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Equilibrium Phase Properties of the Methanol-Isobutane Binary System

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Vapor and liquid equilibrium phase compositions were determined at 0.0, 50.0, 100.0, 125.0, 131.0, 133.0, and 150.0 °C for the methanol-isobutane binary system. Measurements were made at each temperature from the vapor pressure of the methanol to the vapor pressure of the isobutane or to the maximum azeotropic or critical pressure, whichever was higher. Equilibrium ratios for each component were calculated at each temperature from the phase composition data. The azeotropic pressures and associated compositions were measured, and an expression relating azeotropic pressure and composition was developed. The critical temperatures and corresponding critical pressure were measured, and the critical locus was constructed.

Introduction

The phase behavior of methanol-alkane binary mixtures has received increased interest in recent years. This interest has arisen for a variety of reasons, including in particular the role of methanol as a hydrate inhibitor in gas transportation and processing operations and the use of methanol and other alcohols and ethers in motor gasoline. In addition to this industrial interest, methanol-alkane mixtures are often used as model systems for understanding polar-nonpolar mixture behavior and for developing mixing rules and interaction parameters for equation of state work for this class of systems. Vapor-liquid equilibrium in the *n*-butane-methanol binary system was studied by Leu et al. (1) at 0, 50, and 100 °C, and the azeotropic behavior of this system has been reported by Churkin et al. (2). No previous published work has been found for the methanol-isobutane system. In view of the importance of the system and the lack of data on it, the present study was undertaken. The objective was to determine vapor-liquid equilibrium data in the range from 0 to 150 °C and to explore the azeotrope and critical regions wherever they occurred.

Experimental Section

The equipment used and the method of operation for this study were basically the same as that described previously by Huang et al. (3).

Equilibrium was attained by mechanically rocking the entire assembly. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under

isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals. After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was then sampled and analyzed by using a similar procedure.

The azeotropic region was approached isothermally by adjusting pressure or altering the composition through appropriate addition of more material. After the equilibration process had been completed, the azeotropic pressure corresponding to a given experimental temperature was determined using the equilibrium phase compositions as a guide. When the composition difference between the vapor and liquid phases was less than 2×10^{-4} mole fraction, the azeotropic point was considered to have been attained.

The critical point was obtained at isothermal conditions by using an iterative experimental procedure involving changes in pressure and/or composition. As equilibrium was approached in the critical region, minor isothermal adjustments in the pressure were made to observe changes along the phase boundary and to note the critical opalescence. When the critical pressure had been determined, the pressure was increased well into the single-phase region so that the system could be sampled and analyzed to obtain the composition at the critical point.

Temperatures were measured with iron-constantan thermocouples which had been calibrated against a platinum resistance thermometer. Each temperature was read out on a digital voltmeter (HP-3455A). Temperatures are believed known to within ± 0.1 °C or better. Pressures were measured with various strain gauge pressure transducers, depending on the range and magnitude of the pressures encountered during the experiment. These had been calibrated with a precision dead-weight gauge. The various transducers were Druck PA-110/W (0-15 psia; 0.1% full scale (FS)); Statham PA208TC-100-350 (0-100 psia; 0.15% FS); and Statham UGP4-200 (0-200 psig; 0.15 FS), -500 (0-500 psig; 0.15% FS), and -1000 (0-1000 psig; 0.15 FS). The pressure is believed known to within $\pm 0.15\%$ of the full scale or better.

The phase compositions were determined with a Hewlett-Packard Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used for this binary system. The column used was a 2.44-m-length by 3.18-mm-diameter stainless steel tube packed with Porapak-QS and was maintained at 105 °C. The response factor for converting from area fraction to mole fraction for isobutane was 1.7393 with respect

