Salting-Out of Acetone, 1-Butanol, and Ethanol from Dilute Aqueous Solutions

Shaoqu Xie, Conghua Yi, and Xueqing Qiu
School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640,
P.R. China

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The salting-out phase equilibria for acetone, 1-butanol, and ethanol (ABE) from dilute aqueous solutions using potassium carbonate (K_2CO_3) and dipotassium hydrogen phosphate trihydrate ($K_2HPO_4{\cdot}3H_2O$) as outstanding salting-out agents were investigated. Increasing the salt concentration strengthened the salting-out effects and improved the distribution coefficients of all three solvents (ABE) significantly. Temperature had a slight effect on the phase equilibria. The K_2HPO_4 solution (69 wt %) showed a stronger salting-out effect than the K_2CO_3 solution (56 wt %) on recovering ABE from dilute aqueous solutions. Dilute aqueous solutions containing more solvents increased the recoveries of acetone and 1-butanol, while the results showed a negligible effect on the solubility of ABE. The solubility of ABE was also correlated well with the molar number of salt per gram of water in the aqueous phase. A new equation demonstrated this satisfactorily. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 3470–3478, 2015

Keywords: salting-out, acetone + 1-butanol + ethanol, dilute aqueous solutions, phase equilibria, solubility correlation

Introduction

Acetone, 1-butanol, and ethanol (ABE) are industrial solvents and important chemical feedstocks. They can be produced industrially from the petrochemical feedstocks, and originally from existing biomass such as corn grain, corn stovers, and other feedstocks, including dedicated energy grasses. ABE were predominantly produced by fermentation until they could be produced more cheaply from fossil fuels.[1–3] When the fossil fuels are exhausted, they can be obtained again by liquid fermentation techniques.

Ethanol and 1-butanol, which are blended with gasoline in any proportion, can be utilized in internal combustion engines.[4] Bioethanol is already an attractive fuel today. The industrial fermentative biobutanol is an alternative fuel because of its cleanness and renewability.[5] However, 1-butanol has many benefits over ethanol, such as higher energy content, lower vapor pressure, better blending ability with gasoline at higher percentages, and application to existing vehicles without their modifications.[6] Therefore, its important to develop the biobutanol fermentation industry to help mitigate the scarcity of energy.

The percent yield of biobutanol in the ABE fermentation broth was seriously restricted to 1-butanol toxicity even though the genetic modifications of microbes, specifically of the *Clostridium acetobutylicum*, were tested to improve the solvent level and the 1-butanol production ratio.[7] The total solvents (ABE) concentration, which makes few breakthroughs so far, is around 20 g L^{-1}. The recoveries of total solvents from a dilute aqueous solution by multistep distillation utilized a large energy consumption and, therefore, a high cost.[8] That is why developing other *in situ* methods alternately in conjunction with the distillation techniques are so attractive.

Various alternative techniques, such as flash fermentation technology,[9,10] adsorption,[11] pervaporation,[12] gas stripping,[13] and liquid–liquid extraction,[14] had been investigated to recover the solvents from the ABE fermentation broth. Salting-out, as a special energy-saving separation process,[15] however, can recover ABE effectively. This process, which is different from the traditional liquid–liquid extraction using organic solvents as extractants, only requires strong electrolytes.

Because of the important repulsive effect, salting-out was applied to recover bio-based chemicals with the aid of organic solvents as the extractants.[16,17] This process is called salting-out extraction. Finding a suitable extractant and an appropriate salting-out agent usually make the process complicated. The recoveries of 1-butanol and acetone from dilute aqueous solutions using different organic solvents as extractants and different electrolytes as salting-out agents, dating back to 1994, was reported by Malinowski and Daugulis.[18] The distribution coefficients of acetone and 1-butanol were markedly increased, but the product recovery, extractant recovery, and salt recovery challenged the economic tradeoff. Similarly, biobutanol and acetone were separated from fermentation broth using the extrinsic combination of acetone and K_2HPO_4.[19] However, the excess amount of acetone made this process unattractive because of the large energy consumption in the downstream distillation process. A salting-out process which abandons the extractants may overcome this obstacle. A salting-out agent with the merits of cheapness, greenness, and stability takes advantage of its reutilization.

Correspondence concerning this article should be addressed to C. Yi at chyi@scut.edu.cn or X. Qiu at cexqqiu@scut.edu.cn.

Salting-out can also be used to separate bio-based chemicals from the concentrated aqueous solutions or fermentation broths. 2,3-Butanediol from a concentrated fermentation broth was recovered effectively using 53–56 wt % of potassium carbonate.[20] In another case, it was found that the effect of sodium acetate was less important than that of sodium chloride for improving the recoveries of 1-butanol and acetone from concentrated aqueous solutions.[21] A tremendous amount of work had been done to evaluate the salting-out effects of electrolytes. Experimental results showed that the solubilities of bio-based chemicals in the organic phase and aqueous phase could be greatly changed with the increase in the amount of salt in different systems.[22] Therefore, the selection of salting-out agents is most important for the dilute aqueous solutions. The bio-based chemicals at low concentrations in the fermentation broths were difficult to be salted out at a low concentration of a salt.[16] A salt with relatively great solubility in pure water, such as potassium carbonate, is one of the most important alternatives for the dilute aqueous solutions. Dipotassium hydrogen phosphate is also a biocompatible salting-out agent with potential for the salting-out of ABE from the dilute aqueous solutions.[23]

The objective of this study was to investigate the separation of ABE from dilute aqueous solutions by the salting-out method. The salts with relatively great solubilities were used here. The concentrations of ABE were determined by the actual concentrations of ABE found in the fermentation broths. Because of the homogeneous dilute solutions, most of the research was carried out avoiding the ABE losses. Therefore, a priority of the salting-out process was the recovery of the wanted product. Furthermore, the solubility of ABE in the aqueous phase was correlated with the molar number of salt per gram of water in the aqueous phase.

