Separation of isopropanol from aqueous solution by salting-out extraction

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Abstract: A novel salting-out extraction process has been developed to separate isopropanol from aqueous solution. Potassium carbonate was experimentally shown to be effective in modifying the liquid–liquid equilibrium (LLE) of an isopropanol/water/hexane system in favour of the solvent extraction of isopropanol from an aqueous solution with hexane, particularly at suitable salt concentrations. Potassium carbonate enlarged the area of the two-phase region. This effect essentially increased the distribution coefficient of isopropanol between hexane and water and increased the separation factor for isopropanol vs water, which is an important consideration in designing a solvent extraction process. The effects of potassium carbonate concentration, temperature and pH on the LLE were studied. Finally, a $\phi 30\,mm \times 1200\,mm$ reciprocating plate column (RPC) was tested to separate isopropanol from an aqueous solution. When isopropanol in an aqueous solution with composition of isopropanol/water = 1:0.95 (wt/wt) was extracted by hexane assisted with 30% (wt%) potassium carbonate aqueous solution, the alcohol–water ratio increased to 11:1 in the extract.
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Keywords: isopropanol; salting-out effect; extraction; separation

NOTATION

D	Isopropanol distribution coefficient between hexane and the aqueous solution, defined as *the ratio of the isopropanol concentration in the organic phase to that in the aqueous phase*
D_{al}	Isopropanol distribution coefficient between hexane and the aqueous solution, defined as *the ratio of the isopropanol concentration in the organic phase to that in the aqueous phase with salt*
D_0	Isopropanol distribution coefficient between hexane and the aqueous solution, defined as *the ratio of the isopropanol concentration in the organic phase to that in the aqueous phase without salt*
HS	Integral heat of dissolution for salt (kJ mol^{-1}) (Fig 4)
S	Separation coefficient, defined as *the ratio of the distribution coefficient of isopropanol vs the distribution coefficient of water*
X	Isopropanol concentration in aqueous solution (wt%) (Fig 6)
X1	Isopropanol concentration (wt%) (Figs 5, 7 and 8)
X2	Water concentration (wt%) (Figs 5, 7 and 8)

INTRODUCTION

Isopropanol is a basic chemical material and solvent used in the production of many chemicals and intermediates.[1] Isopropanol is usually diluted in these processes, so the concentration and purification of isopropanol from dilute aqueous solutions is an important issue in isopropanol production.

Aqueous isopropanol solutions have a low azeotropic boiling point (80.3 °C). The isopropanol concentration in the azeotrope is 87.4% (wt%), so there is virtually no possibility of producing isopropanol with a purity above 87.4% by normal distillation methods. In industrial production, dilute aqueous isopropanol solutions are often crudely concentrated by distillation to increase the alcohol concentration to close to the azeotropic composition. Then, the concentrated aqueous alcohol solution is dehydrated in an azeotropic distillation column to obtain isopropanol with a purity above 99.5% at the bottom (Fig 1). This conventional process has two serious drawbacks: (1) the reflux ratios during crude concentration and dehydration are large and (2) all the water has to be removed from the top of the azeotropic distillation column as vapour. These drawbacks lead to high energy consumption in the separation process.

To overcome these drawbacks, a novel method was developed using salting out extraction and azeotropic distillation to separate isopropanol from aqueous

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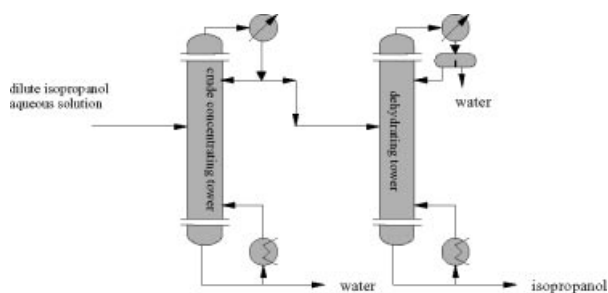*T Zhigang, Z Rongqi, D Zhanting*

Figure 1. Isopropanol and water separation by azeotropic distillation.

solutions (Fig 2). In this coupled process, the salting-out effect helps extract the isopropanol from the aqueous solution by acting as an extracting agent which also serves as a dehydrating agent in the subsequent azeotropic distillation. Then the extract is dehydrated in an azeotropic distillation tower at low reflux ratio to produce isopropanol with a purity above 99.5% at the bottom. The salting-out agent can be refused after regeneration.

