

previously prepared^{1,2} using different ratios of reactants and suggest that it is some type of a substituted polyamide.

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The Discharge of Zinc Ions at the Dropping Mercury Cathode. A Test of the Ilkovic Equation

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The use of the polarograph in this Laboratory for the determination of zinc in plant materials and fertilizers has required an examination of the relation between limiting current and concentration of zinc over a wider concentration range than usual. Lingane and Kolthoff¹ have tested the same relationship over the range 10^{-4} – 10^{-2} molar for four metal ions depositing from 0.1 *M* potassium chloride. On the other hand, a five-fold concentration range is about all that is usually covered in most of the reported methods of polarographic analysis.

The basal solution used here has the composition 0.1 *M* ammonium chloride, 0.02 *M* potassium thiocyanate and 0.0002% methyl red. Like the solution proposed by Stout, *et al.*,² it enables zinc to be determined in the presence of nickel, and any data available about it are of more practical value to those concerned with the determination of zinc than these obtained for potassium chloride solutions, in which zinc and nickel are not resolved.

With this mixed basal solution in the electrolysis cell, the anode potential proved to be equal (to within a few millivolts) to that of the saturated calomel electrode, so that cathode potentials, when referred to the S. C. E. as zero, may be taken as equal to the applied potentials. The deposition potential was found to be -1.02 volts. The temperature coefficient of the limiting current was determined between the temperatures 18 and 28°, the current increasing by 1.72% of its value at 20° for a rise of 1°. All other measurements were conducted at a temperature of $20 \pm 0.15^\circ$ and at a potential of -1.20 volts, limiting current conditions having then been reached. From the table it will be seen that the relation between current and zinc concentration is linear (to within about $\pm 1.5\%$) over a one hundred-fold concentration range.

(1) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

(2) P. R. Stout, J. Levy and L. C. Williams, *Coll. Czech. Chem. Comm.*, **10**, 129 (1938).

Ilkovic³ has shown that the value of i/C can be calculated from the diffusion coefficient, the mass of mercury (m) flowing per second from the cathode, and the drop time (t). Values of the two latter were determined and are given in the table, while the diffusion coefficient was calculated from the ionic mobility at infinite dilution, assuming a value of 47.8 at 20° for the latter. On substituting these values in the Ilkovic equation, it is found that $i/C = 4.67$ microamperes per millimole per liter, which is 9% lower than the observed value of 5.10.

TABLE I
RELATION BETWEEN CONCENTRATION OF ZINC AND
LIMITING CURRENT

$m = 1.392$ mg./sec., $t = 3.61$ sec., $m^2/st^{3/2} = 1.545$ mg.²/sec.^{-1/2}.

<i>C</i> , millimoles/ liter	<i>i</i> , microamp.	<i>i/C</i> microamp./ mmole/liter
0.0500	0.252	5.04
.250	1.016	5.06
.500	2.54	5.08
1.00	5.18	5.18
5.00	25.7	5.14

Mean 5.10

The agreement is good enough to support the view that the mechanism of this particular discharge process is substantially the same as that pictured by Ilkovic. At the same time, the combined errors involved in the measurements of i/C , m and t probably do not exceed 3%, so that the discrepancy cannot be disregarded. Lingane and Kolthoff obtained a similar result for the discharge of zinc from 0.1 *M* potassium chloride, the observed limiting current exceeding the calculated by 5%. They suggested this might be due to the occurrence of the complex ion $ZnCl^+$. If, as here, the electrolyte contains potassium thiocyanate, the tendency toward complex formation may well be greater. Hence, in view of the difficulty of knowing what value to assign to the diffusion coefficient, it is of more interest to combine the four experimentally determined quantities in the form of the ratio $i/Cm^{2/3}t^{1/6}$. The value of this ratio at any one temperature should then be a constant independent of the type of capillary, and should characterize any one particular discharge process. For the data just presented at 20°, it has the value 3.31, or 3.56 at 25°, allowing for a temperature coefficient of 1.48%. This represents the difference between the observed temperature coefficient of the limit-

(3) D. Ilkovic, *ibid.*, **6**, 498 (1934).

ing current (1.72%) and 0.24%, which is the temperature coefficient of the product $m^{2/3}t^{1/6}$.⁴ The corresponding figure calculated from Lingane and Kolthoff's data for zinc at 25° is 3.42.

(4) D. Ilkovic, *Coll. Czech. Chem. Comm.*, **10**, 249 (1938).

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NEW COMPOUNDS

Semicarbazone of the Methyl Ester of Azelaic Half-aldehyde

After splitting methyl 9,10-dihydroxystearate with lead tetraacetate,¹ the aldehydic methyl ester was separated from pelargonic aldehyde by fractional distillation, b. p. 159–164° (26 mm.). By the usual procedure, the semicarbazone of the ester could be prepared easily. From a benzene–ligroin mixture prisms are obtained, m. p. 107°.

