



Sodium sulfate recovery from boric acid liquors



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ABSTRACT

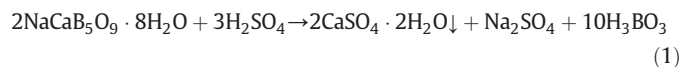
Boric acid has multiple uses in several industries, the pharmaceutical, glass and ceramic industries being some of them. Its obtaining involves the addition of sulfuric acid to slurry of calcium–sodium borate at 70 °C and, after the removal of insoluble undesired material, the crystallization of boric acid by cooling the clear solution to 15–25 °C. The residual mother liquor contains mainly sodium sulfate, sodium chloride and boric acid in concentrations depending on the composition of the borate ore and the temperature at which the boric acid is recovered. The addition of methanol or ethanol to these liquors is proposed to recover selectively most of the sodium sulfate by salting-out. This separation of the main component of the solution would not only produce a more easily disposable liquid waste but it would also reduce its over-all volume as it could be recycled into the main process. 98% of the sodium sulfate can be recovered with a 7:3 volume to volume ratio of alcohol to mother liquor. The recovery is improved when the concentration of boric acid is reduced before the salting-out. Ethanol proved to be 35% more efficient for the selective precipitation process than methanol. Sodium chloride and boric acid do not co-precipitate with the sodium sulfate.

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1. Introduction

Boron minerals are used to obtain refined products such as boric acid and borax. These compounds have different applications in the pharmaceutical, ceramic and glass industries, among many others (Garret, 1998).

In Argentina, boric acid is obtained by the reaction of low grade ulexite (sodium and calcium borate) with sulfuric acid at 70 °C according to Eq. (1).



By-product calcium sulfate together with clay is separated as waste and, by cooling the mother liquors to a temperature of less than 25 °C, boric acid is crystallized and separated by filtration. The remaining liquor is saturated in boric acid and contains sodium sulfate as well as other soluble substances such as sodium chloride contained in the ulexite ore.

In order to minimize water pollution, treatment and disposal of the liquors have been deeply investigated.

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Crystallization by cooling a brine obtained by evaporation is the most common process to separate salts from any aqueous system. Salting-out or drowning-out is another method to precipitate salts by adding a third component to the solution to change the solubility of a given solute.

Mina-Mankarios and Pinder (1991) studied the salting-out of sodium sulfate from a solution of sulfuric acid 38% (w/w), with 80:20 methanol:water volume ratio. They concluded that a high temperature, high crystal suspension density and long residence time are favorable conditions for the production of large sodium sulfate crystals.

Fernández-Lozano et al. (2001) studied the kinetics of crystallization of Na₂SO₄–NaCl from brines using methanol. In this study the Na₂SO₄ obtained was 98% pure and the process efficiency was 94%. The effect of methanol on sodium sulfate crystal size was studied by (Okorafor and Hash, 2008). They pointed out as a necessary condition that the salting-out agent should be more soluble in the original solvent than the solute; hence, the solute can be displaced from the solution. They concluded that the quantity of the salting-out agent has a great influence on the size and morphology of the crystals; crystal size decreases when the amount of methanol increases.

Moreover, when an electrolyte is added, the salting-out procedure causes the decrease of the solubility of a non-electrolyte in water. As an example, the solubility of ethyl ether in water at 25 °C is 0.91 mol%, but in an aqueous solution containing 15% (w/w) of sodium chloride the solubility is just 0.13 mol%. This decrease of solubility can be explained by taking into account that some of the molecules of water cannot dissolve the ethyl ether because they are solvating the

Table 1
Composition of the mother liquors.

g/100 ml	Solution A	Solution B
%B ₂ O ₃	2.043	2.800
%SO ₄ ²⁻	4.781	4.336
%Cl ⁻	0.886	0.303

sodium and chloride ions. In this case two immiscible phases (aqueous and organic) are generated (Solutions of electrolytes, 2014, Encyclopedia Britannica Ed). Another example is the water–ethanol system, which becomes immiscible by adding a salt like potassium carbonate (Smith, 1996).

To our experience, the salting-out of sodium sulfate from boric acid liquor has not been studied. In this paper the use of ethanol and methanol as salting-out agents is proposed. The influence of boric acid in the recovery of sodium sulfate is also analyzed.

Recovering by-product sodium sulfate allows the recycling of the mother liquor, saturated in boric acid, to the beginning of the process thus minimizing the liquid discharge. Sodium sulfate is also valuable as it is used, for example, in dyeing and stamping of fabrics (textile industry), and eliminating calcium from brines in order to obtain lithium carbonate.

2. Experimental

2.1. Materials and methods

Mother liquors from two factories in Salta Province (Argentina) were the matter of study. The liquors were tagged as liquor A and liquor B. The chemical composition of the liquors is shown in Table 1.

The difference between the Cl⁻ contents of each liquor is related to the quality of the raw material that each company uses (ulexite).

The difference in the B₂O₃ concentration is due to the crystallization temperature used by each factory. These values are, of course, lower than the solubility of boric acid at room temperature of 3.85% (w/v).

