[Contribution from the Thompson Chemical Laboratory, Williams College]

# The Conductance of Sulfamic Acid and Some Sulfamates in Water at 25° and Conductance Measurements of Some Long Chain Sulfamates in Water and in Water–Acetone Mixtures at 25°[1]

By Edward G. Taylor, Robert P. Desch and Arthur J. Catotti

Recent work[2] has indicated that the conductance of long chain electrolytes in aqueous media may be markedly affected by the nature of the gegenions. It has been suggested that, among other factors, the size of the gegenion and thus its conductance, may have an important influence on the shape of the conductance curve below the critical concentration. Grieger and Kraus[3] have shown that the maximum phenomenon in mixed solvents appears to be associated with the slower moving gegenions. It was decided to investigate certain long chain sulfamates since the earlier work of Sakurai,[4] Winkelblech[5] and Hantzsch and Stuer[6] on sulfamic acid has shown that the sulfamate ion possesses a relatively low conductance. Furthermore, in view of the reported high strength of the acid we may neglect any effects due to hydrolysis. However, as may be seen from Fig. 1 there are certain inconsistencies in the earlier work on sulfamic acid while for sodium sulfamate there are large discrepancies in the conductance measurements.[4,5] We have therefore measured the conductances of dilute aqueous solutions of sulfamic acid, potassium sulfamate, ammonium sulfamate and silver sulfamate at 25°. The limiting conductance of the sulfamate ion is found to be 48.6 while the dissociation constant of the acid is $1.01 \times 10^{-1}$. We have found evidence of ion pair association in the case of silver sulfamate, for which the dissociation constant is $1.03 \times 10^{-1}$. Finally, conductance measurements in water and in 10% acetone–water mixtures at 25° were made with octadecyltrimethylammonium, hexadecyltrimethylammonium, octadecylpyridonium and hexadecylpyridonium sulfamates.

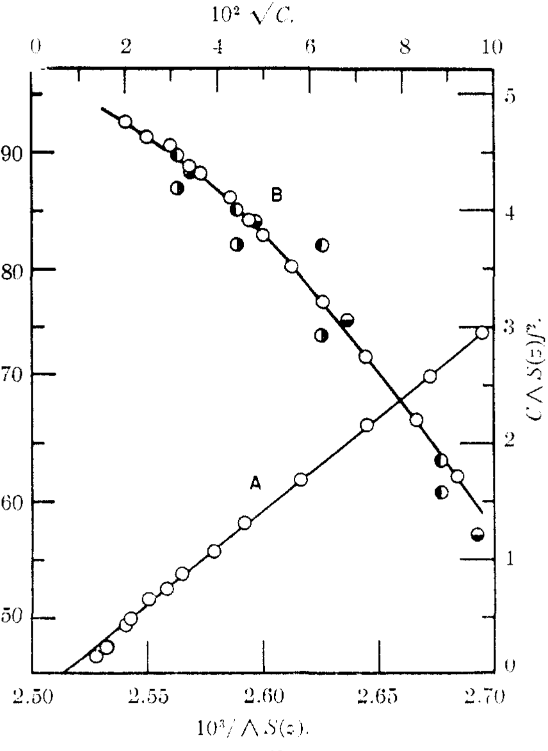

Fig. 1.—Conductance of sulfamic acid in water: A, Shedlovsky plot, bottom and right-hand scales; B, $\Lambda-\sqrt{C}$ plot, top and left-hand scales, ◐ Sakurai, ◑ Winkelblech, ◒ Hantzsch and Stuer, ○ ours.

## Experimental

**Materials.**—Sulfamic acid was purified at least four times according to the method described by Sisler, Butler and Audrieth.[7] Potassium sulfamate was prepared by the interaction of equivalent amounts of potassium hydroxide and sulfamic acid in aqueous solution. The salt was precipitated by the addition of ethanol and recrystallized from ethanol–water and from acetone–water mixtures, m.p. 222.5° (all melting points are corrected). Ammonium sulfamate was similarly prepared from ammonia gas and sulfamic acid dissolved in aqueous ethanol. It was purified by repeated precipitation from aqueous ethanol with acetone, m.p. 130°. Silver sulfamate was obtained by the metathesis of purified ammonium sulfamate and silver nitrate in aqueous solution. The precipitate was thoroughly washed with cold water and the precipitate further purified by precipitation from aqueous solution with acetone.

