

# Vapor-Liquid Equilibria at Subatmospheric Pressures of the Ethylcyclohexane-*n*-Octane System

P. S. PRABHU and M. VAN WINKLE  
University of Texas, Austin, Texas

Vapor-liquid equilibria are reported for the system *n*-octane-ethylcyclohexane at 760, 500, 400, 100, and 50mm. of Hg total pressure. Essentially, the system behaves ideally at all pressures, although the relative volatility increases with increase in pressure.

VAPOR-LIQUID EQUILIBRIA for the system ethylcyclohexane-*n*-octane were determined at 760, 500, 400, 100, and 50mm. of Hg pressure. The investigation, part of a study of the vapor-liquid equilibrium characteristics of mixtures of hydrocarbons of different molecular structure under vacuum conditions, indicated the binary system behaves essentially ideally. Activity coefficients of both components were nearly unity at all pressures and compositions investigated.

## MATERIALS

Table I compares the experimental properties of the materials with those reported in the literature.

The vapor pressure data were calculated from the Antoine equation using the values of the constants reported by Dreisbach (1, 2).

Table I. Properties of Materials

	Ethylcyclohexane	
	Experimental	Literature (1)
$n_D^{30}$	1.42837	1.42859
Density $d_4^{30}$	0.7794	0.77988
N.B.Pt. °C. at 760mm.	131.7	131.78
	<i>n</i> -Octane	
	Experimental	Literature (2)
$n_D^{30}$	1.39287	1.39269
Density $d_4^{30}$	0.6949	0.69445
N.B.Pt. °C. at 760mm.	125.6	125.67

## EXPERIMENTAL PROCEDURE AND EQUIPMENT

A modified form of the Colburn equilibrium still (3) previously described (4) was used in all experiments. Pressure was controlled by the use of a manostat and temperature was measured by an iron-constantin thermocouple in conjunction with a Leeds and Northrup potentiometer.

The procedure was identical with that reported previously (4) and is the standard procedure for this laboratory for vacuum vapor-liquid equilibrium determination.

The compositions of the vapor and liquid equilibrium sample were determined by means of refractive index measurements at 30° C. using a Bausch and Lomb precision refractometer with a sodium D light source.

## DISCUSSION OF DATA

The data derived from the experimental study are

reported in Table II along with the calculated activity coefficients. The activity coefficients are defined by:

$$\gamma_i = (y_i P_T) / (x_i P_i)$$

Table II. Experimental Vapor-Liquid Equilibrium Data  
System: *n*-Octane-Ethylcyclohexane

Temp., ° F.	Mole Fraction <i>n</i> -Octane		$\gamma_0$	$\gamma_{ECH}$
	Liquid	Vapor		
Pressure 760mm.				
268.2	0.119	0.143	1.03	0.98
267.6	0.192	0.220	1.00	0.98
266.1	0.286	0.315	0.98	0.98
264.85	0.388	0.424	0.99	0.98
263.75	0.489	0.525	0.99	0.99
262.45	0.589	0.623	0.99	0.99
261.4	0.689	0.715	0.99	0.99
260.4	0.785	0.806	0.99	0.99
259.4	0.894	0.902	0.99	1.00
Pressure 500mm.				
241.0	0.112	0.132	1.02	0.99
240.0	0.190	0.215	1.00	1.00
239.0	0.290	0.318	0.98	1.01
238.1	0.383	0.416	0.98	1.01
237.2	0.480	0.512	0.98	1.01
236.3	0.591	0.621	0.98	1.01
235.2	0.692	0.716	0.99	1.02
234.2	0.791	0.815	0.99	1.03
233.25	0.906	0.910	0.99	1.05
Pressure 400mm.				
227.7	0.095	0.113	1.03	0.99
226.7	0.191	0.215	0.99	1.00
225.8	0.289	0.317	0.99	1.00
224.8	0.394	0.424	0.98	1.01
223.9	0.481	0.513	0.99	1.01
222.9	0.593	0.623	0.99	1.02
221.9	0.688	0.710	0.99	1.04
221.0	0.795	0.811	0.99	1.04
220.28	0.898	0.908	0.99	1.04
Pressure 100mm.				
155.6	0.099	0.117	1.04	1.00
155.0	0.193	0.217	1.01	1.00
154.5	0.296	0.323	0.99	1.00
153.8	0.385	0.413	0.99	1.00
153.15	0.492	0.522	0.99	1.00
152.55	0.599	0.627	0.99	1.01
151.95	0.689	0.712	0.99	1.02
151.35	0.783	0.797	0.99	1.04
150.70	0.889	0.897	1.00	1.05
Pressure 50mm.				
126.0	0.110	0.127	1.03	0.99
125.6	0.194	0.215	1.00	1.00
125.1	0.289	0.314	1.00	1.00
124.6	0.384	0.414	1.00	1.00
124.1	0.481	0.508	0.99	1.01
123.6	0.593	0.616	0.99	1.01
123.2	0.689	0.708	0.99	1.02
122.7	0.791	0.804	0.99	1.03
122.2	0.898	0.905	1.00	1.04

The values of the experimental activity coefficients are nearly unity which indicates that the binary system behaves essentially ideally at all pressures investigated and over all composition ranges. The very light deviations are attributed to the combined errors in analysis, slight variations in temperature and pressure, and traces of impurities. Certainly the systems can be considered ideal in behavior within the estimated accuracy of the data, about 1%.

