

Theoretical Aspects of Obtaining Pure Inorganic Substances During Crystallization from Solutions

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Abstract

A method for calculating the cocrystallization of components in ternary water-salt systems is proposed. The method allow to obtain a quantitative assessment of the production of pure inorganic substances in the process of crystallization from electrolyte solutions.

Keywords: Cocrystallization coefficient; Activity of component; Isopiestic solution

Introduction

Crystallization from solutions has long been used as a method of separation and the production of pure substances. This method acquired particular importance in the first half of the last century in the preparation of compounds of radioactive elements, its relevance is preserved today in the technology of high purity substances. Technological developments in this field are based on studies of the properties of solutions whose main task is to evaluate the efficiency of the separation of inorganic compounds during crystallization from electrolyte solutions. In the technology of high purity substances, the problem is reduced to the evaluation of the interaction of the major and individual impurity component, since in field of microconcentrations of impurity components it is possible neglect their interaction with each other.

Theory

For the ternary water-salt system according to the Nernst distribution law, the thermodynamics coefficient of cocrystallization of the impurity component can be expressed as

$$D_2^0 = \frac{A_1 B_2}{B_1 A_2} \quad (1)$$

where A and B activity of components in liquid and solid phases; the subscript 1 and 2 refer to the major and impurity component, respectively. Taking the activity of pure component in the solid phase to be unity, the Eq.(2) can be represented also as $D_2^0 = \frac{A_1^0}{A_2^0}$, where A_1^0 is the activity component in its saturated binary solution. The activity of each component in the mixed electrolyte solution according to Allakhverdov GR [1] in the first approximation can be represented as

$$A_i = A_i^* \frac{x_i}{\sum x_i} \quad (2)$$

where A_i^* is the activity of the impurity component in its binary isopiestic solution having the same solvent activity as in the mixed solution; $x = \nu m / W$, ν -stoichiometric coefficient of the electrolyte, m -molality, W - number of moles of the solvent per kilogram ($W=55.51$ for water).

Combining Eqs. (1) and (2) and substitution $B_i = y_i f_i$, where y and f is the mole fraction and activity coefficient of a component in the solid phase, we obtain

$$\frac{A_1^* x_1 y_2 f_2}{A_2^* x_2 y_1 f_1} = \frac{A_1^0}{A_2^0} \quad (3)$$

In the limiting case when $x_2 \rightarrow 0$ also $A_1^* \rightarrow A_1^*$, $f_1 \rightarrow 1$ and the equilibrium cocrystallization coefficient of the impurity component can be defined as

$$D_2 = \lim_{x_2 \rightarrow 0} \frac{x_1 y_2}{y_1 x_2} = \frac{1}{f_2} \frac{A_2^*}{A_2^0} \quad (4)$$

Relation (4) is similar to the Ratner AP [2], with the distinction that liquid-phase interaction is represented here in explicit form as ratio of the impurity activities in different solutions. In this case A_1^* is the activity of the impurity component in its binary isopiestic solution having the same solvent activity as in the saturated solution of the major component. If we use the functional dependence of the osmotic coefficient of the solution on the concentration $\varphi = \varphi(x)$, described in [3-5], then the value of x can be determined from equation: $x\Psi = -\ln a_w$, where a_w is the solvent activity in a saturated solution of major component. Based on the value of φ , the activity coefficient can be determined and then the activity of impurity component. The activity coefficient of the impurity component in the solid phase f_2 according to Allakhverdov GR [6,7] can also be calculated based on the data for the pure components.

Conclusion

Thus, the proposed method makes it possible to predict the change in the concentration of the impurities components during

crystallization of the major component from electrolyte solutions..

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