

## Salting-out separation and liquid–liquid equilibrium of tertiary butanol aqueous solution

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Received 20 December 1998; received in revised form 14 January 2000; accepted 21 January 2000

### Abstract

The separation of tertiary butanol (TB) from aqueous solution was studied by salting-out effect for practical application. The final concentration of alcohol can be concentrated into 96% from its original 60%. More than 20 salts were experimented upon to compare their salting-out capacities. According to the concentration target, potassium fluoride (KF) was chosen as a salting-out agent for TB aqueous solution. The liquid–liquid equilibrium data of TB–H<sub>2</sub>O–KF system and the relationship between the amount of KF and the concentration of TB at different temperatures have been measured and reported. The method of salt addition has been optimized by experiments. KF liquor can be used as salting-out agent. A mathematical model was set up by Pitzer theory and Wilson equation. The Wilson parameters and the Pitzer parameters were obtained by regression. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Salting out; Tertiary butanol; Potassium fluoride; Separation; Liquid–liquid equilibrium

### 1. Introduction

Tertiary butanol (TB) can be used as a material for producing *tert*-butylamine, isobutene, tri-isobutyl aluminium and some medicines. It can also be used as synthetic additive, anti-ageing agent, synthetic musk, antioxidant paint naphtha and so on. Normally, the commercial availability is of aqueous solution containing 87% TB which cannot meet the needs of high concentration for further productions. Because it forms an azeotropic mixture with water, high purity TB cannot be obtained by common distillation methods. A special separation by extractive distillation can be used for obtaining 93% TB, but the process is more complicated and the consumption of energy is also high. The effect of salting-out has been studied long ago, but its application has not been so wide till now. Using the salting-out method diminishes nonelectrolyte solubilities because the ions draw water molecules around themselves and rob the water molecules from the nonelectrolytes (for example tertiary butanol). A product of tertiary butanol can be obtained with higher concentration and lower energy consumption by this method.

Four isomers of butyl-alcohol all have azeotropes with water, but only tertiary butanol is entirely miscible with water because of its strong polarity. Kato [1] considered that the salt concentrations required to cause a phase-separation

in the polar nonelectrolyte aqueous solution are higher than those in the case of non-polar molecules. For salting out in alcohol aqueous solution, Tan [2] considered that basic metal halides are good salting-out agents. Korenman et al. [3] made a research of salting-out of some normal alcohols and found that the order of salting-out capacity is KF>KCl>KBr>KI.

In this work, we select salting-out agent from many inorganic salts and confirm a suitable amount of salt for separating TB aqueous solution. The liquid–liquid equilibrium data of TB–H<sub>2</sub>O–KF system are measured. A mathematical model is set up by Pitzer theory and Wilson equation, and the Pitzer parameters are obtained by regression. The concentration of TB in alcohol phase can go up to 96% and then the salting-out agent in water phase is recovered by simple vaporization for reuse. Another experiment of reusing concentrated KF aqueous solution is carried out. 85% KF concentrated aqueous solution is selected as salting-out agent for commercial production. The results of the study have been put into practice.

### 2. Experimental

#### 2.1. Salt selection

##### 2.1.1. Materials

Tertiary butanol, KF, KBr, KCl, LiCl, NaCl, BaCl<sub>2</sub>, SnCl<sub>2</sub>, NH<sub>4</sub>Cl, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Na<sub>3</sub>PO<sub>4</sub>, KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>,

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$(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{K}_2\text{CO}_3$  are all analytical reagents. Water used is de-ionized water.

### 2.1.2. Analysis methods

The density of TB aqueous solution was measured with a density bottle. Concentration of TB aqueous solution was measured by Sp-501N Gas Chromatograph. The water microanalysis was carried out by Karl Fischer titration.

