Liquid-Liquid Equilibrium for 1-Butanol-Water-KF and 1-Butanol-Water-K₂CO₃ Systems

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Abstract: KF or K_2CO_3 was added into the 1-butanol-water system and two phases were formed: water-rich phase (water phase) and 1-butanol-rich phase (1-butanol phase). The liquid-liquid equilibrium (LLE) data for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems were measured at 25 ℃ and showed that 1-butanol phase contained negligible salt and water phase contained negligible 1-butanol when the concentrations of KF and K_2CO_3 in the water phase were equal to or higher than 27.11% and 31.68%, respectively. Thus water could be separated efficiently from 1-butanol-water by adding KF or K_2CO_3 into the system. A theoretical calculation of LLE data was calculated by using the Pitzer theory to get water activity in the water phase, and by the models, such as the Wilson, NRTL or the UNIQUAC for the 1-butanol phase. For 1-butanol-water-KF system, the experimental data were found in good agreement with the calculated results by using Pitzer theory and Wilson equation, while for 1-butanol-water-K_2CO_3 system, the experimental data were found in good agreement with the calculated results by using Pitzer theory and UNIQUAC equation.

Key words: 1-butanol-water-KF; 1-butanol-water-K_2CO_3; liquid-liquid equilibrium; Pitzer equation; Wilson equation; NRTL equation; UNIQUAC equation; salting-out effect

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The 1-butanol forms azeotrope with water[1], and cannot be extracted to a high concentration from the aqueous solution by the ordinary distillation method. In this case, azeotropic distillation is often used. For azeotropic distillation, however, both the azeotropic entrainer and water must be vaporized into the top of an azeotropic distillation column in order to obtain the anhydrous 1-butanol at the bottom. In addition, the amount of azeotropic entrainer is usually large, which leads to high energy consumption. For this reason, use of KF or K_2CO_3 to separate isopropanol-water[2] and ethanol-acetone-1-butanol-water[3] systems was studied. But no study on the liquid-liquid equilibrium (LLE) of 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems were reported. The LLE data for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems were necessary for separating 1-butanol-water system by using KF or K_2CO_3, and the calculation of LLE data was of practical and theoretical value. In this work, LLE data for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems at 25 ℃ were measured, a theoretical calculation of LLE data was calculated by using the Pitzer theory to get water activity in the water phase, and by the models, such as the Wilson, NRTL or the UNIQUAC for the 1-butanol phase. The ex-

perimental data were found in good agreement with the calculated results for system of 1-butanol-water-KF by using the Pitzer theory and the Wilson equation, while for system of 1-butanol-water-K_2CO_3 by using the Pitzer theory and the UNIQUAC equation.

1 Experimental

1.1 Materials and Analysis

Analytical grade ethanol and 1-butanol (Jinan Chemical Reagents Factory) was purified by fine distillation. Their purities were checked by gas chromatography, and no impurity peaks were found. Analytical grade KF (Zhenjiang Chemical Reagents Factory) and K_2CO_3 (Changshu Chemical Reagents Factory) were dried at 140 °C for 8 h before use. Water distilled twice in the presence of $KMnO_4$ was used.

The concentrations of water and 1-butanol were determined by gas chromatography. The salt content was determined by weighing and mass balance method.

The specifications of the gas chromatograph are as follows. Detector: thermal conductivity detector; Carrier gas: H_2; Column packing: GDX-401; Column length: 3 m; Column temperature:130 °C; Vaporization temperature: 140 °C; TC current: 150 mA; Carrier gas flow rate: 40 mL/min.

1.2 Apparatus and Procedure

Certain volumes of 1-butanol and distilled water were added into the test-tube with pipet, and a certain amount of salt weighed with Ohaus Electric Balance (Ohaus Corp. Florham Park,JN USA) was put into the test-tube, then the test-tube were shaken (150 r/min) at 25 °C for 3 h in a SHA-C Constant-Temperature Shaker with Water Bath(Changzhou Guohua Electric Appliance Co. Ltd.), the temperature was controlled and maintained with an accuracy of within 0. 1 °C. Followed by standing still for 3 h. After that, liquid-liquid equilibrium was reached, 1-butanol was analyzed by SQ-206 Gas Chromatography (Beijing Analytical Apparatus Factory), and salt concentration was obtained by weighing and mass balance method. In order to verify the reliability of experimental results, the liquid-liquid equilibrium data of ethanol-water-K_2CO_3 system at 25 °C were determined and compared with those from the Ref. [4]. The maximum deviation of ethanol content in the ethanol phase was 0. 8% when the concentration of K_2CO_3 in the water phase was the same, which showed that the experimental data were reliable by the present experimental method.

