

High-Temperature VLE for the Tetralin–Quinoline System

Shaukat Mahmood, Qingwen Zhao, and Vinayak N. Kabadi*

Chemical Engineering Department, North Carolina A&T State University, 1601 East Market Street, Greensboro, North Carolina 27411

A flow type high-temperature apparatus has been designed and fabricated for the VLE measurements of multicomponent systems. The apparatus provides easy sampling without disturbing the equilibrium at temperatures up to 500 °C. The new VLE apparatus has been tested by measurement of data for the tetralin–quinoline binary system along an isotherm at 325 °C for which literature data are already available. Furthermore, new data measurements are reported at two higher temperatures, 350 °C and 370 °C. The apparatus will be used in the future to generate high-temperature VLE data for binary mixtures of various coal model compounds.

Introduction

High-temperature, high-pressure thermodynamic measurements in the literature are quite limited. Such data are essential for development of thermodynamic models and correlations which are necessary for design of many chemical processes. A static method has been commonly used for the measurement of vapor–liquid equilibria at high pressures and has allowed the collection of accurate data at low temperatures. In this type of VLE apparatus, the equilibrium cell is kept at constant temperature in a bath. It is filled by known amounts of compounds. The pressure and compositions of the two phases in equilibrium are measured. Many VLE measurements using static cells are available in the literature. They differ by their sampling systems and their range of operation. Traditional static VLE measurements suffered from the drawback that the sampling process disturbed the equilibrium state especially for measurements at high pressures and/or high temperatures. To overcome this problem, a number of new sampling techniques have been devised.

A VLE apparatus with a microexpansion sampling system has been developed by Figuiere *et al.*¹ and has been used by Laugier *et al.*^{2,3} at pressures up to 40 MPa and temperatures up to 623 K for studying mixtures containing hydrogen and hydrocarbons. Samples are directly injected in the carrier gas stream of the gas chromatograph by means of a very brief opening of microvalves. Legret *et al.*^{4,5} used a similar sampling method in their VLE measurements at pressures as high as 100 MPa. Samples were transferred from an equilibrium cell into microcells; each microcell was taken off and attached to the port of a special chemical analysis apparatus. Another modification of the microvalve sampling method called the capillary microvalve sampling system was designed by Guillevic *et al.*^{6,7} especially for water–ammonia systems. Here, a microbore capillary tubing separates the microvalve from the chromatographic injection port, thereby allowing on-line sampling as well as precise individual control of both equilibrium temperature and injection port temperature. A further modified version of this technique has been given by Laugier and Richon⁸ and Richon *et al.*⁹

Meskel-Lesavre *et al.*¹⁰ and Rousseaux *et al.*^{11,12} describe a static VLE apparatus that uses a variable-volume VLE cell and requires no sampling. The components of the mixture are weighed and introduced separately into the equilibrium cell. The cell is brought to the equilibrium temperature inside a constant-temperature fluid bath. The pressure versus volume curve is recorded; the break point displayed in the curve gives the equilibrium bubble point pressure and the saturated volume of the liquid mixture. A similar apparatus was used by Fontalba *et al.*¹³ to simultaneously measure VLE data and saturated densities of hydrocarbon–carbon dioxide systems. They used two different loadings of the variable-volume cell at the same pressure and temperature. In each loading, the volumes of the coexisting vapor and liquid phases were measured. The compositions of the two phases and their densities were then calculated by solving simple mass balance equations. A more recent and modified version of this apparatus for high-pressure measurements has been presented by Richon *et al.*¹⁴ An excellent comprehensive review of static methods for VLE measurements has been given by Richon.¹⁵

Recently, a number of high-temperature VLE data sets have been measured using a flow VLE method. In this type of apparatus, a feed stream of desired composition is held in a feed tank and pumped continuously into the VLE cell. Temperature, pressure, and liquid level in the VLE cell are monitored and controlled accurately. Vapor and liquid streams are continuously removed, sampled, and returned to the feed tank. The two main advantages of this method over the static method are (1) substantial amounts of vapor and liquid samples can be drawn for analysis without disturbing the equilibrium in the cell and (2) materials spend relatively less time in the equilibrium cell, and this allows for high-temperature measurements for thermally sensitive compounds. On the other hand, in the flow method, equilibrium must be achieved dynamically, and special care must be taken to ensure that conditions of equilibrium exist in the equilibrium cell. Three flow VLE apparatuses of special note include those of Niesen *et al.*,¹⁶ Hutchenson *et al.*,¹⁷ and Inomata *et al.*¹⁸ The first two of these use a view cell to monitor the liquid level, whereas the last one uses a capacitance sensor to sense and control the liquid level. The flow apparatus designed and built in

* Corresponding author. E-mail: kabadi@ncat.edu.