### 2.1.3. Specification of the gas chromatograph

Detector: thermal conductivity detector; Carrier gas:  $\text{H}_2$ ; Column length: 2 m; Column packing: Porapak R, 80~100 mesh; Column temperature: 403.2 K; Vaporization temperature: 418.2 K; TC current: 150 mA; Carrier gas flow rate: 22 ml/min; Up-stream column pressure: 1 kg/cm<sup>2</sup>; Sample size: 1  $\mu\text{l}$ ; Attenuation ratio: 1/2

### 2.1.4. Procedure

According to an empirical rule of salt effect in nonelectrolyte–water system, the greater the solubility of salt, the higher a salt effect is. About 20 kinds of salts are tested individually to TB aqueous solution for comparing of the solubility and the TB concentration in alcohol phase. If there is no phase separation with adding salt, the effect of salting-out does not exist. A certain salt is added into a dried 25 ml test-tube, in which there are 15 ml 71.1 (wt.%) TB solution already. The test-tube is vibrated, then put in a thermostatic bath (0.1013 MPa, 318 K), this procedure is repeated three times. When the solution attains equilibrium (about 2 h), the concentrations of TB in alcohol phase and water phase are measured by gas chromatograph.

### 2.2. Determination and correlation of liquid–liquid equilibrium (L–L–E) for the tertiary butanol–water–potassium fluoride system

The L–L–E measurements of TB– $\text{H}_2\text{O}$ –KF are carried out in a CS501 Super-Thermostat Bath and a scaled test-tube with plug. Certain volumes of TB and distilled water are added into the test tube with pipet, and a certain amount of dried salt weighed with analytical balance are put into the test-tube, then the tube is vibrated for 30 min. The test-tube is placed into the super-thermostat bath in which temperature is adjusted to a certain value. The fluctuation of temperature is believed to be less than  $\pm 0.1$  K. The system could be in equilibrium if the concentrations of TB in both phases remained almost constant for 2 h. The compositions of TB in the two phases are measured by a gas chromatograph. The concentrations of KF in two phases were obtained by weighing and mass balance method.

The phase equilibrium data of alcohol–water– $\text{K}_2\text{CO}_3$  system at 298.2 K are measured and compared with those from

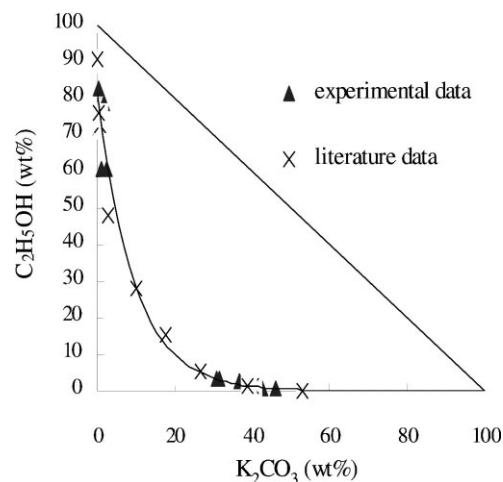


Fig. 1. L–L–E phase diagram of  $\text{C}_2\text{H}_5\text{OH}$ – $\text{H}_2\text{O}$ – $\text{K}_2\text{CO}_3$  system at 298.2 K.

literature. The experimental result is in good agreement with the literature data [4] as shown in Fig. 1.

## 3. Results and discussion

### 3.1. Salt selection

Twenty-one different salts are used for the experiment. About 1 g of the salts are added into 15 ml of 71.1 (wt.%) TB aqueous solution, and the quantity and concentration of the two phases are analyzed. Their salting-out capacities are listed in Table 1. For a concentrated TB aqueous solution, the salting-out capacities of salts can be divided into three types according to phase-separation and TB concentration in alcohol phase. The first type (for example  $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$ , ...) cannot be dissolved completely and the solution will not result in phase-separation. Basically, the salts do not have salting-out capacity. The second type (for example  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ , ...) can result in phase-separation and has a certain capacity for salting-out, but their solubilities are quite low in the TB aqueous solution. Increasing the amount of salt added into solution continuously can not increase the concentration of TB in alcohol phase. The third type (for example  $\text{KF}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ , ...) has a great salting-out capacity and the solubilities in solution are big. The salts of this type in water phase are not yet saturated (see Table 1) and the concentration in alcohol phase can be increased if more salt is added. When  $\text{KF}$  as a salting-out agent is selected, the maximum concentration value of TB in alcohol phase is obtained. The TB concentration in alcohol phase will be higher than 96%. The other advantage with using  $\text{KF}$  as salting-out agent is that the content of TB in water phase almost approaches zero. Table 2 gives some maximum concentrated results of TB aqueous solution with some salts at normal temperature and shows that the salting-out effect of  $\text{KF}$  is notable.

