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Azeotropes at Elevated Pressures for Systems Involving Cyclohexane, 2-Propanol, Ethyl Acetate, and Butanone

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A new stainless steel apparatus for measuring azeotropic points of binary as well as multicomponent systems at elevated pressures has been developed. The azeotropic temperatures and compositions of six binary systems composed of cyclohexane, 2-propanol, ethyl acetate, and butanone were determined at elevated pressures, correlated by empirical equations with pressure, and predicted by the UNIFAC group contribution method. The calculations demonstrate that the correlated data are in good agreement with experimental values.

Introduction

Azeotropic data are very important in many chemical engineering processes, such as separation, purification, extractive distillation, and azeotropic distillation. Moreover, azeotropic mixtures have also been used for some special solvent systems. On the other hand, azeotropic data can also be used in thermodynamic modeling and in the prediction of vapor−liquid equilibrium behavior. Thus, such information is of great interest in the study of solution properties, but of great practical value in chemical engineering process design as well.

Many studies have already been done on azeotropes. Most of the collected azeotropic data[1−3] are those at normal or lower pressures. To investigate azeotropic behavior at elevated pressures, as well as to describe the azeotropic properties of multicomponent systems and to predict the vapor−liquid equilibrium behaviors at elevated pressures from the binary azeotropic data, a new all-stainless steel azeotrope apparatus was developed and constructed. In this work, the azeotropic temperatures and compositions of six binary systems composed of cyclohexane, 2-propanol, ethyl acetate, and butanone were determined at pressures up to 902 kPa and correlated by empirical equations with the pressure. The azeotropic data at low pressures for these binary systems have been reported by many authors, compiled by Horsley[1] and Lide,[2] and collected by Gmehling et al.[3,4] The azeotropic data for the system of cyclohexane + ethyl acetate at elevated pressures from 131.9 to 231.3 kPa have been reported by Regenbrecht.[5] Those for the cyclohexane + butanone system at pressures from 199.5 to 395.6 kPa were reported by Renker,[6] and those for pressures from 459.9 to 1289.3 kPa, which were derived from the vapor−liquid equilibrium data, were reported by Swami et al.[7]

Experimental Section

Chemicals. The cyclohexane, 2-propanol, ethyl acetate, and butanone used were of analytical grade and purified by rectifying and collecting the fractions with constant boiling temperatures and refractive indices. The purities of the chemicals were confirmed by gas chromatography analysis and were estimated higher than 99.9%. The normal boiling points, refractive indices, and densities at 293.15 K of the pure chemicals are presented in Table 1 and compared with the literature data.

Table 1. Physical Properties of Pure Substances

	experimental			literature[2]		
substance	T_b (K)	d^{20} (g cm^{-3})	n_D^{20}	T_b (K)	d^{20} (g cm^{-3})	n_D^{20}
cyclohexane	353.82	0.7785	1.4265	353.85	0.7785	1.4266
2-propanol	355.51	0.7855	1.3776	355.57	0.7855	1.3776
ethyl acetate	350.16	0.9005	1.3722	350.21	0.9003	1.3723
butanone	352.75	0.8054	1.3787	352.75	0.8054	1.3788

Apparatus. The apparatus, consisting of a boiler, a high-performance rectifying column, a thermometer well, a condenser, and a sample collector, is shown in Figure 1. The boiler, which has a volume of about 500 mL, was heated with an outer heater. The column, which is 1400 mm high, was packed with highly efficient stainless steel round packing materials and wrapped with rock wool to prevent loss of heat. At the top part of the column, two windows made of 6-mm-thick glass allowed for visual observation and facilitated control of the reflux ratio. The thermometer well was located at the top of the column and inserted about 50 mm into the column to guarantee that no heat loss occurred in temperature measuring, and a secondary standard platinum resistance thermometer accompanied by a Keithley 195A 5-1/2 digital multimeter was employed for the temperature measurements. The uncertainty in the temperature measuring was ±0.001 Ω, estimated to be ±0.01 K. The system pressure was measured and controlled by a four-digit pressure transducer with an accuracy of ±0.1 kPa. The sample collector with a volume of about one-half that of the boiler, 250 mL, was used to collect the light fraction for further distillation, and the valve between the collector and the boiler was closed for light fraction collecting in the rectifying procedure.

