J. Chem. Eng. Data **1988**, *33*, 16-20

Vapor–Liquid and Liquid–Liquid Equilibria for the System *sec*-Butyl Alcohol–Di-*sec*-butyl Ether–Water

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Vapor–liquid equilibrium data for the *sec*-butyl alcohol–di-*sec*-butyl ether–water (SBA–DSBE–water) system are reported over a pressure range of 600–770 mmHg. Liquid–liquid equilibrium data for the SBA–DSBE–water and SBA–DSBE–water–methyl ethyl ketone (MEK) systems were obtained at 311.15 K. Vapor–liquid and liquid–liquid equilibrium data were reduced independently by using the UNIQUAC equation. A compromise set of interaction coefficients reproduce the experimental data very well.

Introduction

Methyl ethyl ketone (MEK) is produced commercially by the catalytic dehydrogenation of *sec*-butyl alcohol (SBA), which is made by hydrating butyl sulfates. An important processing step is the separation of SBA from water and its reaction byproducts. The dehydration is accomplished primarily in an azeotropic distillation tower using one of the reaction byproducts, di-*sec*-butyl ether (DSBE), as the dehydrating agent. Simulation results and experimental measurements, which show that the tower operates with one and two liquid phases on the trays, are presented by Kovach and Seider (*1*, *2*).

Data were found in the literature for the SBA–water (*3*, *4*), SBA–MEK (*5*), MEK–water (*6*, *7*), and SBA–MEK–water (*8*, *9*) systems. However, no liquid–liquid or vapor–liquid equilibrium data were found for either the SBA–DSBE binary or the SBA–DSBE–water ternary systems. Since the interactions with DSBE are exploited in performing this azeotropic distillation, vapor–liquid and liquid–liquid equilibrium data were measured and interaction coefficients for the UNIQUAC equation (*10*) were computed. In addition, because the effect of MEK was unknown, vapor–liquid and liquid–liquid equilibrium data were measured for the SBA–DSBE–water–MEK system. When preliminary simulations showed MEK to be almost entirely in the vapor phase, these data were excluded from the data regression.

Experimental Section

Reagent Chemicals. *sec*-Butyl alcohol and methyl ethyl ketone were supplied by Aldrich Chemical Co. and di-*sec*-butyl ether was supplied by Wiley Organics. All three chemicals were reported as having a minimum purity of 99%. When an analysis by gas chromatograph failed to detect significant impurities, the chemicals were used without purification. Water was distilled and deionized prior to use.

Boiling points of the reagents were measured and are listed in Table I. In addition, vapor pressure data for di-*sec*-butyl ether were measured (Table II). To check the experimental procedure, the boiling point of water was measured at 750, 600, and 296 mmHg and compared to literature values. The maximum deviation was 0.1 K. The vapor pressure data for the other species are presented by Kovach and Seider (*1*).

Table I. Boiling Point (K) at 750 mmHg

	SBA	DSBE	water	MEK
this work	372.0	394.5	372.8	
literature[a]	372.4	394	272.81	353.2

[a] Boiling points were found by using a vapor pressure correlation (SBA), from ref *11* (DSBE), the Steam Tables (water), and as reported by the chemical supplier (MEK).

Table II. Vapor Pressure for Di-*sec*-butyl Ether[a,b]

T, K	P, mmHg	T, K	P, mmHg
353.4	200	384.0	551
364.8	300	386.7	601
373.6	400	389.6	652
380.8	501	394.5	750

[a] $\ln \{P\} = C_1 + C_2/(C_3 + T) + C_4{*}T + C_5{*}T^2$ (K, mmHg), where $C_1 = 112.70$; $C_2 = -16598.3$; $C_3 = 0.00$; $C_4 = -0.24638$; $C_5 = 2.1326 \times 10^{-4}$. [b] Coefficients for SBA, MEK, and water are tabulated by Kovach and Seider (*1*).