This novel method has the following advantages:

(1) The dehydrating agent acts as the extractant, so the extraction and distillation process are coupled, which improves the isopropanol separation.
(2) The concentration tower is not needed and the isopropanol vaporization times are reduced, which lowers the energy consumption.
(3) The salting-out effect of the inorganic salts improves the extraction power of the isopropanol extractant and the separation factor for alcohol vs water and substantially increases the isopropanol/water ratio in the extract. So the steam cost for the azeotropic distillation is greatly reduced.

A major motivation for this work is to determine a suitable salting-out agent and test the feasibility of separating isopropanol from aqueous solutions by salting-out extraction. Experimental and thermodynamic simulation of the salting-out effects of some chlorides on LLE of ethanol/water and butanol/water systems have been reported, but further investigations on the salting-out effects of other inorganic salts for the separation of alcohol and water are not available in the literature.[2–12] In this work, some common inorganic salts were chosen to study the influence of the salting-
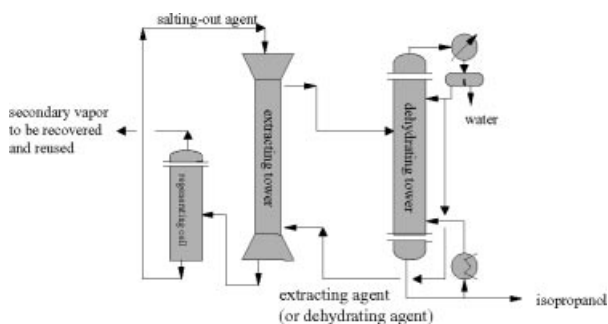

Figure 2. Isopropanol and water separation by salting-out extraction coupled with azeotropic distillation.

out effect on the liquid–liquid extraction (LLE) of isopropanol/water/hexane systems. Further salting-out extraction experiments were carried out at the optimum conditions to test the separation of isopropanol and water.

EXPERIMENTAL
Materials and reagents
The organic solvents isopropanol and hexane and the inorganic salts sodium chloride, potassium chloride, calcium chloride, sodium carbonate, potassium carbonate and potassium ethanoate and other reagents used in this work were all of analytical purity and purchased from the Beijing Chemical Regents Shop, Beijing, PRC.

The raw material for the industrial isopropanol was supplied by the Jinzhou Petroleum Chemical Co, Jinzhou, PRC.

Screening of extracting agent
A suitable extracting agent should have low solubility in water and a high capacity for isopropanol extraction. It should also have a strong dehydrating effect in the subsequent azeotropic distillation so that it can serve as both the extracting agent and the dehydrating agent.

The most common dehydrating solvents, benzene, hexane, ethyl ethanoate and butyl ethanoate, were tested to extract isopropanol from 50% (v%) aqueous solution by added potassium carbonate with a solution concentration of $1 \, mol \, dm^{-3}$ at a volume ratio 1:1:1 (extractant:isopropanol solution:salt solution). The results indicated that the benzene and hexane had similar salting-out effects. Although ethyl ethanoate and butyl ethanoate had better performance, the potassium carbonate concentration in ethyl ethanoate was greater (above 0.5%, wt%) and the boiling point of butyl ethanoate was higher (higher than $126\,°C$, 1 atm). Compared with benzene, hexane has lower toxicity and was chosen as the extracting agent.

Screening of salting-out agent
Sodium chloride, potassium chloride, calcium chloride, sodium carbonate, potassium carbonate and potassium ethanoate were separately weighed and dissolved in deionized water to prepare $1 \, mol \, dm^{-3}$ aqueous salt solutions. Isopropanol and deionized water were mixed to make an aqueous alcohol solution with a concentration of 50%(v%). Different kinds of aqueous salt solutions, aqueous alcohol solutions and hexane were mixed at a pre-determined volume ratio of 1:1:1 (volume ratio) and stirred, then left to equilibrate for 24h. The experimental apparatus was graduated with a minimum graduation of $0.1 \, cm^3$ which could lead to a relative deviation of less than 1%.