Anal. Calcd. for C₁₁H₂₁O₃N₃: C, 54.3; H, 8.6; N, 17.3. Found: C, 54.3; H, 8.7; N, 16.8.

Scanlan and Swern² could not isolate the semicarbazone of the corresponding ethyl ester in a crystalline form.

(1) Hsing and Chuang, *THIS JOURNAL*, **61**, 3589 (1939).

(2) Scanlan and Swern, *ibid.*, **62**, 2305 (1940).

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Quinoline Derivatives

1,2-Dimethyl-1,2,3,4-tetrahydroquinoline zinci-hydrochloride was prepared from 1,2-dimethyl-1,2,3,4-tetrahydroquinoline by the method of Emerson and Davis.¹ After recrystallization from glacial acetic acid, filtration, and washing free of acetic acid with ether, the compound melted at 152–154°.

Anal. Calcd. for 2C₁₁H₁₆N·2HCl·ZnCl₂: Cl, 26.7. Found: Cl, 26.4.

1,2-Dimethyl-1,2,3,4-tetrahydroquinoline hydriodide was prepared by mixing equal volumes of 1,2-dimethyl-1,2,3,4-tetrahydroquinoline and hydriodic acid of sp. gr. 1.50. After crystallization had been induced by adding ethyl acetate, the product was collected on a filter and crystallized from absolute alcohol, m. p. 138.5–140.0°.

Anal. Calcd. for C₁₁H₁₆NI: I, 44.0. Found: I, 43.7.

2,6,8-Trimethylquinoline zinci-hydrochloride was also prepared from 2,6,8-trimethylquinoline by the procedure of Emerson and Davis.¹ It was purified in the usual way, m. p. ca. 200°.

Anal. Calcd. for 2C₁₂H₁₈N·2HCl·ZnCl₂: Cl, 25.8. Found: Cl, 25.7.

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(1) Emerson and Davis, *THIS JOURNAL*, **61**, 2830 (1939).

6-Bromo-3-methoxybenzyl Alcohol and Some Derivatives

6-Bromo-3-methoxybenzyl Alcohol. A.—A mixture of 25 g. of 3-methoxy-6-bromobenzaldehyde¹ and 4 g. of aluminum ethoxide in 100 cc. of absolute ethyl alcohol was allowed to stand at room temperature for ten days. The ethyl alcohol and volatile products were then distilled from an oil-bath heated to 120°. The residue was treated with dilute hydrochloric acid and extracted twice with ether. The ether extracts were dried over anhydrous sodium sulfate and the ether evaporated. The crude 6-bromo-3-methoxybenzyl alcohol remained as a slightly oily, crystalline mass which was sufficiently pure for use, yield, 22–25 g. (88–100%).

B.—To a solution of 24 g. of 3-methoxy-6-bromobenzaldehyde in 150 cc. of hot alcohol was added 0.1750 g. of Adams platinum oxide catalyst² and 0.013 g. of ferrous chloride. The mixture was shaken with hydrogen until absorption ceased. The platinum was coagulated by the addition of 0.5 cc. of 0.5 *N* sodium hydroxide and filtered out. The filtrate was distilled to remove the alcohol and the brown oily residue was dissolved in ether and dried over anhydrous sodium sulfate. The ether solution was evaporated to about 50 cc., petroleum ether added to turbidity and the solution cooled. Small colorless plates were deposited which were filtered out, washed with a little petroleum ether and dried; yield, 20.5 g. (83%). A portion was crystallized from alcohol, m. p. 49°.

Anal. Calcd. for C₈H₉O₂Br: Br, 36.83. Found: Br, 35.63, 35.76.

6-Bromo-3-methoxybenzyl Chloride.—To a solution of 25 g. of 6-bromo-3-methoxybenzyl alcohol in 100 cc. of chloroform there was added 12.5 g. of phosphorus trichloride. The mixture was allowed to stand for twenty-four hours and was then poured onto crushed ice to decompose the unreacted phosphorus trichloride. The mixture was extracted with ether, the ether solution washed with sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of the ether gave 18 g. (66%) of the crude product. A portion was recrystallized from alcohol, m. p. 75.4–76°.

Anal. Calcd. for C₈H₉OClBr: Cl, 15.06. Found Cl, 14.98.

6-Bromo-3-methoxybenzyl Methyl Ether.—To 5.5 g. of sodium in 125 cc. of absolute methyl alcohol there was added 47 g. of 6-bromo-3-methoxybenzyl chloride. The mixture was boiled for two hours. It was allowed to cool and sufficient water was added to dissolve the precipitated salt. The solution was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the ether distilled off. The residue was distilled in a vacuum, yield, 33 g. (72%), b. p. (9 mm.) 126–129°, n_D^{25} 1.5515, d_4^{25} 1.4259.

Anal. Calcd. for C₉H₁₁O₂Br: Br, 34.60. Found: Br, 34.55, 34.52.

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(1) Pschorr, *Ann.*, **391**, 26 (1912).

(2) Adams, Voorhees and Shriner, "Organic Syntheses," Collective Volume I, 452 (1932).