Experimental Section

Materials

Acetone (99.5 wt %) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). 1-Butanol (99.5 wt %) was obtained from Shanghai Lingfeng Chemical Reagent Co. (Shanghai, China). Ethanol (99.7 wt %), water-free potassium carbonate (99.0 wt %), and dipotassium hydrogen phosphate trihydrate (99.0 wt %) were supplied by Guangdong Guanghua Sci-Tech Co. (Shantou, China). These chemicals were used without further pretreatment. Dilute aqueous solutions for the salting-out experiments were prepared using distilled deionized water with electrical conductivity of lower than 1.5×10^{-4} S m^{-1}.

Salting-out experiments

Two types of dilute aqueous solutions were selected according to the compositions of ABE in different fermentation broths.[19,24] The chemical compositions of dilute aqueous solutions are shown in Table 1. The differences between the solutions were the total solvent level and the solvent ratio of acetone:1-butanol:ethanol. Basic electrolytes, such as potassium carbonate (K_2CO_3),[25] dipotassium hydrogen phosphate (K_2HPO_4),[26] are appropriate for the salting-out experiments. The addition of salt or its solution was unlimited until the dilute aqueous solutions split in the organic phase and the aqueous phase. The salting-out system was vigorously mixed well with a magnetic stirrer and then settled until salting-out phase equilibria was achieved at a given temperature. The distribution coefficient D was calculated as the ratio of the equilibrium mass fraction, in the aqueous phase, ω_{i1}, and in the organic phase, ω_{i2}

Table 1. Compositions of Dilute Aqueous Solutions

	Mass Fraction (wt %)			
	Ethanol	Acetone	1-Butanol	Water
Dilute aqueous solution A[24]	0.18	0.54	1.08	98.20
Dilute aqueous solution B[19]	0.33	0.57	1.12	97.98

$$D_i = \frac{\omega_{i2}}{\omega_{i1}} \tag{1}$$

where $i = 2$, 3, and 4, represented ethanol, acetone, and 1-butanol, respectively.

The initial concentration of salt (g kg^{-1}) in the salting-out system was set down to water-based solution. In the evaluations of the preferential salts, K_2CO_3 or $K_2HPO_4{\cdot}3H_2O$ was added to the dilute aqueous solution gradually (from 100 g kg^{-1} to saturated condition at 298.15 K). The temperature was controlled in a water bath and measured by a standard glass-mercury thermometer. The effect of temperature on the salting-out of total solvents was studied at 298.15, 310.15, and 323.15 K. In the evaluations of salt solutions, salting-out factor was defined as the ratio of the volume of a salt solution at 333.15 K to that of a dilute aqueous solution at 298.15 K. The volume of a salt solution and the volume of a dilute aqueous solution were measured with the suction pipettes. Different salt solutions were also used to promote the liquid–liquid phase splitting. Suitable salting-out factor was determined by the recoveries of ABE. The dilute salt solution (the aqueous phase) can be concentrated using vacuum distillation and used again for the recoveries of ABE.

Analytical methods

After the salting-out phase equilibria were reached, the mass fractions of acetone, 1-butanol, ethanol, and water in both phases were analyzed by a TECHCOMP gas chromatography with a thermal conductivity detector and a 2 m (L) × 3 mm (ID) × 5 mm (OD) Porapak Q 80—100 mesh packed column. The flow rate of carrier gas (H_2) was 30 mL min^{-1}. Peak area normalization method was used to conduct all the chromatographic data. Here, all the chromatographic data were obtained under salt-free condition ($\omega_{11F} + \omega_{21F} + \omega_{31F} + \omega_{41F} = 1$). All analytical experiments were performed in duplicate.

The mass fraction of salt was measured at the subsensitive resonance line (404.5 nm) of potassium by flame atomic absorption spectrometry which adopted an external standard method.[27] Samples were pretreated with nitric acid and cesium nitrate. Cesium nitrate was used as an ionization buffer.

Results and Discussion

No interface could be observed if the initial concentration of salt was not up to the critical salt concentration, as shown in Tables 2 and 3. Control represented the dilute aqueous solution A. 1-Butanol + water system is partially miscible.[28] But the dilute aqueous solutions are homogeneous because the concentration of 1-butanol is lower than its solubility in pure water. The cosolvents of acetone and ethanol increased the solubility of 1-butanol in water.[29] The organic molecules, which were attracted to water molecules previously,

Table 2. Distribution Coefficients of Ethanol (D_2), Acetone (D_3), and 1-Butanol (D_4) for Dilute Aqueous Solution A with Different Initial Concentrations of K_2CO_3 at 298.15 K

Concn (g kg^{-1})	D_2	D_3	D_4
Control	1[a]	1[a]	1[a]
100	1[a]	1[a]	1[a]
200	6.75	8.91	131.58
300	20.28	36.91	748.35
400	65.96	258.87	3784.05
500	215.12	1252.47	–
600[b]	327.77	2646.61	–

[a] No phase splitting was observed.
[b] Saturated condition.
–No 1-butanol was detected in the aqueous phase.

