

# Azeotropic Behavior of a Water + *n*-Propanol + Cyclohexane Mixture Using Cyclohexane as an Entrainer for Separating the Water + *n*-Propanol Mixture at 760 mmHg

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In this study, the phase behavior of a water + *n*-propanol + cyclohexane ternary mixture was experimentally investigated for feasibility using cyclohexane as an entrainer to the azeotropic distillation of a water + *n*-propanol azeotrope. The experimental results showed that this ternary mixture is partially miscible and exhibits as a heterogeneous azeotrope. The present experimental data include the binary water + *n*-propanol vapor–liquid equilibrium, the ternary water + *n*-propanol + cyclohexane vapor–liquid–liquid equilibrium, the heterogeneous azeotropic temperature, the bulk azeotropic liquid composition, and the individual liquid compositions at 760 mmHg. The correlation results of the binary data were satisfactory with the NRTL (*AIChE J.* **1968**, *14*, 135) and the UNIQUAC (*AIChE J.* **1975**, *21*, 116) models. The correlation result of the azeotropic ternary mixture with the NRTL model is fair, with the worst AARD % (10.69%) for the vapor composition of water and the AARD % values of the rest of the compositions smaller than 5%. The results with the UNIQUAC model show that the UNIQUAC model is not suitable to represent this azeotropic ternary system because of very large AARD % values. With the residual curve map (RCM) and the obtained liquid–liquid equilibrium curve, two conceptual azeotropic distillation schemes using cyclohexane as the entrainer were proposed to separate the azeotropic mixture of water and *n*-propanol. All of the thermodynamic properties required for constructing the RCM were obtained either from the literature or from the experiments performed in this study and include the boiling temperatures of all three constituent components, the azeotropic data of the constituent binary pairs, and the azeotropic data of the ternary system.

## Introduction

Although many separation processes such as membrane separation, molecular distillation, supercritical fluid extraction, and high rotating distillation (Higee) have been discussed extensively, the conventional distillation is still a very important process for separating liquid mixtures in chemical and related industries. To design a distillation scheme, the comprehensive understanding of the phase behavior of the mixture to be separated is necessary, particularly whether the mixture is azeotropic and whether the azeotrope is homogeneous or heterogeneous. It is well acknowledged that the existence of a ternary heterogeneous azeotropic mixture is important to the process of alcohol purification. For instance, benzene or cyclohexane was usually used as an entrainer added to the azeotropic alcohol and water mixture to form a heterogeneous azeotropic mixture so that further purification could be feasibly carried out.

The study of an azeotropic mixture is not a new subject. The experimental investigations, the empirical or semiempirical correlations, and the predictions of ternary mixtures have been done, and the results were reported in the literature, for instance, the studies by Chapman and Goodwin,<sup>3</sup> Gmehling and Böltz,<sup>4</sup> Wisniak and Segura,<sup>5</sup> and Eckert and Kubicek,<sup>6</sup> etc.

However, few reports were found for the heterogeneous azeotropic mixtures.

When cyclohexane was added to the azeotropic mixture of water and *n*-propanol, a partially miscible liquid mixture will be formed under the pressure of 760 mmHg. This ternary mixture was merely reported as an azeotropic mixture.<sup>7</sup> Because it is partially miscible, one might raise the question of whether this azeotrope is possibly heterogeneous. For this azeotrope, Horsley<sup>7</sup> gave only the azeotropic temperature and an azeotropic composition that must be the vapor composition (also equal to the bulk liquid composition) but not the heterogeneity of the liquid phase. To comprehensively understand the phase behavior of this ternary mixture, experiments were carried out at 760 mmHg to determine (1) the vapor–liquid–liquid equilibrium (VLE) behavior, (2) the heterogeneity of this azeotropic mixture, and (3) the VLE data, the azeotropic temperature, the overall (bulk) liquid azeotropic composition, and the azeotropic compositions of each liquid phase of this ternary mixture.

The experimental VLE data were then correlated with the models of UNIQUAC<sup>1</sup> and NRTL.<sup>2</sup> The correlation results showed that the UNIQUAC<sup>1</sup> model is not suitable to represent this mixture, while the correlation with the NRTL<sup>2</sup> model is reasonable. The pair interaction parameters of the constituent components of this mixture were then determined and reported. The correlation of the experimental azeotropic data had also been tried. Unfortunately, the correlation results showed

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that the estimated azeotropic temperature deviated from the experimental temperature smaller than 1 K, but the estimated azeotropic compositions have very large deviations from the experimental values. Thus, this correlation for azeotropic data was not reported here.

To separate the water and *n*-propanol mixture, two conceptual azeotropic distillation schemes using cyclohexane as the entrainer were proposed based on the boiling temperatures of three constituent components, the azeotropic properties of the constituent binary pairs and the ternary mixture, and the algorithm of the residual curve map (RCM).

### Theoretical Background

**VLE.** For the VLE of a mixture of three components, the phase equilibrium criteria must be of equal temperature and pressure throughout all of the phases and of equal fugacity of all constituent components in each phase expressed as

$$\hat{f}_i^v = \hat{f}_i^{l1} = \hat{f}_i^{l2} \quad i = 1-3 \quad (1)$$

If the fugacities of the vapor and liquid phases are expressed in terms of the fugacity coefficient and activity coefficient, respectively, then the above equilibrium equation becomes eq 2. This approach is called the  $\phi$ - $\gamma$  method for VLE, where  $f_i^{lo}$  is the standard

$$y_i \hat{\phi}_i^v P = x_i^j \gamma_i^j f_i^{lo} \quad i = 1, 2, \dots, n; j = 1, 2 \quad (2)$$

state of the liquid phase of component *i*. If the condensed phase of pure component *i* at the system temperature and pressure is chosen as the standard state and assuming that the condensed phase volume is a very weak function of pressure and is expressed as

$$f_i^l = p_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left[\frac{v_i^l(P - P_i^{\text{sat}})}{RT}\right] \quad (3)$$

then eq 2 is further expressed as

$$y_i P = \frac{x_i^j \gamma_i^j p_i^{\text{sat}}}{\Phi_i} \quad i = 1, 2, \dots, n; j = 1, 2 \quad (4)$$

where

$$\Phi_i = \frac{1}{E} = \frac{\hat{\phi}_i^v}{\phi_i^{\text{sat}}} \exp\left[-\frac{v_i^l(P - P_i^{\text{sat}})}{RT}\right] \quad (5)$$

where *E* is the enhancement factor and the exponential term is the Poynting factor negligible at low pressure. For this study, the fugacity coefficients are calculated by the virial equation of state expressed as eq 6.

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \quad (6)$$

The second virial coefficients of the constituent components are estimated with Pitzer's general correlation method.<sup>8</sup>

The formula for the fugacity coefficient of component *i* is

$$\ln \hat{\phi}_i^v = (2 \sum_j y_j B_{ij} - B) \frac{P}{RT} \quad (7)$$

where the second virial coefficient of the mixture is calculated by the following mixing rule:

$$B = \sum_{i=1}^n \sum_{k=1}^n y_i y_k B_{ik} \quad (8)$$

Actually, the computation results show that the second virial coefficient has a very small value ( $B = -0.0009715 \text{ m}^3/\text{mol}$ ), which indicates that the vapor of the present system is ideal because the operating pressure is at 760 mmHg.

