EXTENSION OF THE TURBIDITY RATIO METHOD TO THE NEAR INFRARED REGION*

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Received August 2nd, 1978

The turbidity ratio method has been extended to the near infrared region. In addition to the usual wavelengths 435·8, 546·1 and 684·3 nm, wavelengths 857·5, 1074 and 1346 nm were also used in the measurements. Using a model system of polystyrene latex, it was shown that the turbidity ratio method could be utilized also in this range of wavelengths. Its advantages and shortcomings were demonstrated.

During fifteen years of its existence, the turbidity ratio method has proved to be very useful, although it has not become too widespread (*cf.*[1-3] and references cited therein). The method allows us to determine the particle size, especially in those cases in which their relative dimensions (related to the respective wavelength) or their relative refractive index go beyond the limits of validity of the simple Rayleigh–Debye theory[4], or when their absolute concentration in the given system remains unknown[5].

Samples investigated are sometimes very opaque; moreover, this opacity cannot be sufficiently varied by dilution (in some cases one must even be satisfied with a single concentration). Using a model system, we would like to demonstrate in this work conditions under which it is possible, by employing higher wavelengths, to raise considerably the transparency of a system with the given particle size[6]. Experimental results should also confirm that for such wavelengths no further extensive calculations are needed, but that one may utilize data and procedures already published[7,8].

EXPERIMENTAL

The polystyrene latex (Kaučuk, Kralupy near Prague) was diluted to an optically suitable concentration by water with 0·5% of stabilizer. The sample preparation and purification were similar to those described earlier[1]; measurements were carried out with suspensions at four concentrations prepared for this purpose. Electron microscopy showed that the sample contained almost monodisperse particles, 679 ± 1·5 nm in size.

The turbidities of individual samples were measured in cells 1·00 thick with a Perkin–Elmer model 340 spectrophotometer, within the wavelength range from 400 to 2600 nm. Since water

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* Part XXV in the series Light Scattering; Part XXIV: This Journal *44*, 2064 (1979).

in NIR absorbs light, the wavelengths used were 435·8, 546·1, 684·3, 857·5, 1074 and 1346 nm. The spectrophotometer just mentioned is particularly suited for the given purpose because of its optical and electronic parameters. Its main advantages consist in: *a*) high sensitivity and accuracy in the range of very low and high extinctions, *b*) the possibility of exact reading of turbidity for the required wavelength (by means of increased resolution and digital interpolation of data), *c*) the possibility of exact correction for the extinction of the solvent by automatic recording of the difference curve (here, extinction means the sum of turbidity and absorbancy).

RESULTS AND DISCUSSION

For the purposes of this work, let us first recall some basic relationships allowing the particle size to be determined by the turbidity ratio method. By creating the ratio of specific turbidities $(\tau/c)_0$ determined for the pair of wavelengths λ_a, λ_b and extrapolated for $c \rightarrow 0$, concentration disappears in the eventual expression, and it holds

$$(\tau_a/\tau_b) = (\lambda_b/\lambda_a)(\alpha_b/\alpha_a)^3 (S_a/S_b) = (\lambda_a/\lambda_b)^2 (S_a/S_b) = T_{ab}\,, \qquad (1)$$

where τ is turbidity, λ is the wavelength of light in the given medium, $\alpha = \pi L/\lambda$ (L is the particle size in nm), and S is a complicated scattering function[1,7,8]. The measurement can be performed at one or more pairs of wavelengths. For monodisperse systems, the particle sizes determined by such measurements are nearly identical in all cases. Since, however, T_{ab} is at the same time a function of particle size and of the chosen pair of wavelengths, measurements at two and more pairs of wavelengths provide us with preliminary information on the degree of polydispersity of the system[1].

We have also shown[7,8] that in using this method, it is advantageous to employ a constant ratio $\lambda_b/\lambda_a = \varkappa = 1{\cdot}2531$ between the individual terms of the given sequence of wavelengths. For an arbitrary pair of turbidities τ_a and τ_b it holds, then,

$$T_{ab} = \tau_a/\tau_b = \varkappa^{-2(b-a)}\, S_a(\alpha/\varkappa^a, m)/S_b(\alpha/\varkappa^b, m)\,. \qquad (2)$$

It is desirable that the difference $(b - a) = \delta$ should not exceed 3 (at a sufficiently small dispersion of the relative refractive index, m).

