Isobaric Vapor–Liquid Equilibrium Data for the System *n*-Hexane–2-Propanol

John M. Rotter and Harold N. Knickle*
Department of Chemical Engineering, The University of Rhode Island, Kingston, Rhode Island 02881

Vapor–liquid equilibrium data have been determined at 760 ± 2 and 380 ± 1 mmHg in an Altsheler still. The binary mixtures were analyzed by density composition data. The activity coefficient curve for *n*-hexane at 380 mmHg exhibits a maximum. The experimental data at both pressures were thermodynamically consistent when tested by Herrington's method.

Isobaric vapor–liquid equilibria for the binary system *n*-hexane–2-propanol have previously been measured at 684 mmHg (*10*). In this study, the vapor–liquid equilibrium data for *n*-hexane–2-propanol are presented at 380 and 760 mmHg.

Experimental Section

The vapor–liquid equilibria were determined using an Altsheler still (*1*). The 2-propanol used was anhydrous reagent from Union Carbide Corporation. The *n*-hexane was purchased from Phillips Petroleum Company and was a pure grade 99. mole % minimum reagent. Physical properties of the reagents are compared with values from the literature in Table I.

Othmer (*6*) has suggested having a large surge tank connected to the vent of the still to maintain constant pressure for vacuum work. Boiling is started and the exhauster is closed off after the desired pressure is reached. The only way for the pressure to change in an air-tight system is by the change in height of the condensing liquid in the condenser. This would be due to a change in the boil-up rate while approaching equilibrium. This type of pressure control is very simple and effective. This method was used to control pressure under a nitrogen atmosphere in the vacuum work and in the atmospheric work when the pressure was above 760 mmHg. Alternately, when the pressure was between 758 and 760 mmHg, the system was vented to the atmosphere and when below 758 mmHg no run was made. A schematic diagram of the pressure control system is presented in Figure 1.

Table I. Physical Properties of Pure Grade Chemicals Used

Material	Specific gravity		Normal bp	
	Exptl	Lit.	Exptl	Lit.
n-Hexane	0.6587 d_4^{20}	0.6603 d_4^{20} (*3*)	68.15	68.73 (*2*)
2-Propanol	0.7839 d_4^{20}	0.7855 d_4^{20} (*3*)	82.1	82.4 (3)

Table II. Density Composition Data for *n*-Hexane–2-Propanol at 23 °C

Mole fraction of *n*-hexane	Density	Mole fraction of *n*-hexane	Density
1.0000	0.6554	0.3355	0.7216
0.8430	0.6654	0.2530	0.7338
0.7252	0.6764	0.1821	0.7455
0.6062	0.6867	0.1119	0.7586
0.5061	0.6990	0.0594	0.7689
0.4195	0.7104	0.0000	0.7819

Atmospheric pressure was measured with a Fortin barometer. The vacuum was simultaneously measured by two methods, a vacuum gauge and a mercury manometer. The pressure control was 760 ± 2 and 380 ± 1 mmHg.

Boiling point temperature in the overhead expansion bellows

Table III. Equilibrium Data and Computed Activity Coefficients for the *n*-Hexane–2-Propanol System at 760 mmHg

760 mmHg mole fraction of *n*-hexane		Temp, °C	γ_1	γ_2
Liquid	Vapor			
0.023	0.136	77.70	4.501	1.065
0.060	0.257	70.05	4.112	1.330
0.117	0.424	68.25	3.680	1.192
0.210	0.558	64.70	3.022	1.209
0.246	0.600	64.10	2.828	1.179
0.286	0.637	63.90	2.600	1.141
0.398	0.672	62.25	2.080	1.325
0.417	0.672	62.20	1.988	1.372
0.493	0.691	61.90	1.746	1.508
0.593	0.706	61.55	1.501	1.819
0.657	0.720	61.60	1.379	2.051
0.673	0.725	61.65	1.353	2.107
0.728	0.727	61.60	1.257	2.521
0.872	0.758	61.80	1.087	4.702
0.923	0.799	62.50	1.058	6.273
0.975	0.856	63.90	1.025	12.930

Table IV. Equilibrium Data and Computed Activity Coefficients for the *n*-Hexane–2-Propanol System at 380 mmHg

