BEHAVIOR OF A MINUTE AMOUNT OF FURFURAL IN DISTILLATION OF AQUEOUS ETHANOL SOLUTION UNDER REDUCED PRESSURE

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To clarify the behavior of a trace component during distillation under reduced pressure, the vapor-liquid equilibrium ratio and the plate efficiency of the trace component are needed.

Vapor-liquid equilibria of aqueous ethanol solution containing about 0.05 wt % furfural (trace component) were measured at 25.3 kPa and 12.7 kPa by use of an Othmer-type still. The equilibrium ratio of furfural varies only slightly with the reduction of pressure.

Distillation experiments were carried out by use of an Oldershaw-type column at atmospheric pressure, 25.3 kPa and 12.7 kPa. A method for calculating the plate efficiency from the concentrations of distillate and bottoms was derived. The calculated results show that the Murphree vapor efficiency is little affected by pressure in the range of 12.7 kPa to atmospheric pressure.

By reducing the pressures, the bubble point of the system decreases remarkably, but the change of behavior of a trace component in distillation becomes quite small.

Introduction

To investigate the behavior of a trace component in distillation, the vapor-liquid equilibrium and the plate efficiency of the trace component are required. For the last decade several studies on these problems have been carried out by the authors.¹⁻⁸⁾ They, however, have been confined to distillation at atmospheric pressure. The behavior of a trace component in distillation under reduced pressure has not been reported up to this time.

In this study aqueous ethanol solutions containing a minute amount of furfural were used. Furfural is known as a representative trace impurity encountered in liquor production.

The vapor-liquid equilibria were measured by use of an Othmer-type still with a reduced pressure control system. The equilibrium ratios of furfural were obtained at 25.3 kPa and 12.7 kPa. Distillation experiments were carried out at atmospheric pressure, 25.3 kPa and 12.7 kPa by use of an Oldershaw-type column.

A simple mathematical model employing Murphree vapor efficiency as an adjustable parameter was derived. The efficiency of the trace component was obtained from the experimental concentrations of

distillate and bottoms.

The effect of pressure on the equilibrium ratio as well as the Murphree vapor efficiency (abbreviated EMV) of the trace component is discussed.

1. Vapor-Liquid Equilibrium

1.1 Experiment

For the measurement of vapor-liquid equilibrium, an Othmer-type still with a reduced pressure control system was used. A schematic diagram of the experimental apparatus is shown in Fig. 1. The pressure in the apparatus was maintained substantially constant by use of a needle valve and a buffer tank of about 20 liters.

An aqueous ethanol solution containing about 0.05 wt % furfural was charged in the still. The apparatus was operated for about 7 hours under the desired pressure. After the vacuum pump was stopped and the pressure was returned to atmospheric pressure, samples for both phases were withdrawn for analysis.

The density of the sample was measured at 25°C and the concentration of ethanol was determined from the density curve. The concentration of furfural was determined by spectrophotometry. After dilution of the sample with water, the absorbance of the peak at about 277 nm was measured and the concentration of furfural was determined with the calibration curve.

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Fig. 1. Schematic diagram of apparatus for vapor-liquid equilibrium measurements.

1.2 Results and discussion

The results of vapor-liquid equilibrium measurements are shown in Figs. 2 and 3.

Figure 2 shows the vapor-liquid equilibrium relation of the major components, water and ethanol. The co-ordinates of this figure, x'_2 and y'_2 , are respectively the mole fraction of ethanol in liquid and vapor phase, on a trace component free basis:

$$x'_2 = x_2 / (x_1 + x_2) \quad \text{and} \quad y'_2 = y_2 / (y_1 + y_2).$$

These x'_2 - y'_2 curves were compared with x_2 - y_2 curves obtained from the binary data¹⁰⁾ of the water-ethanol system at the same pressure. Both curves are substantially coincident. It can be found that the vapor-liquid composition curve of the major components is only slightly affected by the reduction of pressure.

