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Drowning-out crystallisation of sodium sulphate using aqueous two-phase systems

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Abstract

A novel method to obtain crystals of pure, anhydrous salt, using aqueous two-phase systems was studied. A concentrated salt solution is mixed with polyethylene glycol (PEG), upon which three phases are formed: salt crystals, a PEG-rich liquid and a salt-rich liquid. After removal of the solid salt, a two-phase system is obtained. Both liquid phases are recycled, allowing the design of a continuous process, which could be exploited industrially. The phase diagram of the system water–Na_2SO_4–PEG 3350 at 28°C was used. Several process alternatives are proposed and their economic potential is discussed. The process steps needed to produce sodium sulphate crystals include mixing, crystallisation, settling and, optionally, evaporation of water. The yield of sodium sulphate increases dramatically if an evaporation step is used.

Keywords: Aqueous two-phase systems; Drowning-out crystallisation; Sodium sulphate

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1. Introduction

Aqueous two-phase systems (ATPSs) have been known for more than 30 years and they have been used extensively in the separation of biomaterials. In recent years ATPSs have also been used to separate metal ions [1–3]. The only reference to the use of ATPSs to carry out a crystallisation is given by Berry et al. [4] who mention it as an alternative amongst several separation schemes. This is an interesting article that evaluates different separation alternatives, amongst them ‘‘drowning-out’’ which is crystallisation by the addition of a foreign component.

Ho-Gutierrez et al. [5] show experimental data for aqueous mixtures of polyethylene glycol (PEG) with Na_2SO_4 and NaCl. They determined the concentration of solute using atomic absorption spectroscopy and the concentration of PEG through measurements of the refractive index. They also measured the densities of the solutions and studied the influence of the molecular mass of PEG and temperature.

Few references exist involving drowning-out crystallisation. Hull and Owens [6] showed that KI and KIO_3 can be separated from an aqueous solution of both electrolytes by the addition of 1,4 dioxane. Alfassi and Feldman [7] used this method for the preparation of Br by separation of KBr and $KBrO_3$ by addition of acetone. Ata and Alfassi [8] found that it is possible to separate KNO_3 from KNO_2 using acetone, acetonitrile and tetrahydrofuran. We-

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ingartner et al. [9] reported extractive crystallisation from aqueous solutions by addition of a solvent and then recovery by changes in temperature. They propose an industrial process to crystallise chloride or sodium carbonate with 1-butanol or 1-propanol.

This paper describes a novel method for the obtention of crystals of pure anhydrous sodium sulphate using an ATPS containing PEG, water and the salt.

2. Results and discussion

Aqueous solutions of some inorganic salts with carbonate, sulphate, chloride, nitrate and phosphate anions form two aqueous immiscible phases if PEG is added and some of the salt may crystallise if it is in sufficiently high concentration:

$$H_2O + \text{Salt} + \text{PEG} \rightarrow \text{Phase 1 (PEG-rich)} + \text{Phase 2 (salt-rich)} + \text{salt crystals}$$

In these systems the water is distributed in both phases, most of the PEG is concentrated in the top phase and most of the inorganic salt in the bottom phase. The salt crystallises as the proportion of water decreases. The PEG acts as a salting-out agent for anhydrous salts at low temperatures, increasing areas of crystallisation or opening new ones. This allows the crystallisation of anhydrous salts, which, in the absence of PEG, can only be obtained in the hydrated state.

The ternary phase diagram for Na_2SO_4–PEG–water at 28°C [5] is shown in Fig. 1. Based on this diagram four processes were designed to obtain sodium sulphate, each includes a mixer, a crystalliser and a separator as shown in Fig. 2. In these processes the feed (F) is mixed with the recirculation streams rich in PEG (stream 3) and with part of the aqueous phase rich in salt (stream 4). The feed consists of 100 ton/day of decahydrate (44%, w/w, sodium sulphate, 56%, w/w, water). This mixture (stream 1) is within the crystallisation field of Na_2SO_4. After separating the crystals the remaining biphasic solution, (stream 2) is separated into two phases and recirculated. This corresponds to a type I process. Fig. 3 shows the phase diagram with the compositions of the streams in Fig. 2 of a potential type I process (No. 4 in Table 1).

