Depolarization ratio and distribution analysis of polydispersions

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The conditions of using the practical relationship $\varrho(90°) = 1.89\,(m-1)^2\bar{\alpha}$ to determination of the size of polydispersion particles were investigated on the basis of theoretical study involving the influence of polydispersity on the relationship $\varrho(90°) = f(\bar{\alpha})$. In studying the influence of polydispersity on spectral dependence of the depolarization ratio ϱ, the dispersion of the index of refraction was taken into account. The obtained working relations may be used for determining the parameters of the lognormal distribution function of negative order.

На основании теоретического изучения влияния полидисперсности на зависимость $\varrho(90°) = f(\bar{\alpha})$ были обсуждены условия использования практического соотношения $\varrho(90°) = 1{,}89\,(m-1)^2\bar{\alpha}$ для определения размера частиц в полидисперсных системах. При изучении влияния полидисперсности на спектральную зависимость деполяризационного фактора ϱ принималась во внимание дисперсия показателя преломления; полученные рабочие зависимости можно использовать для определения параметров логарифмически нормальной функции распределения отрицательного порядка.

The depolarization measurements of scattered light play an important role in distribution analysis of the size of colloid dispersion particles.

Provided the primary luminous ray is nonpolarized, the light scattered at the angle $\Theta = 90°$ by a spherical isotropic particle is fully polarized for $\alpha \rightarrow 0$. For higher values of α, the scattered light is only partially polarized and the degree of polarization may be a criterion of the size of spherical particles.

The degree of polarization is usually expressed by the depolarization ratio ϱ, *i.e.* the ratio of the flux of the scattered light corresponding to horizontal component to the flux of the light corresponding to vertical component in nonpolarized primary ray.

The measurement of the dependence of polarization ratio on angle to the purpose of determining the parameters of the lognormal distribution of particle sizes was proposed by *Kerker et al.* [1]. This procedure necessitates to compare the experimental relation $\varrho(\Theta)$ with the theoretical one calculated on the basis of the Mie theory [1]. *Stevenson et al.* used the dependence of polarization ratio on wavelength at a given angle of observation Θ for distribution analysis of the *Heller* populations [2]. In this case, the dispersion of refractive index in the used range of wavelengths was neglected. From the view-point of determining only the mean size of polydispersion particles, the paper published by *Graessley* and *Zuffall* [3] is remarkable. As a matter of fact, these authors observed that $\varrho(90°)$ keeps its monotonic character up to $\alpha = 10$ for sufficiently wide distributions. They resolved the relations $i_1 = f(\alpha)$ into monotonic and oscillating functions. As the heterodispersity averages the above functions, they replaced the periodic terms by their mean values.

This paper deals with the influence of polydispersity on the relation $\varrho(90°) = f(\bar{\alpha})$ and also gives attention to the variation of the relative index of refraction with wavelength as regards the theoretical processing of the relations $\varrho(90°) = f(\lambda_0)$ in polydispersions with lognormal distribution of particle sizes.

Theoretical

The scattering of electromagnetic radiation by an isotropic, nonabsorbing, spherical particle is described by the theory of *Mie* [4, 5]. The radiation scattered by a spherical particle according to this theory may be expressed by the scalar components A_1, A_2 of the vector of secondary electrical field

$$kA_1(m, \alpha, \Theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \tag{1}$$

$$kA_2(m, \alpha, \Theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n) \tag{2}$$

The meaning of individual symbols is: n — positive integer, α — size parameter, $\alpha = 2\pi r/\lambda = kr$, r is the radius of particle and λ is the wavelength of radiation in dispersion medium, m — relative index of refraction, Θ — scattering angle, a_n, b_n — Lorenz—Mie coefficients, π_n, τ_n — angle coefficients.