Table 1  
Comparison of salting-out capacities of some salts on 71.1 (wt.%) TB aqueous solution

Type of salt effect	Salt	Quantity of salt added (g)	TB concentration (wt.%) in		Note
			Alcohol phase	Water phase	
First	NaNO <sub>3</sub>	0.2979	71.1	71.1	No phase separation
	NaF	0.2980	71.1	71.1	No phase separation, salt saturated
	Ca(N <sub>3</sub> ) <sub>2</sub>	0.2996	71.1	71.1	No phase separation
	CH <sub>3</sub> COONa	0.9575	71.1	71.1	No phase separation, salt saturated
	CuSO <sub>4</sub>	0.9456	71.1	71.1	No phase separation, salt saturated
	Na <sub>3</sub> PO <sub>4</sub>	0.9386	71.1	71.1	No phase separation, salt saturated
	SnCl <sub>2</sub>	0.9885	71.1	71.1	No phase separation, salt saturated
Second	BaCl <sub>2</sub>	0.9928	72.1	0.292	Salt saturated
	KNO <sub>3</sub>	1.0005	75.2	4.50	Unsaturated
	Na <sub>2</sub> SO <sub>4</sub>	0.9847	74.5	≈0	Salt saturated
	Na <sub>2</sub> SO <sub>3</sub>	0.9874	79.0	≈0	Salt saturated
	NaCl	1.0095	89.1	≈0	Salt saturated
	KCl	0.9922	88.4	2.63	Salt saturated
	CaCl <sub>2</sub>	0.9950	85.8	≈0	Salt saturated
Third	KBr	0.9861	82.2	3.372	Unsaturated
	K <sub>2</sub> CO <sub>3</sub>	0.9890	82.7	≈0	Unsaturated
	KF	1.0011	82.0	≈0	Unsaturated
	NH <sub>4</sub> NO <sub>3</sub>	1.1095	82.1	3.21	Unsaturated
	NH <sub>4</sub> Cl	1.0012	88.5	4.83	Unsaturated
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.9949	83.5	≈0	Unsaturated
	LiCl	0.9880	86.0	0.336	Unsaturated

### 3.2. The relations between tertiary butanol concentration and some operating conditions

The effect of salt quantity added, temperature and lay up time are studied. For every experiment, 10 ml 60% TB aqueous solution ( $\rho=0.9023$  g/ml, 298.2 K) or 10 ml 70% TB aqueous solution is used. Fig. 2 shows that the TB concentration of alcohol phase increases with the increase of salt added, but the salting-out effect will decrease when the TB concentration of alcohol phase is higher than 90%. Therefore, if the salting-out method is used for concentrating tertiary butanol, a suitable quantity of KF should be added around 2~3 g/10 ml 70% TB aqueous solution on the experimental condition. Otherwise, the method will not be economical. Table 3 presents the once salting-out experimental data and the effect of temperature and lay up time on TB concentration in alcohol phase. It is clear from Table 3 that the effect of temperature is not significant. Especially, when the content of TB approaches 95%, the effect of temperature is almost null. The concentration of TB will increase slightly with an increase of lay up time. Generally, the concentration of TB no longer increases remarkably in 2 h lay up time. When the content of TB approaches