The data are consistent by the Redlich (5) test.

The values of the constants in the Margules equation were calculated and are reported in Table III.

$$\ln \gamma_1 = A_1 x_2 + B_1 x_2^2$$

$$\ln \gamma_2 = A_2 x_1 + B_2 x_1^2$$

The values of these constants are very small and approach zero. For an ideal system, the constants would be zero.

This system is interesting because, contrary to the tendency in most binary systems, the relative volatility tends to increase with increase in pressure. This is shown in Figure 1, the equilibrium composition curves at the pressures tested. Examination of the vapor pressure curves of the two components indicates that they diverge slightly as the pressure is increased, thereby increasing the relative volatility.

Figure 2 is a plot of the equilibrium vaporization ratios ( $K = y/x$ ) for the two compounds vs. temperature at constant pressure.

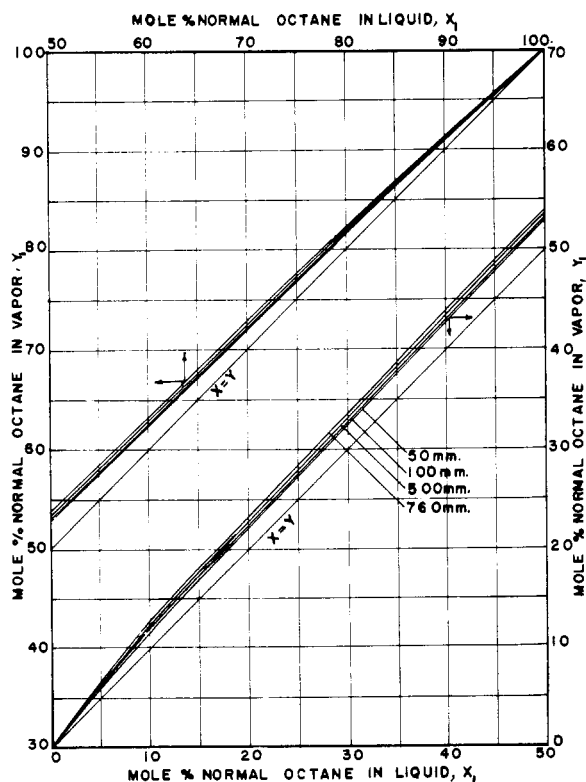


Figure 1. Vapor-liquid equilibrium diagram for the *n*-octane-ethylcyclohexane system at 760, 500, 100, and 50 mm. of Hg absolute

Table III. Margules Constants

Press., Mm. of Hg	$A_1$	$B_1$	$A_2$	$B_2$
760	-0.046	-0.023	-0.012	0.069
500	-0.069	0.065	0.00	0.052
400	-0.023	0.023	-0.012	0.058
100	-0.046	0.058	-0.035	0.081
50	-0.058	0.058	0.00	0.046

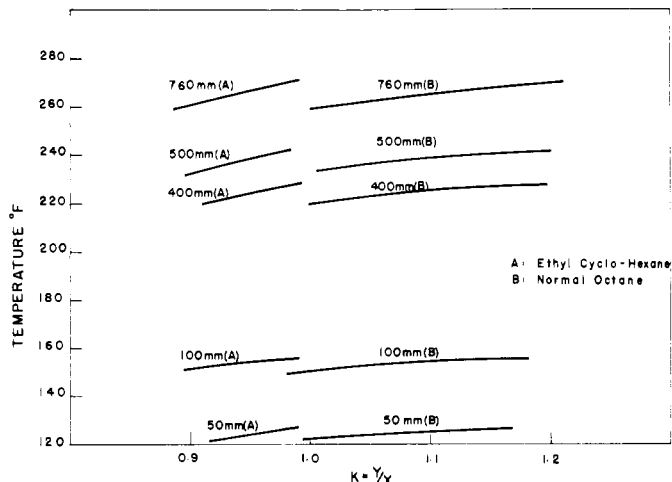


Figure 2. Plot of  $K$  vs. temperature for the *n*-octane-ethylcyclohexane system at different pressures

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#### NOMENCLATURE

- $A, B$  = Margules constants  
 $P_i$  = vapor pressure of component  $i$   
 $P_T$  = total pressure  
 $x, y$  = mole fraction in liquid and vapor, respectively

#### Subscripts

- ECH = ethylcyclohexane  
 O = *n*-octane  
 $i$  = any component  
 1 = *n*-octane  
 2 = ethylcyclohexane

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