Effect of polydispersity in the use of transmission light scattering methods

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The effect of polydispersity on the course of functional dependence of the methods of specific turbidity and turbidity ratios as well as the possibility of determining the mean particle diameter of PVAc latices by these procedures were investigated. It was shown that the working relationship of the turbidity method valid for monodisperse system may be used for arbitrary polydisperse systems with $\bar{\alpha}$ ranging from 8 to 10. Except for rather heterogeneous systems the effect of polydispersity in the method of turbidity ratios is also small, within the range of particle sizes from 200 to 1400 nm which is of direct importance to practical purposes as well.

In preceding papers [1, 2] the problem of determining the mean diameter of the particles of PVAc latex by the transversal light scattering methods has been studied. The topic of this paper is the application of transmission measurements, *i.e.* the method of specific turbidity and the method of turbidity ratios. As known [3], these procedures may be successfully applied to monodisperse systems but the presence of the particles with various sizes often brings about certain complications.

In the case of polydisperse systems the distribution function or merely the mean diameter of particles should be found. From the point of view of transmission light scattering methods this problem may be solved by various procedures [3]. For instance, *Wallach* and *Heller* [4] proposed to measure turbidity at different wavelengths. On the basis of these measurements the modal parameter as well as the width parameter of the corresponding distribution may be determined. *Shchyogolev* and *Klenin* [5] developed a method of the simultaneous determination of the sizes, refractive index, and volume concentration of dispersed phase from the measurements of turbidity spectrum.

The present paper is concerned with the effect of polydispersity on the course of functional dependence of the methods of specific turbidity and turbidity ratios and the possibility of determining the mean particle diameter of PVAc latex by these procedures.

Relationship between turbidity and particle size

The turbidity τ of a system containing N equal spherical particles of radius r per unit volume may be expressed by the relationship

$$\tau = N \pi r^2 Q, \tag{1}$$

where it holds for the scattering efficiency Q according to the Mie theory [3]

$$Q = \frac{2}{\alpha^2} \sum_{n=1}^{\infty} (|a_n|^2 + |b_n|^2)/(2n + 1). \tag{2}$$

The symbols a_n and b_n stand for the complex functions of α ($\alpha = 2\pi r/\lambda$, λ is the wavelength of the radiation applied in the system) and m ($= n_p/n_0$) is the ratio of the refractive indices of particles n_p and medium n_0.

The following relation is valid for the turbidity of polydisperse system [6]

$$\tau = \left[\frac{\lambda}{2\pi n_0}\right]^3 \int_0^\infty Q\, \alpha^2\, f(\alpha)\, d\alpha. \quad (3)$$

In order to express $f(\alpha)$, *Evva* [6] used a logarithmic distribution in the form

$$f(\alpha) = C \exp[-K(\ln \alpha/\alpha_0)^2], \quad (4)$$

where K was the width parameter and α_0 the modal parameter of distribution while $f(\alpha) = C$ for $\alpha = \alpha_0$. From this then ensues the following relationship for the calculation of specific turbidity [6]

$$(\tau/c)_0 = \frac{3\pi n_0 \int_0^\infty Q\, \alpha^2 \exp[-K(\ln \alpha/\alpha_0)^2]\, d\alpha}{2\varrho \lambda_0 \int_0^\infty \alpha^3 \exp[-K(\ln \alpha/\alpha_0)^2]\, d\alpha} = k\, \frac{\bar{Q}}{\bar{\alpha}}. \quad (5)$$

If we construct the graph expressing $\bar{Q}/\bar{\alpha}$ as a function of $f(\bar{\alpha})$, the experimental value of $(\tau/c)_0$ may be used for the determination of $\bar{\alpha}$, *i.e.* also of the diameter of particles.

The size of particles may be also estimated by determining the turbidity at two wavelengths and for the so-called dispersion quotient DQ it holds according to *Teorell* [7]

$$DQ = \tau_1\, \lambda_{0,2}^2/\tau_2\, \lambda_{0,1}^2 \quad (6)$$

and eventually with respect to (*1*)

$$DQ = \lambda_{0,2}\, Q(\lambda_{0,1})/\lambda_{0,1}\, Q(\lambda_{0,2}). \quad (7)$$

With respect to (*5*) it may be written for polydisperse system

$$\overline{DQ} = \frac{\lambda_{0,2} \int_0^\infty Q(\lambda_{0,1})\, \alpha^2 \exp[-K(\ln \alpha/\alpha_0)^2]\, d\alpha}{\lambda_{0,1} \int_0^\infty Q(\lambda_{0,2})\, \alpha^2 \exp[-K(\ln \alpha/\alpha_0)^2\, d\alpha}. \quad (8)$$

By constructing the graph of the function $\overline{DQ} = f(\bar{\alpha})$ and comparing to the experimental value of $[(\tau/c)_0]_1/[(\tau/c)_0]_2$ the needed diameter of particles may be determined.