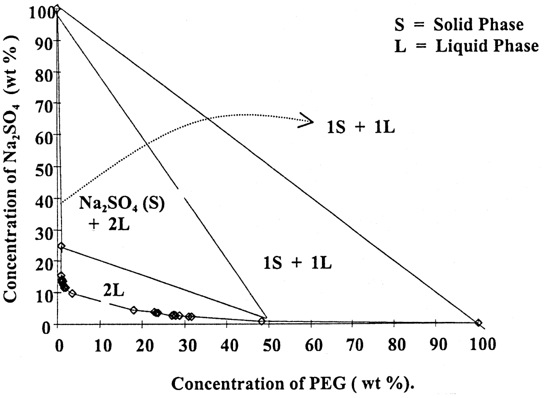

Fig. 1. Phase diagram for a Na_2SO_4–PEG–water system at 28°C [5]. The average molecular mass of the PEG was 3350. Regions of two liquid phases (2L), one solid and one liquid (1S+1L) and one solid and two liquid phases are shown. The solid is anhydrous Na_2SO_4. Near the origin, below 10% Na_2SO_4 and at low concentrations of PEG only one phase exists.

For the selection of process conditions a total recycle of the PEG has been chosen. We have studied four alternatives, which have an equal crystal yield of 58%, permitting recovery of approximately 25 ton/day of anhydrous sulphate. The difference between the alternatives is in the recirculation streams and in the magnitude of the purge. Table 1 shows the results of the balances for the four points selected.

Another alternative was investigated to increase the yield of the crystallisation by evaporating part of the water from the salt mixture and recycling it to the process (type II process). This is shown in Fig. 4. An evaporator must be added to the process and the

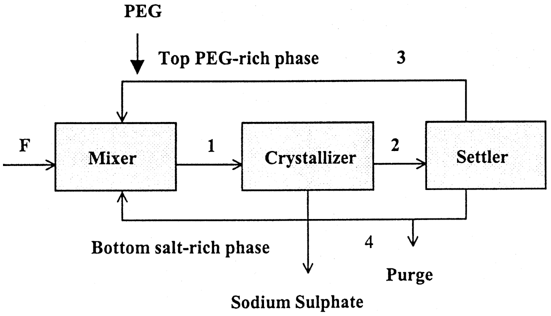

Fig. 2. Type I process flow sheet for the production for sodium sulphate. F=Feed.

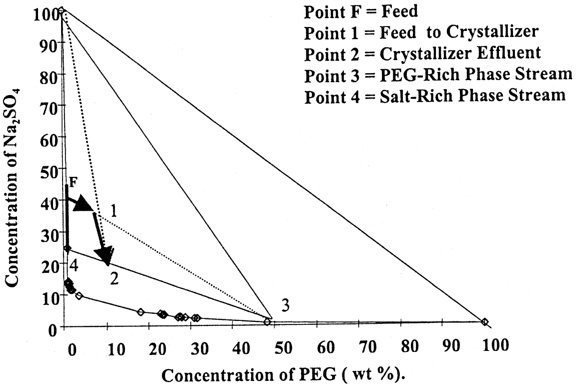

Fig. 3. Identification of streams in the phase diagram Na_2SO_4–PEG–water of a type I process to obtain Na_2SO_4 crystals (Fig. 2). The average molecular mass of the PEG was 3350.

by-product, water, which is scarce in the north of Chile where there is a natural abundance of inorganic salts, could be used in the plant. The value of this by-product is 2 US$/ton.

By the inclusion of an evaporator four new alternatives are generated. These are shown in Table 2 (Nos. 5–8) which includes results obtained from the mass balance and profit calculations with different flow-rates of evaporated water. In this Table alternative 4, which does not include evaporation, is shown for comparison. Fig. 5 shows the phase diagram with the composition of the streams in Fig. 4 of a type II process. To compare the different process alternatives proposed, the bulk balances and profits were calculated using MATLAB (The MathWorks, Boston, MA, USA). A price of 1.5 US$/kg for PEG [10], and 115 US$/ton for sodium sulphate [11] was considered. The gross profits were calculated as the difference between the cost of the products less that of the reagents and was 30.89 US $/ton of product for cases 1 to 4. The cycle of the process for alternative 4 is shown on the phase diagram in Fig. 3. In Table 1 alternative 4 would be the most advantageous economically as it involves smaller flow-rates, which would imply smaller equipment size. This novel type of crystallisation process using ATPSs, permits the use of a settling tank to separate the two phases and this represents an advantage over other processes using solvents which require a distillation column whose capital and operational costs are far higher.