For practical purpose we define the dimensionless intensity functions

$$\begin{aligned} i_1(m, \alpha, \Theta) &= k^2 A_1 A_1^* \\ i_2(m, \alpha, \Theta) &= k^2 A_2 A_2^* \end{aligned} \tag{3}$$

where A_1^* and A_2^* are complex conjugate functions with respect to A_1 and A_2.

The degree of polarization of the light scattered by a polydisperse system consisting of spherical particles may be then expressed by the following equation

$$\varrho(\Theta) = \frac{\int_0^\infty i_2(m, \alpha, \Theta) \cdot \mathrm{f}(\alpha)\, \mathrm{d}\alpha}{\int_0^\infty i_1(m, \alpha, \Theta) \cdot \mathrm{f}(\alpha)\, \mathrm{d}\alpha} \tag{9}$$

where $\mathrm{f}(\alpha)$ is the distribution function of particle sizes. In this study, the validity of two frequently used lognormal distribution functions is assumed. The form of these distribution functions is as follows

$$\mathrm{f}(\alpha) = \left(\frac{K}{\pi}\right)^{1/2} \alpha^{-1} \exp\left[-K \ln^2 \frac{\alpha}{\alpha_\mathrm{M}}\right] \tag{10}$$

(lognormal distribution of negative order — NOLD [6]) and

$$\mathrm{f}(\alpha) = C \exp\left[-K \ln^2 \frac{\alpha}{\alpha_\mathrm{M}}\right] \tag{11}$$

(*Evva* distribution [7])
where α_M is the medial parameter of distribution, K describes the width of distribution, and $\mathrm{f}(\alpha)$ is equal to C for $\alpha = \alpha_\mathrm{M}$.

Results and discussion

The theoretical relations $\varrho(90°) = \mathrm{f}(\bar{\alpha})$ and $\varrho(90°) = \mathrm{f}(\lambda_0)$ were calculated on the basis of eqn (*9*). The integrals in this equation were computed by numerical integration with a computer Siemens 4004 in twofold accuracy, the step being $\Delta\alpha = 0.05$.

Fig. 1 represents the influence of polydispersity on the relation $\varrho(90°) = \mathrm{f}(\bar{\alpha})$ for a system with the relative index of refraction equal to 1.10 (Evva distribution).

As obvious from Fig. 1, the practical application of the functional relations is limited because of ambiguity of data. But this figure is important from the view-point of confrontation of the above-mentioned exact procedure with the approximate method according to Graessley and Zuffall. According to these authors, the limiting depolarization may be described for sufficiently wide distribution by the simple equation

$$\bar{\varrho}(90°) = 1.89\,(m-1)^2\,\bar{\alpha} \tag{12}$$

On the basis of this relation *e.g.* for $\bar{\alpha} = 5$, $m = 1.10$, $\bar{\varrho} = 0.095$, which is in a very good agreement with the result obtained from the relation $\varrho(90°) = \mathrm{f}(\bar{\alpha})$ (Fig. 1) for $K = 10$. Thus in a system with the medium degree of polydispersity ($K = 10$), the use of eqn (*12*) is completely justified. But the use of the theoretical relation

