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

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

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 λ and λ' to give the corresponding angles θ and θ'. Suppose further that $\lambda = 4000$, $\lambda' = 3000$, $\theta = 89°$ and $\theta' = 70°$.

From the definition of y and the values for λ and θ 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 λ'. 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

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

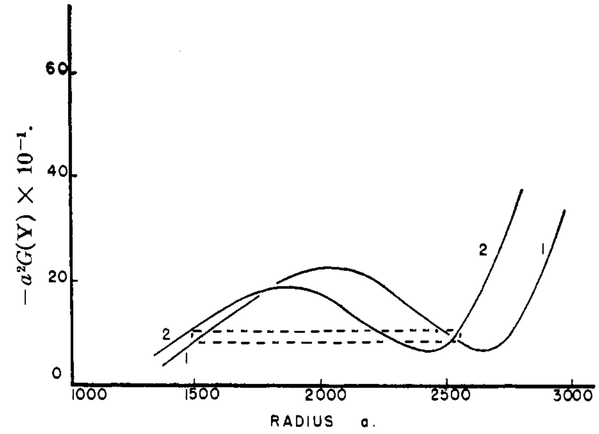

Fig. 1.

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).

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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[1] Abstracted in part from a thesis by R. Kent Murmann, presented to the Graduate Faculty of Northwestern University, in partial fulfillment of the requirements for the degree of Master of Science in chemistry, August, 1951.

[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).

derivatives melting at the same point. In general the method of O'Gee and Woodburn[5] was superior to that of Aspinall.[6]

N-Isopropyl- and N-*n*-butylethylenediamine were prepared by the method of O'Gee except that the free amines were dried with sodium before distillation.

N-*n*-propylethylenediamine was obtained by the courtesy of Dr. H. M. Woodburn at the University of Buffalo. It was redistilled over sodium.

The amines were fractionated through an eleven-inch column packed with stainless steel spiral and had the following boiling ranges

N-Alkylethylenediamines ($RNHCH_2CH_2NH_2$) R	B.p., °C.
Me	114–115
Et	125–126
i-Pr	137–138
n-Pr	152–153
n-Bu	75–77 (20 mm.)

These agree well with those reported by O'Gee and Woodburn.[5]

Preparation of Solutions and Titrations.—The amines were diluted with distilled water until they were 3 to 5 molar and then standardized against standard acid by means of conductometric titrations. The primary standard for all acid–base titrations was a sample of 99.96% potassium hydrogen phthalate obtained from the Bureau of Standards.

The constant ionic strength nitric acid solution containing barium nitrate was made by preparing a solution approximately 0.1 N in boiled nitric acid and adding reagent grade chemicals to make the solution 0.50 M in KNO_3 and 0.05 M in $Ba(NO_3)_2$. The nitric acid was then titrated against standard base using phenolphthalein as the indicator.

A Beckman *p*H meter model G was standardized against Beckman standard buffers at a *p*H of 4.00 and 9.00 before each run. A Beckman 1190–90 glass electrode was used which is accurate to *p*H's of 11 without corrections in the absence of sodium ion. The solutions were maintained at a constant temperature by means of a constant temperature bath at 25 ± 0.1° and by an intimate mixture of ice and water at 0 ± 0.1°.

The titration of the standard nitric acid solution with standard amine was accomplished by means of a microburet capable of being read to ± 0.001 ml. The hydrogen ion was followed by means of a *p*H meter which could be read to ± 0.02 *p*H unit.

A sample titration at the appropriate regions of *p*H along with calculated values of pK_1 and pK_2 are indicated in Table I. One notices the good agreement of the various pK values. In each case these values were checked by determining the respective *p*H's of two separate solutions which fall in the first dissociation constant range and in the second dissociation constant range. The constants calculated from these solutions agreed with those obtained from the titration within ±0.01 pK unit.