In this study, the liquid-phase activity coefficients are estimated with the NRTL model<sup>1</sup> of Renon and Prausnitz and the UNIQUAC model<sup>2</sup> of Abrams and Prausnitz. Because both models can be found from open literature or textbooks, these two models are not repetitively described here.

**Heterogeneous Azeotrope.** For a heterogeneous azeotropic mixture, the phase equilibrium relation is identical to that of the previous VLE. Thus,

$$y_i \hat{\phi}_i^v P = x_i^j \gamma_i^j f_i^{\text{sat}} \quad i = 1, 2, \dots, n; j = 1, 2, \dots, \pi \quad (9)$$

The material balance equation for the heterogeneous azeotropic mixture is

$$y_i - \bar{x}_i = y_i - \sum_{j=1}^{\pi} \xi_j^j x_i^j = 0 \quad i = 1, 2, \dots, n \quad (10)$$

where  $\bar{x}_i$  is the mole fraction of component *i* in the bulk liquid and  $\xi_j^j$  is the mole fraction of the *j*th liquid phase in the overall bulk liquid, so that

$$\sum_{j=1}^{\pi} \xi_j^j = 1 \quad (11)$$

and

$$\sum_{i=1}^n \bar{x}_i = 1 \quad (12)$$

Other material balance equations regarding the vapor phase and each liquid phase are

$$\sum_{i=1}^n y_i = 1 \quad (13)$$

and

$$\sum_{i=1}^n x_i^j = 1 \quad j = 1, 2, \dots, \pi \quad (14)$$

It is obvious that the equations

$$y_i = \bar{x}_i \quad i = 1, 2, \dots, n \quad (15)$$

are satisfied by both homogeneous and heterogeneous azeotropic mixtures. Equations 4–13 were used to solve

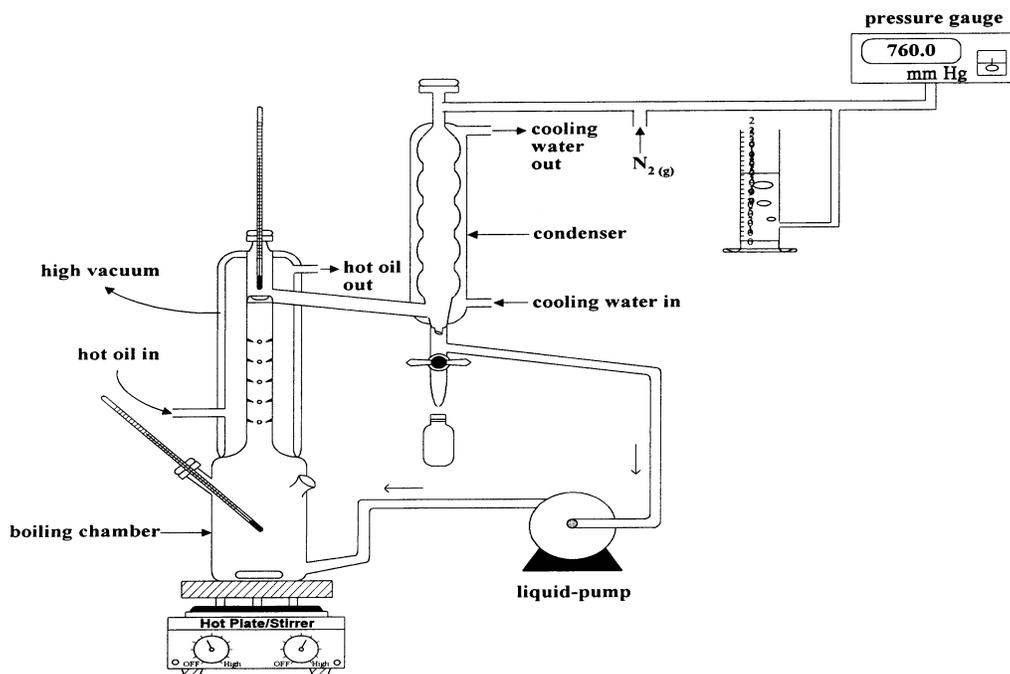


Figure 1. Apparatus for VLE and VLLE experiments.

the azeotropic temperature and the compositions of each individual liquid and vapor phase. All of the compositions must satisfy the following restrictions:

$$0 \leq x_i^j \leq 1 \quad i = 1, 2, \dots, n; j = 1, 2, \dots, \pi \quad (16)$$

$$0 \leq y_i \leq 1 \quad i = 1, 2, \dots, n \quad (17)$$

$$0 \leq \xi^j \leq 1 \quad j = 1, 2, \dots, \pi \quad (18)$$

## Experiments

**Chemicals.** The chemicals used in this study are GR grade ethanol, *n*-propanol, and cyclohexane with purity higher than 99.5%. All chemicals are the products of Merck Co. and were used without further purification. Water was generated from a Millipore water generator with an electric resistance of less than  $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ .

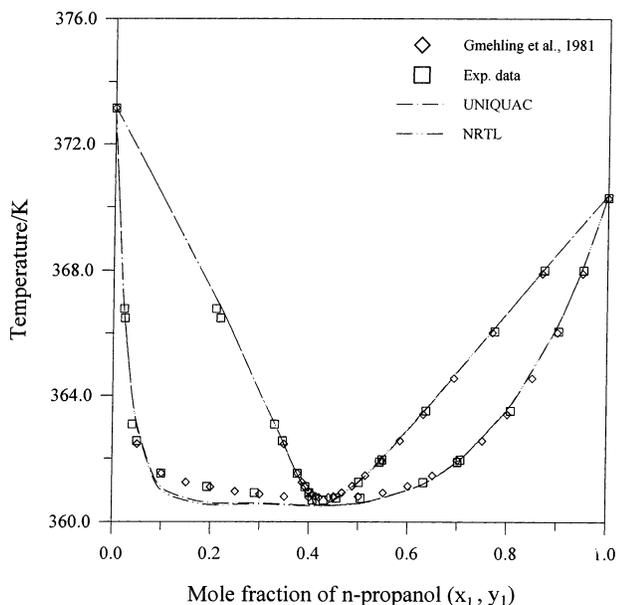
**VLLE Experiment.** An Othmer-type equilibrium cell with vapor condensation recirculation shown in Figure 1 was used for the present VLLE experiment. The cell was designed in such a way that liquid entrainment was avoided because of the baffles on the inner cell wall, and the heat loss through the vapor path wall was prevented by the insulation of the vacuum jacket and by heating with silicon oil in another jacket. It indeed improved the experiment to reach and maintain the equilibrium temperatures of the vapor and liquid phases easier. The vapor and liquid temperatures were measured with the mercury thermometers (Amarell Co.), which have been calibrated at the boiling temperature of pure water, with a finest division of 0.1 K. The liquid phase was stirred uniformly by a magnetic stirrer. About  $6 \text{ mL} \cdot \text{min}^{-1}$  of liquid was vaporized, condensed, and recirculated back to the cell. During the experiment, the condensed vapor might form two liquid phases on the return path to the cell such that the lighter phase always remains above the denser phase and would not return to the cell. To overcome this difficulty, a liquid pump was then installed to force these two liquid phases to circulate back into the cell. According to our experience, the VLLE will

be reached in 1 h after the temperatures of the vapor and liquid phases are maintained identical and stable. The condensed vapor was taken with a syringe for analysis. Because the vapor formed two liquid phases when condensed, pure ethanol was used as a cosolvent to homogenize the vapor sample. The peak area of ethanol must be excluded from gas chromatography analysis to obtain the correct vapor composition. About 8 mL of the liquid phase was sampled, put in a liquid-liquid equilibrium (LLE) bottle that was kept at the same temperature as that of the VLLE experiment, and allowed to separate into two liquid phases. After the LLE was reached, two liquid phases were then sampled separately for composition analysis.

