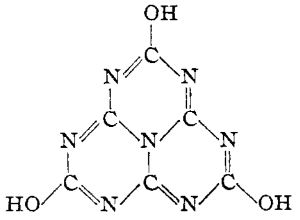
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, NO. 748]

Some Derivatives of Cyameluric Acid and Probable Structures of Melam, Melem and Melon

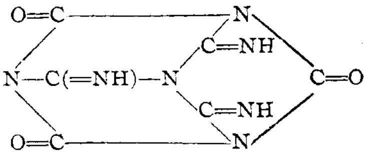
BY C. E. REDEMANN AND H. J. LUCAS

Since it has been shown recently that the structure proposed by Pauling and Sturdivant for the cyameluric acid nucleus,[1] I, accounts more satisfactorily for the acidic strength and for the products of hydrolysis[2] than any other proposed structure, and because of the prediction made by these authors[1] that there should be a group of cyameluric compounds analogous to the cyanuric compounds, attempts have been made to prepare some of these analogs.

Cyameluric acid forms a blue-lavender cupric ammonium salt, $CuNH_4(C_6N_7O_3)NH_3$, entirely analogous to that of cyanuric acid,[3] $CuNH_4(C_3N_3O_3).NH_3$. The insoluble cupric ammonium cyamelurate is useful in purifying cyameluric acid since the acid is readily regenerated from the salt by suspending it in water and acidifying with hydrochloric acid.



Pauling and Sturdivant
I



Franklin
II

In the case of the mercuric salts the parallelism is not so satisfactory. While Hantzsch[4] reported two different mercuric cyanurates with the formula $Hg_3(C_3N_3O_3)_2$, one called an oxygen salt, the other a nitrogen salt, specimens of mercuric cyamelurate, $Hg_3(C_6N_7O_3)_2$, obtained under conditions shown by Hantzsch to give different salts with the former gave only a single salt with the latter. This salt gave an immediate precipitate of yellow mercuric oxide with aqueous sodium hydroxide, hence it would be called the oxygen salt from the Hantzsch point of view. Although in this case the analogy with cyanuric acid is not complete, nevertheless the behavior of the mercury salt favors structure I rather than structure II, for of the latter only a nitrogen salt is possible. This argument is, however, open to criticism, for if the N–Hg bond has sufficient ionic character the salt would be expected to react with sodium hydroxide.

Cyanuryl trichloride, $C_3N_3Cl_3$, and cyameluryl trichloride, $C_6N_7Cl_3$, are completely analogous. Hydrolysis of the two chlorides is similar except that cyameluryl chloride hydrolyzes more rapidly, as might be expected since it is the acid chloride of the stronger acid.[2] When heated with acetic acid each acid chloride yields the respective acid and acetyl chloride; upon alcoholysis each yields the respective acid and an alkyl chloride.

Esters of cyameluric acid are more difficult to prepare than are those of cyanuric acid. Two series of esters are known for the latter: the oxygen esters, and the nitrogen esters. Potassium cyamelurate does not react readily with alkyl halides at room temperature. After standing with methyl iodide for nineteen months, only a small amount of iodide ion was formed and no ester could be isolated. Likewise, cyameluryl trichloride with sodium methoxide (or benzoxide) failed to give the ester. Potassium cyamelurate and allyl bromide gave an allyl derivative at 100° which was not obtained pure. A tribenzyl ester was obtained from benzyl chloride and potassium cyamelurate at 156°. This ester is a nitrogen ester since it gave benzylamine and no benzyl alcohol upon hydrolysis. Cyanuric acid[5] also forms the nitrogen ester at elevated temperatures.

From cyameluric acid and diazomethane was obtained a mixture of monomethyl esters with the nitrogen ester predominant, and also a trimethyl ester which was entirely a nitrogen ester.

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(1) Pauling and Sturdivant, *Proc. Natl. Acad. Sci.*, **23**, 615 (1937).

(2) Redemann and Lucas, THIS JOURNAL, **61**, 3420 (1939).

(3) (a) Benrath and Meckenstock, *Z. anorg. allgem. Chem.*, **151**, 35 (1926); (b) Claus and Putensen, *J. prakt. Chem.*, [2] **38**, 216 (1888).

