Dedicated to Professor Valer Fărcăşan
at his 85th anniversary

STUDIES ON THE NATRIUM SULPHATE SALTING-OUT CRYSTALLIZATION. I. EQUILIBRIUM OF THE CRYSTALLIZATION

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ABSTRACT. The separation of anhydrous natrium sulphate through salting-out crystallization with methanol and ethanol has been analysed and discussed. The equilibrium data for the systems natrium sulphate – water – methanol and natrium sulphate – water – ethanol at different temperatures have been reported. On the basis of selective solubility and mass balance the optimal mixing ratio inorganic phase/organic solvent and maximum potential for the best degree separation have been established.

INTRODUCTION

Crystallization is the process where solid particles are formed from a homogeneous phase. In crystallization the solution is concentrated and usually cooled until the solute concentration becomes, at that temperature, higher than its solubility. Thus, the solute comes out of the solution under the form of crystals of relatively high purity.

The salting-out crystallization is the method by means of which, in contrast to the crystallization induced by evaporation, the desired salt can be selectively precipitated in organic solvents – water mixtures [1].

The method of crystallization of inorganic salts with organic solvents is often used for the recovery of inorganic salts from fibre spinning baths, metallurgical wastes and other effluents. A special case of salting-out crystallization is the dehydration of salt hydrates, when anhydrous salt can be obtained from a single component solution.

The first industrial application of the crystallization with organic solvents is the manufacturing of KNO_3 (1970) from KCl and HNO_3 using isobutanol [2]. The success of this first process has stimulated the studies of the equilibrium and kinetics of other inorganic compound(s) crystallization with organic solvents, the most important being natrium sulphate [3-6].

Natrium sulphate has many industrial applications among which the manufacture of glass, cellulose and paper, natrium sulphide, detergents and sometimes the storage up of the heat. The production is related to its processing from natural deposits, from intermediate or by-products from industrial processes such as: a) chlorination of pyrite ashes b) manufacture of natrium bicromate, potassium chloride c) treatment of wastewaters from cellulose.

An important source of natrium sulphate is the wastewater from fibre spinning baths of the viscose plants. A possibility to improve the recovery of natrium sulphate from this source is the selective method of salting-out crystallization with organic solvents, particularly methanol and ethanol. Another advantage of this kind of crystallization is that it proceeds without heat in the crystallizer.

The literature data refer to the following systems: natrium sulphate – ammonia; natrium sulphate – water – ammonia; natrium sulphate – ethanol; natrium sulphate – methanol; natrium sulphate – water – methanol; natrium sulphate – isopropanol; natrium sulphate – water – glycol at normal temperature [7–10]. These data allow only a comparison between different separation efficiency in normal conditions of temperature. New studies are required to establish the phase equilibrium for the natrium sulphate – water – organic solvent systems.

The present research aims at obtaining the equilibrium data for the systems natrium sulphate – water – methanol and natrium sulphate – water – ethanol at different temperatures and establishing the optimum mixing ratio for inorganic phase/organic solvent with the best degree of separation by means of the process of salting-out crystallization.

EXPERIMENTAL

The most suitable solvents for the salting-out crystallization of natrium sulphate are methanol, ethanol, acetone, propanol as well as their mixtures with one another and also with water [11]. The precipitating solvents used in this research are methanol and ethanol. The experiments were carried out in a batch isothermal stirred vessel of 0.5 l. Stirring was achieved mechanically by using a blade stirrer. The temperature was regulated by a thermostated batch and measured by a thermometer.

The solubility of natrium sulphate in mother liquor was determined gravimetrically with barium chloride. The solid phase was analysed by drying the waste at 200 ^{0}C.

RESULTS AND DISCUSSION

In almost all cases, the solubility of the salt decreases considerably if the solvent contains an organic component. During crystallization, temperature is another important factor in the nucleation and growth of crystals. It is known that the equilibrium and kinetics of the crystallization are very sensitive to the variation of the temperature. The relationship between solubility and temperature is exponential. [12]

The main results of our study include the effect of both the temperature and the concentration of the organic solvent on the solubility of the natrium sulphate. Table 1 lists the solubility of natrium sulphate in ethanol solutions versus temperature.

The values of the solubility in brackets are registered for the decahydrate ($Na_2SO_4 . 10H_2O$) known as Glauber's salt. This hydrate appears at low temperature (25 – 30 ^{0}C) and low concentration of ethanol (< 50%). In all other cases, the solid phase was separated as anhydrous natrium sulphate.