Table 3. Distribution Coefficients of Ethanol (D_2), Acetone (D_3), and 1-Butanol (D_4) for Dilute Aqueous Solution A with Different Initial Concentrations of K_2HPO_4 at 298.15 K

Concn (g kg^{-1})	D_2	D_3	D_4
Control	1[a]	1[a]	1[a]
100	1[a]	1[a]	1[a]
200	1[a]	1[a]	1[a]
250	6.74	9.36	140.50
300	13.29	20.74	318.62
400	42.08	100.22	1868.84
500	162.83	678.17	–
700[b]	411.91	1525.30	–

[a] No phase splitting was observed.
[b] Saturated condition.
–No 1-butanol was detected in the aqueous phase.

rearranged themselves in anion-bridged polar–polar contact through the alcohol OH groups after adding enough salt into the salting-out system.[30] A certain amount of ions attracted the water molecules to make the organics saturated for the liquid–liquid partition. The distribution coefficients of ABE were always improved with the increase in salt concentration in the dilute aqueous solution A. A notable distinction among the distribution coefficients was their sequence ($D_2 < D_3 < D_4$) at the same salt concentration. The results were in agreement with the initial contents of these solvents, and essentially conformed to the polarity indexes: ethanol (5.2) > acetone (5.1) > 1-butanol (4.0).[31] 1-Butanol with a lower polarity index was preferentially salted out and totally recovered with a sufficient addition of salt, especially under saturated condition. A large amount of K_2CO_3 or K_2HPO_4 ionized in polar solvent to produce cations and anions that repelled the aggregates of organics. So, it is necessary to enrich total solvents by increasing the concentration of salt.

The experimental results of the salting-out process at different temperatures using K_2CO_3 as a salting-out agent are shown in Figure 1 and Table 4. Figure 1a shows the influences of temperature and initial K_2CO_3 concentration on the mass fraction of water in the organic phase. It decreased with the increase in the initial concentration of K_2CO_3 (from 200 g kg^{-1} to saturated condition) at 298.15 K. The increasing ions preferred to associate with water molecules for hydration. By contrast, the mass fraction of water in the aqueous phase under salt-free condition increased, as shown in Figure 1b. The total solvents in the organic phase were enriched. It can be seen that temperature has a slight effect on the phase equilibria.

The influence of temperature on the salting-out process using $K_2HPO_4·3H_2O$ as a salting-out agent are presented in Figure 2 and Table 4. After the pretreatment by $K_2HPO_4·3H_2O$, the results in Figure 2 showed the analogous tendencies with the results in Figure 1. The effect of temperature on the mass fraction of water in the organic phase and the mass fraction of water in the aqueous phase under salt-free condition were more noticeable, which verified the endothermic behavior of the salting-out process. The solubility of K_2HPO_4 in pure water increases greatly with the increase in temperature,[32] which is related with the more remarkable salting-out effect of K_2HPO_4 than that of K_2CO_3 under saturated condition at higher temperatures, as shown in Figure 2a. Meanwhile, a smaller amount of ABE detected in the aqueous phase was attributed to the stronger repulsive interaction with increasing ion additives, together with the slight endothermic effect.

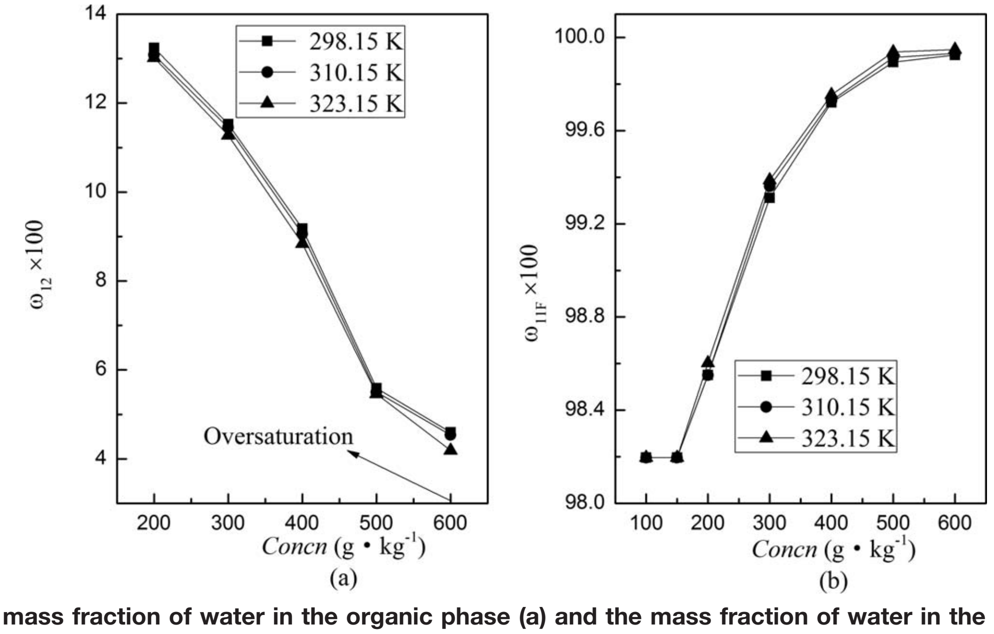


Figure 1. The mass fraction of water in the organic phase (a) and the mass fraction of water in the aqueous phase under salt-free condition (b), plotted against initial concentration of potassium carbonate.

