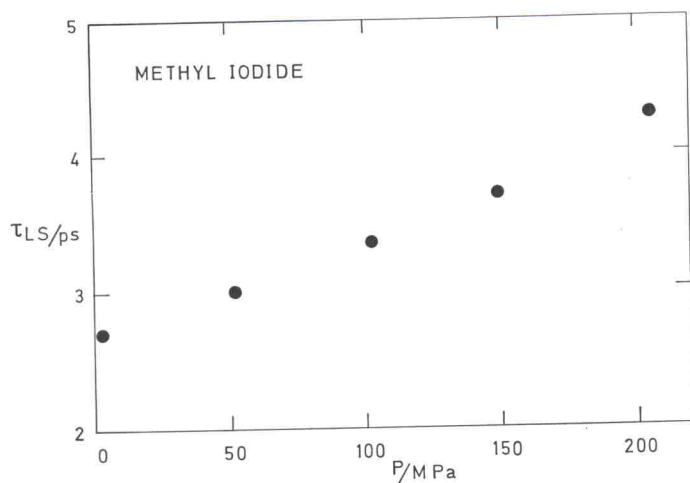


Fig. 7. Light scattering rotational relaxation time for methyl iodide versus pressure.

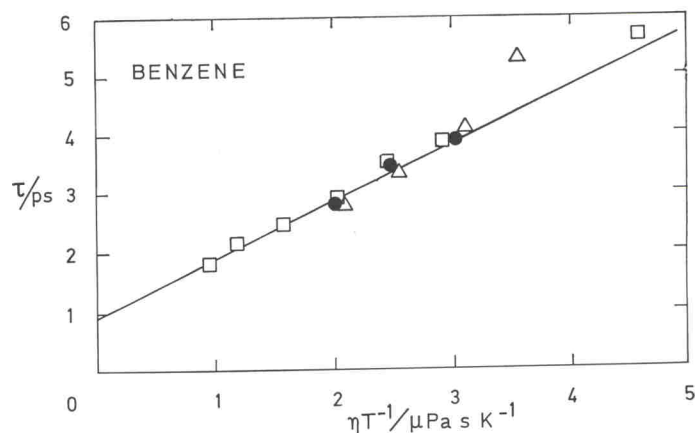


Fig. 8. Rotational relaxation times for benzene versus viscosity $\times T^{-1}$: $\bullet\bullet\bullet$, pure liquid, high pressure Rayleigh, 298 K, this work; $\square\square\square$, solution, Rayleigh, 297 K, ref. [6]; $\triangle\triangle\triangle$, pure liquid, high pressure Rayleigh, 296 K, ref. [10]. The line is a least squares fit of the \bullet high pressure data.

ence might be due to a change in the proton quadrupolar coupling constant with pressure. If we compare our τ_{LS} results to the τ_1 Raman results, it appears that pair correlations are decreasing as pressure is increasing.

Using eq. (8) and the reported values of fN and gN , we find that τ_{LS} should increase faster than τ_1 with increasing pressure simply due to the increase in N , the number of scatterers in the scattering volume. This does not appear to be the case from Fig. 10. It is possible that either f or g , or both, are changing with pressure, and this change could explain the observed results. There is also the possibility that some assumptions used in obtaining τ_1 from the Raman data are not applicable at high pressure. Specifically, there may be significant vibration-rotation interaction at high pressures and/or the non-orientational relaxation processes may not affect the isotropic and anisotropic Raman spectra in the same way [24]. This could also help explain the large discrepancy between the Raman and NMR data.

C. Methyl iodide

Our high pressure depolarized Rayleigh relaxation times for methyl iodide measured using interferometry are given in Fig. 11, along with high pressure Raman results of Campbell et al. [9], and high pressure depolarized Rayleigh results of Dill et al. [10]

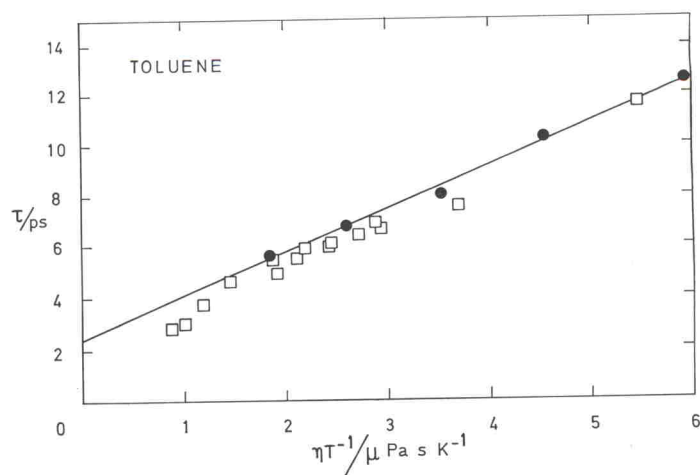


Fig. 9. Depolarized Rayleigh rotational relaxation times for toluene versus viscosity $\times T^{-1}$: $\bullet\bullet\bullet$, pure liquid, high pressure, 298 K, this work; $\square\square\square$, solution, 297 K, ref. [6]. The line is a least squares fit of the high pressure data.