Vapor–Liquid Equilibrium. The recirculation still in Figure 1 was used to measure vapor-liquid equilibrium data. In operation, the circulation loop is filled to just below the vapor disengagement region (B). A small stream of nitrogen (J) is introduced at the bottom of the left leg of the circulation loop (A) to encourage the upward movement of the liquid. This leg is heated and the mixture vaporizes causing the upward movement of the liquid. In section B, the vapor disengages from the liquid and rises into section C where it is heated slightly to prevent condensation. The liquid drops down into the right leg of the still (H). The vapor is condensed in the glycol-cooled condenser, section E, and continues into section G where a small reserve accumulates for sampling. The thermocouple well (D) is used to verify that a small temperature gradient exists and that the vapor entering section C is not superheated (to prevent vaporization of entrained liquid). The temperature of the acetone and dry ice trap, section F, is low enough to condense or freeze any vapor that escapes from the condenser, with none detected during the experiments. Condensate is returned to the circulation loop through section G which contains a three-way valve to allow sampling. The thermocouple well (I) in the right leg of the circulation loop allows the measurement of temperatures in the liquid phase.

Temperature measurements were made using an iron–constantan thermocouple and a digital multimeter (Doric Trendicator 410a) with 0.1 K temperature increments. The temperature generally became steady after 30 min of operation with samples taken at least 90 min later. For measurements near azeotropic compositions, the system was allowed to equilibrate for approximately 3 h. The pressure measurements were accurate to within ±2 mmHg.

Liquid–Liquid Equilibrium. The apparatus for measurement of the liquid–liquid equilibrium data is shown in Figure 2. The liquid temperature was maintained within 0.1 K of the set point by a Lauda heating circulation bath, Model MS3, and measured in increments of 0.01 K. The vessel was charged and shaken vigorously every 20 min. Samples were taken after 2–4 h.

Analysis. Hydrocarbon analyses were performed using a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and a Shimadzu Chromatopac C-R1A electronic integrator. The injector and detector temperatures were maintained at 513 and 523 K, respectively.

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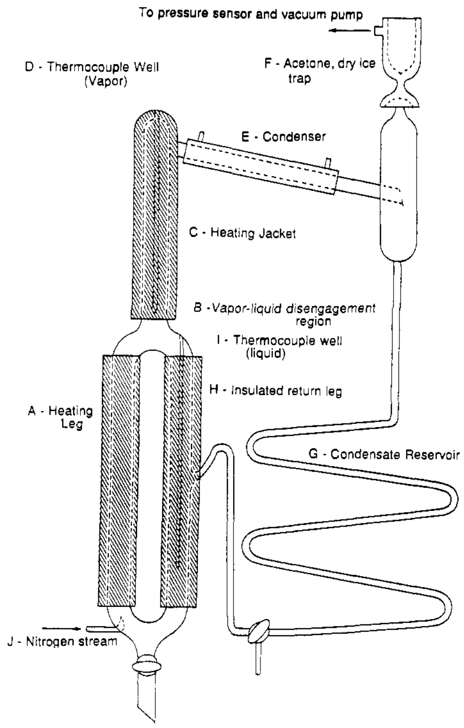

Figure 1. Recirculation still for measurement of vapor-liquid equilibria.

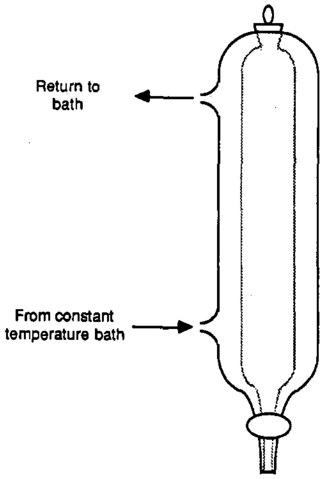

Figure 2. Apparatus for measurement of liquid-liquid equilibrium data.

Two chromatograph columns were used with the redundant results checked for consistency. All columns were 1.81 m long with an internal diameter of 0.51 cm. Column one was packed with 5% Carbowax 20M on 100-120 Supelcoport and operated isothermally at 388 K. Column two was packed with 10% Carbowax 1200 on Carbopack and was operated at 388 K for 2 min, increased to 458 K over 3.5 min, and held for 2.5 min. Calibration analyses were carried out to convert the peak area ratio to the weight composition of the mixture. The composition of the samples differed by less than 5 wt % from the nearest calibration point. Concentration measurements were generally accurate to within a relative error of 1%.

