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Chemistry

THE EQUILIBRIA BETWEEN DI-n-DECYLAMINE AND SULFURIC ACID

K. A. Allen

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Kenneth A. Allen

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THE EQUILIBRIA BETWEEN DI-n-DECYLAMINE AND SULFURIC ACID

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ABSTRACT

Benezene solutions of di-n-decylamine have been equilibrated with aqueous sulfuric acid at 25°. The amine salts remain in the organic phase, and the data are interpreted on the basis of aggregation of these species. Equilibrium constants for the formation of colloidally dispersed amine sulfate and for sulfate-bisulfate exchange within the colloid are evaluated. The precipitation of pure di-n-decylamine bisulfate at a given acid activity independent of total amine concentration is attributed to a maximum bisulfate content for a stable colloidal dispersion corresponding to approximately equal moles of sulfate and bisulfate.

I. INTRODUCTION

High molecular weight amines in organic diluents have been shown to extract a wide variety of substances from aqueous solutions. Some of these extractions are useful in analytical procedures[1] and others show promise of possible application to industrial purifications.[2] The fundamental processes underlying this behavior of the long chain amines are therefore of some interest. A somewhat more extensive discussion of the background material relative to project interest in these phenomena is to be found in ORNL-1977.[4]

Solubility and extraction data obtained in the systematic studies have provided considerable evidence indicative of association of the amine salts in the organic phases.[2] Titrations of benzene solutions of di-n-decylamine (hereinafter this amine will be referred to as DDA) with sulfuric acid have been shown by Baes to support this view, and the extraction of iron by DDA sulfate has been interpreted from this standpoint.[3] The mole percent of amine bisulfate formed by DDA in the solvent Amsco G was found by Horner to be a very nearly linear function of the pH of half molar sulfate aqueous phases containing sulfuric acid and sodium sulfate.[2]

The present investigation was undertaken with the object of obtaining more evidence as to the nature of the equilibria involved in these reactions.* In a previous paper it was shown

*Much of the material contained in this report is also being published in the Journal of Physical Chemistry (June, 1956, expected); the equilibration data of Tables I and II, however, as well as some other material of particular value for project application, will not be available in the journal article, and it was felt that interested project personnel should have access to a more complete presentation of this information.

that the sulfuric acid extraction behavior of tri-n-octylamine was consistent with a quantitative treatment based on partial aggregation of the sulfate species.[4] The present results are in accord with those of the earlier work, and the treatment is along the lines of that found applicable in the case of the tertiary amine, although specific differences in behavior between the two amines have been observed.

II. EXPERIMENTAL

Materials. The di-n-decylamine used in this work was prepared in the following way.* Armeen 10D (a mixture of 8, 10 and 12 carbon straight chain saturated primary amines, principally n-decylamine) was fractionated in a Podbielniak-type still; 900 g of product with a boiling range of 216-217° at 725 mm were collected. This material was heated in a reaction vessel under argon with about 200 g Raney nickel and 400 ml ethyl alcohol. The alcohol was allowed to evaporate slowly without reflux. Rapid ammonia evolution commenced at 140°, continuing until the temperature of the reaction mixture reached 150° over a period of about ten minutes. Further heating for 20-30 minutes raised the temperature to 220° with markedly decreased ammonia evolution. The cooled partially solidified mixture was taken up with chloroform and filtered. Fractional distillation resulted in a center cut of 450 g DDA in the boiling range 195-196° at 5.0 ± 0.1 mm.

*The preparation, purification and analyses of this amine were carried out by W. J. McDowell of this laboratory.

This material was subjected to both total and differential titrations.[5] The resulting apparent molecular weight was 298.6 (theoretical for DDA:297.6). The primary amine content was found to be less than 0.5%, and the tertiary 3 ± 1%, using the methods referred to. Titration curves constructed from the sulfuric acid equilibration data given in the following section showed inflection points at 98.0 ± 0.5% of theoretical for DDA concentrations in benzene ranging from 0.05 to 0.5 M. Assuming tertiary amine to be the only impurity, and that its behavior is similar to that of tri-n-octylamine, inspection of the comparative titration curves for the latter and DDA (Figure 1) shows that at the inflection point for DDA only a negligible amount of acid will have been consumed by the tertiary impurity. On this basis the sulfuric acid equilibrations indicate a tertiary amine content of 2.0 ± 0.5%, in agreement, within experimental error, with the value obtained by differential analysis. Free amine concentrations below the equivalence point were therefore calculated from 98.0% of the concentrations given below (e.g., in this range, the 0.05 M solution was treated as being 0.0490, the 0.1 M solution as 0.0980, etc.).

Above the equivalence point the salt forms of DDA and tri-n-octylamine behave very similarly, as is shown by Figure 1. Consequently, in the bisulfate range the tertiary impurity was ignored and all calculations were based on the total concentrations shown. The 0.5 M solution was prepared on a weight basis, using the apparent molecular weight obtained by analysis. The other solutions were obtained by dilution from the half molar