Table 4. The Mass Fraction of Water in the Organic Phase (ω_{12}), and the Mass Fraction of Water in the Aqueous Phase Under Salt-Free Condition (ω_{11F})

Concn (g kg^{-1})	$\omega_{12} \times 100$ (298.15 K)	$\omega_{12} \times 100$ (310.15 K)	$\omega_{12} \times 100$ (323.15 K)	$\omega_{11F} \times 100$ (298.15 K)	$\omega_{11F} \times 100$ (310.15 K)	$\omega_{11F} \times 100$ (323.15 K)
K_2CO_3						
200	13.2	13.1	13.0	98.6	98.6	98.6
300	11.5	11.5	11.3	99.3	99.4	99.4
400	9.2	9.1	8.8	99.7	99.7	99.8
500	5.6	5.5	5.5	99.9	99.9	99.9
600[a]	4.6	4.5	4.2	99.9	99.9	100.0
K_2HPO_4						
250	15.6	14.8	14.7	98.6	98.7	98.7
300	14.0	13.8	13.8	99.1	99.1	99.1
400	13.5	12.8	11.8	99.6	99.6	99.7
500	10.4	10.1	9.4	99.9	99.9	99.9
700[a]	6.8	4.9	3.7	99.9	99.9	100.0

[a] Saturated condition.

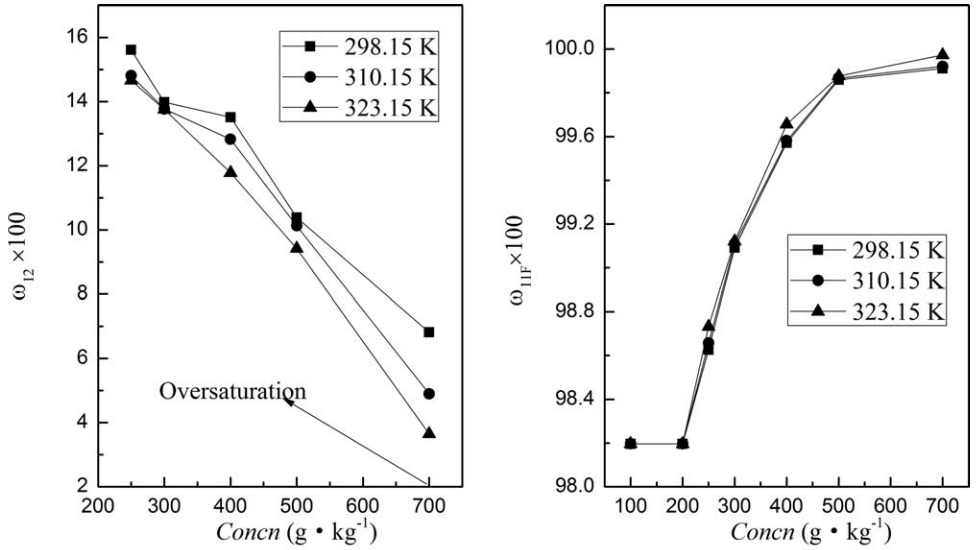
From an industrial point of view, it is practical to use salt solutions as salting-out agents to recover the solvents instead of the crystallized salts. That means, salt solutions with higher concentrations should be in preparation for reducing the dampening effect of the additional water (water from salting-out agent). As previously described, the preparations of the K_2CO_3 solution and the K_2HPO_4 solution were done with the mass fractions of 56 and 69% at 60°C, respectively. Figure 3 shows the organic residues in the aqueous phase after the salting-out of ABE from the dilute aqueous solution A using the K_2CO_3 solution. It may be seen that the mass fraction of 1-butanol shows a sharper decline than that of acetone or ethanol with increasing the salt concentration. The raise of the salting-out factor increased the salt concentration. It becomes more prone to recover 1-butanol with the lowest polarity index accordingly, as shown in Figure 4. Meanwhile, the recovery of acetone is the equivalent of that of ethanol. The recovery of 1-butanol, acetone, or ethanol was calculated by the following formula

$$R_i = \frac{m_0\omega_{i0} - m_1\omega_{i1}}{m_0\omega_{i0}} \tag{2}$$

where R_i is the recovery of acetone, 1-butanol, or ethanol ($i = 2$, 3, and 4, represented ethanol, acetone, and 1-butanol, respectively), m_1 is the mass of the aqueous phase, ω_{i1} is the mass fraction of each component in the aqueous phase, m_0 is the mass of the dilute aqueous solution, ω_{i0} is the mass fraction of each component in the dilute aqueous solution, m_1 and m_0 could be determined by gravimetrical analysis.

The K_2HPO_4 solution showed a more obvious salting-out effect on the dilute aqueous solution A because of the higher solubility of K_2HPO_4 in water at a higher temperature. The signal of 1-butanol could not be detected at the salting-out factor of 1.5:1 and the mass fraction of acetone indicated that the K_2HPO_4 solution was more favorable to increase its recovery, as shown in Figure 5. This recovery was synchronized with that of ethanol. Increasing the salting-out factor was proposed for increasing the recovery of acetone or ethanol in the ABE separation, as shown in Figure 6. The salt solution that worked best appeared to be a K_2HPO_4 solution with a greater proportion of K_2HPO_4 in it.

The levels of total solvents which were obtained in batch fermentations or pseudocontinuous fermentation processes varied because of some internal and external conditions.[33] Different strains also changed the solvent ratio of acetone:1-butanol:ethanol.[34] The effect of the total solvents' level on the salting-out process was studied by combining the dilute



(a)

(b)

Figure 2. The mass fraction of water in the organic phase (a), and the mass fraction of water in the aqueous phase under salt-free condition (b), plotted against initial concentration of dipotassium hydrogen phosphate.