After equilibrium, the aqueous volume had different volumes due to the different salting-out effects. Different volumes of water were added to the different solutions, stirred, then allowed to settle so that all of

the aqueous solutions had the same volume. Thus the salting-out effects of the different salts were compared based on equal aqueous salt concentrations (since the potassium carbonate concentration in the organic phase was less than 100 ppm, the loss of potassium carbonate in the organic phase could be ignored). The equilibrium potassium carbonate aqueous concentration was $0.782\,mol\,dm^{-3}$.

The equilibrium phases were carefully separated and their compositions were analyzed. The isopropanol distribution coefficient between the hexane and the aqueous solution was calculated as ratio of *the isopropanol concentration in the organic phase to that in the aqueous phase*. The inorganic salt that provided the best isopropanol distribution coefficient was chosen as the salting-out agent.

The experiments were repeated at least three times and had average deviations of less than 5%.

Factors effecting LLE

The experiments were repeated at least three times and had average deviations of less than 2%.

Salting-out agent concentration

Potassium carbonate provided the best extraction performance, so it was chosen as the salting-out agent. Potassium carbonate was dissolved in deionized water to prepare 9.7% (wt%) aqueous salt solutions. Isopropanol was mixed with deionized water at different volume ratios, such as 0.25:1, 0.5:1, 1:1, 1.5:1, 2:1, 3:1, 4:1… etc, to prepare a series of alcohol aqueous solutions with different isopropanol concentrations. These isopropanol aqueous solutions were mixed with the above salt solutions and hexane at a volume ratio of 1:1:1 (isopropanol solution:salt solution:hexane). After equilibrium, different volumes of deionized water were added to the different solutions, stirred, then allowed to settle so that all of the aqueous solutions had the same volume. Samples were taken from the two phases to analyze the composition. Thus the LLE data based on equal aqueous salt concentra-

tions (since the potassium carbonate concentration in the organic phase was less than 100 ppm, the loss of potassium carbonate in the organic phase could be ignored) were plotted. The equilibrium potassium carbonate aqueous concentration was $94.50\,g\,dm^{-3}$.

The salt solution concentrations were changed to 19.6%, 28.4% (wt%) and the above procedures were repeated. The LLE data were obtained and plotted for equilibrium aqueous salt concentrations of $190.1\,g\,dm^{-3}$ and $278.2\,g\,dm^{-3}$.

Temperature

LLE was evaluated at different water bath temperatures from 30 °C to 50 °C to study the effect of temperature on the salting-out extraction. The methods were analogous to the above procedure.

pH

HCl and NaOH were added to adjust the pH to evaluate the effect of hydrogen ion concentration in the aqueous solution on LLE for pH values 10.9, 12.1, 12.9. The methods were analogous to the above procedure.

Salting-out extraction experiments

A Reciprocating Plate Column (RPC) was used for salting-out extraction of isopropanol from aqueous solutions (Fig 3).

The feed (isopropanol:water = 1:0.95, by weight) was drawn from the feed container by a peristaltic pump at a flow rate of $6.25\,dm^3\,h^{-1}$ and injected into the middle of the RPC (Fig 3). The salting-out agent was drawn from the feed container by a peristaltic pump at a flow rate of $6.25\,dm^3\,h^{-1}$ and injected into the top of the RPC. The extractant (isopropanol: water:hexane = 5 :20: 75, by weight) was drawn from the feed container by a peristaltic pump at a flow rate of $17\,dm^3\,h^{-1}$ and injected into the bottom of the RPC. The outflow from the top was the extract while the outflow from the bottom was the raffinate. The
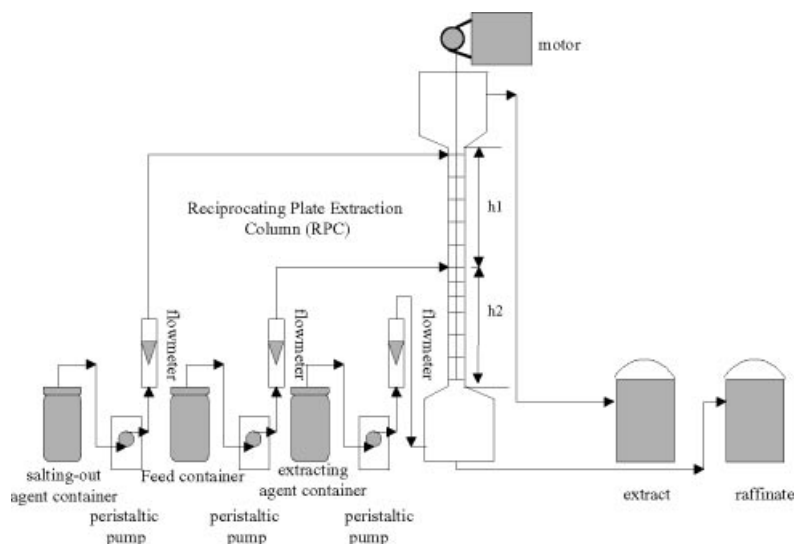