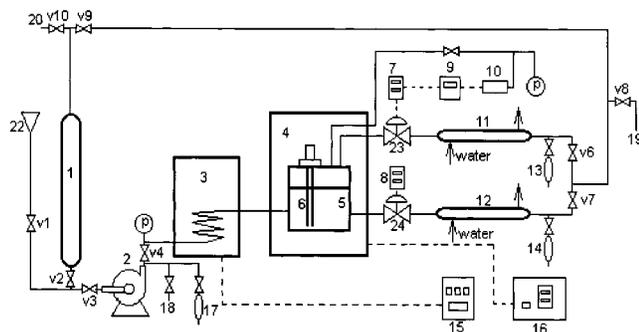


Figure 1. VLE flow diagram with the following labeled parts: (1) feed tank; (2) pump; (3) preheat oven; (4) main oven; (5) equilibrium cell; (6) liquid level probe; (7) pressure controller; (8) liquid level controller; (9) chart recorder; (10) pressure transducer; (11, 12) heat exchangers; (13, 14, 17) sampling bottles; (15) preheater temperature controller; (16) main oven temperature controller; (18, 19) system drain ports; (20) system vent port; (22) feed funnel; (23, 24) control valves; (p) pressure gauges.

this work uses a number of features of the above three apparatus.

In the following discussion, we will describe our flow VLE apparatus and the procedure for data measurements. Data are measured and reported for three high-temperature isotherms for the tetralin–quinoline binary system. One of the isotherms is a repetition of data available in the literature and serves as a performance check of our apparatus. Results are also presented for a successful application of thermodynamic consistency tests to the measured data.

Experimental Section

Apparatus. The apparatus can be divided into four sections, that is, feed section, equilibration section, sampling section, and the control-panel section. The maximum design temperature and pressure for the system are 500 °C and 14 MPa, respectively. All parts and tubing, including the ones exposed to the high-temperature zones, are made of type 316 stainless steel. The tubing used in the fabrication ranges from 0.3 cm to 0.9 cm in diameter. The fittings used are compression type, made of the same material. A schematic of the apparatus is shown in Figure 1, in which all the parts of the apparatus are clearly labeled. The pump is a Pulsafeeder positive displacement metering pump with a capacity of 9 L/h and a pressure rating from ambient to 21 MPa. The flow rate is regulated by adjusting the stroke frequency in the range 0 to 400 strokes/min. The main and the preheater ovens are made by Applied Test Systems, Inc. The main oven has a temperature range of -25 °C to $+500$ °C, and the temperature is controlled to within 1 °C by Honeywell's UDC 5000 digital controller. The heat exchangers on the vapor and liquid exit lines are fabricated in-house by welding concentric tubing of larger diameter and circulating cold water through the jacket. The control panel for the apparatus consists of main and preheater oven controls, level and pressure chart recorder, controllers for the pressure and level control loops, one thermocouple switch and display, and pressure gauges.

The critical part of the apparatus is the VLE cell, a cross section of which is shown in Figure 2. It is cylindrical and made of type 316 stainless steel with an outside diameter of 15 cm, an overall height of 15 cm, and a wall thickness of 2.5 cm. It is fitted with a threaded lid sealed by a vented inconel metal O ring with a silver coating made by Advanced Products Company. The inside dimensions of the

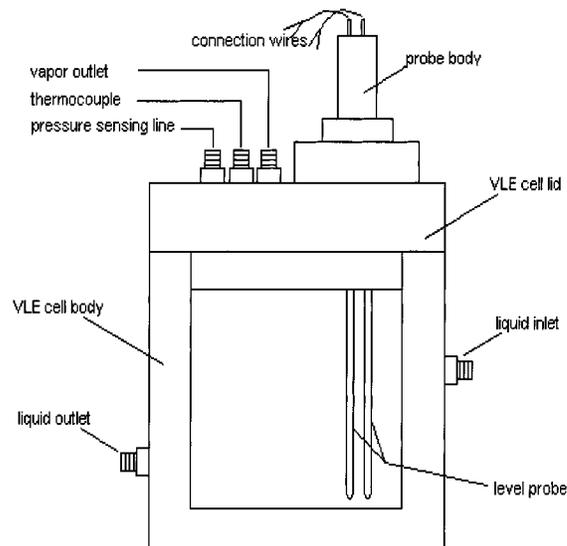


Figure 2. Equilibrium cell with a conductivity liquid level probe.