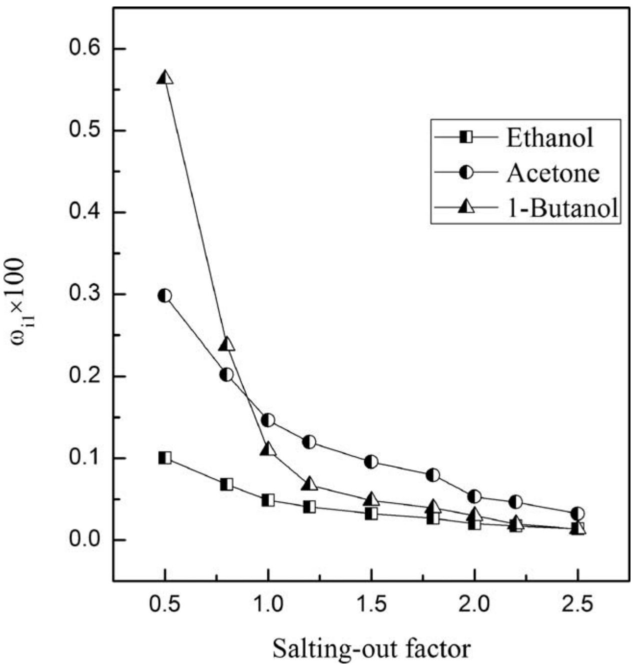


Figure 3. The mass fraction of acetone, 1-butanol, or ethanol in the aqueous phase, plotted against salting-out factor at 25°C (K_2CO_3 solution).

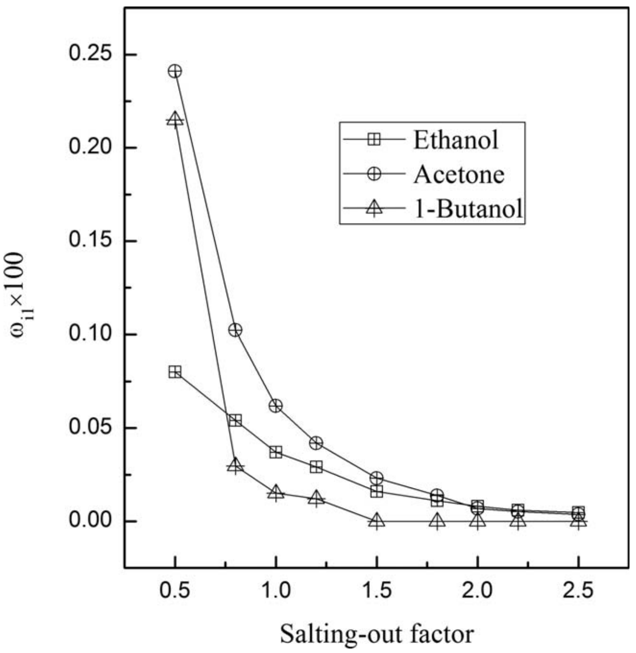


Figure 5. The mass fraction of acetone, 1-butanol, or ethanol in the aqueous phase, plotted against salting-out factor at 25°C (K_2HPO_4 solution).

aqueous solution B with the dilute aqueous solution A. The mass fraction of acetone or 1-butanol in the aqueous phase was found to decrease with the increase in the total solvents' level, whereas the trend was reverse for that of ethanol, as shown in Figures 7 and 8. It seems that a higher total solvents' level avails the aggregates of acetone molecules or 1-butanol molecules. The increasing ethanol molecules in the aqueous phase were substituted for the vacant positions made by the acetone molecules or 1-butanol molecules with lower polarity indexes. These ethanol molecules were attracted by the water molecules without hydration. Less amounts of acetone and 1-butanol were detected with the same volume of K_2CO_3 solution for dilute aqueous solution B and even 1-butanol was totally recovered at the salting-out factor of 1.5:1.

Taking the advantage of the K_2HPO_4 solution into account, the recovery of ethanol, acetone, or 1-butanol was extended to the expected maximization. Therefore, the effect of the total solvents' level on the salting-out process using the K_2HPO_4

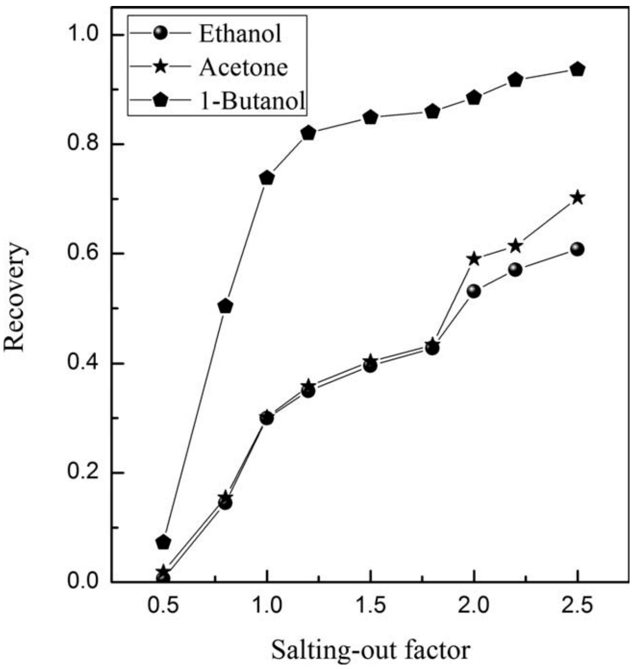


Figure 4. The recovery of acetone, 1-butanol, or ethanol, plotted against salting-out factor (K_2CO_3 solution).

