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Absolute Rayleigh Ratios of Four Solvents at 488 nm

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Argon ion lasers are being used increasingly as the light source in both static and dynamic light scattering experiments from liquids and polymer solutions.[1] In many applications it is necessary to know the absolute Rayleigh ratio for typical solvents at the wavelength of the light source in order to calibrate the scattering apparatus.[2] However, only sporadic literature values exist for the Rayleigh ratios of typical organic solvents at 488 nm—the wavelength of the most-used argon ion laser line. In fact, upon converting typical literature Rayleigh ratios measured at other wavelengths for the most common polarization conditions used in nonlaser light scattering experiments to those used in typical laser experiments, we found that the spread in these values at a given wavelength was rather large. Thus, extrapolation of the existing literature values to 488 nm was not considered to be a satisfactory procedure for obtaining values at 488 nm of the precision required in modern experiments. We have therefore measured the Rayleigh ratios of four commonly used organic solvents at 488 nm.

Experimental Section

The solvents used in this study were all certified ACS reagent grade. The linear polystyrene used was from Pressure Chemical Co. and was reported to have $M_w = 392\,000$ and $M_w/M_n < 1.10$ (batch no. 3b). The sample cells used were cylindrical NMR tubes 10 mm in diameter (Wilmad Glass Co., cut to 75-mm length). The sample cells were cleaned of dust by repeatedly rinsing filtered (0.22-μm Millipore filters) solvent through the cells until 488-nm light scattered from the solvent-filled cells showed no dust when observed through a 12× microscope. A stock solution of the polymer in cyclohexane was prepared by taking the supernatant from a polymer solution which had been centrifuged at 8000*g* for 20 min. The polymer samples were prepared in clean sample cells by diluting transferred aliquots of the stock solution with known amounts of filtered solvent. The concentration of the polymer stock solution was taken as the average between the concentration determined by gravimetric analysis after evaporation and UV-vis analysis.

The total intensity experiments were performed with a newly constructed apparatus.[3] In this apparatus, the light scattered from a sample contained in a thermostated index-matching bath (Brookhaven Model BI-TCA) was measured by seven fixed-position shutter assemblies which were stationed at angles between 30° and 90°. The shutters were connected by fiber optic cables to a cooled photomultiplier (EMI 9502-RF) which had a dark count of approximately 5 counts per measuring period at each angle. An electronic controller was used to consecutively open each shutter to the scattered light, open an electronic gate for 426 ms, and then close the shutter. The time required to complete a cycle of the shutter stations and send the results to a laboratory computer was 8.52 s. The stability of the incident light intensity was checked after every two solvent samples by measuring the intensity of the light scattered from a toluene sample. The relative collection efficiencies of the different shutter assemblies were determined by measuring the angular dependence of the scattered intensity (assumed to be constant) of toluene. All measurements were performed at 25 °C.

Results

The first experiment performed measured the ratios of the scattering intensity from the various solvents to that of toluene. In all cases the data taken at each angle were the average of at least 240 collection cycles, with typical count rates ranging from 5000 to 70 000 counts per cycle. In all cases, the intensity of the scattered light showed no angular dependence. The Rayleigh ratios observed relative to toluene are given in column one of Table I.

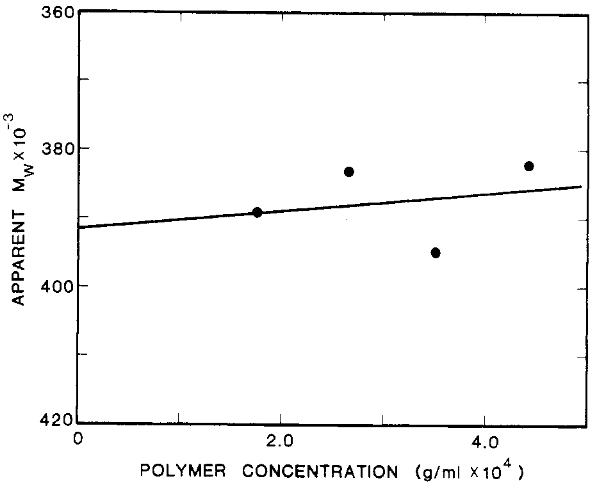

Figure 1. R_v/KC vs. polystyrene concentration after subtraction of solvent scattering and extrapolation to zero scattering angle. The ordinate value at the zero-concentration intercept gives the molecular weight of the polymer.

In order to assign absolute intensities to the ratios of the Rayleigh ratios observed, we measured the molecular weight of a well-characterized linear polystyrene dissolved in cyclohexane. The value for the change in polymer solution refractive index with change in concentration (dn/dc) was extrapolated from the tables in ref 2. The data from 50° to 90° angles were fit to the exact form factor for a Gaussian coil model.[4] Since the product of the scattering vector and the radius of gyration for the polymer was small at all angles (<0.32), the extrapolation to zero angle was not model dependent. The results obtained from our analysis are summarized in Figure 1. Since our intensities were measured relative to toluene, we used the known molecular weight of the polystyrene to obtain a Rayleigh ratio of toluene equal to 39.6×10^{-6} cm^{-1}. Using this Rayleigh ratio, we calculated the remaining Rayleigh ratios in the second column of Table I.