(4) Hantzsch, (a) *Ber.*, **35**, 2717 (1902); (b) *ibid.*, **39**, 139 (1906); (c) *Z. anorg. allgem. Chem.*, **209**, 219 (1932).

(5) Hantzsch and Bauer, *Ber.*, **38**, 1009 (1905).

Cyanuryl chloride and cyameluryl chloride both react with ammonia, the former to produce a monochlordiamide and a triamide, melamine, and the latter to produce a diamide and apparently some triamide, although not pure.

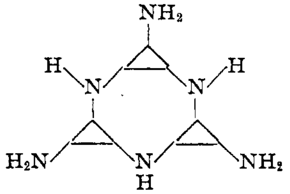
The resemblance of the derivatives of cyameluric acid to the corresponding derivatives of cyanuric acid indicates that cyameluric acid contains hydroxyl groups and suggests that formula I, or $C_6H_7(OH)_3$, is the one which most closely resembles $C_3N_3(OH)_3$.

On the basis that cyameluric acid is represented by I, satisfactory structures can be assigned to melam, melem and melon. Melam,[6] empirical formula $C_6H_9N_{11}$, is probably tetraaminodicyanurimide,[7] III. This structure accounts for the feebly basic property of melam, and is supported by the behavior of melam with 30% aqueous ammonia[8] at elevated temperatures to yield melamine and ammeline; also by Liebig's[6] observation that when boiled with nitric acid melam yields cyanuric acid and ammonium nitrate.

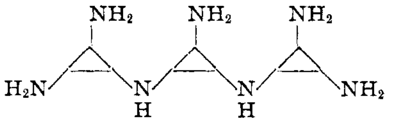
Melem,[6] empirical formula $C_6H_6N_{10}$, is probably cyameluryl triamide, IV. This structure satisfactorily accounts for the formation of large quantities of ammelide upon hydrolysis, and for the fact that melem is more resistant to hydrolysis than melam. Structures III and IV account satisfactorily for the observation that melam is a stronger base than melem, for the latter is derived from much the stronger acid.

$[3.5\text{-}(NH_2)_2C_3N_3]_2NH$	$C_6N_7(NH_2)_3$	$(HN{=}C_3H_3)_2NH$
Melam	Melem	Melon; Franklin
III	IV	V

Melon, with empirical formula $C_6H_3N_9$,[9,10] was assigned structure V by Franklin.[7b] But since melon gives good yields of cyameluric acid upon alkaline hydrolysis[11] a satisfactory structure for melon must involve the planar nucleus characteristic of cyameluric acid, I. Such a structure results from melem, IV, by the loss of ammonia from two or more molecules. One possibility is that shown by structure VI, where three molecules of ammonia have been split out from three molecules of cyameluric triamide. This compound, the molecule of which has three cyameluric nuclei, has the formula $C_{18}H_9N_{27}$, three times $C_6H_3N_9$, the accepted formula for melon. Here the side chains are $-NH_2$ groups, the $=NH$ group forming part of a new ring. Larger molecules of the compact type, where the maximum number of ring closures had taken place would have a higher carbon, lower hydrogen and lower nitrogen content. In such a molecule hydrogen is found only along the periphery. The symmetrical triangular molecule with six cyameluric nuclei is $C_{36}H_{12}N_{52}$ or more simply $C_6H_2N_{8^2/_3}$. As condensations extend indefinitely the empirical formula approaches asymptotically the limit C_3N_4, Franklin's carbonic nitride. Another type of condensation product, in which the cyameluric nuclei, except for the two terminal ones, are joined to only two other nuclei (structure VII), would approach $C_6H_3N_9$ if extended indefinitely.



VI



VII

Melon[12]

On this basis it is possible to account for the lack of constancy of composition of melon observed by Liebig, Franklin and others. The hydrogen content of Franklin's preparations varied from 1.1 to 2.0%, while for the accepted formula, $C_6H_3N_9$, the hydrogen content is 1.5%. By taking extreme precautions to dry mercuric thiocyanate at 150° in the vacuum of a mercury vapor pump before decomposing it to melon, Franklin was able to obtain a product with a hydrogen content of only 0.6%. This corresponds closely to a compact condensation product, triangular in form, with twenty-one nuclei, and molecular formula $C_{126}H_{21}N_{175}$ or more simply $C_6HN_{8^1/_3}$with a hydrogen content of 0.5%. Franklin's material was probably composed of both larger and smaller units, giving an average value corresponding to the above figures. It is probably incorrect to assign any one structure to melon, for it is more than likely a mixture of

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[6] Liebig, *Ann.*, **10**, 10 (1834).