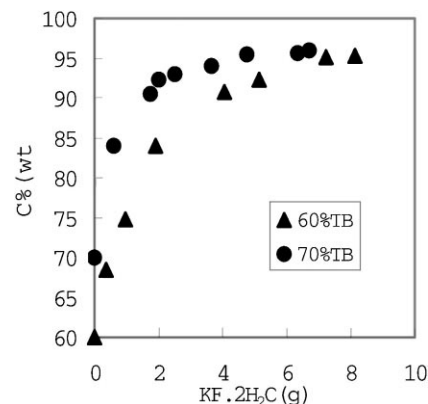


Fig. 2. The relation between the concentration of TB and the quantity of KF·2H<sub>2</sub>O.

96%, the relative amount of salt  $W_r$  can be calculated as follows:

$$\begin{aligned}
 W_r &= \frac{\text{weight of KF} \cdot 2\text{H}_2\text{O added}}{\text{weight of solution treated}} \\
 &= \frac{9.1254}{0.9023 \times 10} = 1.0113
 \end{aligned}$$

Table 2  
Maximum concentrated results of TB solution with some salts at normal temperature

Salt	LiCl	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	KBr	KNO <sub>3</sub>	NH <sub>4</sub> Cl	K <sub>2</sub> CO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KF
TB concentration in alcohol phase (wt.%)	87.5	84.5	83.1	79.5	83.9	92.0	93.0	96.6

Table 3  
The effect of temperature and lay up time on TB concentration  $C_1$  (wt.%) in one-time salting-out experiment

$W$ (g)	$W_r$	Lay up time (at 298.2 K)		Temperature (lay up for 1 h)	
		2 h	24 h	313.2 K	323.2 K
0.3604	0.0399	68.5	70.2	71.2	72.0
0.9692	0.1074	74.8	79.5	80.0	80.2
1.9030	0.2109	84.0	86.1	86.5	86.6
4.0531	0.4492	90.8	92.3	92.6	92.7
5.1416	0.5698	91.3	93.5	93.7	93.8
7.2314	0.8014	95.1	95.3	95.3	95.4
8.1251	0.9005	95.3	95.5	95.5	95.5
9.1254	1.0113	95.8	96.0	96.0	96.0

### 3.3. Optimization of the number of salt adding times

A multi-salting-out method can be used to concentrate TB aqueous solution. After the first-time salting-out operation, the first water phase is separated off, then the salt is added again into the first alcohol phase for concentrating TB and separating off water phase in the second salting-out operation, and then the third-time salting-out operation will be carried out. Because water content is very low in the first alcohol phase, a smaller amount of salt for second operation will be needed and the second water phase has a higher salt concentration. A total salt requirement for attaining a certain TB concentration with multi-salting-out method will be reduced remarkably.

Twice salting-out experiments were carried out with different quantities of salt added in the once salting-out operation. For the first salting-out operation, 25 ml 60% TB aqueous solution was used. For the second salting-out operation, 10 ml of alcohol phase solution separated off in

the first operation was used. Table 4 shows that a total relative amount ( $W_{tr}$ ) of KF is the least, if the quantity of salt added each time is equal to one-half of total salt amount (i.e. 4.5507 g). When 96.8% concentration of TB can be attained,  $W_r$  in twice salting-out operation is about 0.4275. In the concentration, the total salt amount  $W_t$  and the relative salt amount  $W_{tr}$  in twice salting-out can be calculated as follows:

$$W_t = 4.5507 + \frac{2.7677}{10} \times 18.4 = 9.6433 \text{ (g)}$$

$$W_{tr} = \frac{9.6433}{(25 \times 0.9023)} = 0.4275$$

A salt requirement for salting out 10 ml 60% TB aqueous solution can be calculated as follows,

$$W = 9.6433 \times \frac{10}{25} = 3.8573 \text{ (g/10 ml)}$$

Table 5 presents the experimental results of three-time salting-out process. 40 ml of TB 60% aqueous solution ( $\rho=0.9023$  g/ml) is used for first experiment. Then 20 ml 80.5% of TB solution is used from the alcohol phase of first experiment. Finally, 10 ml 91% of TB solution is used for the third experiment.