The weight fraction of water was determined by Karl Fischer analysis using Hydranal, a Eugen Scholz reagent manufactured by Riedel-deHaen, and was generally accurate to within a relative error of 0.5%.

Results and Discussion

There is little scatter in the experimental data and the goodness of fit suggests that the data are thermodynamically consistent. Furthermore, the liquid-liquid equilibrium measurements for the SBA-water and SBA-water-MEK systems compared well with data in the literature (see Table III). The system is modeled using the UNIQUAC equation for the liquid-phase activity coefficients (*10*) and assuming the vapor phase to be ideal.

Table III. A Comparison of Liquid-Liquid Equilibrium Mole Fractions with the Data of Altsybeeva and Morachevskii (*12*)

		ref *12* (313.15 K)	this work (311.15 K)	abs diff
binary				
org phase	SBA	0.3300	0.3320	0.0020
	water	0.6700	0.6680	−0.0020
aq phase	SBA	0.0460	0.0472	0.0012
	water	0.9540	0.9528	−0.0012
ternary				
org phase	SBA	0.2760	0.2582	0.0178
	water	0.6950	0.7127	−0.0177
	MEK	0.0290	0.0291	−0.0001
aq phase	SBA	0.0480	0.0434	0.0046
	water	0.9450	0.9502	−0.0052
	MEK	0.0070	0.0064	0.0006

Table IV. UNIQUAC Parameters from the Reduction of Binary and Ternary Vapor-Liquid Equilibrium Data

Size and Shape Parameters

	r	q	q'
SBA	3.9235	3.6640	4.0643
DSBE	6.0909	5.1680	5.7409
water	0.9200	1.4000	1.6741

Interaction Coefficients, a_{ij}, cal/mol

	SBA	DSBE	water
SBA	0.000	−192.374	461.126
DSBE	415.417	0.000	287.611
water	128.233	3923.53	0.000

Table V. Experimental Vapor-Liquid Equilibrium Data for the SBA-DSBE System

data point	press., mmHg	temp, K	mole fractions	
			x_{SBA}	y_{SBA}
1	600	365.7	0.9458	0.9355
2	601	365.6	0.9187	0.9061
3	601	366.0	0.9731	0.9654
4	746	371.3	0.8571	0.8585
5	748	371.6	0.9470	0.9362
6	749	371.4	0.9046	0.8985
7	749	371.7	0.8840	0.8799
8	749	371.8	0.9688	0.9618
9	755	372.7	0.6446	0.7265
10	755	373.7	0.5568	0.6855
11	764	372.5	0.8705	0.8679
12	764	372.6	0.7908	0.8083
13	764	372.6	0.8990	0.8933
14	764	372.7	0.8513	0.8509
15	767	373.1	0.9572	0.9477
16	768	372.8	0.9296	0.9198

Because the binary azeotropes must be accurately modeled when simulating the distillation tower, the binary interaction coefficients for the SBA-DSBE and SBA-water binaries were determined first. These binary coefficients served as initial estimates when reducing the combined binary and ternary equilibrium data to obtain the UNIQUAC coefficients (Table IV). The experimental data are shown graphically in Figures 3 and 4, and in tabular form in Tables V, VI, and VII.

For the liquid-liquid equilibrium data, the initial UNIQUAC coefficients were computed using the CHEMTRAN program by ChemShare Corp. These coefficients were adjusted manually to obtain a better fit. The final interaction coefficients and shape parameters are shown in Table VIII. The liquid-liquid

Table VI. Experimental Vapor-Liquid Equilibrium Data Used To Determine the Initial Interaction Coefficients for the SBA-Water System

data point	ref	press., mmHg	temp, K	mole fractions x_{SBA}	mole fractions y_{SBA}
1	*13*	600	354.67	0.4490	0.3820
2	*13*	600	354.69	0.3890	0.3770
3	*13*	760	360.68	0.4490	0.3950
4	*13*	760	360.74	0.5100	0.4130
5	*13*	760	361.15	0.5890	0.4430
6	*13*	760	362.18	0.6930	0.5040
7	*13*	760	364.21	0.7860	0.5870
8	*14*	760	366.95	0.9300	0.7580
9	*14*	760	368.95	0.9600	0.8400

