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# The influence of temperature on liquid–liquid–solid equilibria for (water + 2-propanol + KCl +$NH_4Cl$) quaternary system

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ABSTRACT

The influence of temperature on liquid–liquid–solid (L–L–S) equilibria for (water + 2-propanol + KCl + $NH_4Cl$) quaternary system with different KCl/$NH_4Cl$ mass ratios (1/0, 1/3, 1/1, 3/1, 0/1) were systematically investigated. Phase-transition temperature under different salt ratios was determined, seven diagrams of liquid–liquid–solid equilibria around these temperatures were measured and the transitions between two different shapes (L–L–S and L–S equilibria) were studied. Mutual solubility, binodal curve and tie-line data for quaternary system in different temperature were obtained, and it was found that the effect of temperature on phase equilibrium was significant, but insignificant on the variation of binodal curve under the same salt ratio. Moreover, binodal curve data with KCl/$NH_4Cl$ mass ratios (1/0, 1/3, 1/1, 3/1, 0/1) at different temperatures were fitted by three-parameter equation. The relation between phase-transition temperature and different salt mass fraction was established by a polynomial equation with five parameters, and result shows that the lowest splitting temperature is around 18.6 °C corresponding with 71.1% (wt%) $NH_4Cl$. In addition, both temperature and 2-propanol amount affect the salt precipitation, which varies with 2-propanol concentration at different temperature in quadratic polynomial mode.



## 1. Introduction

Potassium is an important mineral and widely used in various fields, it is an essential element for plant growth and development in agriculture, but also the basic material for potash production in industry [1,2], and potassium in human and other organisms plays a significant role in physical quality and bodily functions [3–5]. Recent years have seen the great consumption of potassic salt ore and the decline of saline lake minerals, and many countries start seeking potassium resource from the sea which contains plenty storage of KCl. One cost-effective method is to utilize the zeolites with excellent potassium adsorption capacity for adsorption of potassium from seawater [6]. In the recycling of zeolites, $NH_4Cl$ could be used as a good eluting agent for swapping the adsorbed KCl due to their similar chemical property [7,8]. However, the separation of KCl and $NH_4Cl$ in the potassium rich solution is a challenge, which can form solid solution in the course of crystallization.

In our previous studies [9–11], water–1-propanol–KCl–$NH_4Cl$ aqueous two-phase system (ATPSs) was established for the separation of KCl and $NH_4Cl$ from aqueous solution, and the corresponding liquid–liquid equilibrium and selective partition of salts were systematically studied. To expand our work, another extractant 2-propanol is employed for the separation process. Compared with 1-propanol, 2-propanol is also a common good chemical organic solvent and often used as the extractive agent in chemical experiments [12,13]. Besides, the boiling point of 2-propanol is lower, which is an advantage in the recovery of extractant by evaporation [14,15].

The present work continues the systematic methodology suggested previously and aims to investigate the influence of temperature on the liquid–liquid–solid equilibria for (water + 2-propanol + KCl + $NH_4Cl$) quaternary system. Phase diagrams with different KCl/$NH_4Cl$ mass ratios (1/0, 1/3, 1/1, 3/1, 0/1) were systematically studied, mutual solubility, binodal curve and tie-line data under different temperature were measured. The variation of phase-transition temperature, binodal curve and the precipitation of salt were correlated with appropriate parameter equations.

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**Table 1**
Chemical sample description.

| Chemical name | Source | Initial mass fraction purity | Purification method | Final mass fraction purity | Analysis method |
|---|---|---|---|---|---|
| KCl | Benchmark chemical reagent co., LTD (Tianjin, China) | 0.995 | None | | – |
| $NH_4Cl$ | Benchmark chemical reagent co., LTD (Tianjin, China) | 0.995 | None | | – |
| 2-propanol | BoDi Chemical Reagent Factory. (Tianjin,China) | 0.995 | None | | GC[a] |

[a] Gas chromatography.

**Table 2**
Solubility (wt%) of salts in different solvents at different temperature and $p = 1$atm[a].

| $t$/°C | Composition/% (wt%) | | | | | |
|---|---|---|---|---|---|---|
| | Water | | Aqueous alcohol (5 wt%) | | 2-Propanol | |
| | KCl | $NH_4Cl$ | KCl | $NH_4Cl$ | KCl | $NH_4Cl$ |
| 25 | 26.35 | 28.03 | 23.47 | 27.00 | 0.014 | 0.374 |
| 30 | 27.08 | 29.25 | 24.13 | 28.09 | 0.019 | 0.387 |
| 35 | 27.84 | 30.36 | 24.86 | 29.07 | 0.020 | 0.401 |
| 40 | 28.62 | 31.41 | 25.67 | 30.06 | 0.021 | 0.426 |
| 45 | 29.41 | 32.50 | 26.52 | 31.22 | 0.022 | 0.459 |

[a] Standard uncertainties u are u(T) = 0.1 °C, u(w) = 0.002, and u(p) = 10 kPa.