The function $T_{ab}(\alpha)$ varies considerably according to the region: for $\Lambda_a = 435{\cdot}8$ nm, $\Lambda_b = 546{\cdot}1$ nm and $m = 1{\cdot}20$ (Λ being the wavelength of light *in vacuo*) the function is monotonic within the range $\alpha = 0$ to $1{\cdot}9$, and particularly between 3·2 and 16·5 (when it is approximately linear); in the other regions there are considerable primary and secondary oscillations (the problem of fine structure of scattering functions is dealt with in detail elsewhere[9]). The first critical region of this type lies between $\alpha = 1{\cdot}6$ and 2·75, where the determination gives two or three values of α for one T_{ab}; for $\lambda_b/\lambda_a = \varkappa = 1{\cdot}2531$, the critical T_{ab} values lie between 1·76 and 1·84.

The sample was chosen so that its particle size (expressed in α units for individual wavelengths) lies predominantly beyond the critical region – α values lie within the range 2 to 7; hence, only for the wavelengths $\Lambda_4 = 1074$ ($\alpha \approx 2·75$) and $\Lambda_5 = 1346$ nm ($\alpha \approx 2·2$) they interfere with the critical region mentioned above. The data obtained are reviewed in Tables I and II. The directly measured turbidity values lay between 0·04 and 1·8, which also illustrates possibilities offered by the device (0·001 to 4·00). Turbidity decreases with increasing wavelength, reaching gradually 68·7% (at 546·1 nm), 44·1% (684·3 nm), 27·4% (857·5 nm), 17·0% (1 074 nm) and 9·8% (1 346 nm) of its original value at 435·8 nm. It may be demonstrated that within the given range of particle sizes turbidity decreases approximately with Λ^{-2}, and that consequently at the last three wavelengths the transparency of the sample is three to ten times higher than that at 435·8 nm. With solvents which do not absorb in the NIR, measurements may be extended to include another three wavelengths (1 687, 2 114 and 2 649 nm), where the transparency of the sample increases by 15 to 35 times.

The values of relative specific turbidity, τ/c_x (Table I), do not virtually change with concentration, which was confirmed by measurements taken at four relative concentrations obtained by dilution of the stock solution (dilution scheme: 1·00, 0·75, 0·50, 0·25). A natural consequence that follows is that also the turbidity ratios

TABLE I

The Turbidity of an Aqueous Suspension of Polystyrene Latex at Wavelengths $\Lambda = 435·8$ to 1 346 nm

Relative concentration of suspension, c_x: $c_1 = 1·00$, $c_2 = 0·75$, $c_3 = 0·50$, $c_4 = 0·25$. Measurements were carried out in cells 1·00 cm thick.

Λ	435·8	546·1	684·3	857·5	1 074	1 346
			Turbidity, τ			
c_1	1·779	1·234	0·795	0·493	0·303	0·176
c_2	1·374	0·947	0·611	0·377	0·233	0·136
c_3	0·918	0·631	0·406	0·252	0·157	0·090
c_4	0·465	0·316	0·200	0·126	0·078	0·045
			Relative specific turbidity, τ/c_x			
c_1	1·779	1·234	0·795	0·493	0·303	0·176
c_2	1·832	1·263	0·814	0·502	0·311	0·182
c_3	1·837	1·262	0·813	0·504	0·314	0·179
c_4	1·860	1·263	0·801	0·504	0·313	0·179
$\bar{c}$	1·827	1·255	0·806	0·501	0·310	0·179

and particle sizes determined in the measurements are almost independent of concentration (Table II). This also confirmed an earlier observation[1], which may now be extended to include the near infrared region.

It was found, however, that the observed particle sizes depend somewhat on the wavelength. Between 435·8 and 684·3 nm all the deviations vary within the usual limits of experimental error. At 857·5 and 1074 nm they reach 5–10%, while at 1346 nm they come up to 20%. The cause of different values found for particle sizes by the electronmicroscopic method (number average particle size) and by the light scattering methods (weight average particle size) is usually seen in the polydispersity of the sample, which in the given case would be rather low. The view that the given sample contains only a small fraction of larger particles is corroborated by an electron microscopic observation of the sporadic occurrence of large particles (aggregates,

TABLE II

The Turbidity Ratios $T_{ab} = \tau_a/\tau_b$ and the Respective Particle Sizes of Polystyrene Latex (L, nm) Determined at Various Pairs of Wavelengths

The subscripts at τ are related to the respective wavelengths: 0 (435·8), 1 (546·1), 2 (684·3), 3 (857·5), 4 (1 074), 5 (1 346 nm). Relative concentrations of suspension, c_x: $c_1 = 1·00$, $c_2 = 0·75$, $c_3 = 0·50$, $c_4 = 0·25$.