1.3 Measurement of Liquid-Liquid Equilibrium Data

The LLE data for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems were measured at 25 °C when the concentrations of KF and K_2CO_3 in the water phase were equal to or higher than 27. 11% and 31. 68% (m/m), respectively. No 1-butanol in the water phase was detected by gas chromatography and the salt content in 1-butanol phase was 1. 0×10^{-4}, so the LLE data with negligible 1-butanol in water phase and negligible salt in 1-butanol phase were listed in Table 1 and Table 2, which demonstrated that water could be separated from 1-butanol-water by adding KF or K_2CO_3 into the system.

Table 1　LLE data and calculated results in mass fraction for system of 1-butanol -water -KF at 25 °C　　　　%

No.	Experment data				Calculated results[1]				Calculated results[2]				Calculated results[3]			
	water phase		1-butanol phase		water phase		1-butanol phase		water phase		1-butanol phase		water phase		1-butanol phase	
	ω_2	ω_3	ω_2	ω_1	ω_2	ω_3	ω_2	ω_1	ω_2	ω_3	ω_2	ω_1	ω_2	ω_3	ω_2	ω_1
1	72. 89	27. 11	5. 93	94. 07	71. 81	28. 19	6. 26	93. 74	68. 69	31. 31	7. 09	92. 91	71. 24	28. 76	6. 24	93. 76
2	70. 13	29. 87	5. 35	94. 65	69. 77	30. 23	5. 45	94. 55	66. 42	33. 58	6. 31	93. 69	68. 08	31. 92	5. 72	94. 28
3	67. 82	32. 18	4. 68	95. 32	67. 18	32. 82	4. 85	95. 15	63. 61	36. 39	5. 70	94. 30	64. 37	35. 63	5. 30	94. 70
4	64. 16	35. 84	4. 10	95. 90	64. 62	35. 38	4. 00	96. 00	60. 95	39. 05	4. 81	95. 19	61. 05	38. 95	4. 64	95. 36
5	61. 88	38. 12	3. 64	96. 36	62. 35	37. 65	3. 54	96. 46	58. 72	41. 28	4. 30	95. 70	58. 26	41. 74	4. 24	95. 76
6	59. 20	40. 80	3. 10	96. 90	59. 47	40. 53	3. 06	96. 94	55. 70	44. 30	3. 74	96. 26	54. 84	45. 16	3. 79	96. 21
7	56. 74	43. 26	2. 96	97. 04	58. 62	41. 38	2. 66	97. 34	54. 89	45. 11	3. 28	96. 72	53. 88	46. 12	3. 40	96. 60
8	54. 75	45. 25	2. 75	97. 25	57. 29	42. 71	2. 37	97. 63	53. 59	46. 41	2. 94	97. 06	52. 35	47. 65	3. 09	96. 91
9	52. 63	47. 37	2. 08	97. 92	52. 58	47. 42	2. 09	97. 91	48. 82	51. 18	2. 60	97. 40	47. 04	52. 96	2. 79	97. 21
10	49. 60	50. 40	1. 76	98. 24	49. 75	50. 25	1. 74	98. 26	45. 92	54. 08	2. 18	97. 82	43. 86	56. 14	2. 38	97. 62
Absolute mean deviation					0. 80	0. 80	0. 22	0. 22	3. 25	3. 25	0. 66	0. 66	3. 48	3. 48	0. 52	0. 52

Note:absolute mean deviation is $\sum\limits_{i=1}^{N} | \omega_{cal} - \omega_{exp} | / N$;No. :experiment number;ω_1 ,ω_2 ,ω_3 :Mass fraction of 1-butanol, water and KF, resecptively;

　　1) Based on the experiment data by using Pitzer and Wilson equations;
　　2) Based on the experiment data by using Pitzer and NRTL equations;
　　3) Based on the experiment data by using Pitzer and UNIQUAC equations

