Measurement and Prediction of Quaternary Azeotropes for Cyclohexane + 2-Propanol + Ethyl Acetate + Butanone System at Elevated Pressures

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The azeotropic data of the cyclohexane + 2-propanol + ethyl acetate + butanone quaternary system were measured by using a stainless steel azeotrope apparatus developed by the authors at elevated pressures of 101.3, 302.0, 502.0, 702.0, and 902.0 kPa and predicted by using the Wilson and NRTL activity coefficient models with the paired energy parameters obtained from binary azeotropic data of the six corresponding systems. The calculated results demonstrate that the predicted data are in good agreement with the experimental, and the Wilson and NRTL equations are of comparable accuracy in the prediction of azeotropes for this miscible quaternary system at elevated pressures.

Introduction

The azeotropic point is a distinctive point in vapor−liquid equilibrium, at which the compositions and many other properties, such as enthalpies of vaporization, enthalpies of solvation, etc., are identical for both the vapor and liquid phases. Investigations of the behavior of azeotropic mixtures are of keen interest to theoretical studies and are equally important for industrial and engineering applications. Naturally, It is of great practical importance to predict and calculate multicomponent azeotropes, including ternary, quaternary, or higher-order ones, from readily available binary azeotropic or vapor−liquid equilibrium data. Therefore, many recent attempts have been made to predict the compositions and temperature for ternary azeotropes using vapor−liquid equilibrium data.

Kudryavtseva et al.[1] proposed a method to calculate the compositions for multicomponent azeotropes from the data of binary azeotropes and the pure components. However, it could not be guaranteed that unique azeotropic compositions could be obtained. Eduljee and Tiwari[2] reported a method for predicting ternary azeotropic compositions and temperature from unlike interaction parameters of binary azeotropic mixtures in conjunction with binary azeotropic information according to a general classification of liquids based on their hydrogen bonding capabilities. Tamir and Wisniak[3] employed the Redlich−Kister equation to calculate the azeotropes for ternary systems, but multicomponent (ternary) interaction parameters were required in addition to binary ones. Later, Tamir[4] developed a method for predicting multicomponent azeotropes by using the Wilson equation with parameters estimated from multicomponent vapor−liquid equilibrium data. Kudryavtseva and Toome[5] proposed a simple method to predict ternary azeotropic data that was based on a topographic feature of the ternary mixtures and only required information on binary azeotropes and pure components. Recently, Vahdat and Sather[6] used the Wilson and NRTL equations to derive equations that predict the compositions and temperature of multicomponent azeotropes from binary equilibrium data. This model was successfully used for ternary and quaternary systems, but entropy data of vaporization were required in the calculations. Lan and Mansoori[7] developed a hard sphere expansion conformal solution theory, based on statistical mechanics and the molecular theory of fluid mixtures, to predict the vapor−liquid equilibrium properties of multicomponent mixtures, and an equation of state for multicomponent fluid was developed. The vapor−liquid equilibria as well as azeotropic properties of several binary and ternary nonpolar mixtures were predicted. The proposed approach provides a detailed insight into the peculiar behavior of the azeotropic mixtures. However, all of these prediction methods were mainly proposed and used at normal and lower pressures, but no models and algorithms have been tested and confirmed at elevated pressures. One of the objectives of this work is to provide a more reliable and efficient algorithm, which can predict azeotropic points for multicomponent systems, including ternary, quaternary, and higher-order ones, at elevated pressures from binary azeotropic or vapor−liquid equilibrium data.

The azeotropic and vapor−liquid equilibrium data of the cyclohexane + 2-propanol + ethyl acetate + butanone quaternary system at elevated pressures are not reported in the literature. The azeotropic data for this system were determined at elevated pressures up to 902 kPa in this work.

