

## Correlations between the Rayleigh ratio and the wavelength for toluene and benzene

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### ABSTRACT

The values of the Rayleigh ratio of two pure liquid, toluene and benzene, at various wavelengths have been collected from the literature, and a correlation between the Rayleigh ratio and the wavelength in the form of power law has been developed for each liquid and can be used to compute accurately the Rayleigh ratio at any wavelength between 420 and 700 nm. The Rayleigh ratio scales with the wavelength with a power of  $-4.17$  and  $-4.38$ , respectively, for toluene and benzene, which deviate significantly from the Rayleigh law ( $-4.0$ ). However, if the effect of the wavelength on their refractive indexes is accounted for, the power is reduced to  $-4.0$  and  $-4.2$  for toluene and benzene, respectively.

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### 1. Introduction

Static light scattering (SLS) is one of the most commonly used techniques for determination of molecular (mass) weight,  $M_w$ , radius of gyration,  $R_g$ , and second virial coefficient,  $A_2$ , of macromolecules (e.g., polymers, proteins, etc.) in disperse medium, based on the Zimm plot [1]. The essential quantity required in such SLS applications is the Rayleigh ratio,  $R_{ref}$ , of a reference (pure) liquid (e.g., toluene, benzene, cyclohexane, etc.). The Rayleigh ratio is also important for conformational characterization of flexible molecules based on the optical anisotropy [2]. The value of the Rayleigh ratio is a function of the wavelength of the incident light,  $\lambda$ , and has been repeatedly measured by different researchers for several wavelengths such as  $\lambda = 488, 514.5, 546$  and  $633$  nm. However, with continuous progress in laser technology, diode-pumped solid-state (DPSS) lasers of many different wavelengths (e.g.,  $\lambda = 457, 473, 523, 532, 660, 671$  nm, etc.) have been introduced in the light scattering applications, at which reliable values of the Rayleigh ratio are difficult to find or missing in the literature, thus, requiring new measurements at these wavelengths.

On the other hand, in principle, for the above pure liquids, the Rayleigh scattering law,  $R_{ref} \sim \lambda^{-4}$ , can be well applied, and then, with known values of the Rayleigh ratio at some specific wavelengths, one can calculate the values at the other wavelengths based on the Rayleigh law. In fact, Finnigan and Jacobs used the

values of the Rayleigh ratio at a few wavelengths measured before 1970s and demonstrated that they did follow the Rayleigh law [3]. However, more recently, Wang and Sorensen reported that the variation of the Rayleigh ratio with the wavelength does not follow the Rayleigh law, with a power of  $-4.6$ , instead of  $-4$  [4].

Therefore, in this work we have collected from the literature as many as possible values of the Rayleigh ratio at different wavelengths for two most commonly used reference liquids, toluene and benzene. The objective is to derive a reliable power-law correlation that can be used to predict any values of the Rayleigh ratio for toluene and benzene, in the range of the wavelengths between 420 and 700 nm, without further experimental measurements. Meantime, we can estimate how much the obtained correlations deviate from the Rayleigh law.

As a reference, the values of the Rayleigh ratio collected from the literature and reported here correspond to the scattering geometry at  $90^\circ$  with an unpolarized incident light and detection of the scattered light without a polarizer, denoted by  $R_u$ . If one is using a vertically polarized incident light and detection without a polarizer, the Rayleigh ratio,  $R_v$ , can be easily computed from  $R_u$  by [5]

$$R_v = 2R_u / (1 + \rho_u) \quad (1)$$

where  $\rho_u$  is the depolarization factor for unpolarized incident light, whose values are collected from the literature as well. Moreover, in the case of vertically polarized incident light and detection with vertical polarizer, the Rayleigh ratio,  $R_{vv}$ , is given by

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$$R_{vv} = R_u(2 - \rho_u)/(1 + \rho_u) \quad (2)$$

Most of the collected data were measured at  $t = 25^\circ\text{C}$ , but some of them were done at  $t \in (20, 25)^\circ\text{C}$ . The latter have been corrected to  $t = 25^\circ\text{C}$ . In the case of benzene, this is done using the following well-known temperature dependence of  $R_{vv}$  [6]:

$$R_{vv}^t = R_{vv}^{25}[1 + 0.00368(t - 25^\circ\text{C})] \quad (3)$$

In the case of toluene, since such an expression is unavailable, the few values of the Rayleigh ratio at  $t \in (20, 25)^\circ\text{C}$  have also been corrected with Eq. (3). This is obviously not rigorous, but from molecular viewpoint, toluene differs from benzene by only a methyl.