A total relative amount of salt  $W_{tr}$  in three-time salting-out can be calculated as follows:

$$W_t = 4.4478 + 2.3306 \times \frac{30}{20} + 1.3957 \times \frac{18.5}{10} \times \frac{30}{20} = 11.6668 \text{ (g)}$$

$$W_{tr} = \frac{11.6668}{(40 \times 0.9023)} = 0.323$$

Comparing the results of above experiments (i.e. the once salting-out:  $W_r=1.011$ , twice salting-out:  $W_r=0.43$ ,

Table 4  
Results of twice salting-out experiment at 298.2 K

First salting-out				Second salting-out					Total salt consumed		
$W$ (g)	$W_r$ (g)	$V_2$ (ml)	$V_1$ (ml)	$C_1$ (wt.%) <sup>a</sup>	$W$ (g)	$W_r$ (g)	$V_2$ (ml)	$V_1$ (ml)	$C_1$ (wt.%) <sup>a</sup>	$W_t$ (g)	$W_{tr}$ (g)
5.4521	0.2417	9.6	18.4	86.9	2.2949	0.1872	2.0	9.2	96.5	9.6747	0.4289
4.5507	0.2017	8.9	18.4	86.1	2.7677	0.2258	2.6	9.1	96.8	9.6433	0.4275
3.3911	0.1503	7.9	19.0	82.6	3.3043	0.2783	3.0	9.0	96.4	9.6693	0.4287
2.3970	0.1063	7.1	19.1	78.5	3.8177	0.3233	3.8	8.6	96.3	9.6888	0.4295
2.0477	0.0908	6.5	19.3	74.9	3.9662	0.3393	3.6	8.6	96.1	9.6995	0.4300

<sup>a</sup> Lay up 2 h.

Table 5  
Results of three-time salting-out experiment at 298.2 K

Run	$V$ (ml)	$C$ (wt.%)	$W$ (g)	Lay up time (h)	$V_2$ (ml)	$V_1$ (ml)	$C_1$ (wt.%)
First	40	60.0	4.4478	12	12.0	30.0	80.5
Second	20	80.5	2.2306	5	2.5	18.5	91.0
Third	10	91.0	1.3957	2	1.2	9.7	96.3

the three-time salting-out:  $W_T=0.323$ ), shows that twice salting-out is suitable for separation of TB aqueous solution when economics are considered.

### 3.4. Determination and correlation of L–L–E data for the tertiary butanol–water–KF system

The L–L–E data of TB–H<sub>2</sub>O–KF system are measured at 293.2, 298.2, 308.2 and 318.2 K, and under atmospheric pressure (see Table 6). Fig. 3 presents a L–L equilibrium diagram of TB–H<sub>2</sub>O–KF system at 298.2 K as an example.

In the salting-out process, tertiary butanol–water–KF system can be separated into two phases. There is a small amount of water and little of KF in alcohol phase, and a small amount of TB in water phase. We can consider that the alcohol phase belongs to alcohol–water binary system and water phase belongs to salt–water binary system approximately. The alcohol–water system can be correlated with Wilson equation. The KF–water system can be correlated with Pitzer theory [5].

Activity  $\alpha_2$  of water in KF aqueous solution can be calculated by Pitzer model [6,7].

$$\ln \alpha_2 = -0.036 m \left[ -0.3944 \frac{\sqrt{m}}{1 + 1.2\sqrt{m}} + m(\beta^{(0)} + \beta^{(1)} e^{-2\sqrt{m}}) + m^2 c + 1 \right] \quad (1)$$