[7] (a) Klason, *J. prakt. Chem.*, [2] **33**, 287 (1886); (b) Franklin, THIS JOURNAL, **44**, 507 (1922).

[8] Rathke, *Ber.*, **23**, 1675 (1890).

[9] Laurent and Gerhardt, *Ann. chem.*, [3] **19**, 85 (1847).

[10] Vockel, *Pogg. Ann.*, **58**, 151 (1834).

[11] Volhard, *J. prakt. Chem.*, [2] **9**, 30 (1874).

[12] In VI and VII, each triangle represents C_6H_7, the cyameluric nucleus.

molecules of different sizes and shapes. This gives rise to its amorphous character.

It is seen that there is a formal resemblance between melon and graphite, in that the molecules are infinitely large and planar. The formal resemblance becomes even more pronounced if in the molecule of melon the void between the three cyameluric nuclei is filled by writing in three atoms of carbon and one of nitrogen. Taking the density of graphite as 2.25 and neglecting the hydrogen, we can predict a density for melon of less than 1.7. An observed value is 1.40 at 25°, which value may differ considerably with different preparations. Anhydrous cyameluric acid, which is not predicted to have large void spaces in its structure corresponding to those in melon, is found to have a density of 1.75 at 25°. The high stability of melon, like that of graphite, may be explained in terms of the enormous number of resonating forms contributing to the structure of the compound.

Experimental

Cupric Ammonium Cyamelurate.—To a solution of 2 g. of cyameluric acid trihydrate in 200 ml. of hot 0.5 *N* ammonium hydroxide, there was added an excess of cupric ammonium sulfate solution. After cooling, the resulting lavender precipitate was filtered off, washed and air dried. The color changed to a very blue shade of lavender upon drying, probably due to the loss of either ammonia to form a less amminated compound, or to the loss of water of crystallization.

Anal. Calcd. for $CuNH_4(C_6H_7O_3)\cdot NH_3$: Cu, 20.08. Found: Cu (iodometrically), 19.84, 20.13.

This salt is much less soluble than the one obtained from cyanuric acid under the same conditions.

Mercuric Cyamelurate.—Two samples of mercuric cyamelurate were prepared under conditions which Hantzsch[4] found to yield two different types of salts in the case of cyanuric acid. (A) To a solution of 2 g. of pure potassium cyamelurate in 50 ml. of boiling water was added a slight excess of a boiling solution of mercuric chloride. The white flocculent precipitate of the mercury salt which separated immediately was well washed with water and dried.

Anal. Calcd. for $(C_6N_7O_3)_2Hg_3$: Hg, 57.99. Found: Hg, 58.31, 58.33. The high values for mercury probably are due to adsorption of mercury by the semi-gelatinous precipitate.

(B) The same procedure was followed except that mercuric chloride was replaced by mercuric acetate, and the solutions were ice-cold. Both salts looked alike and gave immediate precipitates of yellow mercuric oxide when treated with a cold 1 *N* sodium hydroxide. Upon standing overnight, nearly colorless crystals of trisodium cyamelurate separated in each case.

Cyameluryl Trichloride.—(A) From tripotassium cyamelurate. Thirty grams of the salt dried at 150° for forty-eight hours and 60 g. of phosphorus pentachloride were ground to a fine mixture in a mortar. This was sealed in a large bomb tube and heated in a boiling water-bath for seven hours. The tube was opened to relieve the pressure, then after resealing heated for an additional nine hours at 139° (*m*-xylene vapor-bath). After phosphorus oxychloride had been removed by letting stand in a desiccator over flake sodium hydroxide in a thin layer, the residue was crushed into a coarse powder and slowly sprinkled into and well stirred with an ice-water mixture to remove potassium chloride and any remaining phosphorus compounds. The light yellow solid was filtered off and dried in a vacuum desiccator over concentrated sulfuric acid. The yield of light yellow crystalline powder, which under the microscope was seen to consist of thin pale yellow platelets, was 23 g. (93%).

