The existence of the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate has been established.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Solubility Relations of the Ternary System Zinc Nitrate–Nitric Acid–Water at 25°

BY WARREN W. EWING, ATWOOD J. RICARDS, WILLIAM J. TAYLOR, JR., AND DAVID W. WINKLER

This further investigation[1] was undertaken to confirm the existence of certain hydrates of zinc nitrate, and to determine methods of preparation of these salts for calorimetric and vapor pressure measurements which are being made in this Laboratory. Malquori[2] investigated this system at 20°, but gives only fragmentary data for the hexahydrate and the tetrahydrate regions.

Experimental

The apparatus and the technique used have been described in a previous article.[3] The only change was to use glass wool instead of a sintered glass plate as the filter medium. This was necessitated by the viscous solutions encountered. The glass wool was packed in a bell-shaped portion extending beyond a constriction in the filtering tube. All solutions were filtered.

The methods of preparing and purifying the zinc nitrate and the nitric acid, and the methods of analysis, have been described in previous articles.[1,3] The compositions of the solid phases were established by analyzing the moist residues and plotting "tie lines."

TABLE I

COMPOSITION OF THE TERNARY SYSTEM $Zn(NO_3)_2$–HNO_3–H_2O AT 25°

Solution		Residue		
% HNO_3	% $Zn(NO_3)_2$	% HNO_3	% $Zn(NO_3)_2$	Solid phase[a]
0.0	56.1			VI
3.5	53.1			VI
9.5	49.4			VI
15.5	46.8			VI
16.6	47.6	6.1	57.8	VI
15.5	49.7	10.3	56.0	VI–IV
24.0	41.5			IV
36.7	34.6			IV
38.6	34.5	22.1	50.7	IV
39.2	35.0			IV

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(1) Ewing, McGovern and Mathews, THIS JOURNAL, **55**, 4827 (1933).

(2) Malquori, *Gazz. chim. ital.*, **58**, 209 (1928).

(3) Ewing and Klinger, THIS JOURNAL, **55**, 4825 (1933).

TABLE I (*Concluded*)

Solution		Residue		
% HNO_3	% $Zn(NO_3)_2$	% HNO_3	% $Zn(NO_3)_2$	Solid phase[a]
38.0	37.5			IV
35.1	41.4			IV
31.6	45.9			IV
24.5	54.0	17.1	59.6	IV
18.5	60.5	11.6	64.9	IV
16.8	62.2	11.9	65.5	IV[b]
14.9	64.2	10.2	66.9	IV[b]
17.9	62.2	9.9	68.9	IV–II
12.8	65.9	11.9	67.0	II[b]
22.6	57.9	14.9	66.4	II
26.6	55.2			II
42.1	44.6			II
43.5	44.9			II
42.2	46.7			II
36.9	52.6	20.0	67.4	II
37.4	52.1	9.0	81.8	I
47.4	43.5	22.0	69.1	I
64.6	28.9			I
65.5	28.1			I
78.9	15.3			I
85.9	11.6	42.9	51.3	I
86.9	10.9			I
88.5	10.1			I
88.8	9.9			I

[a] VI = hexahydrate, IV = tetrahydrate, II = dihydrate, I = monohydrate

[b] Metastable solid phases.

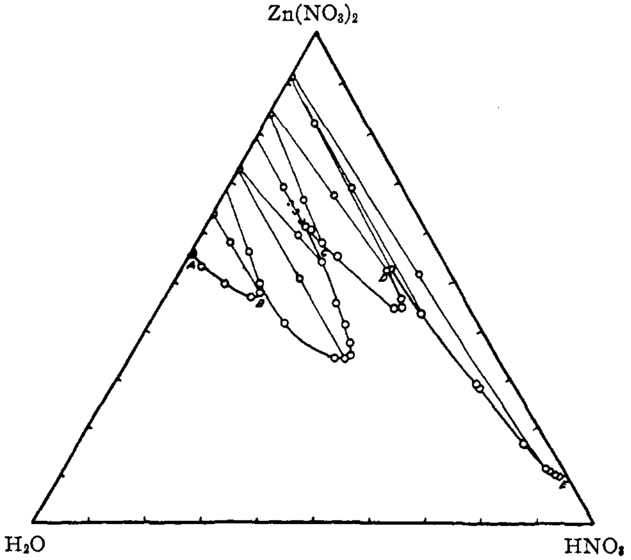

Fig. 1.—Ternary diagram of zinc nitrate–nitric acid–water.

Results

The data obtained are tabulated in Table I, and plotted in Fig. 1. The saturated solutions lying along portion AB of the curve are in equilibrium with the hexahydrate crystals; along BC, with the tetrahydrate; along CD, with the dihydrate, and along DE, with the monohydrate. These are the same hydrates that were found by the freezing point method for the binary system zinc nitrate–water.[1] No evidence was obtained of the existence of the trihydrate.

Summary

The equilibrium diagram for the ternary system zinc nitrate–nitric acid–water at 25° has been established.

The forms of zinc nitrate in stable equilibrium with nitric acid at 25° are the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate.

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The Fluidity of Dioxane–Water Mixtures[1]

BY JOHN A. GEDDES

I. Introduction

Because of the wide range of dielectric constants which can be obtained by the use of dioxane–water mixtures, these have become of considerable importance in the study of dilute electrolytic solutions.[2] The viscosity is also a contributing factor in this study, and although some measurements have already been made,[3] it is evident that corrections are necessary, the value of a 10% water–90% dioxane mixture at 20° being obviously in error. In addition, the fluidity–temperature plot of pure dioxane does not give the smooth curve which should be obtained. This is doubtless caused by incomplete purification, the melting point of the dioxane used having been reported as 11.0°, whereas a later method[4] affords a compound melting several tenths of a degree higher.

This investigation was undertaken to examine the effect of addition of water on the fluidity of dioxane, to correct existing data, and to furnish data at 25° in particular for application to the study of the conductivity of dilute solutions in these mixtures.

(1) The author wishes to express his appreciation to Dr. Eugene C. Bingham, who afforded the facilities of his laboratory for this investigation.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 476 (1933); **55**, 1019 (1933).

(3) Herz and Lorentz, *Z. physik. Chem.*, **140**, 407 (1929).

(4) Vingee, Thesis, Brown University, 1931.