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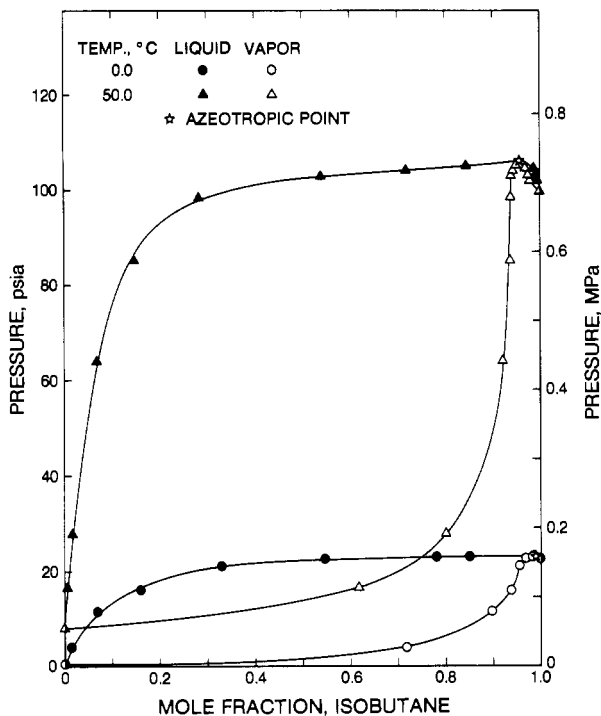


Figure 1. Equilibrium phase compositions in the binary system containing methanol and isobutane at 0 and 50 °C.

to methanol. This was obtained using gravimetrically prepared standard mixtures for the calibrating chromatographic runs. At least six samples of each phase were taken for analysis. The reported compositions are the result of averaging at least four out of six determinations. The precision of the analysis was generally better than 2% relative standard deviation.

When the physical properties in the critical region were determined, the given experimental temperature was considered to be the critical temperature. The corresponding critical pressure was determined by averaging the two values obtained from isothermal compression and expansion observations, as described earlier.

Materials

High-performance liquid chromatographic grade methanol of 99.9 mol % purity was obtained from the Fisher Scientific Co. Instrument grade 2-methylpropane (isobutane) of 99.5+ mol % minimum purity was obtained from Matheson Gas Products, Canada, Inc. Gas chromatograms were run on these two compounds, but no detectable impurities were found. Thus, these materials were used without further purification. The methanol was degassed in the equilibrium cell before the addition of isobutane.

Results and Discussion

The experimental measurements of the equilibrium phase composition for the methanol–isobutane system are given in Table I. The vapor- and liquid-phase envelopes for this system are shown in Figure 1 for two isotherms at 0.0, and 50.0 °C and in Figure 2 for four isotherms at 100.0, 125.0, 133.0, and 150.0 °C. The calculated equilibrium ratios K_i for each component in the binary system at each of the seven isotherms are also given in Table I. The values for four temperatures are shown in Figure 3.

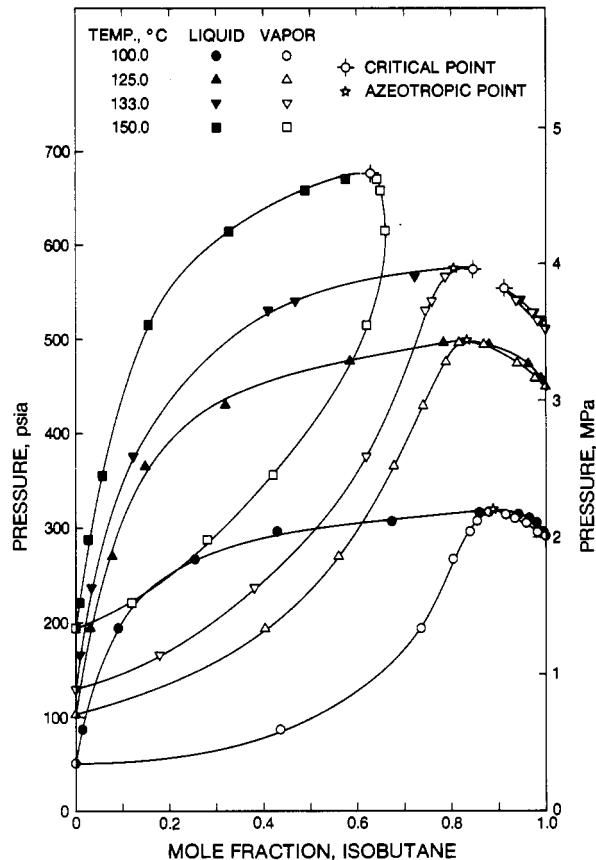


Figure 2. Equilibrium phase compositions in the binary system containing methanol and isobutane at four temperatures, including the critical and azeotrope regions.

