

# The Ternary System: Water–Zirconyl Nitrate–Zirconyl Chloride at 0 °C

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**The aqueous ternary system of zirconyl nitrate and zirconyl chloride, in excess mineral acid, was investigated by solubility measurements at 0 °C. Solid phases were analyzed and studied by x-ray diffraction. Apparently, solid solutions between zirconyl nitrate pentahydrate and zirconyl chloride octahydrate were formed at 0 °C and a total acid content close to 8.2 N. Isothermal invariant points and ternary compounds corresponding to double salt hydrates of definite composition were not detected in the regions of the diagram that we studied.**

The aqueous ternary system of zirconyl nitrate and zirconyl chloride in excess mineral acid solution was investigated by solubility and x-ray methods to determine the nature and composition of solid phases formed. It is long known that  $ZrOCl_2 \cdot 8H_2O$  crystallizes easily from hydrochloric acid solution. On the contrary, in excess nitric acid, the formation of solid  $ZrO(NO_3)_2$  hydrates proves to be very difficult due to higher solubility of these salts and probably supercooling effects. Therefore, for ternary mixtures having low  $Cl^-/NO_3^-$  values, at constant acidity, long waiting times (up to 1 year) were needed for crystallization.

## Experimental Section

**Materials.** All chemicals used were reagent grade. The AR zirconyl chloride used was tested for impurities, especially Th (5, 6).

**Solutions.** Large excesses of HCl and  $HNO_3$  were needed to prevent hydrolysis of zirconyl salts.

A special grade of zirconium oxide, with low water content, was used to prepare concentrated solutions. It was made by the following method. Zirconium hydroxide is precipitated from  $ZrOCl_2$  solution by ammonia as usual, and washed with hot water. The paste containing 80% water was dehydrated partially by heterogeneous distillation with dry toluene. A fine powder, easily soluble in acids and retaining only 19% water, was obtained by this way.

Using this  $ZrO_2$  a stock solution was prepared by dissolving in a mixture of concentrated, reagent grade, HCl and  $HNO_3$ . A gentle heat was applied to aid dissolution of  $ZrO_2$ , and some nitrogen oxides were lost. After cooling to 25 °C the clear solution was carefully analyzed.

The following results were obtained:  $ZrO^{2+}$ , 3.01;  $NO_3^-$ , 5.70;  $Cl^-$ , 2.30 mol  $l^{-1}$ .

In nine volumetric flasks of 100 ml capacity, 80-ml portions of the stock solution were mixed with 20 ml of various mixtures of 10 N HCl and 10 N  $HNO_3$ . Mixtures no. 1 to 9 were obtained in this way.

Densities of the above nine solutions were measured pycnometrically at 25 °C. They varied from 1.481 (solution 1) to 1.507 (solution 9).

**Analytical Methods.** The chemical composition of all solutions was based on wet chemical analyses. Chloride ion was titrated by Volhard's method (1, 7).  $NO_3^-$  was determined by alkalimetry,

after reduction to ammonia by Devarda's metal (3). Zirconyl ion  $ZrO^{2+}$  was determined gravimetrically after precipitation with  $NH_4OH$  and calcination at 900 °C for 3 h.

The accuracy of gravimetric results was better than 0.1%, as may be seen from Table I, column 3 (the weight percent of Zr in all solids was the same). The precision of volumetric determinations was approximately 0.2%.

**Total Acidity.** Total acid is defined as the total concentration of HCl and  $HNO_3$  used to dissolve  $ZrO_2$  and to make up the solution. It includes combined acids and free acids.

Therefore, total acidity of mixtures 1 to 9 was 8.4 N. The molarity of Zr in all mixtures 1 to 9 was 2.41.

For each solution weight percents were calculated from molarity and density data. Calculated percentages agreed very well with analytical results.

Mixtures 10 to 13 were prepared similarly. In these solutions total acidity was 7.94 N,  $ZrO^{2+}$  was 2.68 M and densities were respectively 1.500, 1.503, 1.505, and 1.508 at 25 °C.

**Equilibration.** The clear solutions prepared were equilibrated at 0 °C in conical stoppered flasks for periods of 100–350 days. The flasks were shaken at regular intervals. Long waiting times were needed to attain crystallization, and this period seemed to be inversely proportional to  $Cl^-/NO_3^-$  ratios. Seeding with zirconyl chloride or zirconyl nitrate crystals was not effective in accelerating crystallization. When the amount of crystals obtained seemed to remain unchanged they were filtered and washed with ethyl ether cooled to 0 °C.

