VAPOR-LIQUID EQUILIBRIA OF A MINUTE AMOUNT OF FURFURAL IN WATER-ETHANOL-1-PROPANOL SYSTEM

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Vapor-liquid equilibria of water-ethanol-1-propanol system containing a minute amount of furfural were measured at atmospheric pressure by use of an Othmer-type still.

The experimental results are represented by two triangular diagrams against the liquid compositions of the major components (water, ethanol and 1-propanol), in which one diagram shows the vapor compositions of ethanol and 1-propanol, and another diagram shows the equilibrium ratio of the trace component (furfural).

The curved surface of the equilibrium ratio of the trace component exhibits a bow-shaped downward plane in the water-rich area and shows a ridge in the neighborhood of the water-1-propanol side. In the alcohol (ethanol and 1-propanol)-rich area it exhibits a saddle-shaped face.

Introduction

To clarify the behavior of a trace component in distillation, information regarding the vapor-liquid equilibrium of the trace component is required. In recent years, the experimental data of the vapor-liquid equilibrium of the system containing a trace component have gradually accumulated. These data are, however, those of the trace component in the major system consisting of one solvent or binary solution, except for the vapor-liquid equilibria of a trace component (furfural) in the ternary (water-methanol-ethanol) system measured by the authors (Ikari *et al.*, 1997).

In this paper, the water-ethanol-1-propanol system was selected as the major system, and the vapor-liquid equilibria of the ternary system containing a minute amount of furfural were measured at atmospheric pressure by use of an Othmer-type still.

The water-1-propanol system and the ethanol-1-propanol system containing a minute amount of furfural were also measured and the equilibrium ratio curves of the trace component were obtained.

The equilibrium ratio of the trace component in the ternary system is represented by a curved surface on the triangular diagram of the major components. It is found to exhibit a unique saddle-shaped face.

1. Experiment

1.1 Materials

Furfural was purified by distilling a guaranteed reagent under reduced pressure in a stream of

nitrogen. Distilled water was used.

Reagent grade ethanol for test and research was fractionally distilled after being left for more than 3 days with about 3.5 g of m-phenylenediamine hydrochloride per 1 liter. Guaranteed grade 1-propanol was fractionally distilled. When anhydrous ethanol or 1-propanol was required, the distillate was dehydrated by distillation after being boiled under reflux with about 5 g of magnesium foil per 1 liter and a small amount of iodine as a catalyst.

1.2 Apparatus and procedure

Experiments were performed at atmospheric pressure by use of an Othmer-type still.

A mixed solution of prescribed proportions of water, ethanol and 1-propanol containing approximately 0.05 wt% furfural was charged in the still. The apparatus was operated for 8 h. Upon cooling to room temperature, samples of vapor and liquid phases were drawn for analysis.

1.3 Analysis

1.3.1 Determination of a minute amount of furfural

The concentration of furfural was measured by an absorptiometric method. The sample was diluted properly with water, and absorbance was measured in the range of 350 – 250 nm. From the absorbance of the peak, the concentration of furfural was determined by use of a calibration curve shown in Fig. 1.

A double-beam spectrophotometer (Hitachi, Model 124) was used.

1.3.2 Density curves of binary systems The density of the samples was measured at 298.2 K by a digital density meter (Anton Paar, DMA-40).

In Fig. 2, the density curves of three binary systems were drawn for the purpose of plotting the three sides of a triangular diagram described in the next section.

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Fig. 1 Calibration curve of furfural

Fig. 2 Density curves of three binary systems at 298.2 K and atmospheric pressure

The concentration of 1-propanol in a water-1-propanol system containing a minute amount of furfural was obtained by use of the density curve of the water-1-propanol system shown in Fig. 2.

