Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Extraction of Sulfuric Acid in the Tri-*n*-caprylamine-Benzene System

T. K. Kim[a]; V. Chiola[a]
[a] Sylvania Electric Products, Inc. Chemical and Metallurgical Division Towanda, Pennsylvania

To cite this Article Kim, T. K. and Chiola, V.(1968) 'Extraction of Sulfuric Acid in the Tri-*n*-caprylamine-Benzene System', Separation Science and Technology, 3: 5, 455 — 465

To link to this Article: DOI: 10.1080/01496396808052229

URL: http://dx.doi.org/10.1080/01496396808052229

SEPARATION SCIENCE, 3(5), pp. 455–465, Oct., 1968

Extraction of Sulfuric Acid in the Tri-*n*-caprylamine–Benzene System

T. K. KIM and V. CHIOLA
SYLVANIA ELECTRIC PRODUCTS, INC.
CHEMICAL AND METALLURGICAL DIVISION
TOWANDA, PENNSYLVANIA

Summary

Solvent extraction, molecular weight determination, and infrared analysis have been used to study the nature of the amine salt present in the organic phase in the extraction of sulfuric acid by tri-*n*-caprylamine. Tri-*n*-caprylamine in the concentration range of 0.05–0.25 *M* extracts sulfuric acid to form either the normal sulfate or the bisulfate salt, depending on the concentration of acid in the aqueous phase. The normal sulfate is monomeric, while the bisulfate is dimeric. Characteristic infrared absorption bands, attributable to the normal sulfate and the bisulfate salt form, were observed.

The extraction of various acids by the use of the acid-binding properties of high molecular weight aliphatic amines was first reported by Smith and Page (*1*). A number of papers concerning the extraction of nitric, hydrochloric, and sulfuric acids by high molecular weight amines have appeared since then (*2–4*). The first quantitative study of sulfuric acid extraction by tri-*n*-octylamine was made by Allen (*5*). Later, the nature of amine sulfate was investigated by a light-scattering method (*6*). The extraction of sulfuric acid by high molecular weight amines has since been studied extensively by various workers (*7–11*).

High molecular weight amines in general show unusual capabilities for extracting metal ions and it has been widely shown that amine salts are involved in the extraction. Elucidation of the formation and nature of the amine salt is essential for understanding the mechanism of metal extraction.

The present work is part of a broader investigation of soluble tungstate species by solvent extraction with tri-*n*-caprylamine (*12*). During the course of this work it became necessary to determine the distribution of sulfuric acid between the aqueous phase and a benzene solution of amine. The amine salt formed was studied by vapor-pressure osmometry, the extraction isotherm, and its infrared spectrum.

EXPERIMENTAL

Tri-*n*-caprylamine was obtained as a commercial grade of symmetrical tertiary amine from General Mills' Chemical Division (Alamine 336). Purification was accomplished by distillation at 4–5 torr to remove the fraction boiling below 110°C. The fraction remaining in the distillation flask was taken as the purified amine. The molecular weight of this fraction, as determined by vapor-pressure osmometry, was 387.61. The tertiary-amine content was 96% and was determined by nonaqueous potentiometric titration with perchloric acid in a mixture of glacial acetic acid and acetic acid anhydride.* The purified amine was used throughout this work. All other chemicals were reagent grade.

Procedure

A sulfuric acid solution of known concentration was shaken mechanically at 25 ± 0.5°C for 1 hr with an equal volume of organic extractant containing a known concentration of the amine in benzene. Two hours were allowed for settling and phase separation. The optimum equilibration time was determined previously.

A Fisher Titralyzer was used to determine the acid content of the aqueous phase by titration with standard NaOH solution. The acidity of the organic phase was determined from the difference in the initial acidity of the aqueous phase and its residual acidity after equilibration. In some cases, the acidity of the organic phase was determined by nonaqueous titration (*10*), in order to verify the material balance. Results of the two methods were within ±4%.

---

* J. W. Roddy, Oak Ridge National Laboratory, Oak Ridge, Tenn., private communication.

The vapor-pressure measurement of the amine and the amine salts in benzene solution were made at 20°C with a Mechrolab Vapor Pressure Osmometer, Model 302. With benzil (Eastman Organic Chemicals) as a standard for calibration, the calibration curve was essentially linear.

