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Phase equilibria in the system Na^+, $K^+//SO_4^{2-}$-$(CH_2OH)_2$-H_2O and Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O at 328.15 K

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ABSTRACT

An experimental study on phase equilibria at 328.15 K in the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O) and its subsystem (Na^+, $K^+//SO_4^{2-}$-$(CH_2OH)_2$-H_2O) was carried out by the method of isothermal solution saturation. In these systems, the initial mass fraction of ethylene glycol is 30% in the salt-free binary solvent (water + ethylene glycol). The solubilities, densities, viscosities, and refractive indices of saturated solutions have been measured for the two systems. According to the experimental results, solubility curves and physical properties (ρ, η, n_D) curves are plotted. In the subsystem (Na^+, $K^+//SO_4^{2-}$-$(CH_2OH)_2$-H_2O), there are two invariant points, three invariant curves, and three fields of crystallization corresponding to K_2SO_4, $Na_2SO_4{\cdot}3K_2SO_4$, Na_2SO_4. In the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O), there are five crystallization fields, seven univariant curves, and three eutonic points corresponding to three salts, that is (K_2SO_4 + $Na_2SO_4{\cdot}3K_2SO_4$ + KCl), (Na_2SO_4 + $Na_2SO_4{\cdot}3K_2SO_4$ + KCl) and (Na_2SO_4 + NaCl + KCl), respectively. No solvate phases with ethylene glycol are observed and no solid solutions are found. All the physical properties (ρ, η, n_D) of both systems change regularly with concentration change of the liquid phase. In comparison with the phase diagram of the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O) at 328.15 K and this quaternary system (Na^+, $K^+//Cl^-$, SO_4^{2-}-H_2O) at 323.15 K, the size of the salt crystallization fields changes significantly. The experimental results reveal that the presence of ethylene glycol significantly reduces the solubility of the salts in the aqueous solution. These changes between phase diagrams at different solvents and temperatures will be very useful for extracting the salts. According to this work, the measured values and phase equilibrium diagrams can be used for a new technology to design and optimize the production of K_2SO_4 by the conversion process with industrial KCl and mirabilite aqueous mixtures, and provide fundamental data support for chemical industry development.

1. Introduction

In many industrial cases, chemical reactions do not deliver the desired product alone, separation processes are required. Thus, a wide variety of efforts have been undertaken to research the separation (purification) processes. Crystallization is normally regarded as a separation technique with the apparent advantage of lower energy [1]. The addition of organic solvent to the aqueous solution of soluble inorganic salts normally decreases the solubility of the salt, which is termed "drowning out" and has a number of potential advantages over alternative crystallization techniques since it creates the possibility of carrying out the operation at ambient temperature, yielding crystals of high purity [2]. In fact, it is expected that the phase diagram provides the required knowledge of aqueous or solvent electrolyte mixtures to design the crystallization process. The measurement of SLE for mixtures is important for analysing the solubility of every salt and for designing separation technology processes [3].

During the past decades, many studies are available in the literature on solubility of various salts in (water + organic) solvents, the objectives of which have been to evaluate the potential applicability of the drowning-out procedure as a technique for separation of salts. For example, Gomis et al. [4–6] have investigated twelve ternary aqueous systems including NaCl and KCl in 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and (water + NaCl + 1-pentanol/2-pentanol/3pentanol/2-methyl-2-butanol/2-methyl-1-butanol) at 298.15 K. Their experimental results show that the salting-out effects of these kinds of alcohols are similar except for 2-methyl-2-butanol which presents the most significant

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decrease in the solubility of this ternary system. Moreover, Zhou et al. [7] have reported on the solubility of the ternary systems (ethylene glycol + NaCl + H_2O), (ethylene glycol + KCl + H_2O), (ethylene glycol + RbCl + H_2O), and (ethylene glycol + CsCl + H_2O).

Potassium sulfate is an important low index salt and high quality compound potassium salt [8], which makes it a superior fertilizer to KCl and results in its widespread use in agricultural fields. Apart from its application as a fertilizer, K_2SO_4 has industrial uses as well [9]. Based on abundant sulfate-type saline resources in China, a technology of the production potassium sulfate based on potassium chloride and Na_2SO_4 [10] by the following double decomposition reaction.

$$KCl + Na_2SO_4 = K_2SO_4 + 2NaCl \quad (1)$$

The above reaction is accomplished by the following two steps:

$$6KCl + 4Na_2SO_4 = Na_2SO_4 \cdot 3K_2SO_4 + 6NaCl \quad (2)$$

$$2KCl + Na_2SO_4 \cdot 3K_2SO_4 = 4K_2SO_4 + 2NaCl \quad (3)$$

For the method, there is little quality of Na_2SO_4, K_2SO_4 and $Na_2SO_4{\cdot}3K_2SO_4$ existing in the mother liquid, which is difficult to process and separate. In order to isolate impurity, anti-solvent crystallization is applied to crystallize K_2SO_4. SLE measurements play an important role in separation process with mixtures.

Ethylene glycol is an important chemical used in the petroleum and chemical industries. Ethylene glycol in the liquid state has, like water, a developed spatial network of hydrogen bonds [11], which largely determines its physical and chemical properties. Studies [12,13] have shown that in an ethylene glycol–water mixture no distinct complexes are formed, except at very low temperatures. Ethylene glycol is used as an anti-solvent or an additive in crystallization to obtain solid materials of desirable physical quality and chemical purity [14,15]. Therefore, a better understanding of salting-out effects and solubility behaviour are necessary for the effective design and implementation of optimum operating conditions and equipment for processes involving such complex systems.