We believe that the long periods of time that were required to attain equilibrium in this system were due mainly to an intense supercooling effect that could not be overcome by shaking or by seeding. It is also probable that "induced solubilization" due to higher solubility of zirconyl nitrates played some role.

Both the solid phases and remaining mother liquors were carefully analyzed by the above mentioned chemical wet methods.

After filtration of solids, total acidity in mother liquors was obtained from  $Cl^-$  and  $NO_3^-$  concentrations in the filtrates. It was  $8.0 \pm 0.2$  N, which may be considered as practically constant. It is obvious that after separation of solid  $ZrOCl_2$  and  $ZrO(NO_3)_2$  mixtures, the amounts of  $Cl^-$  and  $NO_3^-$  ions in the liquid phase will diminish.

The  $H^+$  concentration in the original solutions remained constant after crystallization, with a precision of  $\pm 0.2$  N. This was calculated from eq 2, explained in the following section. This result is in agreement with the finding that solid phases obtained were not more acidic or more basic than the usual zirconyl compounds.

## Results

The components of this system are  $Cl^-$ ,  $NO_3^-$ ,  $ZrO^{2+}$ ,  $H^+$ , and  $H_2O$ . If  $X_{Cl^-}$  is the mole percent of chloride ion and other  $X$  values are indexed similarly, the following equations hold:

$$X_{Cl^-} + X_{NO_3^-} + X_{ZrO^{2+}} + X_{H^+} + X_{H_2O} = 100 \quad (\text{mass balance}) \quad (1)$$

**Table I. The System Water, Zirconyl Nitrate, and Zirconyl Chloride at 0 °C. Compositions in Weight Percent**

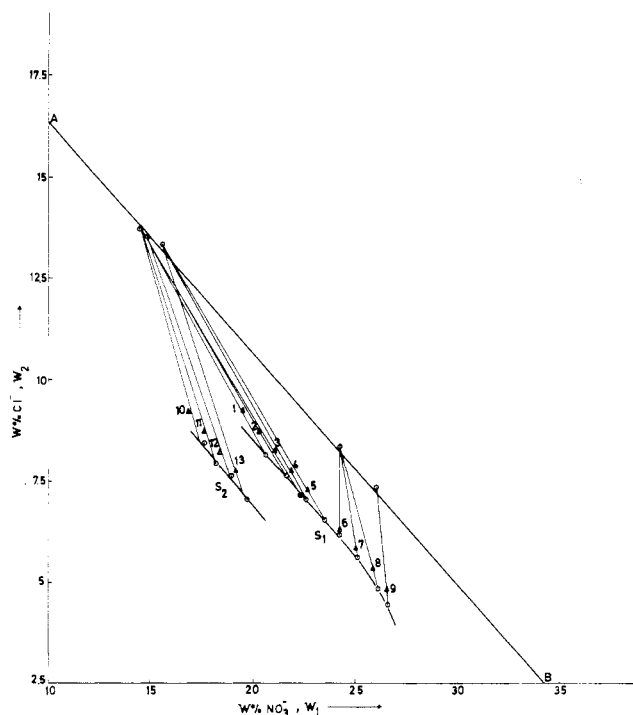
Mixture no.		Initial comp	Liquid phase	Solid phase
Total acid = 8.4 N				
1	NO <sub>3</sub> <sup>-</sup>	19.45	20.6	14.5
	Cl <sup>-</sup>	9.2	8.1	13.7
	Zr	14.7	11.48	28.2
2	NO <sub>3</sub> <sup>-</sup>	20.26	21.6	14.5
	Cl <sup>-</sup>	8.7	7.6	13.7
	Zr	14.7	11.51	28.2
3	NO <sub>3</sub> <sup>-</sup>	21	22.3	14.5
	Cl <sup>-</sup>	8.2	7.1	13.7
	Zr	14.65	11.88	28.2
4	NO <sub>3</sub> <sup>-</sup>	21.8	22.6	15.5
	Cl <sup>-</sup>	7.7	7.0	13.3
	Zr	14.63	12.86	28.2
5	NO <sub>3</sub> <sup>-</sup>	22.6	23.5	15.5
	Cl <sup>-</sup>	7.25	6.5	13.3
	Zr	14.60	12.88	28.2
6	NO <sub>3</sub> <sup>-</sup>	24.2	24.2	24.2
	Cl <sup>-</sup>	6.27	6.1	8.3
	Zr	14.55	13.2	28.2
7	NO <sub>3</sub> <sup>-</sup>	25.0	25.1	24.2
	Cl <sup>-</sup>	5.8	5.6	8.3
	Zr	14.52	13.4	28.2
8	NO <sub>3</sub> <sup>-</sup>	25.8	26.1	24.2
	Cl <sup>-</sup>	5.3	4.7	8.3
	Zr	14.49	11.52	28.2
9	NO <sub>3</sub> <sup>-</sup>	26.5	26.6	26.5
	Cl <sup>-</sup>	4.8	4.4	7.3
	Zr	14.47	12.2	28.2
Total acid = 7.94 N				
10	NO <sub>3</sub> <sup>-</sup>	16.8	17.6	14.5
	Cl <sup>-</sup>	9.16	8.4	13.7
	Zr	16.25	13.95	28.2
11	NO <sub>3</sub> <sup>-</sup>	17.6	18.2	14.5
	Cl <sup>-</sup>	8.7	7.9	13.7
	Zr	16.24	14.29	28.2
12	NO <sub>3</sub> <sup>-</sup>	18.3	18.9	14.8
	Cl <sup>-</sup>	8.2	7.6	13.5
	Zr	16.22	14.46	28.2
13	NO <sub>3</sub> <sup>-</sup>	19.1	19.7	15.5
	Cl <sup>-</sup>	7.7	7.0	13.3
	Zr	16.20	14.80	28.2

