Molality	0.01	0.05	0.1	0.5	1
			KNO_3		
α	0.991	0.973	0.959	0.895	0.845
K	.87	1.09	1.19	1.11	.91
φ'	.978	0.947	0.919	0.855	.803
			$CsNO_3$		
α	0.991	0.966	0.948	0.877	0.821
K	.87	.85	.91	.86	.66
φ'	.978	.950	.924	.839	.784

Whilst these osmotic coefficients can have little quantitative significance, especially for more concentrated solutions, the purpose of the calculation is achieved by showing that the effect of incomplete dissociation is such as to lead to osmotic coefficients of a more reasonable order.

The osmotic coefficients of the alkali acetates are much higher than one would expect from a consideration of their molal volumes. Davies' equation, however, gives no indication of incomplete dissociation and it is probable that the abnormally high values for all but the lithium salt as well as the reversal in the normal order Li > Na > K > Rb > Cs will find an explanation in the asymmetrical distribution of charge in the acetate ion.

There seems to be no purpose at present in attempting a theoretical explanation of the coefficients of the polyvalent salts. It may, however, be pointed out that, as Fig. 2 shows, the departure from the limiting Debye–Hückel equation at high concentrations is no more marked for polyvalent electrolytes in general than it is for a typical uni-univalent salt such as potassium chloride.

Finally I wish to record my thanks to Professor G. Scatchard, who has helped me with much information regarding his theory and to the Chemical Society for a grant which assisted in the purchase of rubidium and cesium salts.

Summary

1. Osmotic and activity coefficients have been determined by the isopiestic vapor pressure method for thallous nitrate, perchlorate and acetate, rubidium and cesium nitrate and acetate, barium chloride, lanthanum chloride, potassium ferrocyanide and aluminum sulfate. The data for rubidium chloride, bromide and iodide and cesium bromide and iodide have been redetermined.

2. The possibility of incomplete dissociation of sodium, potassium, cesium and thallous nitrate has been discussed and it is shown that not only is this hypothesis consistent with Davies' extension of the conductivity equation but it also explains the abnormally low values found for the osmotic and activity coefficients of these salts.

AUCKLAND, NEW ZEALAND RECEIVED AUGUST 12, 1936

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OHIO STATE UNIVERSITY]

The Use of Crotonaldehyde to Reduce the Postprecipitation of Zinc on Copper Sulfide

BY JOHN R. CALDWELL[1] AND HARVEY V. MOYER

It has been known for many years that copper sulfide, precipitated in the presence of zinc, will carry down appreciable quantities of zinc even when the precipitation is made in a normal acid solution. Various theories of mixed crystal formation, of solid solution and of coprecipitation have been proposed as explanations. Comparatively recent studies have been made by Kolthoff and Pearson,[2] Knowles and Martin,[3] Balarew[4] and Kolthoff and Moltzau.[5] Kolthoff has presented evidence which seems to indicate that an adsorbed layer of hydrogen sulfide on the surface of the copper sulfide causes the postprecipitation of the zinc as sulfide.

Recently we have found that certain organic compounds may be used to alter the nature of analytical precipitates.[6–9] In a study of the separation of zinc and cobalt, it was found that if zinc sulfide was precipitated in the presence of a small amount of certain aldehydes, acrolein in particular, the quantity of cobalt carried down is

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[1] Present address, Tennessee Eastman Corporation, Kingsport, Tennessee.

[2] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

[3] Knowles and Martin, *Trans. Faraday Soc.*, **31**, 502 (1935).

[4] Balarew, *Z. anal. Chem.*, **102**, 408 (1935).

[5] Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).

[6] Caldwell, THIS JOURNAL, **57**, 96 (1935).

[7] Caldwell and Moyer, *ibid.*, **57**, 2372 (1935).

[8] Caldwell and Moyer, *ibid.*, **57**, 2375 (1935).

[9] Caldwell and Moyer, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 38 (1935).

so small that it is possible to make a quantitative separation of the metals in one precipitation. It seemed quite probable that this same procedure could be applied to the separation of copper and zinc.