Preparation of the Amine Salts for Molecular Weight Determination

A known concentration of the amine in benzene solution was converted to the amine salt by equilibration with a known concentration of sulfuric acid. After equilibration, the salt was washed three times with deionized water in order to remove excess sulfuric acid. The washed product was subjected to reduced pressure (0.5 torr) in order to prepare benzene- and water-free amine salt.

Infrared Measurements

Infrared measurements on the amine salt was obtained with a Perkin-Elmer Model 221 which was equipped with thallium halide windows.

RESULTS AND DISCUSSION

Acid-Extraction Isotherm

The transformation of a tertiary amine to the corresponding amine salt, which is accomplished by the equilibration of the free amine with sulfuric acid solution, may give rise to either the amine normal sulfate or the amine bisulfate.

To determine which salt form predominates in the organic phase, extraction isotherms (equilibrium curves) of 0.05, 0.10, 0.15, 0.22, and 0.25 *M* concentrations of amine in benzene solution were constructed. The extraction isotherms of 0.15 and 0.22 *M* amine solutions are shown in Figs. 1 and 2. These show three regions in which the magnitudes of the acid-extraction coefficients differ significantly.

Very high extraction coefficients of acid are obtained when the equilibrium concentration of acid in the aqueous phase does not exceed about 0.02 *M*. This is the region where the amine sulfate exists predominantly. The reaction between the amine and sulfuric acid may be represented as follows:

$$2R_3N_{(org)} + (H_2SO_4)_{(aq)} \rightleftharpoons [(R_3NH)_2SO_4]_{(org)} \qquad (1)$$

where R_3N represents free amine and (org) and (aq) represent organic and aqueous phases, respectively.

The equilibrium constant *K* can be written as follows on the assumption that the concentrations in the organic phase are equal to the activities.

$$K = \frac{[(R_3NH)_2SO_4]_{(org)}}{(AH_2SO_4[R_3N]^2)_{(org)}} \qquad (2)$$

AH_2SO_4 represents the activity of aqueous sulfuric acid. Values of the mean ionic activity coefficient of sulfuric acid ($\gamma^{\pm}$) were taken from Harned and Owen (*13*).

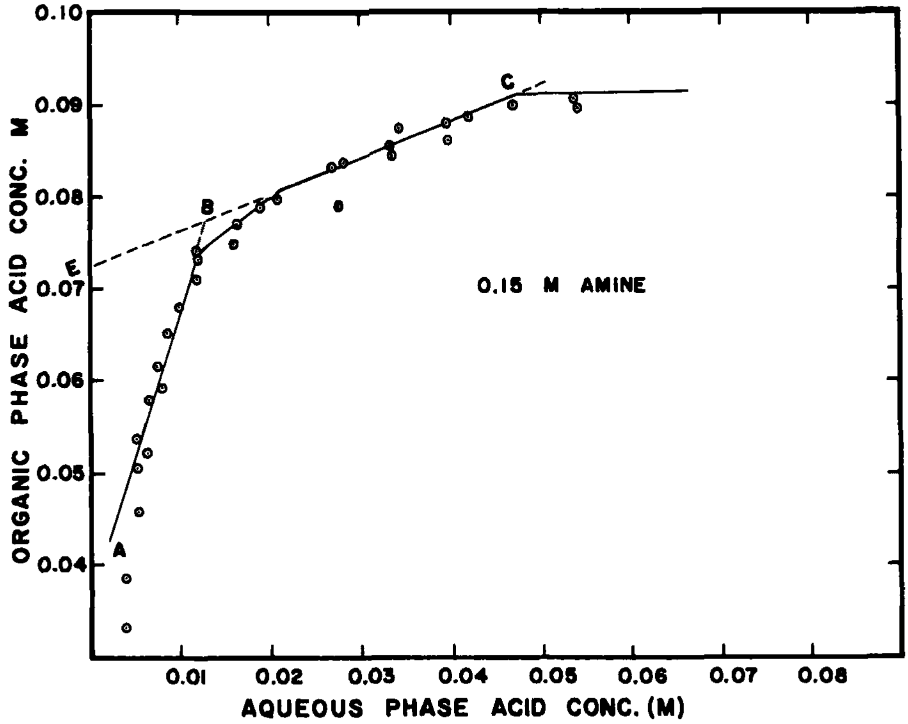

FIG. 1. Extraction isotherm: 0.15 *M* tricaprylamine in benzene; various concentrations of sulfuric acid.