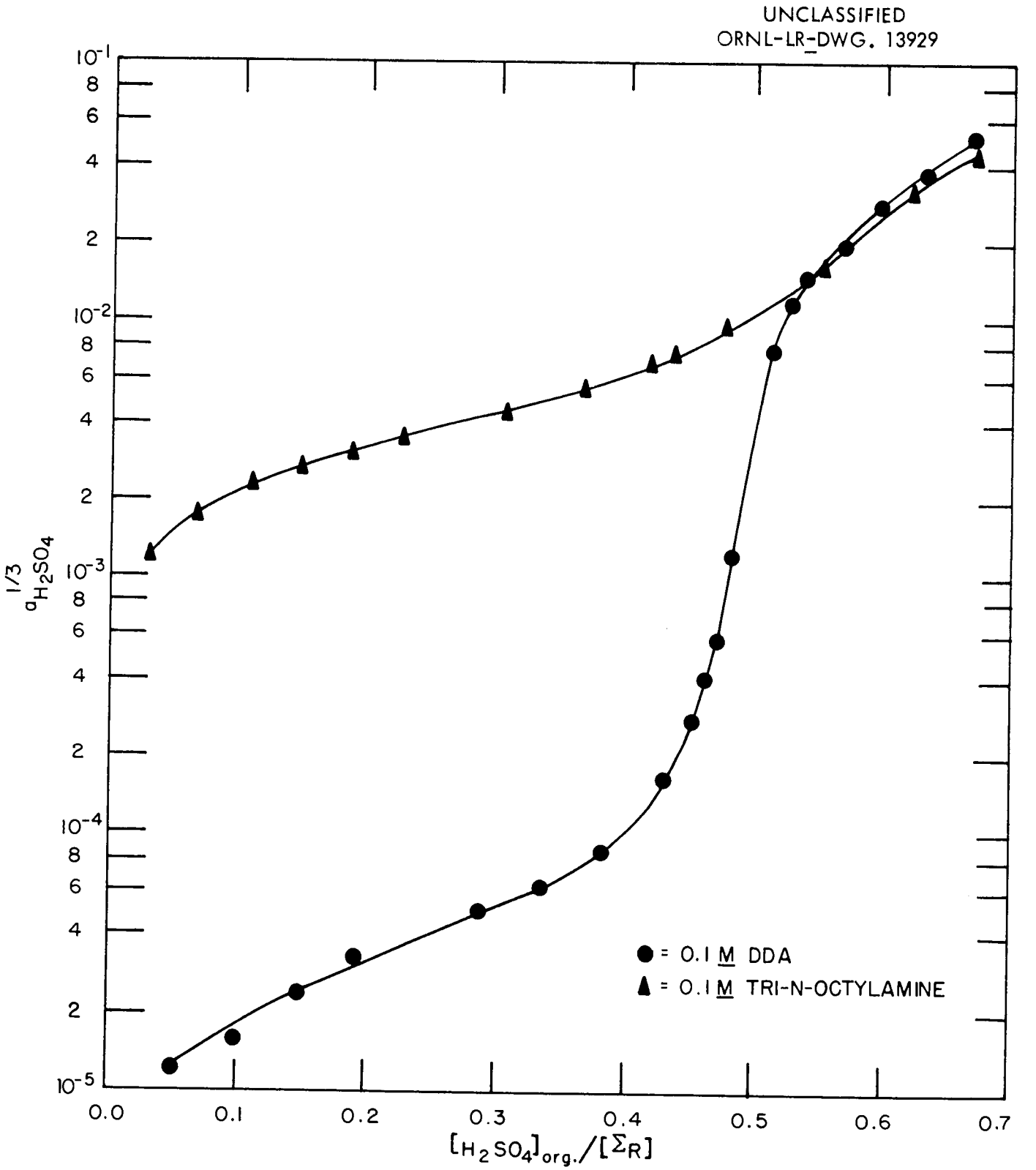

FIGURE 1. TITRATION CURVES

stock. These benzene solutions were prepared at 25° and stored in a 25.00 ± 0.05° thermostat throughout their period of use. The other materials used were of the usual reagent grade furnished by the large chemical supply houses.

Procedure and Analyses. The apparatus and technique employed for the equilibrations were the same as those described for tri-n-octylamine.[4] A series of preliminary rate studies showed that equilibrium was attained by all the DDA solutions *vs.* widely varying amounts of sulfuric acid in at most 30 minutes. The data reported below are based on shaking times of one hour or more at 25.0 ± 0.1°C. Aqueous acid concentrations greater than 10^{-3} *M* were determined volumetrically with standard base. The lower sulfuric acid molarities reported were obtained by pH measurement, using a Beckman Model G meter and an experimentally determined calibration curve. These results are shown with two and three significant figures, but it should be pointed out that they may be in error as much as ± 10%, and possibly more in the very low range. This source of error, together with the known impurity of the amine, is considered to account for the scatter observed in the points calculated for the data below the equivalence point. The reliability of the data above this point is comparable to that encountered in the case of tri-n-octylamine.[4]

Sulfuric acid absorbed into the organic phases was measured by titration with standard sodium ethoxide.[6] When necessary free amine was then determined in the same sample by potentiometric titration with perchloric acid in dioxane.

III. RESULTS AND DISCUSSION

The aqueous sulfuric acid activities used in the graphs and equilibrium constant expressions given below were obtained from Harned and Owen[7] using the graphical method described previously.[4] For brevity and convenience in the following discussion reacting sulfuric acid is written in the undissociated form and the symbol R is used to denote the amine molecule $(C_{10}H_{21})_2NH$.

The results of equilibrations below the equivalence point of DDA solutions ranging from 0.05 to 0.5 M are given in Table I. The reaction for normal sulfate formation is

$$H_2SO_4 + 2R = R_2H_2SO_4 \qquad (1)$$

and the corresponding equilibrium constant, assuming true solution behavior and unit activity coefficients for the benzene soluble species, should be

$$K' = \frac{[R_2H_2SO_4]}{a_{H_2SO_4}[R]^2} \qquad (2)$$

Values of log $a^{1/3}_{H_2SO_4}$ vs. log $[R_2H_2SO_4]/[R]^2$ calculated from the data of Table I are plotted in Figure 2. It is apparent that the data do not conform to the behavior predicted by (2), although in one case (that of the least concentrated solution, 0.05 M) the straight line connecting the points has the required slope of 3. There is no indication of any tendency on the part of the lines for the different concentrations to

Table I

EQUILIBRATION DATA BELOW EQUIVALENCE POINT

A. DDA = 0.0490 M

$[H_2SO_4]_{aq}$	$a^{1/3}_{H_2SO_4}$	$2[H_2SO_4]_{org}$	[R]
3.28×10^{-5}	5.10×10^{-5}	.00952	.0395
5.35×10^{-5}	8.23×10^{-5}	.01909	.0299
7.22×10^{-5}	1.10×10^{-4}	.02868	.0203
1.18×10^{-4}	1.78×10^{-4}	.03813	.0109
1.94×10^{-4}	2.89×10^{-4}	.04259	.00641
2.50×10^{-4}	3.66×10^{-4}	.04483	.00422*
4.66×10^{-4}	6.60×10^{-4}	.04607	.00294*
6.80×10^{-4}	9.30×10^{-4}	.04753	.00157*
1.01×10^{-3}	1.32×10^{-3}	.04830	.00082*
1.48×10^{-3}	1.85×10^{-3}	.04838	.00081*
1.91×10^{-3}	2.31×10^{-3}	.04865	.00063*

B. DDA = 0.0980 M

$[H_2SO_4]_{aq}$	$a^{1/3}_{H_2SO_4}$	$2[H_2SO_4]_{org}$	[R]
7.6×10^{-6}	1.20×10^{-5}	.0096	.0884
1.01×10^{-5}	1.57×10^{-5}	.0193	.0787
1.50×10^{-5}	2.35×10^{-5}	.0300	.0690
2.10×10^{-5}	3.28×10^{-5}	.0386	.0594
3.09×10^{-5}	4.81×10^{-5}	.0578	.0402
3.91×10^{-5}	6.05×10^{-5}	.0676	.0304
5.47×10^{-5}	8.40×10^{-5}	.0771	.0209
1.05×10^{-4}	1.59×10^{-4}	.0866	.0114
1.85×10^{-4}	2.75×10^{-4}	.0911	.0069
2.74×10^{-4}	4.00×10^{-4}	.0930	.0050
3.96×10^{-4}	5.66×10^{-4}	.0948	.0033*
9.01×10^{-4}	1.20×10^{-3}	.0969	.0013*

Table I (Cont'd.)