cell are 10 cm diameter and 7.5 cm long with a total volume of 590 cm³. Openings are provided for feed inlet, vapor and liquid outlet, thermocouple sensor, pressure sensor, and liquid level sensor. Temperature was measured by a factory-calibrated J-type iron–constantan thermocouple sensor (accuracy $\Delta T = \pm 0.01$ K). The thermocouple was successfully tested using melting ice and boiling water. Pressure was measured by a Rosemount model 1151 GP pressure transmitter with a pressure range from 7.5 kPa to 41.37 MPa and an accuracy of 0.1%.

The liquid level sensor is a Model LC 2300 conductivity probe made by Delta M Corporation. The liquid level probe is mounted on a 7.5 cm diameter flange which is bolted to the top of the VLE cell. It is also sealed using a metal O ring made by Advanced Products Company. The sensing element in the LC2000 Series level probes is a wire the electrical resistance of which is a function of temperature and thermal conductivity of the surrounding medium. The thermal conductivity of the liquid whose level is to be measured is generally significantly greater (as much as 100 times) than the vapor phase above it. Therefore, an increment of resistance (ΔR) in the sensor wire is directly proportional to the length not submerged in the liquid. With many level sensing techniques, a change in the process temperature will alter the operation of the device, requiring many calibrations over the desired range of temperatures. The LC2000 Series design avoids this problem by having two probes, a heated probe that is at a slightly higher temperature than an unheated reference probe that is maintained at the process temperature. The sensor signal is the difference in resistances of the two probes, which is relatively temperature independent. After calibration, the 4 to 20 mA signal output of the level sensor corresponds to 0 to 100% liquid in the cell. The signal is then used to record and control the liquid level. With proper calibration the accuracy of this sensor is about 1%.

Procedure. The liquids used were tetralin (99.9% pure) and quinoline (99% pure) from Aldrich Chemical Co. The two chemicals were mixed in desired proportions, and the feed was charged in the feed tank. Feed from the feed tank (1) was filtered through a pair of strainers of 60 and 230 μm and was pumped by a positive displacement metering pump (2), to the preheater oven (3). The liquid stream was heated while it passed through a coil-shaped tubing in the preheater oven. The temperature of the liquid was raised to within 5 °C of the desired experimental temperature.

The feed then entered the second coil placed inside the main heater oven (4), where the temperature of the liquid stream was raised to the desired temperature before it entered the vapor–liquid equilibrium cell (5). The vapor and liquid flow rates out of the VLE cell were controlled by two control valves (23, 24), placed in the respective lines. The two controllers (7, 8) manipulated these valves to maintain a constant pressure and required liquid level in the cell. The vapor and liquid from the cell were cooled by two jacketed heat exchangers (11, 12), combined together, and returned to the feed tank. Before the point where these streams are combined, each line is provided with a sampling port (13, 14). The third sample point (17) is provided on the feed input line near the outlet of the pump. The samples of the feed, the vapor, and the liquid streams were taken once the equilibrium conditions were established. The quantities of the samples removed were easily controlled with the use of metering valves. Once the samples were collected, they were tested and analyzed by liquid chromatography. The pressure and liquid levels were controlled by two feedback control loops. The pressure in the VLE cell was measured by a Rosemount pressure transmitter, which sent a 4 to 20 mA signal to the controller which then manipulated the flow rate of the vapor out of the VLE cell through a Badger control valve placed in the vapor line. The liquid level inside the VLE cell was measured by a Delta-M LC2300 level sensor. The probe, after sensing the level, sent the signal to the controller, which manipulated the control valve in the liquid outlet line to keep the level constant.