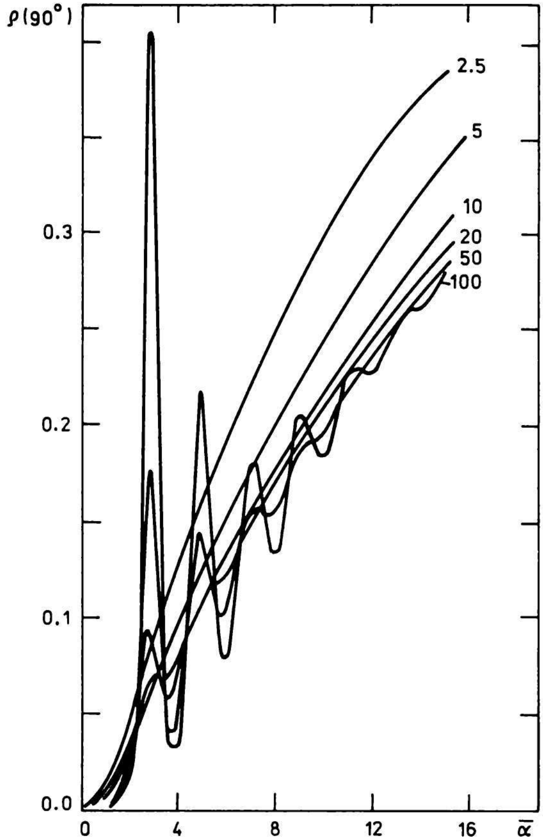
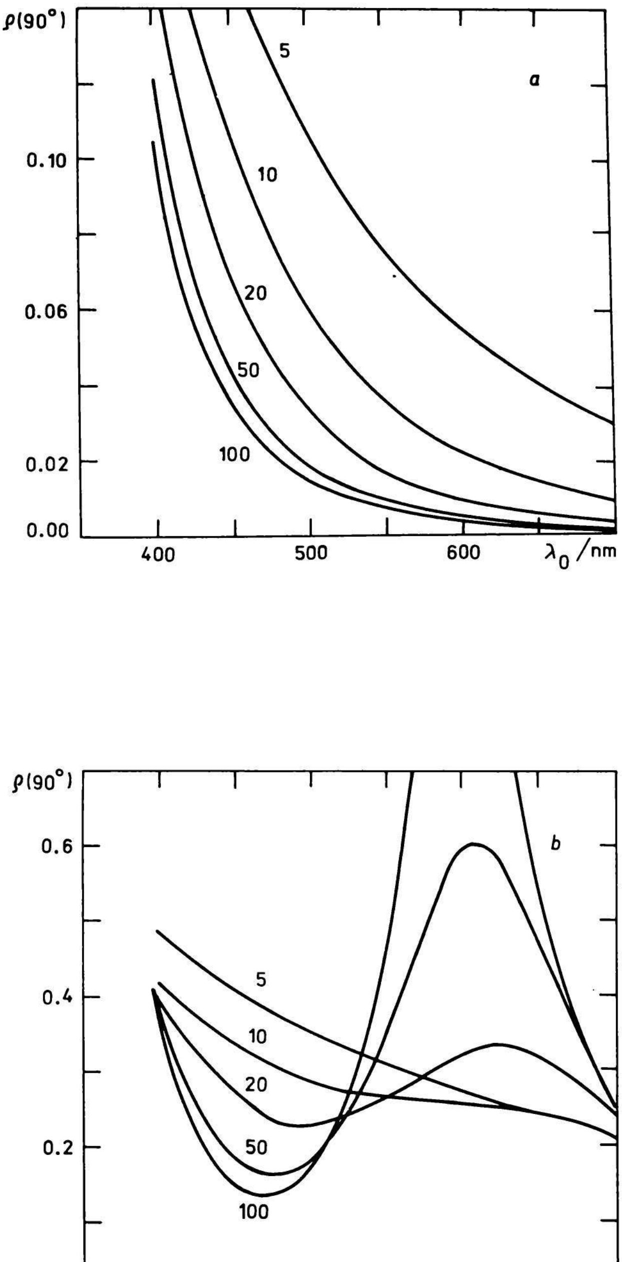
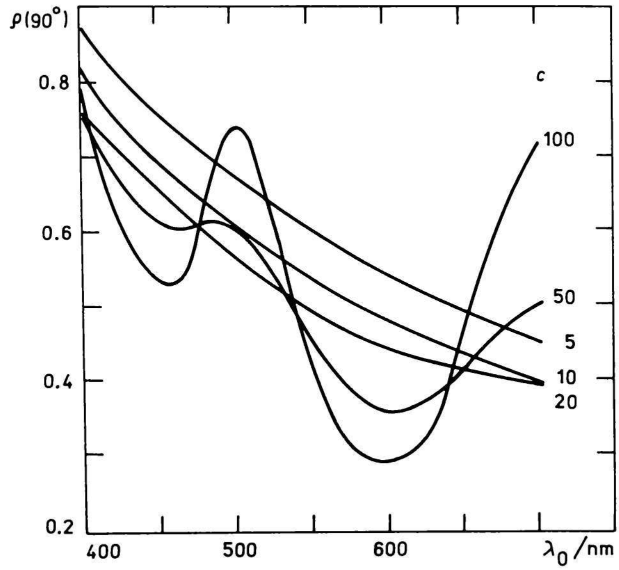