Experimental

The starting material used as well as the preparation of samples for measurements was described in paper [1]. The turbidities were measured on a Perkin—Elmer (model 450) spectrophotometer using 4 cm long cells. In order to remove disturbing effects [8], the inlet and outlet parts of the cell were equipped with a slit of 3-mm diameter and the side walls were covered with a layer absorbing light. The measurements were carried out at the wavelengths of 360, 436, 546, 600, and 700 nm. Fig. 1 shows the relations $(\tau/c) = f(c)$ for the above wavelengths from which the values of $(\tau/c)_0$ were determined by extrapolating to $c = 0$ (the method of least squares). In Fig. 2 the concentration dependence of individual DQ is presented.

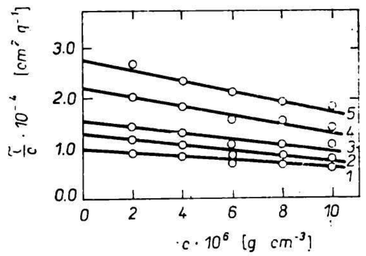

Fig. 1. Variation of specific turbidity with concentration for five wavelengths of the radiation used.
1. 700 nm; *2.* 600 nm; *3.* 546 nm; *4.* 436 nm; *5.* 360 nm.

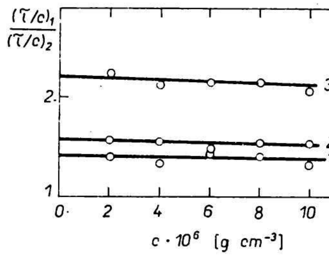

Fig. 2. Concentration dependence of turbidity ratios for three pairs of wavelengths.
1. 436/546 nm; *2.* 546/700 nm; *3.* 436/700 nm.

Results and discussion

The theoretical values of $\bar{Q}/\bar{\alpha} = f(\bar{\alpha})$ for various degrees of polydispersity are given in Fig. 3 while the significance of the corresponding width parameters of the chosen distribution is obvious from Fig. 4. In order to calculate the values of $\bar{Q}/\bar{\alpha}$ relationship (*5*) was used in the form [6]

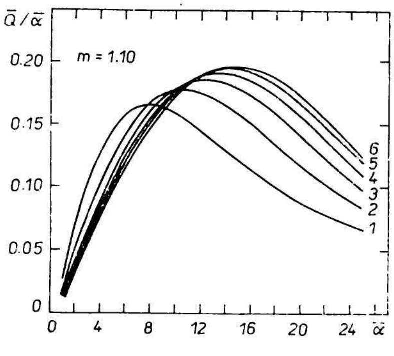

Fig. 3. Dependence of $\bar{Q}/\bar{\alpha}$ on $\bar{\alpha}$ for different values of the width parameter K of the Evva distribution.
1. $K = 2.5$; *2.* $K = 5$; *3.* $K = 10$; *4.* $K = 20$; *5.* $K = 50$; *6.* $K = \infty$.

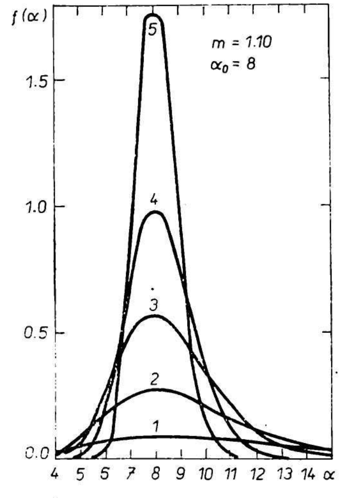

Fig. 4. Logarithmic distribution of the particle size for different degrees of polydispersity.
1. $K = 2.5$; *2.* $K = 5$; *3.* $K = 10$; *4.* $K = 20$; *5.* $K = 50$.

$$\frac{\bar{Q}}{\bar{\alpha}} = \frac{\int_0^\infty Q\, \alpha^2 \exp[-K(\ln \alpha/\alpha_0)^2]\, d\alpha}{\alpha_0^4\, (\pi/K)^{1/2} \exp(4/K)} . \tag{9}$$

The relation between α_0, $\bar{\alpha}$, and K is given by the expression

$$\alpha_0 = \bar{\alpha} \exp(-3/4\, K). \tag{10}$$

The numerator of the fraction in eqn (*9*) was solved by numerical integration (program in language Fortran IV for a computer CDC 3300). For the calculation of Q for $0.6 < \alpha < 20$ eqn (*2*) was used and the summation was performed up to $n = 25$ while for $\alpha < 0.6$ the approximative relation of Schoenberg and Jung [9] was employed

$$Q = \frac{8}{3}\, \alpha^4 \left[\frac{m^2 - 1}{m^2 + 2}\right]^2 \left[1 + \frac{6(m^2 - 2)}{5(m^2 + 2)}\, \alpha^2\right]. \tag{11}$$

