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journal homepage: www.elsevier.com/locate/jiec1 Salting-out extraction systems of ethanol and water induced by
2 high-solubility inorganic electrolytes

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ABSTRACT

The salting-out extraction systems of ethanol and water induced by the high-solubility inorganic electrolytes were investigated at 25 °C. More than 99.90% of ethanol was salted out into the organic phase. The salt content of the organic phase is only about 0.01 wt%, which is negligible for the application of the ethanol–salt salting-out extraction. More than 90% of water can be retained in the aqueous phase. It is concluded that the salting-out effects of four salting-out agents on the aqueous solution of ethanol are ordered in the sequence: $K_4P_2O_7 > K_3PO_4 > K_2HPO_4 > K_2CO_3$.

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5 Introduction

6 Salting-out extraction systems composed of alcohols and salts
7 are often used for separating value-added chemicals or fuels from
8 aqueous solutions [1,2]. However, the low-solubility salt or the
9 insufficient addition of the high-solubility salt resulted in the loss
10 of ethanol, the incomplete recovery of products or the interfusion
11 of salt in the organic phase [3,4]. Thus the liquid–liquid equilibria
12 for the ethanol+water+salt system should be investigated to
13 select the suitable salting-out extraction systems.

14 In the study of the salting-out effects of different salts on the
15 phase separation of the ethanol+water miscible system, it was
16 found that NaCl was a very poor salting-out agent [5]. But
17 NaF was a preferable salting-out agent because 5 wt% of
18 NaF and 20–30 wt% of NaCl showed the similar effects on the
19 separation of alcohol from the aqueous solution. According
20 to the Hofmeister series, $CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > F^- > Cl^- > Br^-$
21 $> NO_3^- > I^- > ClO_4^- > SCN^-$, F^- shows stronger salting-out effect
22 than Cl^- [6,7,8]. However, the outstanding drawback of NaF is the
23 lower solubility of it in pure water. Different kinds of salting-out
24 agents, such as $(NH_4)_2SO_4$, NaCl, NH_4Cl , Na_2SO_4 , Na_3PO_4 , Na_2CO_3
25 and $NaNO_3$ were used for the phase separation of ethanol+water
system, which could be applied to the analyses of lixiviums of two

26 brands of plastic wrapping film [9]. It was found that $(NH_4)_2SO_4$
27 was the most suitable electrolytes because of its stronger salting-
28 out effect and higher solubility in water. The recoveries of
29 hydrophobic phthalate esters were in the range of 84.1–110% [9].
30 However, the results showed that the aqueous phase contained
31 5 wt% of ethanol when 40 wt% of $(NH_4)_2SO_4$ dissolved in the
32 ethanol+water system [10]. This kind of salting-out system was
33 also demonstrated to efficiently separate biobutanol from the
34 aqueous solution or acetone+1-butanol+ethanol (ABE) from
35 fermentation broth [11]. The ethanol+ Cs_2SO_4 +water system was
36 investigated at (10, 30, and 50) °C [12]. However, the mass
37 fraction of ethanol in the aqueous phase was about 2 wt% when
38 the Cs_2SO_4 content rose to 60 wt%. Liquid–liquid equilibrium data
39 for ethanol+ $MgSO_4/ZnSO_4$ +water systems were determined at
40 (303.15 and 313.15)K [13]. But the ethanol content of the aqueous
41 phase which suggested the loss of ethanol declined less than
42 favorably. Thus the selections of suitable electrolytes for the
43 phase splitting of ethanol+water system and the higher recovery
44 of ethanol were of crucial importance.

45 The objective of this study was to investigate the extreme
46 separation of ethanol from an aqueous solution by the high-
47 solubility inorganic electrolyte at 25 °C. Afterwards, the efficient
48 ethanol–salt salting-out extraction systems were selected accord-
49 ing to the recovery of ethanol, the removal of water and salt
50 content of the organic phase. Meanwhile, the salting-out effects of
51 different salts on the aqueous ethanol solution were also
52 demonstrated.

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Nomenclature

Abbreviations and symbols

b	Molality
C_1	Initial salt concentration
DR	Dehydration ratio
m_1	Mass of the aqueous phase
m_2	Mass of the organic phase
m_0	Mass of the aqueous ethanol solution
M	Molar mass of salt
R	Recovery
s	Solubility of ethanol
α, β	Constants
ω_{ij}	Mass fraction of one component in one phase (subscript i=1,2,3 represent water, ethanol, and salt, respectively; subscript j=1,2 represent the aqueous phase and organic phase, respectively)

Experimental

Materials

The reagents used in the experiments were ethanol, anhydrous potassium carbonate (K_2CO_3), dipotassium hydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$), tripotassium phosphate trihydrate ($K_3PO_4 \cdot 3H_2O$), pyrophosphate potassium trihydrate ($K_4P_2O_7 \cdot 3H_2O$) and deionized water. Their sources and purity are shown in Table 1 and they were used without further purification. The other reagents used in the experiments were of analytical grade.