Test of Temperature−Pressure Dependence. The temperature−pressure dependence is very important in measuring the azeotropic temperature. The boiling temperatures of pure water at pressures from 102.45 to 1011.05 kPa were measured. The water was deionized and redistilled, and its normal boiling point was 373.14 K. The observed vapor pressures and boiling temperatures are presented in Table 2. The subscripts exptl and calc in the table heading refer to experimental and calculated data,

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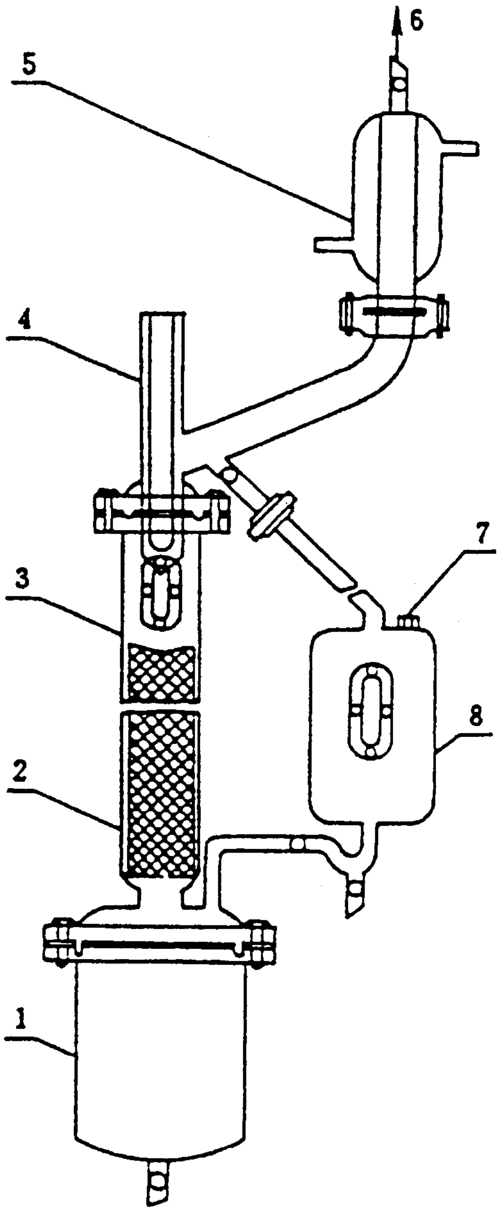

Figure 1. Scheme of the azeotrope apparatus at elevated pressures: 1, boiler; 2, packing materials; 3, high-performance rectifying column; 4, thermometer well; 5, condenser; 6, connection to pressure control unit; 7, feed inlet; 8, sample collector.

Table 2. Test of Temperature−Pressure Dependence for Pure Water

P_{exptl} (kPa)	T_{exptl} (K)	P_{calc} (kPa)	T_{calc} (K)	$100(P_{\mathrm{exptl}} - P_{\mathrm{calc}})/P_{\mathrm{exptl}}$	ΔT (K)
102.45	373.42	102.27	373.47	0.17	−0.05
205.42	394.19	205.09	394.24	0.16	−0.05
304.93	407.32	305.46	407.26	−0.18	0.06
397.24	416.49	396.72	416.54	0.13	−0.05
497.52	424.86	498.07	424.82	−0.11	0.04
615.74	432.97	615.07	433.01	0.11	−0.04
697.94	438.04	698.67	438.00	−0.10	0.04
803.16	443.74	803.17	443.74	−0.00	0.00
912.25	449.10	912.36	449.09	−0.01	0.01
1011.05	453.54	1011.38	453.53	−0.03	0.01
average				0.10	0.035

respectively. The Antoine equation in the literature[8]

$$\ln(P/\mathrm{kPa}) = 16.23135 - 3778.22/(T/\mathrm{K} - 47.8154) \quad (1)$$

is used to calculate either the pressure or the temperature at the experimental conditions, i.e., the pressure was calculated at the experimental temperature from the above Antoine eq 1 and compared to the observed pressure, and the same for the temperature. This indicates that the temperature and pressure are consistent and that the boiling temperatures measured by this apparatus are reliable.

