

## The Determination of Particle Sizes from Tyndall Spectra

W. Heller, H. B. Klevens, and H. Oppenheimer

Citation: [The Journal of Chemical Physics](#) **14**, 566 (1946); doi: 10.1063/1.1724197

View online: <http://dx.doi.org/10.1063/1.1724197>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/9?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Determination of particle size distributions from acoustic wave propagation measurements](#)

Phys. Fluids **11**, 1065 (1999); 10.1063/1.869977

[Determination of Particle Size by Diffraction of Light](#)

Am. J. Phys. **42**, 320 (1974); 10.1119/1.1987680

[Determination of Particle Size Distributions of Dispersions of Small Superconducting Particles from Magnetic Measurements](#)

J. Appl. Phys. **38**, 2687 (1967); 10.1063/1.1709971

[Tyndall Spectra, Their Significance and Application](#)

J. Chem. Phys. **14**, 565 (1946); 10.1063/1.1724196

[Particle Size Determination from XRay Line Broadening](#)

J. Appl. Phys. **17**, 687 (1946); 10.1063/1.1707771

---



"geloids" which are responsible for gel formation. The size of these aggregates varies with the experimental conditions, such as temperature, protein concentration, and composition of the solvent.

<sup>1</sup> W. Heller and E. Vassy, *Phys. Rev.* **63**, 65 (1943).

<sup>2</sup> G. Mie, *Ann. d. Physik* **25**, 377 (1908).

## The Determination of Particle Sizes from Tyndall Spectra\*

W. HELLER

*Chemistry Department, Wayne University, Detroit, Michigan*

AND

H. B. KLEVENST† AND H. OPPENHEIMER

*Chemistry Department, University of Chicago, Chicago, Illinois*

June 24, 1946

TYNDALL spectra in light scattering systems without selective absorption furnish a hitherto neglected principle for the determination of particle sizes within an important range of ultramicroscopic dimensions. The principle, based on the decrease of the wave-length exponent,  $n$ , with increasing particle diameter, above dimensions of  $\sim \frac{1}{10}$  of the wave-lengths used, was outlined in a previous paper<sup>1</sup> and it has now been used for a quantitative method. For this purpose, particle size determinations were carried out with the slit ultramicroscope, using model systems described below. The data obtained were correlated with the wave-length exponent which was obtained, on the same systems, from spectrophotometric measurements of the conservative absorption, the latter being equivalent to spectrophotometric measurements of the global Tyndall effect. Two instruments, the visual Pulfrich spectrophotometer and the Beckman photoelectric spectrophotometer were used for the experiments. The range of wave-lengths covered was 4000–6500Å for the latter and about 1000Å less for the former. Using the principle outlined previously,<sup>1</sup> true absorption—which would interfere with the measurements—was found to be practically absent above 3800Å. The calibration curves, obtained on the variation of  $n$  with particle size, depend slightly on the amount of Tyndall light radiated in the direction of the primary beam. The respective solid angle was defined for the Pulfrich instrument, under the conditions used, by  $\leq 4^\circ$ , depending on the slit width (turbidity). The angle is larger

for the Beckman instrument where it is constant by virtue of the standard construction of the apparatus. The wave-length exponent obtained for a given particle size decreases slightly with increasing concentration of the particles. This effect was excluded by compiling  $n$  in each instance for a series of concentrations and by extrapolating to infinite dilution. The latter value generally differs by not more than 5 percent from the lower value obtained at a concentration of 0.1 percent, the latter being approximately the highest concentration used in all experiments.

The model systems used were aqueous emulsions of polystyrene, polyisoprene and styrene-isoprene copolymer. Ultramicroscopic observations showed that these particles were spherical (in contradistinction to the molecules of which they are composed). Extensive optical investigations of the authors on the locus and mechanism of emulsion polymerization, by means of a spectrophotometric-interferometric method,<sup>2</sup> and with the ultramicroscope—selected results have already been published<sup>3</sup>—showed that the size of these particles can be varied and controlled by varying the reaction time and temperature, and the nature and concentration of the emulsifier used. The information thus gained made it possible to vary the average particle diameter systematically between  $<500$  and  $\sim 3000$ Å, the size range desired for calibrations of  $n$  against particle sizes. Because of the courtesy of the United States Rubber Company, electron-microscopic material could be examined which showed that the size distribution curve in systems as those used is—if prepared in the presence of a stabilizer—generally fairly symmetrical and has a half-width of approximately 200Å. The results obtained for the calibration curves, therefore, do not differ appreciably from those to be expected from strictly monodisperse systems.