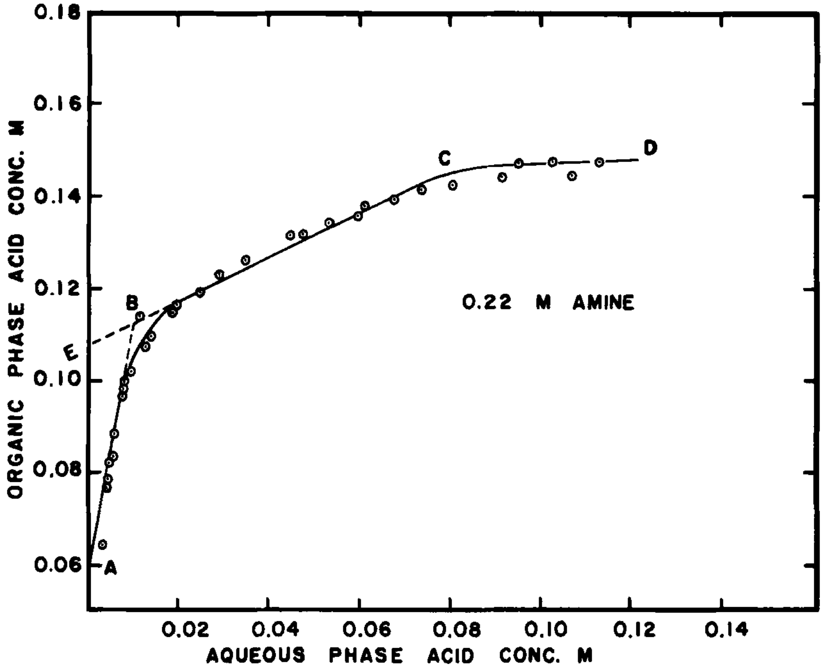

FIG. 2. Extraction isotherm: 0.22 *M* tricaprylamine in benzene; various concentrations of sulfuric acid.

The molar activity of sulfuric acid is obtained from the following equation:

$$AH_2SO_4 = 4\gamma^{\pm}M^3 \tag{3}$$

where *M* represents the acid concentration of the aqueous phase after equilibration.

The total amine concentration $\Sigma[R_3N]$ is as follows:

$$\Sigma[R_3N] = [R_3N] + 2[(R_3NH)_2SO_4] \tag{4}$$

where $[R_3N]$ denotes the concentration of free amine. The calculated values for *K* are given in Table 1. The averaged equilibrium constant is 3.24×10^8 when the amine concentration is 0.05–0.22 *M*. When the amine concentration was 0.25 *M*, *K* values were unusually high.

TABLE 1

Equilibrium Constant

Amine conc.	K
0.05	2.85×10^8
0.10	3.17×10^8
0.15	3.49×10^8
0.22	3.46×10^8
0.25	6.78×10^9

Allen (5), using tri-*n*-octylamine, reported K values of 1.90×10^8. Wilson also obtained K values of 1.4×10^8 for tri-*n*-octylamine.* Verstegen and Ketelaar (*10*), using tri-*n*-octyl- and tri-*n*-hexylamine, found K values of 1.87×10^7 and 0.45×10^7, respectively.

Logarithmic plots of AH_2SO_4 versus $[(R_3NH)_2SO_4]/[R_3N]^2$ for all of the amine concentrations examined resulted in essentially straight lines having slopes equal to about 1. Figure 3 shows typical plots for 0.05 and 0.10 M amine in benzene. From these data, it is concluded that (a) the reaction takes place according to Eq. (1) and (b) the predominant species which exists in the region is the amine normal sulfate. It can be seen that there is a systematic departure point in the plot when the acid concentration in the equilibrium aqueous phase exceeds about 0.02 M. This is the point where amine bisulfate is thought to start to form.

