The use of spectral dependence of light scattering dissymmetry for distribution analysis of dispersions

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Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

The influence of polydispersity on the relations between the dissymmetry of scattered light and mean size of particles, or wavelength of the used light was theoretically studied. It has been disclosed that both these relations may be used for distribution analysis of polydispersions.

Теоретически изучалось влияние полидисперсности на зависимость диссимметрии рассеянного света от средней величины частиц и длины волны используемого света. Оказалось, что обе эти зависимости можно использовать при дистрибуционном анализе полидисперсий.

The determination of size or size distribution of the particles in colloidal dispersions is of fundamental importance for research and practice. For this purpose, the light scattering is successfully used and the method of dissymmetry may be regarded as a classical procedure [1]. In this method, we define the coefficient of dissymmetry as ratio of two scattered light fluxes

$$Z=\frac{\Phi(\theta_1)}{\Phi(\theta_2)} \tag{1}$$

usually measured in angles of observation of 45° and 135° with respect to the primary beam. In accordance with the theory of Mie, Z is a function of the relative index of refraction m and of the parameter of size $\alpha=\pi D/\lambda$ (D is the diameter of particle and λ is the wavelength of the radiation used in the system) and can be calculated for monodisperse systems by using the tabulated intensity functions of Mie for spherical particles [2] and different combinations of m and α. However, the theoretical relationship exhibits oscillating character. The ambiguousness of data may be eliminated by measuring the dissymmetry with nonpolarized or vertically and horizontally polarized beam [3]. The method of dissymmetry was used for estimating the size of particles of polydisperse latexes by *Maron et al.* [4].

It appeared that the obtained results were dependent not only on the size distribution of particles but also on the wavelength of the radiation used. Thus this fact led us to the idea to study theoretically

1. the influence of polydispersity on the relation $Z = f(\bar{\alpha})$,
2. the spectral dependence of the coefficient of dissymmetry with the aim to use these relations for distribution analysis of polydisperse colloidal systems with $m = 1.10$ and $m = 1.20$.

Theoretical

The theoretical expression of the coefficient of dissymmetry is based on the equation (nonpolarized primary beam)

$$Z_n(45/135) = \frac{\int_0^\infty [i_1(m, \alpha, 45) + i_2(m, \alpha, 45)] f(\alpha)\, d\alpha}{\int_0^\infty [i_1(m, \alpha, 135) + i_2(m, \alpha, 135)] f(\alpha)\, d\alpha} \quad (2)$$

where i_1 and i_2 are the intensity functions according to Mie [2].

Owing to frequent applicability, it was assumed that the distribution function of particle sizes could be expressed as a lognormal distribution of negative order — NOLD in the form [5]

$$f(\alpha) = \left(\frac{K}{\pi}\right)^{1/2} \alpha^{-1} \exp\left[-K \log^2 \frac{\alpha}{\alpha_M}\right] \quad (3)$$

where α_M is the medial size and K is the breadth parameter. The meaning of the breadth parameter is illustrated in Fig. 1.

The Mie intensity functions for vertically i_1 or horizontally i_2 polarized primary beam may be written in the form [6]

$$i_1(m, \alpha, \theta) = \left| \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \right|^2 \quad (4)$$

$$i_2(m, \alpha, \theta) = \left| \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n) \right|^2 \quad (5)$$

where π_n and τ_n are angular coefficients expressed in terms of the Legendre polynomials and a_n, b_n are coefficients defined by means of the Bessel functions. The number of the terms in series (*4*) and (*5*) was determined by means of the following empirical equation (*7*)

$$n_{max} = 1.84\alpha^{0.904} + 4$$

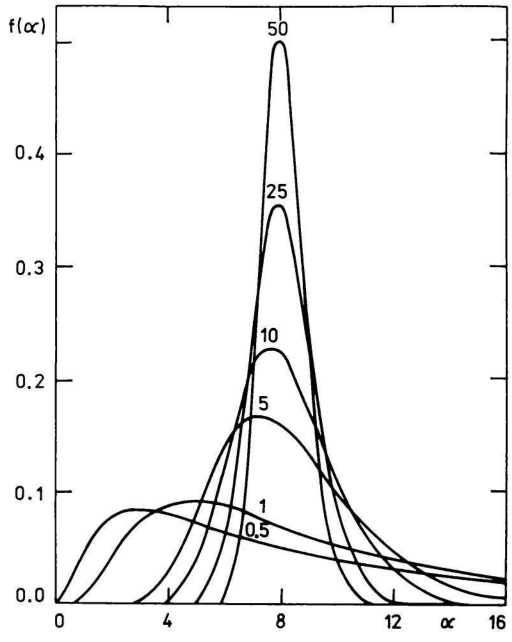


Fig. 1. NOL distribution for $\alpha_M = 8$ and different degrees of polydispersity.