EQUILIBRATION DATA BELOW EQUIVALENCE POINT

C. DDA = 0.196 M

$[H_2SO_4]_{aq}$	$a^{1/3}_{H_2SO_4}$	$2[H_2SO_4]_{org}$	$[R]$
4.6×10^{-6}	7.3×10^{-6}	.0484	.1476
6.4×10^{-6}	1.0×10^{-5}	.0726	.1234
1.50×10^{-5}	2.3×10^{-5}	.1209	.0751
2.25×10^{-5}	3.5×10^{-5}	.1451	.0509
4.40×10^{-5}	6.8×10^{-5}	.1692	.0268
7.92×10^{-5}	1.21×10^{-4}	.1822	.0138
1.10×10^{-4}	1.66×10^{-4}	.1834	.0126
1.23×10^{-4}	1.85×10^{-4}	.1868	.0092
2.03×10^{-4}	3.00×10^{-4}	.1878	.0082
2.39×10^{-4}	3.50×10^{-4}	.1911	.0050*
3.96×10^{-4}	5.66×10^{-4}	.1916	.0045*
4.98×10^{-4}	7.00×10^{-4}	.1947	.0015*
8.24×10^{-4}	1.11×10^{-3}	.1943	.0020*

D. DDA = 0.490 M

$[H_2SO_4]_{aq}$	$a^{1/3}_{H_2SO_4}$	$2[H_2SO_4]_{org}$	$[R]$
1.0×10^{-6}	1.6×10^{-6}	.0971	.3929
1.0×10^{-6}	1.6×10^{-6}	.1939	.2961
1.5×10^{-6}	2.4×10^{-6}	.2900	.2000
7.0×10^{-6}	1.1×10^{-5}	.3898	.1002
4.50×10^{-5}	5.96×10^{-5}	.4596	.0304
5.35×10^{-5}	8.23×10^{-5}	.4716	.0184
2.12×10^{-4}	3.13×10^{-4}	.4829	.0072*
2.50×10^{-4}	3.66×10^{-4}	.4827	.0074*
4.45×10^{-4}	6.31×10^{-4}	.4866	.0038*

*These values of $[R]$ have been corrected for bisulfate formation in accordance with the footnote on p. 10.

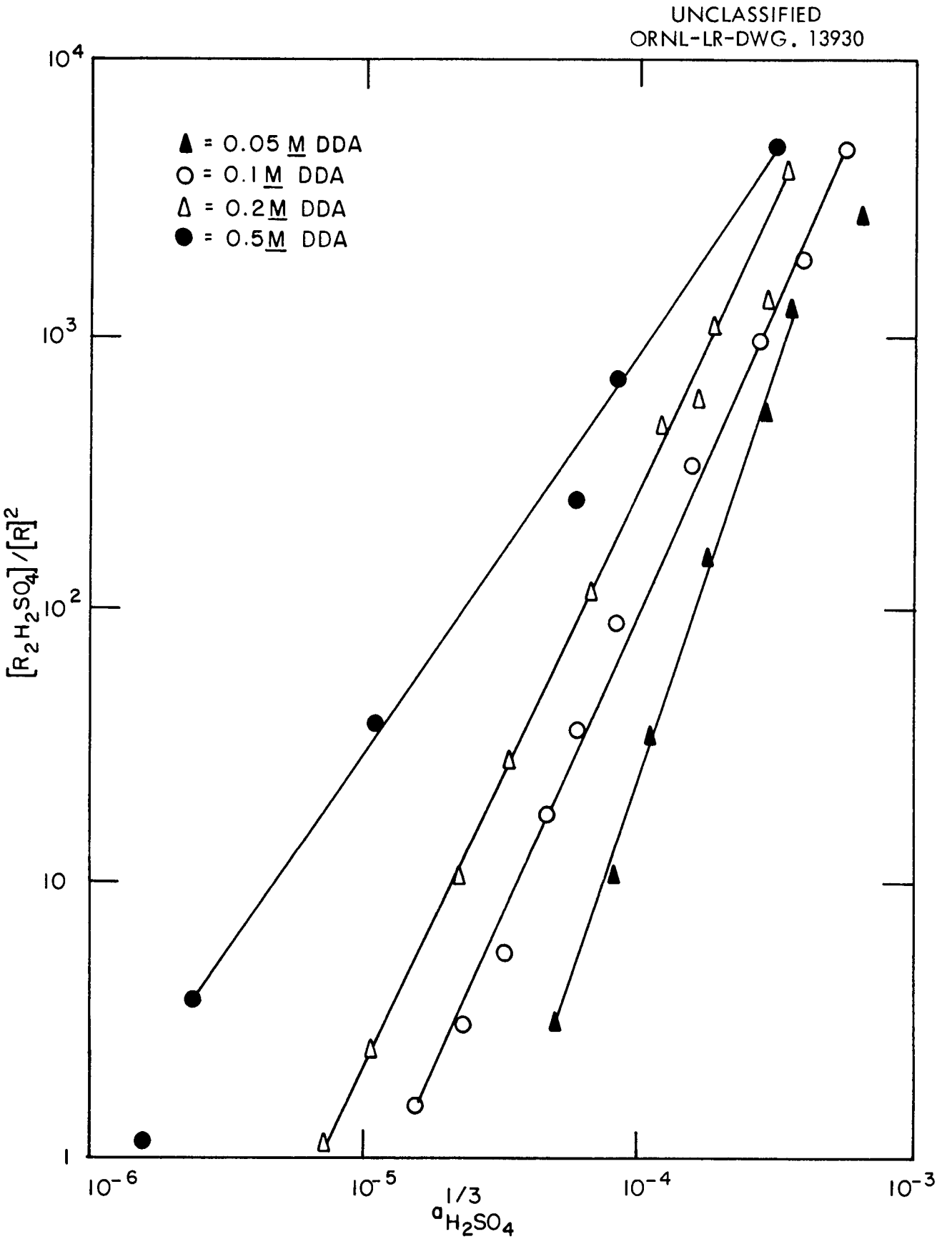

FIGURE 2. NORMAL SULFATE FORMATION

approach coincidence at low organic sulfate levels, as was the case with tri-n-octylamine. Indeed, the opposite appears more likely, and it may be tentatively concluded that with DDA aggregation occurs immediately on the formation of the first amine sulfate.

