[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE COLLEGE OF WASHINGTON]

Binary Liquid Systems. II. The Azeotropic Composition of Carbon Tetrachloride–Ethyl Acetate Mixtures as a Function of the Pressure

BY PHILIP W. SCHUTZ AND ROBERT E. MALLONEE

In the first article[1] of this series it was pointed out that, judging from the then existing values for the composition of the azeotrope formed by carbon tetrachloride–ethyl acetate mixtures at different pressures, it appeared that this system was unique since the rate of change of the azeotropic composition with pressure decreased as the pressure decreased.

The rapid change in composition with pressure at higher pressures evidenced by these data would indicate that in the vicinity of 900 mm. a complete separation of these compounds by ordinary fractional distillation would be possible (see curve 1, Fig. 1). As the data were so few in number and the phenomenon an entirely new one, the present work was undertaken in order to obtain a complete set of data over a wider pressure range.

Experimental

The materials and apparatus were identical with those previously described[1] except that a pressure regulator was incorporated, which, with careful operation, controlled the pressure within ±0.3 mm. All runs were made as described earlier. As we were interested only in the composition of the azeotrope and since the quantities of materials were limited, we did not cover the entire range of compositions at any pressure other than 685 mm. The azeotropic composition was determined at each pressure by means of the x–y diagram familiar in the analysis of distillation problems. The composition of the liquid (x) was plotted against that of the vapor (y), both in terms of the same constituent. A forty-five degree line on such a plot represents vapors and liquids of the same composition. The intersection of the curve through the points representing equilibrium compositions of the vapor and liquid on either side of the azeotrope with this forty-five degree line represents the azeotropic composition at the pressure under which the data were obtained. At each pressure, three or more vapor–liquid equilibrium compositions were determined on each side of the azeotropic composition. In every case the intersection was at such an angle as to lead to no uncertainty as to the azeotropic composition. All analyses were made by refractive index (n^{20}D) and all compositions are believed accurate to well within ±0.1 mole %.

Discussion of Results

The data obtained are given in Table I and plotted as composition *vs.* pressure in curve 2, Fig. 1. It is apparent from this curve that the rate of change of composition of the azeotrope formed by this system with pressure is increasing as the pressure is decreased. This result is in accord with all available data of a similar nature on other systems. It is also apparent that the present results are not in very good agreement with the three earlier values, indicated by curve 1 of Fig. 1, and we are unable to explain the large discrepancies at the present time. The value of 43 mole per cent. at 760 mm. given by Young[2] and by Lecat[3] has been widely quoted, but it is impossible

TABLE I

AZEOTROPIC DATA AT DIFFERENT PRESSURES

P, mm.	B. p., °C.	Mole % CCl_4
789.2	76.15	55.60
583.7	66.72	60.75
484.5	61.32	63.75
385.2	55.22	67.75
285.7	47.36	72.60

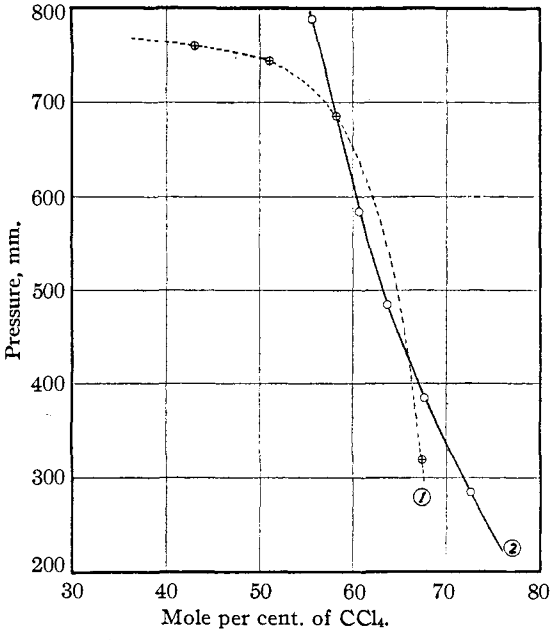

Fig. 1.—Change in composition of the azeotrope formed by the system carbon tetrachloride–ethyl acetate with pressure: 1, plot of data from Reference 1; 2, plot of data from Table I.

---

(1) THIS JOURNAL, 61, 2691 (1939).

(2) Young, "Distillation Principles and Processes," Macmillan and Company, London, 1922, p. 52.

(3) Lecat, "l'Azeotropisme," Lamertin, Brussels, 1918, p. 136.

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.

PULLMAN, WASH. RECEIVED MARCH 5, 1940

[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

BY HAROLD P. KLUG AND LEROY ALEXANDER

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

---

[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).