A quasi-ternary wet residue method applied to solid-liquid equilibrium systems

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ABSTRACT

Solid-liquid equilibrium data are the basis of extraction processes. Traditional wet residue method is known as the most commonly used technique for analyzing equilibrium data for ternary solid-liquid systems. However, when the solid phase contains more than two substances, the wet residue method is restricted. Aiming at this problem, we proposed a novel quasi-ternary wet residue approach that is specialized for analyzing the composition of solid phase for quaternary and more complex systems. To evaluate the applicability of the proposed technique, case studies were introduced in this paper: For a quaternary water-sugar system composed of D-glucose, D-xylose, L-arabinose and H_2O, experimentally obtained solid-liquid equilibrium data were utilized to determine the composition of pure solid phase at different temperatures and; For two quaternary water-salt systems, i.e., NaCl-KCl-MgCl$_2$-H$_2$O and NaCl-CaCl$_2$-MgCl$_2$-H$_2$O, compositions of solid phase were methodologically analyzed, respectively. The results allow for effective investigating relations of solid-liquid phase equilibria for quaternary and more complex systems via the proposed technique.

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1. Introduction

Solid-liquid equilibrium is considered as fundamental in chemical thermodynamics, which is of great significance to the separation and purification of chemical products. Typically, measurement methods on solid-liquid equilibrium include equilibrium [1], synthetic [2] and thermal analysis [3], etc. For example, Du et al. [4] determined a quaternary solid-liquid equilibrium system composed of terephthalic acid, isophthalic acid, phthalic acid and N-methylpyrrolidone using the equilibrium method; Barroug et al. [5] measured a ternary solid-liquid equilibrium system of H_2O-$Cu(NO_3)_2$-$Al(NO_3)_3$ via the synthetic method; Coto et al. [6] employed the thermal analysis technique to determine solid-liquid equilibrium data of paraffin in petroleum mixtures.

In ternary solid-liquid equilibrium systems, the determination of solid phase composition is essential for the design of material separation processes. Among others, wet residue method [7] is one of the most commonly used approach to determine the

composition of pure solid phase by analyzing the liquid phase and the wet residue. In this technique, compositions of liquid phase and wet residue can be determined via analytical means. Though wet residue method has been applied primarily in ternary systems, some researchers expanded it to quaternary systems. For example, Song [8] depicted equilibrium data of a quaternary solid-liquid system, in which the pure solid phase was determined by using the wet residue method in a tetrahedron. The selected vertex was projected to the bottom of the tetrahedron, and solid phase composition was investigated thereafter by the projection plane. However, it is very tedious and inefficient to evaluate solid-liquid equilibrium data for quaternary and more complex systems in which the solid phase contains more than two substances via the traditional wet residual method, since three-dimensional (3D) phase diagrams must be employed.

To date, a great variety of studies with respect to solid-liquid equilibrium are concentrated on systems in which two [9—11] or three [12—14] substances in solid phase were participated. Researches of quaternary systems constituting of three substances in solid phase and water as liquid phase are primarily focused on water-salt systems [15,16]. As for the water-sugar system, quaternary systems composed of three kinds of sugars and water have rarely been reported. For gramineous plants, monosaccharides in

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solution after the hydrolysis of hemicellulose are generally existed in the form of D-glucose, D-xylose and L-arabinose. Analyzing solid-liquid equilibrium data for such water-sugar systems is a preliminary procedure for the extraction of monosaccharides. Hence in this paper, solid-liquid equilibria in an aqueous system composed of D-glucose, D-xylose, L-arabinose are investigated. Aiming at limitations of the traditional wet residue method, a novel quasi-ternary wet residue technique which can be employed in quaternary and more complex systems for analyzing solid-liquid equilibrium data is proposed. The relations of solid-liquid equilibria in two quaternary water-salt systems are studied to verify the proposed method.

2. Theory

2.1. Traditional wet residue method

In a solid-liquid equilibrium system, the composition of liquid phase can be measured by using appropriate analytical approaches (e.g. chemical analysis [17], HPLC [18], ICP-OES [19] etc.). However, the separation of pure solid phase in solid-liquid equilibrium systems is very difficult, giving rise to a dilemma that the composition of pure solid phase cannot be readily determined. Traditional wet residue method is a technique that has been widely applied to analyze the composition of solid phase in ternary solid-liquid equilibrium systems. In the plane phase diagram, lines of wet residue composition and liquid phase composition pass through the composition of pure solid phase. At the same temperature, wet residue lines converge at a point. This point indicates the composition of pure solid phase.

2.2. Quasi-ternary wet residue method

In quaternary and more complex solid-liquid equilibrium systems, traditional wet residue method is restricted due to the utilization of 3D phase diagrams as mentioned above. Aiming at this problem, a novel quasi-ternary wet residue method is proposed, as follows:

For a solid-liquid equilibrium system composed of n solutes and a solvent, there are n-1 solutes reach co-saturation in the solution, while a solute is not saturated. If n-1 solutes reached co-saturation are considered as a component, the complex system can be simplified to a ternary system, i.e., an unsaturated solute, a saturated solute and a solvent. By acquiring compositions of liquid phase and wet residue, such the solid-liquid equilibrium system can be analyzed in a plane phase diagram.