Experimental Section

Chemicals. All of the chemicals, cyclohexane, 2-propanol, ethyl acetate, and butanone, were of analytical grade and were further purified by rectifying and collecting the fraction with constant boiling temperature and refractive index. All of the pure chemicals were confirmed by gas chromatography analysis, and the purities were estimated to be higher than 99.9%. The physical properties of the chemicals used in these measurements were compared to literature data and presented in the previous work.[8]

Apparatus. The stainless steel azeotrope apparatus described in the previous work[7] was employed for the determining of quaternary azeotrope. The high-performance rectifying column was packed with high-efficient stainless steel round packing materials and wrapped with rock wool to minimize heat losses. A pressure control unit

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Table 1. Experimental Tests of Composition Analysis of Prepared Mixtures for the Quaternary System Cyclohexane (1) + 2-Propanol (2) + Ethyl Acetate (3) + Butanone (4)

prepared				deviations			
x_1	x_2	x_3	x_4	Δx_1	Δx_2	Δx_3	Δx_4
0.4256	0.2982	0.1054	0.1697	0.0042	0.0011	−0.0005	−0.0048
0.4098	0.4746	0.0459	0.0696	−0.0058	0.0042	0.0005	0.0011
0.3924	0.5816	0.0174	0.0236	−0.0049	0.0037	0.0006	0.0006
0.2630	0.6735	0.0109	0.0524	0.0038	−0.0049	0.0001	0.0010
0.2515	0.7109	0.0203	0.0181	0.0014	−0.0028	0.0008	0.0006
0.3515	0.6003	0.0311	0.0171	−0.0018	0.0030	−0.0009	−0.0003
0.5107	0.2104	0.1109	0.1680	0.0047	−0.0009	−0.0018	−0.0020
0.5547	0.1874	0.0837	0.1742	0.0029	0.0019	−0.0011	−0.0038
0.4448	0.2017	0.2617	0.0918	−0.0038	−0.0012	0.0041	0.0009
				0.0037	0.0026	0.0012	0.0017

with a digital pressure transducer was designed to control and measure the system pressure with an accuracy of ±0.1 kPa. The thermometer well is located at the top of the column, and a secondary standard platinum resistance thermometer, accompanied with a 5−1/2 digital multimeter, was used for the temperature measurement. The accuracy of measured resistance is ±0.001Ω, which is equivalent to ±0.01 K for the azeotropic temperature.

Composition Analysis. The compositions of the quaternary mixtures were analyzed and determined by a Shimazu gas chromatograph equipped with a thermal conductivity detector. The chromatograph column was packed with Porapak-Q packing materials (Waters Associates, Inc.). The flow rate of the carrier gas, H_2, was 60 mL·min^{-1}. The column temperature was maintained around 443.15 K. The compositions were determined by the relative area method whose accuracy was estimated to be 0.003 mole fraction for quaternary mixtures. Some test results for prepared mixtures are given in Table 1. The prepared samples were analyzed three times independently, and every final result was taken from the average of the values of these three measurements.

Test of Quaternary Azeotropic Compositions. As to the quaternary systems, the variation of boiling temperature is not notable, but that of the composition is too sensitive in the vicinity of the azeotrope. Sometimes the change in a quaternary composition will amount to 0.1 mole fraction even though the temperature change is less than only 0.05 K. Thus, it is imperative to propose a reliability test for quaternary azeotropic compositions before working on measurements at elevated pressures. Because quaternary azeotropic data for this system at normal and elevated pressures are not available in the literatures, the azeotropic temperature and composition for this system were determined at 101.3 kPa with different prepared starting compositions. Each of them was distilled seven times at the same reflux ratio. The light fraction was collected up to about one-half of the starting volume, and the remnant mixtures in the boiler were replaced by the collected light fractions for further distillation. The temperature was measured, and the composition was analyzed in each cycle. The test results of the last four cycles are presented in Table 2 with first three cycles omitted. It demonstrates that the temperature and composition tend to a certain value after six cycles, and the final azeotropic temperature and composition was almost uniform, even when starting from different prepared compositions. It also indicates that the quaternary azeotropic data measured by this apparatus are accurate and reliable.