380 mmHg mole fraction of *n*-hexane		Temp, °C	γ_1	γ_2
Liquid	Vapor			
0.033	0.150	61.20	2.898	1.126
0.057	0.248	59.15	2.970	1.132
0.070	0.328	56.70	3.475	1.164
0.093	0.465	52.40	4.305	1.195
0.114	0.529	50.75	4.235	1.179
0.135	0.574	49.25	4.095	1.188
0.144	0.590	48.10	4.114	1.233
0.187	0.637	46.80	3.587	1.239
0.277	0.701	44.60	2.890	1.305
0.390	0.730	43.90	2.195	1.457
0.423	0.740	43.65	2.072	1.505
0.466	0.750	43.80	1.894	1.550
0.574	0.756	43.65	1.559	1.914
0.670	0.769	43.65	1.358	2.339
0.742	0.775	43.60	1.238	2.922
0.765	0.783	43.50	1.218	3.113
0.753	0.780	43.60	1.228	2.985
0.777	0.784	43.60	1.196	3.246
0.820	0.795	43.35	1.160	3.874
0.841	0.797	43.40	1.132	4.330
0.890	0.817	43.80	1.080	5.508
0.940	0.850	44.40	1.041	7.986
0.965	0.887	45.20	1.027	9.835

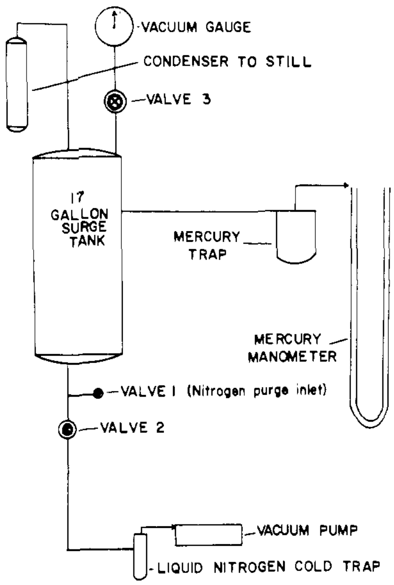

Figure 1. Schematic diagram for the pressure control system.

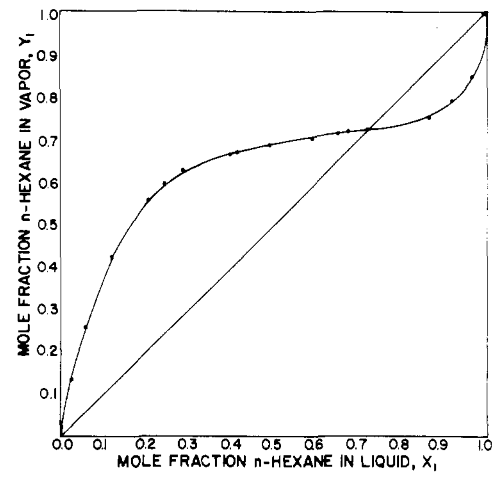

Figure 2. Equilibrium data for the *n*-hexane–2-propanol system at 760 mmHg.

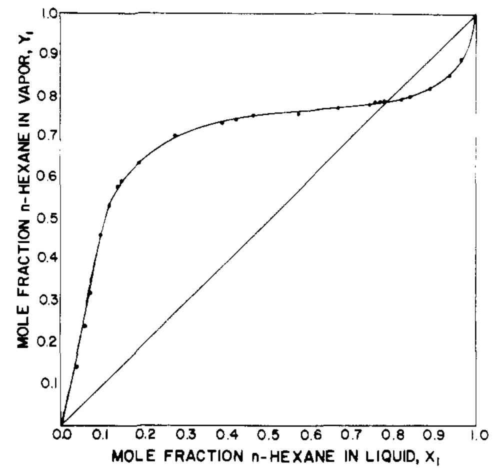

Figure 3. Equilibrium data for the *n*-hexane–2-propanol system at 380 mmHg.