## 2. Experimental

### 2.1. Materials

KCl (>99.5 mass%, analytical grade) and $NH_4Cl$ (>99.5 mass%, analytical grade) were supplied by Tianjin Benchmark chemical reagent co., LTD (Tianjin, China). 2-Propanol (>99.5 mass%, analytical grade) was purchased from Tianjin BoDi Chemical Reagent Factory (Tianjin, China), and the purity of 2-propanol was checked by gas chromatography. All chemicals were used without further purification. Water used in experiments was double distilled. Description of chemical samples is presented in Table 1.

### 2.2. Apparatus and procedures

#### 2.2.1. Mutual solubility

Water–2-pronaol is completely miscible system and it is impossible to investigate the mutual solubility. The solubility of salt (KCl and $NH_4Cl$) in solvent (water and 2-propanol) at varied temperature was determined in a crystallizer equipped with a magnetic stirrer and isothermal fluid water bath with an uncertainty of within ±0.1 °C. The hybrid systems were made by mixing excessive salt with solvent, which should be sufficiently stirred for 24 h to ensure homogeneous mixing and settled for a further 4 h [9]. After

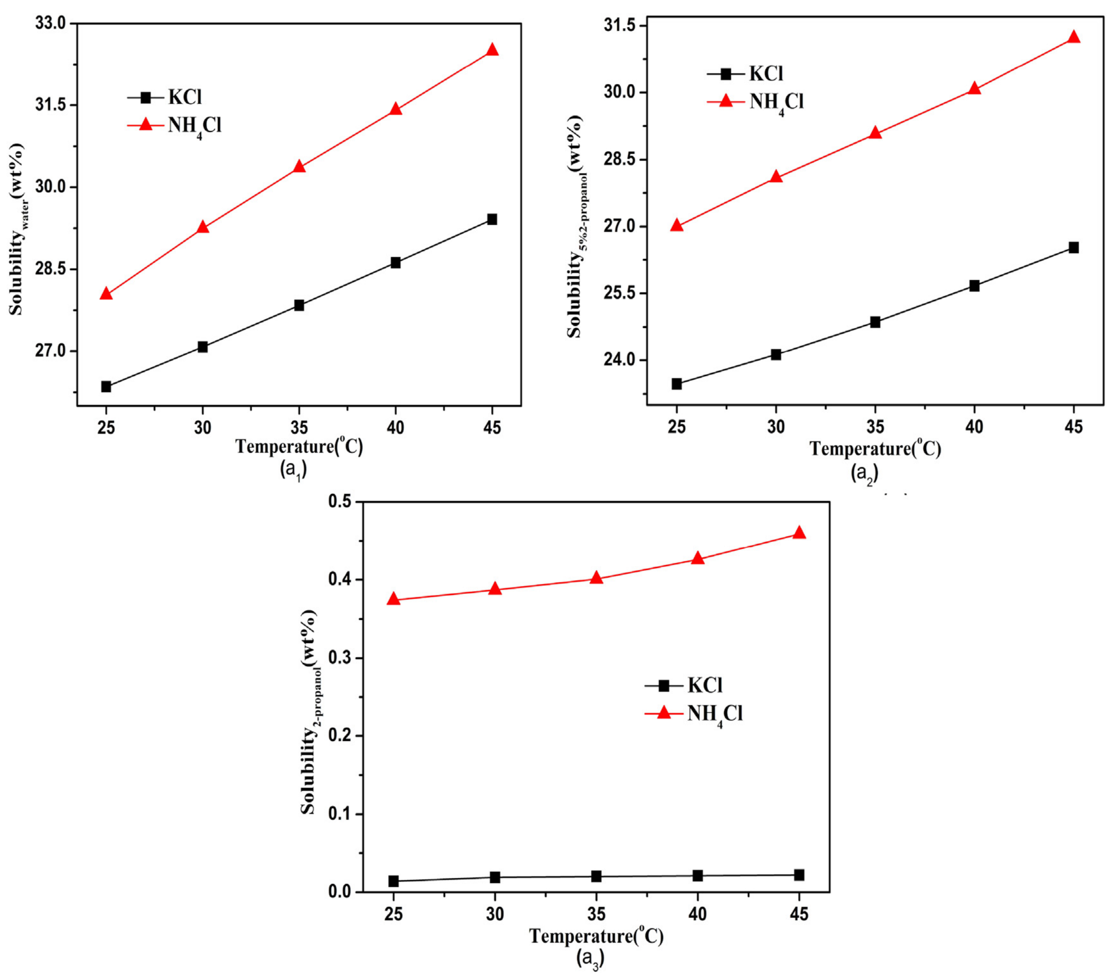


**Fig. 1.** Solubility of KCl and $NH_4Cl$ in different solvents ($a_1$, water; $a_2$, 5% aqueous alcohol; $a_3$, 2-propanol).