Salting-out experiments

An aqueous solution containing 40 wt% of ethanol was prepared in a sealed glass vial. A certain amount of K_2CO_3 , $K_2HPO_4 \cdot 3H_2O$, $K_3PO_4 \cdot 3H_2O$ or $K_4P_2O_7 \cdot 3H_2O$ was added to the 20 mL headspace bottles. An appropriate amount of 40 wt% aqueous ethanol solution was added to the headspace bottles according to the anticipated initial salt concentration. The initial salt concentration (C_1) in the unit of g/kg was defined as,

$$C_1 = \frac{m_{salt}(g) \times 1000}{m_{salt}(g) + m_{water}(g)} \quad (1)$$

where m_{salt} is the mass of salt, and m_{water} is the mass of water from the 40 wt% aqueous ethanol solution and the crystal water. Then the headspace bottles were sealed with tan PTFE/white silicone septa.

The salting-out system was shaken for 1 h to promote the phase splitting and then settled for 24 h to reach the liquid–liquid equilibrium at 25 °C. The temperature was controlled in a water bath and measured by a standard mercury-in-glass thermometer. Two phases formed because of the salting-out effect. The upper

layer was ethanol-rich phase (organic phase) and the lower phase was water-rich phase (aqueous phase). The contents of ethanol and water in each phase were obtained by taking 0.6 μ L of liquid from the aqueous phase or organic phase with a microsyringe for GC analysis. The organic phase was subjected to atomic absorption spectroscopy analysis to determine the salt content. The mass fraction of salt in the aqueous phase was calculated according to the mass balance.

When the contents of ethanol, water, and salt in each phase was determined, the recovery of ethanol (R) from the aqueous solution was calculated as,

$$R = \frac{0.4m_0 - m_1\omega_{21}}{0.4m_0} \quad (2)$$

where m_1 is the mass of the aqueous phase, m_0 is the mass of the ethanol aqueous solution, ω_{21} is the ethanol content of the aqueous phase.

The dehydration ratio (DR) was defined as,

$$DR = \frac{0.6m_0 - m_2\omega_{12}}{0.6m_0} \quad (3)$$

where m_2 is the mass of the organic phase, ω_{12} is the water content of the organic phase.

Analytical methods

The gas chromatography (Techcomp GC7900, China), equipped with a 2 m(L) \times 3 mm(ID) \times 5 mm(OD) Porapak Q 80–100 mesh packed column and a thermal conductivity detector was adopted to detect ethanol and water [14,15]. The column temperature was maintained at 393.5 K for 10 min, and the injector and detector temperatures were fixed at 453.15 K. The mass fractions of ethanol and water in two phases were determined by normalizing by GC peak area. The salt content of the organic phase was assayed by the flame atomic absorption spectrophotometer (Shimadzu AA-6800F, Japan) at the wavelength of 766.5 nm [16].

Results and discussion

The liquid–liquid equilibria

As can be seen from the experimental results in Table 2, ethanol formed an insoluble new phase with water and a small amount of K_2CO_3 as the initial concentration of K_2CO_3 was equal to or greater than 100 g/kg. The upper liquid phase in the headspace bottle is the organic phase and the lower liquid phase is the aqueous phase.

Table 2 shows the effect of initial concentration of K_2CO_3 on the separation efficiency of the ethanol aqueous solution at 25 °C. The separation of ethanol was not obvious at low initial concentrations of K_2CO_3 , because the water content of the organic phase and the ethanol content of the aqueous phase were very high. Though the aqueous two-phase system can be used for salting-out extraction of some value-added chemicals, the loss of ethanol and the loss of salt are considered to be the top problems. When the initial concentration of K_2CO_3 increased, the water content of the organic phase and the ethanol content of the aqueous phase declined.

Table 1
Materials.

Reagents	Manufacturer	Purity
Ethanol	Guanghua Chemical Plants Co. Ltd.,	99.7%
$K_2HPO_4 \cdot 3H_2O$	Guanghua Chemical Plants Co. Ltd.,	99.0%
$K_3PO_4 \cdot 3H_2O$	Guangzhou Chemical Reagent Factory	99.0%
K_2CO_3	Shanghai Lingfeng Chemical Reagent Co., Ltd.,	99.0%
$K_4P_2O_7 \cdot 3H_2O$	Tianjin Damao Chemical Plants Co. Ltd.,	99.0%
Deionized water	Ultra Pure Water System	(Electrical conductivity $< 1.5 \times 10^{-4} S m^{-1}$)

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