*n*-Octadecyl and *n*-hexadecyl iodides were prepared from the corresponding alcohols using the method described by Levene, West and van der Scheer.[8] *n*-Octadecyl iodide was recrystallized from hexane, m.p. 34–35°; *n*-hexadecyl iodide was purified by distillation, m.p. 22.5–23.5°.

The alkyltrimethylammonium iodides were prepared by heating the corresponding alkyl iodides with excess of trimethylamine in methanol solution at 60° for several days. The excess of trimethylamine was removed on a steam-bath and the salts recrystallized from anhydrous ethyl acetate, from ethanol–ether mixtures and by precipitation from ethanol solution using acetone. The alkylpyridonium iodides were obtained by heating the alkyl iodides with excess pyridine at 60° for several hours. *n*-Octadecylpyridonium iodide was recrystallized from ligroin–ethanol mixtures, m.p. 103–104°, while *n*-hexadecylpyridonium iodide was recrystallized from mixtures of absolute ethanol and ether, m.p. 98–99°.

The sulfamates were prepared by metathesis of the corresponding quaternary iodides with silver sulfamate in ethanol. After filtering and evaporation of the filtrate to dryness these salts were repeatedly recrystallized from acetone containing about 10% of absolute ethanol: *n*-octadecylpyridonium sulfamate, m.p. 97–98°; *n*-hexadecylpyridonium sulfamate, m.p. 92–93°. It was not possible to determine accurate melting points for the alkyltrimethylammonium sulfamates because of pronounced shrinkage effects during heating.

The specific conductance of the solvents used for the runs was always about $1 \times 10^{-6}$ ohms$^{-1}$ or less.

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(1) This paper comprises parts of theses submitted by Arthur J. Catotti (June, 1949) and Robert P. Desch (June, 1950) in partial fulfillment of the requirements for the Degree of Master of Arts at Williams College.

(2) Grieger, ref. 1, *Ann. N. Y. Acad. Sci.*, **56**, 827 (1949).

(3) Grieger and Kraus, This Journal, **70**, 3803 (1948).

(4) Sakurai, *J. Chem. Soc.*, **69**, 1654 (1896).

(5) Winkelblech, *Z. physik. Chem.*, **36**, 546 (1901).

(6) Hantzsch and Stuer, *Ber.*, **38**, 1022 (1905).

(7) Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 178.

(8) Levene, West and van der Scheer, *J. Biol. Chem.*, **20**, 525 (1915).

**Apparatus.**—The weight dilution method was used throughout. Due doubtless to the uncertainty surrounding the solvent correction it was not possible to obtain accurate measurements much below $4 \times 10^{-4}$ $N$ in aqueous solutions of the long chain sulfamates. Resistances were measured using an alternating current Wheatstone bridge essentially the same as that described by Luder.[9]

Several conductance cells of the Erlenmeyer type described by Kraus and Fuoss[10] were used. They were fitted with small lightly platinized electrodes. At least two conductance runs were made with each compound, the latter being recrystallized between the runs.

## Results

In Tables I, II and III are presented the values of the equivalent conductance and the square root of the concentration in moles per liter of solution. The densities of the solutions have been taken as that of the pure solvent.