T_{ab}	τ_0/τ_1	τ_0/τ_2	τ_0/τ_3	τ_1/τ_2	τ_1/τ_3	τ_1/τ_4	τ_2/τ_3	τ_2/τ_4	τ_2/τ_5	τ_3/τ_4	τ_3/τ_5
Turbidity ratios, $T_{ab} = \tau_a/\tau_b$											
c_1	1·442	2·238	3·611	1·552	2·504	4·069	1·614	2·622	4·522	1·625	2·802
c_2	1·451	2·250	3·647	1·550	2·513	4·065	1·621	2·622	4·485	1·618	2·767
c_3	1·456	2·260	3·644	1·552	2·503	4·015	1·613	2·587	4·536	1·604	2·812
c_4	1·473	2·322	3·688	1·576	2·504	4·037	1·588	2·561	4·481	1·612	2·815
$\bar{c}$	1·456	2·267	3·648	1·558	2·506	4·046	1·609	2·598	4·503	1·615	2·799
Particle sizes, L, nm											
c_1	740	721	737	699	724	778	771	804	872	859	909
c_2	726	728	726	702	723	779	736	804	881	962	925
c_3	719	711	726	699	724	778	771	827	869	1 005	904
c_4	697	680	713	661	724	778	827	850	881	984	904
$\bar{c}$	721	710	726	690	724	778	777	821	876	952	911

Note: For the sake of comparison, earlier measurements of turbidity ratios performed with a CF4 Optica Milano spectrophotometer (cell 0·50 cm) are given; they are a mean from the values determined at six concentrations (data in the brackets are newly measured values taken for comparison): $\tau_0/\tau_1 = 1·458 \pm 0·006$ ($1·456 \pm 0·013$), $\tau_0/\tau_2 = 2·273 \pm 0·041$ ($2·267 \pm 0·037$), $\tau_1/\tau_2 = 1·566 \pm 0·034$ ($1·558 \pm 0·003$).

agglomerates), along with the predominant majority of almost monodisperse particles. Scattering measurements in the visible region also confirm such view, because the particle sizes determined in the measurements are only by some 3–5% higher than data obtained by electron microscopy. Moreover, the agreement of data (Table II) measured by employing several independent procedures in various time intervals and using two quite different spectrophotometers indicate not only the correctness and reproducibility of measurements, but also the absence of any observable trend towards further aggregation.

In interpreting data obtained by the turbidity ratio method one should be very careful, however, even if the sample involved contains a relatively small fraction of larger particles. The resulting turbidity ratios of such sample (which are not a mere sum of the turbidity ratios of individual components) are completely determined by the character of the dependence of (τ/c) on α in the respective region of α values (on the other hand, however, the specific turbidities of components related to their weight fraction may be summed up). The scattering behaviour of a mixture of two monodisperse components A and B having different particle size ($L_A < L_B$) may be estimated by the following reasoning: Let the turbidity ratio of the mixture, τ_a^{AB}/τ_b^{AB}, be defined by

$$\frac{\tau_a^{AB}}{\tau_b^{AB}} = \frac{x(\tau_a^A/c)_0 + (1-x)(\tau_a^B/c)_0}{x(\tau_b^A/c)_0 + (1-x)(\tau_b^B/c_0)} = T_{ab}^{AB}\,, \tag{3}$$

where x is the fraction of the component A in the mixture. For the turbidity ratio of the component A alone ($x = 1$) it holds, of course, that $T_{ab}^A = \tau_a^A/\tau_b^A$. The question arises under what conditions the resulting turbidity ratio of the mixture, T_{ab}^{AB}, will be smaller than T_{ab}^A (the component A alone instead of the mixture AB). By dividing Eq. (*3*) by T_{ab}^A, we obtain

$$\frac{x + (1-x)(\tau_a^B/\tau_a^A)}{x + (1-x)(\tau_b^B/\tau_b^A)} = Q\,. \tag{4}$$

Hence, T_{ab}^{AB} will be smaller than T_{ab}^A, if $Q < 1$, and thus also

$$\tau_a^B/\tau_a^A < \tau_b^B/\tau_b^A\,; \quad \tau_a^B/\tau_b^B < \tau_a^A/\tau_b^A\,. \tag{5}$$

Since $L_A < L_B$, this condition is fulfilled for those regions of the function $T_{ab}(\alpha)$ in which the turbidity ratio $T_{ab} = \tau_a/\tau_b$ decreases with increasing α (*i.e.* with increasing relative particle size, L/λ), and *vice versa*. For the given relative refractive index $m = 1{\cdot}200$, the function T_{ab} (where a corresponds to 435·8 and b to 546·1 nm) increases within the range $\alpha = 2{\cdot}0$ to $2{\cdot}4$, and after that within the range $\alpha = 17{\cdot}5$ to $25{\cdot}0$ (further maxima are omitted); within the ranges $\alpha = 0$ to $2{\cdot}0$ and $2{\cdot}4$ to $17{\cdot}5$ the

