Determination of the Rayleigh ratios of pure liquids by means of a photometer Spekol

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The possibility of using a photometer Spekol for determination of the Rayleigh constants of pure liquids has been studied. It appears that the correction for the index of refraction $n^{1.85}$ may be used to the determination of $R(90°)$ of pure liquids at the wavelengths 442—633 nm.

Изучена возможность использования фотометра Спекол для определения констант Релея чистых жидкостей. Показалось, что поправку на показатель преломления $n^{1.85}$ можно применить для определения $R(90°)$ чистых жидкостей при длинах волн 442—633 нм.

The study of interactions in binary and ternary mixtures enabling us to determine fundamental thermodynamic quantities belongs to important applications of the method of light scattering measurement [1, 2]. As the use of spectral colorimeter Spekol with accessories (Zeiss, Jena) appears to be profitable to this purpose, we took up, in the first stage, the determination of $R(90°)$ of liquid standards by means of this photometer.

Theoretical

The determination of the Rayleigh ratios of pure liquids was based on the following equation [3]

$$R(90°) = C\,C_{n_1}\frac{1}{t_a^2 t_1^2(1-4A^2)}\,(I'(90°) - 2AI'(90°)) \qquad (1)$$

where

C is the calibration constant of the instrument,
C_{n_1} is the so-called correction for the index of refraction,
$t_a = 1 - f_a$, where $f_a = \left(\frac{n_g - 1}{n_g + 1}\right)^2$

(Fresnel correction for the reflection of light at the interface cell glass—air [4]),

$t_l = 1 - f_l$, where $f_l = \left(\dfrac{n_g - n_l}{n_g + n_l}\right)^2$

(Fresnel correction for the reflection of light at the interface glass—liquid [4]),

$A = f_l + t_l f_a$,

n_g and n_l are indices of refraction of cell glass and measured liquid,

$I'(90°)$ is luminous flux of scattered radiation at the angle of 90° according to galvanometer reading.

The calibration constant C may be calculated on the basis of the measurement of $I'(90°)$ in convenient standard (benzene) and tabulated value of its Rayleigh ratio $R_b(90°)$ from the equation

$$C = \frac{1}{C_{n_b}} \frac{R_b(90°)}{\dfrac{1}{t_a^2 t_l^2 (1 - 4A^2)} (I_b'(90°) - 2AI_b'(90°))} = \frac{1}{C_{n_b}} \frac{R_b(90°)}{I_b(90°)} \tag{2}$$

Since it is valid for the ratio of the distance of photomultiplier from the centre of cell (R) and the radius of cell (r) $R/r \gg 1$, the correction C_{n_l} incident to Spekol may be expressed [5] as follows

$$C_{n_l} = (n_l)^m \tag{3}$$

Now the value of exponent m should be ascertained. It may be determined from the measurements of light scattering in a few liquids with known values of $R(90°)$. Eqn (1) is to be written in the following form

$$R(90°) = \frac{R_b(90°)}{I_b(90°)} \left(\frac{n_l}{n_b}\right)^m I(90°) \tag{4}$$

or

$$\frac{R(90°)}{I(90°)[I_b(90°)]^{-1}} = (n_l)^m \frac{R_b(90°)}{(n_b)^m} \tag{5}$$

On taking logarithm of eqn (5), the value of m can be determined from the slope of the relationship

$$\log\left(\frac{R(90°)}{I(90°)[I_b(90°)]^{-1}}\right) = \mathrm{f}(\log n_l) \tag{6}$$

Experimental and results

We used seven liquid standards for determining m. All chemicals used were anal. grade reagents. They were dried and purified by multiple distillation and filtration before measurements. The measurements of light scattering were carried out with the above-described spectrometer by using a fluorescence adapter with photomultiplier detection. The adapter was fitted with a diaphragm placed in front of the photomultiplier while the rear-view mirror of the adapter was not in use.