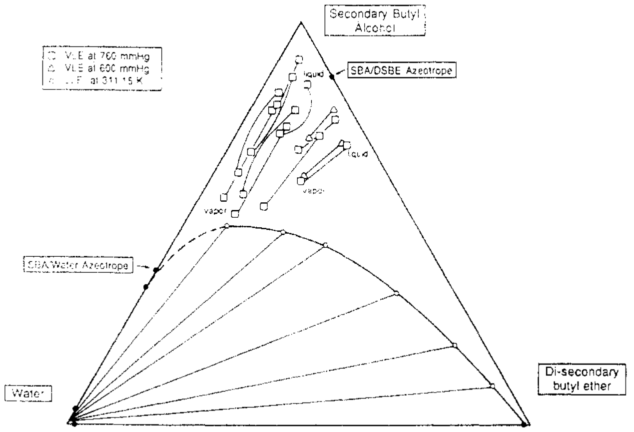

Figure 3. Vapor-liquid and liquid-liquid equilibrium data (mole fractions).

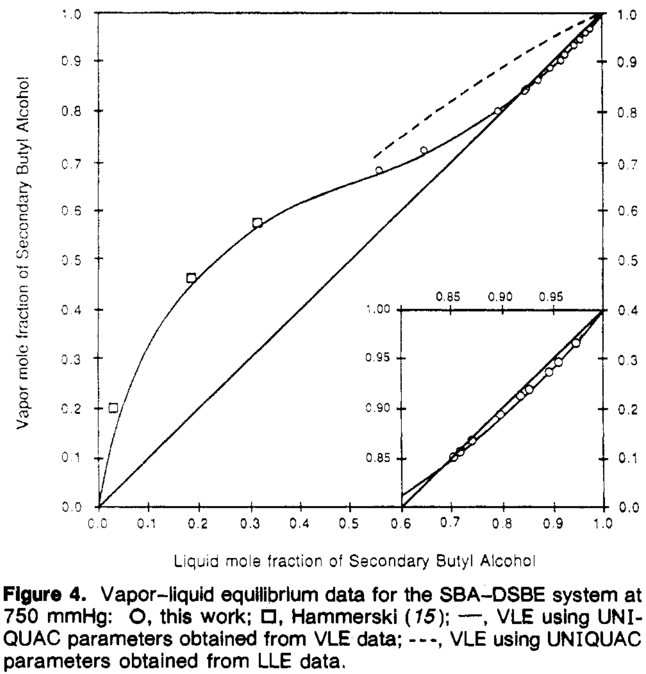

Figure 4. Vapor-liquid equilibrium data for the SBA-DSBE system at 750 mmHg: ○, this work; □, Hammerski (*15*); —, VLE using UNIQUAC parameters obtained from VLE data; ---, VLE using UNIQUAC parameters obtained from LLE data.

equilibrium data are reported in Tables IX and X and a comparison of the experimental data and the calculated liquid-liquid equilibria using the UNIQUAC equation, with the interaction coefficients of Table VIII, is presented in Figure 5. This figure also shows the results of vapor-liquid equilibrium calculations using the vapor pressure data in Table II. These results differ greatly from the experimental data, as exemplified by the $K_{SBA} = K_{DSBE}$ curve which should intersect the SBA-DSBE axis at 87 mol % SBA. The isotherm at 370 K and $P = 1.1816$ bar illustrates the variation in liquid mole fractions at fixed temperature and pressure.