Figure 3. Salting-out extraction unit with RPC.

countercurrent extraction was completed in the RPC with the aid of the vibrations of the sieve plate.

The vibration of the plate was driven by a motor at a vibration frequency of 100 rpm. The glass column was 30 mm in diameter and 1200 mm in height with $h_1 = h_2 = 600$ mm. The spacing between the stainless steel sieve plates was 50 mm with each having 50% free area.

The experiments were repeated at least nine times and had average deviations of less than 5%.

Analytical methods

The equilibrium phases from the LLE experiments were carefully separated and their compositions were analyzed with a Perkin-Elmer Autosystem X1 gas chromatograph using a 1.8 m × 3.2 mm Chromosorb 102 column and a thermal conductivity detector. The chromatograph was linked to a personal computer using the GS station software supplied by the BeiFen Co. All analyses were carried out with 30 cm³ min⁻¹ of helium and an oven temperature of 200 °C. The system was calibrated based on the integrated peak area of the components in 2 mm³ samples of known compositions. The maximum average error of the analyses was found to be within ±0.1% (wt) over the entire composition range of the mixture.

The potassium carbonate concentration in each of the equilibrium phases was determined by titration.[13] A specified amount of strontium nitrate was added to the sample which is excessive against the potassium carbonate. After the deposited strontium carbonate was removed, the strontium concentration was determined by titration against EDTA with methylthymol blue as the indicator. Thus the potassium carbonate concentration was calculated.

Since the reaction involved in the titration is essentially an aqueous phase reaction, the sample taken from the organic phase was mixed with a sufficient amount of deionized water to give a homogeneous mixture which was agitated for 2 h in a water bath at 25 °C before carrying out the titration. This procedure gave consistent and reproducible results.

RESULTS AND DISCUSSION
Screening of salting-out agent

The distribution coefficients for isopropanol between the hexane and the aqueous solution using sodium chloride, potassium chloride, calcium chloride, sodium carbonate, potassium carbonate and potassium ethanoate are listed in Table 1. D_{al} is the

isopropanol distribution coefficient defined as the ratio of *the isopropanol concentration in the organic phase to the isopropanol concentration in the aqueous phase*. D_0 is the isopropanol distribution coefficient between the two phases without salt added.

As shown in Table 1, the isopropanol distribution coefficient for the hexane/water system is obviously improved by adding inorganic salt to the system. The salting-out effect increased in the order of potassium chloride < sodium chloride < potassium ethanoate < calcium chloride < sodium carbonate < potassium carbonate.

The above order may be due to the different interactions between different inorganic salt molecules and the water molecules in the aqueous solution. Stronger interactions between the salt molecules and water molecules resulted in more destruction of the isopropanol–water interaction structure which forms in aqueous solutions without salt. Thus, the isopropanol is more easily excluded from the aqueous solutions because of the stronger interaction of the salt with the water, which results in a larger isopropanol distribution coefficient between the hexane and the aqueous solution.