$$X_{Cl^-} + X_{NO_3^-} = X_{H^+} + 2X_{ZrO_2^{2+}} \quad (\text{charge balance}) \quad (2)$$

As outlined in the preparation of solutions, ZrO<sub>2</sub><sup>2+</sup> concentration and total acidity (X<sub>Cl<sup>-</sup></sub> + X<sub>NO<sub>3</sub><sup>-</sup></sub>) were kept constant in each of the two sets of initial solutions. It follows from eq 2 that

$$X_{H^+} = \text{constant} \quad (3)$$

At constant temperature and pressure, and under the condition specified by eq 3, the system investigated is divariant. Therefore, to draw the phase diagram, only two independent variables will be sufficient. The other three concentrations may be calculated from eq 1–3. Choosing rectangular coordinates, we have plotted the weight percent of nitrate ion, W<sub>1</sub>, horizontally and the weight percent of chloride ion, W<sub>2</sub>, vertically. Figure 1 shows a portion of the diagram obtained, the region of W<sub>1</sub> greater than 10 and W<sub>2</sub> greater than 2.5. The intercept of line AB with W<sub>1</sub> axis (0% Cl<sup>-</sup>) is at 38.59% by weight, corresponding to zirconyl nitrate pentahydrate. The intercept of AB with W<sub>2</sub> axis (0% NO<sub>3</sub><sup>-</sup>) is at 22.03%, which corresponds to zirconyl chloride octahydrate. Detailed solubility information is summarized in Table I. The composition of initial mixtures, saturated liquids in equilibrium, and solid phases, all expressed in weight percent, are given in



**Figure 1.** Phase diagram of the system water–zirconyl nitrate–zirconyl chloride at 0 °C. S<sub>1</sub> pertains to a total acid of 8.4 N. S<sub>2</sub> pertains to a total acid of 7.94 N.

three columns. For each mixture a tie-line is drawn through the three experimental points presented in Table I. The solubility curve S<sub>1</sub> pertains to a total acidity of 8.4 N, and the solubility curve S<sub>2</sub> to a total acidity of 7.94 N. This shows clearly that the solubility is lower at a lower acidity.

It is seen that, within the precision of chemical analyses, all the solid phases obtained fall on the line AB. This result is in support of solid solution formation between zirconyl nitrate pentahydrate and zirconyl chloride octahydrate, provided x-ray examinations are not in contradiction with the existence of such mixed crystals.

The molecular weights of the two solids, ZrOCl<sub>2</sub>·8H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O, differing only by one unit (322.3 and 321.3), Zr content, should be approximately constant in the mixed solids. Our experimental results are in agreement with this conclusion. In column 3 of Table I we see that Zr content is 28.2% in all solid phases. We can deduce also that the ternary solids are mixed salts that are not more basic, nor more acidic than the usual zirconyl compounds. That means in all solids obtained we have

$$X_{Cl^-} + X_{NO_3^-} = 2X_{ZrO_2^{2+}} \quad (4)$$

Isothermal invariant points were not detected in the regions of diagram that we studied.

**X-Ray Data.** Debye–Scherrer diffraction patterns for all powders prepared were recorded on photographic films. After Delaunay reduction (2), the crystal parameters were calculated. For some mixtures, the chemical composition of solids obtained was very close together. On the other hand, the precision of crystallographic measurements does not allow a distinction to be made between, say, powders 1 and 12. It was therefore sufficient to consider only three main groups of powders for x-ray study. The results obtained are summarized in Table II. Every result is the mean of at least four measurements.

