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SPECTROTURBIDIMETRIC STUDY OF PARTICLE SIZE DISTRIBUTION IN SiO_2 SOLS

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For the study of particle size distribution in the SiO_2 sols, methods of a specific turbidity and turbidity ratios were applied. Distribution parameters of these polydispersions were searched by a numerical optimalization (SIMPLEX method). Our version of spectroturbidity methods is presented for the distribution analysis of standard SiO_2 sol (Ludox) and for the granulometric description of a SiO_2 sol-gel transformation. The best estimates of distribution parameters of Ludox proved a certain degree of polydispersity with harmony to the electrone microscopy. In the aging proces in SiO_2 sols it was found that in the initial phases the breadth of particle size distribution increases, while for the later aging intervals this parameter does not change any more, only the size of aggregates increases.

INTRODUCTION

Transmission and transversal methods of classical light scattering have become standard procedures with a distribution analysis of diluted colloid dispersions [1]. From a point of view of an experimental simplicity and attainability, the methods of specific turbidity and turbidity ratios step into a foreground [2].

In the submitted work, these methods have been applied in a modified version for granulometric description of standard "monodisperse" SiO_2 sol (Ludox), as well as for a similar study of the SiO_2 sol in an initial phase of a sol-gel transformation.

THEORETICAL PART

The turbidity of a monodisperse system of nonabsorbing spherical particles with a radius r is defined by a relation [3]:

$$\tau^{\mathrm{calc}}(r;m,\lambda) = N\pi r^2 Q(r;m,\lambda) \tag{1}$$

with $Q(r;m,\lambda)$ a scattering coefficient, m a relative refractive index (ratio of refractive indexes of a particle and of medium) and λ a wavelength in the medium. The number of scattering particles in a unit of volume N can be expressed by:

$$N = \frac{3c}{4\pi r^3 \rho_2} \tag{2}$$

with c a mass concentration and ρ_2 a density of dispersed particles.

Scattering coefficient can be expressed with respect to the exact Lorenz-Mie Theory [4, 5] of light scattering by:

$$Q(r;m,\lambda) = \frac{2}{\alpha^2}\sum_{n=1}(2n+1)^{-1}\left(|a_n|^2+|b_n|^2\right) \tag{3}$$

with a_n, b_n Lorenz-Mie coefficients and $\alpha = 2\pi r\lambda^{-1}$ is a so called size parameter.

In case of a polydispersion system of spherical particles, distribution of which is defined by a continual distribution (usually biparametrical) function f(r) the relations (1) and (2) must be used in a form of integrals [6]:

$$\tau^{\mathrm{calc}}(r_{\mathrm{M}},\sigma,m,\lambda) = N\int_0^{\infty}\pi r^2 Q(r;m,\lambda)\,\mathrm{f}(r;r_{\mathrm{M}},\sigma)\,\mathrm{d}r \tag{4}$$

$$N = \frac{3c}{4\pi\rho_2}\frac{3}{\int_0^{\infty} r^3\mathrm{f}(r;r_{\mathrm{M}},\sigma)\,\mathrm{d}r} \tag{5}$$

with $\mathrm{f}(r;r_{\mathrm{M}},\sigma)$ a normalized biparametric particle size distribution function with parameters r_{M} and σ.

By a combination of equations (4) and (5) a relation for a calculation of specific turbidity of polydisperse system $(\tau/c)^{\mathrm{calc}}$ can be obtained:

$$\left(\frac{\tau}{c}\right)^{\mathrm{calc}}(r_{\mathrm{M}},\sigma,m,\lambda) = \frac{3}{4\rho_2}\frac{\int_0^{\infty} r^2 Q(r;m,\lambda)\,.\mathrm{f}(r;r_{\mathrm{M}},\sigma)\,\mathrm{d}r}{\int_0^{\infty} r^3\mathrm{f}(r;r_{\mathrm{M}},\sigma)\,\mathrm{d}r} \tag{6}$$