In a typical run, the pump was started from cold and the stroke frequency was set between 200 and 250 strokes/min which corresponded to a liquid flow rate in the range (80 to 100) mL/min. The preheater oven and the main oven temperatures were steadily increased to the set point values. The cell pressure was manipulated by manually adjusting the control valve on the vapor outlet line to a low enough value so that the cell showed no liquid level. The pressure was steadily increased until the liquid level as indicated by the level sensor increased to about 3.5 cm. The set point for pressure was set to the pressure at that point, and both the pressure control and the liquid level control loops were activated. The system was allowed to run for 2 h monitoring the fluctuations of the temperature, pressure, and the liquid level. The feed flow rate was then steadily reduced to a pump stroke frequency of about 150 strokes/min. The system was allowed to run for another hour. The first samples of vapor and liquid phases were withdrawn and immediately analyzed. The feed flow rate was reduced in steps of 15 strokes/min allowing 1 h for equilibrium at each step. At each step samples were withdrawn and analyzed. This was continued until consecutive feed flow rates did not show appreciable changes in vapor and liquid compositions. This generally happened when the stroke frequency was between 100 and 120 strokes/min which corresponds approximately to a feed flow rate between 15 and 30 mL/min. At this point two more sets of samples were withdrawn at intervals of 0.5 h. The final data corresponded to the averages of temperatures, pressures, vapor compositions, and liquid compositions for the three measurements. Overall fluctuations in temperatures and pressures after equilibration were observed to be $\Delta T = \pm 1$ K and $\Delta P = \pm 0.4\%$ which corresponds to ± 0.8 kPa at a pressure of 2 bar and ± 6 kPa at a pressure of 15 bar.

The analysis of the sample obtained from the apparatus was carried out by liquid chromatography. Some details

of the instrument and the method are listed below:

Instrument:	Perkin-Elmer LC410 pump
Detector:	Perkin-Elmer UV spectrophotometric detector kept at 254 nm
Column:	Perkin-Elmer 3 cm \times 3 mm C-18 column
Mobile Phase:	65% acetonitrile, 35% water
Flow Rate:	1.8 mL/min
Sample Concentration:	One part sample to two parts solvent by volume
Sample Size:	6 μ L
Column Pressure:	11.7 MPa (1700 psi)
Data Analysis:	Millipore chromatographic software

With this method we were able to reproduce measurements on test samples to within 1% at all times.

Results and Discussion

To test the newly designed and built flow VLE apparatus, we chose the tetralin–quinoline binary system. The goal was to measure one of the isotherms already available in the literature¹⁹ and then measure a couple of isotherms at higher temperatures. A quick review of the literature for thermophysical properties of the two pure components showed that consistent sets of data for critical properties and vapor pressures are available for tetralin, but this is not true for quinoline, especially at high temperatures above 350 °C. Discrepancies are observed in high-temperature vapor pressures and critical pressure of quinoline. We, therefore, decided to measure vapor pressure data of quinoline in the temperature range from 250 °C to 400 °C. This was done by the procedure described above, but only the liquid phase was circulated, and the vapor phase was held static. The vapor pressure data measured are shown in Table 1. The only high-temperature vapor pressure data available in the literature are those of Glaser and Ruland,²⁰ Sebastian *et al.*,²¹ and Niesen and Yesavage.²² The first of these data sets covers a more extensive temperature range from 237.7 °C to 462 °C. Our data agree fairly well with these literature data with deviations of less than 1%. The discrepancies in quinoline vapor pressure representation come from smoothed data extended to the critical temperature, and correlations that have been developed using these smoothed data. Two such data sets in the literature are found in the API Monograph Series²³ and the Engineering Sciences Data Unit.²⁴ Two prominent correlations available are both based on the Cox equation, one by Chao *et al.*²⁵ and the other by Das *et al.*²⁶ An accepted value for the critical temperature of quinoline is 782 K measured by Ambrose.²⁷ A reliable measurement for critical pressure, however, is not available. Two values are available: 46.6 bar given in the API Monograph Series²³ and the tables of Reid *et al.*,²⁸ and 48.6 bar extrapolated from their correlation by Das *et al.*²⁶ In this work, using $T_c = 782$ K and $P_c = 46.6$ bar, and using the data sets of Steele *et al.*²⁹ and Glaser and Ruland²⁰ and the data of Table 1, we regressed the four parameters in the Wagner equation (Reid *et al.*²⁸) given below

$$\ln(P_r^{\text{sat}}) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6)/T_r \quad (1)$$

where T_r and P_r are reduced temperature and pressure and $\tau = (1 - T_r)$.