On this basis (2) may be rearranged, giving

$$a_{H_2SO_4}[R]^2 = \frac{[R_2H_2SO_4]_c}{K'} \qquad (3)$$

where the subscript c denotes the colloidal salt of constant activity. The right hand side of (3) should be a constant, and we write

$$K'' = a_{H_2SO_4}[R]^2, \qquad (4)$$

again assuming unit activity coefficient for the free amine. In Figure 3 log $a^{1/3}_{H_2SO_4}$ is plotted against log $[R]$ for the data of Table 1.* Although the points on this plot exhibit serious scatter, there is no evidence of any systematic

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*As in the case of tri-n-octylamine, bisulfate corrections were found necessary for the low $[R]$ values at high acid activities. These corrections were much smaller here, however, because of the greater basicity of DDA. Free amine concentrations were calculated from the material balance relation

$$R = [\sum R] - 2[\sum S]\frac{1}{1+X} \qquad (5)$$

where $[\sum R]$ and $[\sum S]$ denote, respectively, total amine and total organic sulfate in moles per liter, and the equivalent fraction X of bisulfate was obtained from

$$K_2 = \frac{X^2}{a_{H_2SO_4}(1-X)} = 2600 \text{ (see below)}.$$

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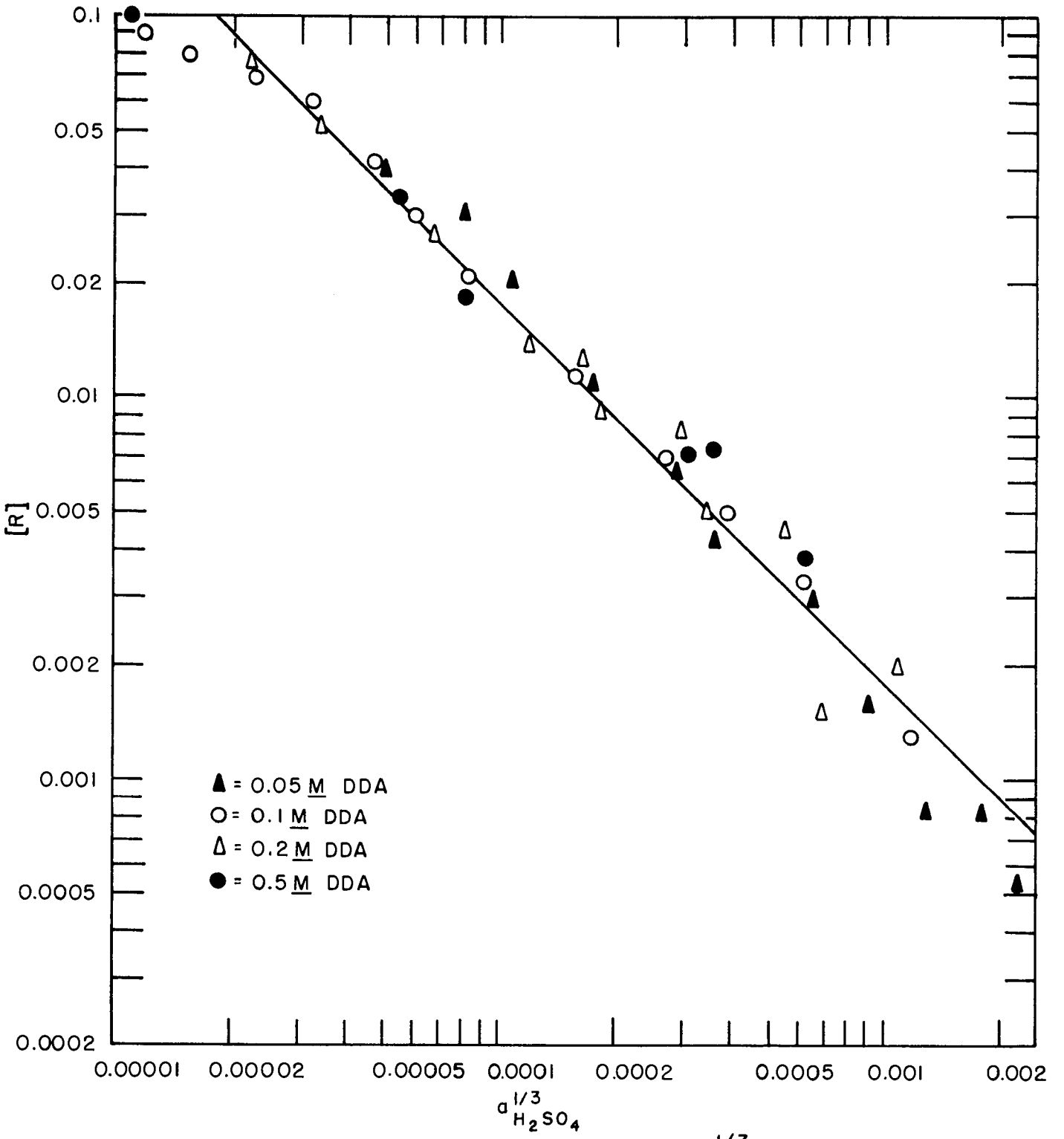

FIGURE 3. FREE AMINE vs $a^{1/3}_{H_2SO_4}$

departure as a function of total amine concentration from the line shown. There is some indication of a general, and possibly real, curvature toward the theoretical slope at high activities. Along the line, the apparent amine sulfate concentrations vary appreciably (e.g., at $[R] = 0.04$, the ratio between $[R_2H_2SO_4]$ for the 0.5 M data and that for the 0.05 M data is ca. 45), and it may be concluded, within the experimental error indicated by the observed scatter, that below the equivalence point the relationship between acid activity and free amine concentration is independent of the amount of salt present.

The line of Figure 3, being of slope -1 instead of -3/2 as predicted by equation (4), leads to an empirical constant of the form

$$K_1 = a_{H_2SO_4}[R]^3 \sim 6\times10^{-18}(\text{moles/liter})^6 \qquad (6)$$

which is consistent with an activity coefficient for the free amine in benzene $\gamma_R \propto [R]^{1/2}$. Tri-n-octylamine was found to obey (4) in this region after correcting for a hypothesized distribution of free amine between solvent and colloid, implying at least a constant activity coefficient.