Supposing that a solid-liquid equilibrium system is composed of n solutes and a solvent, solutes n_1, n_2, ..., n_{n-1} reach co-saturation. Mass fraction of solutes in the liquid phase are y_1, y_2, ..., y_{n-1}, respectively, and mass fraction of the unsaturated solute n_n in liquid phase is x_1. Mass fraction of solutes n_1, n_2, ..., n_{n-1} in wet residue are y'_1, y'_2, ..., y'_{n-1}, respectively, and solute n_n is x'_1 in wet residue. Assuming that mass fraction of solutes n_1, n_2, ..., n_{n-1} in pure solid phase are y_{1a}, y_{2a}, ..., $y_{(n-1)a}$, respectively, and the unsaturated solute n_n is x_{1a}.

If saturated solutes in the solution were considered as a component, mass fraction of such the component in liquid phase, wet residue and pure solid phase can be expressed as $\sum_{i=1}^{n-1} y_i$, $\sum_{i=1}^{n-1} y_i'$ and $\sum_{i=1}^{n-1} y_{ia}$, respectively.

In ternary phase diagrams, i.e., Figs. 1–3, the composition of liquid phase can be written as $(x_1, \sum_{i=1}^{n-1} y_i)$, the composition of wet residue can be written as $(x'_1, \sum_{i=1}^{n-1} y_i')$ and the composition of pure solid phase can be written as $(x_{1a}, \sum_{i=1}^{n-1} y_{ia})$.

Mass fraction of co-saturated solutes in the wet residue y'_1, y'_2, ..., y'_{n-1} can be expressed by y_1, y_2, ..., y_{n-1} and y_{1a}, y_{2a}, ..., $y_{(n-1)a}$, as:

$$y'_1 = \frac{my_1 + py_{1a}}{m + p}, \qquad (1)$$

$$y'_2 = \frac{my_2 + py_{2a}}{m + p}, \qquad (2)$$

$$\vdots$$

$$y'_{n-1} = \frac{my_{n-1} + py_{(n-1)a}}{m + p} \qquad (3)$$

where m denotes the mass of solution in wet residue and p denotes the mass of pure solid. So:

$$\sum_{i=1}^{n-1} y'_i = \frac{m \sum_{i=1}^{n-1} y_i + p \sum_{i=1}^{n-1} y_{ia}}{m + p} \qquad (4)$$

and

$$x'_1 = \frac{mx_1 + px_{1a}}{m + p} \qquad (5)$$

Combining Eqs. (4) and (5), the composition of wet residue can be expressed as: $\left(\frac{mx_1 + px_{1a}}{m+p}, \quad \frac{m\sum_{i=1}^{n-1} y_i + p\sum_{i=1}^{n-1} y_{ia}}{m+p} \right)$

The linear equation through composition points of liquid phase and wet residue can be deduced, as:

$$y = \frac{\sum_{i=1}^{n-1} y_{ia} - \sum_{i=1}^{n-1} y_i}{x_{1a} - x_1} x - \frac{x_{1a} \sum_{i=1}^{n-1} y_i - x_1 \sum_{i=1}^{n-1} y_{ia}}{x_{1a} - x_1} \qquad (6)$$

If $x = x_{1a}$, substituting it into Eq. (6), $y = \sum_{i=1}^{n-1} y_{ia}$ can be derived. As a consequence, the composition point of pure solid phase lands up on wet residue lines.

It is important to note that the proposed quasi-ternary wet residue method has two major limitations:
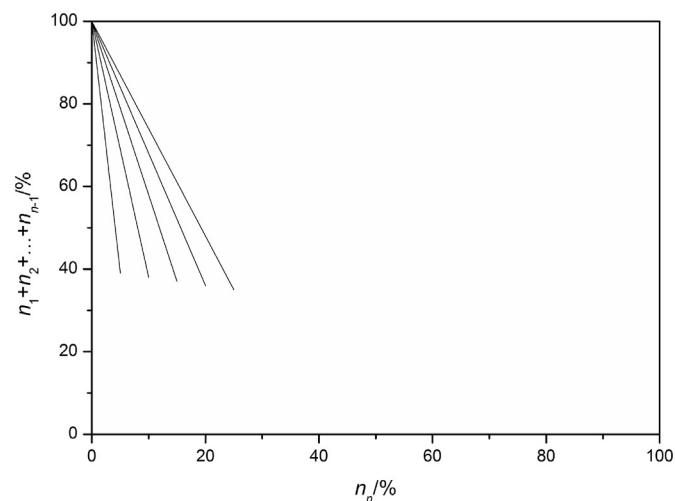

Fig. 1. Wet residue lines intersect at y-axis ($x = 0$, $y = 100$). All curves were qualitatively plotted.