The natrium sulphate solubility

Temp. (^{0}C)	Ethanol concentration (mass %)						
	3	10	20	30	50	60	80
25	[18.5]	[11.83]	[5.98]	[2.60]	[0.52]	0.18	0.002
30	[26.8]	[19.0]	10.42	[4.45]	0.60	0.19	0.004
35	29.0	20.5	11.38	4.80	0.64	0.204	0.006
40	28.5	20.2	11.32	5.01	0.69	0.215	0.009
45	28.31	20.0	11.34	5.22	0.73	0.228	0.01
50	27.82	19.65	11.31	5.37	0.76	0.243	0.014
60	27.25	19.46	11.33	5.67	0.84	0.268	0.018
70	26.84	19.3	11.32	5.71	0.89	0.289	0.02

At low ethanol concentration it is difficult to obtain a general correlation between solubility and temperature. The values from the first two columns in Table 1 show that the solubility has a maximum at 35 ^{0}C and 3 % (mass concentration of ethanol) and at 35 ^{0}C and 10 % ethanol.

At higher concentration of ethanol, more than 20 %, the variation of the solubility of natrium sulphate increases continuously and rapidly with the temperature. Simultaneously the presence of the organic alcohol decreases the solubility of the salt, with the increase of ethanol concentration.

These observations show that in order to achieve the best degree of separation, the process must take place at a temperature lower than 25 ^{0}C and at a higher concentration of alcohol in solution. For the experiments developed in the conditions represented in Table 1, the maximum degree of separation for the equilibrium condition was attained at 25 ^{0}C and 80 %, when the mother liquor has only 0.002 % natrium sulphate.

Table 2 lists the temperatures of the system during the transition of decahydrate Na_2SO_4 .10 H_2O to anhydrous natrium sulphate with ethanol concentration. These data were obtained by means of the analysis of the equilibrium diagram for the system natrium sulphate – water – ethanol at different temperatures.

The variation of temperature for the transition of Na_2SO_4 .10 H_2O to Na_2SO_4 (with ethanol concentration).

Concentration of ethanol (%)	Temperature of transition (^{0}C)	Solubility of Na_2SO_4 (%)
0.00	32.4	33.27
3.09	31.6	29.38
11.33	31.0	20.14
25.34	30.65	7.247
33.17	30.0	3.356
45.85	27.5	0.943
52.25	25.2	0.409
56.56	20.0	0.194

The presence of ethanol changes the temperature of the transition to lower values. In the binary system Na_2SO_4 – water the transition point is at 32.4 ^{0}C. In this way, in a saturated solution of Na_2SO_4, the decahydrate $Na_2SO_4.10 H_2O$ will crystallize in normal conditions.

These data show that at 56.6 % ethanol the anhydrous salt Na_2SO_4 could be separated even at 20 ^{0}C. By extrapolation it can be concluded that at higher ethanol concentrations, the temperature of crystallization can be further decreased. This conclusion is an important industrial advantage in the salting-out crystallization. The precipitation with organic alcohol represents the direct way to obtain the anhydrous inorganic salt at normal temperature. Dehydration of decahydrate $Na_2SO_4.10 H_2O$ can be performed without heating.

The results of the salting-out crystallization with methanol at 25 ^{0}C are listed in Table 3.

The listed values in Table 3 show a gradual increase in the efficiency of separation with methanol concentration. Simultaneously, the concentration of methanol influences the composition of the solid phase. At 25 ^{0}C and methanol concentration lower than 10 % the separated solid phase obtained is decahydrate $Na_2SO_4.10 H_2O$. At the concentration of 17.27 % methanol, the solid phase is registered as heptahydrate $Na_2SO_4.7H_2O$ whereas at the concentration of 21.2 % a mixture of heptahydrate $Na_2SO_4.7H_2O$ and anhydrous Na_2SO_4 is determined. In the range of 22 % and 57.67 % methanol concentrations, the separated solid phase was determined as anhydrous natrium sulphate.

Table 3.

