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Salt-forming regions of seawater type solution in the evaporation and fractional crystallization process

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ABSTRACT

Phase diagrams are important tools for design of fractional crystallization processes. However, besides that metastable behaviors are typically found, evaporative crystallization processes are often operated at nonequilibrium with conditions due to high evaporation rates. In such case, the salt-forming regions can be different and more complex than expected based on the equilibrium diagram. Thus in this work, the concepts and principle of salt-forming regions including primary region, extreme region, and conditional region are theoretically proposed to present the complex behaviors of salt-formation. Furthermore, the metastable zones and salt-forming regions are experimentally determined for a typical ternary system of Na^+, Mg^{2+}//$SO_4{}^{2-}$–H_2O at 348 K by the experimental method of isothermal boiling evaporation with an evaporation rate of $2.2\,g\,(L\,min)^{-1}$ (water). The primary regions (or extreme regions) of Thenardite, Loweite and Sakeite are enlarged and they are 1.16 (1.64), 1.28 (1.34) and 1.33 (1.96) times bigger, respectively, than those in solubility diagram, whereas Vanthoffite' region is reduced. The conditional regions accounts for 26.83% of the diagram's total region, where the salts precipitating maybe one or another or together which depend on the non-thermodynamic conditions, such as crystal seed, evaporation rate, mechanical, and so forth. Thus, knowledge of salt-forming region, especially the conditional region, would be extremely valuable to industry process design and control.

1. Introduction

Information on the salt(s) to be encountered in a given electrolyte system as a function of temperature is essential for the design of fractional crystallization processes. Industrial evaporation processes such as with sea water, are often operated at high evaporation rates and different pressure, where the metastable phenomena cause more complex behavior. In such case, the salt-forming regions are usually difficult to be accurately described by either the solubility diagram or the metastable diagram, making it necessary to learn more about the phenomena and mechanisms of salt formation at non-equilibrium state.

1.1. Solubility diagram

The solubility diagram corresponding to a stable state with absolute minimum free energy of the system, is also known as phase equilibrium diagram or stable phase diagram. Beginning with Van't Hoff, solubilities in sea water and related systems have been studied for more than 100 years [1]. Based on thermodynamic laws and the phase rule, the methodology of 'isothermal solubility equilibrium' [2] or 'isothermal decrease of the supersaturation' [3] for the experimental determination of SLE data, graphical representation [4] and thermodynamic models [1,5–7] have been developed and used to guide experiments and processes development.

1.2. Metastable diagram

Metastable phenomena occurring in complex system, cause a deviation of the salt precipitation sequence from the solubility diagrams. A well-known example is the 'solar phase diagram' of Na^+, K^+, Mg^{2+}//Cl^-, $SO_4{}^{2-}$–H_2O system at 298 K (partial) which was published by Kurnakov and Nikolaev [8]. By using Kurnakov's method, the isothermal natural evaporation method, metastable equilibrium data of sulfate, carbonate, borate and Li^+, Mg^{2+}, Rd^+ containing systems at ambient temperature were determined by Jin et al. [9–11], Sang et al. [12,13], Deng et al. [14–16], Zeng et al. [17,18]. The metastable equilibrium in salt water systems corresponds to a relative minima free energy of the system, where equilibria exist between metastable solid salt and solute species in the liquid phase while the stable solid salt is absent. Therefore, several metastable states may exist separately for a system at one temperature, and the actual metastable state present depends on which species of

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the solid salt is present. An example is the stable and metastable states in the system $MgSO_4–MgCl_2–H_2O$ at 348 K [19].

1.3. Salt-forming region

Industrial evaporation processes such as multi-effect evaporation are often operated at the compulsive nonequilibrium stable or dynamic state in high evaporation rates at boiling temperature usually from 323 to 393 K. Salt-forming behavior in such case is even more complex and difficult to be predicted accurately by either the solubility diagram or the metastable diagram. For example, four-effect evaporative crystallizers are running stably in Loweite and Kieserite solubility regions, but produce the desired salt of NaCl in the salt plant of Qarun Salt Lake (Egypt) [20]. The previous results of Na^+, $Mg^{2+}//SO_4{}^{2-}–H_2O$ system at 373 K [21], K^+, $Mg^{2+}//SO_4{}^{2-}–H_2O$ system at 348 K [22], Na^+, $Mg^{2+}//Cl^-$, $SO_4{}^{2-}–H_2O$ system at 348 K [23,24] and 373 K [25] show that (1) two salts are not always simultaneously co-precipitated from the co-saturated solution, (2) the salt-forming region at a given temperature is commonly different from its solubility region, (3) an overlap region typically exists among the salt-forming regions where which salt is formed depends on the nonthermodynamic conditions, such as crystal seed, etc. However, in spite of the classical concept of a solubility diagram and so-called metastable diagram, the knowledge about salt-forming region, such as the principle of its determination, the mechanism and deviation from the solubility region, and its stability in industry process, is under-exploited.