The integrals in eqn (*2*) were solved by numerical method with a step $\Delta\alpha = 0.05$ using a computer Siemens 4004.

The program of calculation was constructed in language Fortran IV and all calculations were carried out in twofold accuracy. The reliability of calculations was tested by means of the data published by *Wallace* and *Kratohvil* who presented the angular function $I_1 = f(\theta)$ for polydisperse polystyrene (PS) latex [8]; I_1 is the intensity of scattered light (vertically polarized primary beam) in the system.

Results

Fig. 2 demonstrates the influence of polydispersity on the relationship $Z_n(45\text{-}/135) = f(\bar{\alpha})$ for polydisperse colloidal systems ($m = 1.10$, $\lambda_0 = 546$ nm).

It is obvious that the use of this relationship for determining the size of spherical particles gives multivalidity of data except for considerably polydisperse system ($K = 1$). This ambiguity, as described in paper [4], may be eliminated by measuring $Z(45/135)$ with vertically as well as horizontally polarized primary beams. The theoretical relations $Z_v(45/135)$ and $Z_h(45/135)$ necessary for finding the corresponding distribution parameters are represented in Figs. 3 and 4.

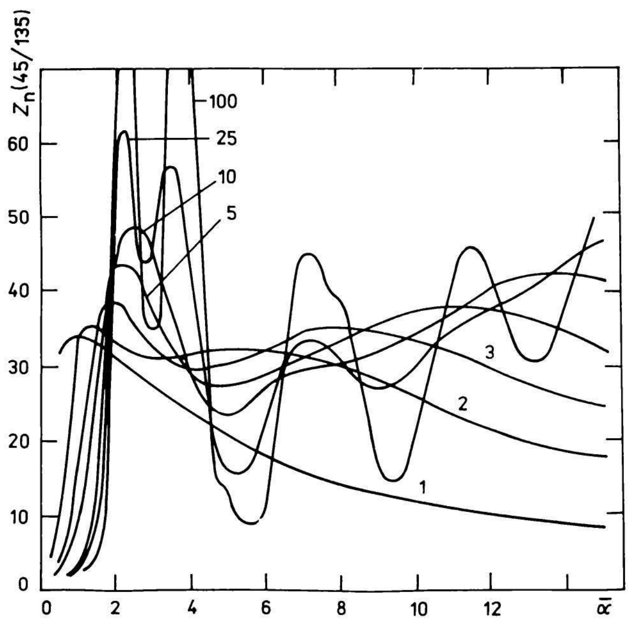


Fig. 2. Variation of the coefficient of dissymmetry (nonpolarized primary beam) with mean value of α for $\lambda_0 = 546$ nm and $m = 1.10$; NOL distribution, $K = 1, 2, 3, 5, 10, 25, 100$.

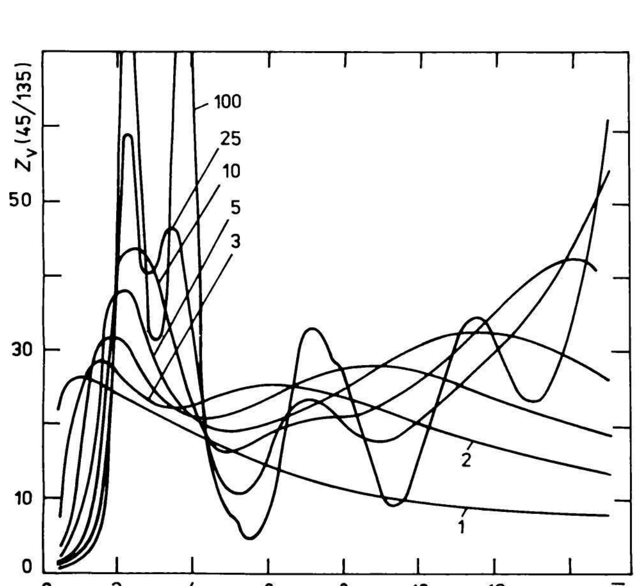


Fig. 3. Variation of the coefficient of dissymmetry (vertically polarized primary beam) with mean value of α for $\lambda_0 = 546$ nm and $m = 1.10$; NOL distribution, $K = 1, 2, 3, 5, 10, 25, 100$.