Fig. 1. Variation of the depolarization ratio ϱ (90°) with the mean value of α, Evva distribution. ($K = 2, 5; 5, 10, 20, 50$, and 100.) $\lambda_0 = 546$ nm; $m = 1.10$.

ϱ (90°) = f (λ_0) appeared to be more convenient for distribution analysis of polydispersions. Assuming the validity of NOLD for polydispersions in the range $r_M = 100$—1000 nm and for the parameters of width $K = 5$, 10, 20, 50, 100, the working relationships were calculated while the dispersion of the index of refraction was taken into account [8].

The theoretical relations ϱ (90°) = f (λ_0) which are represented in Fig. 2 may be used for determination of the distribution parameters NOLD up to $r_M = 1000$ nm (if r_M is greater than 1000 nm, the working curves gradually become confluent and analysis is difficult). The distribution parameters may be found by using either graphical or numerical comparison of theoretical and experimental data. They may be also found from the intersection of the relation $K = f(r_M)$ for the wavelengths


ρ(90°)
0.10
0.06
0.02
0.00
5
10
20
50
100
a
400
500
600
λ0 /nm
ρ(90°)
0.6
0.4
0.2
0.0
5
10
20
50
100
b
400
500
600
λ0 /nm


ρ(90°)
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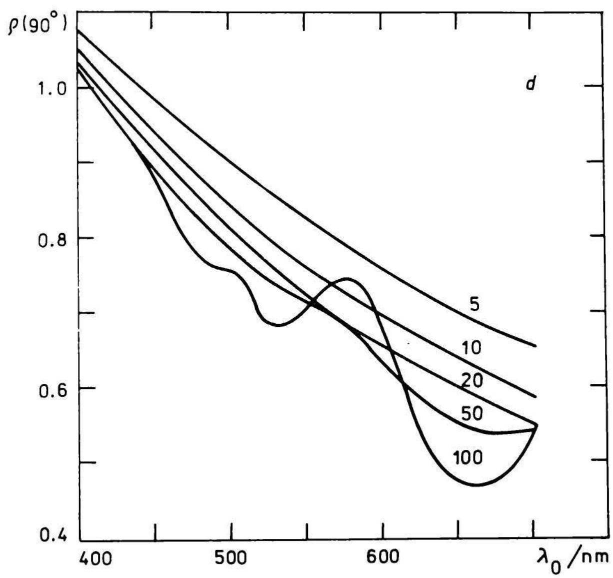
0.6
0.4
0.2
400
500
600
λ0/nm
c
100
50
5
10
20