From the practical point of view, a inverse problem has a more important practical purpose – to define a distribution of size particles of the studied polydispersed system from measurement of a dependence of the turbidity on wavelength. From an experimental determination of a light attenuation by passing through a path length l the relations $(\tau/c)_i = \mathrm{f}(c)$ will be obtained, extrapolation of which to an infinite dilution values of

$$\lim_{c\to 0}\left(\frac{\tau}{c}\right)_i = \left(\frac{\tau}{c}\right)_i^{\mathrm{exp}}$$

can be defined for $i = 1, 2 \ldots M$ values of the wavelength λ_i of primary radiation. (Here $\tau = (\ln 10 \log \Phi_0/\Phi)/1$ with Φ_0, Φ light fluxes of the primary and attenuated radiation). Since a direct inversion of the equation (6) is not possible, distribution parameters are searched by a numerical optimalization. Assuming, that the values of specific turbidity have been determined with a constant variance, the best estimates of distribution parameters r_M and σ can be obtained by a minimalization of a objective function in the form of an nonweighted sum of squares of deviation between the theoretical and experimental values of the specific turbidity:

$$U(r_M, \sigma) = \sum_{i=1}^{M} \left[\left(\frac{\tau}{c}\right)^{\mathrm{calc}} (r_M, \sigma, m, \lambda_i) - \left(\frac{\tau}{c}\right)^{\mathrm{exp}}_i \right]^2 = \min \tag{7}$$

Instead of specific turbidities it is advisable to minimalize the sum of deviation squares of turbidimetric ratios T_{ij}. The turbidimetric ratio for two wavelengths $\lambda_i < \lambda_j$ has been introduced with respect to a validity of the following:

$$T_{ij} = \left(\frac{\tau}{c}\right)_{\lambda_i} / \left(\frac{\tau}{c}\right)_{\lambda_j} > 1$$

The objective function is then as follows:

$$U(r_M, \sigma) = \sum_{i=1}^{M-1} \sum_{j=i+1}^{M} \left[T_{ij}^{\mathrm{calc}} (r_M, \sigma, m, \lambda_i, \lambda_j) - T_{ij}^{\mathrm{exp}} \right]^2 = \min \tag{8}$$

The objective function is in both instances a function of only two variables r_M and σ and the minimalization can be carried out by a non-gradient method or by gradient method with numerical calculation of the gradient.

The estimate of standard deviations of parameters r_M and σ can be obtained, if course of function $U(r_M, \sigma)$ in the vicinity of minimum $U(r_M^*, \sigma^*)$ is substituted by a quadratic form [6]:

$$U(r_M, \sigma) = U(r_M, \sigma) - U(r_M^*, \sigma^*) = \boldsymbol{X}^T \mathrm{A}\, \boldsymbol{X} \tag{9}$$

where $\boldsymbol{X}$ and $\boldsymbol{X}^T$ are a column or row vectors of deviations r_M and σ from their optimal values r_M^* and σ^* and A is a Hess information matrix. The values of deviations $s(r_M)$ and $s(\sigma)$ and a covariency of parameters $\mathrm{cov}(r_M, \sigma)$ shall be calculated from elements of an inversion matrix $(\mathrm{A}^{-1})_{ij}$ as follows:

$$s(r_M) = \left[(\mathrm{A}^{-1})_{11} U_{\min} / (M-2) \right]^{1/2} \tag{10}$$

$$s(\sigma) = \left[(\mathrm{A}^{-1})_{22} U_{\min} / (M-2) \right]^{1/2} \tag{11}$$

$$\mathrm{cov}(r_M, \sigma) = (\mathrm{A}^{-1})_{12} U_{\min} / (M-2) \tag{12}$$

Details of the procedure of the parameter deviation estimate have been published in the study [7].

RESULTS AND DISCUSSION

Suitability of the proposed method of calculation of SiO_2 sol distribution parameters has been tested on experimental data of the relationship of specific turbidity to the wavelength, published by Deželic and Kratochvíl [8] for stabilized SiO_2 sol (Ludox), as well as on turbidity spectra of SiO_2 sols, made by natrium silicate neutralization [9]

The calculation of best estimates of parameters of the particle size distribution has been carried out by a method, stated in the preceding part, according to own software, produced in the language Fortran.

The Gauss' distribution and logarithmic distribution of the negative order (NOLD) have been chosen for the description of particle size distribution in polydisperse systems:

$$f(r; r_M, \sigma) = \frac{1}{(2\pi)^{1/2} \sigma r} \exp\left[-\frac{1}{2\sigma^2} \ln^2 \frac{r}{r_M} \right] \tag{13}$$

where r_M is median of distribution and σ is a standard deviation $\ln r$.