TABLE I

THE CONDUCTANCES OF SULFAMIC ACID AND SOME SULFAMATES IN WATER AT 25°

| $10\sqrt{C}$ | $\Lambda$ | $10\sqrt{C}$ | $\Lambda$ |
|---|---|---|---|
| Sulfamic acid | | Potassium sulfamate | |
| 2.041 | 392.3 | 1.526 | 120.8 |
| 2.491 | 391.1 | 1.942 | 120.2 |
| 2.976 | 390.3 | 2.395 | 119.9 |
| 3.410 | 388.6 | 2.938 | 119.5 |
| 3.623 | 388.0 | 3.248 | 119.1 |
| 4.282 | 385.8 | 3.406 | 119.2 |
| 4.668 | 384.2 | 3.877 | 118.6 |
| 4.976 | 382.6 | 4.565 | 118.0 |
| 5.570 | 379.9 | 4.633 | 118.0 |
| 6.276 | 377.0 | 4.879 | 117.7 |
| 7.199 | 372.3 | 5.613 | 117.1 |
| 8.326 | 366.8 | 5.967 | 116.9 |
| 9.205 | 362.0 | 6.569 | 116.2 |
| 9.966 | 357.9 | 7.380 | 115.6 |
| | | 7.835 | 115.2 |
| | | 8.342 | 114.8 |
| Ammonium sulfamate | | Silver sulfamate | |
| 1.629 | 120.8 | 1.589 | 109.1 |
| 2.103 | 120.1 | 2.069 | 108.4 |
| 2.740 | 119.5 | 2.560 | 107.7 |
| 3.222 | 119.2 | 2.981 | 107.2 |
| 3.486 | 118.9 | 3.719 | 106.3 |
| 4.011 | 118.4 | 4.400 | 105.3 |
| 4.540 | 118.0 | 4.987 | 104.4 |
| 5.206 | 117.4 | 5.644 | 103.4 |
| 6.162 | 116.5 | 6.069 | 102.7 |
| 8.300 | 115.0 | 7.515 | 100.4 |
| | | 8.065 | 99.39 |

TABLE II

THE CONDUCTANCES OF SOME LONG CHAIN SULFAMATES IN WATER AT 25°

| $10\sqrt{C}$ | $\Lambda$ | $10\sqrt{C}$ | $\Lambda$ |
|---|---|---|---|
| *n*-Octadecyltrimethylammonium sulfamate | | *n*-Hexadecyltrimethylammonium sulfamate | |
| 1.048 | 67.25 | 1.732 | 67.93 |
| 1.565 | 65.43 | 2.298 | 67.85 |
| 1.925 | 64.06 | 2.678 | 67.32 |
| 2.172 | 61.74 | 3.247 | 66.88 |
| 2.509 | 57.80 | 3.533 | 66.06 |
| 3.274 | 50.47 | 4.452 | 58.88 |
| 4.068 | 45.21 | 4.830 | 55.77 |
| Data for 2 further runs not included; points included in Fig. 2 | | 5.548 | 50.78 |
| *n*-Octadecylpyridonium sulfamate | | *n*-Hexadecylpyridonium sulfamate | |
| 0.754 | 68.18 | 1.294 | 69.22 |
| 1.048 | 68.05 | 2.064 | 68.56 |
| 1.509 | 67.88 | 2.844 | 67.84 |
| 2.027 | 67.15 | 2.956 | 67.85 |
| 2.250 | 65.31 | 3.721 | 62.65 |
| 2.504 | 61.84 | 4.281 | 58.10 |
| 3.053 | 55.47 | 4.357 | 57.58 |
| 3.543 | 51.46 | 5.653 | 49.76 |
| 3.758 | 48.97 | 6.359 | 46.65 |
| 4.529 | 44.68 | | |
| 5.130 | 40.91 | | |

TABLE III

THE CONDUCTANCES OF SOME LONG CHAIN SULFAMATES IN 10% ACETONE–WATER MIXTURES AT 25°

| $10\sqrt{C}$ | $\Lambda$ | $10\sqrt{C}$ | $\Lambda$ |
|---|---|---|---|
| *n*-Octadecyltrimethylammonium sulfamate | | *n*-Hexadecyltrimethylammonium sulfamate | |
| 1.512 | 54.66 | 1.210 | 56.21 |
| 1.954 | 56.03 | 1.988 | 55.78 |
| 2.459 | 60.27 | 2.707 | 55.50 |
| 2.981 | 62.00 | 3.300 | 55.63 |
| 3.477 | 61.43 | 3.625 | 55.95 |
| 3.740 | 60.47 | 4.378 | 56.98 |
| 4.912 | 55.17 | 5.061 | 56.77 |
| | | 6.070 | 55.08 |
| *n*-Octadecylpyridonium sulfamate | | *n*-Hexadecylpyridonium sulfamate | |
| 0.8578 | 55.61 | 1.189 | 56.63 |
| 1.196 | 56.52 | 1.642 | 56.68 |
| 1.787 | 58.37 | 2.469 | 56.46 |
| 2.510 | 65.45 | 3.174 | 56.64 |
| 2.798 | 66.36 | 3.743 | 58.09 |
| 3.282 | 65.38 | 4.376 | 58.80 |
| 3.846 | 62.97 | 4.578 | 59.90 |
| 4.541 | 58.91 | 5.122 | 58.23 |
| 5.166 | 55.35 | 5.920 | 56.62 |
| | | 6.044 | 56.04 |
| | | 7.409 | 52.48 |