The compositions of all of the components were analyzed by gas chromatography with a thermal conductivity detector. The column used was an 80/100 Porapak Q, 6 ft  $\times$   $1/8$  in. The optimum operation conditions for the present analysis are as follows: injection temperature, 160 °C; oven temperature, 180 °C; detector temperature, 170 °C; detector current, 180 mA; carrier gas (helium) flow rate,  $28 \text{ mL} \cdot \text{min}^{-1}$ .

The VLLE system was controlled at 760 mmHg with a simple apparatus also shown in Figure 1 by applying the advantage of the local atmospheric pressure as always lower than 760 mmHg. In this apparatus, the nitrogen gas was supplied at constant 760 mmHg to the still and a scaled glass column filled with water. The water level was determined by the daily local atmospheric pressure measured by a Fortin barometer. The accuracy of the pressure control is  $\pm 1 \text{ mmHg}$ . During the experiment, we carefully examined the peaks of gas chromatography analysis and observed that the peak of nitrogen did not appear. This showed that nitrogen in the pressure control system did not affect the present phase equilibrium.

The reliability of this phase equilibrium apparatus and operation technique had been tested by the measurement of the vapor-liquid equilibrium (VLE) of the *n*-propanol + water mixture at 760 mmHg. The experimental equilibrium compositions and the activity coef-



**Figure 2.** Experimental and correlated VLE data of the water + *n*-propanol mixture.

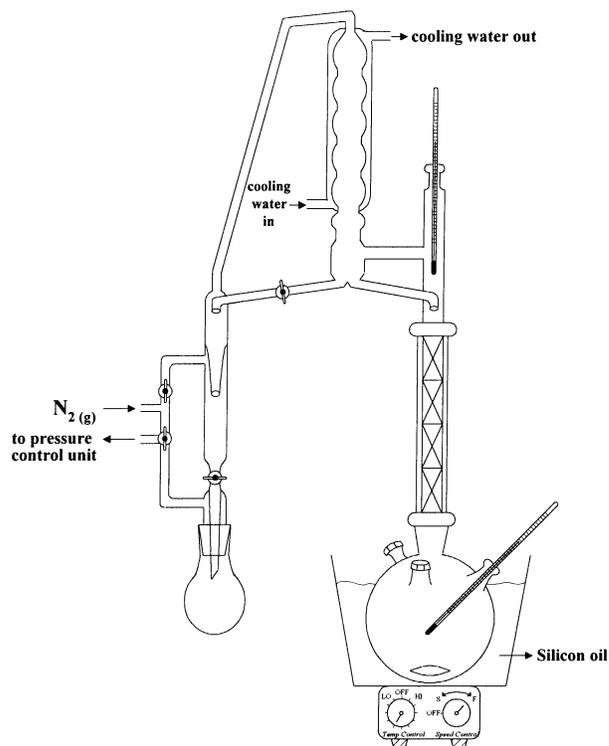
**Table 1. Experimental VLE Data of *n*-Propanol (1) + Water (2) at 760 mmHg**

no.	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	$\gamma_1$	$\gamma_2$
1	373.15	0.0000	0.0000		1.001
2	366.78	0.0215	0.2079	11.113	1.018
3	366.48	0.0233	0.2173	10.838	1.019
4	363.08	0.0395	0.3287	10.991	1.008
5	362.55	0.0493	0.3451	9.435	1.013
6	361.53	0.0991	0.3759	5.317	1.059
7	361.11	0.1928	0.3918	2.895	1.171
8	360.92	0.2893	0.4001	1.985	1.321
9	360.69	0.4066	0.4291	1.528	1.519
10	360.75	0.5040	0.4550	1.304	1.732
11	361.25	0.6313	0.5006	1.122	2.095
12	361.89	0.7002	0.5423	1.069	2.306
13	361.96	0.7061	0.5473	1.067	2.321
14	363.51	0.8067	0.6352	1.020	2.686
15	366.06	0.9023	0.7733	1.006	3.011
16	368.01	0.9514	0.8728	1.001	3.168
17	370.29	1.0000	1.0000	1.003	

ficients of the two components are given in Table 1, and the good agreement with the literature data of Gmehling et al.<sup>9</sup> (1981) is given in Figure 2. This mixture showed the azeotropic composition of *n*-propanol at the mole fraction of 0.42.

**Azeotrope Determination Experiment.** The azeotropic temperature and the composition of the present *n*-propanol + cyclohexane + water mixture was determined by a packed distillation column as shown in Figure 3. This packed column is equivalent to a 15-tray column. The final azeotropic mixture was obtained by a consecutive distillation of the top products of each batch distillation. The original mixture was fed into the bottom vessel of the packed column and distilled. The vapor condensate was collected and then used as the feed for the next distillation. One would obtain the azeotrope after two or three consecutive distillation operations (dependent on the original feed composition); otherwise, a pure compound should be obtained as the vapor product of the last distillation if the original mixture is nonazeotropic.

The pressure control and the analysis of the samples of this azeotrope determination experiment were similar to those of the previous VLLE experiment.



**Figure 3.** Packed column for determining the existence of the azeotrope.

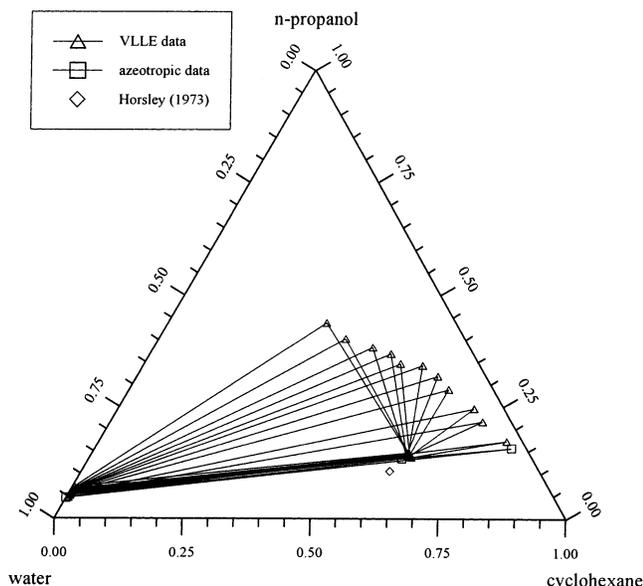
**Table 2. Experimental and Literature Azeotropic Data for *n*-Propanol (1) + Cyclohexane (2) at 760 mmHg**

	<i>T</i> <sup>az</sup> /K	<i>y</i> <sub>1</sub> <sup>az</sup>
present work	347.91	0.2395
Horsley <sup>7</sup>	347.84	0.2412
Hiaki et al. <sup>9</sup>	347.68	0.2490

To test the reliability of this distillation column and the operation technique of this experiment, the azeotropic temperature and the composition of the *n*-propanol + cyclohexane mixture at 760 mmHg was determined by this apparatus. The original composition of the mixture for the first distillation was prepared close to the azeotropic point to save time and effort. During the experiment, the condensate was totally refluxed to the column. The present experimental and literature (Horsley<sup>7</sup> and Hiaki et al.<sup>10</sup>) azeotropic temperature and composition are listed in Table 2. It is obvious that all three data sets agree well with each other.