1.3.3 Constant density curves of water-ethanol-1-propanol system

The densities of 76 mixtures of the three major components were measured at 298.2 K and plotted on a triangular diagram. By dividing the interval between every two adjacent data points in proportion, the spots of the rounded-value density were obtained. The constant density curves were drawn by connecting these spots with smoothed curves. The triangular diagram is shown in Fig. 3.

1.3.4 Measurement of the ratio of 1-propanol to

Fig. 3 Diagram of constant density lines of water-ethanol-1-propanol system at 298.2 K and atmospheric pressure

Fig. 4 Calibration curve for ratio of 1-propanol to ethanol

ethanol As can be seen in Fig. 3, the constant density lines are parallel to the base of the triangular diagram. To determine the concentration of the ternary system, the concentration ratio of 1-propanol to ethanol is required in addition to the density. Taking into account that the samples contained water to a considerable extent, a steam gas chromatograph (Ohkura, GC-103) was used to measure the concentration ratio.

Figure 4 shows the calibration curve prepared previously.

1.3.5 Determination of water concentration The wt% of ethanol, which was obtained from the weight ratio of 1-propanol to ethanol, is plotted on the base of the triangular diagram shown in Fig. 3. A straight line joining this spot and the apex of the triangle is

Table 1 Vapor-liquid equilibrium data at atmospheric pressure for water-1-propanol-furfural systems

Exp. No.	Concentration in liquid phase [mol %]			Concentration in vapor phase [mol %]			Equilibrium ratio of furfural [—]
	Water	1-Propanol	Furfural	Water	1-Propanol	Furfural	
1	100.0	0	0.00629	100.0	0	0.0586	9.32
2	100.0	0	0.00661	100.0	0	0.0487	7.38
3	97.8	2.2	0.00962	76.8	23.1	0.0452	4.70
4	96.9	3.1	0.0101	73.6	26.4	0.0295	2.90
5	95.2	4.8	0.0110	67.0	33.0	0.0220	2.01
6	93.0	7.0	0.0112	65.7	34.3	0.0181	1.61
7	88.5	11.5	0.0125	63.7	36.3	0.0135	1.09
8	83.7	16.3	0.0157	62.2	37.8	0.0122	0.776
9	79.9	20.1	0.0152	61.1	38.9	0.00978	0.644
10	75.3	24.7	0.0166	61.3	38.7	0.00917	0.552
11	62.9	37.1	0.0198	58.5	41.5	0.00778	0.394
12	50.5	49.5	0.0213	55.2	44.8	0.00661	0.311
13	42.3	57.7	0.0261	51.8	48.2	0.00743	0.284
14	31.3	68.7	0.0284	48.5	51.5	0.00790	0.279
15	15.2	84.8	0.0345	34.8	65.2	0.0103	0.298
16	9.3	90.6	0.0314	22.5	77.5	0.00952	0.304
17	0	100.0	0.0331	0	100.0	0.0120	0.362

Table 2 Vapor-liquid equilibrium data at atmospheric pressure for ethanol-1-propanol-furfural systems

Exp. No.	Concentration in liquid phase [mol %]				Concentration in vapor phase [mol %]				Equilibrium ratio of furfural [—]
	Water	Ethanol	1-Propanol	Furfural	Water	Ethanol	1-Propanol	Furfural	
1	0.09	99.9	0	0.0241	0.11	99.9	0	0.00549	0.228
2	0.26	91.9	7.8	0.0258	0.35	94.6	5.0	0.00621	0.241
3	0.28	82.0	17.7	0.0285	0.34	90.8	8.8	0.00713	0.250
4	0.20	72.9	26.9	0.0315	0.30	84.0	15.7	0.00825	0.262
5	0.26	60.6	39.1	0.0339	0.42	74.8	24.8	0.00966	0.285
6	0.10	51.4	48.5	0.0347	0.16	67.2	32.7	0.00999	0.288
7	0.31	45.4	54.3	0.0321	0.63	61.6	37.8	0.00971	0.303
8	0.41	29.5	70.1	0.0347	0.83	45.0	54.2	0.0113	0.325
9	0.07	21.9	78.0	0.0346	0.20	35.2	64.6	0.0118	0.342
10	0.13	13.3	86.5	0.0359	0.32	23.3	76.4	0.0123	0.341

drawn. The points of intersection of the straight line and two constant density lines, which are the upper and lower sides of the density of the sample, were obtained. The wt% of water, which corresponds to the density of the sample, was determined by dividing the interval between the two points in proportion.