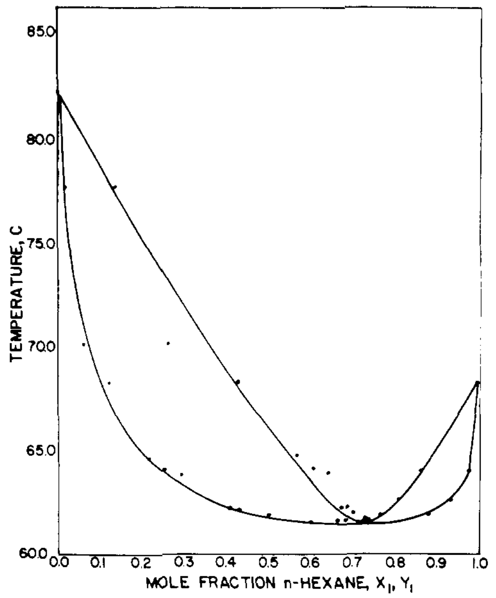

Figure 4. Boiling point composition diagram for the *n*-hexane–2-propanol system at 760 mmHg.

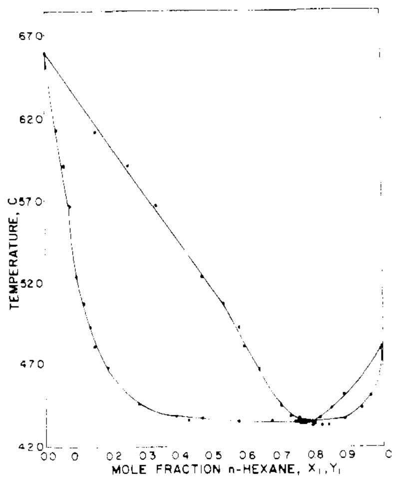

Figure 5. Boiling point composition diagram for the *n*-hexane–2-propanol system at 380 mmHg.

of the Altsheler still was used to determine when equilibrium was obtained. A Cromel–Alumel thermocouple was used for temperature measurement. The potentiometer used was also connected in parallel to a strip chart recorder to allow for continuous temperature monitoring. The still was allowed to run for a half hour at constant temperature to ensure equilibrium was obtained. Temperature measurement was estimated to be accurate to ±0.1 °C.

Analytical data in the form of a density composition curve was used. Table II lists these data at 23 ± 0.2 °C which were measured by a Christian Becker specific gravity balance. The balance was standardized with demineralized water.

Mixtures of *n*-hexane and 2-propanol were carefully prepared and weighed to 0.1 mg. Weight fractions were converted to mole fractions by molecular weight constants obtained from Perry's Handbook (*7*).

Using the above described pressure control and the experimental operating procedures of Altsheler (*1*), the equilibrium data were determined at 760 and 380 mmHg and are plotted and tabulated in Tables III and IV and Figures 2 and 3, respectively. Figures 4 and 5 represent the temperature composition diagrams at 760 and 380 mmHg, respectively.

Liquid Phase Activity Coefficients. The liquid phase activity coefficients were determined with the following relation:

$$\gamma_i = y_i P / x_i P_i^s$$

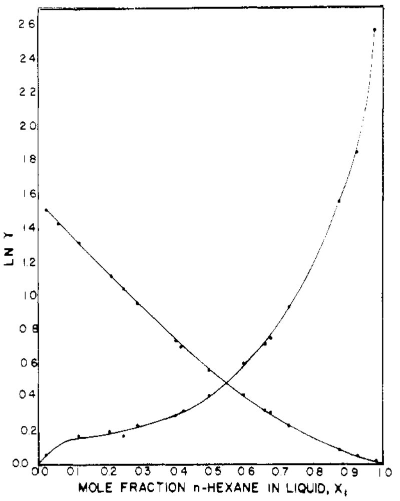

Figure 6. Activity coefficients vs. mole fraction of *n*-hexane in liquid at 760 mmHg.

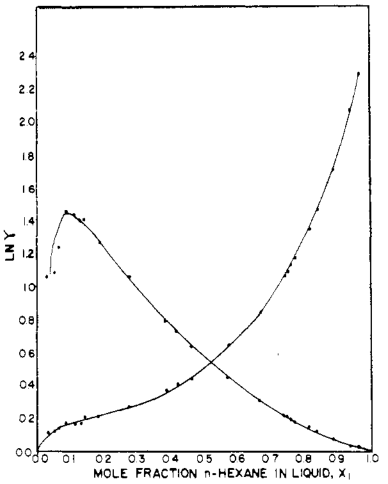

Figure 7. Activity coefficients vs. mole fraction of *n*-hexane in liquid at 380 mmHg.