## Discussion

The results for sulfamic acid and silver sulfamate have been treated by the Shedlovsky method[11] to obtain values of $\Lambda_0$ and $K$. As may be seen from Fig. 1, except for a few points in the dilute region, for which the experimental errors are relatively large, $1/\Lambda S(z)$ is found to be a linear function of $C\Lambda S(z)f^2$. Values of $\Lambda_0$ were obtained from the intercepts on the $1/\Lambda S(z)$ axes; from the slopes of large-scale plots the dissociation constants of sulfamic acid and silver sulfamate are found to be $1.006 \times 10^{-1}$ and $1.032 \times 10^{-1}$, respectively. In the cases of potassium and ammonium sulfamates the $\Lambda/\sqrt{C}$ plots are straight lines and the corresponding values of $\Lambda_0$ were calculated from the individual $\Lambda$ values using the Onsager relation $-\Lambda_0 = (60.19\sqrt{C} + \Lambda)/(1 - 0.229\sqrt{C})$. The $\Lambda_0$ values obtained according to these procedures are pre-

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[9] Luder, THIS JOURNAL, **62**, 89 (1940).

[10] Kraus and Fuoss, *ibid.*, **55**, 21 (1933).

[11] Fuoss and Shedlovsky, *ibid.*, **71**, 1496 (1949).

sented in Table IV along with the values of the limiting conductance of the sulfamate ion which have been calculated using the generally accepted values of the cation conductances.[12]

TABLE IV

LIMITING CONDUCTANCES OF SULFAMIC ACID AND SOME SULFAMATES IN WATER AT 25°

| | $\Lambda_0$ | $\Lambda_0^+$ | $\Lambda_0^-$ |
|---|---|---|---|
| Sulfamic acid | 393.31 | 349.82 | 48.49 |
| Silver sulfamate | 110.60 | 61.92 | 48.68 |
| Potassium sulfamate | 122.07 | 73.52 | 48.55 |
| Ammonium sulfamate | 122.03 | 73.4 | 48.63 |
| Mean value of the limiting conductance of the sulfamate ion | | | 48.59 |

In Figs. 2, 3 and 4 are shown the $\Lambda/\sqrt{C}$ plots for the long chain sulfamates using the data presented in Tables II and III. In water the features of the $\Lambda/\sqrt{C}$ curves are those usually found for a long chain electrolyte. The breakpoint, generally associated with the incidence of appreciable micelle formation, occurs at about $4 \times 10^{-4}$ $N$ in the case of the octadecyl salts whereas it is at approximately $13 \times 10^{-4}$ $N$ for the hexadecyl salts. It is apparent that in the dilute region the curves are straight lines although the experimental data for these solutions are not sufficiently precise for an exact treatment. However, the limiting equivalent conductances for hexadecyltrimethylammonium, octadecylpyridonium and hexadecylpyridonium sulfamates are obviously around 69, 69 and 70, respectively. The scattered data for the octadecyltrimethylammonium sulfamate precludes all but a very rough extrapolation but it is obvious that its limiting conductance must be around 69.

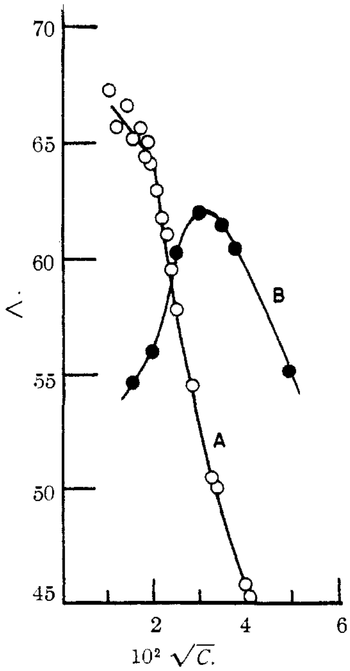

Fig. 2.—Conductance of octadecyltrimethylammonium sulfamate: A, in water; B, in 10% acetone-water mixture.

