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Scott Whittenburg
University of New Orleans, swhitten@uno.edu

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Depolarized Rayleigh scattering study of pyridine in cyclohexane

S. L. Whittenburg, Dane R. Jones,[a] D. H. Christensen,[b] and C. H. Wang

University of Utah, Salt Lake City, Utah 84112
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The depolarized Rayleigh scattering spectrum of a liquid composed of anisotropic molecules reflects the reorientation of molecular pairs as well as single particle reorientation. A depolarized Rayleigh scattering study can thus yield direct information about single particle reorientation and about orientational pair correlation (OPC). According to the Stokes–Einstein model the single particle reorientation time, τ_s, is known to be proportional to η/T, where η is the shear viscosity and T is the absolute temperature. Thus, it has been proposed that τ_s can be obtained from a concentration dependent depolarized Rayleigh light scattering study. The depolarized Rayleigh reorientation time, τ_{Ray}, extrapolated to infinite dilution in an optically isotropic solvent is equal to τ_s. This assumes, however, that the τ_{Ray} values at each concentration can be scaled to a value corresponding to the viscosity of the neat liquid.

While the Stokes–Einstein model for single particle reorientation requires $\tau = C\eta/T$, where C is a constant depending upon the boundary conditions used in the calculation, for some molecular systems the light scattering experiments yield a finite intercept in the τ_s vs η/T plot.[3] Under this circumstance it is necessary to take the finite intercept into account when scaling the τ_{Ray} values.

For solute–solvent systems with weak intermolecular interaction viscosity scaling of the relaxation times according to a Stokes–Einstein relation have been shown to give reliable single particle relaxation times.[1,2] In systems with stronger interactions such as hydrogen bonding or complex formation this method has shown mixed results. For example, in the pyridine–CCl_4 system with a strong solute–solvent interaction due to complex formation between the lone pair electrons on the nitrogen atom and the chlorine atoms the scaled relaxation times when extrapolated to infinite dilution give accurate values for τ_s.[3] For the hydrogen bonding pyridine–H_2O system, however, viscosity scaling fails

drastically.[4] In this note we report the results of a depolarized Rayleigh light scattering study of the pyridine–cyclohexane system which also exhibits a significant solute–solvent interaction. The interaction is displayed in a strongly nonlinear viscosity–concentration relation.[5]

The experimental setup and method by which the depolarized Rayleigh relaxation times are extracted from the experimental spectra have previously been given.[3] τ_{Ray} is related to τ_s by[6]

$$\tau_{Ray} = \tau_s(1 + fn)/(1 + gn) , \tag{1}$$

where f is the static OPC factor, g is the dynamic OPC factor, and n is the number density of scatters. A recent calculation suggests that for linear and symmetric top molecules dynamic OPC does not affect τ_{Ray}.[7] This result is however challenged by Wolynes and Deutch.[8] While pyridine is strictly an asymmetric top it is isoelectronic with benzene with a polarizability tensor nearly equal to that of an oblate symmetric top.[8] Also, experimental evidence for other asymmetric tops suggests g is nearly zero in the light scattering experiment.[9,10] Therefore, for pyridine we have $\tau_{Ray} \simeq \tau_s(1 + fn)$. In Table I we have given the measured τ_{Ray} and η values as a function of pyridine concentration. Also given are the scaled relaxation times, scaled to the viscosity of neat pyridine.

One notes that, to within the experimental accuracy, the scaled relaxation times are independent of pyridine concentration. This is in agreement with the results of

TABLE I. τ_{Ray}, η, and viscosity scaled relaxation times as a function of pyridine concentration in cyclohexane.