The heat of dissolution for salt is one of the macroscopic parameters that reflects the interaction strength between salt molecules and water molecules. Stronger interactions absorb more energy, while weaker interactions absorb less energy. The salting-out strength is compared with the dissolution enthalpy of salts[14] in Fig 4, showing that the integral heat of dissolution for the salts correlates with the salting-out strength of the salts. In Fig 4, the abscissa represents the isopropanol concentration in aqueous solution (x, wt%) while the left ordinate presents the distribution
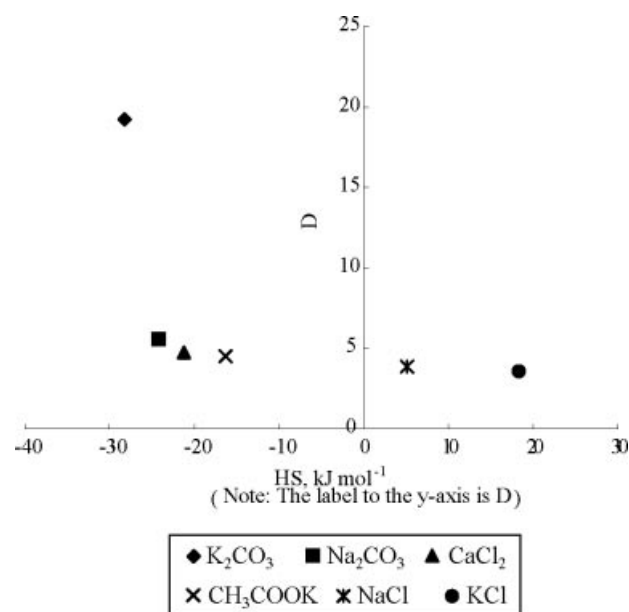

Figure 4. Comparison of salting-out strength with integral heat of dissolution for salt (D_{al}/D_0 data were adapted from Table 1; dissolution heat data collected from Ref 14) symbol "−" represents "heat-absorbing" and "+" represents "heat-releasing".

Table 1. Salting-out effects of different inorganic salts[a] (20 °C)

	Salt					
	K_2CO_3	Na_2CO_3	$CaCl_2$	CH_3COOK	$Nacl$	KCl
D_{al}/D_0	19.23	5.55	4.73	4.5	3.86	3.54

[a] Salt concentration in equilibrium aqueous solution was 0.782 mol/dm⁻³ and D_0 is 0.92.

(*D*) and the right ordinate is the separation coefficient (*S*).

The salting-out effect mechanism of potassium carbonate in an isopropanol/water/hexane system is comparatively complex and will be analysed in a later study.

Because the salting-out strength of potassium carbonate was the largest for the experimental conditions, its chemical properties are stable and it is not corrosive, potassium carbonate was chosen as the salting-out agent in the following experiments.

Factors effecting LLE

The potassium carbonate concentration was less than 100 ppm in the organic phase, so the distribution of potassium carbonate between the two phases can be neglected, so the quaternary system isopropanol/water/hexane/potassium carbonate has been simplified to a ternary isopropanol/water/hexane system in the following discussion.

Potassium carbonate concentration

The LLE of an isopropanol/water/hexane system at different potassium carbonate concentrations is plotted in Fig 5 for a temperature of 28 °C. The two-phase region area increases with increasing potassium carbonate concentration. The extrapolated curves in Fig 5 are 'trend curves' of the experimental data at the same conditions plotted by the graph software Microsoft Excel.

The isopropanol distribution coefficients and separation coefficients of isopropanol vs water at different salting-out agent concentrations in the aqueous solutions are shown in Fig 6. The separation
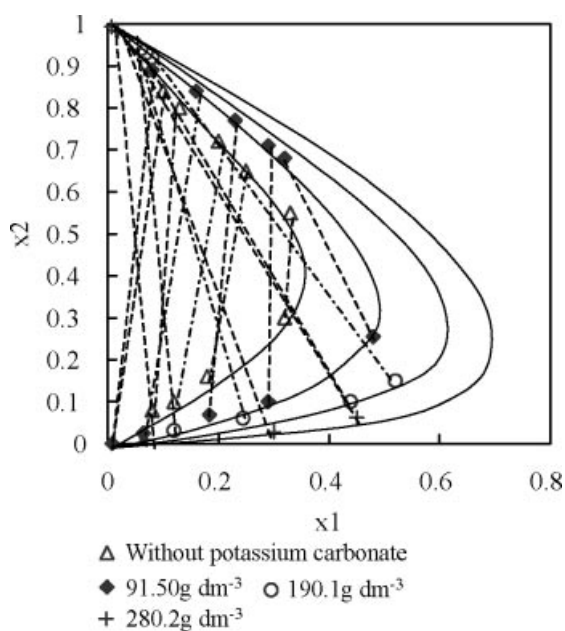
coefficient *S*, which is defined as *the ratio of the distribution coefficient of isopropanol to the distribution coefficient of water* is shown on the right vertical axis of