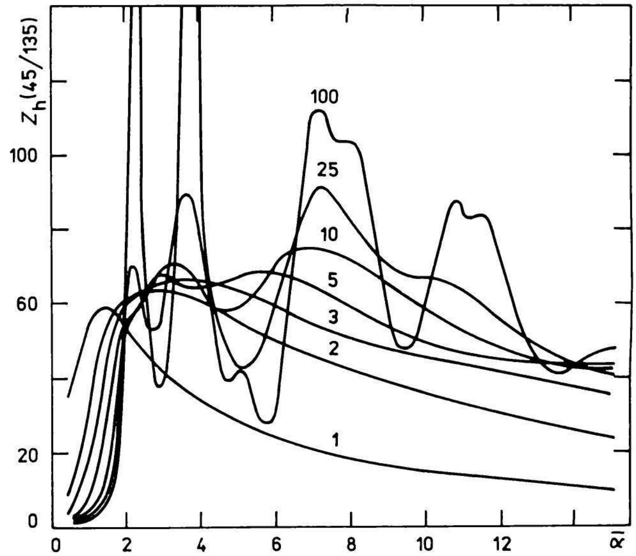


Fig. 4. Variation of the coefficient of dissymmetry (horizontally polarized primary beam) with mean value of α for $\lambda_0 = 546$ nm and $m = 1.10$; NOL distribution, $K = 1, 2, 3, 5, 10, 25, 100$.

Subsequently, the relationships $Z_n(45/135) = f(\lambda_0)$ were constructed for various wavelengths. The theoretical relationships $Z_n(45/135) = f(\lambda_0)$ were calculated for polystyrene polydisperse populations with medial radii in the range $r_M =$ 100—1000 nm and $K = 5$, 10, 20, 50, and 100. Owing to significant role of the dispersion of the index of refraction, the corresponding index of refraction was inserted into calculations for each wavelength. The indices of refraction were ascertained on the basis of the Cauchy equations [9]

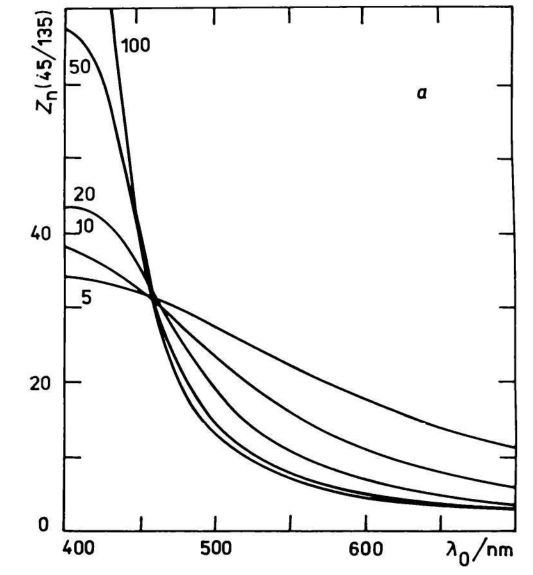
$$n_{PS} = 1.5683 + 10.087 \times 10^3\ \text{nm}^2/\lambda_0^2$$

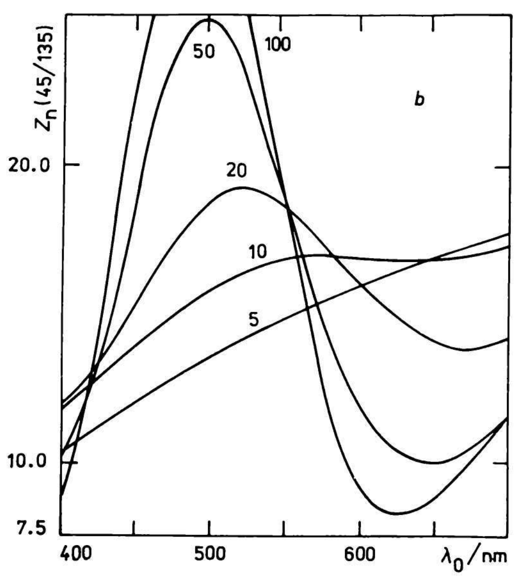
$$n_W = 1.324 + 3.046 \times 10^3\ \text{nm}^2/\lambda_0^2$$

where n_{PS} and n_W are indices of refraction of PS and water and λ_0 is the wavelength of light in nm.