Although a number of aldehydes were found to be effective in reducing the postprecipitation of zinc on copper sulfide, the unsaturated aldehydes containing the structure, RCH=CHCHO, proved superior to all others tried. Acrolein, cinnamic aldehyde and crotonaldehyde contain this structure and all were found to reduce greatly the quantity of zinc carried down. Acrolein is probably the best but it is troublesome to prepare and polymerizes so readily that it is difficult to keep. Cinnamic aldehyde tends to form an insoluble resinous product which interferes with filtration. Crotonaldehyde does not have these objectionable properties and was chosen for this investigation although it is not as effective as acrolein in the separation of zinc from cobalt. Benzaldehyde and formaldehyde were tried but were not as satisfactory as the unsaturated aldehydes. It was found that formaldehyde was quite effective in reducing the quantity of zinc carried down, but it seemed to prevent the quantitative precipitation of the copper. A few tenths of a milligram of copper always remained in solution after saturation with hydrogen sulfide.

Experimental

Materials.—The benzaldehyde and crotonaldehyde were distilled through a small laboratory fractionating column. Formaldehyde was used in the usual 40% solution.

A reagent grade of copper sulfate was recrystallized twice.

A reagent grade of zinc sulfate was recrystallized once.

Procedure.—A solution containing 0.125 g. of zinc and 0.125 g. of copper as sulfates with varying quantities of sulfuric acid was diluted to 100 ml. in a 250-ml. Erlenmeyer flask. Precipitations were made in pairs, one without aldehyde and the other containing approximately 0.05 ml. of an aldehyde. The flasks were connected to the same source of hydrogen sulfide through a Y-tube to ensure an equal supply of gas to each solution. A mechanical shaker kept the solutions in constant agitation during precipitation. Hydrogen sulfide was passed into the open flasks for five minutes to remove the air, then the flasks were stoppered and the gas was kept in contact with the solutions for fifteen minutes at the pressure of about 15 cm. of water. The flasks were removed, stoppered and allowed to stand for different lengths of time varying from thirty minutes to six hours.

In order to determine the quantity of zinc carried down, the solution was filtered through filter paper, washed with hot water and then five 10-ml. portions of 6 *N* hydrochloric acid were poured through the filter. This procedure was carried out in a hood since the aldehyde and hydrogen sulfide react to form a compound with a very unpleasant odor. The zinc was extracted by the hydrochloric acid and it was observed that if more than 10 mg. of zinc was present, there was a vigorous evolution of hydrogen sulfide. A few milligrams of copper always dissolved and this was removed before the zinc was determined. The solution was evaporated to dryness, moistened with nitric acid and again brought to dryness to destroy organic matter. The residue was dissolved in 100 ml. of water which was made normal with hydrochloric acid and the trace of copper precipitated with hydrogen sulfide. After filtration, the solution was evaporated to dryness and the zinc was determined turbidimetrically with potassium ferrocyanide according to the method described by Yoe.[10] In order to be certain that all the zinc was extracted from the copper sulfide, several precipitates, some formed in the presence of aldehyde and some formed in its absence, were dissolved in nitric acid and reprecipitated in the presence of crotonaldehyde. No zinc was found in any of the filtrates.

Benzaldehyde was tried in the first quantitative experiments. Although copper sulfide is usually precipitated in a solution 0.5 to 1 *N* in sulfuric acid, a lower normality was chosen in order to bring out the protective action of the aldehydes to the fullest extent. In the presence of 0.05 ml. of benzaldehyde, the zinc carried down with the copper sulfide varied from 0.2 to 1.2 mg., whereas, in the absence of the aldehyde, the quantity of zinc varied from 1.5 to 15 mg. Although considerable reduction in the zinc carried down was brought about by the benzaldehyde, it was not considered a satisfactory protective agent because of rather large variations in the results.

Crotonaldehyde was found to be effective in reducing the post-precipitation of zinc even in 0.36 *N* acid. In a series of determinations carried out as described above, approximately seventy times as much zinc was found on an average in the copper sulfide precipitates which were formed in the absence of the aldehyde. In four determinations in which filtration was made immediately after precipitation, an average of 0.07 mg. of zinc was found in those precipitated with aldehyde and an average of 4.0 mg. was found in the blanks. In ten determinations in which the precipitates were allowed to stand from two to three hours, an average of 0.11 mg. of zinc was found in those treated with aldehyde and an average of 8.0 mg. was found in the untreated ones. Five determinations on standing from four to six hours showed an average of 0.25 mg. of zinc when precipitated with aldehyde and an average of 18.0 mg. in its absence. A change of acid concentration from 0.36 to 0.5 *N* caused no significant difference in the results.