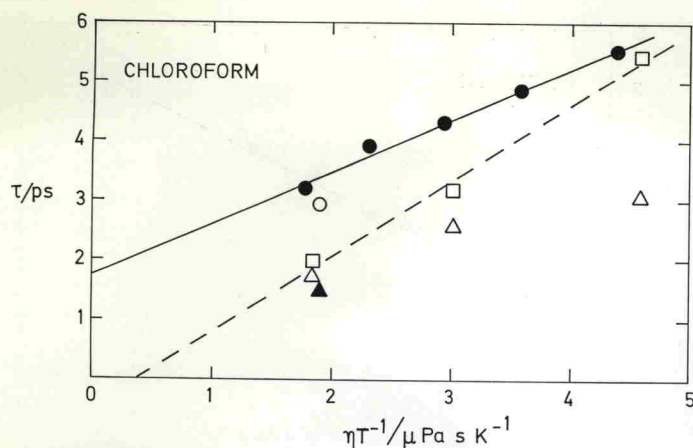


Fig. 10. Rotational relaxation times for pure chloroform versus viscosity $\times T^{-1}$: $\bullet\bullet\bullet$, high pressure Rayleigh, 298 K, this work; $\square\square\square$, high pressure Raman, 296 K, ref. [8]; $\triangle\triangle\triangle$, high pressure NMR, 296 K, ref. [8]; \circ Rayleigh, 295 K, ref. [7]; \blacktriangle NMR, 295 K, ref. [7]. The line is a least squares fit of the high pressure data.

measured using a grating spectrometer. Again, the Raman experiments should yield single particle relaxation times. In comparing our τ_{LS} results to the τ_1 Raman times we find a situation similar to that for chloroform, that is, pair correlations appear to be significant at atmospheric pressure. However, the τ_{LS} of Dill et al. do not agree with our τ_{LS} values and are significantly smaller than the Raman times.

The depolarized Rayleigh spectra obtained using spectrometers consist of two prominent features: an intense narrow peak at the laser frequency, and a broad "Rayleigh wing" which extends, in many cases, for several hundreds of wavenumbers. In an interferometric experiment this "wing" appears as a flat background due to the overlapping of adjacent orders and does not interfere with measurement of the narrow component. In order to obtain the narrow component from the experimental grating spectrometer spectrum the contribution of the "wing" must be "subtracted out" in some manner.

Since the nature of the wing spectrum is not totally understood, Dill et al. separated out the narrow part by assuming the second moment of the narrow band was the classical, single particle value, $6kT/I$. The second moment will differ from the classical value in the presence of pair correlations. There is also evidence that the single particle second moment can differ significantly

from $6kT/I$. Campbell et al. [9] have measured the second moment of methyl iodide at pressures up to 200 MPa and at temperatures ranging from 273 K to 363 K. In all cases the second moment was found to be significantly less than $6kT/I$. Other investigations have yielded various values for the second moment of methyl iodide.

In the absence of knowledge concerning the magnitude of pair correlations and reliable second moment values we feel there are limitations involved in obtaining τ_{LS} values from depolarized Rayleigh experiments performed using grating spectrometers.

Our τ_{LS} values and the Raman τ_1 values approach each other at high pressures, as was the case for chloroform. This behaviour can be explained as arising either from changes in f and g with pressure, or effects of vibration-rotation interaction and non-orientational processes on the Raman spectra, or both.

Conclusion

We have shown that accurate depolarized Rayleigh light scattering measurements using interferometry can be performed at high pressure. By changing the pressure, the viscosity can be varied over a wide range while keeping chemical composition constant.

The light scattering relaxation times of pure benzene and toluene measured at high pressures are a linear function of viscosity at constant temperature. This viscosity dependence agrees well with previous results obtained over a range of concentrations at atmospheric pressure. The effect of pair correlations on the light scattering relaxation time is small and one is essentially measuring the single particle relaxation time. For chloroform and methyl iodide the light scattering relaxation time is also a linear function of viscosity. Pair correlations seem to be significant in these two liquids. At higher pressures, the light scattering and Raman rotational relaxation times approach each other. This suggests either the magnitude of the static and dynamic contributions to the pair correlations are changing with pressure, or the approximations used to obtain the single particle Raman rotational relaxation times from the polarized and depolarized Raman spectra are not valid at high pressure, or both.

Acknowledgement

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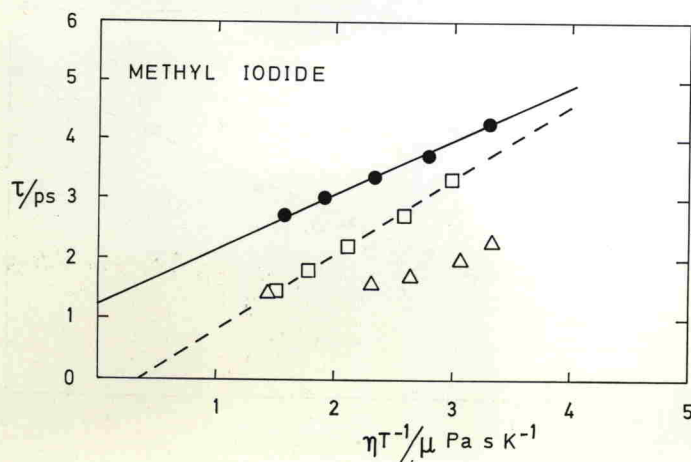


Fig. 11. Rotational relaxation times for pure methyl iodide: $\bullet\bullet\bullet$, high pressure Rayleigh, 298 K, this work; $\square\square\square$, high pressure Raman, 303 K, ref. [9]; $\triangle\triangle\triangle$, high pressure Rayleigh, 296 K, ref. [10]. The line is a least squares fit of the \bullet high pressure data.