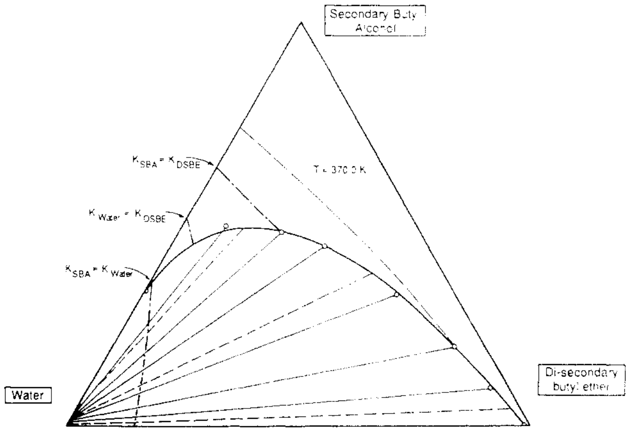

Figure 5. Liquid-liquid equilibrium data, mole fractions (○). Dashed tie lines and binodal curve computed with the UNIQUAC equation and interaction coefficients in Table VIII. 370 K isotherm and $K_{SBA} = K_{DSBE}$, $K_{water} = K_{DSBE}$, $K_{SBA} = K_{Water}$ curves computed by using vapor pressure data (Table II) and the UNIQUAC equation with interaction coefficients in Table VIII.

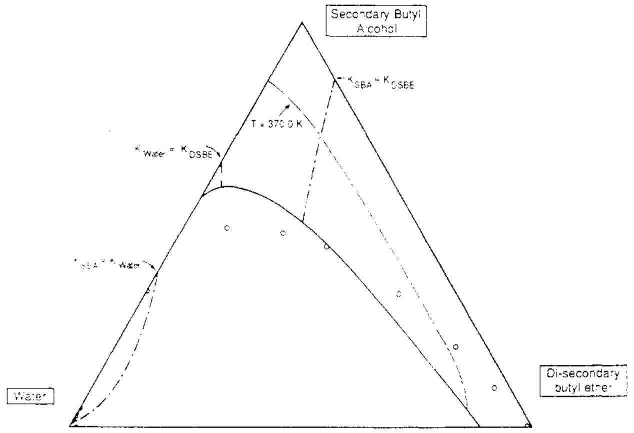

Figure 6. Liquid-liquid equilibrium data, mole fractions (○). Binodal curve (solid) computed with the UNIQUAC equation and interaction coefficients in Table IV. 370 K isotherm and $K_{SBA} = K_{DSBE}$, $K_{water} = K_{DSBE}$, $K_{SBA} = K_{Water}$ curves computed by using vapor pressure data (Table II) and the UNIQUAC equation with interaction coefficients in Table IV.

Excellent agreement with the VLE data was obtained when the UNIQUAC equation was used with the interaction coefficients in Table IV. Moreover, an important measure of the suitability of the data fit for analysis of distillation towers is the accuracy with which the relative volatility (K_i/K_j) contours are reproduced. The contours along which two species have the same volatility ($K_i/K_j = 1$) are most noteworthy as their intersection with the axes occurs at the binary azeotropes. Figure 6 shows that the $K_{SBA} = K_{DSBE}$ and the $K_{SBA} = K_{Water}$ curves accurately reproduce the binary azeotropes. The second intersection of the $K_{SBA} = K_{Water}$ curve with the SBA-water axis suggests a second azeotrope, a possibility supported by the vapor-liquid and liquid-liquid equilibrium data in the literature. Unfortunately, however, poor agreement is obtained between the LLE data and the results of the LLE calculations when these interaction coefficients are used.

In summary, the liquid-liquid and vapor-liquid equilibrium data are accurately modelled *independently* by the UNIQUAC equation. However, an accurate fit of both the VLE and LLE data with a single set of UNIQUAC parameters does not seem possible. Figures 5 and 6 were plotted by using the interaction

Table VII. Experimental Vapor-Liquid Equilibrium Data for the SBA-DSBE-Water System. Calculated Mole Fractions Using Vapor Pressure Data (Table II) and the UNIQUAC Equation with Interaction Coefficients in Table IV

