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Experimental Determination of Absolute Turbidities of Pure Liquids and Standard Polystyrene Solutions*

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Rayleigh ratios and turbidities of some pure liquids and standard polymer samples (benzene, toluene, Cornell polystyrene, and D.C./P.J. 3 polystyrene) were measured by use of the Oster-Aminco photometer. The problem of proper optical correction factors was thoroughly elucidated and a connection between the refractive index and volume correction of Carr and Zimm and other workers, and the n^2-correction of Hermans and Levinson was found. Measurements were performed at wavelengths 546 and 436 mμ. The values are somewhat lower than the larger part of data in literature, but agree with recent data obtained by carefully performed measurements.

INTRODUCTION

Pure liquids, especially those of the aromatic series, are very convenient standards for calibration of light scattering photometers. They are chemically fully defined, are readily available substances, and they can be successfully clarified by distillation. Moreover, the scattering intensities are mostly nearer to the intensities of polymer solutions — nowadays the most important systems investigated by light scattering — than the intensities of other scattering standards whose turbidities are determined by the transmission method.

There are two points causing some uncertainty in calibration data obtained by pure liquids: (1) the Rayleigh ratios reported in the literature vary in a range greater than the actual experimental error of intensity measurements, and (2) the existence of various optical correction factors causing sometimes improper evaluation of instrument readings.

The standard samples of polymers in solution are not so convenient for calibration purposes, because they cannot be distributed over the whole world for an indefinitely long time. The clarification of these solutions is more difficult, it is usually performed by filtration, which allows some variations in experimental conditions. Otherwise there are same reasons for uncertainty in calibration as mentioned before.

In a recent paper[1] a critical survey of the literature on the calibration of light scattering photometers as well as on the Rayleigh ratios of pure liquids and turbidities of standard solutions of polystyrene in toluene has been made.

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In the present paper the results of own measurements, discussed in that survey, are given together with more experimental details and a critical study of proper optical correction factors.

EXPERIMENTAL

Light scattering measurements were carried out by use of the Oster-Aminco photometer[2] connected to a »Philips« Model PE 4222 electronic voltage stabilizer. The apparatus was used with improvements described earlier[3]. The measurements were performed as before[4], and the apparatus was calibrated with »Ludox« colloidal silica using the method of Maron and Lou[5]. The lineary polarized light was obtained by placing carefully adjusted polaroid discs before the photomultiplier tube. Used were semioctagonal cells made by Hellma GMBH, Müllheim/Baden, Germany. All measurements were made at room temperatures (21—25^{0}C).

Pure liquids (benzene, toluene) were reagent grade chemicals. The purification and clarification was performed by distillation over sodium several times shortly before use. This was enough to obtain samples without dust and with a dissymmetry very close to unity.

The standard samples of polystyrene —Cornell polystyrene and D.C./P.J.3 polystyrene* — were prepared as 0.5% solutions in toluene following the prescriptions and clarified by filtration through sintered glass filters (Schott & Gen., Mainz, Germany, porosity G5M) under nitrogen pressure.

OPTICAL CORRECTION FACTORS

The intensity of the scattered beam reaching the detector depends on the refractions and reflections of rays on the cell walls. There are many papers dealing with corrections which must be made in order to obtain right values of absolute light scattering quantities. Since the first paper of Carr and Zimm[6], formulating firstly the refractive and volume corrections, till the present time these problems were throughly elucidated and the derived mathematical expressions checked experimentally, but the picture is still somewhat confusing.

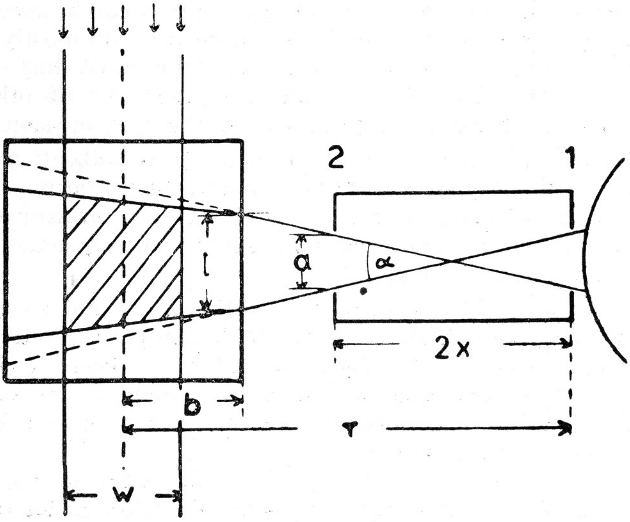

Fig. 1. Geometry of light scattering cell and detector.

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* These samples were obtained through the courtesy of Professor P. Debye, of Cornell University, U.S.A. (Cornell Polystyrene), and Professor P. Johnson, of the University of Cambridge, England (D. C./P. J. 3 Polystyrene).