(a)

(b)

(c)

● Isopropanol distribution coefficient (*D*)
○ Separation coefficient (*S*) for isopropanol vs water
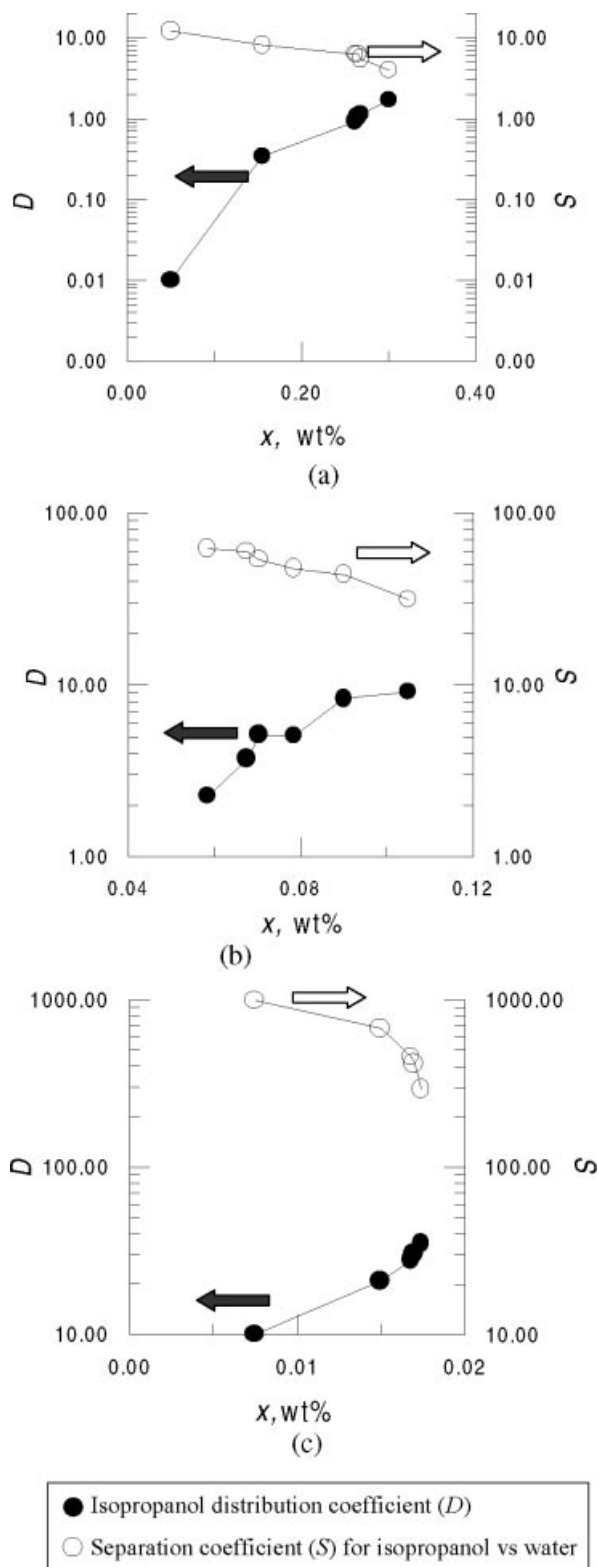
Figure 6. Distribution coefficients of isopropanol and separation coefficients of isopropanol vs water at different salt concentrations (28 °C). (a) equilibrium aqueous potassium carbonate concentration was 94.50 g dm^{-3}; (b) equilibrium aqueous potassium carbonate concentration was 190.1 g dm^{-3}; (c) equilibrium aqueous potassium carbonate concentration was 278.2 g dm^{-3}.

