PHASE EQUILIBRIA STUDY OF THE BORIC ACID-SODIUM SULPHATE-WATER SYSTEM AT 50°C AND 70°C[1]

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Abstract

The study of the ternary systems containing boric acid are of great industrial importance because the possibility to choose best conditions to separation this compound from borates ores. For them, it is convenient to make an isothermal study of this system and to plot curves show equilibrium conditions of the solid substance and the ternary liquid. For that the solubility of each substance in aqueous solution with changeable quantity of them must be determined, at constant pressure and temperature. In this paper we are showing the result of the experimental study of the equilibrium of the H_3BO_3-Na_2SO_4-H_2O system at 50° C and 70° C, and atmospheric pressure. The results are presented in a ternary phase diagram form. The solubility curve of H_3BO_3 in Na_2SO_4 saturated solutions are constructed too, showing that solubility of the first one is increasing as the concentration of the second one is increasing. In the temperature and composition domain studied, the solid phases observed were H_3BO_3, Na_2SO_4 and a mixture of them.

Key words: Boric acid; Sodium sulphate; Equilibrium ternary diagram.

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INTRODUCTION

In this paper the boric acid behavior in saturated solutions of sodium sulphate was investigated, with the aim of find the best conditions to separation this acid from solutions of borates minerals treatment, as the ulexite, when it is treated with sulphuric acid. The behavior in the equilibrium of H_3BO_3-Na_2SO_4-H_2O system was investigated by preparing several saturated solutions of them at 50° C and 70° C of temperature and atmospheric pressure.

Generally, the equilibrium conditions between liquid and solid phases, are represented by different kind of diagrams. In this case, we prefer the ternary diagram, because it shows how the two solid components and water systems with the three components systems in general are related.[1]

All compositions, e. g., bulk compositions, liquid compositions and compositions of solid phases, on ternary diagrams may be expressed in terms of the three end member component, which define the system. These three components are located at the apices of a triangle.

Each side of the ternary diagram represents combinations of the two substances indicated on the extremity of that side. One point inside of diagram represents a ternary solution, so the concentrations sum, expressed in mass percentage will be 100 % always.[1] This ternary diagram allows to observe directly the solid phase composition in equilibrium with the dissolution.

MATERIALS AND METHOD

All chemicals used in the determination of the liquid-solid equilibrium at 50°C and 70°C were Anedra**,** analytical grade: H_3BO_3, 99,84 %, and Na_2SO_4 99,75 %. Water distillated, pH: 6,7 was used.

The experiments were carried out in a device constructed in the laboratory. It is an transparent acrylic cylinder of 10 cm of diameter and 15 cm height, closed, provided with stirring and entry on de upper part to put ph-meter, if necessary, and side entries to allow put thermometer and take samples. This device was placed in a thermostat at determined temperature.

The experimental method consisted basically in preparing duplicates of heterogeneous mixtures of known overall composition, by intensive stirring (400 - 600 rpm), and settling several times at constant temperature to ensure that equilibrium was reached. To confirm the equilibrium was reached, the solutions were monitored by testing some of the ions, Na^+, to determine any variation between two or three determinations.[1]

When the equilibrium was reached, samples were taken from both phases, liquid and solid, and analyzed by conventional methods: boric acid by titulation with NaOH in mannitol presence; Na_2SO_4 through the sodium, by atomic absorption spectrometry in a Shimadzu AAS 6500.

RESULTS AND DISCUSSION

Tables 1– 2 show the experimental data obtained for the systems investigated, for 50°C and 70°C, respectively. These results are in similar coincidence with the literature data.[2,3] Solid phases present are indicated as B, if it is boric acid, or S, if sodium sulphate.