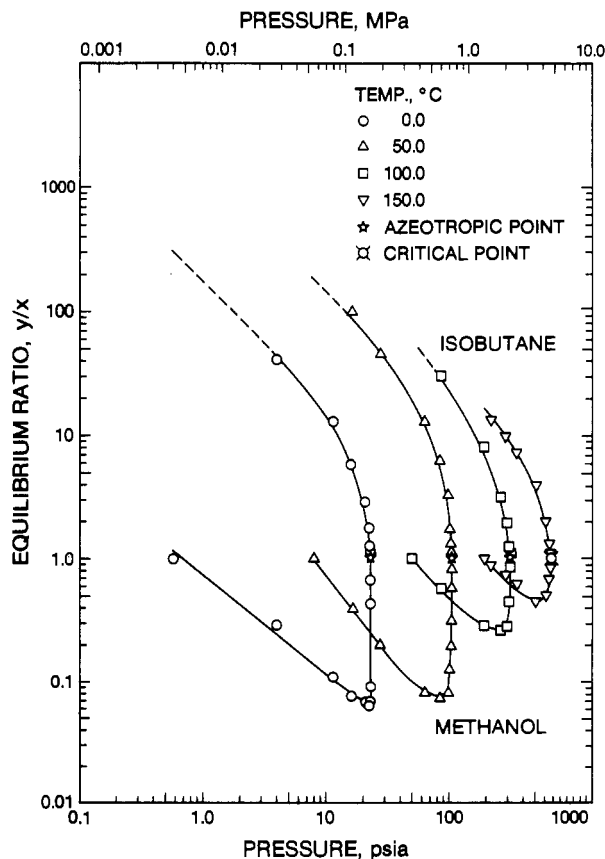


Figure 3. Equilibrium ratios for methanol and isobutane in the binary system.

Table I. Equilibrium Phase Properties of the Methanol (1)–Isobutane (2) System: Pressure p , Liquid-Phase Mole Fraction x_2 , Vapor-Phase Mole Fraction y_2 , and Equilibrium Ratio K_1 at Temperature t