The formulation of Carr and Zimm, independently developed by Brice *et al.*[7], was applied and improved by Sedlaček[8], Maron and Lou[9], Carpenter and Krigbaum[10] and Kerker *et al.*[11] The refractive index correction C_n for rectangular cells mentioned everywhere is given as

$$C_n = n^2 \left(1 - \frac{b}{r} \; \frac{n-1}{n}\right)^2 \tag{1}$$

where n is the refractive index of scattering medium, r and b are geometrical constants involved in Fig. 1. The volume correction varies from one type of apparatus to another.

A different approach to light scattering corrections was made by Hermans and Levinson[12]. These authors pointed out that in case the detector does not »see« past the edges of the incident beam the refractive index correction should be proportional simply to n^2. They discussed several cases of cell and detector geometry and criticized also expression (1). Later it will be shown that the n^2-correction, if taken as a relative one, consists of both the relative refractive and volume corrections. For these reasons it appears that the correction of Hermans and Levinson has the character of a total optical correction. The n^2-correction was successfully applied in experimental work, especially in connection with absolute light scattering photometers[13–17].

Other corrections, based on the reflection effects on cell walls are of importance only in determining light scattering quantities from the geometrical constants of the apparatus. The most important of these is the reflection correction C_o based on Fresnel's reflection formulas[3,8]. A review of these corrections is given by Sedlaček[8].

In the following the method of correcting measured values obtained with a rectangular cell (for semioctagonal cells the same formulas are valid) by a relative photometer (*i.e.* a photometer which should be calibrated by a substance of standard turbidity) will be discussed. To simplify the relations and to render possible comparison between existing approaches the detector should »see« within the edges of the incident beam, a requirement fulfilled by the Oster-Aminco photometer.

If the calibration of the photometer was performed with a liquid of refractive index n_1, data obtained on a liquid of refractive index n_2 must be corrected by the relative correction factor

$$C_i' = C_{i,2} \; / \; C_{i,1} \tag{2}$$

The total relative optical correction factor is represented by the product $C'_n \cdot C'_v \cdot C'_o$.

The C'_o factor is very small. So in the case of comparison of the optical systems water-glass-air and benzene-glass-air $C'_o = 1.002$ (in the wavelength range 578—405 mμ), a value much smaller than the experimental error of light scattering measurements, which allows to neglect this correction. In absolute photometers this correction is of importance because C_o takes in most cases values in the range 0.955 — 0.965.

In the case of the Oster-Aminco photometer the relative refractive index correction factor C'_n can be used in the form (1). For the volume correction two different forms of expressions exist. The first one is given by Carr and Zimm[6]:

$$C_v = 1 - \frac{b\,(a + l) \,/\, (r - b)}{2nl + b\,(a + l) \,/\, (r - b)} \tag{3}$$

and has to be applied to cell and detector geometries with the light stop 2 (Fig. 1) placed directly onto the cell wall or very close to it*. All constants are as in Fig. 1.

The second type of volume correction, calculated for geometries as shown in Fig. 1, is given by Kerker *et al.*[11] Using the symbols of Fig. 1 this correction factor can be written as follows

$$C_v = 2 \left[\left(\frac{r - b - x}{x} + \frac{2b}{n\sqrt{a^2 + 4x^2}} \right)^2 + 1 \right]^{-1} \tag{4}$$

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* It should be noted that the expression for C_v involved in the original paper of Carr and Zimm[6] is erroneous (it is probably a misprint), causing a frequent quoting and using of this incorrect expression. Only Sedlaček[8] gives the correct expression (3).

if the light stops of the receiver nosepiece are square and equal. If the light stops are rectangular with the width a and height h, expression (4) takes the form:

$$C_V = 2\left[\left(\frac{r - b - x}{x} + \frac{2b}{n\sqrt{a^2 + 4x^2}}\right)\left(\frac{r - b - x}{x} + \frac{2b}{n\sqrt{h^2 + 4x^2}}\right) + 1\right]^{-1}. \qquad (4a)$$

If a^2, $h^2 \ll 4x^2$ a simpler expression results:

$$C_V = 2\left[\left(\frac{r - b - x}{x} + \frac{b}{nx}\right)^2 + 1\right]^{-1} \qquad (4b)$$

Using expressions (1) and (4b) the total relative optical correction factor can be obtained:

$$C'_n \cdot C'_V = \frac{n_2^2\left\{\left[\frac{r}{x}\cdot\frac{n_1(r - b - x) + b}{n_1(r - b) + b}\right]^2 + 1\right\}}{n_1^2\left\{\left[\frac{r}{x}\cdot\frac{n_2(r - b - x) + b}{n_2(r - b) + b}\right]^2 + 1\right\}}\,. \qquad (5)$$