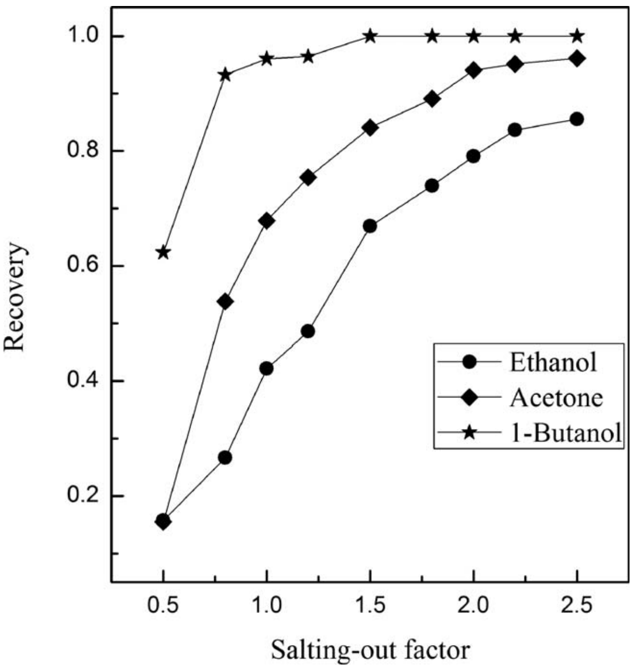


Figure 6. The recovery of acetone, 1-butanol, or ethanol, plotted against salting-out factor (K_2HPO_4 solution).

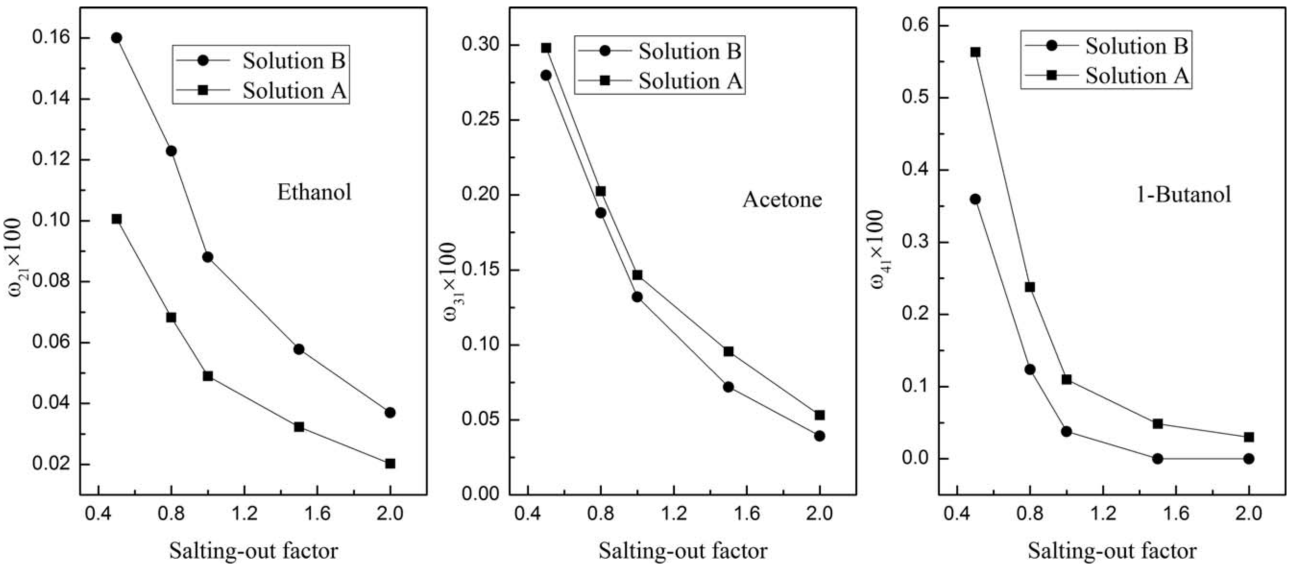


Figure 7. The difference of the mass fraction of ethanol, acetone, or 1-butanol in the aqueous phase between dilute aqueous solution A and dilute aqueous solution B after salting-out by K_2CO_3 solution.

solution as a salting-out agent was a little different. The gap of the mass fractions of ethanol in two aqueous phases at the same salting-out factor was narrowed by the more concentrated K_2HPO_4 solution. However, it was undeniable that a high ethanol level in the aqueous solution resulted in more ethanol molecules left in the aqueous phase.

All the experimental results showed that the solubilities of ABE in the aqueous phase were related with a given salt concentration. The solubilities of ABE were measured as the saturated concentrations per 100 g of water. The dilute aqueous solutions became oversaturated solutions after plenty of water molecules were attracted by the ions. A specific performance of the salting-out process was the decreasing solubilities of ABE in the aqueous phase with increasing the concentration of salt. Thus, ABE were salted out. It seems that the solubilities of ABE can be predicted over a wide range of conditions. The salting-out effect of salt on the solubility of the protein can be expressed by an equation of the type[35]

$$\log s = \alpha c + \beta \tag{3}$$

where s is the protein solubility, c is the salt concentration, and α and β are the constants. Equation 3 was commonly used in the physical chemistry of the proteins, but it was unsuited for the salting-out of ABE. Thus, other correlations should be designed.