As evident from Fig. 5, the relationships $Z_n(45/135) = f(\lambda_0)$ may be used for determining the distribution parameters of the NOL distribution up to $r_M =$ 1000 nm (as for higher values of r_M, the graphical relationships for $K = 5$, 10, 20 practically coalesce).

For determining the distribution parameters of the particle size distribution we may use either graphical or numerical comparison of the theoretical relationships $Z(45/135) = f(\lambda_0)$ with the experimental ones. In the graphical method, the experimental relationship $Z_n = f(\lambda_0)$ is drawn on transparent paper and the


$Z_n(45/135)$
100
50
a
20
10
5
40
20
0
400
500
600
λ_0/nm


$Z_n(45/135)$
50
100
b
20.0
20
10
5
10.0
7.5
400
500
600
λ_0/nm

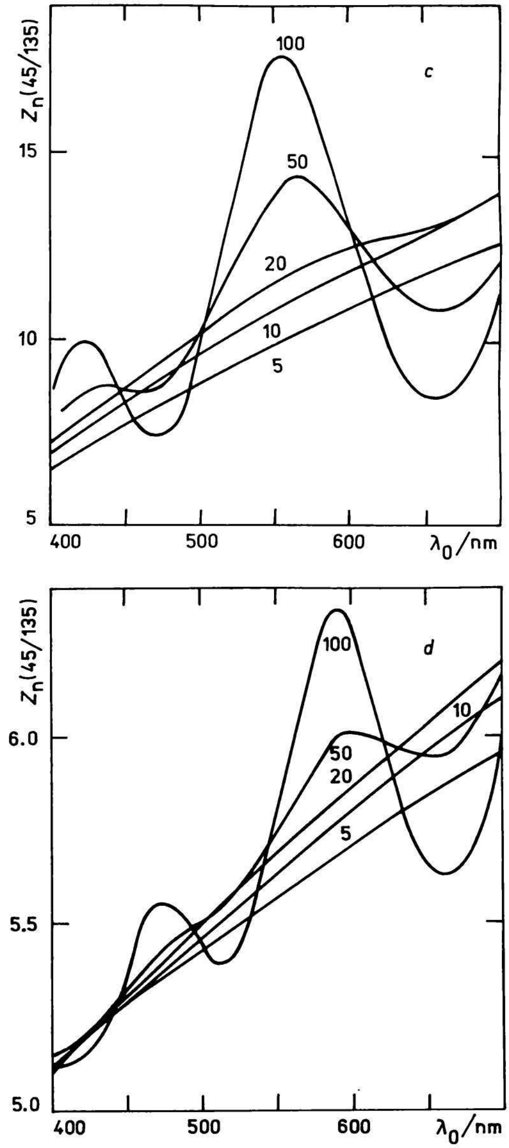
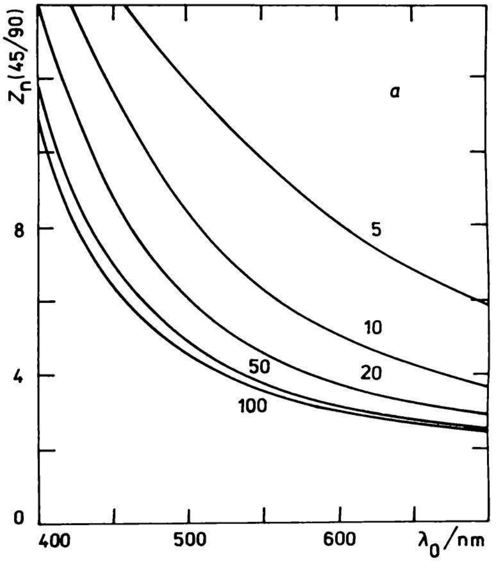
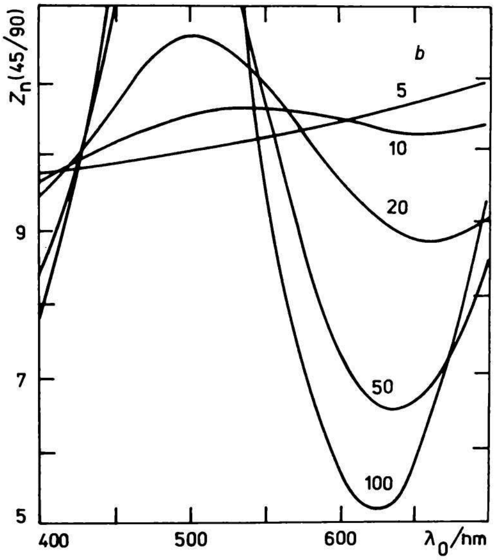
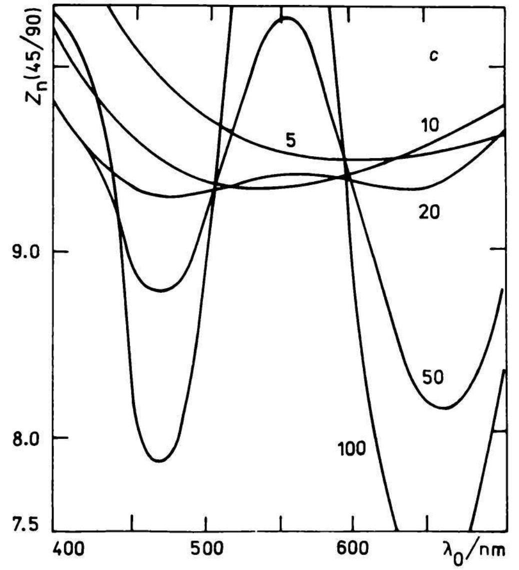