The results of equilibrations in the bisulfate range are given in Table II. These data were treated as in the previous paper[4]; the formation of amine bisulfate is regarded as an exchange reaction, viz.,

$$2HSO_4^- + R_2H_2SO_4 = 2RH_2SO_4 + SO_4^=. \qquad (7)$$

The sulfate and bisulfate species are considered to form a

Table II

EQUILIBRATION DATA IN BISULFATE RANGE

$[\Sigma R]$	$[H_2SO_4]_{aq}$	$a^{1/3}_{H_2SO_4}$	$2[H_2SO_4]_{org}$	X	$X^2/1-X$
.0500	.00905	.00800	.0518	.036	.00135
"	.0137	.0109	.0528	.056	.00333
"	.0230	.0158	.0550	.100	.0111
"	.0370	.0220	.0575	.150	.0265
"	.0603	.0305	.0620	.240	.0759
.100	.00847	.00760	.1033	.033	.00113
"	.0151	.0117	.1060	.060	.00383
"	.0208	.0148	.1088	.088	.00845
"	.0210	.0149	.1093	.093	.00951
"	.0312	.0196	.1143	.143	.0239
"	.0520	.0278	.1198	.198	.0489
"	.0522	.0279	.1214	.214	.0582
"	.0821	.0372	.1270	.270	.100
"	.1325	.0507	.1346	.346	.183
.200	.0187	.0137	.2125	.0625	.00416
"	.0342	.0208	.2254	.127	.0185
"	.0570	.0294	.2383	.192	.0453
"	.1033	.0430	.2582	.291	.119
"	.1104	.0449	.2639	.320	.150
.500	.0172	.0129	.525	.050	.00263
"	.0348	.0211	.558	.116	.0153
"	.0559	.0290	.587	.174	.0367
"	.0766	.0355	.611	.222	.0634
"	.0949	.0407	.626	.252	.0849
"	.1123	.0455	.640	.280	.109

series of ideal solutions within the colloid, and their activities are taken equal to their respective equivalent fractions.[8] Accordingly,

$$K_2' = \frac{a_{SO_4} = X^2_{RH_2SO_4}}{a^2_{HSO_4} - X_{R_2H_2SO_4}} \qquad (8)$$

Here, for brevity, we put $X = X_{RH_2SO_4} = [RH_2SO_4] / [\sum R]$, and since it is apparent from K_1 that in this region only negligible quantities of amine remain uncombined $X_{R_2H_2SO_4} = 1-X$. The aqueous ion activity ratio can be readily shown to be proportional to $1/a_{H_2SO_4}$ and we obtain the simpler equivalent expression

$$K_2 = \frac{X^2}{a_{H_2SO_4}(1-X)} \qquad (9)$$

In Figure 4 $\log X^2/1-X$ is plotted against $\log a_{H_2SO_4}$, calculated from the data of Table II. Here the 0.05 and 0.1 M data are superimposed on a straight line of the slope (unity) required by (9), but systematic departures are evidenced by the data for the two higher concentrations. These departures are in the direction which would be expected for true solution behavior, although their magnitude is by no means sufficient for any actual correlation on this basis. It seems more reasonable to attribute them to failure of the activity relationship assumed for the colloidal species and expressed in (8) as equivalent fractions. The line shown leads to a value for K_2 of 2600 ± 400 $(\text{moles/liter})^{-3}$, with the restrictions