Allen (5) demonstrated that a logarithmic plot of AH_2SO_4 versus $[(R_3NH)_2SO_4]/[R_3N]^2$ gave a straight line having a unit slope when sulfuric acid was extracted by tri-*n*-octylamine of 0.05, 0.1, 0.25, and 0.5 M concentration in benzene. He found also that the formation of normal sulfate occurs when the acidity of the aqueous phase at equilibrium is less than 0.02 M. Above 0.02 M, it was considered that aggregation of the salt begins. The conclusion was based on the evidence of the systematic departure point in the logarithmic plot of AH_2SO_4 versus $[(R_3NH)_2SO_4]/[R_3N]^2$. Verstegen and Ketelaar (*10*) also found that tri-*n*-octylamine normal sulfate forms predominantly at low acidities, that is, when the sulfuric acid concentration of the aqueous phase after equilibration is less

---

* A. S. Wilson, Battelle Memorial Northwest Laboratory, Richland, Wash., private communication.

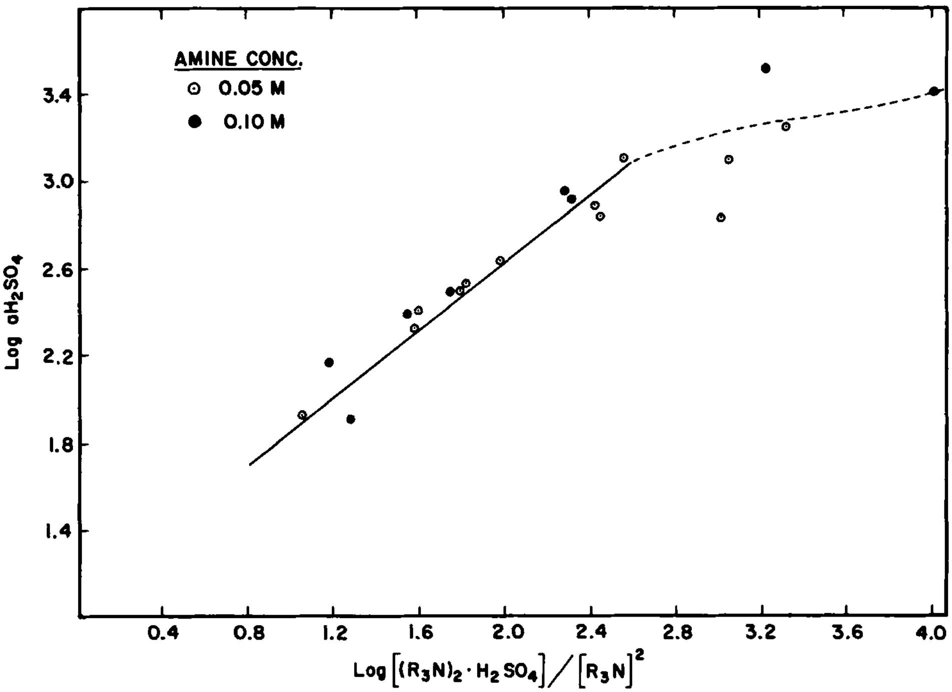

FIG. 3. Activity of sulfuric acid versus $[(R_3N)_2 \cdot H_2SO_4]/[R_3N]^2$.

than 0.02 *M*. When tri-*n*-hexylamine is the extractant, normal sulfate salt forms if acid concentration is less than 0.03 *M*.

At higher acid concentrations, deviations were found in the plot of free-amine concentration versus $\sqrt[3]{AH_2SO_4}$. Such deviations were ascribed to the point where the formation of amine bisulfate began.

Following the region of very efficient acid extraction, the extraction coefficient decreases gradually. This is the region where an additional acid molecule is extracted and amine bisulfate starts to form. The reaction may be represented as follows:

$$[(R_3NH)_2SO_4]_{(org)} + (H_2SO_4)_{(aq)} \rightleftharpoons 2[(R_3NH)HSO_4]_{(org)} \quad (5)$$

Examination of the extraction isotherms shows two regions where straight lines may be drawn. One of these corresponds to the region where the amine sulfate exists predominantly and another to the region where amine bisulfate is forming. The line BC, corresponding to bisulfate formation in Figs. 1 and 2, can be extrapolated to intersect the vertical axis at E.