Figure 5. LLE of hexane/isopropanol/aqueous solution with different potassium carbonate concentrations at 28 °C. (Note: The extrapolated curves are 'trend curves' plotted using Microsoft Excel of the experimental data at the same conditions.)

△ Without potassium carbonate
◆ 91.50 g dm^{-3} ○ 190.1 g dm^{-3}
+ 280.2 g dm^{-3}

each figure with isopropanol concentration in the aqueous solution on the abscissa. Here, the definition of the isopropanol distribution coefficient was the same as in the above with the water distribution coefficient defined as the ratio of *the water concentration in the organic phase to the water concentration in the aqueous phase*.

The results in Fig 6 show that the isopropanol distribution coefficient increased with increasing aqueous isopropanol concentrations while the separation coefficient for isopropanol vs water decreased with increasing aqueous isopropanol concentrations at the same salting-out agent concentration. Moreover, the isopropanol distribution coefficient and the separation coefficient for alcohol vs water all obviously improved an order of magnitude with increasing salting-out agent concentration from $94.50\,\mathrm{g\,dm^{-3}}$ to $190.1\,\mathrm{g}$ $\mathrm{dm^{-3}}$. Another order of magnitude increase occurred when the salting-out agent concentration was increased from $190.1\,\mathrm{g\,dm^{-3}}$ to $280.2\,\mathrm{g\,dm^{-3}}$.

Increasing the salt concentration to more than 30% (wt%) would further improve the salting-out effect but the salt solution viscosity would be so high that it would weaken the mass transfer in the extraction column. So, 30% potassium carbonate aqueous solution was selected as the salting-out regent for the salting-out extraction on PRC.

Temperature
The LLE of a hexane/isopropanol/30% potassium carbonate aqueous solution system at 30 °C, 40 °C and 50 °C are plotted in Fig 7. Increasing the temperature decreased the two-phase region size as the salting-out effect was weakened. The extrapolated curves in Fig 7 are 'trend curves' of the experimental data at the same conditions plotted using Microsoft Excel.
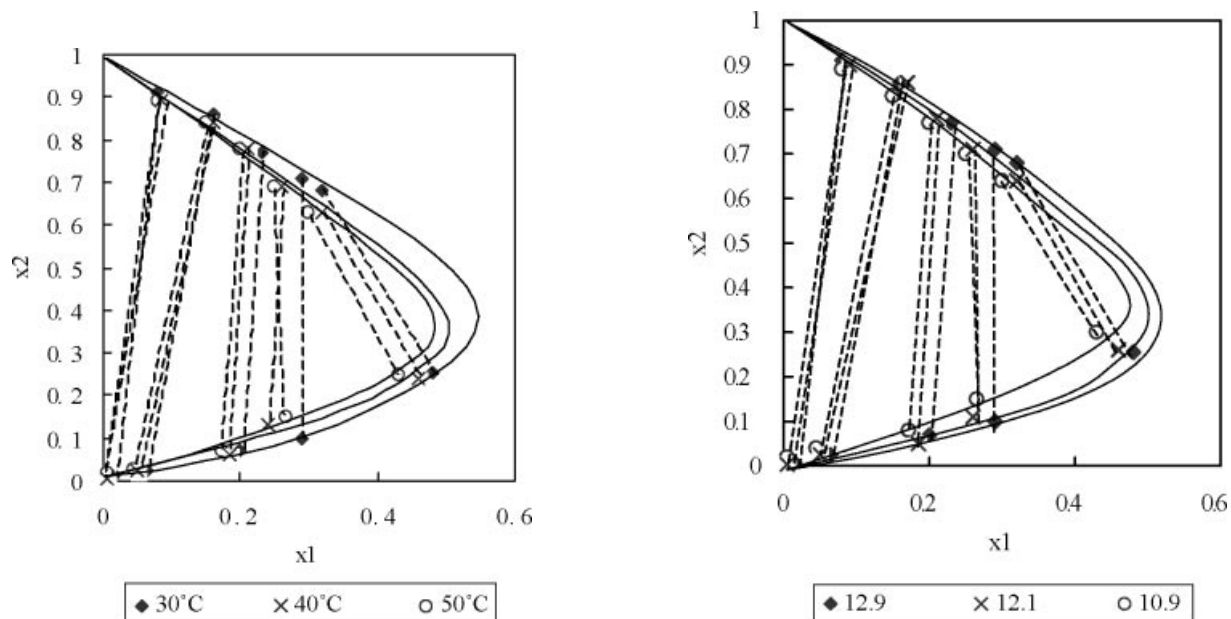
pH
The LLE of a hexane/isopropanol/30% potassium carbonate aqueous solution system at pH 10.9, 12.1 and 12.9 are plotted in Fig 8. By increasing the acidity of the aqueous solution, CO_3^{2-} is likely to change to HCO_3^- which weakens the salting-out effect. If the acidity is increased further, the HCO_3^- may change to CO_2. So a suitable pH is higher than 12. The decrease in the salting-out effect with pH can also be explained in terms of increasing isopropanol solubility with decreasing pH. The extrapolated curves in Fig 8 are 'trend curves' of the experimental data at the same conditions plotted using Microsoft Excel. The mechanism for the pH effect will be studied in later experiments.