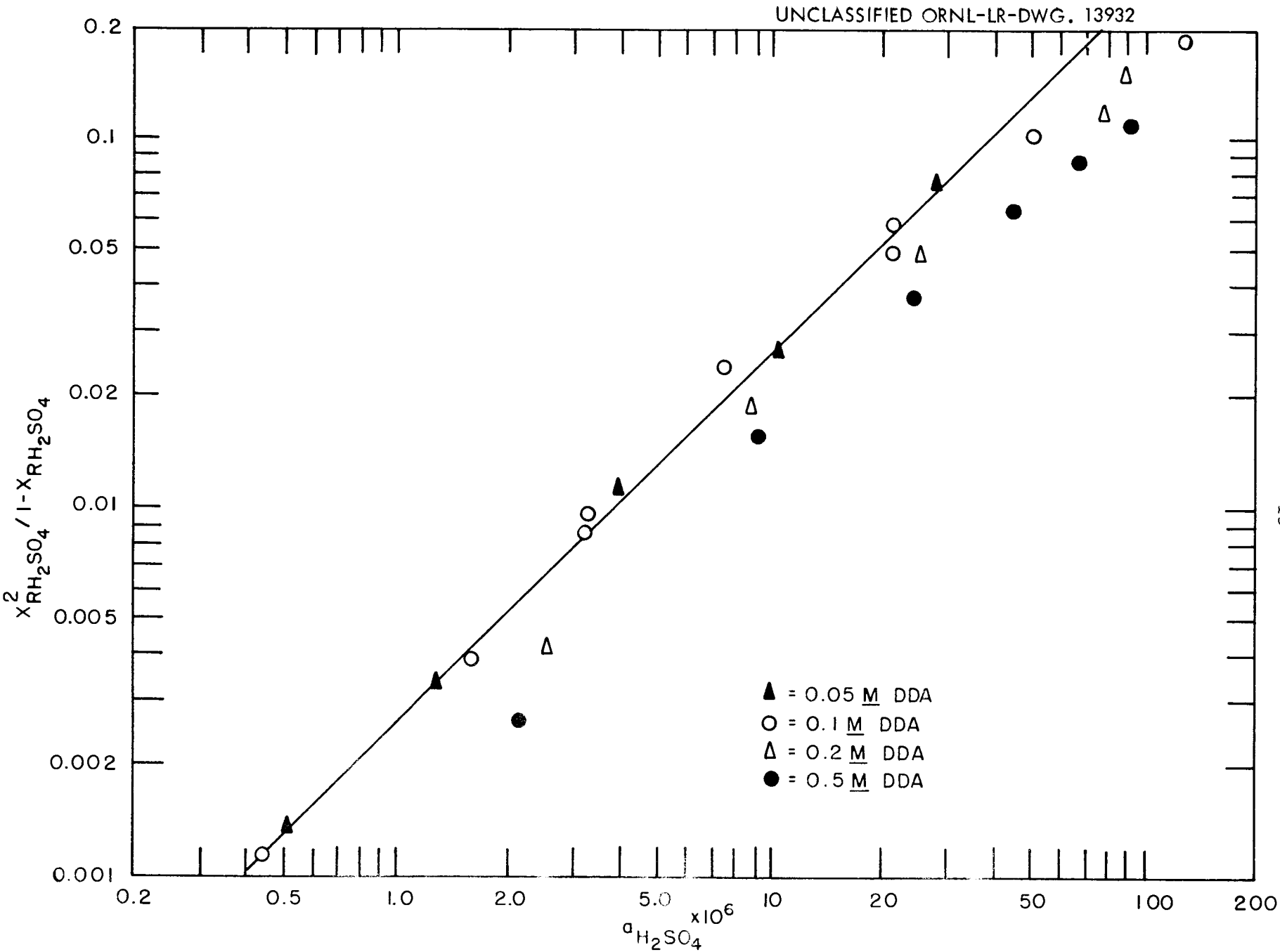

FIGURE 4. BISULFATE EQUILIBRIA

that this constant holds only for total amine concentrations between 0.05 and 0.1 M and for equivalent fractions of bisulfate less than 0.25.* Bisulfate formation in 0.1 M DDA equilibrated with half molar sulfate solutions of varying acid activity was found by Baes[3] to be several percent less than is shown here in the range over which K_2 is valid. On the plot of Figure 4, his data would fall between the line and the points for the 0.2 M solution; this difference may in part be attributed to uncertainty in the values of $a_{H_2SO_4}$ for the half molar sulfate solutions. Unpublished data obtained with one molar sulfate indicate that this trend continues in at least a qualitatively consistent manner.[9]

The curvature away from the line exhibited by the three more concentrated solutions at higher activities is apparently real, and may be taken as an indication of a gradually decreasing tendency for the salt to absorb more bisulfate. Increasing the aqueous sulfuric acid concentration to still higher levels results in the appearance of a precipitate at an acid activity of ca. 1.6×10^{-4}. This solid was found to be the pure bisulfate both from direct analysis[9] and material balance differences (see Table III). A rough estimate of the upper limit of its solubility in benzene at 25° was made by contacting successively diluted DDA solutions with large volumes of half molar sulfuric acid. This experiment limited the solubility of the bisulfate to less than 0.001 M, by visual inspection of the equilibrated organic phases.

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*The bisulfate data obtained by Horner[2] for DDA and dilaurylamine in aromatic mineral spirits at about 35° lead to a value for K_2 (as defined by Equation 9) of ca. 600.

Table III

EQUILIBRATION DATA WITH PRECIPITATED BISULFATE

$[\Sigma R]$	$[H_2SO_4]_{aq}$	Solution		
		$[R]$	$[H_2SO_4]_{org}$	$[H_2SO_4]_{org}/R$
0.1	0.273	0.0212	0.0306	0.69
.1	.365	.0130	.0177	.73
.2	.196	.0766	.111	.69
.2	.297	.0282	.0397	.71
.5	.198	.0550	.0816	.67

$[\Sigma R]$	$[H_2SO_4]_{aq}$	Precipitate		
		R(mmoles)	H_2SO_4 (mmoles)	H_2SO_4/R
0.1	0.273	1.388	1.385	1.00
.2	.196	1.778	1.811	1.02
.5	.198	8.368	8.160	0.97

In another series of equilibrations 0.05, 0.1, 0.2 and 0.5 M DDA solutions were contacted with successively increasing aqueous acid concentrations at 25°. Favorably large aqueous/organic phase ratios were used, and at each acid level a sufficient number of equilibrations were made to ensure equilibrium at a known acid activity. By visual inspection, again, it was shown that in all four amine solutions precipitation occurred between $a_{H_2SO_4} = 1.6 \times 10^{-4}$ and $a_{H_2SO_4} = 1.8 \times 10^{-4}$, which corresponds to the pH range 0.9 to 1.0 for 0.5 M sulfate. In the range of amine molarities used it is therefore concluded that this effect is essentially independent of total amine concentration.

The data shown in Table III were obtained in order to further elucidate this phenomenon, with particular emphasis in this case on the composition of the species remaining in solution after an appreciable fraction of the amine has been precipitated. The mole ratios of sulfate to amine in the species remaining dispersed are very close to two thirds, with slight increases for the 0.1 and 0.2 M solutions at the higher acid concentrations shown. This ratio corresponds to the composition $(R_2H_2SO_4 \cdot RH_2SO_4)_n$ for the aggregate, and is considered to represent an approximate value for an upper limit of bisulfate content consistent with colloidal stability. This effect may be likened to the solubilization phenomena known to occur in other colloidal systems, such as soap solutions. It is evident here that the normal sulfate is capable of forming a co-aggregate with at least an equal molecular proportion of

bisulfate. The bisulfate salt of tri-n-octylamine, on the other hand, was found to be appreciably soluble in benzene,[4] although the hypothesized distribution of free amine between solvent and colloid which was assumed in treating the data obtained with the tertiary amine is related to the co-aggregation observed here.

IV. SUMMARY

The distribution of sulfuric acid between water and benzene solutions of di-n-decylamine ranging from 0.05 to 0.5 M has been shown to be consistent with a treatment based on association of the amine salts in the organic phase. Two constants have been evaluated;

$$K_1 = a_{H_2SO_4}[R]^3 \sim 6\times10^{-18}(\text{moles/liter})^6$$

and

$$K_2 = \frac{X^2_{RH_2SO_4}}{a_{H_2SO_4}\ X_{R_2H_2SO_4}} = 2600 \pm 400(\text{moles/liter})^{-3}.$$

The first describes empirically the formation of colloidally dispersed amine sulfate of constant activity from the reaction between free amine and sulfuric acid. This equilibrium is understandable in terms of the corresponding stoichiometry if the free amine may be regarded to require an activity coefficient proportional to the square root of its molarity in the benzene. The second constant, which describes sulfate-bisulfate exchange within the colloid, is valid only for total

amine concentrations from 0.05 to 0.1 M and equivalent fractions of bisulfate less than 0.25.

Within these limits, in contrast to tri-n-octylamine,[4] the behavior of di-n-decylamine is apparently ideal with respect to the activity relationship implicit in the equivalent fraction ratio.

Above an equilibrium aqueous sulfuric acid activity of ca. 1.6×10^{-4} di-n-decylamine bisulfate is precipitated from the organic phase. This effect is independent of total amine concentration, and the data indicate that the maximum bisulfate content of a stable colloidal dispersion corresponds to the formula $(RH_2SO_4 \cdot R_2H_2SO_4)_n$. At higher aqueous acid levels the dispersed species changes only slightly in composition while amine is rapidly removed from solution as the bisulfate.