Table 1. Solubility of boric acid in saturated solutions of sodium sulphate, at 50° C. B: H_3BO_3; S: Na_2SO_4

% Na_2SO_4	0,00	4,50	9,00	13,30	18,00	23,00	26,00	30,00	30,60	31,50
% H_3BO_3	10,20	10,35	10,90	11,50	11,90	12,50	12,90	13,30	6,00	0,00
Solid phase	B	B	B	B	B	B	B	B + S	S	S

Table 2. Solubility of boric acid in saturated solutions of sodium sulphate, at 70°C**.** B: H_3BO_3; S: Na_2SO_4

% Na_2SO_4	0,00	5,00	10,00	15,00	20,00	24,00	28,00	28,50	29,50	31,00
% H_3BO_3	15,10	15,30	15,80	16,40	16,90	17,00	17,40	12,30	7,00	0,00
Solid phase	B	B	B	B	B	B	B+S	S	S	S

As we can see in Figure 1, the graphical representation of the equilibrium data results in similar diagrams for the two systems investigated. In it we can observe that boric acid solubility increases as sodium sulphate concentration is increasing, until a certain point**,** in the temperature range studied.

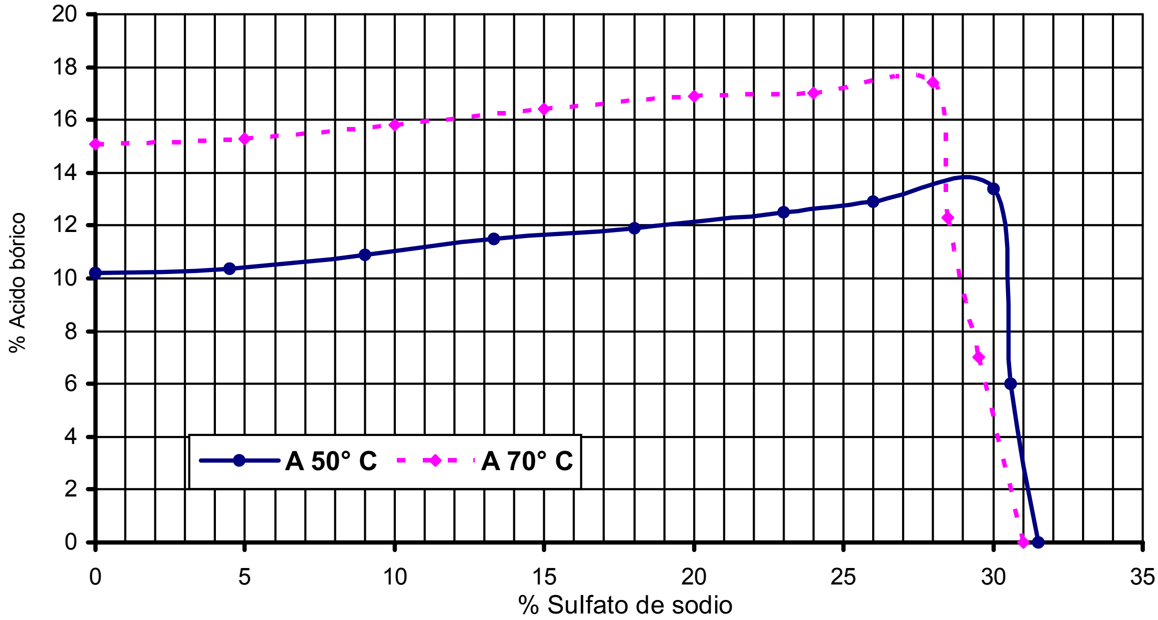

Figure 1. Solubility of boric acid in saturated solutions of sodium sulphate.

In order to show these data in a ternary diagram we consider that each apex of the triangle representing the ternary system express 100 % of the component at that apex. The side of the triangle, directly opposite that apex, represents 0 % of the apex component. Compositions of points which lie along the outside edge of the triangle are a mixture of the two components at each end of that line, with 0 % of the third component.

For any point inside the ternary diagram, the sum of distances parallely traced from this point to the three sides will be always equal to one triangle side. Then, taking one side as unity and expressing the three components quantities like totality fraction, it is possible to represent compositions of any ternary system by one point in the diagram. So, if each triangle apex represents a pure component, that is, H_2O, H_3BO_3 or Na_2SO_4, the distance from a point inside the triangle to any side, parallely measured to one of another sides gives the proportion of component represented by opposite apex. Any point inside the triangle represents three components. But, if the point is situated on a side, that indicates only two components, that are represented by both of apices of this side.[(1)]

When two substances, like H_3BO_3 and Na_2SO_4 in this case, don't form a compound, the isothermal solubility curve, that shows composition of dissolutions with both of them, in different proportions, in equilibrium with the solid H_3BO_3 or Na_2SO_4, are similar to showed in Figure 2 a) if the experience was realized at 50° C, or 2 b) if it was at 70° C.