Experimental results of the natrium sulphate salting-out crystallization with methanol at 25^{0}C

Exp. Nr.	Na_2SO_4 (%)	Methanol (%)	Water (%)	Efficiency of separation (%)	The separated solid phase
1	25.30	4.66	70.03	19.32	$Na_2SO_4.10 H_2O$
2	22.18	9.52	68.30	29.20	$Na_2SO_4.10H_2O$
3	15.80	17.26	66.84	51.21	$Na_2SO_4.7H_2O$
4	12.96	21.18	65.83	59.60	$Na_2SO_4.7H_2O + Na_2SO_4$
5	3.75	25.79	70.61	88.04	Na_2SO_4
6	3.07	30.37	66.51	90.20	Na_2SO_4
7	1.68	39.90	58.42	94.64	Na_2SO_4
8	0.84	47.40	51.76	97.32	Na_2SO_4
9	0.673	53.22	46.19	97.86	Na_2SO_4
10	0.38	57.78	42.04	98.78	Na_2SO_4

From the results obtained so far, the experimental conditions for the direct obtaining of the anhydrous natrium sulphate can be settled. The solubility of Na_2SO_4 in methanol/water mixture decreases considerably with the increase of methanol fraction. On the basis of this diagram the optimal mixing ratio m_A/m_B (A – inorganic phase; B – methanol or organic alcohol) could be established. The solubility of natrium sulphate in the system natrium sulphate – water – methanol at 40 ^{0}C is shown in Figure 1.
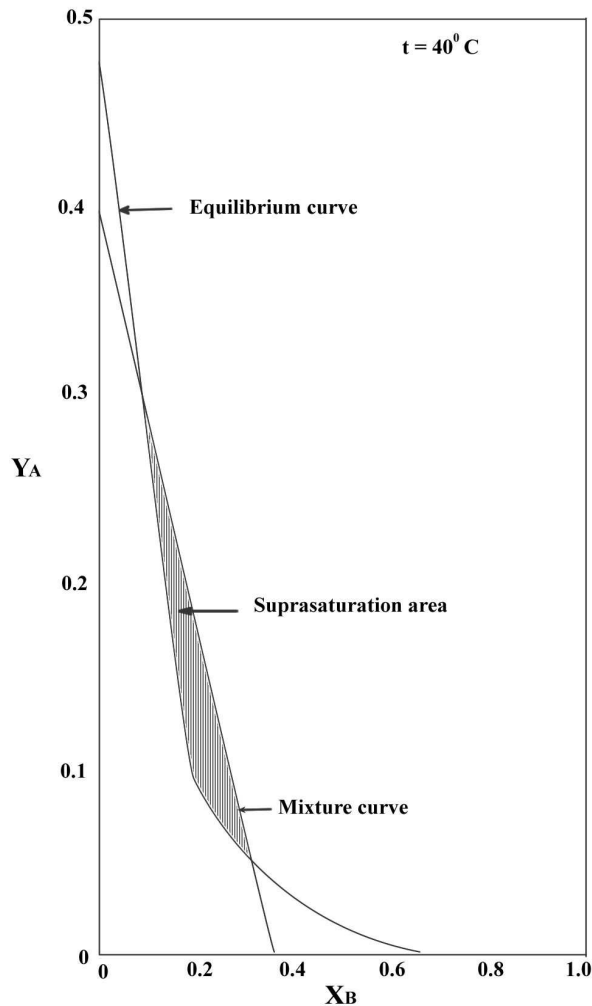
Fig. 1. Solubility of natrium sulphate in the system– water – methanol at 40 ^{0}C
(Y_A = kg Na_2SO_4/kg water; X_B = kg CH_3OH/kg water).

Figure 1 offers the possibility of getting acquainted with the field of crystallization in strict dependence on the natrium sulphate and methanol concentration.

To illustrate the used method, the operation curve (mixture curve) for the mixture with Y_A = 0.4 kg Na_2SO_4/kg water and B_E = 0.35 kg methanol/kg water is drawn on the diagram. The solution (mother liquor) and the solid crystals are in contact for a long time, long enough to reach an equilibrium. The crystallization equilibrium is attained when the solution of mother liquor is saturated and the natrium sulphate concentration reaches constant values. The

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concentration of the salt can be described as a point in the field of supersaturated solution or unsaturated solution, depending on the mixing ratio m_a/mb_o.

In conclusion, at an optimal mixing ratio the supersaturated solution yields the maximum amount of crystals. This ratio can be obtained from the mass balance. The optimisation of the salting-out crystallization can be carried out in two stages: a) at maximum solid concentration in suspension; b) at maximum amount of crystals.