The regressed constants are $A = -6.98143$, $B = -0.0017808$, $C = -1.48936$, and $D = -4.73306$. Equation 1 was found to agree very well with the data, with a maximum deviation of less than 0.8%. The results of the three correlations and the experimental data are shown in Figure 3. The correlation predictions are shown as curves, and the data are represented by symbols. The data

Table 1. Measured Vapor Pressure of Quinoline

$t/^\circ\text{C}$	vapor pressure/bar	$t/^\circ\text{C}$	vapor pressure/bar
250.2	1.358	325.0	5.213
260.0	1.689	329.6	5.564
269.8	2.053	340.1	6.628
275.0	2.196	350.6	7.750
280.0	2.425	360.2	8.828
289.9	2.938	369.9	10.03
300.0	3.454	380.0	11.49
310.0	4.120	390.1	13.08
320.0	4.850	400.0	14.89

Table 2. VLE Data for the Tetralin (1) + Quinoline (2) Binary System

$t/^\circ\text{C}$	P/bar	x_1	y_1	γ_1	γ_2	G^E/RT
325.0	5.213	0.0	0.0			
	5.500	0.062 ± 0.002	0.103 ± 0.004	1.1423	1.0028	0.0109
	5.860	0.143 ± 0.004	0.216 ± 0.005	1.1015	1.0130	0.0249
	6.220	0.242 ± 0.005	0.337 ± 0.007	1.0677	1.0195	0.0305
	6.740	0.376 ± 0.007	0.484 ± 0.009	1.0504	1.0358	0.0405
	7.220	0.527 ± 0.009	0.627 ± 0.007	1.0302	1.0431	0.0356
	7.870	0.732 ± 0.006	0.798 ± 0.005	1.0119	1.0689	0.0265
	8.667	1.000	1.000			
350.0	7.597	0.0	0.0			
	7.940	0.057 ± 0.002	0.086 ± 0.003	1.0968	1.0057	0.0106
	8.410	0.140 ± 0.004	0.197 ± 0.004	1.0712	1.0159	0.0232
	8.900	0.243 ± 0.005	0.320 ± 0.006	1.0483	1.0234	0.0290
	9.630	0.400 ± 0.008	0.490 ± 0.010	1.0363	1.0314	0.0328
	10.20	0.525 ± 0.009	0.611 ± 0.008	1.0281	1.0395	0.0330
	10.92	0.700 ± 0.006	0.763 ± 0.005	1.0123	1.0566	0.0251
	12.13	1.000	1.000			
370.0	10.04	0.0	0.0			
	10.40	0.057 ± 0.002	0.080 ± 0.003	1.0635	1.0031	0.0065
	10.98	0.135 ± 0.003	0.180 ± 0.004	1.0526	1.0171	0.0216
	11.60	0.245 ± 0.005	0.310 ± 0.006	1.0403	1.0229	0.0268
	12.62	0.435 ± 0.008	0.513 ± 0.010	1.0299	1.0278	0.0283
	13.15	0.530 ± 0.009	0.605 ± 0.008	1.0258	1.0328	0.0287
	13.92	0.685 ± 0.006	0.743 ± 0.005	1.0129	1.0443	0.0225
	15.49	1.000	1.000			

from the Engineering Sciences Data Unit²⁴ and predictions of the Chao *et al.*²⁵ correlation are significantly lower than our data and those of Glaser and Ruland²⁰ with deviations of as much as 18% at the highest measured temperature. On the other hand, the Cox equation of Das *et al.*²⁶ agrees very well with our fitted Wagner equation at temperatures up to 470 °C. Deviations observed at higher temperatures are because of different values of critical pressures used in the two correlations. With the current status, the critical properties used here and the correlation based on the Wagner equation provide as good a method for vapor pressure calculation for quinoline. A more reliable value for the critical pressure is much desired.

