DEPENDENCE OF TRANSVERSELY SCATTERED LIGHT FLUX ON CONCENTRATION IN COARSE POLYDISPERSE SUSPENSIONS

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The flux of light scattered by a polydisperse system at 90°, integrated along the optical path of the incident beam, exhibits an extremum in dependence on the suspension concentration, and is formally described by the same equation as holds for monodisperse systems. The coefficients in this equation are the mean values of the individual coefficients of the monodisperse components.

It has been shown previously[1] that in dependence on concentration in a monodisperse system, the flux density of scattered transversely passed light integrated along the incident beam pathway, exhibits an extremum whose position on the concentration coordinate is directly proportional to the linear dimension of the particles suspended. The model derived can be employed in the study of the behaviour of polydisperse systems, which is the objective of the present work.

EXPERIMENTAL

The model substance was corundum, similarly as in ref.[1], and the apparatus was also similar as previously[1]. The suspension concentration was varied in three ways: by weighing-in into a given volume (weighing-in method) or by stepwise addition of small amounts of corundum to the suspension (additions method) or by stepwise isochoric dilution of the suspension (replacement method). Different size fractions of corundum were used and mixed. In the additions method, the weight of a batch was determined for each fraction as the average of ten replicate batches; it was 29·1 to 158·5 mg according to the particle size used. Special tiny glass vials served as the dispensing device.

For the replacement method, an apparatus[2] was set up consisting of two interconnected syringes (Fig. 1) and a six-way valve whose two outlets were interfaced to the syringes, two other outlets were connected to the disperse system, one was connected to a pure water reservoir and one served as discard drain. During the suction stroke, one syringe was filled with water while the other sucked the chosen volume from the suspension. After turning the valve position, water from the one syringe was expelled into the suspension system while the suspension from the other syringe was discarded.

For corundum fractions up to 22 − 32 µm particle size the replacement method was employed owing to the high turbidity of the fine fractions, application of the additions method would have required the use of too small vials.

For monodisperse systems, the dependences of the electric signal induced by the light flux, J_r, on the total molar concentration of the suspension, C, were measured using the three methods, and identical results were obtained. Since the additions and replacement methods are much more rapid than the weighing-in method, only the two former were used in the subsequent experiments. For the additions method, the aqueous polydisperse corundum systems were so prepared that two fractions were added successively in a preselected order to the cell containing a given volume of water, and the steady-state J_r value was recorded after each addition. The increase in the total volume was allowed for when calculating the total concentration.

For the replacement method, the most concentrated suspension of the polydisperse system under study was diluted stepwise and the steady-state J_r value was recorded. The experimental conditions were chosen such that typically 10 dilutions were carried out before the extremum and 10 dilutes after the extremum.

While in the additions method the concentration changed in an arithmetic sequence, in the replacement method it changed in a geometric sequence, which allowed a considerably wider concentration span to be encompassed.

THEORETICAL

For monodisperse systems, the validity of the equation describing the dependence of J_r on concentration,

$$J_r = A_1[1 - \exp(-A_2C)]\exp(-A_3C) \qquad (1)$$

has been verified[1]. The A_1 coefficient is independent of the particle size whereas A_2 and A_3 are not and correspond to the turbidities in the directions parallel with an perpendicular to the incident light beam, respectively. Assuming that the individual
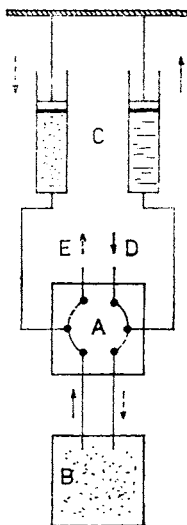

FIG. 1

Device for isochoric suspension dilution. A Six-way two-position valve, B cell with suspension, C syringes, D connection to water reservoir, E discard drain