The equilibrium ratio of the trace component ($\equiv y_3/x_3$) is plotted against x'_2 in Fig. 3, in which the data⁹⁾ at atmospheric pressure are also plotted for comparison. The curves at 25.3 kPa and 12.7 kPa show nearly identical results and are located slightly above the curve at atmospheric pressure. The effect of pressure on the equilibrium ratio of furfural appears to be relatively small.

On the contrary, the bubble point is affected remarkably by the reduction of pressure. In the case of 50 mol% ethanol solution, the bubble point changes from 80°C at 101.3 kPa to about 50°C at 25.3 kPa and 36°C at 12.7 kPa.

2. Distillation Experiments

2.1 Apparatus and procedure

Distillation experiments were carried out by use of a ten-stage Oldershaw-type column, 50 mm in diameter by 45 mm tray spacing, with vacuum jacket. A schematic diagram of the apparatus is shown in Fig. 4. The apparatus was connected with the same reduced pressure control system as shown in Fig. 1. The still consisted of a 1-liter flask with three necks, in one of which a capillary tube was mounted to prevent bumping. Thermocouples for temperature measure-

Fig. 2. Vapor-liquid composition curves of the major component (water-ethanol).

Fig. 3. Equilibrium ratio curves of the trace component (furfural).

Fig. 4. Schematic diagram of apparatus for distillation experiments.

ment were located at six points.

A feed solution of the specified concentration was charged in the still. Under a desired pressure the apparatus was operated for 3 to 6 hours according to the vapor rate until steady state. Samples were withdrawn from the reservoir and the still. They were analysed by the same method as stated in the previous section.

2.2 Experimental results

The experimental conditions and results of the first series of experiments are shown in **Table 1**. To reveal the effect of pressure and the vapor rate, these runs were carried out at a constant reflux ratio ($=8$) and at nearly constant feed compositions.

In the next section we determine the EMV of the trace component by using the experimentally obtained concentrations in distillate and bottoms. In these calculations we need the ethanol concentration in the liquid on each plate in the column, because the equilibrium ratio of the trace component is a function of ethanol concentration. It is assumed that the ethanol concentrations are obtained by the distillation calculation, as will be mentioned in the next section.

The error inherent in the calculated ethanol concentration may cause some error in the determination of EMV of the trace component. To eliminate the error an azeotropic mixture of water and ethanol containing a minute amount of furfural was used as a feed solution in the second series of experiments. The experimental conditions and results of this series are shown in **Table 2**.

3. Calculation of Plate Efficiency

3.1 Derivation of equations

A schematic model of our distillation experiments is shown in **Fig. 5**.

The following assumptions have been made.

- (1) The condenser is a total condenser.
- (2) The conditions of constant molal overflow are applied.
- (3) The EMV of the major component and that of the trace component are each assigned a constant value throughout the column.
- (4) The efficiencies at still are unity.
- (5) The presence of a trace component does not affect the equilibrium relation of only the major component.
- (6) The equilibrium ratio of a trace component is a function of the concentration of the major component, but is independent of the concentration of the trace component.

From the equilibrium relation ($y_n^* = K_n x_n$) and the definition of EMV, the following equation is derived.

$$y_n = EK_n x_n + (1 - E)y_{n+1} \quad (1)$$

Assumptions (1) and (4) yield, respectively,

$$y_1 = x_D = x_0 \quad (2)$$

$$y_{N+1} = K_{N+1} x_{N+1} \quad (3)$$

Material balances around the bottom and an arbitrary plate n ($1 < n \leq N$) result in, respectively,

$$x_N = (V/L)y_{N+1} - (D/L)x_D \quad (4)$$

$$x_{n-1} = x_n + (V/L)(y_n - y_{n+1}) \quad (5)$$

Here, Eq. (1) through Eq. (5) hold for any component, but only two of the EMV's are independent of each other.