In the ethanol-1-propanol-furfural system, a minute amount of water was also present. The concentration of water in the system was determined with a Karl Fisher water analyzer (Mitsubishi Chemical Industry, CA-02).

2. Results and Discussion

Experimental vapor-liquid equilibrium data at atmospheric pressure are listed in **Tables 1–3**.

2.1 Water-1-propanol-furfural system

From the data of Table 1, the mole fractions on a trace component free basis and the equilibrium ratio of furfural were obtained by the following equations and plotted in **Figs. 5 and 6**.

$$x_3' = x_3/(x_1 + x_3), \quad y_3' = y_3/(y_1 + y_3), \quad K = y_4/x_4$$

In Fig. 5, binary data, which were obtained from a data book (Kogan, 1974), are also plotted for comparison.

Figure 6 shows the equilibrium ratio of the trace component (furfural) in the water-1-propanol system. For comparison, those in a water-methanol system (Ikari *et al.*, 1997) and in a water-ethanol system (Ikari and Toya, 1971) are also plotted in Fig. 6. It can be seen that the equilibrium ratio curve of furfural in the

Table 3 Vapor-liquid equilibrium data at atmospheric pressure for water-ethanol-1-propanol-furfural systems

Exp. No.	Concentration in liquid phase [mol %]				Concentration in vapor phase [mol %]				Equilibrium ratio of furfural [—]
	Water	Ethanol	1-Propanol	Furfural	Water	Ethanol	1-Propanol	Furfural	
1	5.53	89.3	5.14	0.0276	5.96	91.6	2.48	0.00661	0.239
2	5.35	85.1	9.59	0.0251	6.01	89.0	5.02	0.00591	0.236
3	4.47	5.17	90.4	0.0356	11.7	8.89	79.5	0.0125	0.353
4	10.5	84.5	5.00	0.0268	11.5	86.2	2.34	0.00631	0.235
5	10.4	79.3	10.3	0.0306	11.4	83.2	5.45	0.00713	0.233
6	10.0	59.9	30.1	0.0288	13.2	69.0	17.8	0.00717	0.249
7	9.54	49.7	40.8	0.0329	13.5	60.5	26.0	0.00843	0.256
8	9.52	40.2	50.3	0.0343	14.3	51.6	34.1	0.00949	0.276
9	10.3	28.8	60.8	0.0341	17.3	39.8	42.9	0.0100	0.294
10	9.99	9.80	80.2	0.0324	20.0	15.7	64.3	0.0102	0.315
11	9.53	4.96	85.5	0.0326	20.2	8.45	71.4	0.0106	0.325
12	9.88	2.38	87.7	0.0351	20.4	4.00	75.6	0.0120	0.341
13	20.1	75.4	4.58	0.0249	19.3	78.4	2.28	0.00617	0.248
14	20.4	69.7	9.89	0.0254	20.1	74.4	5.52	0.00611	0.241
15	19.8	59.9	20.4	0.0268	21.3	66.6	12.1	0.00654	0.244
16	20.4	39.6	40.0	0.0258	24.1	49.5	26.4	0.00667	0.259
17	20.1	19.7	60.2	0.0273	29.7	26.2	44.1	0.00790	0.289
18	20.1	9.58	70.3	0.0323	32.0	14.5	53.6	0.00968	0.299
19	20.6	4.86	74.6	0.0300	32.9	7.48	59.7	0.00905	0.302
20	20.0	2.22	77.8	0.0321	35.1	3.37	61.5	0.00993	0.310