Results and Discussion

Determination of Quaternary Azeotropic Data. As discussed above, it is more difficult to determine a quaternary azeotrope than a binary one because especially large deviations probably occur in the azeotropic compositions. The prepared starting mixtures should be distilled with all of the light fractions returned to the rectifying column for longer than 1 h, and a larger reflux ratio should be maintained during the entire measuring procedure. The compositions should also be sampled and analyzed for every circulation. If the amount of the remnant liquid mixture is too small to continue measuring after several cycles, the liquid mixture should be prepared again according to the last analyzed composition, and then continue rectifying until both the temperature and composition remain unchanged. In this way, the azeotropic temperatures and compositions for the cyclohexane + 2-propanol + ethyl acetate + butanone quaternary system were determined at elevated pressures up to 902 kPa. They are presented in Table 3 and in Figures 1 and 2.

Ordinarily, because the requirements to form a quaternary azeotrope are very sensitive to changes and complicated, it is not easy to form a quaternary azeotrope. The quaternary azeotrope probably degenerates into a ternary azeotrope, or even to a binary one, when the system pressure changes even slightly. In this study, the quaternary azeotrope of the cyclohexane + 2-propanol + ethyl acetate + butanone system degenerated into a ternary azeotrope at 502 kPa and into a binary one at pressures higher than 702 kPa.

Prediction of Quaternary Azeotropic Data. In this work, quaternary azeotropic data were predicted by using an activity coefficient method as discussed for ternary azeotropic temperatures and compositions at normal and lower pressures.[9] According to the vapor−liquid equilibrium criterion, the fugacities of the vapor and the liquid phases should be equal when equilibrium is achieved:

$$z_i P y_i = \gamma_i p_i^0 x_i \qquad (i = 1-4) \tag{1}$$

where x and y are the mole fractions for the liquid and the

Table 2. Measurements of Quaternary Azeotropic Compositions at 101.3 kPa for System Cyclohexane (1) + 2-Propanol (2) + Ethyl Acetate (3) + Butanone (4)

	starting composition	fourth cycle		fifth cycle		sixth cycle		seventh cycle	
	x	T/K	x	T/K	x	T/K	x	T/K	x
x_1	0.5016	341.84	0.4901	341.70	0.4914	341.68	0.4862	341.68	0.4881
x_2	0.2011		0.2519		0.2662		0.2793		0.2864
x_3	0.2178		0.1715		0.1607		0.1507		0.1500
x_4	0.0795		0.0863		0.0817		0.0842		0.0815
x_1	0.4088	341.73	0.4743	341.69	0.4824	341.68	0.4853	341.68	0.4894
x_2	0.3142		0.2811		0.2737		0.2704		0.2739
x_3	0.1203		0.1403		0.1511		0.1590		0.1573
x_4	0.1567		0.1043		0.0910		0.0853		0.0794

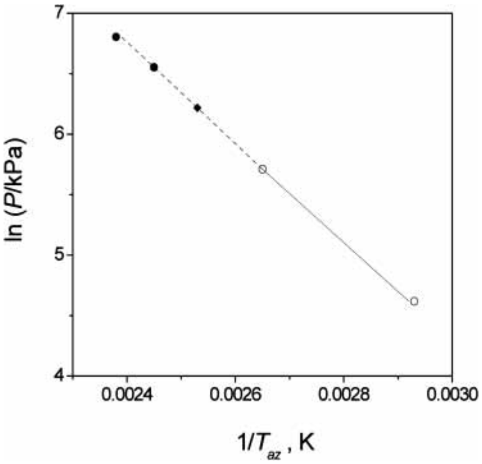

Figure 1. Plot of the logarithm of pressure versus the reciprocal of azeotropic temperature for the quaternary system: ○, experimental, quaternary azeotrope; ◆, ternary azeotrope; ●, binary azeotrope; −, Wilson equation; ···, NRTL equation; - - -, extrapolated from quaternary.

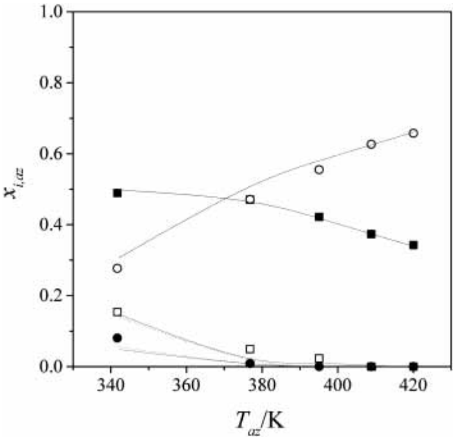

Figure 2. Plot of the quaternary azeotropic compositions versus the azeotropic temperature: ■ experimental, x_1; ○, x_2; □, x_3; ●, x_4; −, Wilson equation; ···, NRTL equation.