For tetralin, on the other hand, consistent data sets for vapor pressure are available. A review and analysis of literature data has been given by Niesen and Yesavage,¹⁹ and smoothed data up to the critical temperature are listed in the API Monograph Series.³⁰ The only vapor pressure data that were measured for tetralin in this work are the end points of the three VLE isotherms. The three isotherms that were measured for the binary tetralin–quinoline system are 325 °C, 350 °C, and 370 °C. The data are listed in Table 2, and *PXY* diagrams for the three isotherms are shown in Figure 4. Our vapor pressure values for tetralin agree very well (within 1% error) with the smoothed data in the API Monograph Series³⁰ and the data of Simnick *et al.*³¹ and Natarajan and Viswanath.³² However, the tetralin vapor pressures reported by Niesen and Yesavage¹⁹ in the temperature range 300 °C to 340 °C are on the average 2% lower than the data from other sources. Figure 5 shows a comparison of our 325 °C isotherm with that of Niesen and Yesavage.¹⁹ The two data sets agree very well, except

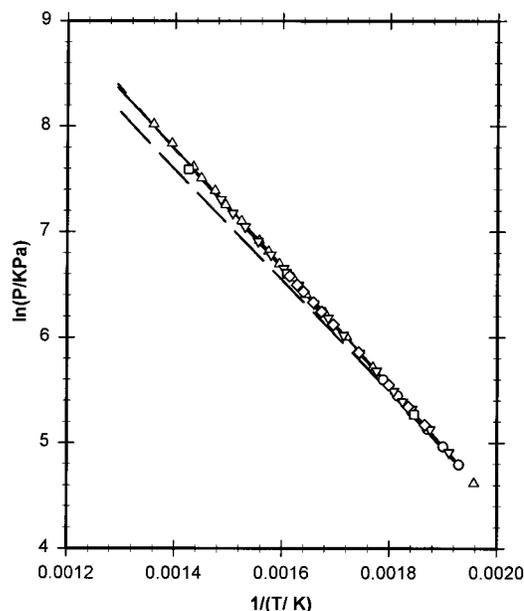


Figure 3. Experimental data and correlations for the vapor pressure of quinoline (P in kPa and T in K). Symbols represent experimental data, and curves represent correlations as follows: Δ , Glaser and Ruland;²⁰ ∇ , this work; \square , Sebastian *et al.*;²¹ \diamond , Niesen and Yesavage;²² \circ , Steele *et al.*;²⁹ —, Wagner equation of this work; - - -, Cox equation of Das *et al.*;²⁶ - - - -, Cox equation of Chao *et al.*²⁵

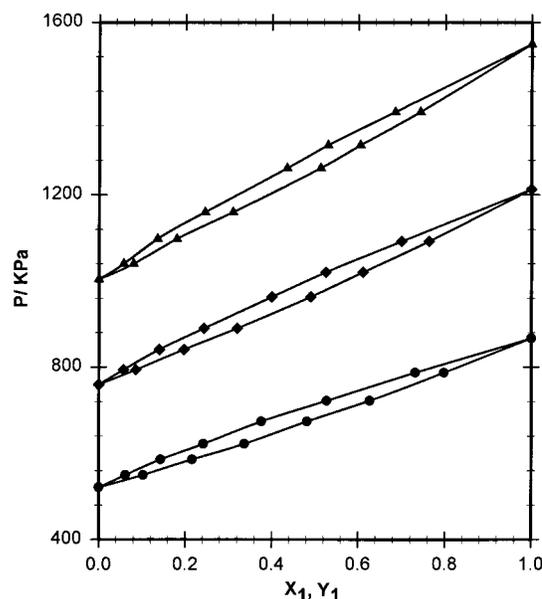


Figure 4. VLE data for the tetralin–quinoline system: \bullet , 325 °C; \blacklozenge , 350 °C; \blacktriangle , 370 °C.

for the tetralin-rich end point where our vapor pressure is 8.667 bar compared to their value of 8.428 bar. In Table 2, the liquid and the vapor mole fractions represent average values of four sample measurements each; upper and lower limits of the measurements are also reported. Data at the temperatures 350 °C and 370 °C provide isotherms previously not available for this system.