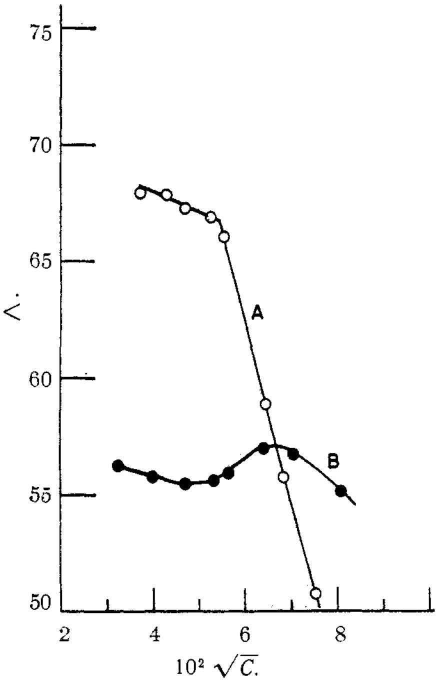

Fig. 3.—Conductance of hexadecyltrimethylammonium sulfamate: A, in water; B, in 10% acetone-water mixture.

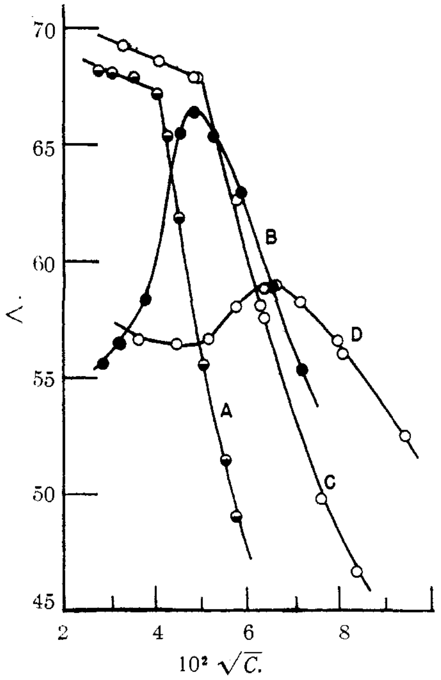

Fig. 4.—Conductance of octadecylpyridonium (A, B) and hexadecylpyridonium (C, D) sulfamates: A and C in water; B and D in 10% acetone-water mixture.

In 10% acetone-water mixtures the $\Lambda/\sqrt{C}$ plots reveal quite interesting features. In all four cases pronounced maxima are present. For hexadecyltrimethylammonium sulfamate and perhaps for the hexadecylpyridonium salt straight lines are approached at the experimentally accessible low concentration end of the curve. The limiting conductances are obviously around 57 for the hexadecyltrimethylammonium salt and about 58 for

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[12] MacInnes, *J. Franklin Inst.*, **225**, 661 (1938).

the hexadecylpyridonium salt. Accordingly, the $\Lambda_0$ values for the octadecyltrimethylammonium and octadecylpyridonium must sulfamates lie around 57–58. It is thus clear that, except for hexadecyltrimethylammonium sulfamate, in which case the maximum value of $\Lambda$ is approximately the same as that of $\Lambda_0$, the values of $\Lambda$ at the maxima lie appreciably above the limiting equivalent conductances. The values of $(\Lambda_{\max.} - \Lambda_0)$ for octadecyltrimethylammonium, octadecylpyridonium and hexadecylpyridonium sulfamates are approximately 5, 8 and 1, respectively. Kraus and others[13] have reported values of 7 and 10.7, respectively, for $(\Lambda_{\max.} - \Lambda_0)$ in the cases of octadecyltrimethylammonium bromate and formate in 10% acetone–water mixture. The conductances of the bromate and formate ions are 55.8 and 54.6, respectively. It therefore appears that the height of the conductance peak is not dependent entirely on the conductance of the gegenion since in view of the lower conductance of the sulfamate ion we might expect a higher maximum. It is interesting to note that the position of the maximum appears to depend only on the nature of the long chain—it occurs at about $2 \times 10^{-3}$ $N$ for the hexadecyl chain and at about $9 \times 10^{-4}$ $N$ for the octadecyl chain.