Table 3. Experimental Azeotropic Temperatures and Compositions of the Quaternary System Cyclohexane (1) + 2-Propanol (2) + Ethyl Acetate (3) + Butanone (4)

P/kPa	T/K	x_1	x_2	x_3	x_4
101.3	341.68	0.4887	0.2771	0.1536	0.0804
302.0	376.82	0.4706	0.4710	0.0495	0.0089
502.0	395.09	0.4221	0.5548	0.0230	0
702.0	408.90	0.3736	0.6264	0	0
902.0	420.03	0.3422	0.6578	0	0

vapor phases, respectively, P is the total pressure, p^0 is the saturated vapor pressure of the pure component, γ is the activity coefficient for the liquid phase, and z is the nonideal correction factor for the vapor phase. By using a virial equation of state truncated after the B term, the correction factor could be reduced if the effect of pressure on molar volume of the pure component liquid is neglected, thus

$$z_i = \exp\left[\frac{(B_{ii} - v_i^{\mathrm{L}})(P - p_i^0)}{RT}\right] \tag{2}$$

where the second virial coefficients B_{ii} were calculated by the Tsonopoulos[10] method, $v_{\mathrm{i}}^{\mathrm{L}}$ is the molar volume of the pure liquid, and the vapor pressures p_i^0 were calculated by the Antoine equation with the constants taken from Stephenson and Malanowski.[11] The activity coefficients in eq 1 were calculated from the multicomponent Wilson equation reformulated by Orye and Prausnitz:[12]

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{4} G_{ji}x_j - \sum_{j=1}^{4} \frac{G_{ij}x_j}{\sum_{k=1}^{4} G_{kj}x_k} \tag{3}$$

where

$$G_{ji} = \frac{v_i^{\mathrm{L}}}{v_j^{\mathrm{L}}} \exp\left(-\frac{g_{ji} - g_{ii}}{RT}\right) \tag{4}$$

and the multicomponent NRTL equation[13]

$$\ln \gamma_i = \frac{\sum_{j=1}^{4} \tau_{ji}G_{ji}x_j}{\sum_{k=1}^{4} G_{ki}x_k} + \sum_{j=1}^{4} \frac{G_{ij}x_j}{\sum_{k=1}^{4} G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{l=1}^{4} \tau_{lj}G_{lj}x_l}{\sum_{k=1}^{4} G_{kj}x_k}\right) \tag{5}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{6}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{7}$$

where $g_{ji}-g_{ii}$ and $g_{ij}-g_{jj}$ are the Wilson and NRTL paired energy parameters.

Furthermore, the predictive calculations were made for multicomponent azeotropic points from the corresponding binary azeotropic temperatures and compositions by using the Wilson and NRTL activity coefficient models. A prediction of a multicomponent azeotrope is done by searching a set of compositions of equilibrium vapor that equal those of the coexisting liquid phase. At the azeotropic point, the vapor−liquid equilibrium relationship eq 1 becomes eq 8 because of the identical composition for the vapor and liquid phases:

$$\gamma_i = \frac{z_i P}{p_i^0} \qquad (i = 1{-}4) \tag{8}$$

Hence, two paired activity coefficients could be calculated more accurately from the azeotropic temperatures and pressures by using this equation than from the measurement of equilibrium compositions. The activity coefficients calculated with this equation and the compositions were then substituted into the two-component Wilson[14] or NRTL equations ($\alpha_{ij} = 0.47$) for each coupled system, and two paired energy parameters were calculated by an iteration algorithm. Thus, six pairs of energy parameters for calculating the activity coefficients of the quaternary systems could be obtained from the azeotropic data of the six corresponding binary systems. In this calculation, the azeotropic data of the related binary systems were taken from the correlation equations with the pressures reported previously.[8] The obtained Wilson and NRTL paired energy parameters are tabulated in Table 4.