The dissociation constants at 0 and 25° along with the heats of neutralization are summarized in Table II. A graphic representation of these pK values is shown in Fig. 1. Although these compounds have comparable dissociation constants, it does appear that with the straight chain alkyls there is a gradual change in going from methyl to butyl with a slight maximum in the region of N-ethylethylenediamine. It is likewise noteworthy that although one may expect a more marked change in case of the pK_2 values as compared to changes in pK_1, this was not observed.

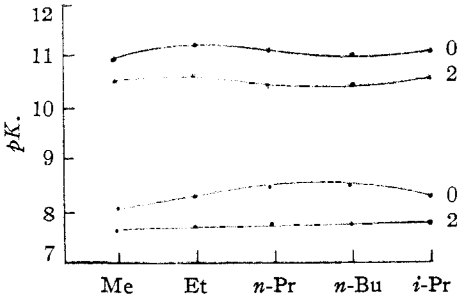

Fig. 1.—Dissociation constants of N-alkylethylenediamines.

TABLE I

DISSOCIATION CONSTANTS OF N-ETHYLETHYLENEDIAMINE AT 0°

Diamine, ml.	*p*H	C_{En}	C_{H}	pK_1
1.002	7.91	0.06223	0.10254	8.16
1.039	8.00	.06449	.10247	8.16
1.077	8.10	.06679	.10239	8.16
1.111	8.19	.06886	.10232	8.16
1.150	8.28	.07123	.10224	8.17
1.187	8.36	.07346	.10217	8.17
1.220	8.43	.07545	.10210	8.17
1.252	8.50	.07739	.10204	8.17
1.291	8.57	.07974	.10196	8.16
1.328	8.65	.08197	.10189	8.16
			Av.	8.16
				pK_2
2.050	10.50	0.12477	0.10048	11.12
2.085	10.53	.12681	.10041	11.11
2.120	10.55	.12885	.10034	11.10
2.160	10.59	.13110	.10026	11.11
2.191	10.62	.13300	.10006	11.11
2.337	10.72	.14146	.09992	11.10
2.413	10.77	.14585	.09978	11.11
2.481	10.80	.14976	.09965	11.10
2.594	10.85	.15624	.09944	11.10
2.709	10.90	.16282	.09922	11.08
			Av.	11.11

TABLE II

DISSOCIATION CONSTANTS AND HEATS OF NEUTRALIZATION OF N-ALKYLETHYLENEDIAMINES

$RNHCH_2$-CH_2NH_2 —R—	pK_1 0°	pK_1 25°	pK_2 0°	pK_2 25°	ΔH, kcal. pK_1	ΔH, kcal. pK_2
Me	8.00	7.56	10.83	10.40	− 6.55	− 6.30
Et	8.16	7.63	11.11	10.56	− 7.90	− 8.20
n-Pr	8.24	7.54	11.04	10.34	−10.4	−10.4
n-Bu	8.11	7.53	10.93	10.30	− 8.65	− 9.40
i-Pr	8.30	7.70	11.15	10.62	− 8.95	− 7.90

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[5] R. C. O'Gee and H. M. Woodburn, THIS JOURNAL, **73**, 1370 (1951).

[6] S. R. Aspinall, *ibid.*, **63**, 852 (1941).

Chromatographic Investigations Related to Photographic Theory. II. Adsorption of Developing Agents and Sodium Sulfite[1]

BY T. H. JAMES AND W. VANSELOW

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In a preceding paper,[2] the technique of elution chromatography was used to show that the photographic developing agents, *p*-phenylenediamine and hydrazine, are adsorbed by silver bromide. These agents displaced the adsorbed dyes, phenosafranin and 3,3′-diethyloxacarbocyanine, from the silver bromide surface. Hydroquinone and catechol, on the other hand, caused the dyes to be held even more tightly, and this suggested a coöperative adsorption of the negatively-charged developing agent

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[1] Communication No. 1473 from the Kodak Research Laboratories.

[2] T. H. James and W. Vanselow, THIS JOURNAL, **73**, 5617 (1951).