## Experimental Results

**VLLE.** The 23 experimental data points of VLLE of the water + *n*-propanol + cyclohexane mixture are listed in Table 3. It shows that the boiling point of this mixture varied in a small temperature range and also shows that the composition of water in the aqueous phase and the composition of the vapor phase varied slightly. The projection of the ternary VLLE data from a three-dimensional diagram to a plane is plotted as Figure 4 where the organic, water, and vapor phases of each equilibrium point were located. It is observed that the vapor phase composition was confined in a small area and should not be a linear projection in this diagram. This implicated that the surface of VLLE in a three-dimensional space had a very sharp curvature so that the vapor composition of this partially miscible liquid



**Figure 4.** Projection diagram of the experimental VLE and the experimental and literature azeotropic data of the water + *n*-propanol + cyclohexane mixture.

**Table 3.** Experimental VLE Data of Water (1) + *n*-Propanol (2) + Cyclohexane (3) at 760 mmHg

no.	<i>T</i> (K)	<i>x</i> <sub>1</sub> '	<i>x</i> <sub>2</sub> '	<i>x</i> <sub>1</sub> ''	<i>x</i> <sub>2</sub> ''	<i>y</i> <sub>1</sub>	<i>y</i> <sub>2</sub>
1	340.46	0.2533	0.4365	0.9269	0.0687	0.2369	0.1451
2	340.44	0.2452	0.4264	0.9278	0.0680	0.2290	0.1456
3	340.44	0.2334	0.4011	0.9315	0.0644	0.2360	0.1378
4	340.30	0.2246	0.3968	0.9311	0.0647	0.2420	0.1433
5	340.35	0.1900	0.3815	0.9333	0.0625	0.2426	0.1418
6	340.36	0.1760	0.3859	0.9333	0.0625	0.2402	0.1431
7	340.34	0.1612	0.3673	0.9351	0.0607	0.2420	0.1414
8	340.33	0.1682	0.3593	0.9346	0.0612	0.2321	0.1427
9	340.34	0.1537	0.3451	0.9355	0.0603	0.2349	0.1436
10	340.30	0.1379	0.3360	0.9358	0.0599	0.2396	0.1419
11	340.36	0.1120	0.3411	0.9372	0.0586	0.2380	0.1420
12	340.33	0.0946	0.3236	0.9385	0.0574	0.2435	0.1393
13	340.37	0.0943	0.3170	0.9390	0.0568	0.2422	0.1403
14	340.26	0.0849	0.2996	0.9395	0.0563	0.2443	0.1387
15	340.25	0.0875	0.2875	0.9407	0.0551	0.2390	0.1379
16	340.50	0.0568	0.2523	0.9442	0.0517	0.2438	0.1385
17	340.27	0.0589	0.2448	0.9436	0.0520	0.2383	0.1374
18	340.29	0.0612	0.2196	0.9456	0.0503	0.2342	0.1382
19	340.34	0.0587	0.2202	0.9460	0.0499	0.2377	0.1369
20	340.25	0.0582	0.2178	0.9456	0.0503	0.2334	0.1378
21	340.30	0.0567	0.2154	0.9457	0.0498	0.2398	0.1381
22	340.57	0.0529	0.2125	0.9474	0.0484	0.2393	0.1384
23	340.34	0.0313	0.1713	0.9507	0.0452	0.2364	0.1351

mixture was found only in a small region. It is also observed that the aqueous liquid phase is always a high-purity product (typically water). The connection of the two equilibrium liquid compositions and the vapor phase would form a triangle, as shown in Figure 4. It is comprehensible that the height of the triangle in this figure decreased when the composition of the VLE approached the heterogeneous azeotropic point, and finally this height disappeared and the triangle became a linear line when the mixture met the azeotropic composition.

**Azeotropic Behavior.** The present water + *n*-propanol + cyclohexane mixture forms a minimum temperature azeotrope under 1 atm of pressure, as reported by Horsley,<sup>7</sup> and also was determined by a consecutive distillation of vapor condensate in a packed column in this study. After three independent batch distillations begun from different feed compositions,

**Table 4.** Experimental and Literature Azeotropic Data for Water (1) + *n*-Propanol (2) + Cyclohexane (3) at 760 mmHg

	run 1	run 2	run 3	ave values	Horsley <sup>7</sup>
<i>T</i> <sup>az</sup> (K)	339.95	340.00	339.98	339.98	339.70
<i>y</i> <sub>1</sub> <sup>az</sup>	0.2516	0.2609	0.2562	0.2562	0.2937
<i>y</i> <sub>2</sub> <sup>az</sup>	0.1313	0.1325	0.1333	0.1324	0.1036
<i>x</i> <sub>1</sub> <sup>az</sup>	0.0304	0.0273	0.0301	0.0293	<i>a</i>
<i>x</i> <sub>2</sub> <sup>az</sup>	0.1585	0.1525	0.1565	0.1558	<i>a</i>
<i>x</i> <sub>1</sub> <sup>'az</sup>	0.9559	0.9557	0.9561	0.9559	<i>a</i>
<i>x</i> <sub>2</sub> <sup>'az</sup>	0.0441	0.0443	0.0439	0.0441	<i>a</i>

<sup>a</sup> Unavailable.

the present experiment showed that this azeotrope is heterogeneous with two liquid phases. Unfortunately, Horsley<sup>7</sup> did not mention this phenomenon. The compositions of two liquids and vapor phases and the available literature values are listed in Table 4. The azeotropic temperatures of the present experiment and that of Horsley agreed with each other very well (less than 0.28 K deviation), while the azeotropic composition has a deviation of up to 27.8% for *n*-propanol (0.1324 vs 0.1036). We mention that Horsley<sup>7</sup> reported only the azeotropic vapor composition that is equal to the bulk liquid composition. Actually, it could be explained that the present experimental data are more reasonable than Horsley's. (1) The vapor composition varied slightly for all of the different equilibrium points, as shown in Table 3. This implied that the phase surface in a three-dimensional space had very sharp curvature and all of the vapor compositions were very near to the azeotropic point. (2) The azeotropic composition of Horsley<sup>7</sup> is more away from the VLE points than the present experimental azeotropic composition shown in Figure 4; i.e., the correct azeotropic composition is more unlikely located at Horsley's azeotropic composition. Besides, the present experimental compositions of the three phases of this heterogeneous azeotropic point lying along a straight line showed that the present experimental data are more reliable.