For $\alpha > 20$, equation of van de Hulst [9] was applied

$$Q = 2 - \frac{16m^2 \sin \varrho}{(m + 1)^2\, \varrho} + 4\, \frac{1 - m \cos \varrho}{\varrho^2} + 7.53\, \frac{z - m}{z + m}\, \alpha^{-1.772}, \tag{12}$$

where

$$\varrho = 2\alpha(m - 1) \tag{13}$$

and

$$z = [(m^2 - 1)\, (6\alpha/\pi)^{2/3} + 1]^{1/2}. \tag{14}$$

The values of Q were also obtained by means of a computer.

Then they were confronted with some values published earlier [10]. On the basis of Fig. 3 it may be stated:

a) The value of $(\bar{Q}/\bar{\alpha})_{\max}$ decreases with increasing polydispersity and shifts towards smaller values of $\bar{\alpha}$.

b) In the case of small particles ($\bar{\alpha} < 8$) the turbidity of polydisperse system is greater in comparison with a monodisperse one but it is opposite for larger particles ($\bar{\alpha} > 12$). The effect of polydispersity on the turbidity of systems with $\bar{\alpha} \approx 10$ is small.

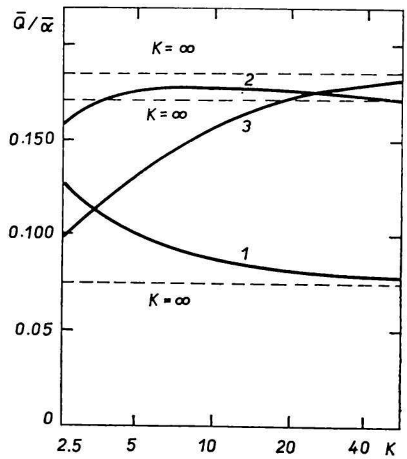

Fig. 5. Effect of the degree of polydispersity on the values of $\bar{Q}/\bar{\alpha}$ for different particle size; $\bar{\alpha} = 4$ (*1*), $\bar{\alpha} = 10$ (*2*), $\bar{\alpha} = 18$ (*3*).

These relations are illustrated in Fig. 5, where $\bar{Q}/\bar{\alpha}$ is represented as a function of K ($\bar{Q}/\bar{\alpha} = f(K)$) for $\bar{\alpha} = 4$, 10, and 18. As obvious, with decreasing polydispersity the values of $\bar{Q}/\bar{\alpha}$ converge to the corresponding values of the monodisperse system ($K = \infty$). If $\bar{\alpha} = 10$, the curve ascends initially and approximately from $K = 5$ to higher values of K it decreases slightly while it does not deviate too much from the value of Q/α corresponding to monodisperse system. This relationship shows a similar character for $\bar{\alpha} = 8$ or 9 as well, so that it is possible in the first approximation to use the relationship $Q/\alpha = f(\alpha)$ valid for monodisperse system for the practical determination of particle size in the systems with $\bar{\alpha}$ ranging from 8 to 10.

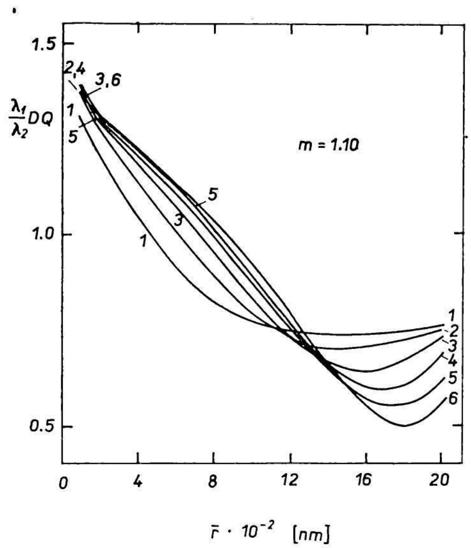

Fig. 6. Effect of the degree of polydispersity on the course of the curves $DQ = f(\bar{r})$ for $\lambda_{0,1} = 436$ nm and $\lambda_{0,2} = 546$ nm; $K = 2.5$ (*1*), $K = 5$ (*2*), $K = 10$ (*3*), $K = 20$ (*4*), $K = 50$ (*5*), and $K = \infty$ (*6*).

