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Solid-liquid phase equilibria of ternary system $Na_2S_2O_3$-Na_2SO_4-H_2O in a wide range of temperatures: Measurement and application

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ABSTRACT

In order to provide a fundamental basis for treatment of wastewater from desulfurization of coke oven gas to recover pure salt, solid-liquid equilibrium data of $Na_2S_2O_3$-Na_2SO_4-H_2O system at T = (278.15, 283.15, 291.15, 333.15 or 353.15) K were measured. The experimental data was obtained using the isothermal solution saturation method and Schreinemaker's wet residue method. The solid-liquid phase diagrams of the ternary system were constructed. The ternary phase diagrams turned out to be simple eutectic type containing one invariant point, two univariant curves, and two single-salt crystallization regions. It was found that the crystallization region of Na_2SO_4 is larger than that of $Na_2S_2O_3$ and expands with the increasing of temperature. But the crystallization region of $Na_2S_2O_3$ decreases with the increasing of temperature. Through analyzing the thermodynamic characteristics of $Na_2S_2O_3$ and Na_2SO_4, two crystallization methods for separating the mixture of $Na_2S_2O_3$-Na_2SO_4 were put forward. A simple comparison of the two crystallization methods was carried out.

1. Introduction

Steel and iron industry is pillar industries of many countries, including China. Coking process provide necessary hard coke for steel and iron industry [1]. Nevertheless, during the coking process, lots of coke oven gas which need further treatments will be generated. As one of the treatments, desulfurization of coke oven gas can get rid of impurities such as hydrogen sulfide. But on the other hand, lots of wastewater will be generated from the desulfurization processes. Generally, the wastewater from desulfurization of coke oven gas is composed of organic and inorganic contaminants. The organic contaminants mainly include phenolic compounds, polynuclear aromatic hydrocarbons (PAHs), polycyclic nitrogen-containing aromatics and acyclic compounds which are toxic, mutative and carcinogenic and may produce long-term environmental and ecological impacts [2–7]. The inorganic components in wastewater from desulfurization of coke oven gas mainly include sodium thiocyanate, sodium sulfate and sodium thiosulfate.

Desulfurization wastewater with a high salt concentration is forbidden to be directly discharged. Hence, at present, after treated by biochemical method or chemical oxidization method, wastewater from desulfurization of coke oven gas is often delivered to evaporation ponds, producing huge amounts of mixed salts with many kinds of impurities. Mixed salts can lead to secondary pollution with rainfall infiltration and thus are often identified as hazardous wastes [8–10].

To solve these problems, technology needs to be developed to extract pure sodium sulfate and sodium thiosulfate, which can be reused by other industries, from the salt mixtures or directly from wastewater. For the separation of two inorganic salts, crystallization is a frequently used unit operation. Generally, the crystallization method development and design is based on phase equilibrium of the water-salt system. Hence, the measurement and analysis of the phase diagrams of $Na_2S_2O_3$-Na_2SO_4-H_2O system is of both theoretical and practical importance. However, very little phase equilibrium data of the ternary $Na_2S_2O_3$-Na_2SO_4-H_2O system has been reported in literature. Neither has the crystallization method of $Na_2S_2O_3$-Na_2SO_4 mixture been reported. In this study, the solid-liquid phase equilibria of the ternary $Na_2S_2O_3$-Na_2SO_4-H_2O system at T = (278.15, 283.15, 291.15, 333.15 or 353.15) K were investigated using the isothermal solution saturation method. Base on the determined phase diagrams of

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Table 1
The purities and suppliers of chemicals used in this study.

Agents	CAS	Mass fraction purity[a]	Grade	Sources
Na_2SO_4	7757-82-6	≥0.995	GR	Tianjin Kermel Chemical Reagent Co. Ltd., China
$Na_2S_2O_3$	7772-98-7	≥0.990	AR	Tianjin Kermel Chemical Reagent Co. Ltd., China
I_2	7553-56-2	≥0.998	AR	Tianjin Yuxiang Technology Co. Ltd., China
KI	7681-11-0	≥0.990	AR	Shanghai Macklin Biochemical Co. Ltd., China
$Pb(NO_3)_2$	10099-74-8	≥0.990	AR	Tianjin Yuanli Chemical Co. Ltd., China
Anhydrous ethanol	64-17-5	≥0.997	AR	Tianjin Real&Lead Chemical Technology Co. Ltd., China

[a] Data provided by suppliers.

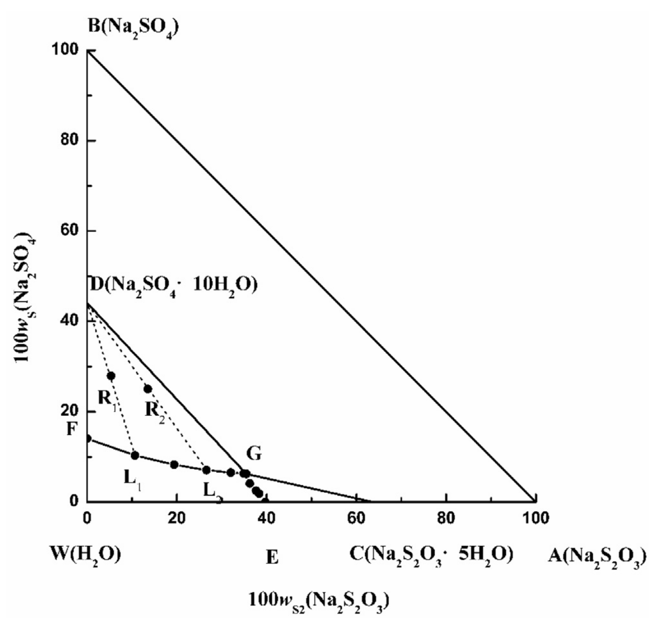

Fig. 1. Principal sketch of Schreinemakers's graphical method. The L_i is the saturated liquids, the R_i is the wet residues, and D is the solid composition.