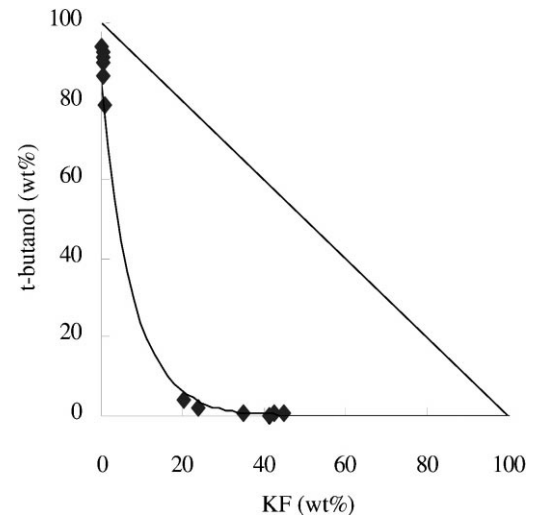


Fig. 3. L–L–E phase diagram of TB–H<sub>2</sub>O–KF system at 298.2 K.

Correlation of alcohol phase: In equilibrium state, the activity values of water in two phases must be equal, namely  $\alpha_{21}=\alpha_{22}$ . The alcohol phase is a homogeneous system, the activity  $\alpha_2$  of water in alcohol phase can be calculated by Wilson equation.

$$\alpha_2 = \gamma_2 x_2 \quad (2)$$

Table 6  
L–L equilibrium data of TB–water–KF system at 293.2, 298.2, 308.2 and 318.2 K

Temperature (K)	Run	Water phase (wt.%)			Alcohol phase (wt.%)			Total composition (wt.%)		
		Water	TB	KF	Water	TB	KF	Water	TB	KF
293.2	1	67.06	1.20	31.75	13.4	86.43	0.17	48.96	29.50	21.54
	2	61.64	1.00	37.36	9.26	89.89	0.85	94.72	32.03	25.25
	3	62.04	0.89	37.06	9.79	90.12	0.087	40.48	37.72	21.80
	4	82.62	5.78	11.60	21.79	78.11	0.10	77.11	12.18	10.71
	5	78.48	3.00	18.53	16.56	83.21	0.23	58.36	28.81	12.83
	6	54.95	0.06	44.98	6.46	93.05	0.49	45.92	15.81	38.27
	7	56.19	0.41	43.41	8.22	91.19	0.59	42.51	25.61	31.88
298.2	1	56.84	0.56	42.55	10.88	89.71	0.41	40.33	30.24	29.43
	2	80.30	4.02	20.08	20.29	79.10	0.61	63.66	19.35	16.99
	3	74.52	1.88	24.00	12.94	86.77	0.49	48.95	36.70	14.35
	4	54.55	0.45	45.00	7.26	92.45	0.28	36.05	35.27	28.17
	5	64.16	0.75	35.09	8.48	91.16	0.36	39.55	39.22	21.24
	6	58.59	0.22	41.19	5.59	94.21	0.19	49.71	15.11	35.18
308.2	1	82.57	2.32	15.11	18.95	80.94	0.11	75.07	11.46	13.47
	2	81.58	1.90	16.52	20.41	79.47	0.12	59.46	29.95	10.59
	3	56.73	0.43	42.58	4.24	95.67	0.09	49.97	12.68	37.35
	4	49.39	0.10	50.51	1.86	98.12	0.02	41.00	15.55	45.45
	5	51.49	0.15	48.36	3.36	96.69	0.05	45.52	11.55	42.93
318.2	1	67.33	1.34	31.33	8.46	90.98	0.56	51.33	25.85	22.68
	2	73.32	1.46	25.22	11.78	87.13	1.09	63.29	16.06	20.65
	3	75.61	1.55	22.88	13.17	84.18	1.96	62.74	19.07	18.18
	4	57.04	0.11	42.86	4.31	95.64	0.05	44.47	22.44	33.39
	5	54.48	0.02	45.1	4.73	94.94	0.32	46.63	14.18	39.19