				mole fractions				
data point	source	press., mmHg	temp, K	x_{SBA}	x_{DSBE}	y_{SBA}	y_{DSBE}	y_{water}
1	exptl	765	364.1	0.7723	0.0504	0.5549	0.0578	0.3873
	calcd					0.5585	0.0532	0.3883
	% error					-0.7	-8.0	0.3
2	exptl	763	365.6	0.8109	0.0498	0.6138	0.0575	0.3287
	calcd					0.6134	0.0526	0.3340
	% error					-0.1	-8.4	1.6
3	exptl	763	367.4	0.8556	0.0506	0.6898	0.057	0.2532
	calcd					0.6924	0.0545	0.2530
	% error					0.4	-4.4	-0.1
4	exptl	762	369.6	0.8979	0.0494	0.7840	0.0575	0.1585
	calcd					0.7851	0.0554	0.1595
	% error					0.1	-3.6	0.6
5	exptl	762	363.5	0.7325	0.1012	0.5140	0.1009	0.3851
	calcd					0.5226	0.0938	0.3836
	% error					1.7	-7.0	-0.4
6	exptl	752	364.6	0.7711	0.1009	0.5656	0.0989	0.3355
	calcd					0.5808	0.095	0.3241
	% error					2.7	-3.9	-3.4
7	exptl	751	368.3	0.8373	0.0969	0.7162	0.0998	0.1840
	calcd					0.7069	0.0969	0.1962
	% error					-1.3	-2.9	6.7
8	exptl	750	364.6	0.7091	0.1850	0.5358	0.1552	0.3090
	calcd					0.5520	0.1491	0.2989
	% error					3.0	-3.9	-3.3
9	exptl	600	361.2	0.6884	0.2460	0.6070	0.2094	0.1836
	calcd					0.5888	0.1929	0.2185
	% error					-3.0	-7.9	19.0
10	exptl	600	362.5	0.7739	0.1869	0.7043	0.1675	0.1282
	calcd					0.6940	0.1700	0.1360
	% error					-1.4	1.5	6.1
11	exptl	744	366.6	0.7504	0.2000	0.6713	0.1675	0.1612
	calcd					0.6631	0.1708	0.1660
	% error					-1.2	2.0	3.0
12	exptl	749	366.9	0.6863	0.2598	0.6003	0.2008	0.1989
	calcd					0.6145	0.1995	0.1860
	% error					2.4	-0.7	-6.5

Table VIII. UNIQUAC Parameters from the Reduction of Ternary Liquid-Liquid Equilibrium Data

Size and Shape Parameters

	r	q	q'
SBA	3.9235	3.6640	3.6640
DSBE	6.0909	5.1680	5.1680
water	0.9200	1.4000	1.4000

Interaction Coefficients, a_{ij}, cal/mol

	SBA	DSBE	water
SBA	0.000	89.591	331.559
DSBE	-100.288	0.000	1834.309
water	139.216	126.950	0.000

Table IX. Liquid-Liquid Equilibrium Mole Fractions for the SBA-DSBE-Water System at 311.15 K

data point	aqueous phase		organic phase	
	x'_{SBA}	x'_{DSBE}	x''_{SBA}	x''_{DSBE}
1	0.0472	0.0000	0.3320	0.0000
2	0.0288	<0.0001	0.4910	0.0980
3	0.0234	0.0001	0.4785	0.2234
4	0.0190	<0.0001	0.4420	0.3330
5	0.0177	0.0001	0.3226	0.5480
6	0.0173	<0.0001	0.1963	0.7388
7	0.0104	0.0001	0.0926	0.8675
8	0.0000	0.0142	0.0000	0.9860

Table X. Liquid-Liquid Equilibrium Mole Fractions for the SBA-DSBE-Water-MEK System at 311.15 K

data point	aqueous phase			organic phase		
	x'_{SBA}	x'_{DSBE}	x'_{water}	x''_{SBA}	x''_{DSBE}	x''_{water}
1	0.0434	0.0000	0.9502	0.2582	0.0000	0.7127
2	0.0231	<0.0001	0.9737	0.4355	0.0935	0.4317
3	0.0216	0.0001	0.9749	0.4200	0.2209	0.3153
4	0.0143	0.0001	0.9834	0.3764	0.3409	0.2423

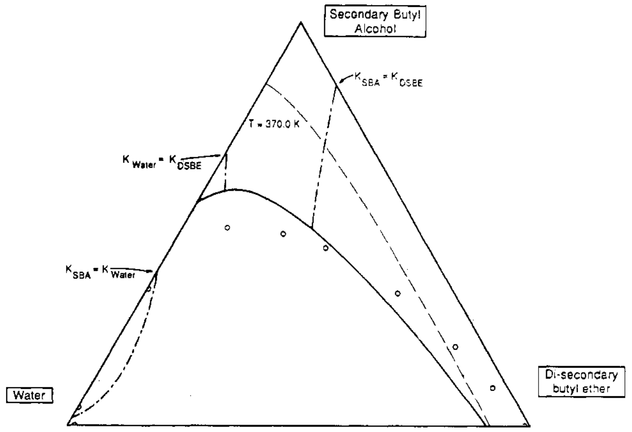

Figure 7. Liquid–liquid equilibrium data, mole fractions (O). Calculated results using the UNIQUAC equation with compromise interaction coefficients in Table XI. See Figures 5 and 6.

parameters determined from the liquid–liquid and vapor–liquid equilibrium data, respectively.