21	30.5	67.2	2.33	0.0248	25.6	73.4	1.06	0.00635	0.256
22	30.0	65.1	4.90	0.0240	25.7	71.5	2.83	0.00619	0.258
23	30.3	59.6	10.1	0.0228	27.5	66.2	6.39	0.00575	0.252
24	30.2	59.0	10.8	0.0240	27.7	65.7	6.65	0.00603	0.251
25	29.8	39.8	30.4	0.0233	31.6	48.1	20.4	0.00600	0.258
26	29.8	30.1	40.1	0.0245	34.3	37.4	28.3	0.00655	0.267
27	29.6	15.1	55.3	0.0273	38.7	20.3	41.1	0.00782	0.286
28	29.9	5.09	65.0	0.0289	41.9	7.39	50.7	0.00881	0.304
29	29.6	2.66	67.7	0.0281	42.4	3.96	53.7	0.00846	0.301
30	29.5	1.16	69.3	0.0311	43.7	1.71	54.6	0.00920	0.295
31	40.3	54.9	4.77	0.0232	32.6	64.1	3.32	0.00639	0.276
32	40.2	49.7	10.1	0.0237	34.0	59.1	6.97	0.00675	0.285
33	40.1	39.8	20.1	0.0218	36.4	48.7	14.9	0.00611	0.280
34	39.7	19.6	40.7	0.0255	42.7	26.5	30.8	0.00732	0.287
35	40.0	9.80	50.2	0.0257	45.9	13.8	40.3	0.00765	0.297
36	39.6	4.66	55.7	0.0262	48.6	6.85	44.6	0.00807	0.308
37	50.5	39.3	10.2	0.0201	39.6	51.7	8.72	0.00652	0.325
38	50.2	24.7	25.0	0.0229	44.4	34.1	21.6	0.00738	0.323
39	49.8	9.93	40.2	0.0215	50.2	14.4	35.3	0.00696	0.324
40	49.6	4.73	45.6	0.0246	52.5	7.31	40.2	0.00799	0.324
41	49.7	2.22	48.1	0.0246	53.4	3.39	43.2	0.00803	0.326
42	55.7	39.7	4.62	0.0179	39.5	56.2	4.27	0.00637	0.355
43	60.7	29.3	10.0	0.0174	44.6	44.6	10.8	0.00703	0.405
44	60.4	19.8	19.8	0.0183	48.2	31.2	20.6	0.00687	0.375
45	60.1	9.89	30.0	0.0185	52.8	16.2	31.0	0.00685	0.371
46	60.0	2.07	37.9	0.0226	55.9	3.64	40.5	0.00860	0.381
47	71.3	23.8	4.91	0.0165	47.7	44.8	7.46	0.00893	0.541
48	71.1	14.5	14.4	0.0162	52.1	27.6	20.3	0.00836	0.515
49	71.0	9.32	19.7	0.0188	54.7	18.0	27.3	0.00935	0.498
50	70.8	4.74	24.5	0.0169	57.0	9.58	33.5	0.00805	0.476
51	70.4	2.03	27.6	0.0175	58.5	4.26	37.3	0.00831	0.474
52	81.3	14.1	4.61	0.0131	52.7	36.4	10.9	0.0104	0.796
53	81.1	9.38	9.50	0.0158	56.0	23.7	20.3	0.0121	0.762
54	81.0	4.66	14.3	0.0158	58.1	12.2	29.8	0.0115	0.727
55	91.3	4.40	4.26	0.0109	61.1	18.8	20.1	0.0172	1.58
56	100.0	0	0	0.00612	100.0	0	0	0.0438	7.15

Fig. 5 Comparison of vapor-liquid composition curve at atmospheric pressure for the major component system (water-1-propanol) in this work with that of binary system (water-1-propanol)

Fig. 7 Comparison of vapor-liquid composition curve at atmospheric pressure for the major component system (ethanol-1-propanol) in this work with that of binary system (ethanol-1-propanol)

Fig. 6 Equilibrium ratio curves at atmospheric pressure of the trace component (furfural)

water-1-propanol system is a bow-shaped curve and similar to that in the water-ethanol system.