It is observed that the variation of parameters, plotted as a function of the Cl<sup>-</sup>/NO<sub>3</sub><sup>-</sup> ratio, is linear. It can be suggested that solid solutions have been formed by inclusion of ZrO(NO<sub>3</sub>)<sub>2</sub> into the ZrOCl<sub>2</sub> lattice.

Table II. Summary of Crystallographic Data

Solid no.	Dimensions, Å			Unit cell
	a	b	c	
1, 2, 3, 10, 11, 12	16.58	22.11	17.27	Orthorhombic
4, 5, 13	16.47	21.98	17.13	Orthorhombic
6, 7, 8	15.80	21.38	16.50	Orthorhombic

### Discussion

Although the tie-lines are converging to three different centers on the line AB (except one), ternary compound formation was not confirmed by x-ray studies, and isothermal invariant points were not found on the diagram. This is another support for the opinion that ternary compounds are not formed in this system. We believe that solid solutions between  $ZrO(NO_3)_2 \cdot 5H_2O$  and  $ZrOCl_2 \cdot 8H_2O$  are crystallized at 0 °C, at least for a total acidity close to 8.2 N. Although formation of solid solutions between two hydrates with differing degrees of hydration seems to be rather unusual, we were not able to prove the formation of any ternary compound of known composition. Similarly, existence of isothermal invariant points was not detected on the phase diagram, at least in the regions that we studied.

Pure zirconyl chloride octahydrate and pure zirconyl nitrate hydrates were similarly studied by the x-ray diffraction method. For zirconyl chloride octahydrate we have obtained the following parameters (mean value of four measurements):  $a = 12.9 \text{ \AA}$ ,  $b = 12.9 \text{ \AA}$ ,  $c = 10.6 \text{ \AA}$ .

They are very close to literature data. Accordingly, this salt belongs to the tetragonal system.

We have also prepared pure zirconyl nitrate dihydrate  $Zr(NO_3)_2 \cdot 2H_2O$  and measured the crystallographic dimensions:  $a = 9.44 \text{ \AA}$ ,  $b = 12.85 \text{ \AA}$ ,  $c = 9.85 \text{ \AA}$  (mean value of four measurements).

According to the above results, this salt belongs to the orthorhombic system.

As for the zirconyl nitrate pentahydrate, we were not able to

prepare crystals corresponding exactly to  $Zr(NO_3)_2 \cdot 5H_2O$  and having a constant composition (4). It appears that the pentahydrated nitrate is stable only in the form of solid solutions.

When the total acid was increased to 9.4 N, we were able to prepare solutions more concentrated than shown by the line AB. Solid phases which crystallized from these mixtures at 0 °C were apparently mixed salts formed between zirconyl chloride octahydrate and hydrates of zirconyl nitrate with water molecules less than five (4, 3, and 2). X-Ray results were more difficult to interpret, and it was not possible to show the existence of a ternary compound.

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### Glossary

$X_i$	mole percent of species $i$
$W_1$	weight percent of $NO_3^-$
$W_2$	weight percent of $Cl^-$
N	normality
S	solubility curve

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## Thermodynamic Properties of the System Toluene-1,2-Dichloroethane

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Data on heats of mixing at 30 °C, vapor-liquid equilibrium, latent heats of vaporization at 686 mmHg, and vapor pressures for the system toluene-1,2-dichloroethane are presented.

This paper presents the experimental data on vapor-liquid equilibrium, latent heats of vaporization, vapor pressure, and heats of mixing of mixtures of toluene and 1,2-dichloroethane. Earlier work from this laboratory has been reported (17, 18). A literature survey revealed that the system toluene-1,2-dichloroethane has been studied and Table I shows the extent of study on the system. In addition to these available data, Barker (2) has reported activity coefficients for the system at 30, 40, and 50 °C determined by gas-liquid chromatographic techniques.

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### Material Used and Purification

Analar toluene and laboratory grade 1,2-dichloroethane supplied by British Drug House, Bombay, were purified by the methods described by Weissberger (30) and Riddick and Bunger (19). The purities were checked against refractive index and density, and are reported in Table II. Vapor phase chromatographs were obtained for the liquids using an AIMIL-NCL dual column gas chromatograph using Silicone gum rubber S.E. 30 as column material. A single peak was obtained for all the liquids.

### Vapor Pressure Data

Vapor pressures of 1,2-dichloroethane were obtained up to laboratory pressure in a Brown still and at higher pressures in a Swietoslawsky type still. The present values together with data