## Size Distribution of Spheres by Light Scattering[1]

BY F. BUECHE

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Several methods have been proposed during the past few years for determining the range of sizes of spherical particles in solution.[2] The purpose of this note is to outline another method which the author believes has some practical advantages over the others so far presented. This method makes use of the fact that for a solution of spheres of unequal size the position of the first angular intensity minimum does not yield the same sphere size for two different wave lengths. The method makes use of some relations derived by W. B. Dandliker[3] who apparently failed to notice the inherent simplicity of a method based upon them.

If one assumes that the Debye theory[4] may be applied to scattering by a solution of spheres, it may be shown that the condition which exists at the first minimum leads to the relation[3]

$$a_1^2G(y_1) = a_2^2G(y_2)$$

To obtain this relation one replaces the actual distribution of sizes by a rectangular distribution extending from radii of $a_1$ to $a_2$. The quantity $y_1$ is equal to

$$\frac{4\pi a_1}{\lambda} \sin ({}^1/{}_2\theta_m)$$

and similarly for $y_2$. The function $G(y)$, a function of $y$ alone, is given in the table. Its algebraic form is given in reference 3.

| $y$ | $-G(y)$ | $y$ | $-G(y)$ |
|---|---|---|---|
| 1.5 | 0.06 | 5.0 | 3.50 |
| 2.5 | 1.21 | 5.5 | 1.60 |
| 3.5 | 4.70 | 6.0 | 1.37 |
| 4.0 | 5.95 | 6.5 | 3.79 |
| 4.5 | 5.50 | 7.0 | 7.39 |

The use of this result may be best illustrated by an example. Suppose one has measured the position of the angular minimum (for light plane polarized with plane perpendicular to the plane of observation) at two wave lengths $\lambda$ and $\lambda'$ to give the corresponding angles $\theta$ and $\theta'$. Suppose further that $\lambda = 4000$, $\lambda' = 3000$, $\theta = 89°$ and $\theta' = 70°$.

From the definition of $y$ and the values for $\lambda$ and $\theta$ one may write $y = 0.0022\ a$. Since each $y$ determines a value of $G(y)$ as shown in the table, one is able to plot curve 1 of the figure which shows $a$ *vs.* $a^2/G(y)$. This curve does not uniquely determine either $a_1$ or $a_2$. However, to find unique values one need only plot a similar curve for the data obtained at $\lambda'$. This is curve 2 of the figure.

At the values of $a = a_1$ and $a = a_2$ both of these curves must satisfy equation 1. Therefore one must have

$$a_1^2G_1 = a_2^2G_2$$
$$a_1^2G_1^1 = a_2^2G_2^1$$

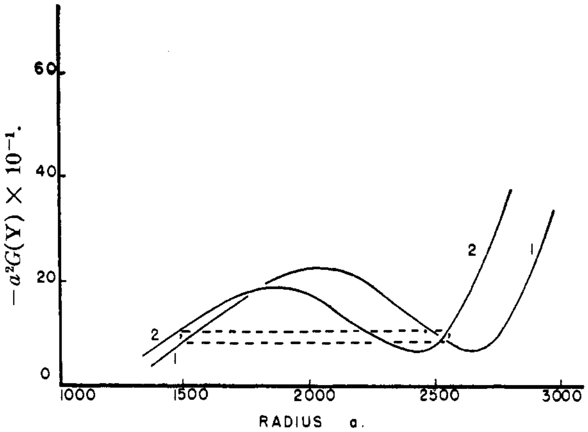

Fig. 1.

That is to say, the actual values of $a_1$ and $a_2$ will be such that at these two values the vertical coördinates of curve 1 equal each other and also the vertical coördinates of curve 2 equal each other. By inspection it is seen that this is true for $a_1 = 1500$ and $a_2 = 2600$. These tell us that the actual particle size distribution may be approximated by a rectangular distribution having limiting radii of 1500 and 2600.

It should be mentioned that when the distribution is very broad it may be necessary to use values $G(y)$ above $y = 8$. In that event the above treatment can only be considered as approximate since the simple Debye relations begin to fail in that region.

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[1] This work was carried out under a contract with the Office of Rubber Reserve, R. F. C., in connection with the U. S. Government's Synthetic Rubber Program.

[2] M. Kerker and V. K. LaMer, THIS JOURNAL, **72**, 3616 (1950); I. Johnson and V. K. LaMer, *ibid.*, **69**, 1184 (1947).

[3] W. B. Dandliker, *ibid.*, **72**, 5112 (1950).

[4] See for example the review article by G. Oster, *Chem. Rev.*, **43**, 336 (1948).

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## Dissociation Constants of N-Alkylethylenediamines[1,2]

BY FRED BASOLO AND R. KENT MURMANN

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The acid–base dissociation constants of ethylenediamine,[3] diethylenetriamine and triethylenetetramine[4] have been determined. In the course of investigating steric effects on the binding of metal ions with N-alkylethylenediamines, it was necessary to determine the acid–base dissociation constants or "hydrolysis" constants of the amines. Since the N-alkylethylenediamines form an interesting series of compounds, this paper reports the acid–base dissociation constants of five such diamines. The constants were determined in the presence of 0.05 *M* $Ba(NO_3)_2$ and 0.50 *M* $KNO_3$ by the method of Bjerrum.[3]

### Experimental

**Reagents.**—N-Methyl- and N-ethylenediamine were each prepared by two methods which gave identical products with

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[2] This investigation was supported by a grant-in-aid from the National Institutes of Health—Grant No. G-3239.

[3] J. Bjerrum and P. Anderson, *K. Danske Vidensk. Selsk. Mathfys. Medd.*, **22**, No. 7 (1945).

[4] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).