Test of Azeotropic Temperature and Composition. To confirm that the azeotropic data determined by this apparatus are correct, the azeotropic temperature and composition for the benzene + ethanol system were determined at 101.33 kPa with different starting compositions. In each operation, the light fraction was collected to about one-half of the starting volume, and the remnant liquid mixtures in the boiler were replaced by the light fractions for further distillation. In this way, the mixtures of liquid were distilled for four cycles at the same reflux ratio. The temperature was measured, and the composition was analyzed in each cycle. The results of the test runs are presented in Table 3. The temperature and composition tend to certain values after two cycles, and the final azeotropic temperature and composition are almost uniform from different starting compositions and are also in good agreement with the literature values.[9]

Composition Analysis. The differences in the densities of the pure components of the binary mixtures cyclohexane (1) + ethyl acetate (3), 2-propanol (2) + ethyl acetate (3), and ethyl acetate (3) + butanone (4) systems were sufficient to allow composition analysis of the mixtures by density measurements. The densities of the mixtures were measured by a five-digit density meter (Anton Paar model DMA45). For the systems of cyclohexane (1) + 2-propanol (2) and cyclohexane (1) + butanone (4), the refractive indices were measured for composition analysis by an Abbe refractometer. The analysis uncertainty in the mole fraction is estimated to be about ±0.001.

The compositions of the 2-propanol (2) + butanone (4) mixtures were analyzed and determined by a Shimazu gas chromatograph (model GC-7A) equipped with a thermal conductivity detector. The chromatography column was packed with Porapak-Q (Waters Associates, Inc.). The flow rate of the carrying gas, H_2, was 60 mL/min. The column temperature was maintained at 443 K. The compositions were determined by the relative area method, with an uncertainty in the mole fraction of around ±0.001.

Results and Discussion

Determination of Azeotropic Data. The azeotropic temperatures and compositions of the six binary systems consisting of cyclohexane (1), 2-propanol (2), ethyl acetate (3), and butanone (4) were determined at pressures up to 902 kPa. The results are presented in Tables 4−9, and some literature data at 101.3 kPa[1] and at superatmospheric pressures[3] are also listed for comparison.

To ensure the accuracy of the temperature measurements, good insulation should be carefully considered to prevent loss of heat from radiation because the apparatus is made of stainless steel. Therefore, the rectifying column was wrapped with aluminum silicate rock wool, which has a low thermal conductance.

Correlation of Azeotropic Temperatures and Compositions. At the azeotropic point, the compositions of the vapor and liquid are identical; thus for binary systems, only two variables are independent, and two equations are required to correlate the azeotropic data. The experimental results demonstrate that plots of the logarithm of pressure versus the reciprocal of the azeotropic temperature and of

Table 3. Test of Azeotropic Temperature and Composition for the Benzene (1) + Ethanol System[a]

starting composition	1st cycle		2nd cycle		3rd cycle		4th cycle	
x_1	T (K)	x_1	T (K)	x_1	T (K)	x_1	T (K)	x_1
0.2218	341.06	0.5390	340.99	0.5477	340.98	0.5492	340.98	0.5498
0.5301	340.99	0.5475	340.98	0.5472	340.98	0.5494	340.98	0.5488
0.7795	341.10	0.5671	340.99	0.5499	340.98	0.5503	340.98	0.5499

[a] Literature values:[9] $T_{\mathrm{az}} = 340.95$, $x_{1,\mathrm{az}} = 0.5525$.

Table 4. Experimental, Predicted, and Literature Azeotropic Data for the Cyclohexane (1) + 2-Propanol (2) System

system 1 + 2							
experimental			UNIFAC		literature[1]		
P (kPa)	T (K)	x_1	T (K)	x_1	P (kPa)	T (K)	x_1
101.3	342.64	0.5887	343.57	0.5978	101.3	341.95	0.5918
302.0	377.35	0.4735	377.14	0.4757	101.3	341.75	0.5918
502.0	396.15	0.4100	395.35	0.4173	101.3	342.75	0.5951
702.0	409.17	0.3740	408.48	0.3786	101.3	342.55	0.6028
902.0	420.17	0.3426	418.95	0.3498	101.3	342.75	0.6028

Table 5. Experimental, Predicted, and Literature Azeotropic Data for the Cyclohexane (1) + Ethyl Acetate (3) System

system 1 + 3							
experimental			UNIFAC		literature[1,3]		
P (kPa)	T (K)	x_1	T (K)	x_1	P (kPa)	T (K)	x_1
101.3	344.66	0.4784	345.37	0.4152	101.3	345.95	0.4714
302.0	383.38	0.4048	383.49	0.3709	101.3	344.75	0.4513
502.0	404.55	0.3620	404.80	0.3441	131.9	353.00	0.4463[3,a]
702.0	420.83	0.3377	420.39	0.3223	176.0	362.62	0.4319[3,a]
902.0	433.30	0.3166	432.95	0.3037	231.3	372.63	0.4153[3,a]