Table 2　LLE data and calculated results in mass fraction for system of 1-butanol -water -K₂CO₃ at 25 ℃　　　%

No.	Experiment data				Calculated results[1]				Calculated results[2]				Calculated results[3]			
	water phase		1-butanol phase		water phase		1-butanol phase		water phase		1-butanol phase		water phase		1-butanol phase	
	ω_2	ω_1	ω_2	ω_1	ω_2	ω_4	ω_2	ω_1	ω_2	ω_1	ω_2	ω_1	ω_2	ω_4	ω_2	ω_1
1	68.32	31.68	10.20	89.80	72.34	27.66	8.37	91.63	72.11	27.89	8.92	91.08	74.28	25.72	8.93	91.07
2	65.00	35.00	9.18	90.82	70.17	29.83	7.06	92.94	69.12	30.88	7.82	92.18	69.44	30.56	8.15	91.85
3	62.08	37.92	8.11	91.89	67.67	32.33	6.03	93.97	65.87	34.13	6.88	93.12	64.82	35.18	7.43	92.57
5	57.24	42.76	6.20	93.80	62.58	37.42	4.54	95.46	59.94	40.06	5.38	94.62	57.32	42.68	6.18	93.82
6	55.19	44.81	5.57	94.43	60.67	39.33	3.98	96.02	57.87	42.13	4.77	95.23	54.96	45.04	5.63	94.37
7	52.91	47.09	5.02	94.98	58.90	41.10	3.40	96.60	56.02	43.98	4.13	95.87	52.91	47.09	5.02	94.98
8	51.24	48.76	4.35	95.65	56.58	43.42	3.00	97.00	53.70	46.30	3.68	96.32	50.41	49.59	4.57	95.43
9	49.32	50.68	3.90	96.10	54.89	45.11	2.58	97.42	52.10	47.90	3.19	96.81	48.71	51.29	4.06	95.94
10	47.50	52.50	3.49	96.51	53.28	46.72	2.21	97.79	50.51	49.49	2.75	97.25	47.16	52.84	3.58	96.42
Absolute mean deviation					5.38	5.38	1.67	1.67	3.15	3.15	0.95	0.95	1.62	1.62	0.38	0.38

Note: ω_1 is mass fraction of K₂CO₃, others is same as Table 1

2　Calculation of Liquid-Liquid Equilibrium Data

2.1　Calculation Basis

Experimental data show that the 1-butanol-water-salt system can be separated into two phases: water-salt phase(water phase) and 1-butanol-water phase (1-butanol phase). The water phase can be calculated by the Pitzer theory and the 1-butanol phase by either the Wilson equation, NRTL equation or the UNIQUAC equation.

2.2　Calculation Method

2.2.1　Water phase

The water phase consisting of water and salt can be calculated by the Pitzer theory[5].

$$\begin{cases} I = \dfrac{1}{2}\sum_i m_i Z_i^2 \\[2mm] \Phi = -\mid Z_M Z_X \mid A_\Phi \dfrac{I^{0.5}}{1+1.2I^{0.5}} + m\dfrac{2v_M v_X}{v} \\[2mm] \qquad \cdot [\beta^{(0)} + \beta^{(1)} e^{-2I^{0.5}}] + m^2 \dfrac{2(v_M v_X)^{3/2}}{v}c + 1 \\[2mm] \ln a_2 = -\dfrac{vmM_2}{1\,000}\Phi \end{cases}$$

where I (mol/kg) is the ionic strength, m_i (mol/kg) is the i-ion mass molar concentration, Z_i is the number of the i-ion charges, Φ is the Osmotic parameter for aqueous electrolytes, Z_M and Z_X are the charges (in electronic units) on ions M and X while v_M and v_X are the numbers of these ions in the formula, also $v = v_M + v_X$, A_Φ is the Debye-Hückel coefficient, $\beta^{(0)}$, $\beta^{(1)}$ and c are Pitzer parameters, m (mol/kg) is the salt mass molar concentration, M_2 is water molecular weight, a_2 is water activity

in water phase.