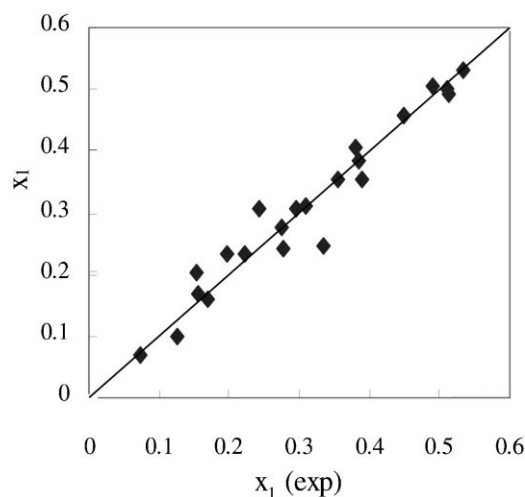


Fig. 4. Comparison of experimental and calculated values of concentration in alcohol phase.

$$\ln \gamma_2 = -\ln(x_2 + \lambda_{21}x_1) + x_1 \left( \frac{\lambda_{21}}{x_2 + \lambda_{21}x_1} - \frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} \right) \quad (3)$$

By Eqs. (1)–(3)

$$\ln \alpha_2 = \ln \gamma_2 + \ln x_2 = -0.036m \left[ -0.3944 \frac{\sqrt{m}}{1 + 1.2\sqrt{m}} + m(\beta^{(0)} + \beta^{(1)}e^{-2\sqrt{m}}) + m^2c + 1 \right] \quad (4)$$

Rearrangement,

$$-\frac{1}{0.036m^2} \left[ \ln \frac{1}{1 + \lambda_{21}(x_1/x_2)} + x_1 \left( \frac{\lambda_{21}}{x_2 + \lambda_{21}x_1} - \frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} \right) \right] + 0.3944 \frac{1}{\sqrt{m} + 1.2m} - \frac{1}{m} = \beta^{(0)} + \beta^{(1)}e^{-2\sqrt{m}} + mc \quad (5)$$

$$\lambda_{12} = \frac{V_2}{V_1} e^{-(A_{12}/RT)} \quad (6)$$

$$\lambda_{21} = \frac{V_1}{V_2} e^{-(A_{21}/RT)} \quad (7)$$

The correlated Wilson parameters are:  $A_{12}=1500.0444$  and  $A_{21}=801.3780$ .

Table 8  
Results of twice salting-out experiment with different concentrations of KF liquor at 298.2 K

Properties of salting-out agent (KF liquor)		First salting-out			Second salting-out			Salt consumed	
$C_{KF}$ (wt.%)	$\rho$ (g/ml)	V (ml) (60%TB solution)	W (g)	$C_1$ (wt.%)	$V_1$ (ml)	W (g)	$C_1$ (wt.%)	W (g/20 ml)	W (g/10 ml)
67.384	1.4543	20	5.8798	86.1	10	5.8798	94.8	14.5231	7.2616
79.595	1.5359	20	6.1225	88.8	10	5.5012	95.9	14.3092	7.1546
83.000	1.5793	20	5.2433	89.1	10	3.9325	96.1	10.9454	5.4727
89.300	1.6329	20	5.1053	87.8	10	3.6466	96.5	10.4658	5.2329

Table 7  
Pitzer parameters in experimental temperatures

Temperature (K)	$\beta^{(0)}$	$\beta^{(1)}$	$c$
293.2	0.858938	18.4536900	-0.0016932
298.2	0.5540528	-8.5728290	-0.0361430
308.2	0.156329	20.3195600	0.0071533
318.2	0.3418024	13.5410400	-0.154853

Pitzer parameters at high concentration are correlated and presented in Table 7. The equilibrium compositions of alcohol phase of TB–water–KF system are calculated with the Wilson equation and Pitzer parameters. Fig. 4 shows that the calculated values in experimental temperatures are in good agreement with the experimental results.