TABLE I

Mixed $\langle A \rangle_2$ and $\langle A \rangle_3$ coefficients for binary corundum mixtures ($\alpha_1 + \alpha_2 = 1$) determined

l_1 μm	l_2 μm	$\alpha_1 = 1$		$\alpha_1 = 0.467$	
		$\langle A \rangle_2$	$\langle A \rangle_3$	$\langle A \rangle_2$	$\langle A \rangle_3$
30— 40	60— 80	40.1 ± 1.5	2.88 ± 0.09	24.88 ± 2.3	1.93 ± 0.13
		—	—	25.06 ± 1.2	1.82 ± 0.08
60— 80	100—125	11.88 ± 0.95	0.91 ± 0.08	8.16 ± 0.66	0.59 ± 0.06
		—	—	7.62 ± 0.71	0.61 ± 0.06
100—125	160—200	3.9 ± 0.5	0.35 ± 0.04	2.86 ± 0.15	0.27 ± 0.03
		—	—	2.90 ± 0.27	0.29 ± 0.05

particles of the polydisperse system scatter light independent of each other, the resulting coefficients $\langle A \rangle_j$ ($j = 1, 2, 3$) will be given by the proportions of the individual size fractions,

$$\langle A \rangle_j = \sum \alpha_i A_{ji} , \tag{2}$$

where $\alpha_i = C_i/C$ is the mole fraction of the i-th size fraction with a degree of aggregation n_i and concentration C_{ni}, whose contribution to the total molar concentration ($C = \sum C_i$) is $C_i = n_i C_{ni}$. The A_{ji} terms in Eq. (2) are the j-th coefficients of the i-th size fraction regarded as a monodisperse system. For $\langle A \rangle_1$ we have

$$\langle A \rangle_1 = \sum \alpha_i A_{1i} = \sum \alpha_i A_1 = A_1 . \tag{3}$$

Using Eqs (2) and (3), Eq. (1) is generalized to

$$J_r = A_1 [1 - \exp(-\langle A \rangle_2 C)] \exp(-\langle A \rangle_3 C) \tag{4}$$

which is formally identical with Eq. (1) for monodisperse systems[1] and displays an extremum in dependence on C; this extremum, for constant α_i values, lies at

$$C_m = \langle A \rangle_2^{-1} \ln(1 + \langle A \rangle_2/\langle A \rangle_3) . \tag{5}$$

Since for coarse suspensions (with linear particle size $l \geqq 0.5$ μm) the turbidity $\tau_{ji} = H_{ji} C_{ni}$ is proportional to the particle surface area[3,4] and they can be treated by geometrical optics[5,6], the H_{ji} coefficients must also be proportional to the surface area and hence, to $n_i^{2/3}$. Replacing the concentration C_{ni} for the i-th size fraction

TABLE I (*Continued*)

by the additions method (upper rows) and calculated (lower rows)

$\alpha_1 = 0.226$		$\alpha_1 = 0$	
$\langle A \rangle_2$	$\langle A \rangle_3$	A_2	A_3
17.37 ± 1.5	1.43 ± 0.10	11.88 ± 0.95	0.91 ± 0.08
18.25 ± 1.07	1.35 ± 0.08	—	—
5.81 ± 0.19	0.44 ± 0.04	3.9 ± 0.5	0.35 ± 0.04
5.70 ± 0.6	0.47 ± 0.05	—	—
2.45 ± 0.17	0.27 ± 0.05	—	—
2.53 ± 0.12	0.28 ± 0.02	2.03 ± 0.08	0.25 ± 0.05

TABLE II

Mixed $\langle A \rangle_2$ and $\langle A \rangle_3$ coefficients for binary corundum mixtures with a fraction ratio 1 : 3 measured by the replacement method (averages of triplicate determinations, upper rows) and calculated (lower rows)