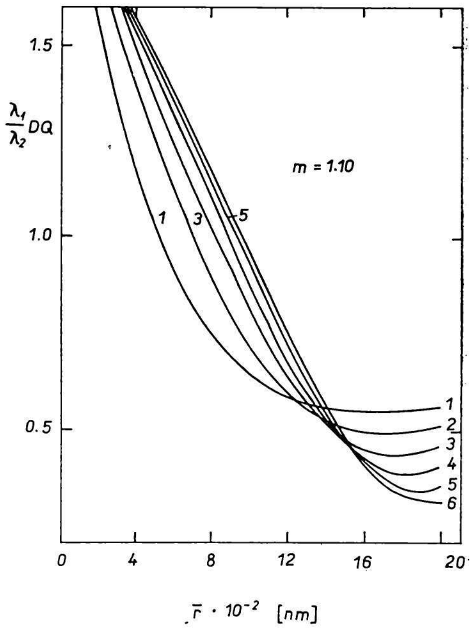

Fig. 7. Effect of the degree of polydispersity on the course of the curves $DQ = f(\bar{r})$ for $\lambda_{0,1} = 436$ nm and $\lambda_{0,2} = 700$ nm; $K = 2.5$ (*1*), $K = 5$ (*2*), $K = 10$ (*3*), $K = 20$ (*4*), $K = 50$ (*5*), and $K = \infty$ (*6*).

The theoretical relationships $\overline{DQ} = f(\bar{r})$ were calculated for three pairs of wavelengths on the basis of equation $\bar{Q}/\bar{\alpha} = f(\bar{\alpha})$ and are presented in Figs. 6—8. For $K > 10$, the effect of polydispersity is small in the radius range from 200 to 1400 nm which is also of direct importance to practical purposes.

The results of the confrontation of experimental values (Figs. 1 and 2) with theoretical relations (Figs. 3, 6—8) are summarized in Tables 1 and 2.

As it follows from the results listed in Tables, the values of diameter D vary within the range from 940 to 1200 nm. This small difference is in agreement with theoretical conclusions. The data obtained by the method of turbidity ratios for $K = 10$ are in

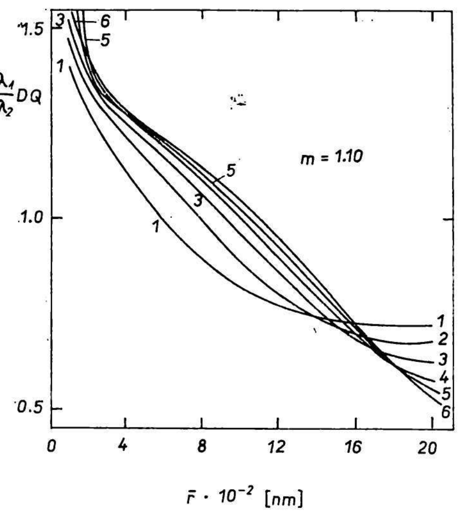

Fig. 8. Effect of the degree of polydispersity on the course of the curves $DQ = f(\bar{r})$ for $\lambda_{0,1} = 546$ nm and $\lambda_{0,2} = 700$ nm; $K = 2.5$ (*1*), $K = 5$ (*2*), $K = 10$ (*3*), $K = 20$ (*4*), $K = 50$ (*5*), and $K = \infty$ (*6*).

excellent agreement with the value of 980 nm determined by electron-optical method. In this case the calculated distribution curve complies best with the distribution curve constructed on the basis of electron microscopic data. The results obtained ($\bar{D} = 1000$—1200 nm) are in good agreement with the results of other methods [1, 2], *i.e.* the methods

Table 1

Mean diameter of the particles of PVAc latex for three wavelengths and $K = 2.5$, 10, 50, and ∞ (method of specific turbidity)

λ_0 [nm]	$\bar{Q}/\bar{\alpha}$	$\bar{\alpha}$				$\bar{D}$ [nm]			
		2.5	10	50	∞	2.5	10	50	∞
436	0.181	—	11.0	11.2	11.4	—	1150	1160	1190
546	0.161	7.0	8.4	9.0	9.2	916	1100	1180	1200
700	0.132	4.4	6.3	6.8	7.1	735	1050	1140	1190

Table 2

Mean diameter of the particles of PVAc latex for three pairs of wavelengths and $K = 2.5$, 10, 50, and ∞ (method of turbidity ratios)

$\lambda_{0,1}$ [nm]	$\lambda_{0,2}$ [nm]	$[(\tau/c)_0]_1/[(\tau/c)_0]_2$	$\bar{D}$ [nm]			
			2.5	10	50	∞
436	546	1.40	600	1040	1200	1240
436	700	2.19	560	980	1160	1200
546	700	1.56	520	940	1080	1120

of minimum intensity (1030 nm), scattering ratio (1180 nm) and dissymmetry in the range of angles from 0 to 90° (1030 nm).

The problem of the significance of the assumed distribution will be the subject of subsequent investigation.

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