Cyameluryl trichloride is highly insoluble in all organic solvents tested, which included chloroform, anisole, nitrobenzene, acetonitrile, *o*-dichlorobenzene and glacial acetic acid (with which it reacted giving acetyl chloride and cyameluric acid). The compound was shown to be essentially free from inorganic salts by ignition upon platinum foil where no ash remained. No melting was observed, but the compound gradually disappeared by a combination of oxidation and perhaps sublimation. Attempts to secure purification by sublimation at atmospheric pressure and under high vacuum were unsuccessful. Analyses were finally run on the dry material without further purification.

Anal. Calcd. for $C_6N_7Cl_3$: N, 35.44; Cl, 38.49. Found: N (Kjeldahl), 35.76, 35.32; Cl (Carius), 32.83, 37.4, 37.4.

Results of the analysis indicate that the compound was slightly impure cyameluric trichloride. When completely decomposed by digesting with nitric acid, the solution gave but a faint test for phosphorus with ammonium molybdate.

(B) From cyameluric acid. Two grams of the acid which had been dried for several days at 150° and six grams of phosphorus pentachloride were ground and intimately mixed. The mixture was sealed in a heavy walled bomb-tube and heated to 218° (naphthalene vapor-bath) for thirty-six hours. The tube was opened periodically to relieve the pressure. The contents of the tube were worked up, as in A. The yield was 2.3 g. (92%) of product closely resembling that prepared from tripotassium cyamelurate.

N-Tribenzyl Cyamelurate.—A mixture of 5 g. of anhydrous trisodium cyamelurate and 17 ml. of freshly distilled benzyl chloride in a sealed bomb-tube was heated for twenty-three hours in a boiling water-bath. As little reaction appeared to take place at this temperature, heating was continued for an additional twelve hours in a vapor-bath at 156° (boiling bromobenzene). The contents were transferred to a Soxhlet extractor and extracted for four hours with boiling benzene. Following removal of volatile compounds by distillation under 18 mm. pressure, the residue was crystallized from boiling benzene; 4.2 g. (36%). After two additional recrystallizations from ethyl alcohol very small white needles melting at 283–284° (cor.) were obtained.

Anal. Calcd. for $C_{27}H_{21}N_7O_3$: mol. wt., 491; N, 19.96;

C, 65.96; H, 4.31. Found: mol. wt. (Rast camphor), 497; N (Kjeldahl), 19.54, 19.57; C, 65.46; H, 4.46.

Saponification of 0.2 g. of tribenzyl cyamelurate by refluxing for one hour with 10 ml. of aqueous 6 *N* potassium hydroxide, followed by distillation of the reaction mixture, gave a faintly cloudy distillate with an odor suggestive of ammonia. Extraction of this with ethyl ether following acidification with hydrochloric acid gave no trace of benzyl alcohol. However, extraction of the aqueous solution with ether after the addition of an excess of sodium hydroxide gave a few drops of a viscous residue which reacted readily with benzoyl chloride. The resulting solid after crystallization from aqueous ethyl alcohol melted at 105.5–106.0°, and melted at the same temperature when mixed with an authentic sample of N-benzylbenzamide, m. p. 105°. This shows that benzylamine but not benzyl alcohol is formed when tribenzyl cyamelurate is saponified and that the tribenzyl compound is a nitrogen, not an oxygen ester.

Action of Cyameluryl Trichloride on Benzyl Alcohol.—A mixture of 1.0 g. of cyameluryl trichloride and 1.5 g. of dry benzyl alcohol reacted spontaneously. The mixture became very hot and the yellow color of the cyameluryl trichloride changed to a pure white. The mixture was then boiled for one minute, cooled and 2 ml. of benzene added. The solid was removed by filtration and the filtrate was fractionally distilled. The fraction boiling between 170–190° had an unmistakable odor of benzyl chloride. This was confirmed by converting into the *p*-bromobenzenesulfon-*p*'-anisidide, m. p. 169.5–170.0° (uncor.), after recrystallizing from ethanol. The melting point was 170.0–0.5 when mixed with a known sample, m. p. 170–171°.[13]

The white residue was shown to be cyameluric acid by its solubility in sodium bicarbonate solution, from which the trisodium salt was precipitated in characteristic colorless needles upon adding an excess of strong sodium hydroxide solution.