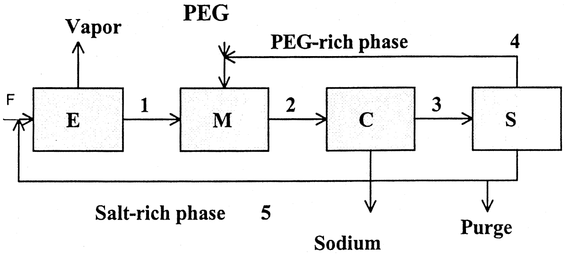

Fig. 4. Type II process flow sheet that includes an evaporation stage. F = Feed, E = evaporator, M = mixer, C = crystalliser, S = settler.

In Fig. 5 it can be seen that in the process shown in Fig. 4 the mass ratio of streams 5 and 4 is nearly 4 (this can also be seen in Fig. 3 with no evaporation), hence in this separation the continuous phase will be the larger salt phase [12,13] as has been observed in the laboratory in a batch process. The salt phase is also the less viscous so in this case phase separation is very fast [14]; hence separation of the salt-rich phase from the PEG-rich phase will be relatively straightforward.

It is observed in Table 2 that profit and yield increase significantly upon evaporation of water. In alternative 6 (evaporation of 18.93 ton/water day) profit is almost doubled with respect to alternative 4. Evaporation of all the water (alternative 9) eliminates

Table 1
Flow-rates of streams in a type I process for a constant sodium sulphate yield of 58% (Fig. 3)

No.	Equipment	Flow-rate (ton/day)				
		Stream 1	Stream 2	Stream 3	Stream 4	Purge
1	M–C–S	627.98	602.86	519.65	7.69	83.21
2	M–C–S	251.19	226.07	138.37	12.18	87.71
3	M–C–S	167.46	142.34	48.78	18.04	93.56
4	M–C–S	125.60	100.48	11.13	13.82	89.34

Table 2
Flow-rates, production of sodium sulphate and profits for a type II process with evaporation (Fig. 5)

No.	Equipment	Flow-rate (ton/day)			Yield (%)	Profits[a]
		Stream 2	Stream 3	Water		
4	M–C–S	125.60	100.48	0.00	58	30.89
5	M–C–S–E	130.44	101.44	11.51	66	49.76
6	M–C–S–E	116.31	84.81	18.93	72	59.46
7	M–C–S–E	106.13	72.13	26.34	77	67.73
8	M–C–S–E	97.62	61.12	33.76	83	74.86
9[b]	M–C–S–E	65.83	21.83	56.00	100	91.41

[a] Profits = value of the products − costs of raw materials.

[b] Corresponds to total evaporation.

the necessity to purge the salt rich phase and permits the recovery of all of the sodium sulphate thus increasing the potential economic benefits. A detailed study of the cost of the evaporation stage will indicate whether this stage is justified and what is the optimum flow of water to the evaporator.

3. Conclusions

A novel method to obtain crystals of pure, anhydrous salt, using ATPSs was studied. Both liquid phases are recycled, allowing the design of a continuous process, which could be exploited industrially. The analysis presented in this paper shows that it is possible to design several different processes of crystallisation for sodium sulphate using ATPSs. The process studied shows a positive economic potential.

The process steps needed to produce sodium sulphate crystals include mixing, crystallisation, settling and, optionally, evaporation of water. The yield of sodium sulphate increases dramatically if an evaporation step is used.

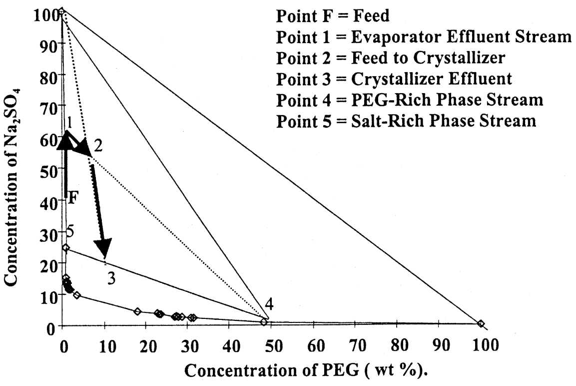

Fig. 5. Identification of streams in the phase diagram Na_2SO_4–PEG–water of a type II process to obtain Na_2SO_4 crystals with evaporation. The average molecular mass of the PEG was 3350.

Acknowledgements

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