In order to present the complex behavior of salt-formation in the nonequilibrium state, in this contribution, we try to improve the concepts and propose the principle of salt-forming region on the bases of solution thermodynamics and the knowledge of crystallization theories. As an example, the salt-forming regions in a typical system Na^+, $Mg^{2+}//SO_4{}^{2-} – H_2O$ at 348 K were experimentally obtained by the method of isothermal boiling evaporation.

2. Theoretical background

Salt-formation means that a solid is built from the liquid solution by nucleation or crystal growth. During nucleation, microscopic nuclei of the salt are formed from the salt building blocks, which grow subsequently to macroscopic crystals. The primary condition necessary for salt-formation is the establishment of supersaturation which may be attained by increasing the salt concentration to above the equilibrium level, commonly, by evaporation or temperature change. There is, however, a threshold in the extent of deviation from equilibrium at which if reached, spontaneous precipitation occurs, whereas the corresponding solubility and the range of supersaturation is in that case defined as supersolubility and metastable zone, respectively. The exact value of supersolubility is not well determined and depends on several factors such as presence of foreign suspended particles, agitation, etc. The width of the metastable zone is quite different from salt to salt, which may causes the difference of salt-forming region from solubility diagram.

2.1. Salt-forming driving force

Supersaturation is, quantitatively, a measure of the deviation of the concentration of a dissolved salt from its equilibrium value, which may be expressed in several types of units. The concentration difference, ΔC, is defined as $\Delta C = C - C_\infty$, where C and C_∞ are the solute concentration in solution and at equilibrium, respectively. The supersaturation ratio (dimensionless), S, is defined as $S = C/C_\infty$, and the relative supersaturation, σ, is defined as $\sigma = (C - C_\infty)/C_\infty$, here $S > 1$ and $\sigma > 0$ for supersaturated solution. For a multi-component solution, one or more salts could be in supersaturated state simultaneously, but the supersaturation for mixed salt cannot be expressed conveniently by method above, thus the saturation index, SI, is therefore introduced as the ratio between the activity and the solubility product. See Eq. (1) [26–28].

$$\mathrm{SI} = \left\{ \frac{\prod \alpha_i^{v_i}}{\exp(-\Delta G^0/RT)} \right\} = \left(\frac{\mathrm{IP}}{K_S^0} \right) \tag{1}$$

where the subscript 0 refers to the equilibrium condition. α denotes the activities of the respective ions. IP and K_S^0 are the ion activity products in the supersaturated solution and at equilibrium, respectively.

The salt-formation in a supersaturated solution starts by the formation of nuclei. According to the classical nucleation theories, the nucleus has a size smaller than the critical size and its chance of growing is small. Nucleus larger than the critical size can continue to grow. Here we consider the equilibrium between a nucleus with critical size and its constituent ions in the supersaturated solution, a critical metastable equilibrium. Corresponding to the critical supersaturation where the spontaneous nucleation or primary nucleation occurs, the supersolubility $\mathrm{SI_{crit}}$ can be expressed by the Kelvin equation for the formation of crystal nuclei in a solution [26,27]. See Eq. (2).

$$\ln \mathrm{SI_{crit}} = \frac{2\sigma V_0}{RTr_{\mathrm{crit}}} \tag{2}$$

where V_0 (m^3) is the molar volume of the salt. σ (J/m^2) is the interfacial tension between nucleus and saturated solvent. r_{crit} (m) is the critical radius of a spherical nucleus.

The essential driving force for the salt-formation is the difference in chemical potential of the solute in the supersaturated solution from the respective value at equilibrium. By using Eqs. (1) and (2), the critical Gibbs energy change for forming a nucleus with the critical size of ns mole salt molecule is evaluated: [26,27]

$$\Delta G^{\mathrm{crit}} = \frac{16\pi\sigma^3 V_0^2}{3(RT \ln \mathrm{SI_{crit}})^2} \tag{3}$$

This is the critical Gibbs energy change for the formation of one nucleus which has the corresponding positive value, and can be considered as the activation energy for forming a spherical nucleus of the critical size. Whereas the chemical potential change $\Delta\mu_{\mathrm{nuc}}$ of the solute at the critical supersaturated and solid–liquid equilibrium, can be calculated by Eq. (4).

$$\Delta\mu_{\mathrm{nuc}} = \frac{\Delta G^{\mathrm{crit}}}{ns} \tag{4}$$

The driving force equations (1)–(3) are commonly used to describe the kinetics of primary nucleation rate or crystal grow rate. However, in complex system, these equations are also the fundament of the salt-forming region.

2.2. Salt-forming region

The salt-forming region is where the salt could be formed either by primary nucleation or by crystal grow. Here the primary nucleation is further distinguished into homogeneous and heterogeneous to denote the situations in which it starts spontaneously or is catalyzed by the presence of foreign particles, respectively. How the salt-formation is changed is determined by the thermodynamic conditions and results in a complex salt-forming region. In our previous work [21–25], the salt-forming region was experimentally distinguished into primary region, extreme region, and conditional region. Here we propose these concepts and principles in thermodynamic raws.

Primary region (PR) is where the homogeneous nucleation for the considered salt could occurs within the isothermal