The mole ratio of amine to acid in the organic phase as determined from the point of intersection was found to be 2:1 in all cases. The intersection point of A–B and B–C is considered the point where the amine is completely transformed to amine salt, and no free amine is available. Beyond the intersection point, amine normal sulfate starts to react with additional acid, as shown by Eq. (5). Following that region, the extraction coefficient decreases until the mole ratio of acid to amine in the organic phase approaches 1.

Vapor-Pressure Measurements of the Amine Salts

The aggregation of the amine salts was studied by vapor-pressure measurements. It has been reported, on the basis of a light-scattering technique, that tri-*n*-octylamine sulfate is monomeric, while tri-*n*-octylamine bisulfate is dimeric (6).

In the preparation of the amine salts for vapor-pressure measurements, the initial acid concentration of the aqueous phase was selected on the basis of extraction-isotherm data, so that there would result predominantly either the normal sulfate or bisulfate form. The average molecular weights of benzene–free amine salts

TABLE 2

Typical Molecular Weight Determinations of Amine Salts

Molecular weight determined by VPO[a]	1011.20	790.54	945.50	774.24
Molecular weight calculated as monomer[b]	485.62	874.23	485.62	874.23
Conc. of initial amine, M	0.22	0.22	0.15	0.15
Acid conc. of aqueous phase, M	0.25	0.10	0.20	0.08
Aggregation no.	~2	~1	~2	~1
Salt form	Bisulfate	Normal sulfate	Bisulfate	Normal sulfate

[a] VPO, vapor-pressure osmometer.

[b] Molecular weight, calculated, based on the average molecular weight of free tri-*n*-caprylamine determined by VPO.

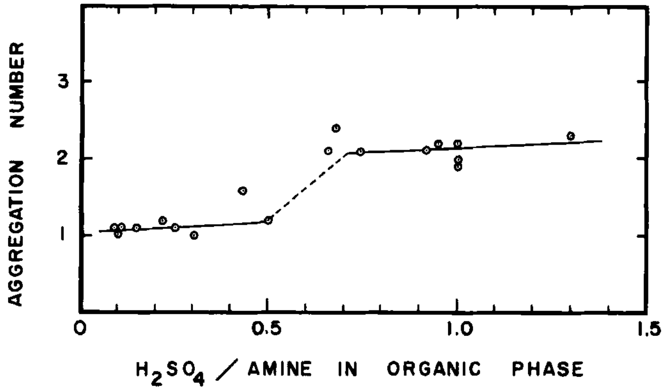

FIG. 4. Aggregation number of amine salts versus the ratio of sulfuric acid to amine in organic phase.

as determined from vapor-pressure measurements are summarized in Table 2.

The aggregation number was found to be about 1 for the normal sulfate, indicating a monomeric form, and about 2 for bisulfate, corresponding to a dimeric form. Figure 4 shows the relationship between aggregation number and the ratio of acid concentration to the amine concentration.

Marcus (*14*) suggested that symmetrical tertiary amine normal sulfates are usually monomeric, while the bisulfate form is dimeric (*14*). On the other hand, nonsymmetrical tertiary amine normal sulfates tend to exhibit larger aggregation numbers, indicating polymeric forms.

Infared Measurements

On the basis of infared-absorption spectra on aqueous solutions of sulfuric acid, characteristic bands attributable to the vibrations of sulfate and bisulfate ions have been assigned (*15*). Characteristic infared-absorption bands due to amine sulfate and amine bisulfate have been reported after the extraction of sulfuric acid by tri-*n*-dodecylamine (*4*) and tri-*n*-octylamine (*16*).

Infared analysis of the organic phase obtained from the extraction of sulfuric acid solutions with 0.1 *M* amine in benzene substantiates extraction-isotherm and molecular weight data. The