Discussion

The study of the postprecipitation of zinc on copper sulfide is complicated by the fact that the precipitate of copper sulfide is variable in composition and its true chemical nature is still unknown. Feigl[11] believes the initial precipitate

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[10] Yoe, "Photometric Chemical Analysis," John Wiley and Sons, Inc., New York, 1928, p. 397.

[11] Feigl, *Z. anal. Chem.*, **72**, 32 (1927).

contains free sulfur because boiling with sodium sulfite gives a considerable quantity of sodium thiosulfate. Recent work by Sauer and Steiner[12] lends support to this view. There is a definite cycle of changes which take place during the precipitation and aging of copper sulfide. During early stages of the precipitation, copper sulfide separates as a fine black sol which remains in suspension in the solution. After three or four minutes the particles begin to clump together and settle. In another five minutes the loose clumps become more compact and dense and assume a brownish color. If the flask is stoppered and allowed to stand, a definite aging process takes place. In two or three hours, the dense brownish-black aggregations begin to disperse and become greenish-black in color. In about ten hours the peptization has reached a point where secondary aggregates are so reduced in size as to be almost invisible to the unaided eye. Microscopic examination shows that minute primary particles predominate. An extremely small concentration of crotonaldehyde exerts a profound influence upon this aging process. When formed in the presence of crotonaldehyde, the precipitate does not peptize to give small primary particles, but on the contrary tends to coagulate into clumps that are even larger than those formed in the beginning. Microscopic examination shows that the clumps consist of many primary particles closely packed into opaque dense masses which show no tendency to disintegrate, even after standing for several days.

Summary

If copper sulfide is precipitated in the presence of a very small concentration of crotonaldehyde, the quantity of zinc carried down is reduced greatly. Apparently the crotonaldehyde reacts with the adsorbed hydrogen sulfide and reduces its value on the surface of the copper sulfide so that it will not cause the postprecipitation of the zinc.

COLUMBUS, OHIO RECEIVED SEPTEMBER 4, 1936

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(12) Sauer and Steiner, *Kolloid-Z.*, **72**, 41 (1935).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Conductivity of Various Salts in *n*-Propyl and Isopropyl Alcohols

BY FRANK HOVORKA AND JOHN COLBERT SIMMS[1]

Introduction

The conductivity of various salts has been determined in methyl and ethyl alcohols by many workers during the last few years. Since only a comparatively few measurements were made in *n*-propyl and isopropyl alcohols, it seemed desirable to carry out a series of conductivity determinations of the more common uni-univalent salts in these two solvents. The dielectric constant of the alcohols gradually decreases as they increase in molecular weight. Therefore, a study of the alcohols as a series ought to give the effect of the solvent as well as that of the dielectric constant on the nature of the electrolytic solutions.

Apparatus.—The assembly comprised a Leeds and Northrup Kohlrausch bridge and dial box type coils of low induction. All the resistances were checked against coils calibrated by the Bureau of Standards. The balance point was detected by Baldwin type telephones using two stage amplification. The other parts used in this "set up" were of the standard type generally used in accurate conductivity measurements.

The cell used in this investigation was of borosilicate glass and was made after a design of Hartley and Barrett.[2]

The thermostat was a large vacuum jar. The temperature was kept constant at 25 ± 0.005°.

Materials and Procedure.—Each of the alcohols containing a little water was refluxed for several hours over barium oxide and then distilled into a Pyrex fractionating flask and column without coming in contact with air. Each was fractionated to a boiling point of 0.05° and then treated with metallic sodium. After two further distillations they were fractionated directly into the conductivity cell which was dried previously by passing dry warm air through it. Usually about 100 g. of alcohol was distilled into the cell. The specific resistance of the *n*-propyl alcohol was 2×10^8 mhos. and of the isopropyl alcohol 9×10^9 mhos. These values were determined by using a direct current of 135 volts and were used in making the solvent correction.

The C. P. salts were recrystallized from water at least three times, dried, and analyzed for final purity. A known amount of each salt was transferred to a 100-cc. Pyrex bottle which had been baked out with a free flame. All of the handling of salts as well as of the alcohols was car-

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(1) This communication is an abstract of a portion of a thesis submitted by John Colbert Simms in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry. Original manuscript received July 24, 1933.

(2) Hartley and Barrett, *Trans. Chem. Soc.*, **103**, 789 (1913).