l_1 μm	l_2 μm	$\langle A \rangle_2$	$\langle A \rangle_3$	C_m	$\langle A \rangle_1$
5— 7	10—15	107.9 ± 2.0	9.22 ± 0.1	0.0235 ± 0.0003	90.5 ± 1.5
		109.7 ± 3.5	8.89 ± 0.08	—	—
10—15	22—32	57.89 ± 1.1	3.49 ± 0.05	0.0496 ± 0.0004	89.7 ± 0.93
		56.49 ± 0.01	3.43 ± 0.01	—	—
22—32	60—80	$25.54 + 0.7$	1.27 ± 0.04	0.1195 ± 0.0004	90.3 ± 1.6
		24.00 ± 0.01	1.34 ± 0.02	—	—
5— 7	15—22	92.00 ± 4.0	7.11 ± 0.22	0.0291 ± 0.0005	91.5 ± 1.8
		96.21 ± 2.1	6.95 ± 0.05	—	90.8 ± 2.7^a
10—15	30—40	52.88 ± 3.9	3.73 ± 0.1	0.0515 ± 0.001	89.3 ± 1.1
		52.57 ± 0.1	3.61 ± 0.01	—	—

a For the individual fractions.

by C_i/n_i in the turbidity relation and denoting H_{ji}/n_i as A_{ji}, we see that this coefficient is inversely proportional to $n_i^{1/3}$. Since this term $n_i^{1/3}$ can be regarded as being proportional to the linear dimension of the particle l_i, we have $A_{ji} = b_j/l_i$. Sub-

TABLE III

Individual A_2 and A_3 coefficients determined from binary mixtures

| l | Addition | | | |
| μm | $k_2 = 3k_1 - 3$ | | $k_2 = 3k_1 - 2$ | |
	A_2	A_3	A_2	A_3
30— 40	$40{\cdot}25 \pm 2{\cdot}7$	$2{\cdot}95 \pm 0{\cdot}10$	$40{\cdot}24 \pm 2{\cdot}1$	$3{\cdot}04 \pm 0{\cdot}1$
60— 80	$11{\cdot}05 \pm 1{\cdot}1$	$1{\cdot}03 \pm 0{\cdot}15$	$12{\cdot}72 \pm 0{\cdot}03$	$0{\cdot}98 \pm 0{\cdot}1$
100—125	$3{\cdot}76 \pm 0{\cdot}5$	$0{\cdot}37 \pm 0{\cdot}03$	$3{\cdot}12 \pm 0{\cdot}45$	$0{\cdot}36 \pm 0{\cdot}02$
160—200	$1{\cdot}97 \pm 0{\cdot}05$	$0{\cdot}27 \pm 0{\cdot}03$	$2{\cdot}04 \pm 0{\cdot}1$	$0{\cdot}26 \pm 0{\cdot}03$

stituting for A_{ji} in Eqs (2) and (5) and rearranging we obtain

$$C_m = \left[b_2 \sum \alpha_i/l_i \right]^{-1} \ln \left(1 + b_2/b_1 \right) \tag{6}$$

which indicates that in polydisperse systems a direct proportionality exists between C_m and the quantity $\left(\sum \alpha_i/l_i \right)^{-1}$ (in monodisperse systems this reduces to a direct proportionality between C_m and the particle size, as found previously[1]).

RESULTS AND DISCUSSION

The validity of Eq. (4) and the additivity of coefficients A_{1i} and A_{2i} (Eqs (2), (3)) were verified in three ways. First, J_r was recorded while increasing the total concentration C and holding the proportion of two different size fractions, hence, the mole fraction α_i, constant. Eq. (4) then was subjected to nonlinear optimization[1] to obtain the values of the coefficients $\langle A \rangle_2$ and $\langle A \rangle_3$, which were compared with those derived from Eqs (2) and (3). The results for isolated fractions and their combinations are given in Table I. In the second procedure, the replacement method was used; the results are given in Table II. The calculated and measured $\langle A \rangle_2$ and $\langle A \rangle_3$ values are in agood agreement for all sizes and their combinations. The last column in Table II also indicates that in accordance with Eq. (4), the $\langle A \rangle_{1i}$ coefficients are constant and equal to the A_1 values for the individual fractions.