If $x \ll (r - b)$, $C'_n \cdot C'_V = n_2^2/n_1^2$, a result identical with the correction of Hermans and Levinson. Even in the cases of $(r - b)$ being only several times larger than x, the ratio of terms in brackets will be small. In the case of the Oster-Aminco photometer $(r - b = 2.73x)$ its largest value obtained for the relative correction of the system benzene-water amounted to 1.02. This shows that the relative n^2-correction of Hermans and Levinson really consists of the relative refractive index correction C'_n and the relative volume correction C'_V, a fact easily understandable if we remember that the light flux of the scattered light reaching the detector is proportional to a product of the scattering volume and the solid angle of the scattered cone[15,17], and that the refractive index correction was derived as a cone angle correction and the volume corrections take into account the changes of the scattering volume.

Table I sets forth numerical calues of relative corrections for the Oster-Aminco photometer. The data are calculated using refractive indexes given by Cantow[18] for pure liquids at 25°C, and taking r = 35.0 mm., b = 14.5 mm., x = 7.5 mm. The C_V' values are calculated from expression (4b). Calculations from (4a) (a = 1.52 mm., h = 2.79 mm.) did not give any significant difference in C_V'. If expression (3) is applied (l = 3.04 mm.) about 7% lower values of C_V' are obtained, showing the unapplicability of this form of volume correction in the case of the Oster-Aminco photometer.

TABLE I

Relative Optical Correction Factors for Data Measured by the Oster-Aminco Photometer Using a Rectangular Cell

n_1 = refractive index of water
n_2 = refractive index of benzene respective toluene

λ_o (mμ)	$(n_2/n_1)^2$	C_n'	C_V'	$C_n' \cdot C_V'$	$C_n' \cdot C_V'/(n_2/n_1)^2$
System: benzene-water					
546	1.268	1.171	1.099	1.287	1.015
436	1.285	1.183	1.105	1.307	1.017
System: toluene-water					
546	1.257	1.164	1.096	1.276	1.015
436	1.275	1.177	1.101	1.296	1.016

RESULTS

In the first experiments with pure liquids all samples, although carefully clarified and showing none or only a few dust particles when observed under a small scattering angle, showed dissymmetries greater than 1.50. It was found that this effect was caused by stray reflections on the edges of light scattering cells. This inconvenience could be eliminated by blackening the outer face of the cell back. In Table II some data are given showing the effect of blackening on the intensity of scattered light (given as galvanometer readings I'_{90}) and on the dissymmetry ($z = I'_{45}/I'_{135}$).

TABLE II

The Effect of Blackening on the Intensity of Scattered Light and Dissymmetry for Benzene Measured in Semioctagonal Cells

	I'_{90}		z	
λ_0 (mμ)	546	436	546	436
unblackened	40.8	11.3	2.80	1.69
blackened	39.8	11.0	1.00	1.00

This blackening procedure gave always satisfactory dissymmetries and should be applied to all solutions whose turbidities are lower than 10^{-2} cm.$^{-1}$ For more turbid media the stray reflections have no influence on the measured scattering intensities and the blackening is unnecessary.

The turbidities were evaluated from the expression

$$\tau = C' \cdot I'_{90} \cdot C_n' \cdot C_v' \cdot C_r \qquad (6)$$

Here τ is turbidity in cm.$^{-1}$, C' is the calibration constant[4], C_n' and C_v' are the optical correction factors defined by expressions (1), (2) and (4b), and C_r is a correction factor introduced especially for the Oster-Aminco photometer owing to the uncertainties of the decade meter multiplier resistors. This correction amounted in some cases to 1.10.

The Rayleigh ratio R_{90} is related to the turbidity by the well known expression

$$R_{90} = (3/16\,\pi) \cdot \tau. \qquad (7)$$

The polarization ratios ϱ_{90} were determined from the relation

$$\varrho_{90} = C_\varrho \, (I'_{90\,H}/I'_{90,V}) \qquad (8)$$

where the indices H and V denote the horizontal and the vertical component of scattered light, respectively, and C_ϱ is the correction factor owing to the different sensitivity of the photomultiplier tube to light beams polarized in different planes. C_ϱ is defined as a ratio of galvanometer readings for light directly incidenting onto the photomultiplier tube [denoted by I'(O)].

$$C_\varrho = I_V'(O)/I_H'(O) \qquad (9)$$

This correction factor varies from tube to tube, taking values usually between 0.9 and 1.1.

The turbidities of standard polystyrene solutions were evaluated as excess turbidities, *i.e.* from the turbidity of the solution the turbidity of the solvent was substracted.

In Tables III and IV the results of measurements at the wavelengths 546 and 436 mμ are given. The data are mean values of several measurements with a standard deviation of less than 2%.