Organic or even mixed solvent systems are much less well understood, partly because detailed solubility and solid-phase stability data are lacking in most cases. The aims of this work are to (I) provide the data of the solid-liquid equilibria and physical properties (ρ, η, n_D) of saturated solutions of the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O) and its subsystem (Na^+, $K^+//SO_4^{2-}$-$(CH_2OH)_2$-H_2O) in mixed solvents containing (30) initial mass% (salt-free binary solvent water + ethylene glycol) ethylene glycol at 328.15 K by the method of isothermal saturation solution, (II) identify the equilibrium solid phases, give the composition of dry salts, and plot the experimental phase diagrams of the two systems, (III) analyse the phase diagrams by comparing with reported data. All these results of this work can be used for a new technology to design and optimize the crystallization separation process involving the reciprocal quaternary system (Na^+, $K^+//Cl^-$, SO_4^{2-}-H_2O) and its ternary system in the mixed solutions at 328.15 K, and provide fundamental data support for chemical industry development.

2. Methodology

2.1. Materials and instruments

The chemicals used are of analytical purity grade. Na_2SO_4, K_2SO_4, NaCl and KCl were purchased from Tianjin Kermel Chemical reagent Co. Ltd., China. The $(CH_2OH)_2$ was provided from Tianjin Damao Chemical reagent Co. Ltd., China. Doubly deionized water (electrical conductivity less than 10^{-4} S·m^{-1}) was used to prepare the solid-liquid phase equilibrium experiments. The purity levels, sources of the chemicals and CAS numbers used in this study are listed in Table 1.

Table 1
The purities and suppliers of chemicals.

Chemical	Mass Percentages Purity[a]	CAS No.	Source
K_2SO_4	≥99.0%	7778-80-5	Tianjin Kermel Chemical reagent Co. Ltd., China
Na_2SO_4	≥99.0%	7757-82-6	Tianjin Kermel Chemical reagent Co. Ltd., China
NaCl	≥99.5%	7647-14-5	Tianjin Kermel Chemical reagent Co. Ltd., China
KCl	≥99.5%	7447-40-7	Tianjin Kermel Chemical reagent Co. Ltd., China
$(CH_2OH)_2$	≥99.8%	107-21-1	Tianjin Damao Chemical reagent Co. Ltd., China

[a] The method of purity analysis is stated by the supplier.

A temperature-controlled vibrator (SHZ-C, made by Shanghai Langgan Laboratory Equipment Co. Ltd., China) with a precision ±0.05 K is used for the solid–liquid equilibrium measurements. An XMTD-4000 type super constant-temperature water bath (Zhengzhou YingYu Yuhua Instrument Co. Ltd., China) was used to keep constant temperature in the experiment. A L5 UV-spectrophotometer (Shanghai Yidian Analysis Instrument Co. Ltd., China) was used for measuring the sulfate ion concentration of the equilibrated solution.

2.2. Experimental method

For the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O) containing (30) initial mass% (salt-free binary solvent water + ethylene glycol) ethylene glycol, equilibrium studies were divided into five experiments according to the number of invariant points for four subsystems. The preparation of the mixtures is presented in Table 2.

The method of isothermal solution saturation was used in this study. The phase equilibrium study was carried out by mixing of known masses of ethylene glycol and water with excess salt. In this work, the initial mass fraction of ethylene glycol was 30% in the salt-free binary solvent (water + ethylene glycol). First, a certain mass of ethylene glycol was weighed and placed into a conical flask and mixed with a fixed mass of water to prepare the solvent. The saturated solutions of the subsystem were acquired by adding the second salts gradually on the basis of their binary saturation points at 328.15 K. That is to say, a certain quantities of K_2SO_4, Na_2SO_4 and solvent are blended together as a series of the samples on the basis of the phase equilibrium composition until saturation was reached. The solid-liquid mixtures in the conical flasks of the subsystem were stirred for 6 h to reach the equilibrium states. Then, the conical flasks with solid-liquid mixtures were placed into a constant-temperature water bath for an additional 12 h to allow remaining solids to settle. The samples of the (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O) system were prepared by adding slowly the third salt containing the fourth ion to the saturated solution of the

Table 2
Preparation of solutions corresponding to different sections of the isotherm for the system (Na^+, $K^+//Cl^-$, SO_4^{2-}-$(CH_2OH)_2$-H_2O).

System	Initial point	Solid Phase	Additive
Na_2SO_4-K_2SO_4-$(CH_2OH)_2$-H_2O	D	K_2SO_4 + Gla[a]	KCl
	E	Na_2SO_4 + Gla[a]	KCl
KCl-K_2SO_4-$(CH_2OH)_2$-H_2O	C	KCl + K_2SO_4	Na_2SO_4
NaCl-Na_2SO_4-$(CH_2OH)_2$-H_2O	A	NaCl + Na_2SO_4	KCl
KCl-NaCl-$(CH_2OH)_2$-H_2O	B	KCl + NaCl	Na_2SO_4

[a] Gla: $3K_2SO_4{\cdot}Na_2SO_4$.