[a] Regenbrecht.[5]

Table 6. Experimental, Predicted, and Literature Azeotropic Data for the Cyclohexane (1) + Butanone (4) System

system 1 + 4							
experimental			UNIFAC		literature[1,3]		
P (kPa)	T (K)	x_1	T (K)	x_1	P (kPa)	T (K)	x_1
101.3	344.88	0.5101	344.56	0.4767	101.3	344.75	0.5065
302.0	383.34	0.4728	383.48	0.4466	101.3	344.95	0.5216
502.0	405.24	0.4503	405.17	0.4253	101.3	344.65	0.5216
702.0	421.60	0.4335	421.12	0.4077	101.3	344.15	0.4750
902.0	434.57	0.4185	434.02	0.3929	101.3	344.95	0.5624
					199.5	366.30	0.5090[3,a]
					395.6	394.05	0.4840[3,a]
					459.9	401.85	0.4330[3,b]
					813.6	429.45	0.3780[3,b]
					1289.3	456.65	0.3560[3,b]

[a] Renker.[6] [b] Swami et al.[7]

the azeotropic composition versus temperature are generally linear, as shown in Figures 2 and 3, respectively. Therefore, the variation of the azeotropic temperature with the pressure is correlated by

$$\ln(P/\mathrm{kPa}) = A - B/(T_{\mathrm{az}}/\mathrm{K} + C) \tag{2}$$

and that of the azeotropic composition with the temperature is correlated by

$$x_{1,\mathrm{az}} = a + b(T_{\mathrm{az}}/\mathrm{K}) \tag{3}$$

The constants in the equations were optimized and are presented in Table 10.

Table 7. Experimental, Predicted, and Literature Azeotropic Data for the 2-Propanol (2) + Ethyl Acetate (3) System

system 2 + 3							
experimental			UNIFAC		literature[1]		
P (kPa)	T (K)	x_2	T (K)	x_2	P (kPa)	T (K)	x_2
101.3	348.28	0.3407	348.52	0.2997	101.3	347.15	0.3400
302.0	383.51	0.5652	382.56	0.5329	101.3	349.05	0.3283
502.0	401.81	0.6820	400.69	0.6494			
702.0	414.51	0.7563	413.64	0.7287			
902.0	424.43	0.8171	423.89	0.7884			

Table 8. Experimental, Predicted, and Literature Azeotropic Data for the 2-Propanol (2) + Butanone (4) System

system 2 + 4							
experimental			UNIFAC		literature[1]		
P (kPa)	T (K)	x_2	T (K)	x_2	P (kPa)	T (K)	x_2
101.3	350.14	0.3779	350.63	0.3621	101.3	350.85	0.3820
302.0	384.65	0.6620	384.30	0.6517	101.3	351.15	0.3820
502.0	402.23	0.8462	402.07	0.7984	101.3	351.05	0.3609
702.0	414.63	0.9512	414.67	0.9002			
902.0	nonazeotrope		415.60	0.9755			

Table 9. Experimental, Predicted, and Literature Azeotropic Data for the Ethyl Acetate (3) + Butanone (4) System

system 3 + 4							
experimental			UNIFAC		literature[1]		
P (kPa)	T (K)	x_3	T (K)	x_3	P (kPa)	T (K)	x_3
101.3	349.95	0.7508	349.91	0.7830	101.3	350.15	0.7885
302.0	387.10	0.7841	387.78	0.7773	101.3	350.20	0.6996
502.0	408.88	0.8081	408.76	0.7824	101.3	350.20	0.8595
702.0	424.14	0.8413	424.05	0.7890			
902.0	436.54	0.8568	436.33	0.7959			

Prediction of Azeotropic Points by UNIFAC. The azeotropic temperatures and compositions were predicted using the UNIFAC group contribution method[10,11] to calculate the activity coefficients in the liquid phase and the B-truncated virial equation to calculate the fugacity coefficients in the vapor phase. The coordination number was calculated by the Skjold−Jorgensen[12] method, and the second virial coefficient was calculated by the Tsonopoulos[13] method. The predicted results are also presented in Tables 4−9.