To determine EMV from the experimentally obtained concentrations of distillate (x_D) and bottoms (x_{N+1}), the following procedure was used. Initially, the value of E is assumed. By use of Eqs. (3), (4), (5) and (1), plate-to-plate calculation is performed from the bottom to the top plate. If the calculated value of y_1 does not agree with x_D within the tolerance, the value of E is adjusted and the calculations are iterated.

For the first series of experiments in **Table 1**, the calculation procedure was adopted first for ethanol among the major components and second for the trace component.

For the second series of experiments in **Table 2**, the calculation procedure was adopted only for the trace component, because the ethanol concentration was almost unchanged on all plates in the column and the equilibrium ratio of furfural was regarded as constant in this ethanol concentration range, as shown in **Fig. 3**.

3.2 Results and discussion

The calculated values of EMV are included in the last columns of **Tables 1** and **2**.

In experiments No. 5 to 12 in **Table 2**, the samples were withdrawn after the pressure was returned to atmospheric pressure. The concentration of furfural in the bottoms was corrected for the liquid on the plates fallen into the bottom by use of the liquid holdup on the plates, which had been determined as about 10% of the liquid in the column. By this correction the EMV of furfural became about 1.8% greater (maximum 2.7%).

The values of EMV in **Table 1** are plotted in **Fig. 6**, which shows that EMV is not affected by the vapor rate when the vapor rate becomes larger than about $30 \text{ g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$. No effect of pressure on the EMV of ethanol can be observed. The EMV of furfural is recognized to become lower by the reduction of pressure, but the effect is not so large.

A typical diagram of the calculated concentration profiles in the column is shown in **Fig. 7**. In the lower part of the column, the concentration of ethanol decreases rapidly and accordingly the concentration of furfural represents a peak.

Table 1. Experimental results of distillation for the water-ethanol-furfural system at constant reflux ratio (=8) and constant feed composition

Exp. No.	Vapor rate [g·cm ⁻² ·h ⁻¹]	Composition in feed [mol%]		Composition in distillate [mol%]		Composition in bottoms [mol%]		Murphree vapor efficiency [—]	
		Ethanol	Furfural	Ethanol	Furfural	Ethanol	Furfural	Ethanol	Furfural
Pressure = atmospheric pressure									
1	24.5	11.61	0.0221	83.24	4.27 × 10 ⁻⁵	4.93	0.0235	0.816	0.714
2	24.8	11.61	0.0221	83.86	4.89 × 10 ⁻⁵	5.06	0.0231	0.884	0.698
3	28.4	11.61	0.0220	84.07	4.30 × 10 ⁻⁵	4.48	0.0225	0.942	0.726
Pressure = 25.3 kPa									
4	17.1	11.86	0.0228	84.70	4.65 × 10 ⁻⁵	6.36	0.0229	0.855	0.744
5	29.4	11.93	0.0223	83.86	1.27 × 10 ⁻⁴	5.66	0.0229	0.804	0.690
6	51.6	11.87	0.0226	83.86	1.58 × 10 ⁻⁴	5.85	0.0230	0.802	0.670
7	59.7	11.92	0.0222	83.45	1.70 × 10 ⁻⁴	5.52	0.0217	0.780	0.668
8	94.7	11.63	0.0217	84.07	2.14 × 10 ⁻⁴	5.25	0.0218	0.822	0.655
Pressure = 12.7 kPa									
9	15.9	11.78	0.0225	84.91	1.89 × 10 ⁻⁴	5.75	0.0226	0.840	0.669
10	28.0	11.85	0.0221	84.70	3.89 × 10 ⁻⁴	5.71	0.0222	0.822	0.610
11	39.3	11.79	0.0219	84.28	4.19 × 10 ⁻⁴	5.06	0.0215	0.794	0.618
12	68.7	11.86	0.0219	85.12	4.75 × 10 ⁻⁴	5.34	0.0218	0.863	0.604

Table 2. Experimental results of distillation for the water-ethanol-furfural system of azeotropic feed mixture (water-ethanol)