p/MPa	x_2	y_2	K_2	K_1	p/MPa	x_2	y_2	K_2	K_1
$t = 0.0\text{ }^\circ\text{C}$									
0.0039	0.000	0.0000		1.000	0.1588	0.9742	0.9889	1.02	0.430
0.0268	0.0173	0.7170	41.4	0.288	0.1589	0.9845	0.9896	1.01	0.671
0.0787	0.0690	0.8976	13.0	0.110	0.1591	0.9906 ^a	0.9906	1.00	1.00
0.1111	0.1615	0.9371	5.80	0.0750	0.1588	0.9935	0.9908	0.997	1.42
0.1443	0.3309	0.9560	2.89	0.0658	0.1581	0.9969	0.9925	0.996	2.47
0.1558	0.5463	0.9715	1.78	0.0628	0.1577	0.9989	0.9954	0.996	4.30
0.1564	0.7819	0.9851	1.26	0.0684	0.1576	0.9995	0.9974	0.997	5.02
0.1580	0.8509	0.9864	1.16	0.0914	0.1574	1.0000	1.0000	1.000	
$t = 50.0\text{ }^\circ\text{C}$									
0.0554	0.0000	0.0000		1.000	0.7262	0.9238	0.9548	1.03	0.593
0.1143	0.0062	0.6167	99.1	0.386	0.7293	0.9209	0.9546	1.04	0.574
0.1910	0.0178	0.8015	45.1	0.202	0.7311	0.9459	0.9554	1.01	0.810
0.4411	0.0707	0.9224	13.1	0.0835	0.7332	0.9562 ^a	0.9562	1.00	1.00
0.5881	0.1482	0.9384	6.33	0.0724	0.7317	0.9633	0.9582	0.995	1.14
0.6787	0.2838	0.9394	3.31	0.0846	0.7205	0.9887	0.9716	0.983	2.53
0.7105	0.5399	0.9419	1.74	0.126	0.7126	0.9926	0.9753	0.983	3.33
0.7181	0.7171	0.9443	1.32	0.197	0.7068	0.9948	0.9786	0.984	4.13
0.7209	0.7953	0.9499	1.19	0.245	0.6877	1.0000	1.0000	1.000	
0.7255	0.8454	0.9516	1.13	0.313					
$t = 100.0\text{ }^\circ\text{C}$									
0.3470	0.0000	0.0000		1.000	2.190	0.8883 ^a	0.8883	1.00	1.00
0.5965	0.0143	0.4329	30.2	0.575	2.167	0.9416	0.9164	0.973	1.43
1.338	0.0914	0.7349	8.04	0.292	2.139	0.9662	0.9359	0.967	1.90
1.843	0.2542	0.8021	3.16	0.265	2.103	0.9828	0.9596	0.976	2.35
2.041	0.4290	0.8397	1.96	0.281	2.036	0.9952	0.9834	0.988	3.45
2.119	0.6730	0.8537	1.27	0.447	2.017	0.9991	0.9961	0.997	4.26
2.180	0.8595	0.8794	1.02	0.858	2.017	1.0000	1.0000	1.000	
$t = 125.0\text{ }^\circ\text{C}$									
0.712	0.0000	0.0000		1.000	3.438	0.8320 ^a	0.8320	1.00	1.00
1.280	0.0333	0.4047	12.1	0.616	3.435	0.8525	0.8457	0.992	1.05
1.866	0.0774	0.5601	7.24	0.477	3.412	0.8793	0.8666	0.986	1.11
2.519	0.1482	0.6762	4.56	0.380	3.264	0.9647	0.9406	0.975	1.68
2.965	0.3198	0.7354	2.30	0.389	3.161	0.9898	0.9765	0.987	2.29
3.289	0.5844	0.7890	1.35	0.508	3.138	0.9943	0.9847	0.990	2.68
3.429	0.7815	0.8157	1.04	0.843	3.104	1.0000	1.000	1.000	
$t = 131.0\text{ }^\circ\text{C}$									
0.8412	0.0000	0.0000		1.000	3.802	0.8421	0.8393	0.997	1.02
1.0825	0.0156	0.2051	16.1	0.761	3.773	0.8816	0.8730	0.990	1.07
1.4762	0.0326	0.3750	11.5	0.646	3.694	0.9308	0.9142	0.982	1.12
1.9602	0.0634	0.5140	8.11	0.519	3.608	0.9540	0.9318	0.977	1.48
2.9261	0.1916	0.6432	3.36	0.441	3.491	0.9812	0.9616	0.980	2.04
3.5687	0.4768	0.7439	1.56	0.490	3.450	0.9940	0.9845	0.991	2.56
3.707	0.6609	0.7742	1.17	0.666	3.420	1.0000	1.0000	1.000	
3.808	0.8126 ^a	0.8126	1.00	1.00					
$t = 133.0\text{ }^\circ\text{C}$									
0.886	0.0000	0.0000		1.000	3.959	0.8048 ^a	0.8048	1.00	1.00
1.136	0.0112	0.1790	16.0	0.830	3.951	0.8465 ^b	0.8465	1.00	1.00
1.633	0.0343	0.3815	11.1	0.640	3.816	0.9130 ^b	0.9130	1.00	1.00
2.586	0.1229	0.6169	5.02	0.437	3.742	0.9452	0.9369	0.991	1.15
3.662	0.4107	0.7434	1.81	0.435	3.651	0.9782	0.9711	0.993	1.32
3.723	0.4671	0.7567	1.62	0.457	3.591	0.9897	0.9833	0.994	1.62
3.920	0.7244	0.7868	1.09	0.773	3.529	1.0000	1.0000	1.000	
$t = 150.0\text{ }^\circ\text{C}$									
1.336	0.000	0.0000		1.000	4.424	0.3279	0.6601	2.01	0.506
1.520	0.0092	0.1209	13.2	0.887	4.542	0.4876	0.6489	1.33	0.685
1.982	0.0285	0.2819	9.90	0.739	4.623	0.5724	0.6400	1.12	0.841
2.448	0.0566	0.4169	7.37	0.618	4.679	0.6254 ^b	0.6254	1.00	1.000
3.555	0.1550	0.6196	4.00	0.450					

^a Azeotrope composition. ^b Critical composition.

The measured azeotropic compositions $x_2(\text{Az})$ and corresponding pressures $p(\text{Az})$ and temperatures $t(\text{Az})$ for this system are presented in Table II and are shown in Figure 4. The measured values cover a temperature range from 0.0 to 133.0 °C. The temperature dependence of the azeotropic mole fraction of isobutane can be expressed analytically as

$$x_2(\text{AZ}) = 0.3231 + 4.9938 \times 10^{-3}((t/^\circ\text{C}) + 273.15) - 9.3531 \times 10^{-6}((t/^\circ\text{C}) + 273.15)^2$$

with the correlation coefficient, $r^2 = 0.9981$, and standard error of 0.0044. The measured critical compositions x_2^c , temperatures t^c and pressures p^c for the system are given in Table III and are also shown graphically in Figure 4.