The solubility curve in a ternary diagram have two parts: from one end to the other of AB curve, that begins at 0,0 % of sodium sulphate and 10,20 % of boric acid and comes to the point which composition is 30,00 % of sodium sulphate and 13,30 % of boric acid, for the experience realized at 50° C, the solid phase in equilibrium with the dissolution is boric acid, while BC curve, that begins in the last point and comes until the point defined by the composition 31,50 % of sodium sulphate and 0,00 % of boric acid, the solid phase is Na_2SO_4. In other words, portions AB and BC of isothermal curve, determine different equilibrium conditions between a ternary solution and a solid phase.

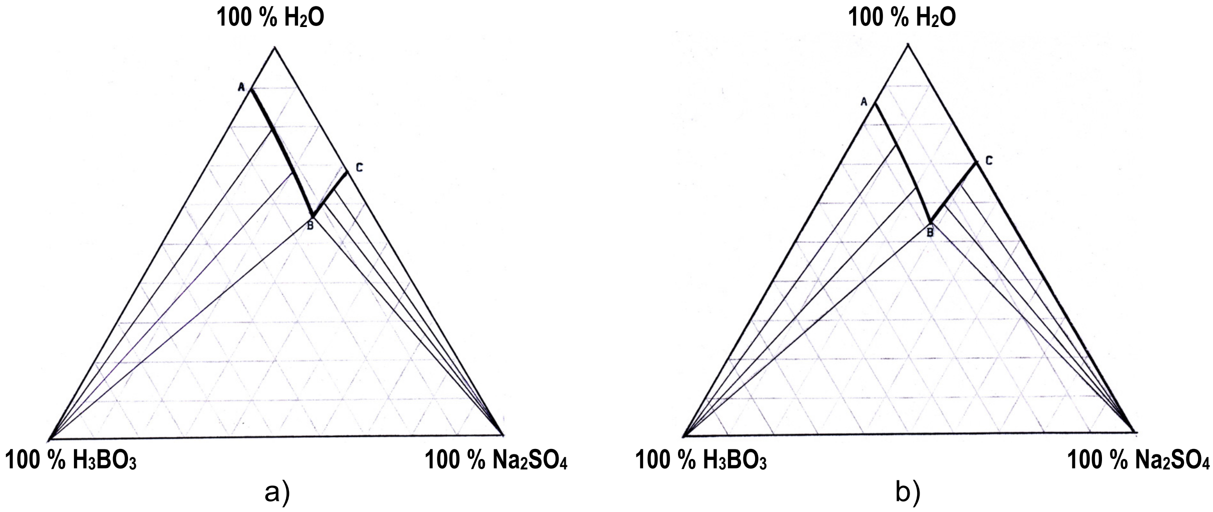

Figure 2. Ternary diagrams of phases equilibria at: a) 50° C; b) 70° C.

The nature of solid phases is left indicated by connection lines between correspondent points to the curves, which indicate saturated solutions compositions, with points determining solid phases composition, for that reason the connection lines are united with the correspondent apex. The B point represents the liquid composition in equilibrium with both solids, H_3BO_3 and Na_2SO_4. Therefore, there are three phases, one liquid phase and two solid phases. The B point is the isothermal invariant point. The solubility curve exhibits a discontinuity when there are more than one solid phase.

A similar interpretation corresponds for the Figure 2 b) diagram, with data from Table 2.

CONCLUSIONS

- The equilibrium phase diagrams may be easily determined by using simple methods.

- The mutual solubility diagrams show the increasing of H_3BO_3 solubility as Na_2SO_4 concentration is increasing.

- In the temperature and pressure domain studied there are these solid phases: H_3BO_3, Na_2SO_4 and a mixture of them.

- The results at 50° C and 70° C show the presence of one isothermal invariant point, in each case.

- The temperature effect on the phase equilibrium is insignificant, in the experimental temperature range.

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