Exp. No.	Reflux ratio [—]	Vapor rate [g·cm ⁻² ·h ⁻¹]	Composition in feed [mol%]		Composition in distillate [mol%]		Composition in bottoms [mol%]		Murphree vapor efficiency of furfural [—]
			Ethanol	Furfural	Ethanol	Furfural	Ethanol	Furfural	
Pressure = atmospheric pressure									
1	8	24.7	88.32	0.0456	89.25	4.26×10^{-5}	87.85	0.0783	0.574
2	4	26.5	88.32	0.0456	89.02	3.96×10^{-5}	88.08	0.0688	0.584
3	2	27.6	89.88	0.0460	89.68	4.76×10^{-5}	89.41	0.0676	0.599
4	1	25.8	89.88	0.0461	89.92	6.30×10^{-5}	89.63	0.0692	0.645
Pressure = 25.3 kPa									
5	8	51.4	90.56	0.0462	91.97	4.50×10^{-5}	90.09	0.0618	0.594
6	4	50.6	90.56	0.0462	91.74	5.56×10^{-5}	90.09	0.0581	0.591
7	2	29.8	90.78	0.0464	91.74	4.44×10^{-5}	90.56	0.0470	0.634
8	1	27.5	90.78	0.0463	91.28	1.08×10^{-5}	90.55	0.0482	0.642
Pressure = 12.7 kPa									
9	8	43.5	91.01	0.0463	92.90	4.25×10^{-5}	90.33	0.0470	0.579
10	4	29.1	91.01	0.0464	92.67	4.46×10^{-5}	90.55	0.0494	0.599
11	2	30.0	91.01	0.0464	91.97	6.11×10^{-5}	90.54	0.0606	0.634
12	1	38.5	91.01	0.0464	91.74	1.20×10^{-4}	90.78	0.0484	0.645

Fig. 5. Model of distillation experiment.

Fig. 6. Murphree vapor efficiencies obtained from the experiments in Table 1.

Fig. 7. Calculated concentration profiles in the column (Exp. No. 6 in Table 1).

The values of EMV in Table 2 are plotted in Fig. 8, which shows that the EMV of furfural in the azeotropic solution of ethanol and water is not affected by the reduction of pressure. The EMV increases slightly as the reflux ratio decreases. The interpretation of this increase is difficult and is left to further examination.

A typical diagram of the calculated concentration profiles in the column is shown in Fig. 9, in which the EMV of furfural varies linearly in contrast to that in Fig. 7.

The differences of EMV of furfural in Table 2 (Fig. 8) with that in Table 1 (Fig. 6) seem to be attributable to the decrease of ethanol concentration in the lower part of the column shown in Fig. 7, because it is noted in the previous paper⁸⁾ that the EMV of furfural increases as the ethanol concentration decreases.

Conclusion

Vapor-liquid equilibria of aqueous ethanol solutions containing a minute amount of furfural were measured at 25.3 kPa and 12.7 kPa. When the pressure is reduced, the bubble point decreases remarkably, but the equilibrium ratio curve of the trace component does not vary significantly.

Distillation experiments were carried out by use of an Oldershaw-type column at atmospheric pressure, 25.3 kPa and 12.7 kPa. The Murphree vapor efficiency of the trace component was determined from the experimental concentrations of distillate and bottoms.

It is shown that the efficiency of the trace component is little affected by pressure in the range of 12.7 kPa to atmospheric pressure.

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Nomenclature

D	= distillate rate (returned to the bottom)	[mol/s]
E	= Murphree vapor efficiency	—
K	= equilibrium ratio	—
L	= liquid rate in the column	[mol/s]
V	= vapor rate in the column	[mol/s]

Fig. 8. Murphree vapor efficiencies obtained from the experiments in Table 2.

Fig. 9. Calculated concentration profiles in the column (Exp. No. 6 in Table 2).

x	= mole fraction in liquid	—
y	= mole fraction in vapor	—
y^*	= y in equilibrium with x	—

<Subscripts>

D	= distillate
N	= number of plates
n	= plate number
1	= water
2	= ethanol
3	= furfural (trace component)

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