### 3.5. Reutilization of KF aqueous solution

KF in water phase should be recovered and reused on a commercial scale, but the reutilization of solid salt by vaporization is not economical and not convenient in continuous process. Concentrated KF liquor can be used as salting-out agent. The twice salting-out experiments are carried with different concentrations of KF liquor for selecting a suitable concentration of KF liquor. For the first salting-out operation, 20 ml of 60% TB aqueous solution is used. For the second salting-out operation, 10 ml of alcohol phase solution separated off in the first operation is used. Table 8 shows that a total salt quantity  $W$  in the twice salting-out operation is decreased with an increase of concentration of KF liquor. When 96.5% TB is attained, the salt requirement with KF liquor in salting-out operation is 5.2329 (g/10 ml), whereas the requirement of solid KF is about 3.8573 (g/10 ml), as shown in Section 3. The salt quantity of KF liquor consumed is more than that of solid KF for the same salting-out result. A dilute solution of KF should be concentrated as high as possible for reduction of salt quantity. In the salting-out of TB aqueous solution, a suitable concentration of KF liquor is higher than 86%.

## 4. Conclusions

The conclusions of the study are:

1. The separation of tertiary butanol (TB) from aqueous solution is feasible by salting-out effect.

2. Potassium fluoride is selected as a salting-out agent. The concentration of TB in alcohol phase and in water phase can be approached to 96% and almost 0%, respectively.
3. When the concentration of TB is greater than 90% (wt), the concentration of TB increases slowly with an increasing salt.
4. Twice salting-out process is suitable for separation of TB. Its total relative amount of salt is at a least of 0.43 g salt/g solution.

## 5. Nomenclature

$c$	Pitzer parameter
$C$	concentration of TB in solution (wt.%)
$C_1$	concentration of TB in alcohol phase (wt.%)
$C_2$	concentration of TB in water phase (wt.%)
$C_{KF}$	concentration of KF in solution (wt.%)
$m$	molality of KF ( $\text{mol ml}^{-1}$ )
$V$	volume of solution (ml)
$V_1$	volume of alcohol phase (ml)
$V_2$	volume of water phase (ml)
$W$	amount of KF (g)
$W_r$	relative amount of KF
$W_t$	total amount of KF (g)
$W_{tr}$	total relative amount of KF
$x_1, x_2$	mole fractions of TB and water in alcohol phase

## Greek letters

$\alpha_{21}$	activity of water in alcohol phase
$\alpha_{22}$	activity of water in water phase
$\beta^{(0)}, \beta^{(1)}$	Pitzer parameters
$\gamma_2$	activity coefficient of water in alcohol phase
$\lambda_{12}, \lambda_{21}$	Wilson parameters

## References

- [1] T. Kato, M. Yudasaka, T. Fujiyama, Salting-out phenomenon and clathrate hydrate formation in aqueous solution of polar nonelectrolyte, *Bull. Chem. Soc. Jpn.* 55 (1982) 1284–1289.
- [2] T.C. Tan, New screening technique and classification of salts for the salt distillation of close-boiling and azeotropic solvent mixtures, *Chem. Eng. Res. Des.* 65 (1987) 421–425.
- [3] I.M. Korenman, Salting-out in a two-phase system. II Higher alcohols–potassium halides–water, *J. Phys. Chem. (Russ.)* 49 (6) (1975) 1490–1493.
- [4] H.T. Stephen, *Solubilities of Inorganic and Organic Compounds*, Vol. 2, Pergamon Press, Oxford, 1979, p. 34.
- [5] K.S. Pitzer, Thermodynamics of electrolytes. I Theoretical basis and general equations, *J. Phys. Chem.* 77 (2) (1973) 268–277.
- [6] K.S. Pitzer, G. Mayorga, Thermodynamics of electrolytes. II Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem.* 77 (19) (1973) 2300–2308.
- [7] W. Xu, Separation of ethanol–acetone–butanol–water system using potassium fluoride (China), *Petrochem. Technol.* 125 (1) (1996) 32–34.