A dual iterative technique was employed in the calculation of the azeotropic temperature and compositions for the quaternary system at a given total pressure, until the

Table 4. Wilson and NRTL Paired Energy Parameters for Systems Involving Cyclohexane (1), 2-Propanol (2), Ethyl Acetate (3), and Butanone (4) in eqs 4 and 6 in J·mol^{-1}

P/kPa	$g_{21}-g_{11}$	$g_{12}-g_{22}$	$g_{31}-g_{11}$	$g_{13}-g_{33}$	$g_{41}-g_{11}$	$g_{14}-g_{44}$	$g_{32}-g_{22}$	$g_{23}-g_{33}$	$g_{42}-g_{22}$	$g_{24}-g_{44}$	$g_{43}-g_{33}$	$g_{34}-g_{44}$
						Wilson Equation						
101.3	1310.18	5461.46	344.01	2755.93	585.71	2921.11	1109.39	1084.89	1702.20	−0.42	483.45	14.61
302.0	195.28	5252.00	714.62	1889.83	573.83	2694.46	1584.65	−426.52	1298.06	−165.05	−1969.40	3386.09
502.0	−275.92	5223.85	819.58	1520.85	473.68	2497.08	3488.51	−2057.85	1418.28	−396.61	−2040.72	3388.32
702.0	−571.17	5191.03	792.45	1349.87	334.66	2378.44	5310.58	−2934.44	−1691.95	4815.17	−1431.44	2186.05
902.0	−774.65	5133.61	663.14	1312.15	164.50	2329.25	5421.83	−2963.46	nonazeotrope		6267.15	−2699.60
						NRTL Equation ($\alpha_{ij} = 0.47$)						
101.3	2534.55	4060.40	639.55	2406.12	1122.05	2335.42	201.87	1953.32	1017.69	675.59	742.81	−248.16
302.0	1714.36	3590.93	1041.16	1542.57	1152.95	2080.33	405.76	748.71	356.99	772.57	−1756.93	3111.02
502.0	1411.34	3409.07	1208.33	1117.67	1076.94	1867.50	2087.32	−720.14	336.45	682.19	−1878.13	3171.35
702.0	1240.39	3264.52	1251.59	879.40	955.81	1736.28	3262.95	−1321.80	−3169.94	6386.25	−1322.34	2068.87
902.0	1137.35	3119.38	1194.64	771.38	798.97	1677.14	3273.88	−1276.15	nonazeotrope		4052.22	−2195.90

Table 5. Predicted Azeotropic Temperatures and Compositions of the Quaternary System Cyclohexane (1) + 2-Propanol (2) + Ethyl Acetate (3) + Butanone (4)

	predicted					deviations				
P/kPa	T/K	x_1	x_2	x_3	x_4	ΔT	Δx_1	Δx_2	Δx_3	Δx_4
					Wilson Equation					
101.3	342.10	0.4973	0.3068	0.1475	0.0484	0.42	0.0086	0.0297	−0.0061	−0.0320
302.0	377.32	0.4736	0.5212	0.0022	0.0030	0.50	0.0030	0.0502	−0.0473	−0.0059
502.0	396.02	0.4152	0.5831	0.0013	0	0.93	−0.0069	0.0283	−0.0217	0
702.0	409.43	0.3726	0.6264	0	0	0.53	−0.0010	0.0000	0	0
902.0	420.08	0.3386	0.6604	0	0	0.05	−0.0036	0.0026	0	0
					NRTL Equation ($\alpha_{ij} = 0.47$)					
101.3	342.15	0.4985	0.3063	0.1396	0.0556	0.47	0.0098	0.0292	−0.0140	−0.0248
302.0	377.32	0.4738	0.5216	0.0020	0.0026	0.50	0.0032	0.0506	−0.0475	−0.0063
502.0	396.01	0.4152	0.5832	0.0013	0	0.92	−0.0069	0.0284	−0.0217	0
702.0	409.43	0.3726	0.6264	0	0	0.53	−0.0010	0.0000	0	0
902.0	420.08	0.3385	0.6604	0	0	0.05	−0.0037	0.0026	0	0
					UNIFAC					
101.3	342.93	0.4945	0.2644	0.0281	0.2129	1.25	0.0058	−0.0127	−0.1255	0.1325
302.0	377.14	0.4627	0.5099	0.0249	0.0025	0.32	−0.0079	0.0389	−0.0246	−0.0064
502.0	395.35	0.4163	0.5816	0.0020	0	0.26	−0.0058	0.0268	−0.0210	0
702.0	408.48	0.3780	0.6208	0	0	−0.42	0.0044	−0.0056	0	0
902.0	418.95	0.3493	0.6497	0	0	−1.08	0.0071	−0.0081	0	0