## 2. The correlation for toluene

In Table 1 are reported values of the Rayleigh ratio collected from the literature for toluene,  $R_{u,T}$ . Note that some of the  $R_{u,T}$  values were obtained from converting the original  $R_{v,T}$  or  $R_{vv,T}$  values based on Eq. (1) or Eq. (2). In addition, some of the  $R_{u,T}$  values were already averaged by the authors from the earlier literature data. In this case, the original papers were not cited. It is seen that the  $R_{u,T}$  values are mostly measured or estimated for the wavelengths,  $\lambda = 488, 514.5, 546.1, 632.8$  and  $647.1$  nm, and occasionally done for some other  $\lambda$  values. For the commonly used wavelengths, the difference between the maximum and minimum  $R_{u,T}$  values at each wavelength varies from 3% to 17%. Let us now average the  $R_{u,T}$  values at each wavelength and plot the obtained  $R_{u,T}$  values as a function of  $\lambda$ , and the results are shown in Fig. 1 (symbols). Then, when the data in Fig. 1 are correlated using a power-law expression, we obtain,

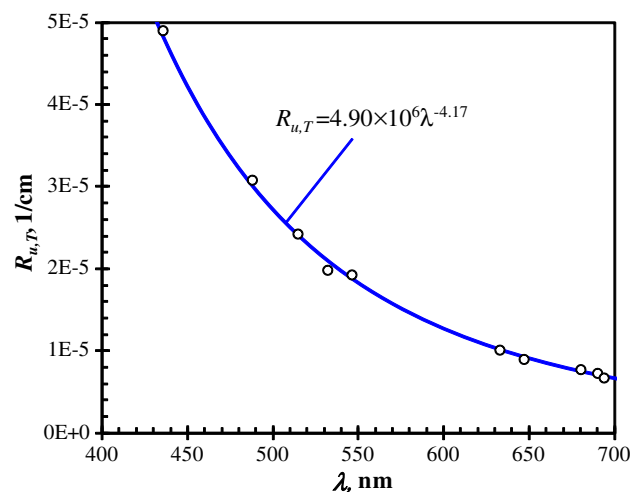
$$R_{u,T} = 4.90 \times 10^6 \lambda^{-4.17} \quad (4)$$

The maximum error between the average values in Fig. 1 and those computed by Eq. (4) is only 6% (at  $\lambda = 532$  nm). Therefore, it can be well used to compute accurately the Rayleigh ratio of toluene for any wavelength in the range between 420 and 700 nm.

**Table 1**

Rayleigh ratio of toluene,  $R_{u,T}$ , and the corresponding depolarization,  $\rho_{u,T}$ , collected from the literature at various wavelengths for unpolarized incident and detected light. Reference angle,  $\theta = 90^\circ$ ; temperature,  $t = 25^\circ\text{C}$ .

$\lambda$ (nm)	$R_{u,T} \times 10^6$ ( $1\text{ cm}^{-1}$ )	$\rho_{u,T}$	Year reported
435.8	49.0	0.495	1956 [10]
488.0	30.7		1987 [5]
488.0	30.6		2002 [4]
488.0	32.1	0.510	1970 [3]
488.0	29.5		1986 [11]
514.5	23.9		1987 [5]
514.5	23.9	0.470	1997 [12]
514.5	24.2		1999 [13]
514.5	26.1		2003 [14]
514.5	23.0		1991 [15]
532.0	18.9		2004 [16]
532.0	20.7		2006 [17]
546.1	18.9	0.468	1970 [3]
546.0	20.9		1987 [18]
546.0	17.9		2002 [19]
630.0	10.4		2002 [19]
632.8	8.77	0.506	1970 [3,20]
633.0	10.5	0.491	1974 [21]
632.8	10.2		2006 [22]
633.0	10.3	0.528	1975 [23]
633.0	10.5		1989 [24]
647.1	8.95		1991 [15]
647.1	8.41		1987 [5]
647.1	9.47		2003 [25]
680.4	7.75		2009 [26]
690.0	7.30		1999 [27]
693.7	6.76		1964 [28]