The scattering characteristics of measured liquids necessary for constructing relationship (6) are given in Table 1. The course of this relationship is represented in Fig. 1. The value of m ascertained from the slope of this straight line is equal to 1.85, the limiting error being ± 0.55.

The values of Rayleigh ratios of the measured pure liquids could be determined with the calibrated device by using the equation

$$R(90°) = \frac{R_b(90°)}{I_b(90°)} \left(\frac{n_l}{n_b}\right)^{1.85} I(90°) \tag{7}$$

Table 1

Rayleigh ratios and indices of refraction of pure liquids literature data ($\lambda_0 = 546$ nm, $t = 25$ °C)

Liquid	$\frac{R(90°) \cdot 10^6}{\text{cm}^{-1}}$	n_l	Ref.
Benzene	16.2	1.502	[6]
Cyclohexanone	4.92	1.450	[7]
Acetone	4.94	1.358	[8]
Cyclohexane	4.56^a	1.425^a	[9]
Toluene	18.9	1.497	[10]
Chloroform	7.45	1.443	[11]
Carbon tetrachloride	6.12	1.461	[12]

a) 20 °C.

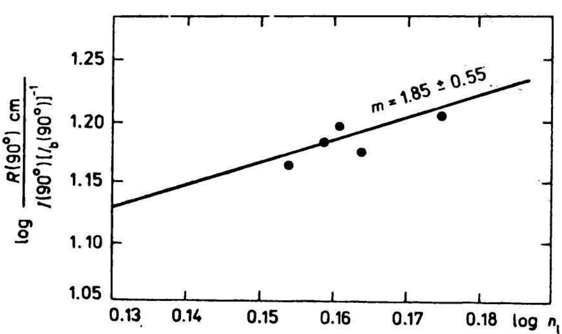

Fig. 1. Variation of $\log \frac{R(90°)\ \text{cm}}{I(90°)[I_b(90°)]^{-1}}$ with $\log(n_l)$ for the fluorescence adapter of instrument Spekol.

The values of $R(90°)$ thus determined are given in Table 2. In consideration of contemporary use of coherent light sources for determining $R(90°)$ of pure liquids, we also measured $R(90°)$ of toluene at 633 nm and of chlorobenzene at 442 nm with this photometer. The value found by us for toluene is $10.2\times10^{-6}\ \mathrm{cm}^{-1}$ (*Pike et al.* [13] found the value $10.4\times10^{-6}\ \mathrm{cm}^{-1}$) and for chlorobenzene $54.4\times10^{-6}\ \mathrm{cm}^{-1}$ (*Rozhdestvenskaya et al.* [14] found the value $54.4\times10^{-6}\ \mathrm{cm}^{-1}$). The values of $R_b(90°)$ for those wavelengths were taken from papers [13, 14].

Table 2

Values of $\dfrac{R(90°)}{I(90°)[I_0(90°)]^{-1}}$ and $R(90°)$ of pure liquids determined with a photometer Spekol (nonpolarized primary ray $\lambda_0 = 546$ nm, temperature 23 °C)

Liquid	$\dfrac{R(90°)\ \mathrm{cm}}{I(90°)[I_0(90°)]^{-1}}$	$\dfrac{R(90°)\cdot10^6}{\mathrm{cm}^{-1}}$
Cyclohexanone	15.7	4.9
Acetone	13.4	4.9
Cyclohexane	14.6	4.7
Toluene	16.0	19.0
Chloroform	15.3	7.4
Carbon tetrachloride	14.9	6.6

We must take into consideration that the value of $R(90°)$ for $\lambda_0 = 442$ nm and $\lambda_0 = 633$ nm was determined on the basis of the value of m found out by calibration at 546 nm. It appears that the influence of wavelength of the used primary radiation on m is negligible and the value $m = 1.85$ may be used in eqn (7) in the whole range of the above-mentioned wavelengths.

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