Methyl Cyamelurate from Cyameluric Acid and Diazomethane.—An excess of an ethereal solution of diazomethane was added to 1.7 g. of very finely powdered cyameluric acid. The evolution of gas, vigorous at first, soon became rather slow. A strong yellow color from excess diazomethane was still present after standing for three days in the refrigerator, although the evolution of gas had become quite slow. The solid was filtered off and dried over concentrated sulfuric acid. The dry pale yellow solid thus obtained weighed 1.8 g. No melting was observed in a capillary tube; no solvent was found from which the material could be purified without some decomposition.

Anal. Calcd. for $C_6H_2N_7O_3(CH_3)$: C, 35.7; H, 2.12; CH_3, 6.38. Found: C, 35.4, 35.1; H, 3.22, 3.05; CH_3 (methoxyl), 0.58, 0.62; CH_3 (methylimide) 6.95, 6.48.

Analysis indicates slightly more than one methyl group per nucleus and some methylation of the hydroxyl groups.

The partially methylated product from the above experiment after fine pulverization was treated again with an excess of diazomethane at room temperature for four days. Since all apparent reaction had ceased, the solid was filtered off, dried over concentrated sulfuric acid, and analyzed.

Anal. Calcd. for $C_6N_7O_3(CH_3)_3 \cdot 1^1/_2H_2O$: C, 36.72; H, 4.12; H_2O, 9.18; CH_3, 15.3. Found: C, 36.22; H, 4.14; H_2O, 9.13; CH_3 (methoxyl), 0.060, 0.062.

When heated on platinum foil the anhydrous compound melted. In a capillary tube no melting was observed up to 290°, but instead extensive charring.

Attempts to Prepare Cyameluric Triamide.—(1) On adding 25 ml. of 15 *N* ammonium hydroxide to 1.19 g. of cyameluryl chloride, a very vigorous reaction took place immediately. The light yellow color of the cyameluryl chloride disappeared and a white flocculent precipitate took its place. After standing for one hour this was filtered off, washed well with cold water and dried in the oven at 75°; weight 0.88 g. As no solvent was found from which this material could be recrystallized, the sample was analyzed without further purification.

Anal. Calcd. for $C_6N_7(NH_2)_3$: N, 64.2; for $C_6N_7(NH_2)_2Cl$: N, 53.1; Cl, 14.93; for $C_6N_7(NH_2)_2OH$: N, 57.6. Found: N (Kjeldahl), 54.28, 54.17; Cl (Carius), 3.32, 3.50.

The analytical data indicate an impure mixture largely composed of one or both diamides, cyameluryl monochlorodiamide, and cyameluryl diamide.

(2) Two grams of cyameluryl chloride was suspended in 100 ml. of anhydrous ethyl ether into which was passed gaseous ammonia until the solution was saturated. It was then allowed to stand for two hours and again saturated with ammonia gas and allowed to stand overnight. Twenty-five ml. of water was then added and the mixture was vigorously shaken. The precipitate was separated by filtration, washed with concentrated ammonium hydroxide, and air dried. It was then crushed and digested with 100 ml. of warm 1 *N* ammonium hydroxide for thirty minutes, filtered, and dried at 100° for one hour. *Anal.* Found: N, 59.88, 60.01.

Since this analytical result agreed most nearly with a possible monohydrate of the triamide or the ammonium salt of the acid diamide the compound was dried for twenty-six hours at 150°. A loss in weight of 4.52% took place, with but little change in the analysis, but the material still appeared to be impure. *Anal.* Found: N, 60.20, 61.96.

(3) Two grams of cyameluryl chloride was sealed in a bomb-tube with anhydrous liquid ammonia and left for twenty hours at room temperature. The tube was opened and the ammonia allowed to evaporate. The residue was extracted with cold water to remove the ammonium chloride. The flocculent solid was collected upon a filter and dried at 100° for four hours. *Anal.* Found: N, 60.34, 60.01.

None of these preparations has a nitrogen content as high as that for the triamide (64.2%), but the purification is hampered because no satisfactory solvent has been found from which the compound can be crystallized.