### Experimental Data Correlation

The experimental VLE data of the binary *n*-propanol + water mixture and the VLE of the ternary water + *n*-propanol + cyclohexane mixture were correlated with the UNIQUAC and NRTL models. The maximum likelihood principle, which assumed that the experimental errors were random and independent and had the advantage of accounting for each concerned variable, was employed. The objection function for the VLE data correlation was

$$Q = \sum_{i=1}^n \left[ \frac{(P_i^{\text{exp}} - P_i^{\text{cal}})^2}{\sigma_{P_i}^2} + \frac{(T_i^{\text{exp}} - T_i^{\text{cal}})^2}{\sigma_{T_i}^2} + \frac{(y_{1i}^{\text{exp}} - y_{1i}^{\text{cal}})^2}{\sigma_{y_{1i}}^2} + \frac{(x_{1i}^{\text{exp}} - x_{1i}^{\text{cal}})^2}{\sigma_{x_{1i}}^2} \right] \quad (19)$$

where  $\sigma_i$  represents the standard deviation of variable *i*. The  $\sigma$ 's for pressure and temperature were estimated by the accuracy of the measurements and the experimenter's reading error, while those for the liquid and vapor compositions were related to the inaccuracy of the calibration curve. For the present study, the values of

**Table 5. Physical Properties of Water, *n*-Propanol, and Cyclohexane<sup>a</sup>**

	water	<i>n</i> -propanol	cyclohexane
MW	18.015	60.096	84.162
<i>T</i> <sub>b</sub> (K)	373.2	370.3	353.8
<i>T</i> <sub>c</sub> (K)	647.3	536.8	553.5
<i>P</i> <sub>c</sub> (bar)	221.2	51.7	40.7
<i>V</i> <sub>c</sub> (cm <sup>3</sup> /mol)	57.1	219	308
<i>Z</i> <sub>ra</sub>	0.2338	0.2541	0.2729
<i>ω</i>	0.344	0.623	0.212
DM (D)	1.8	1.7	0.3
RD (Å)	0.615	2.736	3.261
<i>r</i>	0.92	2.78	3.97
<i>q</i>	1.40	2.51	3.01
<i>q</i> '	1.00	0.89	3.01
<i>η</i> <sub>association</sub>	1.7	1.4	0.0
<i>η</i> <sub>solvation</sub>	1.55 <sup>(1)-(2)</sup>	0.0 <sup>(2)-(3)</sup>	0.0 <sup>(1)-(3)</sup>

Antoine equation

$$\ln P_i^{\text{sat}} (\text{mmHg}) = A - \frac{B}{T(\text{K}) + C} \quad (\text{Reid et al., 1977})$$

	water	<i>n</i> -propanol	cyclohexane
<i>A</i>	18.3036	17.5439	15.7527
<i>B</i>	3816.44	3166.38	2766.63
<i>C</i>	-46.13	-80.15	-50.50
<i>T</i> (K) use range	284-441	285-400	280-380

<sup>a</sup> *Z*<sub>ra</sub>: Rackett parameter for saturated-liquid molar volume correction (Prausnitz et al., 1980). *ω*: acentric factor (Reid et al., 1987). DM: dipole moment (Reid et al., 1987). RD: mean radius of gyration (Reid et al., 1987). *r*: structure volume parameter for the UNIQUAC equation (Prausnitz et al., 1980). *q*: structure area parameter for the UNIQUAC equation (Prausnitz et al., 1980). *q*': structure area parameter for the modified UNIQUAC equation (Prausnitz et al., 1980). *η*: association or solvation parameter (Prausnitz et al., 1980).

these standard deviations were  $\sigma_x = 0.001$ ,  $\sigma_y = 0.01$ ,  $\sigma_T = 0.1$  K, and  $\sigma_P = 1$  mmHg. The physical data and parameters required for correlation are listed in Table 5.

The optimum binary parameters minimizing the above objective function of the *n*-propanol + water mixture are listed in Table 6. The residuals of the experimental and calculated bubble temperature and vapor composition, the root-mean-square deviation (RMSD), and the AADs by the UNIQUAC<sup>1</sup> and NRTL<sup>2</sup> models are listed in Table 7. The *T*-*x*-*y* diagram showing the experimental and calculated values of this binary mixture is given in Figure 2. The data and figure showed that the experimental and correlated values of the *n*-propanol and water mixture matched fairly well by both the UNIQUAC<sup>1</sup> and NRTL<sup>2</sup> models.

The objection function for the ternary VLE data correlation was expressed as

$$Q = \sum_{i=1}^n \left[ \frac{(P_i^{\text{exp}} - P_i^{\text{cal}})^2}{\sigma_{P_i}^2} + \frac{(T_i^{\text{exp}} - T_i^{\text{cal}})^2}{\sigma_{T_i}^2} + \frac{(y_{1i}^{\text{exp}} - y_{1i}^{\text{cal}})^2}{\sigma_{y_{1i}}^2} + \frac{(y_{2i}^{\text{exp}} - y_{2i}^{\text{cal}})^2}{\sigma_{y_{2i}}^2} + \frac{(x_{1i}^{\text{exp}} - x_{1i}^{\text{cal}})^2}{\sigma_{x_{1i}}^2} + \frac{(x_{2i}^{\text{exp}} - x_{2i}^{\text{cal}})^2}{\sigma_{x_{2i}}^2} + \frac{(x_{1i}^{\text{exp}} - x_{1i}^{\text{cal}})^2}{\sigma_{x_{1i}}^2} + \frac{(x_{2i}^{\text{exp}} - x_{2i}^{\text{cal}})^2}{\sigma_{x_{2i}}^2} \right] \quad (20)$$

where the standard deviation of each variable,  $\sigma$ , has a meaning similar to that explained in the paragraph of the VLE correlation.

**Table 6. UNIQUAC and NRTL Model Parameters for the Binary *n*-Propanol (1) + Water (2) Mixture**

<i>A</i> <sub><i>ij</i></sub> /K	UNIQUAC	NRTL
<i>A</i> <sub>12</sub>	-75.39	-17.30
<i>A</i> <sub>21</sub>	-166.24	1013.51
$\alpha_{12}$		0.3
$\alpha_{21}$		0.3

**Table 7. Residual, RMSD, and AAD of the *n*-Propanol (1) + Water (2) Mixture with the UNIQUAC and NRTL Models<sup>a</sup>**

no.	UNIQUAC		NRTL	
	$\Delta T$ (K)	$\Delta y_1$	$\Delta T$ (K)	$\Delta y_1$
1	0.02	0.0000	0.02	0.0000
2	-0.03	0.0125	0.02	0.0110
3	-0.08	0.0139	-0.03	0.0127
4	0.99	-0.0263	0.98	-0.0257
5	0.60	-0.0153	0.55	-0.0138
6	-0.48	0.0161	-0.59	0.0187
7	-0.55	0.0163	-0.62	0.0174
8	-0.36	0.0077	-0.39	0.0069
9	-0.18	-0.0108	-0.20	-0.0130
10	-0.17	-0.0134	-0.18	-0.0159
11	-0.06	-0.0035	-0.06	-0.0053
12	0.00	0.0000	0.01	-0.0011
13	0.01	-0.0005	0.02	-0.0015
14	0.18	0.0073	0.21	0.0073
15	0.25	0.0065	0.27	0.0069
16	0.13	0.0043	0.14	0.0047
17	0.09	0.0000	0.09	0.0000
RMSD	0.36	0.0119	0.37	0.0123
AAD	0.25	0.0096	0.26	0.0101

<sup>a</sup>  $\Delta T = T^{\text{cal}} - T^{\text{exp}}$ ,  $\Delta y_1 = y_{1i}^{\text{cal}} - y_{1i}^{\text{exp}}$ ,  $\text{RMSD} = [\sum_{i=1}^{N_T} (\Delta z)^2 / N_T]^{1/2}$ ,  $\text{AAD} = \sum_{i=1}^{N_T} |\Delta z| / N_T$ , and  $\Delta z = \text{calculated value} - \text{measured value}$ .