**Fig. 1.** Comparison between the  $R_u \sim \lambda$  correlation (solid curve) and the average value at each wavelength (symbols) in Table 1 from the literature for toluene.  $T = 25^\circ\text{C}$ .

It should be particularly noticed that in the correlation, Eq. (4), the scaling of  $R_{u,T}$  with  $\lambda$  with a power of  $-4.17$ , which is significantly different from the Rayleigh scattering law ( $-4$ ). Such deviation would become even more significant in the case of benzene (to be discussed below). The reasons for such deviation were seldom discussed in the literature [4]. However, it is well known that the refractive index  $n$  of a liquid decreases slightly with the wavelength [7]. Then, if the fourth-power local field correction is applied for the Rayleigh ratio [8]:

$$R_u \sim \frac{1}{\lambda^4} \left( \frac{n^2 + 2}{3} \right)^2 \quad (5)$$

one would expect certain effect of the  $n \sim \lambda$  dependence on  $R_u$ , but in practice such effect was not considered in the  $R_u$  determination. We have tried to account for such effect, using Eq. (5), based on the  $n \sim \lambda$  correlation developed by Samoc [7], and found that the power can reduce from  $-4.17$  to  $-4.0$ , thus well justifying the deviation from the Rayleigh law.

For the depolarization factor of toluene,  $\rho_{u,T}$ , only few values can be collected from the literature, which are reported also in Table 1. It is seen that the  $\rho_{u,T}$  value does not vary significantly with  $\lambda$  and there is no clear trend. Thus, when the  $\rho_{u,T}$  value is not available in the literature for a given  $\lambda$  value, we suggest using the average value of all the  $\rho_{u,T}$  values in Table 1, which is  $\rho_{u,T} = 0.492$ . The maximum difference between this average value and those listed in Table 1 is 7.3%.

## 3. The correlation for benzene

The values of the Rayleigh ratio for another commonly used reference liquid, benzene,  $R_{u,B}$ , are collected in Table 2. Similarly, we have averaged the  $R_{u,B}$  values at each  $\lambda$  value, which are reported in Fig. 2. When these  $R_{u,B}$  values are correlated with  $\lambda$  using the power law, we obtain,

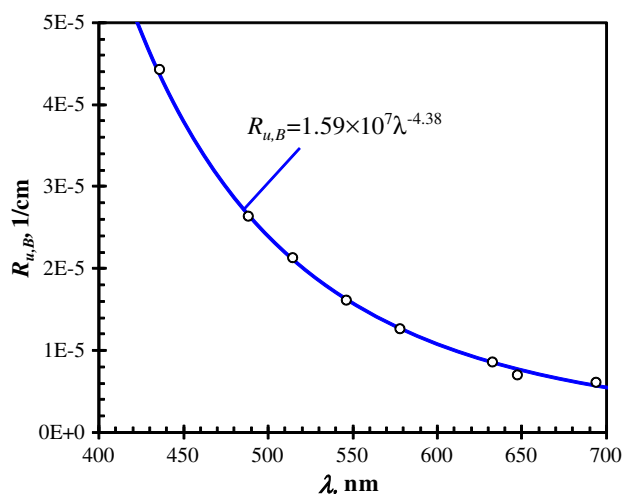
$$R_{u,B} = 1.59 \times 10^7 \lambda^{-4.38} \quad (6)$$

The maximum error between the average values in Fig. 2 and those computed by Eq. (6) is 8.7% (at  $\lambda = 647.1$  nm), and hence, expression 4 can be well used to compute accurately the Rayleigh ratio of benzene for any wavelength in the range between 420 and 700 nm.