The optimisation of the salting-out crystallization dependent on mass fraction of methanol in mixture m_B/m_T is shown in Figure 2. It can be observed that the maximum of solid concentration C_S is obtained at the same fraction of methanol in mixture m_B/m_T at which the potential ΔY is maximum. This potential ensures a high speed of crystallization. Besides, the relative suprasaturation $\Delta Y/Y^*$ becomes lower. In this way the secondary nucleation can be avoided and the quantity of methanol can be reduced in comparison with the other variant (b).
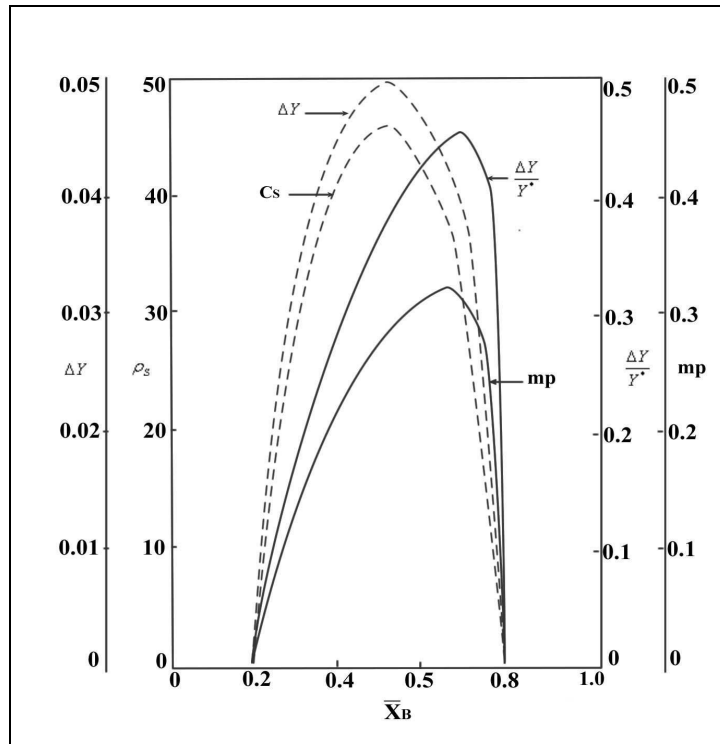

Fig. 2. The optimization of the mixing ratio: ΔY - potential difference (kg/kg);
C_S (ρ_S) – solid concentration in suspension (kg solid/m³ suspension);
$\Delta Y/Y^*$ - relative suprasaturation (kg/kg); Y^* - kg salt/kg methanol;
m_P – sepatated salt (kg recovered salt/kg existing salt);
$\overline{X}_B$ - methanol fraction in the mixture (kg methanol/kg mixture).

On the basis of mass balance it was estabished that at m_B/m_T =0.5, as Figure 2 shows, the entirely mixing ratio, inorganic phase/methanol is m_A/m_B = 1.35. This mixing ratio corresponds to the maximum value of the solid concentration in suspension and also to the maximum potential.

CONCLUSIONS

The analysis of the results obtained points out to the main advantages of the salting-out crystallization with ethanol and methanol. These advantages can be summarized as follows:

1) the salting-out crystallization allows the direct precipitation of the anhydrous sodium sulphate from solutions by using organic alcohols even at room temperature;

2) the process requires a lower amount of alcohol by increasing the salt concentration in the starting solution although the efficiency remains constant

3) the cost of salting-out crystallization can decrease up to 75 % for a separation degree higher than 95 % in contrast to the conventional process.

REFERENCES

1. V. Hopp, *Grundlagen der Chemischen Technologie*, Wiley –VCH 2001, p. 631
2. C. Calistru and C. Leonte, *Tehnologia substanțelor anorganice*, Ed. Didactică şi Pedagogică, Bucureşti, 1972
3. L. Filipescu and E. Pincovski, *Echilibrul solid-lichid. Aplicații în tehnologia sărurilor minerale*, Ed. Tehnică, Bucureşti, 1980
4. K. Winnacker, L. Kuchler, *Chemische Technologie,* 4. Aufl., Carl Hanser Verlag, Munchen, Wien, 1984
5. G. Liebermann and H.H. Emous, *Wiss. Z.T.H.*, Ed. Leuna, Merserburg, 1975, **17**, 553
6. H.D. Kohn, I.Yaron and J.D. Wolf, *J.Appl.Chem.*, London, 1963, 13, 259
7. W.R. Rousseau and R.C. Zumastein, *World Congres III of Chemical Engineering*, Tokyo, 1986, Vol. II
8. O.H. Picht, J. Hung, *J. Ind. Chem.*, 1989, **17(2)**, 179
9. S.J. Jancic and E.J. Jong, *Industrial Crystallization*, Ed. Elsevier, 1984, 1184
10. A. Mersmann, *J. Crystal Growth*, 1990, **30**, 241
11. H. Hoppe, *Chem. Process Eng.*, 1969, 61
12. M. Fedtke, W. Pritzkow, G. Zimmerman,*Technischen Chemie, 6.Aufl.,* Deutscher Verlag fur Grundstoffindustrie, p.92, Stuttgart 1996