In the third procedure the proportion of the two size fractions added was no more held constant, and the A_{1i} and A_{2i} values of the individual fractions were calculated by nonlinear optimization of Eq. (4) for variable α_i. Be k_1 the number of additions (with a weight m_1) of fraction 1 and k_2 the number of additions (with a weight m_2) of fraction 2; then the total molar concentration is $C = \left(k_1 m_1 + k_2 m_2 \right) M^{-1} V^{-1}$

TABLE III
(*Continued*)

patterns

$k_2 = 3k_1 - 1$		$k_2 = 3k_1$		Monodisperse systems	
A_2	A_3	A_2	A_3	A_2	A_3
$40 \cdot 06 \pm 2 \cdot 0$	$3 \cdot 08 \pm 0 \cdot 05$	$40 \cdot 03 \pm 0 \cdot 5$	$2 \cdot 85 \pm 0 \cdot 31$	$40 \cdot 1 \pm 1 \cdot 5$	$2 \cdot 88 \pm 0 \cdot 09$
$12 \cdot 37 \pm 0 \cdot 63$	$0 \cdot 99 \pm 0 \cdot 04$	$11 \cdot 62 \pm 0 \cdot 87$	$1 \cdot 01 \pm 0 \cdot 13$	$11 \cdot 88 \pm 0 \cdot 95$	$0 \cdot 91 \pm 0 \cdot 08$
$3 \cdot 35 \pm 0 \cdot 4$	$0 \cdot 35 \pm 0 \cdot 02$	$3 \cdot 82 \pm 0 \cdot 3$	$0 \cdot 36 \pm 0 \cdot 03$	$3 \cdot 9 \pm 0 \cdot 5$	$0 \cdot 35 \pm 0 \cdot 04$
$1 \cdot 95 \pm 0 \cdot 07$	$0 \cdot 25 \pm 0 \cdot 04$	$2 \cdot 00 \pm 0 \cdot 04$	$0 \cdot 25 \pm 0 \cdot 03$	$2 \cdot 03 \pm 0 \cdot 08$	$0 \cdot 25 \pm 0 \cdot 05$

and the mole fractions are $\alpha_1 = k_1 m_1/(k_1 m_1 + k_2 m_2)$ and $\alpha_2 = k_2 m_2/(k_1 m_1 + k_2 m_2)$.

The results for various sequences of additions $k_2 = f(k_1)$ are given in Table III; they again confirm the additivity described by Eqs (2), (3) as well as the validity of Eq. (4) for the $J_r(C)$ dependence in polydisperse systems.

The C_m values plotted against the calculated $(\sum \alpha_i/l_i)^{-1}$ quantity corresponding to the $J_r(C)$ curve for a constant proportion of the fractions (Fig. 2, open circles) were compared with the C_m vs l plot for the monodisperse fractions (full circles). The open circles are seen to fit well the straight line corresponding to the individual monodisperse fractions. This can be looked upon as a confirmation of the relation (6) and thus of the additivity of coefficients A_{ji} (Eqs (2), (3)) as well as of the $J_r(C)$ dependence according to Eq. (4).

Analogous results have been obtained for other supensions of particles of different size[7] (kaolin, CaO).

FIG. 2

Dependence of C_m (mol l^{-1}) in the extremum of the $J_r(C)$ curve on the $(\sum \alpha_i/l_i)^{-1} \equiv$ $\equiv p$ quantity (μm). Binary corundum mixtures of two size fractions in ratios 1 : 1 and 1 : 3, replacement method (○), additions method (⊗); full circles pertain to monodisperse systems where $(\sum \alpha_i/l_i)^{-1}$ reduces to l_i. Temperature 25°C
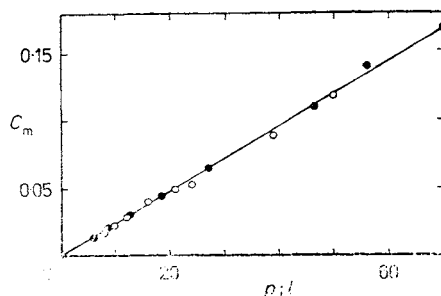
In conclusion, the validity of the relation describing the $J_r(C)$ dependence for coarse $(l_i \geq 0.5 \, \mu m)$ polydisperse systems as well as the interrelations (2), (3) between the mixed coefficients $\langle A \rangle_{ji}$ and the coefficients A_{ji} of the individual fractions can be regarded as proved and applicable to the determination of the distribution or nephelometric reaction course monitoring.

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