The experimental data of water + *n*-propanol + cyclohexane were correlated with the UNIQUAC<sup>1</sup> and NRTL<sup>2</sup> models. Because too extensive experimental and calculated data were included in the correlation and it was impossible to report them all, only the AAD and AARD % values of temperature and the compositions of each constituent component of the two liquid phases and one vapor phase are reported in Table 8. The correlation by the UNIQUAC<sup>1</sup> model was a failure because the AARD % values for the vapor compositions of *n*-propanol and cyclohexane were so large, with 17.03% and 31.80%, respectively, although the AADs in the mole fraction were 0.0405 and 0.0450, respectively. The correlation results by the NRTL<sup>2</sup> model were more satisfactory, with all AARD % values smaller than 5% except the vapor composition of water (10.69%). The difficulty of obtaining a better correlation was due to the presence of cyclohexane in the *n*-propanol + water mixture if one compared to the results discussed in the previous paragraph for the water + *n*-propanol binary mixture. The present results showed that the UNIQUAC<sup>1</sup> model should not be used for this ternary mixture.

The optimum interaction parameters minimizing the above objective function are listed in Table 9. It should be mentioned that the nonrandomness parameter of the NRTL model for the present mixture was not viewed as a constant as reported in some literature. The optimal values of these nonrandomness parameters for the present case are listed in Table 9. During the correlation computations, other sets of designated nonrandomness parameters were tried and always generated worse correlation results than the reported values here.

**Table 8. AAD and AARD % Values of VLLE of Water (1) + *n*-Propanol (2) + Cyclohexane (3) by the NRTL and UNIQUAC Models at 760 mmHg**

	$T/K$	$x_1'$	$x_2'$	$x_3'$	$x_1''$	$x_2''$	$x_3''$	$y_1$	$y_2$	$y_3$
					NRTL					
AAD	0.06	0.0020	0.0117	0.0097	0.0011	0.0011	0.0001	0.0254	0.0046	0.0301
AARD %	0.02	2.00	3.94	1.80	0.12	1.94	3.13	10.69	3.31	4.84
					UNIQUAC					
AAD	0.16	0.0019	0.0124	0.0106	0.0033	0.0035	0.0002	0.0405	0.045	0.0058
AARD %	0.04	2.09	4.16	2.07	0.355	6.19	4.09	17.03	31.80	0.93

**Table 9. UNIQUAC and NRTL Model Parameters of the Water (1) + *n*-Propanol (2) + Cyclohexane (3) Ternary Mixture**

$A_{ij}/K$	UNIQUAC	NRTL
$A_{12}$	135.91	1012.48
$A_{21}$	-476.27	105.87
$A_{13}$	-159.98	1683.92
$A_{31}$	-963.71	1595.86
$A_{23}$	98.48	467.46
$A_{32}$	-309.87	614.99
$\alpha_{12}$		0.442
$\alpha_{13}$		0.582
$\alpha_{23}$		0.311

Because in this research the experimental azeotropic temperature and azeotropic compositions of vapor and heterogeneous liquid phases were already obtained, the representation of the azeotropic behavior had also been tried with the pair parameters obtained from the experimental VLLE data with the UNIQUAC<sup>1</sup> and NRTL<sup>2</sup> models. According to the correlation results, a good agreement between the experimental and calculated azeotropic temperatures was obtained but, unfortunately, a large deviation was obtained between the experimental and calculated compositions. The difficulty of this correlation has not been overcome, and the results could not be reported at present.

### Conceptual Schemes To Separate the Present Mixture by RCM

A RCM is a composite diagram showing all of the azeotropic information of the constituent pairs and the residual curves of the concerned ternary mixture. A residual curve could be determined experimentally or mathematically simulating the experiment. There are rules based on the principle of thermodynamic, material balance, and distillation operation to be followed to construct a RCM.<sup>11</sup> The McCabe–Thiele diagram is viewed as a two-component RCM, while the RCM of a three-component mixture is constructed in a triangular diagram and that of a four-component mixture could be shown in a tetrahedral. A RCM of a mixture containing more than five components is difficult to construct. A RCM could be applied to develop a process to separate a multicomponent mixture particularly for ternary mixtures for which the RCM could be conveniently constructed and visualized. Also, it is realizable that a RCM can also be applied to select a proper entrainer for the azeotropic distillation.

It is known that an azeotropic mixture cannot be separated in a single distillation column. Usually, a specific entrainer is selected for the original mixture, and then an extractive distillation or an azeotropic distillation process is designed to separate this azeotropic mixture. For the azeotropic or extractive distillation, the azeotropic temperature and composition are the information needed for the process design. In a

specific RCM, the azeotropic information is used to draw the distillation boundaries dividing the RCM into several distillation regions that any distillation operation cannot cross.

For the azeotropic distillation or extractive distillation, the VLLE is possibly encountered. The process design for separating a mixture involving VLLE is different from that separating a mixture involving VLE only. However, using the RCM to develop the processes to separate the above mixtures involving VLLE or VLE is very similar. The phase splitting occurring either in the condenser or in the reboiler has two liquid-phase compositions located in two different distillation regions of the RCM. However, all of the compositions of these streams are on a straight line according to the material balance, and the flow rates of the streams are determined by the lever rule in a phase diagram.

In this study, cyclohexane is used as the entrainer to purify *n*-propanol from an aqueous solution. Two conceptual processes, regardless of the economic consideration, were proposed based on the phase equilibrium behavior and the RCM of the ternary water + *n*-propanol + cyclohexane mixture. Such a study has not been reported in the literature.

Following the procedure of constructing a RCM given in the open literature or textbooks, three stable nodes, N1, representing three pure components; three binary saddles, S2, representing three binary azeotropes; and one ternary node, N3, representing the ternary azeotrope, were located in the phase diagram. The azeotropic data of the binary saddles were obtained from the present experiment (water + *n*-propanol mixture) and literature (*n*-propanol + cyclohexane and water + cyclohexane mixtures), and that of the ternary node was obtained from the present experiments; all of the azeotropic data are presented in Figure 5. After all of the required data were put on the diagram, then three distillation boundaries were drawn. Usually, a distillation boundary is a curve because it is relevant to the reflux ratio and stage number of the distillation column. However, Fien and Liu<sup>11</sup> commented that a straight distillation boundary instead of a curved distillation boundary for process development would simplify the work and not affect the accuracy of matching the desired product specification. Thus, only the straight distillation boundaries were considered in this study. These three distillation boundaries separated this RCM into three feasible distillation regions. For development of a separation process, one more phase behavior, the LLE of this ternary mixture, was needed. Thus, the LLE curve by Sørensen and Arlt<sup>12</sup> was also drawn in this RCM.