The literature sources used for comparison with this work are cited in Table I. In order to make the comparisons between the previously reported values for Rayleigh ratios and those in the current work, several corrections were required. To convert R_u to R_v we used the following relations from Huglin:[2]

$$R_u\left(\frac{2}{1+\rho_u}\right) = R_v \tag{1}$$

ρ_u in eq 1 is defined as

$$\rho_u = H_u(90°)/V_u(90°) \tag{2}$$

where H_u and V_u correspond to the horizontally and vertically polarized components of the scattered light at 90°, respectively, and the subscript u denotes unpolarized incident light. In some cases it was necessary to convert data from ρ_v to ρ_u depolarization ratios using the relation

$$\rho_u = 2\rho_v/(1+\rho_v) \tag{3}$$

Having converted literature Rayleigh ratios at various wavelengths into the R_v form, it was necessary to extrapolate these values to the wavelength at which we made our measurements. If the Rayleigh ratios are observed at wavelengths which do not lie close to any electronic absorption bands of the solvent, an approximate form for the

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Table I
Experimental and Literature Results for Rayleigh Ratios at 488 nm and 298 K

	exptl		lit.		lit. after 1962		
	$R_v(90°)/R_v(90°)_{\text{toluene}}$	$R_v(90°)$	$R_v(90°)$	$R_v(90°)/R_v(90°)_{\text{toluene}}$	$R_v(90°)$	$R_v(90°)/R_v(90°)_{\text{toluene}}$	ref
CCl_4	0.447 ± 0.006	17.2	17.3 ± 2.8	0.396 ± 0.50	16.8 ± 1.0	0.395 ± 0.038	5–11
benzene	0.894 ± 0.006	35.4	36.6 ± 3.5	0.875 ± 0.107	37.4 ± 1.4	0.910 ± 0.074	5, 6, 8, 10
toluene	1.000 ± ...	39.6	41.9 ± 3.2	... ± ...	41.1 ± 3.1	... ± ...	5, 6, 8, 10
cyclohexane	0.390 ± 0.006	15.4	13.6 ± ...	0.346 ± ...	13.6	0.331 ± ...	9

wavelength dependence of the Rayleigh ratio is[5]

$$R_v(90°) = \left[\frac{4\pi^2 kT\beta}{\lambda^4}\right]\left[\frac{n}{\alpha}\right]^2\left[\frac{dn}{dT}\right]^2\left(\frac{6+6\rho_u}{6-7\rho_u}\right)\left(\frac{1}{1+\rho_u}\right) \quad (4)$$

where β is the isothermal compressibility, α is the isobaric expansivity, k is Boltzmann's constant, T is the absolute temperature, ρ_u is the previously defined polarization ratio, and n and dn/dT are the refractive index and its temperature derivative. Since both the refractive index and the temperature derivative of the refractive index are wavelength dependent while ρ_u is not strongly wavelength dependent for most solvents, a plot of $\ln [(R_v(90°)/(n(dn/dT))^2]$ vs. $\ln (\lambda)$ for any solvent in a wavelength range far from an absorption band should give a straight line with slope of −4. By the use of various literature sources for the dispersion in the refractive index for the solvents considered,[12,13] the extrapolated Rayleigh ratios in column three of Table I were obtained. Because of the difficulty in measuring Rayleigh ratios precisely, the error bars in the literature values are large even before extrapolation. Columns two and three of Table I clearly show that the Rayleigh ratios measured in this work agree with previous work within the experimental error involved in extrapolating literature values to the 488-nm argon ion line.

During these extrapolations, it was noted that many workers prior to 1962 reported values of R_u at 436 nm which do not show agreement after a λ^4 correction with values for R_u taken by those same workers at 546 nm. Almost all available literature surveyed since the critical review of Kratohvil et al.[10] has shown a reasonable agreement between corrected R_u values at those wavelengths. The source of this discrepancy is not clear, but it would appear that serious errors would result if extrapolations by current workers used only early 436-nm values for R_u. For this reason, we have included post-1962 average literature values for both the Rayleigh ratios and their values relative to the Rayleigh ratio of toluene in columns five and six of Table I. As Table I shows, the Rayleigh ratios and their relative values obtained in our laboratory lie within or close to the error bars of the corresponding literature values obtained from work both before and after 1962.

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Registry No. Ar^+, 14791-69-6; CCl_4, 56-23-5; benzene, 71-43-2; toluene, 108-88-3; cyclohexane, 110-82-7.

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