**Table 2**

Rayleigh ratio of benzene,  $R_{u,B}$ , and the corresponding depolarization,  $\rho_{u,B}$ , collected from the literature at various wavelengths for unpolarized incident and detected light. Reference angle,  $\theta = 90^\circ$ ; temperature,  $t = 25^\circ\text{C}$ .

$\lambda$ (nm)	$R_{u,B} \times 10^6$ ( $\text{cm}^{-1}$ )	$\rho_{u,B}$	Year reported
435.8	45.9	0.425	1962 [29]
436.0	42.6	0.415	1979 [30]
488.0	26.3		2002 [4]
488.0	26.3		1987 [5]
488.0	27.8	0.439	1970 [3]
488.0	25.2		1986 [11]
514.5	20.8		1987 [5]
514.5	21.8		1996 [31]
546.0	16.0	0.420	1979 [30]
546.1	15.6	0.410	1962 [29]
546.0	17.0		1987 [32]
578.0	12.6	0.420	1979 [30]
632.0	8.96	0.420	1979 [30]
632.8	8.35	0.435	1970 [3,20]
632.8	7.64		1995 [33]
633.0	9.06	0.419	1974 [21]
633.0	8.60	0.432	1975 [23]
647.1	7.06		1987 [5]
693.7	6.15	0.425	1964 [28]



**Fig. 2.** Comparison between the  $R_{u,B} \sim \lambda$  correlation (solid curve) and the average value at each wavelength (symbols) in Table 2 from the literature for benzene.  $T = 25^\circ\text{C}$ .

Compared with the case of toluene, the scaling of  $R_{u,B}$  with  $\lambda$  deviates even more significantly from the Rayleigh law, with a power value of  $-4.38$ . We have also tried to compensate such difference by accounting for the dependency of the refractive index on the wavelength, as discussed above, but the obtained power value ( $-4.2$ ) is still significantly larger than the Rayleigh law. This indicates that there are additional factors affecting the Rayleigh ratio through the wavelength. A possible factor is the collision-induced scattering [9]. It is known that most of the reported values of the Rayleigh ratio were obtained from measuring the absolute scattered light without using a Fabry–Perot interferometer, thus including the collision-induced contributions. If the collision-induced scattering has a different wavelength-dependence, it would change the  $R_{u,B} \sim \lambda$  relation. For example, when using a Fabry–Perot interferometer, Floudas et al. [9] obtained a value of  $\rho_{u,B} = 0.2$  for benzene, which corresponds to  $\rho_{u,B} = 0.33$ , significantly smaller than those reported in Table 2. This might suggest significant contributions of collision-induced scattering. Unfortunately, little

information is available in the literature about the dependence of the collision-induced scattering on the wavelength for benzene. In addition, one of course cannot exclude possible overestimation of the Rayleigh ratio in the region of low wavelength (e.g., at  $\lambda = 435.8$  nm), or more generally to higher inaccuracy in the experimental data. However, in both Eqs. (4) and (6), the observed deviations are much smaller than that reported by Wang and Sorenson [4].

The variations of the depolarization factor of benzene  $\rho_{u,B}$  with the wavelength, reported in Table 2, are even more insignificant than those of toluene. The maximum error between the  $\rho_{u,B}$  values in Table 2 and their average value,  $\rho_{u,B} = 0.424$ , is only 3.5%. Thus, considering errors in the measurements, one can well assume that the depolarization factor of benzene is independent of the wavelength and  $\rho_{u,B} = 0.424$  can be used for any wavelengths.

#### 4. Conclusions

Based on the above analysis of the Rayleigh ratio of toluene and benzene reported in the literature, the data for toluene follows very well the Rayleigh scattering law, if the effect of the wavelength on the refractive index is accounted for. For benzene, however, much more significant deviation from the Rayleigh law occurs, which should be related to additional factors such as inclusion of the collision-induced scattering, higher inaccuracy in the experimental data, etc. It is therefore suggested that except for some specific requirement, one should use toluene, instead of benzene, as the reference in SLS applications, and Eq. (4) can be reliably applied to compute the value of the Rayleigh ratio at any wavelength in the range between 420 and 700 nm.

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