TABLE III

Rayleigh Ratio R_{90} (in cm.$^{-1}$) and Polarization Ratio ϱ_{90} for Pure Liquids

λ_0 (mμ)		546	436
benzene	$R_{90} \cdot 10^6$	16.1	46.5
	ϱ_{90}	0.42	0.44
toluene	$R_{90} \cdot 10^6$	17.6	53.3
	ϱ_{90}	0.48	0.50

TABLE IV

Excess Turbidity τ (in cm.$^{-1}$) of Standard Polystyrene Samples in Toluene (0.5 g./100 ml. of Toluene)

	$\tau \cdot 10^4$	
λ_0 (mμ)	546	436
Cornell Polystyrene	12.3	32.4
D.C./P.J.3 Polystyrene	7.82	18.3

DISCUSSION

The data listed in Tables III and IV, if compared with other data available in literature[1], are in agreement with data obtained by carefully performed experiments[13,15,16,17,19,20], but are somewhat lower than the average of all data reported[10]. This subject was very extensively discussed in a previous paper[1]. Here it is only emphasized that many facts confirm the reliability of results reported in this paper.

It appears that a larger part of the results reported in literature may be influenced by errors arising from the use of improper optical correction factors. So for example data obtained by the Brice-Phoenix instruments are mostly evaluated by means of to high residual refraction corrections[21]. The second disadvantage of this type of photometer is the detector's seeing past the edges of the incident beam if standard light stops, as supplied by the manufacturer, are used. Under these conditions the refractive index correction (1) cannot be applied, as pointed out by Hermans and Levinson[12]. This disadvantage can easily be corrected, however, by inserting in front of the photomultiplier tube an additional diaphragm of the same dimensions as that on the front nosepiece. In such a case the geometry is the same as that of Fig. 1 and the same equations for correction factors apply.

In the smaller part of results the calibration procedure was not fully satisfactory (*e.g.* calibration with »Ludox« without extrapolation to zero concentration[2,22], causing also too high results).

The most reliable data appear to be those obtained by »absolute photometers«[15,16] where the turbidity or Rayleigh ratio is determined from the instrument geometry, or by measurements performed on photometers calibrated in a correct manner and having a well-known geometry[13,17,20].

On the other hand, in the experimental procedure described, two sources of uncertainty are possible: (1) the optical correction factors, and (2) the calibration constant. Assuming that the optical corrections used in expression (6) are proper and correct, the reliability of data in Tables III and IV depends upon the accuracy of the calibration procedure. Applying the calibration procedure with »Ludox«, described extensively in another paper[4], very good agreement between particle diameters of monodisperse polystyrene latexes obtained from measurement of scattering at 90° and diameters from other light scattering methods independent of calibration could be achieved[3]. For these reasons it seems that the results given in this paper are very near the best values of Rayleigh ratios and turbidities.

The polarization ratios given are not fully reliable because they were measured by polaroid discs which, as known, do not give 100% polarized light. However, they are in the range of results quoted in literature. For best values of the polarization ratio masurements have to be performed by the use of polarizing prisms.

In all experiments described here the effect of temperature was neglected, although turbidities of benzene and toluene increase about 0.5% per degree, as calculated from Einstein's theory[23], causing a variation of about 2% in data from Tables III and IV. Because the overall experimental error of these measurements was estimated to be about 5%, the error caused by temperature changes cannot be of greater importance. Clearly, it would be desirable to measure turbidities of pure liquids with greater precision, especially for use in calculation of Avogadro's number. For these purposes the precision of a light scattering photometer should be increased by improvements in the optical and electronical part of the apparatus (as it was made in case of specially built instruments) and by controlling the temperature. Only such carefully measured data, used together with reliable values of constants involved in Einstein's equation, will allow exact calculations of Avogadro's number from the light scattering of pure liquids.

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IZVOD

Eksperimentalno određivanje apsolutnih mutnoća čistih tekućina i standardnih uzoraka polistirena

Gj. Deželić

Mjereni su Rayleighovi omjeri i mutnoće nekih čistih tekućina i standardnih uzoraka polistirena (benzena, toluena, Cornell polistirena i D.C./P.J. 3 polistirena) pomoću fotometra Oster-Aminco. Opširno je razmotren problem ispravnih optičkih korekcijskih faktora. Nađena je veza između korekcija za indeks loma i volumena Carra i Zimma i ostalih istraživača, kao i n^2-korekcije Hermansa i Levinsona. Mjerenja su vršena sa svjetlošću valnih dužina 546 i 436 mμ. Dobivene su vrijednosti nešto niže od većine podataka iz literature, ali se slažu s novijim podacima dobivenim iz pažljivo izvedenih mjerenja.

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