Summary

1. Cyameluric acid has been shown to form a group of compounds entirely analogous to those of cyanuric acid. The analogy is complete for

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[13] Gillespie, THIS JOURNAL, **56**, 2740 (1934), gives 167.5°, which is too low.

the cupric ammonium salts, the trichlorides, and the nitrogen esters formed by the reaction of benzyl chloride with the respective alkali salts at elevated temperature. The analogy is less exact for the diamides, the mercuric salts and the oxygen esters.

2. The existence of a trichloride and of an oxygen ester indicates that hydroxyl groups are present in the molecule of cyameluric acid.

3. The analogy with cyanuric compounds and the presence of hydroxyl groups substantiate the planar ring structure for cyameluric acid proposed by Pauling and Sturdivant.

4. Melam is probably dicyanurylimide and melem, cyameluryl triamide.

5. It is proposed that melon is a condensation product of cyameluryl triamide, and that the resulting very large molecules consist of planar cyameluryl rings joined through nitrogen atoms.

PASADENA, CALIF. RECEIVED NOVEMBER 6, 1939

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Ionization Constants of Weak Acids at 25° from Conductance Measurements. A Method of Extrapolating the Data[1]

BY BLAIR SAXTON[2] AND LAWRENCE S. DARKEN[3]

A large number of investigations[4–14] have been conducted in recent years on the determination of ionization constants of weak acids by the conductance method. At the lower concentrations the degree of ionization is determined accurately from conductance data alone by use of the additive law that the specific conductance of the weak acid is equal to the specific conductance of the hydrogen ion and the acid ion as determined from the conductance of the sodium or the potassium salt of the acid, sodium or potassium chloride and hydrochloric acid at the corresponding ionic concentration. The salts and hydrochloric acid are considered completely ionized. The degree of dissociation of the weak acid is set equal to Λ/Λ_e where Λ_e is the equivalent conductance of the theoretical completely dissociated acid at the same ionic concentration. Values of Λ/Λ_e are obtained by a method of successive approximations from the above-mentioned data. From the degree of dissociation of the acid a so-called mass law ionization constant is determined directly according to the relation

$$k = \alpha^2 c/(1 - \alpha) = c_i^2/c_u$$

where α is the degree of dissociation, c is the stoichiometric concentration of the weak acid, c_i is the ionic concentration, and c_u is the concentration of undissociated weak acid. At finite concentrations

$$K = y_\pm^2 k$$

where K is the thermodynamic ionization constant as usually written, and $y_\pm$ is the mean ionic activity coefficient. Several investigators[4–14] have shown that at extremely low concentrations the variation of k with concentration is in good agreement with that predicted by the Debye–Hückel[15] theory of interionic attraction which at low ionic concentrations reduces to this relation

$$\log y_\pm = -A\sqrt{c_i}$$

which combined with the previous equation gives

$$\log K = \log k - 2A\sqrt{c_i}$$

Unfortunately, the range over which this equation holds within an experimental error of one part in a thousand (to give a constant value of log K) is below an ionic concentration of about 0.003 (depending on the acid). Hence, extrapolating to obtain the limiting value of log K from a plot of log k *versus* $\sqrt{c_i}$ is not a convenient method in that it demands high accuracy at low concentrations. It will be shown that the true thermodynamic ionization constant may be determined

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[1] This paper contains material which represents part of the dissertation submitted by Lawrence S. Darken to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1933. Original manuscript received July 20, 1939.

[2] The experimental work and calculations herein reported were completed before the death of Professor Saxton.

[3] Present address: Research Laboratory, United States Steel Corporation, Kearny, New Jersey.

[4] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

[5] Davies, *ibid.*, **54**, 1698 (1932).

[6] Saxton and Langer, *ibid.*, **55**, 3638 (1933).

[7] MacInnes, Shedlovsky, and Longsworth, *Chem. Rev.*, **13**, 29 (1933).

[8] Ives, *J. Chem. Soc.*, 731 (1933).

[9] Brockman and Kilpatrick, THIS JOURNAL, **56** 1483 (1934).

[10] Saxton and Meier, *ibid.*, **56**, 1918 (1934).

[11] Banks and Davies, *J. Chem. Soc.*, 73 (1938).

[12] Saxton and Waters, THIS JOURNAL, **59**, 1048 (1937).

[13] Martin and Tartar, *ibid.*, **59**, 2972 (1937).

[14] Belcher, *ibid.*, **60**, 2744 (1938).

[15] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).