T_{ab} values decrease. If the critical range $T_{ab} = 1{\cdot}76$ to $1{\cdot}84$ (where the determination is not unequivocal) is excluded from our reasonings, it can be said that in the given range the addition of major particles always leads to lower values of the resulting turbidity ratio of the mixture, *i.e.* to a real increase in the resulting particle size. If the particle size of the component A or B overlaps the critical region just mentioned, an opposite effect may appear, but not in all cases. In the case of our sample it seems that owing to the critical region the scattering of values determined at the wavelengths 1 074 and 1 346 nm increases, but a perceptible decrease in the resulting particle size (partial compensation of the effect of the larger particle fraction) occurs only for the wavelength 1 346 nm ($\alpha \approx 2{\cdot}2$), as demonstrated by our measurements (Table II).

To illustrate the argument outlined above, we calculated what fraction of larger particles could lead to the effect observed for the pair of wavelengths Λ_0 and Λ_1. The particle size of component A was taken as 680 nm (determined by electron microscope); that of component B was taken as 981 nm, which corresponds to the triple particle volume of component A. The turbidity ratio $T_{ab}^{A} = \tau_a^A/\tau_b^A$ corresponding to the size 680 nm ($\alpha = 5{\cdot}23$) is 1·490, while the experimentally determined turbidity ratio of the mixture was $T_{ab}^{AB} = \tau_a^{AB}/\tau_b^{AB} = 1{\cdot}456$; hence, the quotient Q was $T_{ab}^{AB}/T_{ab}^{A} = 0{\cdot}977$, and $T_{ab}^{B} = \tau_a^B/\tau_b^B = 1{\cdot}31$. The specific turbidities corresponding to the particle sizes of components A and B were taken from Tables[7]; τ_a^A and τ_a^B were calculated from expressions for T_{ab}^{A} and T_{ab}^{B}. The required values were obtained after substitution into Eq. (*4*) and rearrangement: $x = 0{\cdot}829$ (fraction of A); $1 - x = 0{\cdot}171$ (fraction of B). If the particles of component B were markedly larger, its fraction would be considerably reduced.

Scattering measurements in the NIR region gave particle size values much higher than those given by electron microscopy, namely, by 8–16% or 25–40% (for the highest wavelengths). It is probable that in addition to the effect of the content of larger particles and of the critical region of T_{ab} discussed above, one should also take into account the much greater experimental error in this range, due to instrumental reasons and especially to the presence of absorbing compounds (water, impurities), which may already become operative at 1 346 nm.

The following conclusions may be derived from the results obtained: *1.* The turbidity ratio method provides adequate information on the particle size also in the NIR region, but the data are distinctly less precise. Measurements in this range are therefore advantageous in those cases where the turbidity of the system is very high and cannot be reduced by dilution or by reducing thickness of the sample. *2.* An interpretation of data obtained by the turbidity ratio requires the knowledge of theoretical functions; possible sources of error have been pointed out. By choosing adequate turbidity ratios one could avoid the critical range of T_{ab}. *3.* By measuring turbidity curves (during automatic correction for the extinction of the reference sample), it is possible to make more precise the interpolation of turbidity values while at the same time ruling out or considerably reducing the effect of artefacts (due especially to real absorption).

The author is indebted to Dr F. Lednický for electron-microscopic measurements and to Mrs H. Taucová for careful technical cooperation.

REFERENCES

1. Sedláček B.: *Report*. Inst. Macromol. Chem., Prague 1962. *Preprints, IUPAC International Symposium on Macromolecular Chemistry*, Prague 1965. This Journal *32*, 1374 (1967); *32*, 1398 (1967).
2. Deželić Gj., Deželić N., Težak B.: J. Colloid Interface Sci. *18*, 888 (1963).
3. Hloušek J.: Chem. Prům. *13*, 492 (1963).
4. Kerker M.: *The Scattering of Light and Other Electromagnetic Radiation*. Academic Press, New York 1969.
5. Sedláček B.: Chem. Listy *50*, 30 (1956).
6. Meyerhoff G., Burmeister A.: Makromol. Chemie *175*, 3029 (1974); Burmeister A., Meyerhoff G.: Ber. Bunsenges. Phys. Chem. *78*, 1366 (1974).
7. Sedláček B., Verner B., Bárta M., Zimmermann K.: *Tables of Scattering Functions for Spherical Particles*. Series MACRO, vol. D-2. Inst. Macromol. Chem., Prague 1978.
8. Sedláček B., Verner B., Bárta M., Zimmermann K.: This Journal, in press.
9. Sedláček B.: This Journal, in press.

Translated by L. Kopecká.