2.2 Etanol-1-propanol-furfural system

From the data of Table 2, the mole fractions on a trace component free basis and the equilibrium ratio of furfural were obtained by the following equations and plotted in Figs. 7 and 8.

Fig. 8 Equilibrium ratio at atmospheric pressure of trace component (furfural) in ethanol-1-propanol-furfural system

$$x_2' = x_2 / (x_2 + x_3), \quad y_2' = y_2 / (y_2 + y_3), \quad K = y_4 / x_4$$

In Fig. 7, binary data, which were obtained from the data book (Kogan, 1974), are also plotted for comparison. In Figs. 5 and 7, it can be seen that the vapor-liquid equilibrium curve of the major components, prepared from their mole fractions on a trace component free basis, is coincident with the vapor-liquid equilibrium curve of the corresponding binary system.

Figure 8 shows the equilibrium ratio of the trace component (furfural) in the ethanol-1-propanol system.

2.3 Water-ethanol-1-propanol-furfural system

From the data of Table 3, the mol% of ethanol and 1-propanol in the vapor phase were plotted on each triangular diagram against the mol% of major

Fig. 9 Diagram of constant mol% curves at atmospheric pressure of ethanol and 1-propanol in vapor phase

components (water, ethanol and 1-propanol) in the liquid phase. The constant mol% curves in the vapor phase were drawn in the same way as the constant density curves were prepared, which is described in 1.3.3. Figure 9 shows the constant mol% curves of ethanol and 1-propanol in the vapor phase.

By the same way as the constant mol% curves in the vapor phase were made, the equilibrium ratios of furfural in Table 3 were plotted on a triangular diagram and the constant ratio curves were prepared, and shown in Fig. 10.

The equilibrium ratio of the trace component in the ternary system is represented by a curved surface on the triangular diagram. It can be seen in Fig. 10 that in the upper part of the triangle (water-rich area) the curved surface exhibits a bow-shaped downward plane, but in the lower part (alcohol-rich area) it becomes more complicated. In the neighborhood of the water-1-propanol side there is a ridge, which is parallel to the side. In the alcohol (ethanol and 1-propanol)-rich area, it exhibits a markedly imbalanced saddle-shaped face.

Conclusion

Vapor-liquid equilibria of the following systems containing a minute amount of furfural were measured at atmospheric pressure by use of an Othmer-type still:

- 1) water-1-propanol-furfural system
- 2) ethanol-1-propanol-furfural system
- 3) water-ethanol-1-propanol-furfural system.

From these data and that of the water-ethanol-furfural system, which was formerly studied (Ikari and

Fig. 10 Diagram of constant equilibrium ratio curves at atmospheric pressure of trace component (furfural)

Toya, 1971), the constant mol% curves of ethanol and 1-propanol in the vapor phase, and the constant equilibrium ratio curves of the trace component were drawn on triangular diagrams of the major components in the liquid phase.

It is found that the equilibrium ratio of the trace component exhibits a unique curved surface, which consists of a bow-shaped downward plane and a markedly imbalanced saddle-shaped face.

Accumulation of such information on a trace component seems to be essential to clarify the behavior of a trace component in distillation.

Nomenclature

K	= equilibrium ratio of trace component	[—]
x	= mole fraction in liquid	[—]
x'	= mole fraction in liquid on a trace component free basis	[—]
y	= mole fraction in vapor	[—]
y'	= mole fraction in vapor on a trace component free basis	[—]

<Subscript>

1	= water
2	= ethanol
3	= 1-propanol
4	= furfural

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