Figure 1 represents the calibration curve obtained with a series of polystyrene emulsions. It is valid for a refractive ratio  $m = n_p/n_m$  ( $n_p$ , refractive index of the light scattering particles,  $n_m$ , refractive index of the medium) of 1.23–1.25. The total range of  $m$  covered thus far in the various series extends from 1.18–1.25. Since light scattering is, in absence of true absorption, wholly independent of the chemical nature of the particles, the data obtained may be applied for particle size determinations in any type of dispersed system with spherical particles and refractive ratio  $1.24 \pm 0.01$ . (These refractive ratios were determined interferometrically from the refractive indices of the emulsion and of the medium, using, for the calculation of  $n_p$ , a mixture rule given recently.)<sup>4</sup>

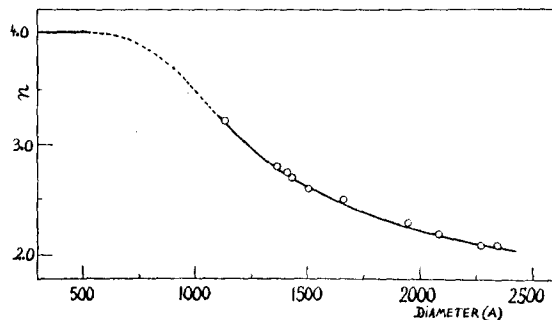


FIG. 1. Variation of wave-length exponent with the diameter of spherical dielectric particles.

TABLE I.

Reaction time (hours)	Percent conversion	$n$	Diameter (Å)
6	<0.5	4.0	500**
9	<0.5	4.0	570**
11	<0.5	3.95	~700**
14	~0.5	3.8	800
18	1.0	3.5	900
36	2.3	2.85	1150
60	3.0	2.5	1500
360	13.8	2.1	2300
540	44.0	2.05	2550
660	59.5	2.0	~2700

\*\* Determined from the quantitative value of light scattering itself, reference 2.

An example of the practical application of the method for rapid particle size determinations is given in Table I which contains data on the variation of the particle diameter of polymer with percent conversion of monomer to polymer in agitated styrene-isoprene reaction mixtures which were kept in bombtubes at 50°C, in presence of 0.2 percent of potassium caprylate as emulsifier. The calibration curve differs here from that in Fig. 1 (in  $<1.23$ ).

\* The work reported in this abstract was done at the University of Chicago in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation. Details of the method and results are given in the restricted reports Comptes rendus 87, 124, 237 (1943); 470 (1944); 845, 846, 858, 888 (1945).

† Present address: Firestone Tire and Rubber Company, Akron, Ohio.

<sup>1</sup> W. Heller and E. Vassy, *J. Chem. Phys.* **14**, 565 (1946).

<sup>2</sup> W. Heller and H. B. Kleven, *Phys. Rev.* **67**, 61 (1945).

<sup>3</sup> W. D. Harkins, *J. Chem. Phys.* **13**, 381 (1945); **14**, 47 (1946).

<sup>4</sup> W. Heller, *Phys. Rev.* **68**, 5 (1945).

### Spectrophotometric Studies on Solubilization of Hydrocarbons\*

W. HELLER

*Chemistry Department, Wayne University, Detroit, Michigan*

AND H. B. KLEVEN†

*Chemistry Department, University of Chicago, Chicago, Illinois*

July 16, 1946

A STRONGLY light scattering emulsion is formed on exceeding the limiting concentration of hydrocarbon,  $c_1$ , which defines its solubility in a soap solution. A quantitative spectrophotometric method for studies on solubilization was based on this known fact.  $c_1$  is characterized by a minimum in light scattering which facilitates the measurements. Special joint studies with H. Oppenheimer showed that the minimum is caused by a decrease in size of molecular aggregates of soap, with increasing oil concentration, at concentrations  $<c_1$ . Solubilization studies on ethylbenzene gave the following results valid at 20°–25°C.

(1)  $c_1$  increases with time, particularly in concentrated solutions where a practically final value is reached only after 60 hours.

