

SOLVATION PROPERTY EFFECT ON CRYSTALLIZATION THROUGH COOLING

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The earlier work (Nayeemuddin *et al* 2000 a), concerning derivation of formulae for determination of various parameters such as heat of crystallization, heat transfer/utilization coefficients, in case of crystallization of magnesium sulphate during cooling of sea bittern, was based on linearity of batch/unsteady state operation. The derived relationships were satisfactorily applied to previous data (Beg *et al* 1989). The said efforts, however, lacked in appropriate explanation regarding the divergent but pertinent theoretical issues such as logic of the linearity of unsteady state data and the basis of low temperature crystallization and its mechanics. The present paper attempts to explore the basic reason lying behind the linearity of unsteady-state batch process; which otherwise is commonly nonlinear. It is worth noting at this stage that sea bittern in indeed a multicomponent solution of different compounds like KBr, MgSO₄, NaCl/KCl and Mg Cl₂ (Beg *et al* 1982). Further in this connection, it would be worthwhile to point of sea bittern (Beg *et al* 1989; Nayeemuddin *et al* 2000 b), it was observed that magnesium sulphate got crystallized as hepta hydrate. It might be revealing at this juncture to refer the plot (Perry 1950), presenting concentration of pure magnesium sulphate against the temperature of crystallizing slurry during cooling of its solution is nonlinear because of the formation of different hydrates of magnesium sulphate at various temperature levels, while in the system, water is acting as a sole solvent. The comparison of the plots obtained during cooling of sea bittern on different occasions (Beg *et al* 1989; Nayeemuddin *et al* 2000 b) with those of pure magnesium sulphate (mentioned above), leads to conclusion that in the former instances, the linearity is solely caused due to the crystallization of single hydrated salt namely MgSO₄·7H₂O, in

which water alone is not acting as solvent. The above discussions have, offered an incomplete answer in respect of the cause of linearity of relationship. A couple of more questions such as "why at all a single hydrated salt is formed? why water alone doesn't act as solvent? and what is actual solvent? have also cropped-up. In this context, it would be appropriate to review in the following paragraphs, different prominent processing steps of sea bittern along with their essential conditions, resulting into recovery of various compounds and formation of complexes:

The processing of desulphated sea bittern-a product obtained subsequent to complete removal of sulphate 'ions' from the raw material (Beg *et al* 1989)-brought the following to the surface.

It was noted that pure sodium chloride crystals are obtained (Beg *et al* 1986), both in direct evaporation of the product within close temperature range of 113 to 117 °C and also during solar evaporation of the solution when its density ranges between 1.22 to 1.28 g ml⁻¹. On attaining density around 1.285 g ml⁻¹ potassium chloride also starts crystallizing alongwith sodium chloride as sylvinite.

When the desulphated product was heated beyond 117 °C, carnallite (KCl, 6Mg Cl₂) crystallized between 123 to 126 °C. The mother liquor of carnallite consisted of magma of almost pure magnesium chloride (4% solution) from which pure magnesium chloride crystals may be obtained by solar evaporation or by controlled heating.

Separation of NaCl-KCl complex (most probably sylvinite) from the carnallite complex was affected by dissolving carnallite into appropriate amount of water, followed by heating the resulting solution to 116 °C.

The following emerges out of the critical review of different processing summarized in the preceding paragraphs.

Firstly, during entire treatment, water alone doesn't appear acting as a solvent. Secondly, within certain specific limits of concentration/temperature or density levels etc. solution as a whole (which apart from active component and some other compounds essentially contains magnesium chloride) forms one phase and the crystallizing compound being the other phase. This in turn leads to conclusion that other compounds present in solution don't interfere with formation of complexes/compounds. Thirdly, during processing, all other salts like magnesium sulphate, sodium/potassium chloride get separated as pure compounds or complexes (which may or may not include magnesium chloride), whereas, under none of the instance pure magnesium chloride gets crystallized at any stage of investigations.

It therefore, transpires from the above discussions that magnesium chloride plays some hidden/vital role in various pro-

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cessing steps of sea bittern or its products. When this situation is reviewed in the light of pertinent literature, (Wells 1950) its key role emerges out to be the solvation property of hydrated magnesium chloride ($MgCl_2 \cdot 6H_2O$) which is most likely due to the presence of as many water molecules as the coordination number of magnesium. This, therefore suggests that sea bittern is an aqueous solution of bromine (as potassium bromide), magnesium sulphate, and chloride of sodium/potassium in the magma of hydrated magnesium chloride; which because of its solvating property during processing results into the formation different compounds/complexes. In the specific case of crystallization of magnesium sulphate, this property is responsible for the formation of its hepta hydrate thereby rendering the concentration temperature curve linear even in batch/unsteady state operations.

Key words: Solvation property, Heat of crystallization, Heat of transfer coefficients, Sea bittern.

References

- Beg M A A, Mahmood S N, Nayeemuddin 1989 Production of marine chemicals in Pakistan, Part-III, Studies on Recovery of magnesium sulphate by chilling. *Pak J Sci Ind Res* **32** 126-132.
- Beg M A A, Nayeemuddin, Mahmood S N 1982 An overview of salt industry in Pakistan. In: *International Symposium on Salt and Marine Chemicals*, Salt Research Institute Bhavanag, India.
- Beg M A A, Nayeemuddin, Mahmood S N, Khan W A, Khan Iqbal S 1986 Production of marine chemicals in Pakistan. Part II, Studies on manufacture of chemicals from sea water bittern. *Pak J Sci Ind Res* **29** 380-396.
- Nayeemuddin, Mahmood S N, Farzana Azmat, Razia Begum 2000a Derivation of relationships and estimation of thermal/thermodynamic parameters, from crystallization data of sea bittern. *Pak J Sci Ind Res* **43** 155-161.
- Nayeemuddin, Mahmood S N, Farzana Azmat 2000b Affects of agitation on recovery of magnesium sulphate during cooling of sea bittern. *Pak J Sci Ind Res* **43** 275-282.
- Perry J H 1950 *Chemical Engineers*, hands Book Mc Graw Hill Book Company New York. PP 1053.
- Wells A F 1950 *Structural Inorganic Chemistry, in Water and Hydrates*, 2nd Ed. Oxford pp 444.