The process design of this separation scheme of the water + *n*-propanol mixture with cyclohexane as the entrainer could be developed completely in the RCM with the LLE curve of this ternary mixture shown in Figure 5. The process scheme 1 developed in the RCM and the corresponding process flow diagram were shown

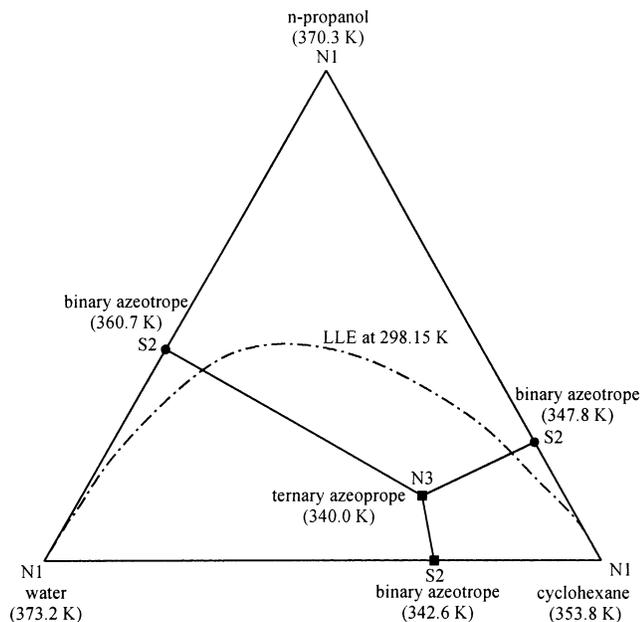


Figure 5. RCM of the water + *n*-propanol + cyclohexane mixture.

in Figures 6 and 7, respectively. The water + *n*-propanol feed, F1, was combined with the bottom stream from the last column, B4, as M1 by the lever rule and fed into column C-1. Water (boiling point at 373.15 K) was removed as the bottom product from this column, and the azeotropic mixture of water + *n*-propanol, D1 (boiling point at 360.7 K), was the top product. To operate beyond the distillation boundary, the recycle stream, Ph1, a cyclohexane-rich organic-phase product from the decanter meets another recycle stream, having a composition identical with that of stream D1, from the top of the third column, C-3, to form a mixture with composition M2. This combined stream was fed into the second column, C-2, from which a ternary heterogeneous azeotropic mixture, D2 (boiling point at 339.7 K), was produced at the top and a binary mixture of the water + *n*-propanol stream, B2 (boiling point is near that of D1), was produced at the bottom of the column. The D2 stream separated into the organic phase Ph1 and the aqueous phase Ph2 connected by the tie line existing at the decanter operation condition. Because the composition of stream B2 is away from the azeotropic composition D1, a further distillation will produce pure *n*-propanol as the bottom product, B3 (boiling point at 370.3 K), and the azeotropic mixture, D1, of water + *n*-propanol as the top product. The aqueous phase of the decanter, Ph2, was distilled in column C-4. The top product of C-4 has the a composition identical with that of the D2 stream and was recycled to combine with another D2 stream from the top of column C-2. The bottom product of column C-4 is B4. An enlarged circle showed the composition difference of streams B4 and Ph2 because these two mixtures had almost the same composition. The flow diagram of this separation scheme is given in Figure 7. This process requires four distillation columns and a decanter and could not be considered as a low-cost process. An alternative scheme of less distillation columns and lower operating cost is proposed in the next paragraph.

Similar to the separation scheme 1, the RCM of this mixture was constructed first. Then the process design was developed based on this RCM as shown in Figure 8. The water + *n*-propanol feed, F1, was mixed with the

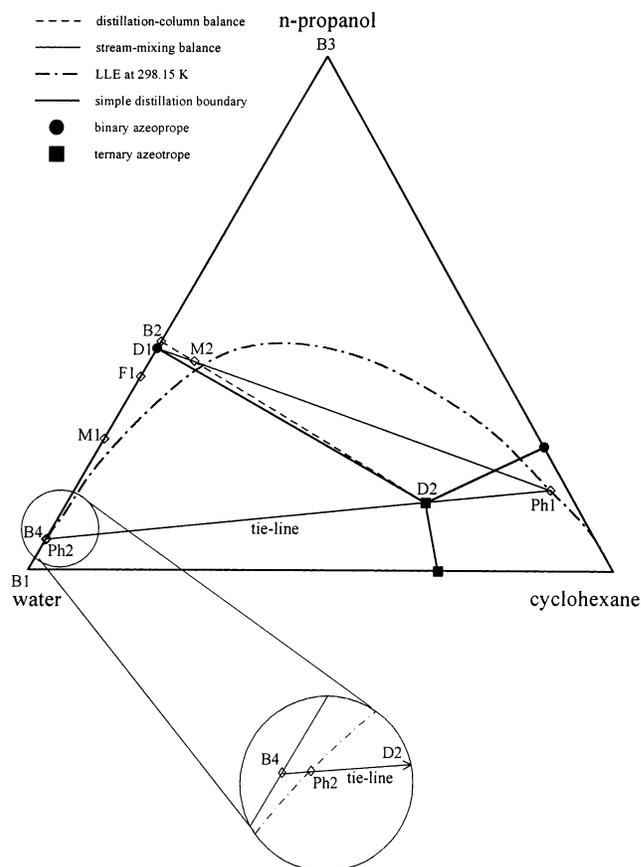


Figure 6. Process scheme 1 developed in the RCM of water + *n*-propanol + cyclohexane.

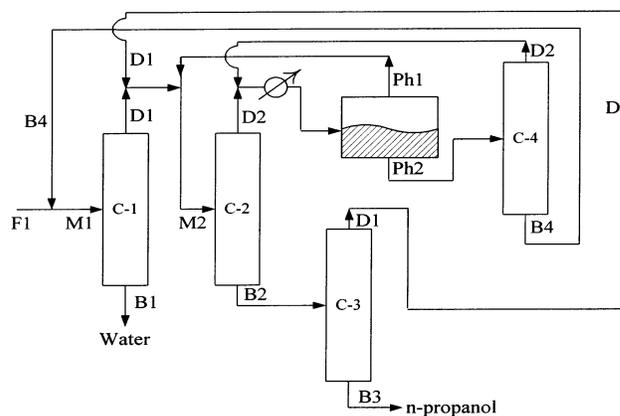
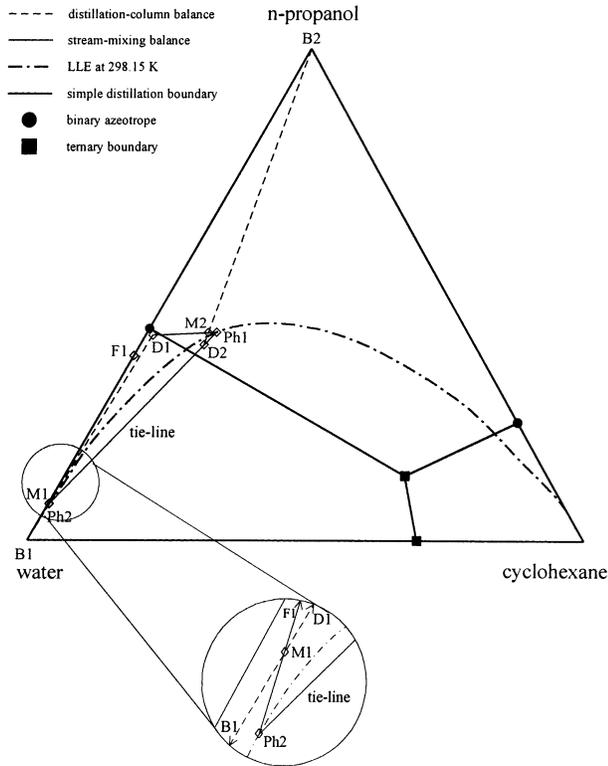