The VLE data were analyzed for thermodynamic consistency by first calculating activity coefficients and then applying the Gibbs–Duhem equation in the form of an area test (see, for example, Prausnitz *et al.*³³). The activity coefficients were calculated using the following equation

$$\gamma_i = (y_i P \Phi_i) / (x_i P_i^{\text{sat}} \Phi_i^{\text{sat}} P_{\text{oynt}}) \quad (2)$$

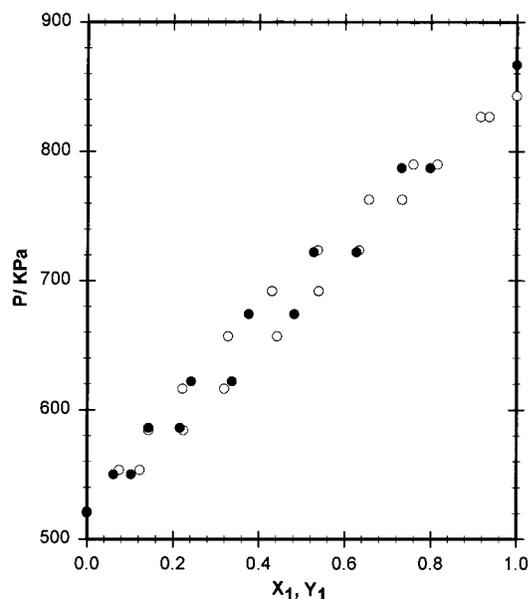


Figure 5. Comparison of our 325 °C isotherm with that of Niesen and Yesavage.¹⁹ ●, our data; ○, data of Niesen and Yesavage.¹⁹

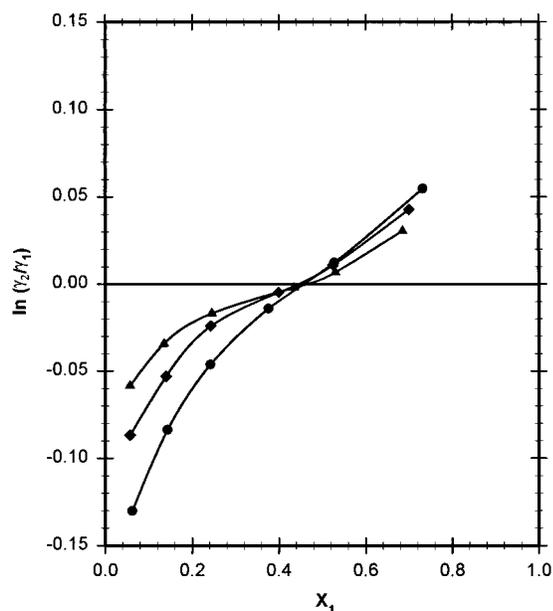


Figure 6. Area test for thermodynamic consistency: ●, 325 °C; ◆, 350 °C; ▲, 370 °C.

where γ_i is the activity coefficient of component i , P is the total pressure, P_i^{sat} is the vapor pressure of pure liquid i at T , Φ_i and Φ_i^{sat} are the fugacity coefficient of component i in the vapor phase and the fugacity coefficient of a pure vapor of component i at equilibrium with liquid at T and P_i^{sat} , respectively, and Poynt is the Poynting correction factor for pure liquid i at T and between the pressures P_i^{sat} and P .

For calculations using eq 2, the following critical properties were used

tetralin	$T_c = 719 \text{ K}$	$P_c = 35.1 \text{ bar}$	$\omega = 0.303$
quinoline	$T_c = 782 \text{ K}$	$P_c = 46.6 \text{ bar}$	$\omega = 0.33$

The Peng–Robinson equation of state³⁴ with $k_{ij} = 0$ was used for the fugacity coefficients. The liquid molar volumes necessary for calculation of the Poynting correction factors were calculated using the HBT method³⁵ for tetralin

and using the modified Rackett equation of Spencer and Danner³⁶ for quinoline with $Z_{\text{RA}} = 0.2679$. The vapor pressures of the two components were calculated using the Wagner equation (eq 1) with the parameters for quinoline given above and the following parameters for tetralin: $A = -5.32759$, $B = -3.06718$, $C = 1.25547$, and $D = -8.67456$ (Wang and Kabadi³⁷).

The calculated activity coefficients and the excess Gibbs free energies are shown in Table 2. The area test for thermodynamic consistency requires that the area under the curve $\ln(\gamma_2/\gamma_1)$ versus x_1 from $x_1 = 0$ to $x_1 = 1$ be zero. Figure 5 shows a plot of $\ln(\gamma_2/\gamma_1)$ versus x_1 . Although it does not cover the entire range from $x_1 = 0$ to $x_1 = 1$, the curves follow a pattern as would be expected of thermodynamically consistent data, such as, crossing the X -axis at around $x_1 = 0.5$. For more accurate and quantitative application of thermodynamic consistency tests, more extensive data measurements would be necessary.

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