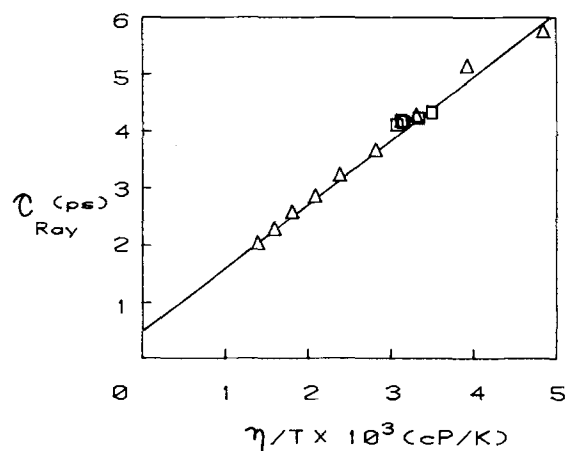| Vol %	τ_{Ray} (ps)	η (cP)	τ_{scaled} (ps)
100	4.3 ± 0.2	0.974	4.3 ± 0.2
80	4.2 ± 0.2	0.913	4.5 ± 0.2
60	4.2 ± 0.2	0.861	4.6 ± 0.2
40	4.1 ± 0.2	0.839	4.7 ± 0.2
20	4.2 ± 0.2	0.853	4.7 ± 0.2

FIG. 1. τ_{Ray} vs η/T for $\triangle$, neat pyridine as a function of temperature; $\square$, pyridine as a function of concentration at 20 °C.

the pyridine–CCl_4 study and confirms that static OPC in pyridine is insignificant. This is in agreement with the experimental observation for benzene.[11] Therefore, viscosity scaling of τ_{Ray} in the pyridine–cyclohexane system is valid in which the viscosity versus concentration curve shows a minimum due to strong solute–solvent interaction. The τ_{Ray} values are plotted versus η/T in Fig. 1 for neat pyridine as a function of temperature and for pyridine as a function of concentration in cyclohexane at 20 °C. The agreement between the two measurements is within the experimental error. Because OPC in pyridine is insignificant, τ_{Ray} in this system is a measure of single particle reorientation.

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a)Present address: Department of Chemistry, California Polytechnic State University, San Luis Obispo, CA 93407.
b)Present address: Chemical Laboratory V, The H. C. Orsted Institute, DK-2100 Copenhagen O, Denmark.

[1]C. K. Cheung, D. R. Jones, and C. H. Wang, J. Chem. Phys. 64, 3567 (1976).
[2]Y. Higashigaki, S. L. Whittenburg, and C. H. Wang, "Light scattering studies of orientational fluctuations of CS_2," J. Chem. Phys. 69, 3297 (1978).
[3]P. -A. Lund, S. L. Whittenburg, C. H. Wang, and D. H. Christensen, "Studies of reorientational relaxation of pyridine in the liquid state and in CCl_4 solutions by depolarized Rayleigh scattering," Mol. Phys. (in press).
[4]P. -A. Lund, D. H. Christensen, S. L. Whittenburg, and C. H. Wang, "Studies of the Reorientational Relaxation of Pyridine in Aqueous Solutions by Depolarized Rayleigh Scattering," Proc. VIth Int. Conf. Raman Spectrosc., Bangalore, India, 1978.
[5]M. Meyer, R. Meyer, B. Brun, J. Salvinien, and J. Metzger, Bull. Soc. Chim. 8, 3132 (1968).
[6]T. Keyes and D. Kivelson, J. Chem. Phys. 56, 1057 (1972).
[7]T. D. Gierke, J. Chem. Phys. 65, 3873 (1976).
[8]P. G. Wolynes and J. M. Deutch, J. Chem. Phys. 67, 733 (1977).
[9]G. M. Searby, P. Bezot, and P. Sixou, Phys. Lett. A 51, 159 (1975).
[10]S. L. Whittenburg and C. H. Wang, J. Chem. Phys. 66, 4995 (1977).
[11]G. R. Alms, S. R. Bauer, J. I. Brauman, and R. Pecora, J. Chem. Phys. 59, 5310 (1973).
[12]G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, J. Chem. Phys. 58, 5570 (1973); 61, 2255 (1974).