Since potassium carbonate is a basic salt formed by a strong base and a weak acid, the pH value of 30% potassium carbonate is about 11. The pH could be controlled to higher than 12 by adding a little sodium hydroxide solution. The corrosiveness of the hydroxyl on the equipment must be considered in industrial processes so stainless steel would be more suitable for full-scale production.

Salting-out extraction experiments
The salting-out extraction process was used to separate isopropanol from industrial material supplied by Jinzhou Petroleum Chemical Co in the experimental set-up illustrated in Fig 3.

The experimental conditions were described in the Experimental section. The experimental results are summarized in Table 2. After extraction the isopropanol purity was greater than 91% (wt%), which was greater than the azeotrope isopropanol concentration (87.4%, wt%) and the isopropanol concentration in

Figure 7. LLE of hexane/isopropanol/10% potassium carbonate aqueous solution at various temperatures. (Note: The extrapolated curves are 'trend curves' plotted using Microsoft Excel of the experimental data at the same conditions.)

Figure 8. LLE of hexane/isopropanol/10% potassium carbonate aqueous solution at various pH values. (Note: The extrapolated curves are 'trend curves' plotted using Microsoft Excel of the experimental data at the same conditions.)

Table 2. Salting-out extraction results

	Run number[a]								
	1	2	3	4	5	6	7	8	9
Isopropanol purity in extract (wt)	91.8%	91.8%	91.9%	91.8%	91.9%	91.8%	91.8%	91.9%	91.8%
Isopropanol concentration in raffinate (wt%)	0.050	0.048	0.043	0.049	0.032	0.040	0.048	0.048	0.045

[a] Note: the run number refers to repeated experiments using recycled reagents.

the raffinate was less than 0.05% (wt%). Isopropanol with a purity of 99.5% was obtained after further azeotropic distillation. Moreover, the separation efficiency remained constant after the salting-out agents were concentrated and reused in extraction.

CONCLUSIONS

1 Experimental results illustrated the salting-out effect on the LLE of isopropanol/water/hexane. Potassium carbonate had the best salting-out effect when sodium chloride, potassium chloride, sodium calcium, chloride carbonate, potassium carbonate and potassium ethanoate were tested to extract isopropanol from 50%(v%) alcohol aqueous solution.

2 Increasing the potassium carbonate concentration intensified the salting-out effect and increased the area of the two-phase region. The two-phase region also enlarged with decreasing temperature and increasing pH for the experimental conditions.

3 Isopropanol was extracted from an aqueous solution with isopropanol/water composition = 1:0.95(wt/wt) with hexane and 30%(wt%) potassium carbonate aqueous solution. The isopropanol extraction performance of hexane was obviously improved with an extraction yield of greater than 99%. The alcohol purity was increased to more than 91% (wt%) in the extract compared with that of 51% (wt%) in the feedstock as the separating factor was improved.

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