Sulfate concentration in the liquors depends on the excess of H₂SO₄ used in the reaction which occurs at pH values 3–3.4 (see Eq. (1)).

96% ethanol and 98.9% methanol were used as salting-out agents.

For the experiments, solutions containing different volume ratios of alcohol and liquor were prepared, specifically: 1:9, 3:7, 4:6, 5:5 and 7:3. They were stirred at a stirring speed of 100 rpm during 1 min, 20 rpm during 5 min and finally, 10 rpm during 10 min. Then, after 48 h of aging at 25 °C, crystals were filtered and dried in a vacuum dryer. The composition of the liquors was determined by chemical analysis. Sulfate concentration was determined by gravimetry, as BaSO₄ adding BaCl₂ to the liquor; RSD of the determination was 6%.

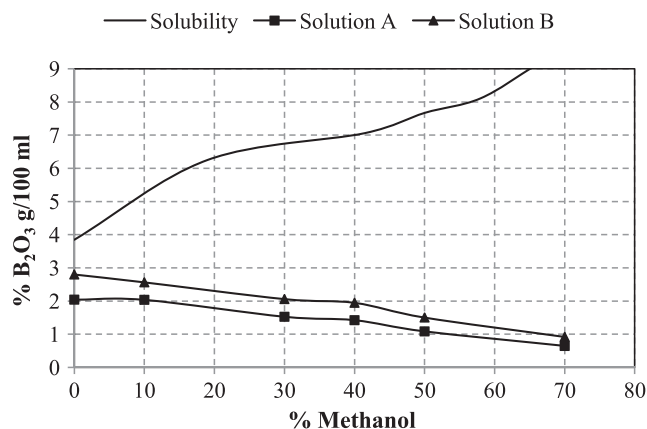


Fig. 1. Solubility (Linke, 1965) and concentration of H₃BO₃ (as %B₂O₃ w/v) in the solutions treated with methanol at 25 °C.

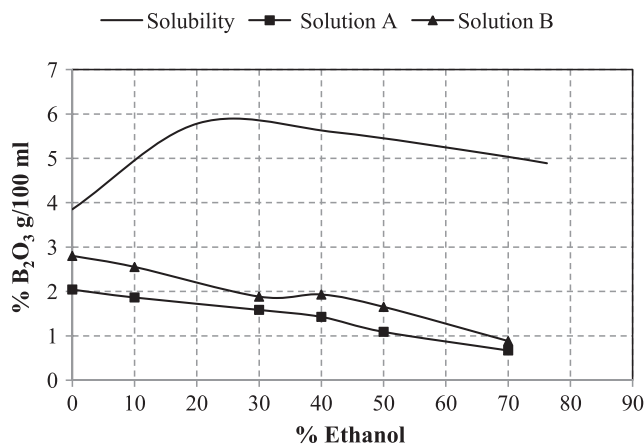


Fig. 2. Solubility (Linke, 1965) and concentration of H₃BO₃ (as %B₂O₃ w/v) in the solutions treated with ethanol at 25 °C.

Chloride was analyzed by volumetry using the Mohr method with a RSD of 4%. B₂O₃ was analyzed applying the acid–base volumetric method using mannitol to increase the boric acid acidity and phenolphthalein as indicator (Flores, 2004); RSD of the titration was 2%.

Another test was made to study the influence of boric acid on the Na₂SO₄ recovery. Boric acid concentration was decreased by cooling the liquor to 8 °C for about 48 h before treatment with alcohol. The boric acid that crystallized was separated by vacuum filtration, and alcohols were added to reach a 4:6 alcohol–liquor volume ratio and then treated under the same conditions of stirring speed as the uncooled liquors.

3. Discussion and results

3.1. Salting out using ethanol and methanol

Figs. 1 and 2 show the variation of the boric acid concentration (expressed as %B₂O₃ w/v) of the liquors after the salting-out procedure. The figures also show the solubility of boric acid in methanol and ethanol solutions at 25 °C. Both salting-out agents increase the boric acid solubility with respect to its solubility in aqueous solutions.

With methanol, boric acid forms highly volatile boric acid methyl ester B(OCH₃)₃ (boiling point 68.7 °C) (Fresenius et al, 1988). This could explain the increase of boric acid solubility; ethanol, on the other hand, decreases boric acid solubility.

Boric acid concentration in liquors A and B before adding alcohol is well below its corresponding solubility in water because of the crystallization process performed at temperatures lower than 25 °C, and also owing to their salinity. The almost lineal decrease of boric acid concentration in both cases is a consequence of the salting-out effect of the alcohols.

Tables 2 and 3 (Linke, 1965) show the NaCl solubility in water–alcohol solutions at 25 °C. Sodium chloride concentrations of the liquors were much lower than the solubility in 70% alcohols, so that NaCl could not suffer any salting-out effect. This was proved by the absence of NaCl in the recovered Na₂SO₄ crystals.

Table 2
NaCl solubility at 25 °C in methanol solutions (Linke, 1965).

Methanol		
% ROH	%NaCl g/100 ml	%Cl ⁻ g/100 ml
0	31.91	19.37
10.45	29.89	18.1
100	10.96	6.65

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