Vapor pressures were determined by use of the Antoine equation and the constants used were obtained from Holmes and Van Winkle (*5*). Activity coefficients are plotted in Figures 6 and 7 and are listed in Tables III and IV at 760 and 380 mmHg, respectively.

Thermodynamic Consistency. In order to test rigorously for thermodynamic consistency heat of mixing data are required over the entire composition range. These data are usually not available and were not in this particular case.

Herrington (*4*) has proposed an empirical test that estimates the heat of mixing. This test gives an indication of the consistency of the data. He states that if his parameters $(D - J) < 10$, the data are probably consistent. For the *n*-hexane-2-propanol data at 760 and 380 mmHg, $(D - J)$ was determined to be -5.3 and 1.9, respectively.

Discussion of Results

The system *n*-hexane-2-propanol is highly nonideal as exemplified by the strong positive deviations from Raoult's law in the activity coefficients and a maximum in the *n*-hexane activity coefficient curve at 380 mmHg. Raol (*8*) has observed maxima for the ethanol-*n*-heptane system at 760 mmHg. Van Ness (*9*) has also observed a maximum in the ethanol activity coefficient for the calculated data of the ethanol-*n*-heptane system and suggests that maxima probably do occur in a number of alcohol-aliphatic hydrocarbon systems.

It should be noted that the activity coefficients were calculated by a simplified expression, which excluded vapor phase nonideality corrections. For mixtures of strongly polar or hydrogen-bonded components, or for mixtures at low temperatures, gas phase corrections may be significant even at low pressures. Since 2-propanol is polar and associates in solution, the *n*-hexane-2-propanol system is highly nonideal and corrections for vapor phase nonideality should be taken into account for highly accurate determination of activity coefficients. Since heat of mixing data were not available to allow rigorous testing for thermodynamic consistency, the activity coefficients were calculated by the simplified expression previously listed. Vapor phase correction terms would allow for a smoother approach to unity of the activity coefficients.

As indicated by the Herrington thermodynamic consistency test, the data are probably consistent.

Glossary

$d_A{}^B$	density at temperature B relative to density at temperature A
D	Herrington's consistency parameter
J	Herrington's consistency parameter
P	total pressure
$P_i{}^s$	vapor pressure of component
T	temperature, °C
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
γ_i	liquid phase activity coefficient of component i

Literature Cited

(1) Altsheler, W. B., Unger, E. D., Kolechov, P., *Ind. Eng. Chem.*, **43**, 2559 (1951).
(2) "API Technical Data Book", 2nd ed, Petroleum Refining, 1970, p 22, Chapter 1.
(3) "Handbook of Chemistry and Physics", 50th ed, Chemical Rubber, Cleveland, Ohio, 1969.
(4) Herrington, E. F. G., *J. Inst. Pet., London*, **37**, 457 (1951).
(5) Holmes, M. J., Van Winkle, M., *Ind. Eng. Chem.*, **62**, 21 (1970).
(6) Othmer, D. F., *Ind. Eng. Chem.*, **35**, 614 (1943).
(7) Perry, J. H., "Chemical Engineer's Handbook", 4th ed, McGraw-Hill, New York, N.Y., 1951, p 322-342.
(8) Raol, J. D., Code, R. K., Best, D. A., *J. Chem. Eng. Data*, **17**, 211 (1972).
(9) Van Ness, H. C., Suczok, C. A., Kochar, N. K., *J. Chem. Eng. Data*, **12**, 346 (1967).
(10) Vijayaraghavan, S. V., Deshpande, P. K., Kuloor, N. R., *Chem. Age India*, **16**, 1267 (1964).

Received for review January 10, 1975. Resubmitted March 23, 1977. Accepted March 23, 1977. John M. Rotter is indebted to the University of Rhode Island for financial support through a graduate teaching assistantship.