For KF since the values of Z_M, Z_X, v_M, v_X and v are 1,1,1,1 and 2, respectivly, and the simplified equations are as follows:

$$\begin{cases} I = m \\[2mm] \Phi = -A_\Phi \dfrac{I^{0.5}}{1+1.2I^{0.5}} + m[\beta^{(0)} + \beta^{(1)} e^{-2I^{0.5}}] \\[2mm] \qquad + m^2 c + 1 \\[2mm] \ln a_2 = -0.036\, m\Phi \end{cases}$$

where the values of $\beta^{(0)}$, $\beta^{(1)}$ and c are taken as $\beta^{(0)} = 0.082$, $\beta^{(1)} = 1.085$, $c = -0.002\,024$[6], respectively; according to the Ref. [6], A_Φ is 0.391 at 25 ℃.

For K₂CO₃, since the values of Z_M, Z_X, v_M, v_X and v are 1,2,2,1 and 3, respectivly, the simplified equations for K₂CO₃ are as follows:

$$\begin{cases} I = 3m \\[2mm] \Phi = -2A_\Phi \dfrac{I^{0.5}}{1+1.2I^{0.5}} + \dfrac{4}{3}m[\beta^{(0)} + \beta^{(1)} e^{-2I^{0.5}}] \\[2mm] \qquad + \dfrac{2^{2.5}}{3}m^2 c + 1 \\[2mm] \ln a_2 = -0.054\, m\Phi \end{cases}$$

where the values of $\beta^{(0)}$, $\beta^{(1)}$ and c are taken as $\beta^{(0)} = 0.128\,8$, $\beta^{(1)} = 1.433\,0$, $c = -0.000\,5$, respectively, according to the Ref. [7], A_Φ is the same as above.

2.2.2　1-Butanol phase

For calculation of the 1-butanol-water-KF and 1-butanol-water-K₂CO₃ systems in phase equilibrium, pure water is selected as the standard state in the water phase and in the 1-butanol phase, thus water activities both in water and 1-butanol phases are equal. If the salt mass molar concentration in water phase is known, water activity can be calculated by using the Pitzer equation, therefore the composition in the 1-butanol phase can be obtained by using either the Wilson equation[6], NRTL

equation[8] or the UNIQUAC equation[9].

The Wilson equation is as follows:

$$\begin{cases} a_2 = \gamma_2 x_2 \\ \ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) \\ \quad + x_1\left[\dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \\ x_1 + x_2 = 1 \end{cases}$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left(-\frac{\Delta g_{12}}{RT}\right), \Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left(-\frac{\Delta g_{21}}{RT}\right),$$

$$V_1^L = 91.97, V_2^L = 18.07^{[1]}$$

a_2 is water activity in 1-butanol phase, γ_2 is water activity coefficient in 1-butanol phase; x_1 and x_2 are molar fraction of 1-butanol and water in 1-butanol phase, respectively; Λ_{12} and Λ_{21} are Wilson equation parameters; V_1^L and V_2^L (mL/mol) are molar volume of pure 1-butanol and water, respectively; Δg_{12} (J/mol) is interaction energy between 1-butanol and water, Δg_{21} (J/mol) is interaction energy of water to 1-butanol; R is gas constant [J/(mol · K)], T (K) is absolute temperature.

The NRTL equation is as follows:

$$\begin{cases} a_2 = \gamma_2 x_2 \\ \ln\gamma_2 = x_1^2\left[\dfrac{\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^2} + \dfrac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \\ x_1 + x_2 = 1 \end{cases}$$

where

$$\tau_{12} = \Delta g_{12}/RT, \tau_{21} = \Delta g_{21}/RT,$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), G_{21} = \exp(-\alpha_{12}\tau_{21})$$

a_2 is water activity in 1-butanol phase; γ_2 is water activity coefficient in 1-butanol phase; x_1 and x_2 are molar fraction of 1-butanol and water in 1-butanol phase, respectively; τ_{12} and τ_{21} are NRTL equation parameters; α_{12} is NRTL equation sequence parameter; Δg_{12} (J/mol) is interaction energy parameter between 1-butanol and water, Δg_{21} (J/mol) is interaction energy of water to 1-butanol; R and T are the same as above.