The minimalization of the sum of squares of deviation between theoretical and experimental specific turbidities, relation (7) and (8), has been carried out by a Simplex method pursuant to Nelder and Mead [10]. Integrals in the equation (6) have been calculated by a trapezoid method and using a disc set of scattering coefficient values $Q(r; m, \lambda)$ tabulated with a constant step $\Delta\alpha = 0.01$.

Table I quotes experimental data $(\tau/c)^{\mathrm{exp}}$ along with calculated values of specific turbidities and the

Table I

Comparison of experimental and calculated specific turbidities for Ludox

Sample	λ_0 nm	$\left(\frac{\tau}{c}\right)^{\mathrm{exp}}$ cm^2g^{-1}	$\left(\frac{\tau}{c}\right)^{\mathrm{calc}}$ cm^2g^{-1}	NOL distr. param.
Ludox 8 $m = 1.100$ $\rho = 2.279$ gcm^{-3}	365.5 404.7 435.8 546.1 578.0	12.20 7.94 5.81 2.29 1.80	11.90 7.84 5.80 2.32 1.84	$r_M = 10.4 \pm$ 0.1 nm $\sigma = 0.02 \pm$ 0.009

best distribution parameters estimates NOL for Ludox.

From the point of view of comparison of the obtained results with results, quoted in the study [8] it must be pointed out, that the authors of the quoted study [8] have defined diameters of the Ludox particles for the individual wavelengths λ_0 (365.5–578 nm) within the range of 10.3–10.7 nm, which proves that the tested Ludox sample cannot be considered for monodisperse. Certain degree of monodispersity is evidenced by results of an electrone microscope study of this system [11], with reference of which the authors are quoting the standard deviation of Ludox particles distribution as $\sigma = 0.22$ nm. This value is identical with the value, that we found using the best estimate of a parameter of the Gauss' distribution of the studied Ludox $\sigma = 0.23 \pm 0.07$ nm, while for $\bar{r}$ we found the value of $\bar{r} = 10.4 \pm 0.05$ nm.

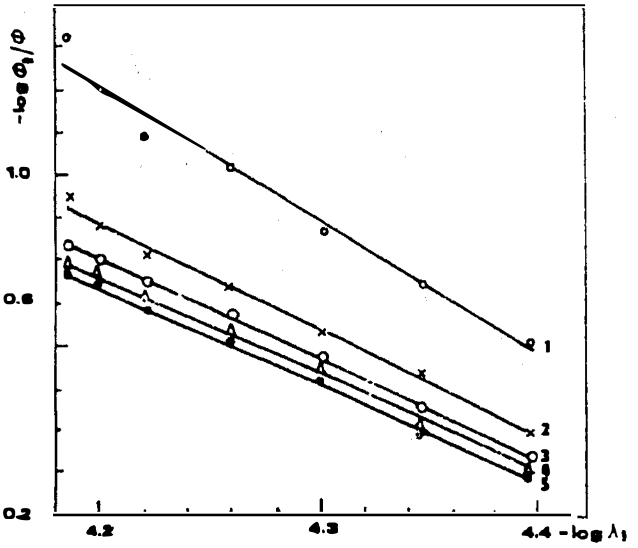

Fig. 1. Relationship of $\log \Phi_0/\Phi = f(\log \lambda_0)$ *for the* SiO_2 *sol with pH = 7.5 and aging intervals t(min): (1) – 60, (2) – 90, (3) – 120, (4) – 180, (5) – 300. [9]*

In a context with another application of a proposed alternative of the spectroturbidimetry the figure 1 shows experimental turbidimetric spectrum of a SiO_2 sol, arising in the course of neutralization of natrium silicate with sulphuric acid to the pH = 7.5 for five aging intervals, derived from literature [9]. As this study does not provide the path length of the scattering system l and definition of the mass concentration of particles c in a system with an ongoing reaction is difficult, we have opted for the search of the best estimates of sol particle size distribution for a given aging interval the sum of squares of turbidity ratios deviations as the objective function (8).

NOL distribution has been chosen for the distribution function, defining the arising polydisperse system. At the calculation of scattering coefficients Q we have assumed the relative refractive index to be constant throughout the whole range of λ_0 and amounting to $m = 1.09$.

The best estimates of NOL distribution parameters r_M and σ together with an estimate of their deviation are summarized in Table II.