V. REFERENCES

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VI. APPENDIX

The plots shown in Figures 5 and 6 are included as a means of presenting the significant results of this investigation in an easily interpreted form. The points were calculated from the equilibrium constants given in the text. Sulfuric acid activities were converted to molarity and then to pH graphically, using an experimentally determined calibration curve for the latter conversion (see Figure 7). In the case of the bisulfate plot (Figure 6) the total di-n-decylamine molarity in benzene should not exceed 0.1 M, although readings at moderately higher concentrations (less than 0.2 M) will not be in serious error. Bisulfate precipitation commences at a pH of about 0.9. The relationships depicted in Figure 5 are independent of total amine concentration.

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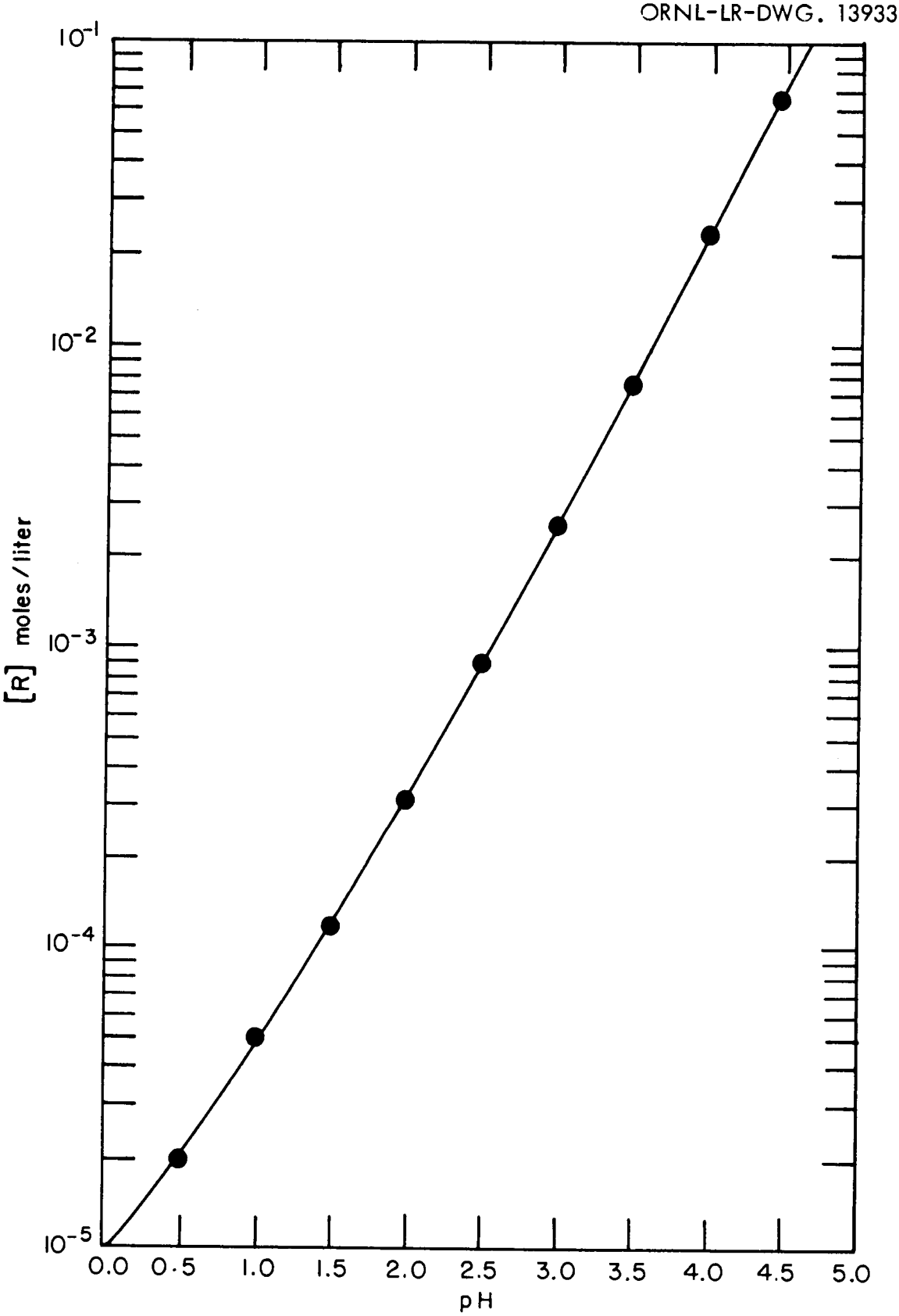