Figure 7. Process flow diagram for process scheme 1.

recycled stream, Ph2, to form the feed M1 and fed into distillation column C-1. The bottom product from this column is water (boiling point at 373.2 K), and the top product, D1 (boiling point near that of water + *n*-propanol at 360.7 K), is the water + *n*-propanol mixture near the distillation boundary in RCM. The recycled stream from the decanter, Ph1, rich in cyclohexane was combined with stream D1 to form a new stream M2 that entered the second distillation column C-2. Because the composition of stream M2 is away from the azeotropic composition of the water + *n*-propanol mixture, a pure *n*-propanol (boiling point at 370.3 K) could be produced from the bottom of distillation column C-2 and the ternary mixture, D2, from the top of the column. This ternary mixture would split into two liquid phases, Ph1 and Ph2, connected by a LLE tie line of this ternary



**Figure 8.** Process scheme 2 developed in the RCM of water + *n*-propanol + cyclohexane.

mixture at the operation temperature of the decanter. From this decanter, the organic-phase stream, Ph1, was recycled to combine with stream D1 and the aqueous-phase stream, Ph2, was recycled to combine with the fresh feed. The enlarged circle clearly shows the different compositions of streams M1 and Ph2. This process needs only two distillation columns, as shown in Figure 9, and is more favorable than the previous process with four distillation columns.

Actually, on the basis of a similar consideration, one can develop other feasible processes to separate other mixtures once the RCM similar to that in Figure 8 was prepared.

## Conclusion

This study began with the fundamental thermodynamic phase equilibrium data of binary and ternary mixtures of water, *n*-propanol, and cyclohexane attained from experiments or literature, and then the feasible azeotropic distillation processes for purifying *n*-propanol from water using cyclohexane as the entrainer were proposed.

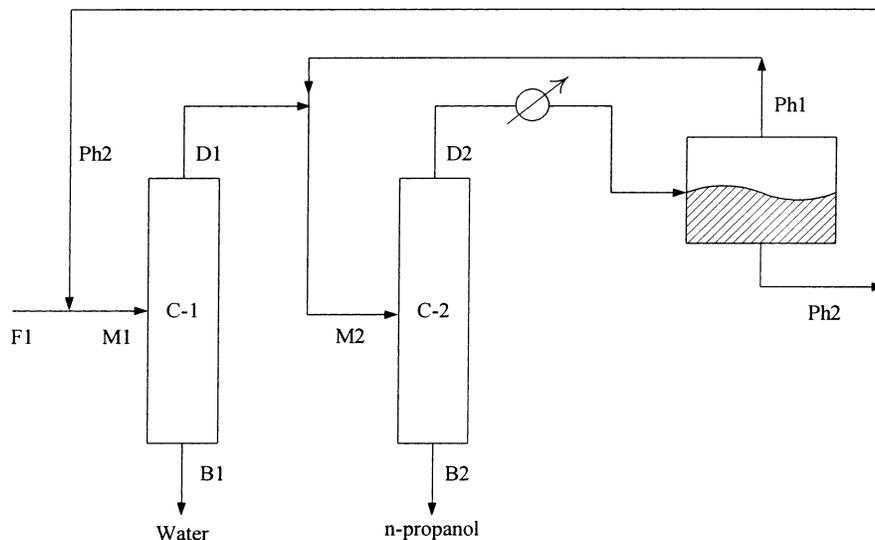
For phase behavior, the present study carried out the experimental measurements of the VLE of the binary water + *n*-propanol mixture and then the VLLE, the azeotropic temperature, and the azeotropic composition of the ternary water + *n*-propanol + cyclohexane mixture. The present experimental azeotropic temperature of this ternary mixture is identical with that given by Horsley<sup>7</sup> but not the azeotropic compositions. The present experimental data should be more reliable than Horsley's, as explained in the earlier paragraph.

The experimental VLLE data correlated fairly well with the NRTL model<sup>2</sup> but unsatisfactorily with the UNIQUAC model.<sup>1</sup> The experimental azeotropic data of the ternary mixture have not yet been successfully correlated.

On the basis of the experimental phase behavior data and the constructed RCM, two conceptual schemes feasible to separate water and *n*-propanol azeotropes were proposed. The first scheme requires four columns to accomplish this purification task, while the second scheme requires two distillation columns less than the first scheme. Thus, the second scheme is the best process between these two schemes.

## Nomenclature

- $B$  = second virial coefficient
- $B_{ij}$  = cross second virial coefficient
- $E$  = enhancement factor
- $f$  = fugacity
- $P$  = pressure
- $Q$  = objective functions defined in eqs 19 and 20
- $R$  = gas constant
- $T$  = temperature
- $v$  = volume
- $x$  = liquid composition



**Figure 9.** Process flow diagram for process scheme 2.

$\tilde{x}_i$  = mole fraction of component  $i$  in the bulk liquid  
 $y$  = vapor composition

*Greek Letters*

$\Phi$  = quantity defined in eq 5  
 $\phi$  = fugacity coefficient  
 $\gamma$  = activity coefficient  
 $\sigma$  = standard deviation of a variable  
 $\xi_j$  = mole fraction of the  $j$ th liquid phase in the overall bulk liquid

*Superscripts*

$\wedge$  = property in a solution  
 $v$  = vapor phase  
 $l$  = liquid phase  
 $\text{sat}$  = saturated

*Subscripts*

$i$  = component  $i$   
 $j$  = liquid phase  $j$

**Literature Cited**

(1) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116.  
 (2) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135.  
 (3) Chapman, R. G.; Goodwin, S. P. A General Algorithm for the Calculation of Azeotropes in Fluid Mixtures. *Fluid Phase Equilib.* **1993**, *85*, 55–69.

(4) Gmehling, J.; Böltz, R. Azeotropic Data for Binary and Ternary Systems at Moderate Pressures. *J. Chem. Eng. Data* **1996**, *41*, 202–209.  
 (5) Wisniak, J.; Segura, H. Heteroazeotropy and Analytical Models for Phase Equilibria. *Ind. Eng. Chem. Res.* **1997**, *36*, 253–263.  
 (6) Eckert, E.; Kubicek, M. Computing Heterogeneous Azeotropes in Multicomponent Mixture. *Comput. Chem. Eng.* **1997**, *21*, 347–350.  
 (7) Horsley, L. H. *Azeotropic Data*; American Chemical Society: Washington, DC, 1973; Vol. III.  
 (8) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*, 6th ed.; McGraw-Hill: New York, 2001; p 102.  
 (9) Gmehling, J.; Onken, U.; Arlt, W. Aqueous–Organic Systems (Supplement 1). *Vapor–Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1981; Vol. I, Part 1a.  
 (10) Hiaki, T.; Tochigi, K.; Kojima, K. Measurement of Vapor–Liquid Equilibria and Determination of Azeotropic Point. *Fluid Phase Equilib.* **1986**, *26*, 83–102.  
 (11) Fien, G.-J. A. F.; Liu, Y. A. Heuristic Synthesis and Shortcut Design of Separation Processes Using Residue Curve Maps: A Review. *Ind. Eng. Chem. Res.* **1994**, *33*, 2505–2522.  
 (12) Sørensen, J. M.; Arlt, W. Binary System. *Liquid–Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1979; Vol. V, Part 1.

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