Table II

Calculated best estimates of NOL distribution of SiO_2 sol for various aging intervals

t	r_M	σ
60	70± 3	0.13± 0.04
90	110± 20	0.31± 0.09
120	112± 17	0.31± 0.06
180	116± 18	0.28± 0.06
300	140± 18	0.27± 0.05

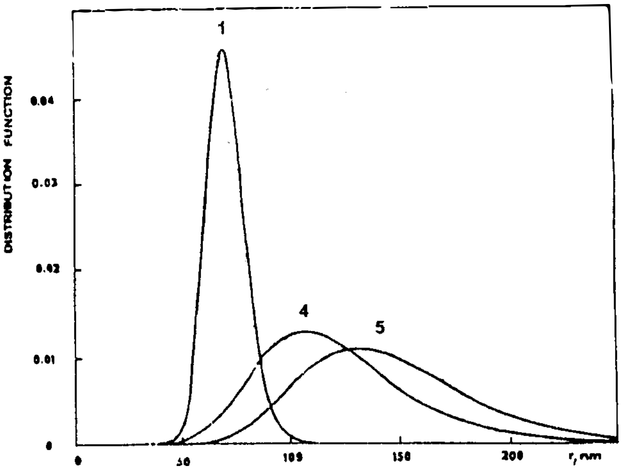

Fig. 2. Granulometric curves of SiO_2 *sol in the aging process. t(min): (1) – 60, (4) – 180, (5) – 300.*

Figure 2 shows the changes of polydispersity of the studied SiO_2 sol during its aging. It is evident from Table II and Figure 2, that in the aging process the primary particles form aggregates of larger size. In the initial phases of aggregation the breadth of the particle size distribution spreads, while in the later aging intervals this parameter distribution does not change any more, only its maximum is shifted towards higher diameters. Our results are thus complementing the results of the experimental SiO_2 sol study [9], where only an increase in the size of aggregates was found.

CONCLUSION

For the study of SiO$_2$ particle size distribution in the sols, methods of a specific turbidity and turbidity ratios have been applied.

Extremely close to the results of the electrone microscopy, the submitted alternative of a specific turbidity method proved a certain degree of polydispersity of the standard SiO$_2$ sol (Ludox). With the granulometric description of a SiO$_2$ sol – gel transformation it has been found with reference to turbidimetric ratios, that in the initial phases of aggregation the breadth of the particle size distribution increases, while for the later aging intervals this parameter does not change any more, only the modal parameter shifts towards larger particle diameters.

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SPECTROTURBIDIMETRICKÉ ŠTÚDIUM DISTRIBÚCIE VEĽKOSTI ČASTÍC V SiO$_2$ SÓLOCH

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Na štúdium distribúcie veľkosti častíc v SiO$_2$ sóloch sa aplikovali metódy špecifickej turbidity a turbiditných pomerov. Najlepšie odhady parametrov distribúcie sa hľadali optimalizáciou váženej, resp. neváženej sumy štvorcov odchýliek teoretických hodnôt turbidít, (vypočítaných na základe Mieovej teórie) a experimentálnych hodnôt určených z meraní spektrálnej závislosti zoslabenia viditeľného svetla prechodom študovaným disperzným systémom.

Výsledky distribučnej analýzy štandardného SiO$_2$ sólu (Ludoxu) vo veľmi dobrej zhode s elektrónovou mikroskopiou poukázali na jeho istý stupeň polydisperzity. Pri granulometrickej charkterizácii SiO$_2$ častíc, vznikajúcich neutralizáciou roztokov kremičitanu sodného sa na základe metódy turbiditných pomerov zistilo, že v procese starnutia sólu dochádza k zhlukovaniu primárnych častíc vo väčšie celky, v dôsledku čoho sa v počiatočných štádiách šírka rozdelenia veľkosti častíc zvyšuje, kým pre pokročilejšie časy sa už tento parameter nemení, len modálny parameter sa posúva k väčším polomerom.

Obe aplikácie ilustrujú dostatočnú citlivosť spektroturbidimetrie pri distribučnej analýze SiO$_2$ polydisperzií.

Obr. 1. Závislosť $\log \Phi_0/\Phi = f(\log \lambda_0)$ *pre sól* SiO$_2$, *pH = 7,5 a časy jeho stárnutia t(min): (1) - 60, (2) - 90, (3) - 120, (4) - 180, (5) - 300. [9]*

Obr. 2. Granulometrické krivky SiO$_2$ *sólu v procese stárnutia t(min): (1) - 60, (4) - 180, (5) - 300.*