ρ(90°)
1.0
0.8
0.6
0.4
400
500
600
λ0/nm
d
5
10
20
50
100

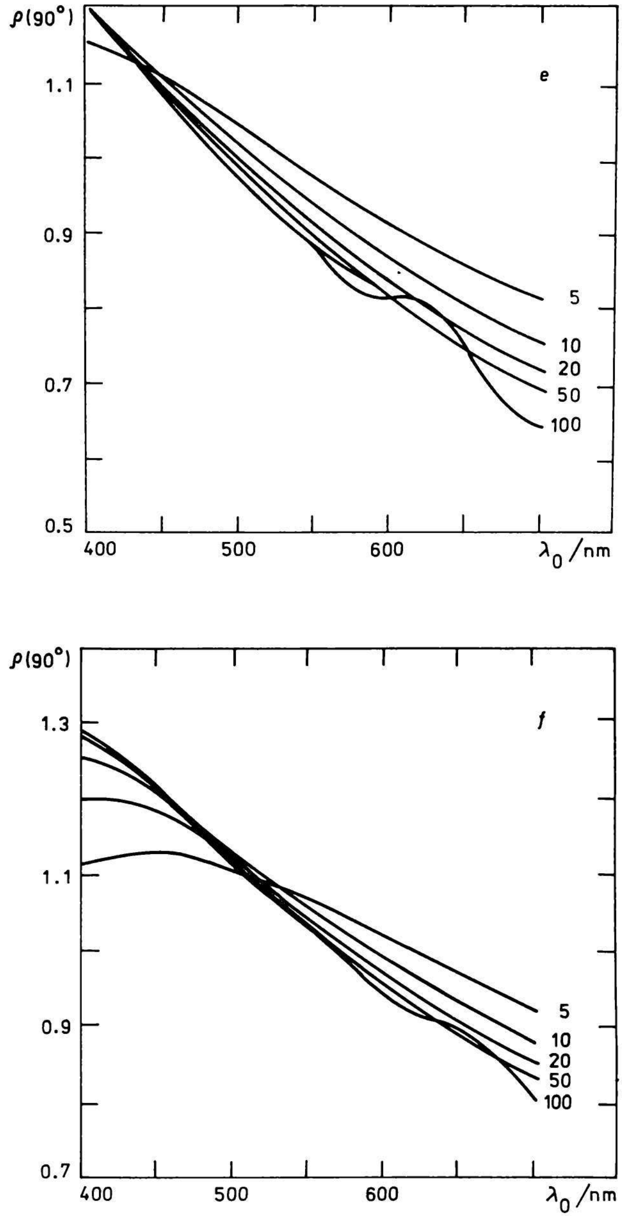


Fig. 2. Spectral dependence of the depolarization ratio ϱ (90°) for PS latex, NOL distribution. ($K = 5$, 10, 20, 50, and 100, r_M/nm: *a*) 100; *b*) 200; *c*) 400; *d*) 600; *e*) 800; *f*) 1000.)

under consideration after reading off the values of K and r_M corresponding to the experimental values of $\varrho(90°)$ determined at these wavelengths (as for detailed procedure, see Ref. [8]).

The influence of dispersion of the index of refraction on the theoretical relation $\varrho(90°) = f(\lambda_0)$ was investigated by comparing the values of $\varrho(90°)$ calculated for $m = 1.20$ and the relative index of refraction corresponding to individual wavelengths. It was revealed that the values of $\varrho(90°)$ obtained for the wavelength region 400—500 nm were lower and those obtained for the wavelength region 550—700 nm were higher than the correct value of $\varrho(90°)$ if the dispersion of the index of refraction was neglected. This statement refers to all investigated parameters of the NOL distribution. For instance, if $\lambda_0 = 436$ nm, this difference is approximately equal to 10% for systems with $r_M = 100$—1000 nm and $K = 5$ whereas it is 12% for systems with narrow distribution of particle sizes ($K = 100$) and $r_M = 100$ nm and reaches even 20% for $r_M = 300$. The difference in $\varrho(90°)$ approximately amounts to 4% for the wavelength of 680 nm and more polydisperse systems ($K = 5$) and may be omitted for $K = 100$.

Besides, the influence of the assumed distribution function on the course of working relations resulting from the method of specific turbidity and on the radiation envelope of polydispersions was studied earlier [6, 9]. In either case, it was revealed that it was not convenient to use the *Heller* distribution [2]. Nevertheless, it results from the comparison of the relations $\varrho(90°) = f(\lambda_0)$ obtained by means of NOL (this paper) and the *Heller* distribution [2] that both distribution functions are equally usable for successful simulation and distribution analysis of polydispersions on the basis of their depolarization ratio.

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