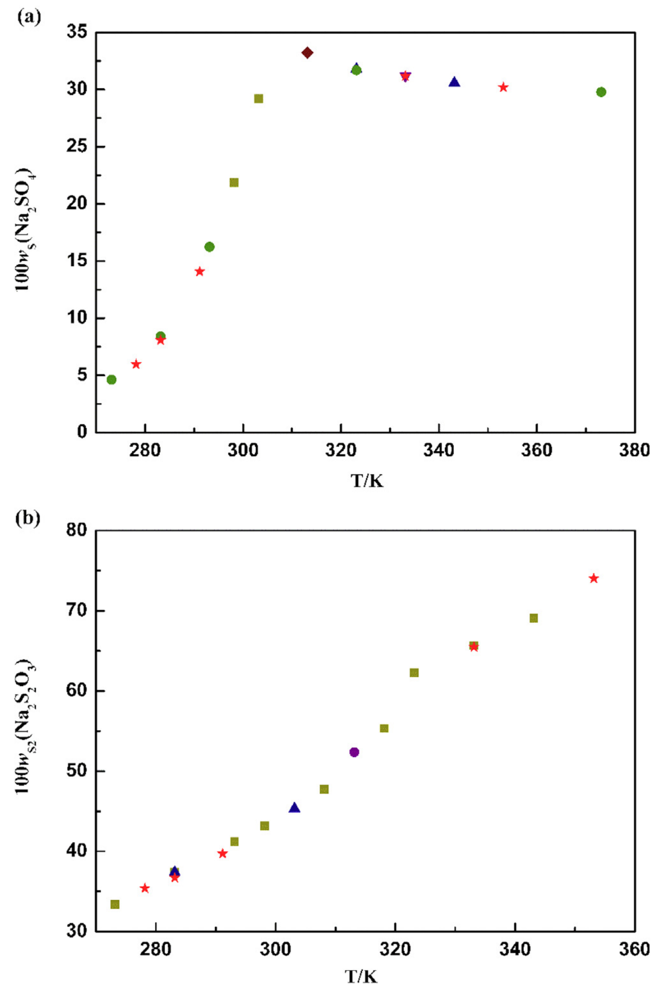

Fig. 2. (a) SLE data for Na_2SO_4-H_2O ■ Ref. [21]; ▲ Ref. [22]; ▼ Ref. [23]; ◆ Ref. [24]; ● Ref. [25]; ★ Experimental results obtained in this work. (b) SLE data for $Na_2S_2O_3$-H_2O ■ Ref. [26]; ▲ Ref. [14]; ● Ref. [27]; ★ Experimental results obtained in this work.

$Na_2S_2O_3$-Na_2SO_4-H_2O system, two crystallization methods for separating $Na_2S_2O_3$-Na_2SO_4 mixture were put forward and discussed.

2. Experimental section

2.1. Materials and instruments

2.1.1. Chemicals

The experimental materials were of high purity (not less than 99.0%) and all of them were directly used without any purification. The sources, purity, grade and CAS numbers of the chemicals used in this work are listed in Table 1. High-purity doubly deionized water, with a resistivity of 18.25 MΩ·cm at ambient temperature, was used to prepare the solutions.

2.1.2. Apparatus

A CKDC-3006 type thermostatic water bath (Nanjing Fandilang Technology Co. Ltd., China) with temperature accuracy of ±0.1 K was used to control the temperature of jacketed glass vessels in the experiments. An EMS-9A type magnetic stirrer (Tianjin Honour Instrument Co. Ltd., China) was used to mixt the solutions. A WDDY-2008 type automatic potentiometric titrator (Taizhou Datang Analytical Instrument Co. Ltd., China) was used to measure the concentrations of $S_2O_3^{2-}$ and SO_4^{2-}. An ICS-5000 type ion chromatography (Thermo Fisher Scientific, The United States) was also used to analyze the concentration of SO_4^{2-}. A standard analytical balance with 110 g capacity and 0.0001 g resolution (AL104, Mettler Toledo Instruments Co. Ltd., Switzerland) was used to weigh the mass of the samples. Rigaku D/max-2500 X-ray diffraction (Rigaku, Japan) analyzer was employed for XRD characterizations.

2.2. Experimental methods

The solid-liquid equilibria in this work were studied in a wide range of temperatures (278.15 K–353.15 K) by the method of isothermal solution saturation [11–13]. A phase equilibrium system was obtained by adding one salt into the saturated solution of the other [14]. In this work, pure $Na_2S_2O_3$ was added into the saturated solution of Na_2SO_4 at fixed temperature. The added amount of $Na_2S_2O_3$ was gradually increased in experiments.