Fig. 5. Spectral dependence of the coefficient of dissymmetry $Z_n(45/135)$ for PS latex; NOL distribution, $K = 5, 10, 20, 50, 100$; r_M/nm: *a*) 100; *b*) 400; *c*) 700; *d*) 1000.

optimum coincidence with its theoretical analogue is to be found by means of Figs. 5 and 6. In the numerical method, the quantities for which the mean quadratic deviation between experimental and theoretical values is minimum are regarded as distribution parameters of the system.


$Z_n(45/90)$
a
8
4
0
5
10
20
50
100
400
500
600
λ_0/nm


$Z_n(45/90)$
b
9
7
5
5
10
20
50
100
400
500
600
λ_0/nm



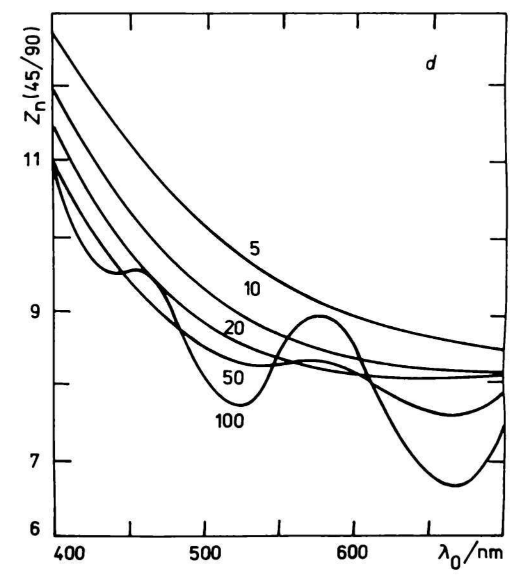


Fig. 6. Influence of polydispersity on spectral dependence of the coefficient of dissymmetry $Z_n(45/90)$ for PS latex; NOL distribution, $K = 5, 10, 20, 50, 100$; r_M/nm: *a*) 100; *b*) 400; *c*) 700; *d*) 1000.

In other method, we may use the relationship $K = f(r_M)$ for particular wavelengths. On the basis of experimental values of Z_n determined for certain wavelengths, we determine all pairs of parameters r_M and K by means of the theoretical relationships $Z_n = f(\lambda_0)$. Then we plot the relationship $K = f(r_M)$ for each wavelength and the intersection of these plots gives the required parameters of that distribution.

Photometer Spekol (Zeiss, Jena) which enables us to alter continuously the wavelengths in the range $\lambda_0 = 400$—700 nm is very suited to experimental investigation of the spectral dependence of the dissymmetry of scattered light. However, for design reasons, we cannot determine the "classical" dissymmetry but the ratio of scattered light fluxes at 45° and 90° by means of this photometer. The working relationships corresponding to these angles $Z_n(45/90) = f(\lambda_0)$ which are needed for determining the distribution parameters are to be seen in Fig. 6. As obvious, the working relationships gradually coalesce also in this case and a detailed distribution analysis becomes difficult for the systems with particles in which the medial radius and the degree of polydispersity are larger than $r_M = 1000$ nm and $K = 5, 10, 20$.

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