Investigation of the Polythermal Solubility System $CaCl_2 \cdot 2H_2O$–$HNO_3 \cdot CO(NH_2)_2$–H_2O

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Calcium chloride is widely used in many fields due to its high hygroscopicity, good solubility in water, and activity at low temperatures, which stimulates significant research in industrial, medical, chemical, energy, and environmental applications. In practice, the complexes formed by calcium chloride with urea are used as de-icing agents [1]. Calcium chloride forms urea complexes in various ratios, including compounds such as $CaCl_2 \cdot 2CO(NH_2)_2$ and $CaCl_2 \cdot 4CO(NH_2)_2$ [2]. Complexes of this type form multiphase systems in solution, which makes it possible to control the physicochemical properties of the solution. In saline soils, calcium chloride ($CaCl_2$) tends to accumulate as a result of natural or irrigation waters [3], and high concentrations of chlorides in the soil have a negative impact on plant growth. Under such conditions, retaining calcium salts in the soil while removing chloride ions is considered one of the important research objectives.

In order to provide a physicochemical justification of the interactions between the components in the $CaCl_2 \cdot 2H_2O$ – $HNO_3 \cdot CO(NH_2)_2$ – H_2O system, the system was studied over a wide range of temperatures and concentrations using the visual polythermal method (Figure 1).

The polythermal solubility diagram of the $CaCl_2 \cdot 2H_2O$ – $HNO_3 \cdot CO(NH_2)_2$ – H_2O system was constructed over the temperature range from −52.0 °C to 48.0 °C on the basis of 9 internal sections and the binary systems $CaCl_2 \cdot 2H_2O$ – H_2O and $HNO_3 \cdot CO(NH_2)_2$ – H_2O. Of the internal sections, lines I–VI were investigated from the $CaCl_2 \cdot 2H_2O$ – H_2O side toward higher $HNO_3 \cdot CO(NH_2)_2$ concentrations, while sections VII–IX were studied from the $HNO_3 \cdot CO(NH_2)_2$ – H_2O side toward the $CaCl_2 \cdot 2H_2O$ apex. In the diagram, the crystallization fields of ice, urea, urea nitrate, calcium chloride dihydrate, calcium chloride tetrahydrate, and calcium chloride hexahydrate were delineated. These crystallization fields converge at four ternary invariant points. The first ternary invariant point corresponds to 8.0 °C and a composition of 57.2% calcium chloride dihydrate, 4.0% urea nitrate, and 38.8% water.

The second ternary invariant point occurs at −6.0 °C and corresponds to 53.6%

calcium chloride dihydrate, 3.6% urea nitrate, and 42.8% water. The third ternary invariant point is observed at −12.0 °C with a composition of 48.0% calcium chloride dihydrate, 3.6% urea nitrate, and 48.4% water. The fourth ternary invariant point corresponds to −52.0 °C and contains 34.0% calcium chloride dihydrate, 4.0% urea nitrate, and 62.0% water.

According to the diagram, ice co-crystallizes with calcium chloride hexahydrate in the temperature range from −51.0 °C to −49.7 °C, and with urea in the range from −34.0 °C to −3.0 °C. Urea nitrate and urea co-crystallize over the temperature range from −6.0 °C to 48.0 °C. Calcium chloride dihydrate co-crystallizes with calcium chloride tetrahydrate in the temperature range from 22.0 °C to 45.2 °C, while calcium chloride dihydrate and urea nitrate co-crystallize at 9.0 °C. Calcium chloride tetrahydrate and calcium chloride hexahydrate co-crystallize in the range from 10.0 °C to 29.7 °C, and calcium chloride hexahydrate and urea co-crystallize at 20.0 °C.

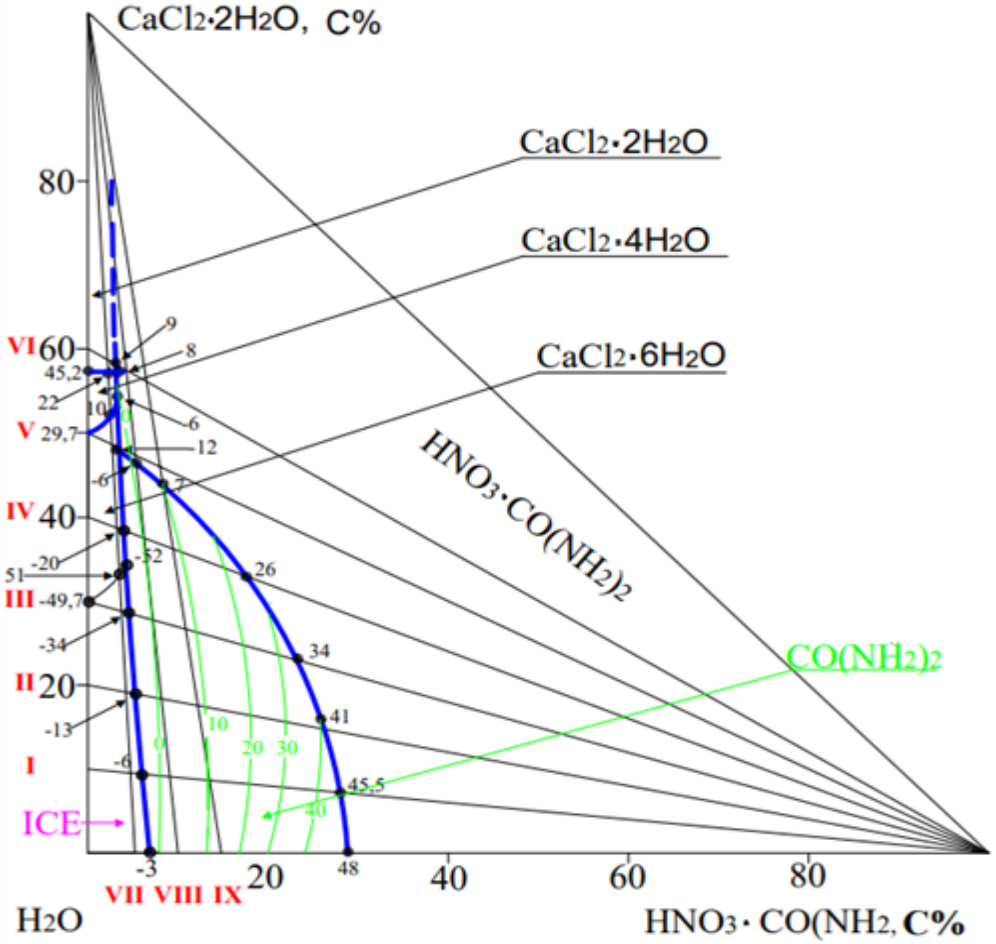

Figure 1. Polythermal solubility diagram of the $CaCl_2·2H_2O$–$HNO_3·CO(NH_2)_2$–H_2O system.

In the polythermal solubility diagram, isotherms were drawn and studied at every 10.0 °C. The system belongs to a simple eutonic type, and no new compounds were formed

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