It is concluded that while the sulfamate ion is not sufficiently slow to allow of the existence of conductance maxima in water its size and other properties are such that unusual aggregation effects are evident in acetone–water mixtures. An interpretation of these phenomena awaits the presentation of more extensive data.

## Summary

1. The conductances of dilute aqueous solutions of sulfamic acid, silver, potassium and ammonium sulfamates have been measured at 25°.

2. The dissociation constants of sulfamic acid and silver sulfamate in water at 25° have been calculated.

3. The limiting conductance of the sulfamate ion has been determined.

4. The conductances of dilute solutions of *n*-octadecyltrimethylammonium, *n*-hexadecyltrimethylammonium, *n*-octadecylpyridonium and *n*-hexadecylpyridonium sulfamates in water and in 10% acetone–water mixtures have been measured at 25°.

5. In water the usual breakpoint in the $\Lambda/\sqrt{C}$ curves is observed.

6. In 10% acetone–water mixture all four salts show maxima in the $\Lambda/\sqrt{C}$ plots.

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[13] Young, Grieger and Kraus, THIS JOURNAL, **71**, 309 (1949).

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[CONTRIBUTION NO. 94 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

# The Salts of Perrhenic Acid. III. Univalent Heavy Metals[1]

BY WM. T. SMITH, JR.

**Preparation of the Salts.**—Water solutions of thallous sulfate and potassium perrhenate, on mixing produced relatively insoluble thallous perrhenate. This white salt was purified by repeated washing and digesting with boiling water. Kraus and Steinfeld[2] have reported this compound and because of its insolubility have suggested its use in the estimation of rhenium.

Silver perrhenate was prepared by treating freshly precipitated silver oxide with a water solution of perrhenic acid. This salt which is more soluble than thallous perrhenate was purified by recrystallization from water. The white salt when pure is not decomposed by sunlight although impure samples darkened slowly. Hönigschmid and Sachtleben[3] reported the preparation of this salt by several metathetical reactions in water solution and found it to be insoluble in concd. nitric acid and soluble in concd. ammonium hydroxide. The salt has been used by Geilmann and Wrigge[4] in a determination of the atomic weight of rhenium.

Freshly prepared cuprous oxide when treated with a perrhenic acid solution produced a blue solution of cupric perrhenate. The very soluble cupric perrhenate was recrystallized from water. The water of crystallization was removed by heating in an oven at 110° and the white anhydrous salt decomposed by heating at 400 to 500° for several days. Rhenium heptoxide and oxygen were volatile products of the decomposition. The brownish-pink residue, similar in color to the hexahydrate of cobalt chloride, remaining after decomposition had ceased was cuprous perrhenate. This salt has not been previously reported.

A water solution of mercurous nitrate on the addition of a solution of potassium perrhenate produced a white basic or oxy-mercurous perrhenate. This substance was digested and washed with hot water. After drying over calcium chloride the substance lost no weight in an oven at 110°. On heating the white solid turned orange at approximately 400° and then melted to a black liquid which decomposed with the evolution of mercury and oxygen. The melt was held between 550 and 600° until no further signs of decomposition were evident and cooled to produce a red solid which changed to orange then yellow and finally to white mercurous perrhenate as the temperature fell. An insoluble mercurous perrhenate has been reported[5] but not quantitatively characterized.

**Freezing Point.**—The freezing points of the salts were determined[6] from cooling curves obtained with a Brown potentiometer and a chromel–

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[1] Presented at the Symposium on the Less Familiar Elements at the A. C. S. Meeting in Detroit, April 17, 1950.

[2] Kraus and Steinfeld, *Z. anorg. Chem.*, **197**, 52 (1931).

[3] Hönigschmid and Sachtleben, *ibid.*, **191**, 207 (1930).

[4] Geilmann and Wrigge, *ibid.*, **199**, 65 (1931).

[5] Heyne and Moers, *Z. anorg. allgem. Chem.*, **196**, 129 (1931).

[6] Smith and Long, THIS JOURNAL, **70**, 354 (1948).