to find the original work in which this value was determined. Young records this value as 57 weight % of carbon tetrachloride. If by chance this should have been 57 mole per cent, the latter value agrees quite well with our results.

Conclusions

1. Data have been presented which show that the system carbon tetrachloride–ethyl acetate behaves in the same manner when subjected to pressure change as do all other systems for which similar data are available. The concentration of carbon tetrachloride in the azeotrope increases as the pressure decreases.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Crystal-Chemical Studies of the Alums. I. Solid Solutions of Potassium Aluminum Alum and Ammonium Aluminum Alum

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Solid solution formation by potassium aluminum alum and ammonium aluminum alum was first observed by Krickmeyer,[1] who proved the existence of a continuous series of solid solutions by density measurements. More recently Hill and Kaplan[2] have studied this pair of alums and made analyses of the conjugate liquid and solid solutions. It was noted that the tie-lines pass through the water apex of the ternary diagram, indicating that the ratio of the two alums is the same in the aqueous phase as in the solid phase. The data when plotted with respect to these two ratios fall nearly upon the true diagonal, giving what Hill and Kaplan regarded as an ideal example of Roozeboom's class 1.[3] This appears to be the first example of this type to be noted. In such a case the deviation of the two phases from the properties of ideal solutions, whatever they are, are quantitatively similar.

It seemed of interest to investigate this series of solid solutions further by means of X-ray diffraction to determine whether they were ideal from the standpoint of Vegard's law,[4] which states that for two compounds of the same crystal structure, forming a continuous series of solid solutions, the lattice constants of the solid solutions are a linear function of the composition. The results of such a study are reported in this communication.

Experimental

The materials used were reagent grade alums each of which was recrystallized from conductivity water slightly acidified with sulfuric acid. To produce fine crystals the solutions were shaken vigorously during crystallization. The crystals were washed successively with water, alcohol, and ether, and then air dried overnight. Analyses of these alums for aluminum by precipitation with *o*-hydroxyquinoline, according to the method of Kolthoff and Sandell,[5] were in excellent agreement with the theoretical composition.

The preparation of the solid solutions followed that of Hill and Kaplan[2] each complex being made up in duplicate so that the final equilibrium solid solution was formed in one case (A) from the potassium alum and in the duplicate case (B) from the ammonium alum. The stoppered bottles containing the complexes were turned in a thermostat at 25 ± 0.1° until equilibrium was attained. Contrary to the observations of Hill and Kaplan, equilibrium was reached much more slowly under the conditions of this experiment. It was necessary to introduce four lengths of 8 mm. Pyrex glass rod into each bottle, thereby producing a miniature rod-mill effect, to prevent the crystals from becoming too coarse. Even under these conditions attainment of complete equilibrium required four months. The crystals of the equilibrium solid solution were filtered off with suction, washed successively with alcohol and ether, and air-dried.

The compositions of the solid solutions were determined by analyzing for ammonia by titrating with calcium hypochlorite solution according to the procedure of Kolthoff and Sandell.[5] This method proved to be much more accurate than the usual Kjeldahl method. From the ammonia content the amount of ammonium alum present was calculated, and the potassium alum determined by difference.

Using a Buerger powder camera[6] of 57.3 mm. radius, precision determinations of the lattice constants of the pure alums and their solid solutions were made at 25°. FeK radiation was used with the films in the asymmetric position,[7] and the camera was thermostated as described by Straumanis and co-workers.[8] For control of the air thermostat a hollow cylindrical mercury regulator[9] was

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(1) Krickmeyer, *Z. physik. Chem.*, **21**, 53 (1896).

(2) Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

(3) Roozeboom, *Z. physik. Chem.*, **8**, 504 (1891).

(4) Vegard, *Z. Physik*, **5**, 17 (1921).

(5) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1936.

(6) Buerger, *Am. Mineralogist*, **21**, 11 (1936).

(7) Ievins and Straumanis, *Z. Krist.*, **94**, 40 (1936).

(8) Straumanis, Ievins and Karlsons, *Z. anorg. allgem. Chem.*, **238**, 175 (1938).

