Solubility in the NaNO₃—NH₄NO₃—KNO₃—H₂O system

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Abstract — Solubility in the NaNO₃—NH₄NO₃—KNO₃—H₂O four-component system was studied for the first time at 25, 40, and 60°C. The crystallization boundaries were determined for individual constituent salts, the double salt 3KNO₃·NH₄NO₃, potassium nitrate-based solid solutions, and ammonium nitrate-based solid solutions. The reported experimental data have been used to optimize a circular isohydric process for preparing potassium nitrate involving additional salts.

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Sodium nitrate, potassium nitrate, and ammonium nitrate, all of chemically pure grade, were used after recrystallization from aqueous solutions. Distilled water, nD = 1.3272, was used to determine solubilities of pure salts and their mixtures. The above-listed chemicals fully satisfied the conditions of our experiments and the precision of the method employed.

Solubility was studied by the isothermal section method at 25, 40, and 60°C [4–6]. The refractive index of a liquid phase was chosen to be the physical property to be measured; it was measured on an IRF-454B2M refractometer [7] for all isotherms with the highest thermostating temperature of 60°C. The precision of water solubility determinations for the individual salts and their mixtures was ±0.5 wt %.

The existence of solid solutions in the NH₄NO₃—KNO₃—H₂O three-component system and in the four-component system was proven by means of X-ray diffraction; changes in unit cell parameters were detected. The unit cell parameters were calculated using Lipson’s method, which was proposed for the orthorhombic system [8], for the reason that our studied compound crystallized just in that system. The existence of the double salt 3KNO₃·NH₄NO₃ was also confirmed by an X-ray diffraction experiment.

We studied potassium nitrate and ammonium nitrate samples, solid solution samples prepared from the NH₄NO₃—KNO₃—H₂O ternary system (sample 1) and the quaternary system (sample 2), and samples of the double salt 3KNO₃·NH₄NO₃ from the ternary

Experimental

The literature lacks solubility data for the NaNO₃—NH₄NO₃—KNO₃—H₂O four-component system, but there is a sufficient amount of solubility data for its boundary ternary systems.

The NH₄NO₃—KNO₃—H₂O system has been studied several times at different temperatures, but data pertaining to the nature of solid phases evolving in this system are divergent [1]. Some researchers state that a continuous solid solution series crystallizes in the system at temperatures in the range 0–100°C. Some others report that one or more chemical compounds are formed, but do not specify their compositions. Karnaukhov [2, 3] found that the 25°C solubility isotherm of the system has three crystallization fields, which belong to two solid solution series (formed by potassium nitrate or ammonium nitrate and the double salt 3KNO₃·NH₄NO₃) and the double salt 3KNO₃·NH₄NO₃.

The NaNO₃—NH₄NO₃—H₂O system has been studied at temperatures in the range from −25 to 100°C [1]. This system is of the simple eutonic type. The 25°C solubility isotherm of the system has three crystallization fields, which belong to sodium nitrate, the double salt 2NaNO₃·NH₄NO₃, and ammonium nitrate [3].

The NaNO₃—KNO₃—H₂O system has been studied in the range of temperatures from 0 to 250°C [2]. The system is of the simple eutonic type. It does not form new chemical compounds or phases of variable composition. The compositions reported by different researchers for eutonic solutions at equal temperatures are not very much divergent, so we have not restudied this system.

Thus, there remains an open question of the existence boundaries of solid solutions and double salts in the boundary systems. Therefore, out study was concentrated on solubility and topology of phase fields in NH₄NO₃—KNO₃—H₂O and NaNO₃—NH₄NO₃—KNO₃—H₂O ternary systems and in the NaNO₃—NH₄NO₃—KNO₃—H₂O quaternary system.
system (sample 3) and the quaternary system (sample 4). Weighed batch samples in flasks were recrystallized on a water bath and exposed in a thermostat at 25°C (sample 1) and 40°C (samples 2–4) under continuous stirring upon equilibration, which was monitored by the refractive index of the liquid phase of a batch exposed to the set temperature for at least 5 h. The solid phase was filtered out and dried to constant weight at 60°C. Cylinder-shaped specimens, each 1 mm high and 0.7 mm in diameter, were prepared from the thus-obtained solid phases. X-ray diffraction patterns were recorded on a URS-55 setup with an RKD chamber (Cr radiation) for 3 h. Line positions were measured on an IZA-2 comparator.

RESULTS AND DISCUSSION

In order to determine the compositions and existence boundaries of solid phases in the \( \text{NH}_4\text{NO}_3–\text{KNO}_3–\text{H}_2\text{O} \) system, we studied (salt solution)–(salt crystals) sections and isohydric sections in the heterogeneous field. Proceeding from the refractive index as dependent on the salt concentration and salt ratio, we found that two solid solution series exist in the system at 25°C, and this is in line with [2, 3]. However, we have not found a \( 3\text{KNO}_3 \cdot \text{NH}_4\text{NO}_3 \) crystallization field at this temperature. The maximal ammonium nitrate concentration in the potassium nitrate-based solid solution is 20.9 wt %, which corresponds with the salt ratio in \( 3\text{KNO}_3 \cdot \text{NH}_4\text{NO}_3 \). The maximal potassium nitrate concentration in the ammonium nitrate-based solid solution is 8.5 wt %.

At 40 and 60°C, there exist crystallization fields of potassium nitrate-based solid solutions whose concentration extent is bound by the ammonium nitrate percentage in the solid phase of 0.0–20.9 wt %, the double salt \( 3\text{KNO}_3 \cdot \text{NH}_4\text{NO}_3 \), and ammonium nitrate. Ammonium nitrate-based solid solutions are absent as shown by our results.

The compositions of solid phases were verified by construction of tie-lies in the crystallization fields of the solid solutions and the double salt [9]. Solubility isotherms of the \( \text{NH}_4\text{NO}_3–\text{KNO}_3–\text{H}_2\text{O} \) system are displayed in Fig. 1; the composition of saturated solutions are found in Table 1.

Our solubility studies show that the pure constituent salts are crystallized in the \( \text{NaNO}_3–\text{NH}_4\text{NO}_3–\text{H}_2\text{O} \) system (Fig. 2). We have not observed the formation of the double salt \( 2\text{NaNO}_3 \cdot \text{NH}_4\text{NO}_3 \). The crystallization of individual salts is verified by the constancy of the refractive index of the liquid phase in heterogeneous mixtures along the sections that originate from the sodium nitrate or ammonium nitrate corners [5].

In order to characterize the solubility isotherm of the \( \text{NaNO}_3–\text{NH}_4\text{NO}_3–\text{KNO}_3–\text{H}_2\text{O} \) system to the full extent, we studied six sections that pass through points lying on sides of the salt basis and the water corner of the constitution tetrahedron. The results obtained on the boundary ternary systems and those sections prove that potassium nitrate and ammonium nitrate