FIGURE 5. FREE DI-N-DECYLAMINE MOLARITY IN BENZENE vs pH OF AQUEOUS SULFURIC ACID AT 25°

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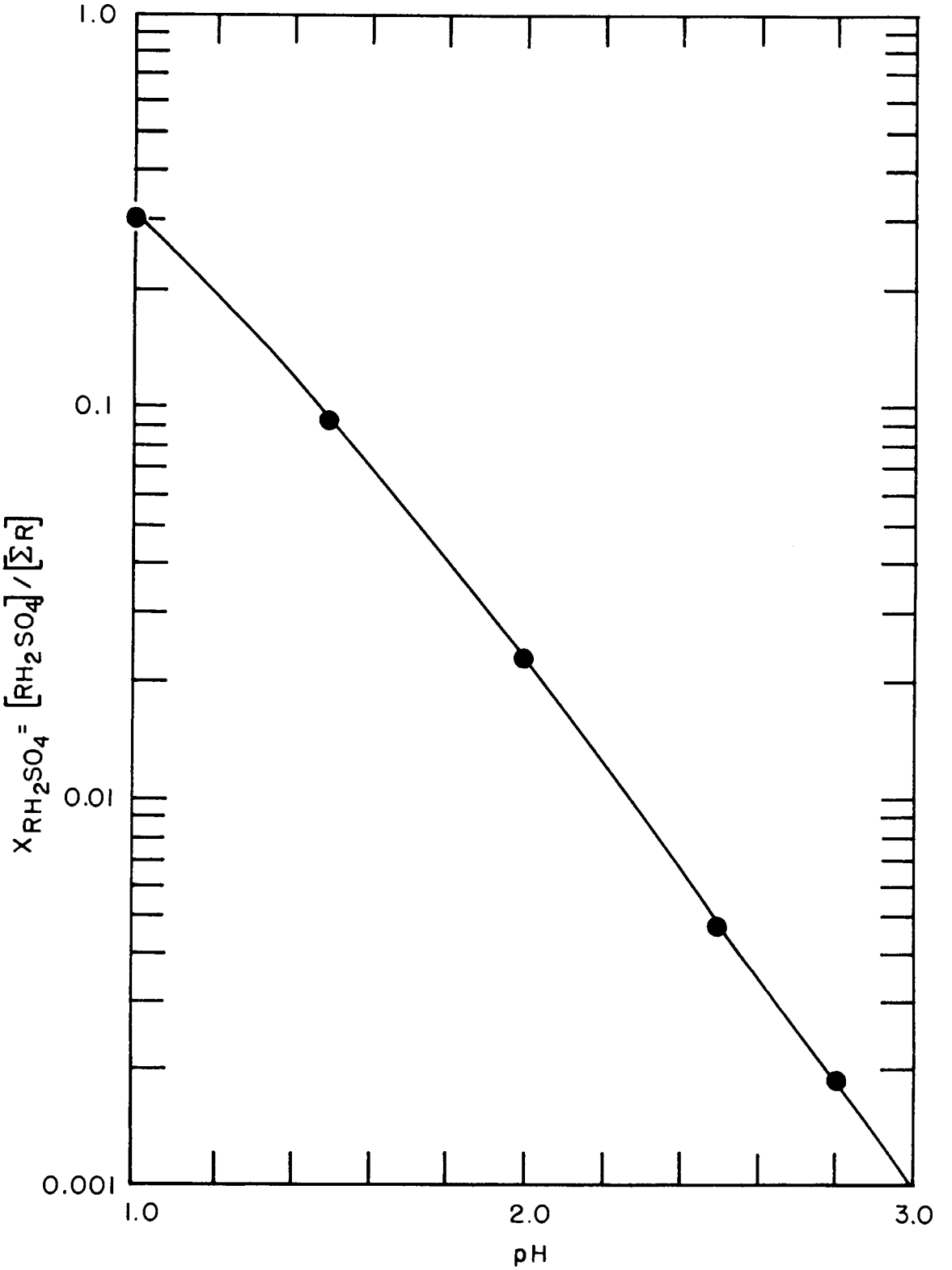

FIGURE 6. COLLOID COMPOSITION AS EQUIVALENT FRACTION OF DI-N-DECYLAMINE IN BISULFATE FORM vs pH OF AQUEOUS SULFURIC ACID AT 25° TOTAL AMINE MOLARITY IN BENZENE MUST NOT EXCEED 0.1M

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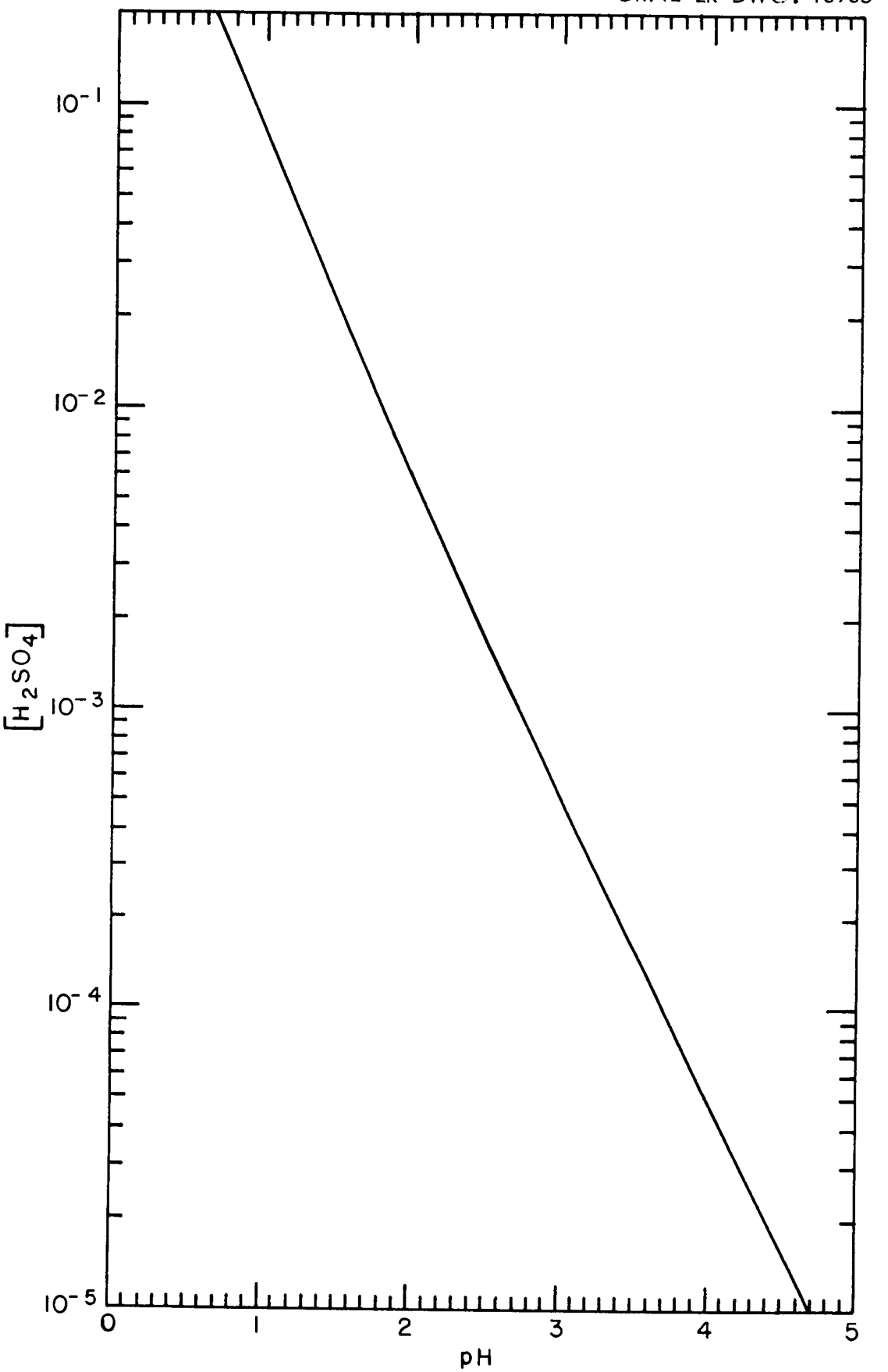

FIGURE 7. SULFURIC ACID MOLARITY vs pH