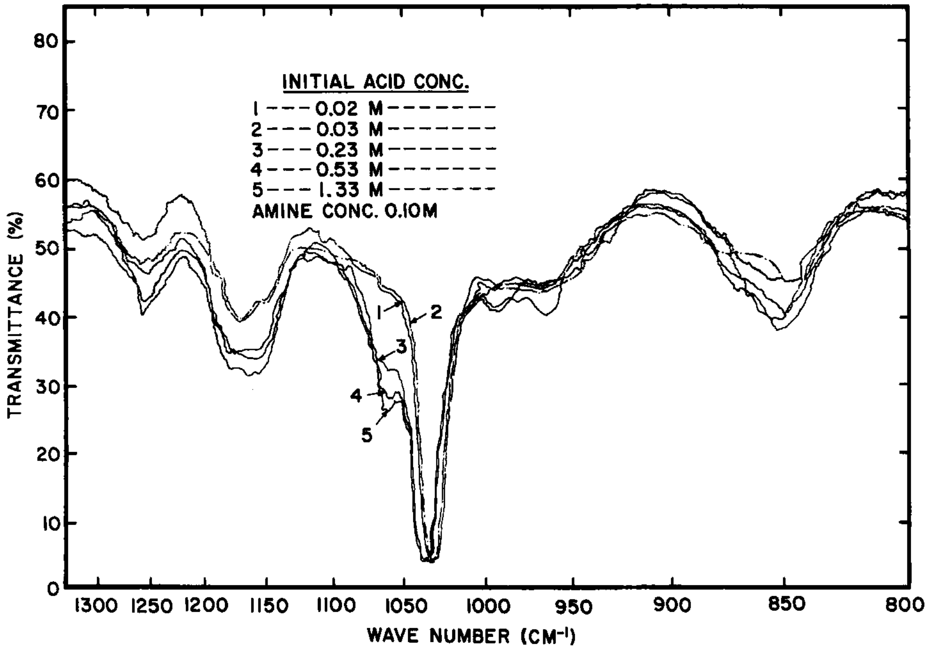

FIG. 5. Infared spectra of organic phases. Extraction of various concentrations of sulfuric acid with 0.10 *M* tricaprylamine.

data given in Fig. 5 and Table 3 show that the bands assigned to the sulfate ion, 1160–1180 and 1040 cm^{-1}, are observed after extraction of 0.02 and 0.03 *M* sulfuric acid solutions. When initial acid concentrations are 0.23, 0.53, and 1.33 *M*, the 1160–1180 cm^{-1} band splits into two bands, 1070 and 1150–1180 cm^{-1}, correspon-

TABLE 3

Infrared Data of the Amine Salt Solution

Alamine 336, *M*	Initial H_2SO_4, *M*	Bands observed, cm^{-1}
0.10	0.02	1040, 1160–1180
0.10	0.03	1040, 1160–1180
0.10	0.23	1040, 1150–1180, 1070, 850, 1250
0.10	0.53	1040, 1150–1180, 1070, 850, 1250
0.10	1.33	1040, 1150–1180, 1070, 850, 1250

ding to the absorption of the bisulfate ion. In addition, there appear two bands at 850 and 1250 cm^{-1} absorption. Intensities due to the bisulfate ion increase with increasing acid concentration.

REFERENCES

1. E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.*, **67**, 48 (1948).
2. F. J. Baroncelli, G. Scibona, and M. Zifferera, *J. Inorg. Nucl. Chem.*, **24**, 405 (1962).
3. P. J. Lloyd and E. A. Mason, *J. Phys. Chem.*, **68**, 3120 (1964).
4. T. Sato, *J. Inorg. Nucl. Chem.*, **24**, 1267 (1962).
5. K. A. Allen, *J. Phys. Chem.*, **60**, 239 (1956).
6. K. A. Allen, *J. Phys. Chem.*, **62**, 1119 (1958).
7. V. V. Fomin, P. A. Zagorets, and A. F. Morgunov, *Zh. Neorgan. Khim.*, **4**, 700 (1959).
8. C. Boirie, *Bull. Soc. Chim. France,* **1958**, 1088.
9. J. M. P. J. Verstegen and J. A. A. Ketelaar, *Trans. Faraday Soc.*, **57**, 1527 (1961).
10. J. M. P. J. Verstegen and J. A. A. Ketelaar, *J. Phys. Chem.*, **66**, 216 (1962).
11. C. F. Coleman and J. W. Roddy, *ORNL P 2354* (1966).
12. T. K. Kim, R. W. Mooney, and V. Chiola, unpublished work.
13. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions,* Reinhold, New York, 1958.
14. Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).
15. G. E. Walrafern and D. M. Dodd, *Trans. Faraday Soc.*, **57**, 1286 (1961).
16. T. Sato, *J. Appl. Chem.*, **15**, 10 (1965).

Received by editor July 5, 1968
Submitted for publication September 5, 1968