Conclusions

A new stainless steel apparatus for measuring azeotropic points of binary as well as multicomponent systems at elevated pressures was developed. The apparatus was tested for running stability, temperature−pressure dependence, and azeotropic compositions; the results demonstrate that the apparatus constructed in this work is reliable and accurate.

All six binary systems, cyclohexane + 2-propanol, + ethyl acetate, + butanone, 2-propanol + ethyl acetate, + butanone, and ethyl acetate + butanone, exhibit minimum-boiling azeotropes at pressures up to 902 kPa, excepting

Table 10. Correlated Constants in Equations 2 and 3 and the Deviations

system[a]	A	B	C	ΔP%	a	b	Δx
1 + 2	16.23231	3876.232	−8.917	0.28	1.6806	−0.003194	0.0028
1 + 3	14.12617	2823.823	−47.696	0.32	1.1092	−0.001835	0.0022
1 + 4	13.39116	2373.037	−74.394	0.10	0.8613	−0.001016	0.0009
2 + 3	20.75762	7844.274	137.759	0.05	−1.8388	0.006264	0.0023
2 + 4	21.67200	8584.693	153.234	0.10	−2.7636	0.008953	0.0090
3 + 4	13.74378	2513.972	−74.433	0.42	0.3123	0.001236	0.0064

[a] 1, cyclohexane; 2, 2-propanol; 3, ethyl acetate; 4, butanone.

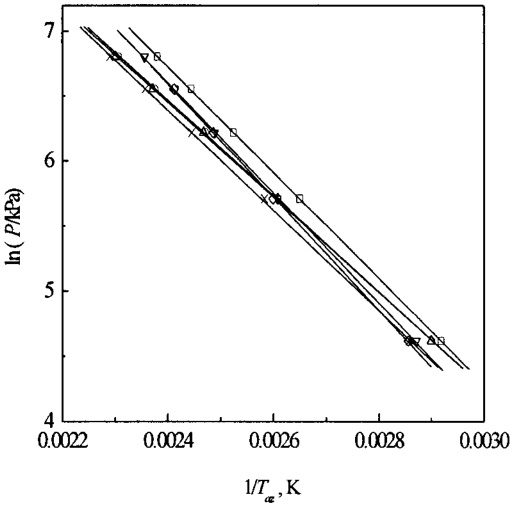

Figure 2. Effect of pressure on azeotropic temperatures: ○, cyclohexane + 2-propanol; □, cyclohexane + ethyl acetate; △, cyclohexane + butanone; ▽, 2-propanol + ethyl acetate; ◇, 2-propanol + butanone; ×, ethyl acetate + butanone; —, correlated.

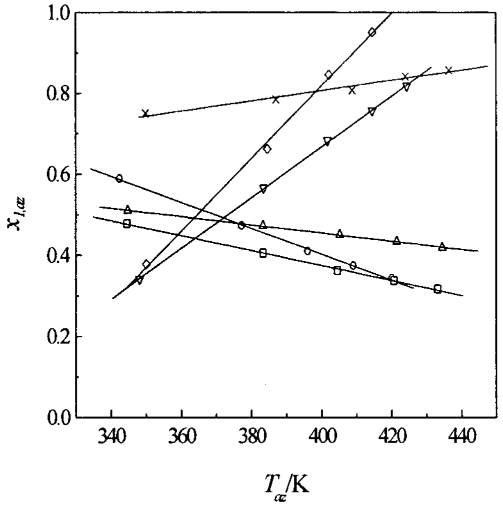

Figure 3. Plots of azeotropic composition versus azeotropic temperature: ○, cyclohexane + 2-propanol; □, cyclohexane + ethyl acetate; △, cyclohexane + butanone; ▽, 2-propanol + ethyl acetate; ◇, 2-propanol + butanone; ×, ethyl acetate + butanone; —, correlated.

the 2-propanol + butanone system at higher pressure. The effect of pressure on the binary azeotropic compositions in the range of elevated pressure was studied and correlated. The variation of the azeotropic temperature with the pressure was correlated by the Antoine-type equation, and the relationship of the azeotropic composition and the azeotropic temperature was correlated by a linear expression. The calculations indicate that the correlated data are in good agreement with the experimental results. The average relative deviation in pressure is 0.21%, and the average absolute deviation in azeotropic composition is 0.0039 mole fraction.

Acknowledgment

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