(2) The number of moles of ethylbenzene, dissolved per mole of soap,  $R_m$ , increases for a given soap concentration, with increasing chain length of the soap molecules.  $R_m$ , implicitly, increases with a decrease in the "critical soap concentration,"  $c_{cr}$ , above which micelles are formed. Considering 15 percent soap solutions, the following  $R_m$  ( $c_{cr}$ ) values were found:  $KC_8$ : 0.0031 (1.62);  $KC_9$ : 0.080 (0.395);  $KC_{10}$ : 0.207 (0.100);  $KC_{12}$ : 0.433 (0.023);  $KC_{14}$ : 0.870 (0.007). The  $c_{cr}$  values, in moles of soap per liter were determined in supplemental experiments by other methods.

(3) With an increase in concentration of a given soap,  $R_m$  first decreases, reaches a minimum, and then increases nearly linearly without definite indication of approaching saturation at a 15 percent concentration. The minimum value of  $R_m$ , is reached at  $c_{cr}$ , providing thereby a new method for determining  $c_{cr}$  from solubilization measurements.  $c_{cr}$  thus found for  $KC_{12}$  is 0.025 mole per liter.

(4) Adopting the concept of the lamellar micelle structure,<sup>1a,1b</sup> using cross-sectional areas of soap molecules as obtained from x-ray measurements and assuming that the density of ethylbenzene absorbed in the micelles is, in the first approximation, identical with that of liquid ethyl-

benzene, one can calculate from  $R_m$ —corrected for oil dissolved by micelles only—the thickness (spacing) of the individual intermicellar ethylbenzene layers. For  $KC_{12}$ , one thus finds, by interpolation, that the oil layer is equivalent to a completed monomolecular layer and a bimolecular layer at a soap concentration of 0.09 and 0.50 mole per liter, respectively. According to extrapolation, a trimolecular layer would be completed at a concentration of 1.08 moles per liter. The corresponding spacings are  $2.7+2\epsilon$ ,  $5.4+2\epsilon$ , and  $8.1+2\epsilon$ Å, respectively, where  $\epsilon$ , a fraction of one Å, represents the unknown distance, at a minimum of potential energy between the hydrophobic ends of the oriented soap molecules and the neighboring ethylbenzene molecules.

\* The work reported in this abstract was done at the University of Chicago in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation. The methods used were developed early in 1943.

† Present address: Firestone Tire and Rubber Company, Akron, Ohio.

<sup>1a</sup>: J. W. McBain, in *Advances of Colloid Science* (Interscience Publishers, New York, 1942), Vol. 1, pp. 99–143; b: several recent papers by W. D. Harkins and co-workers, e.g., W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.* **68**, 220 (1946).

### Refractive Indices of Soaps and Detergents\*

H. B. KLEVEN†

*Department of Chemistry, University of Chicago, Chicago, Illinois*

June 28, 1946

ACCORDING to Hess, Philippoff, and Kiessig,<sup>1</sup> the variation in the refractive indices with the concentration for various soaps is characterized by an intersection of two linear functions. The authors believe that this intersection represents the critical micelle concentration above which micelles are formed. These experiments were repeated and expanded using a Haber-Loewe type of interferometer (layer thickness, 160.290 mm,  $T=23.5^\circ\text{C}$ ) using both cationic and anionic soaps or detergents; a few preliminary data are given below.

The results reported here are those obtained with lauryl amine hydrochloride (LA-HCl) and with potassium laurate ( $KC_{12}$ ). The former was kindly supplied by the Research Laboratories of Armour and Company and was subsequently recrystallized five times; the latter was prepared by multiple fractionation of the methyl ester of lauric acid, followed by saponification and repeated recrystallizations.

The refractive indices change in the case of LA-HCl between 1.332849 and 1.336065 and for  $KC_{12}$  between 1.332828 and 1.335640 over a concentration range from 0.10 percent to 2.00 percent. Plotting of this data gives two straight lines for each series which intersect at 0.29–0.30 percent for the LA-HCl and at 0.61–0.62 percent for the  $KC_{12}$  solutions. The refractive increment,  $(n_t - n_m)/c$ , where  $n_t$  is the refractive index of the solution,  $n_m$  the refractive index of the medium, and  $c$  the concentration in grams per hundred grams solution, reaches a maximum value at 0.29–0.30 percent and at 0.61–0.62 percent for LA-HCl and  $KC_{12}$ , respectively.

More significant is the change with concentration in the refractive index of the solute itself ( $n_s$ ). These values were obtained by use of the new mixture rule reported recently by Heller.<sup>2</sup> These results are plotted in Fig. 1. In both cases,