Conclusion

The experimental measurements obtained in the present investigation have filled a literature gap that existed for the binary

Table II. Azeotropic Properties for the Methanol (1)-Isobutane (2) Binary System: Temperature $t(\text{Az})$, Pressure $p(\text{Az})$, Mole Fraction $x_2(\text{Az})$

$t(\text{Az})/^\circ\text{C}$	$p(\text{Az})/\text{MPa}$	$x_2(\text{Az})$	$t(\text{Az})/^\circ\text{C}$	$p(\text{Az})/\text{MPa}$	$x_2(\text{Az})$
0.0	0.1591	0.9906	125.0	3.438	0.8320
50.0	0.7332	0.9562	131.0	3.808	0.8126
100.0	2.190	0.8883	133.0	3.959	0.8048

Table III. Critical and Corresponding Temperatures t^c and Pressures p^c on the Mole Fractions x_i^c Critical Locus of the Methanol (1)-Isobutane (2) Binary System

x_2^c	$t^c/^\circ\text{C}$	p^c/MPa	x_2^c	$t^c/^\circ\text{C}$	p^c/MPa
0.000	239.4 ^a	8.096 ^a	0.625	150.0	4.679
0.846	133.0	3.951	1.000	135.0 ^a	3.648 ^a
0.913	133.0	3.816			

^aReference 4.

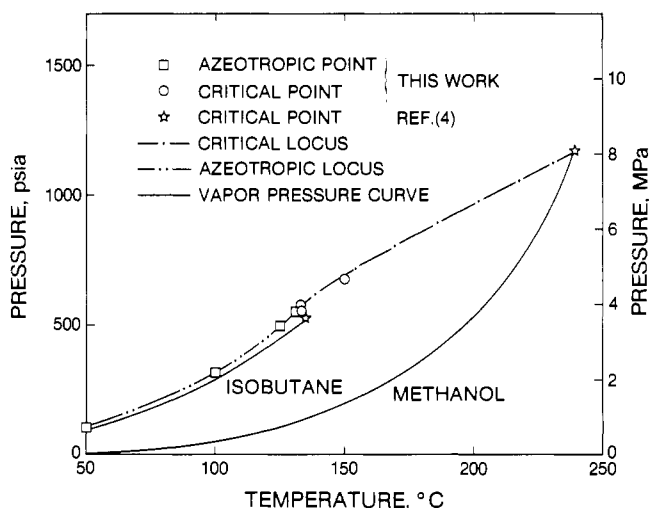


Figure 4. Critical and azeotropic loci in the methanol-isobutane binary system.

vapor-liquid equilibrium data for the isobutane-methanol binary system. The information obtained will be useful for evaluating the optimum binary interaction parameters in equation of state modeling of systems containing this polar-nonpolar binary pair.

The observations made for the system at 133.0 °C merit further discussion. At temperatures above this (150.0 °C), the

system showed the conventional behavior of a binary system in the critical region. At temperatures below, the system showed typical azeotropic behavior with a pressure maximum. At 133.0 °C, as illustrated in Figure 2, the system showed both an azeotrope and two critical points. The two-phase region disappeared between isobutane concentrations of 0.823 and 0.855 mole fraction. At some temperature slightly higher than 133.0 °C, the azeotrope and one critical point presumably merge, and at some point the right-hand lobe of the two-phase region would disappear.

A liquid-liquid miscibility gap was not observed at any of the experimental conditions considered in this investigation.

Acknowledgment

We thank Dr. John Carroll who carried out the correlation of the azeotropic physical properties.

Glossary

Az	azeotropic property
K_i	equilibrium ratio, y_i/x_i
p	pressure, MPa
t	temperature, °C
x_i	mole fraction of component i in liquid phase
y_i	mole fraction of component i in vapor phase

Subscript

i component ($i = 1$, methanol; $i = 2$, isobutane)

Superscript

^c critical property

Registry No. $\text{H}_3\text{CCH}(\text{CH}_3)\text{CH}_3$, 75-28-5; H_3COH , 67-56-1.

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