(9) Heisig and Cameron, *Ind. Eng. Chem., Anal. Ed.*, **5**, 420 (1933).

used with a vacuum tube relay circuit. The temperature within the thermostat could be kept constant at 25 ± 0.2°, and the variation in sample temperature was probably considerably less than this.

The sample consisted of 200-mesh powder stuck on the outside of a fine Pyrex glass capillary tube with an adhesive such as glyptal varnish.

Diffraction lines on the films were measured to ±0.02 mm. Then, using only lines with angle Θ greater than 60°, the lattice constants were calculated by Cohen's analytical method.[10]

Results

In Table I are the compositions of the pure alums and their solid solutions, and their lattice contants at 25°. The criterion for the attainment of equilibrium in the solid solutions was the close agreement in composition for the two members of a pair, each of which had approached equilibrium from opposite directions.

TABLE I

COMPOSITION AND LATTICE CONSTANTS FOR POTASSIUM ALUM AND AMMONIUM ALUM AND THEIR SOLID SOLUTIONS

Substance	Wt. % NH_3 (by analysis)	Mole % $NH_4Al(SO_4)_2 \cdot 12H_2O$	Lattice constant in Å. at 25 ± 0.1°
$KAl(SO_4)_2 \cdot 12H_2O$	0.00	0.00	12.1328
S. S. 1A	1.036	28.52	12.1537
S. S. 1B	1.039		12.1527
S. S. 2A	1.904	51.76	12.1717
S. S. 2B	1.900		12.1722
S. S. 3A	2.770	74.57	12.1926
S. S. 3B	2.767		12.1923
$NH_4Al(SO_4)_2 \cdot 12H_2O$	3.750	100.0	12.2136

The results are presented graphically in Fig. 1. A straight line has been drawn through the points representing the lattice constants of the pure alums. It is seen that the deviations from Vegard's additivity law are extremely small. The deviations are, however, believed to be real, and the pair can be said to be not quite ideal from the standpoint of their solid solutions and Vegard's law.

The values of the lattice constants reported above are believed to be accurate to ±0.001 Å. In the case of the pure alums the values may be compared with those of Lipson and Beevers,[11] who report for $KAl(SO_4)_2 \cdot 12H_2O$, 12.133 Å., and for $NH_4Al(SO_4)_2 \cdot 12H_2O$, 12.215 Å., each with an accuracy of ±0.002 Å., but with no indication of the temperature of their observations.

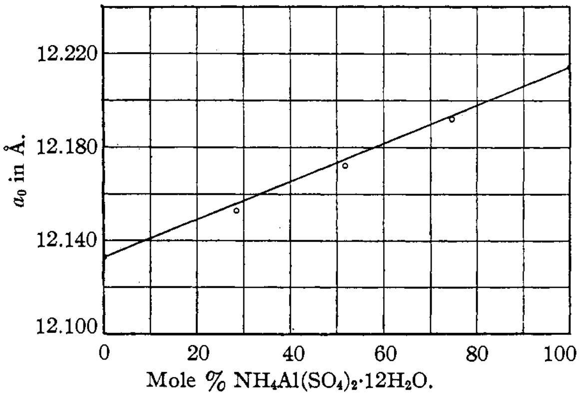

Fig. 1.—Lattice constants as a function of composition for solid solutions of potassium and ammonium alums.

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Summary

1. The solid solutions of potassium aluminum alum and ammonium aluminum alum have been studied by means of X-rays and found to deviate slightly from Vegard's law of additivity.

2. The following values are reported for the lattice constants of the pure alums at 25 ± 0.1°:

$KAl(SO_4)_2 \cdot 12H_2O$ $a_0 = 12.133 \pm 0.001$ Å.
$NH_4Al(SO_4)_2 \cdot 12H_2O$ $a_0 = 12.214 \pm 0.001$ Å.

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(10) Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); **7**, 155 (1936).

(11) Lipson and Beevers, *Proc. Roy. Soc.* (London), **A148**, 664 (1935).