calculated equilibrium vapor composition was equal to the liquid one within a tolerance level. That is

$$|1 - \sum_{i=1}^{4} y_i| \le \epsilon_1 \qquad (9)$$

$$|x_i - y_i| \le \epsilon_2 \qquad (i = 1-4) \qquad (10)$$

where $\epsilon_1 = 0.00001$ and $\epsilon_2 = 0.0001$ are the mole fraction tolerances in this calculation. In this way, quaternary azeotropic points for this system were predicted with the Wilson and NRTL equations and compared with the experimental results. The calculated temperatures and compositions and their deviations from the experimental data are presented in Table 5 and are represented in Figures 1 and 2 by the solid lines for the Wilson equation and the dotted lines for the NRTL equation. Because the quaternary azeotropes degenerate into ternary azeotrope at 502 kPa, and into binary ones at the pressures of 702 and 902 kPa, the azeotropic temperatures deviate slightly from the extrapolation of the quaternary azeotropic temperatures.

Prediction of Quaternary Azeotropic Points by UNIFAC. The quaternary, ternary, and binary azeotropic temperatures and compositions were predicted by using the UNIFAC group contribution method[15,16] to calculate the activity coefficients in the liquid phase, and using the B-truncated virial equation to calculate the fugacity coefficients in the vapor phase. The coordination number was calculated by the Skjold-Jorgensen[17] method, and the second virial coefficient was calculated by the Tsonopoulos[10] method. The predicted results are also presented in Table 5.

Conclusions

The experimental investigation demonstrates that the cyclohexane + 2-propanol + ethyl acetate + butanone quaternary system exhibits a minimum boiling azeotrope, and the azeotropic temperatures and compositions for this system were determined by using a stainless steel azeotrope apparatus at normal and elevated pressures of 101.3, 302.0, 502.0, 702.0, and 902.0 kPa. However, in this observation, the quaternary azeotrope degenerates into a ternary azeotrope at 502 kPa and into a binary one at pressures higher than 702 kPa. It also makes it clear that it is difficult to form a quaternary azeotrope because of the sensitivity of the quaternary compositions and also difficult to accurately determine the quaternary azeotropic compositions because the quaternary temperature-compositions surface is too complanated in the vicinity of the azeotrope.

The variation of azeotropic compositions for multicomponent systems with pressures is usually more complicated than that of binary systems. In general, the relationship of binary azeotropic compositions to azeotropic temperature is linear, but this trend does not always hold for multicomponent systems, especially at elevated pressures. Sometimes it turns around and behaves as a curve as observed in this work (Figure 2) and in the previous work for the ternary system of benzene + n-heptane + ethanol. However, the relationship of the logarithm of pressure versus the reciprocal of azeotropic temperature is essentially linear for binary, ternary, and quaternary azeotropes

(Figure 1), which has been confirmed by many experimental observations.

From the azeotropic temperatures and compositions of the corresponding binary systems, the quaternary azeotropes were predicted with the Wilson and NRTL activity coefficient models in this work. The calculations satisfactorily agree with the experimental results. It shows that the Wilson and NRTL equations could be satisfactorily used to predict quaternary azeotropes from the binary azeotropes at elevated pressures, and that the Wilson and NRTL equations are of comparable accuracy in the prediction of azeotropes for miscible quaternary systems at elevated pressures. This means that vapor−liquid equilibrium behavior at elevated pressures for quaternary systems could also be predicted from the azeotropic data of corresponding binary systems. The quaternary azeotropic azeotropes were also predicted with the UNIFAC group contribution method, but the calculation results suggest that the deviations are larger than those with the Wilson and NRTL models.

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