Firstly, N (mol g^{-1} water) was defined as the molar number of salt per gram of water in the aqueous phase. Then, ABE should be taken as one component, eliminating the interactions of three compounds. Thus, the multicomponent system was simplified. The solubility of ABE in the aqueous phase was given by

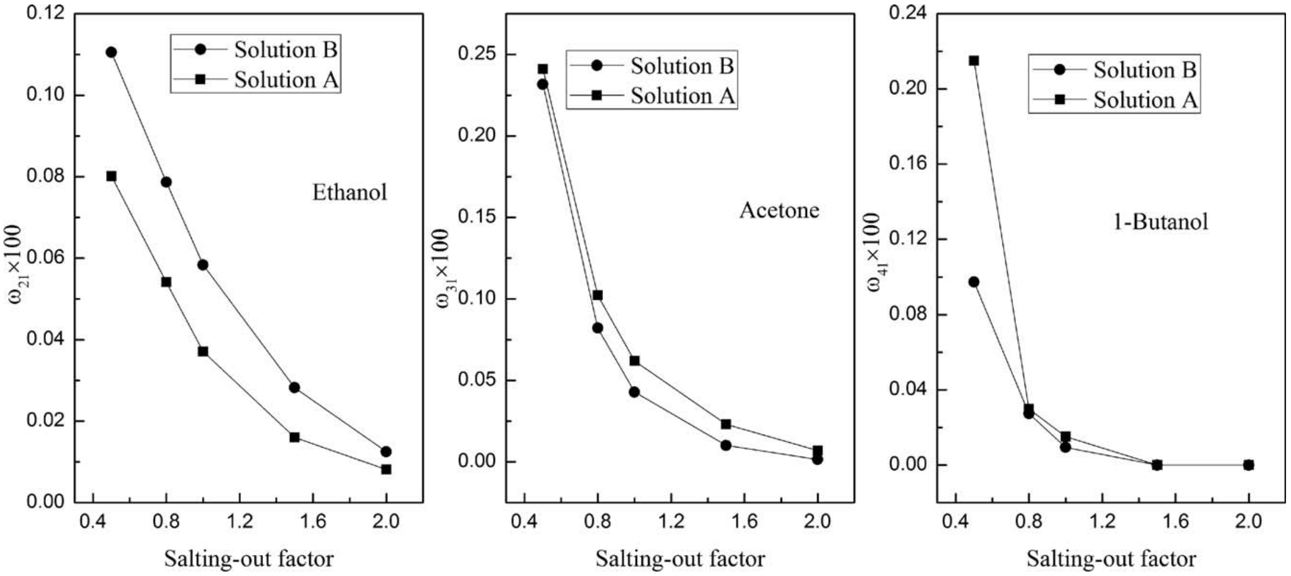


Figure 8. The difference of the mass fraction of ethanol, acetone, or 1-butanol in the aqueous phase between dilute aqueous solution A and dilute aqueous solution B after salting-out by K_2HPO_4 solution.

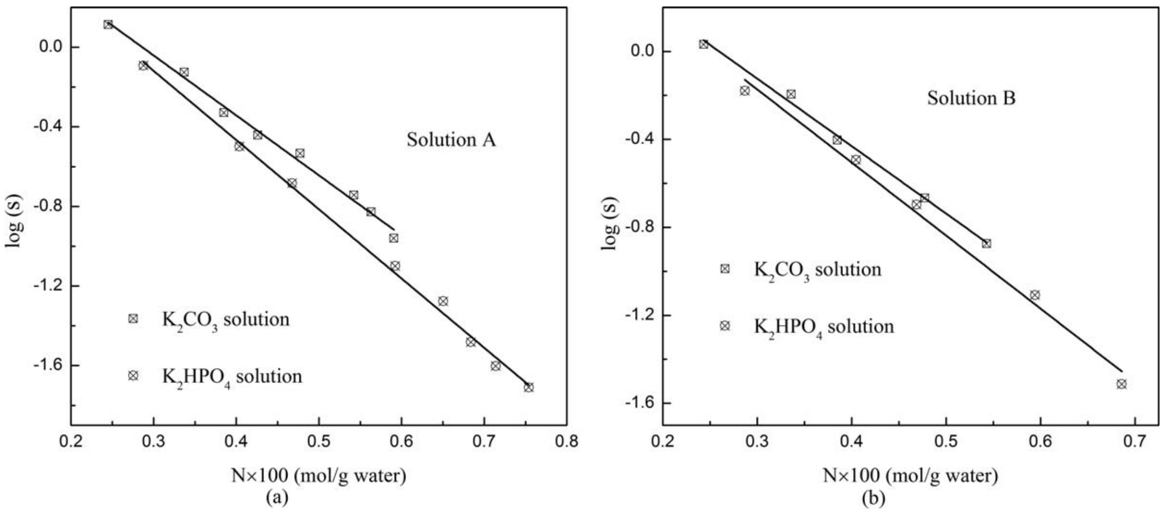


Figure 9. The logarithm of solubility of ABE from dilute aqueous solution A or dilute aqueous solution B, plotted against the molar number of salt per gram of water in the aqueous phase.

$$s=\frac{(\omega_{21}+\omega_{31}+\omega_{41})\times 100}{\omega_{11}} \tag{4}$$

and the molar number of salt per gram of water in the aqueous phase was given by

$$N=\frac{\omega_{51}}{M\times\omega_{11}} \tag{5}$$

where M represented the molar mass of salt, for K_2HPO_4, $M = 174.18$ g mol^{-1}, for K_2CO_3, $M = 138.21$ g mol^{-1}.

The logarithm of the solubility of ABE from the dilute aqueous solution A was plotted against the molar number of salt per gram of water in the aqueous phase, as shown in Figure 9a. The straight lines had been drawn through the points calculated by Eqs. 4 and 5. The empirical constants α, β which fitted to the experimental aqueous-phase ABE-solubility data were listed in Table 5. The α values of two salt solutions were found to be α (K_2HPO_4) $<$ α (K_2CO_3). They were negative. Then with the same variation of N, the reduction of s using the K_2HPO_4 solution was greater than that using the K_2CO_3 solution. It indicated that the salting-out force of K_2HPO_4 was greater than that of K_2CO_3 within the experimental levels. It could be verified by the solubitity of ABE with the same molar number of salt per gram of water in the aqueous phase too, as shown in Figures 9a, b.