The UNIQUAC equation is as follows:

$$\begin{cases} a_2 = \gamma_2 x_2 \\ \ln\gamma_2 = \ln\dfrac{v_2}{x_2} + 5q_2\ln\dfrac{s_2}{v_2} + v_1\left(l_2 - \dfrac{r_2 l_1}{r_1}\right) \\ \quad - q_2\ln(s_1\tau_{12} + s_2) \\ \quad + s_1 q_2\left(\dfrac{\tau_{12}}{s_1\tau_{12} + s_2} - \dfrac{\tau_{21}}{s_2\tau_{21} + s_1}\right) \\ x_1 + x_2 = 1 \end{cases}$$

where

$$\tau_{12} = \exp(-\Delta g_{12}/RT), \tau_{21} = \exp(-\Delta g_{21}/RT),$$

$$l_1 = 5(r_1 - q_1) - (r_1 - 1), l_2 = 5(r_2 - q_2) - (r_2 - 1),$$

$$s_1 = q_1 x_1/(q_1 x_1 + q_2 x_2), s_2 = 1 - s_1,$$

$$v_1 = r_1 x_1/(r_1 x_1 + r_2 x_2), v_2 = 1 - v_1,$$

$$r_2 = 0.92, q_2 = 1.4, r_1 = 3.4543, q_1 = 3.0520^{[1]}$$

a_2 is water activity in 1-butanol phase; γ_2 is water activity coefficient in 1-butanol phase; x_1 and x_2 are molar fraction of 1-butanol and water in 1-butanol phase, respectively; τ_{12} and τ_{21} are UNIQUAC equations parameters; q_1 and q_2 are area parameter of 1-butanol and water, respectively; s_1 and s_2 are area fraction of 1-butanol and water, respectively; r_1 and r_2 are volume parameter of 1-butanol and water, respectively; v_1 and v_2 are volume fraction of 1-butanol and water, respectively; Δg_{12} (J/mol) is interaction energy parameter between 1-butanol and water, Δg_{21} (J/mol) is interaction energy of water to 1-butanol; R and T are the same as above.

Gmehling et al[1] gave energy parameters of the Wilson, NRTL and UNIQUAC equations for the 1-butanol water system which were listed in Table 3. And the equation parametors of Wilson, NRTL and UNIQUAC equations were listed in Table 4.

2.3 Calculation

In order to compare the experimental data with the calculated results for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems, the composition of water phase corresponding to the same composition of the 1-butanol phase and that of 1-butanol phase with the same composition of water phase were calculateded from the equations and the

Table 3　Energy Parameters of Wilson and NRTL and UNIQUAC equations

System	Wilson		NRTL			UNIQUAC	
	Δg_{12}	Δg_{21}	Δg_{12}	Δg_{21}	α_{12}	Δg_{12}	Δg_{21}
1-butanol-water	8 043.56	6 503.44	2 321.71	9 273.28	0.410 6	447.73	2 066.50

Table 4　Equation Parameters of Wilson and NRTL and UNIQUAC equations

System	Wilson		NRTL			UNIQUAC	
	Λ_{12}	Λ_{21}	τ_{12}	τ_{21}	α_{12}	τ_{12}	τ_{21}
1-butanol-water	0.007 657	0.369 2	0.936 6	3.741 0	0.410 6	0.834 8	0.434 5

results were listed in Table 1 and Table 2, which demonstrated that the experimental data were in good agreement with the calculated results for system of 1-butanol-water-KF by using the Pitzer theory and the Wilson equation, while for system of 1-butanol-water-K_2CO_3 by using the Pitzer theory and the UNIQUAC equation.

3 Conclusion

LLE data for 1-butanol-water-KF and 1-butanol-water-K_2CO_3 systems were measured at 25 ℃. 1-Butanol concentrations in 1-butanol phase can reach over 98% and 96% when the concentrations of KF and K_2CO_3 in the water phase are 50.4% and 52.5%, respectively. Thus water can be separated efficiently from 1-butanol-water by adding KF or K_2CO_3 into the system. A theoretical calculation of LLE data was calculated by using the Pitzer theory to get water activity in the water phase, and by the models, such as the Wilson, NRTL or the UNIQUAC for the 1-butanol phase. The experimental data were found in good agreement with the calculated results for system of 1-butanol-water-KF by using the Pitzer theory and the Wilson equation, while for system of 1-butanol-water-K_2CO_3 by using the Pitzer theory and the UNIQUAC equation.

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