Because two liquid phases occur on many of the trays in the azeotropic distillation tower, a compromise set of interaction coefficients was used (Table XI). The agreement with the vapor–liquid equilibrium data was relaxed to gain somewhat better agreement with the binodal curve, as shown in Figure 7. With the exception of the flow rate of the aqueous reflux, the simulation results are in excellent agreement with the experi-

Table XI. Compromise UNIQUAC Parameters

Size and Shape Parameters

	r	q	q'
SBA	3.9235	3.6640	4.0643
DSBE	6.0909	5.1680	5.7409
water	0.9200	1.4000	1.6741

Interaction Coefficients, a_{ij}, cal/mol

	SBA	DSBE	water
SBA	0.000	−193.141	424.025
DSBE	415.855	0.000	315.312
water	103.810	3922.50	0.000

mental measurements for the tower (*1*).

Acknowledgment

Len Fabiano and Walt Mameniskis of ARCO Chemical Co. arranged for and helped with the experimental measurements. John Adams of Chemshare Corp. provided the CHEMTRAN software package for use in the data reduction.

Glossary

a_{ij}	adjustable interaction coefficients
c	regression parameter
K	vapor–liquid equilibrium constant
P	pressure, bar
q	structural area parameter
q'	modified structural area parameter
r	structural size (volume) parameter
T	temperature, K
x'	mole fraction in first liquid phase
x''	mole fraction in second liquid phase
y	vapor mole fraction

Subscripts

i, j	chemical species indices

Registry No. SBA, 78-92-2; MEK, 78-93-3; DSBE, 6863-58-7.

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Received for review August 22, 1986. Revised August 13, 1987. Accepted October 14, 1987. Financial support was provided by the NSF Project CPE-8118023.

Measurements of *PVTx* Properties for the R 13B1 + R 114 System

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The *PVTx* properties for the R 13B1 + R 114 system have been measured by the constant-volume method coupled with several isothermal expansion procedures. The results for four different compositions of 25, 50, 70, and 80 wt % R 13B1 cover the range of temperatures 303–443 K and the range of pressures 0.5–10.3 MPa, which corresponds to the density variation from 150 to 1200 kg/m^3. The experimental uncertainties of the temperature, pressure, density, and mass fraction measurements were estimated to be no greater than 8 mK, 2.0 kPa, 0.15%, and 0.12%, respectively. The dew and bubble points were determined.

Introduction

The *PVTx* properties of refrigerant mixtures have been recently of particular interest not only to the refrigeration industry but also to the power industry since refrigerant mixtures have become regarded as new, prospective working substances. We have been measuring the *PVTx* properties of refrigerant mixtures systematically and the results on the R 12 + R 22 system (*1*) and the R 22 + R 114 system (*2*) were published. In succession we have measured the *PVTx* properties of the R 13B1 + R 114 system. This paper reports the *PVTx* measurements for four different compositions of 25, 50, 70, and 80 wt % R 13B1 in the range of temperatures 303–443 K and the range of pressures 0.5–10.3 MPa, which covers the density range 150–1200 kg/m^3. The dew and bubble points are also reported. The purity of each component supplied was either 99.965 or 99.990 wt % R 13B1 (bromotrifluoromethane, $CBrF_3$) and 99.94 wt % R 114 (dichlorotetrafluoroethane) being an isomeric blend of 95% $CClF_2CClF_2$ + 5% CCl_2FCF_3.

Experimental Section

The *PVTx* measurements of this work have been made by the constant-volume method coupled with several isothermal expansion procedures for a mixture of a given composition. The apparatus and experimental procedure used here have

0021-9568/88/1733-0020$01.50/0