After changing the total solvents' level, the salting-out forces of K_2HPO_4 and K_2CO_3 applied to the dilute aqueous solution B were close to the results of the experiments from dilute aqueous solution A, as shown in Figure 9b and Table 5. After an appropriate simplification, the solubility of ABE in the aqueous phase could be expressed as follows

$$\log\ s=\alpha N+\beta \tag{6}$$

where α and β were the constants, N was the molar number of salt per gram of water in the aqueous phase. In the elaborated experiments, the values of α and β were given,for the K_2CO_3 solution and the dilute aqueous solution A

$$\log\ s=-301.24N+0.86 \tag{7}$$

for the K_2CO_3 solution and the dilute aqueous solution B

$$\log\ s=-306.73N+0.80 \tag{8}$$

for the K_2HPO_4 solution and the dilute aqueous solution A

$$\log\ s=-347.90N+0.93 \tag{9}$$

for the K_2HPO_4 solution and the dilute aqueous solution B

$$\log\ s=-332.20N+0.82 \tag{10}$$

The effect of the salt concentration on the solubility of ABE had been studied by another way. The correlation of the solubility of ABE in the aqueous phase was satisfying. This correlation can be used to assess the losses of ABE in the aqueous phase and helps promote the development of the salting-out process.

Table 5. The constants α, β, and the coefficients of determination R^2

		α	β	R^2
Solution A	K_2CO_3 solution	−301.24	0.86	0.9928
	K_2HPO_4 solution	−347.90	0.93	0.9962
Solution B	K_2CO_3 solution	−306.73	0.80	0.9956
	K_2HPO_4 solution	−332.20	0.82	0.9911

Conclusions

In this study, salting-out phase equilibria for ABE from dilute aqueous solutions using K_2CO_3 and $K_2HPO_4\cdot 3H_2O$ as outstanding salting-out agents were reported in this article. ABE could not be salted out until the initial concentration of salt reached the critical salt concentration. The distribution coefficients of ABE were remarkably improved with the increase in the salt concentration and they were arranged in the order $D_2 < D_3 < D_4$ at the same salt concentration. The greater salting-out effect was heavily dependent on the increase in the salt concentration. The specific performances were the decrease of the mass fraction of water in the organic phase and the increase of the mass fraction of water in the aqueous phase under salt-free condition.

Temperature had a slight effect on the phase equilibria. But, it appeared that the salting-out process was endothermic. Salts with greater solubilities in pure water at a higher temperature could strengthen the salting-out effect.

The K_2HPO_4 solution with a higher proportion of K_2HPO_4 was more favorable than the K_2CO_3 solution to recover ABE from dilute aqueous solutions. At the salting-out factor of 1.5:1, 1-butanol was totally recovered by the K_2HPO_4

solution. More than 85.55 wt % of ethanol and 96.16 wt % of acetone could be recovered by increasing the salting-out factor from 2:1 to 2.5:1. A higher total solvents' level of the dilute aqueous solution strengthened the salting-out effect significantly, which resulted in the decrease in the mass fractions of acetone and 1-butanol in the aqueous phase at the same salting-out factor. But a larger amount of ethanol in the aqueous phase balanced the absences of acetone and 1-butanol.

The solubility of ABE from the dilute aqueous solution A or the dilute aqueous solution B was correlated well with the molar number of salt per gram of water in the aqueous phase by a new equation. The salting-out force of the K_2HPO_4 solution was stronger than that of the K_2CO_3 solution after the experimental verification. The total solvents' levels of the dilute aqueous solutions showed negligible effects on the solubility of ABE in the aqueous phase.

The separation of ABE from dilute aqueous solutions using the salting-out effect was simplified by us. The subsequent separations of ABE can be also simplified because the organic phase contains only a much smaller amount of water. From the economic points of view, the recycling process for a dilute salt solution only involves a single evaporation of the aqueous phase. Then, the salt solution can be reused and the vapor can be used as a heat source.

No organic extractant should be recovered using the salting-out method and the dilute salt solution can be reused. The relatively high salt concentrations could have severely deleterious effects on cells arising from osmotic shock in the fermentation broth.[18] Then, the cells can be filtered out from the organic phase. The original existing salt in the fermentation broth, such as KH_2PO_4, may strengthen the salting-out effect and improve the distribution coefficients of ABE. But, the remaining acids in the fermentation broth should be first neutralized by KOH because of the potassium salts used in our study.

Future work will concentrate on the total recovery of ABE, the cost of salt recovery from the aqueous phase, and the applications of the salting-out process to the ABE fermentation broths. The different salting-out forces of K_2HPO_4 and K_2CO_3 should be further differentiated. With such data, the salting-out process of ABE can be finally applied industrially.

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Notation

Abbreviations and symbols

ABE = acetone + 1-butanol + ethanol
D = distribution coefficient
R = recovery
ω_{ij} = mass fraction of one component in one phase (subscript $i = 1, 2, 3, 4, 5$ represent water, ethanol, acetone, 1-butanol, and salt, respectively; subscript $j = 1, 2$ represent aqueous phase and organic phase, respectively)
ω_{ijF} = mass fraction of one component in one phase under salt-free condition (subscript $i = 1, 2, 3, 4$ represent water, ethanol, acetone, 1-butanol, respectively; subscript $j = 1, 2$ represent aqueous phase and organic phase, respectively; F represent salt-free condition)
m_1 = mass of the aqueous phase
m_0 = mass of the dilute aqueous solution
ω_{i0} = mass fraction of each component in the dilute aqueous solution
c = salt concentration
M = molar mass of salt
N = molar number of salt per gram of water in the aqueous phase
s = solubility of ABE or protein in the aqueous phase
α, β = constants

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