

Table III. Vapor-Liquid Equilibrium Data for the System *o*-Toluidine-*n*-Decane at Atmospheric Pressure^a

x_1	y_1	$T, ^\circ\text{C}$	$y_1(\text{calcd})$	Δy_1
0.019	0.143	197.25	0.144	0.001
0.052	0.269	192.9	0.31	0.041
0.079	0.381	189.2	0.382	0.001
0.114	0.46	185.2	0.441	-0.019
0.192	0.57	180.6	0.514	-0.056
0.22	0.595	179.1	0.525	-0.07
0.532	0.655	176.0	0.692	0.037
0.671	0.727	174.6	0.742	0.015
0.844	0.835	173.8	0.843	0.008
0.909	0.894	174.0	0.895	0.001
0.958	0.942	174.2	0.947	0.005

^a $\Lambda_{12} = 0.2781$; $\Lambda_{21} = 0.6705$; $|\Delta y_1|_{\text{mean}} = 0.023$; $|\Delta T|_{\text{mean}} = 2.14 ^\circ\text{C}$.

Table IV. Vapor-Liquid Equilibrium Data for the System *m*-Xylidine-*n*-Dodecane at Atmospheric Pressure^a

x_1	y_1	$T, ^\circ\text{C}$	$y_1(\text{calcd})$	Δy_1
0.034	0.096	215.6	0.083	-0.013
0.064	0.16	214.1	0.143	-0.017
0.098	0.214	212.5	0.188	-0.026
0.124	0.241	211.8	0.219	-0.022
0.145	0.272	211.0	0.236	-0.036
0.338	0.435	210.1	0.387	-0.048
0.542	0.538	209.9	0.512	-0.026
0.673	0.62	211.1	0.621	0.001
0.818	0.762	213.1	0.764	0.002
0.883	0.82	214.0	0.832	0.012
0.95	0.918	215.5	0.929	0.011

^a $\Lambda_{12} = 0.2961$; $\Lambda_{21} = 1.0987$; $|\Delta y_1|_{\text{mean}} = 0.0195$; $|\Delta T|_{\text{mean}} = 2.86 ^\circ\text{C}$.

In Tables II, III, and IV are listed the results of vapor-liquid equilibrium measurements in the systems aniline-pseudocumene, *o*-toluidine-*n*-decane, and *m*-xylidine-*n*-dodecane, along with the deviations in the vapor phase between the calculated and experimental (observed) compositions, Δy_1 . The compositions x_1 and y_1 are expressed in mole fractions of the more volatile components, viz., hydrocarbons.

The quantities $|\Delta y_1|_{\text{mean}}$ and $|\Delta T|_{\text{mean}}$ (see Tables II-IV) are defined as

$$|\Delta y_1|_{\text{mean}} = \frac{\sum |y_1(\text{calcd}) - y_1(\text{obsd})|}{n}$$

and

$$|\Delta T|_{\text{mean}} = \frac{\sum |T_{\text{calcd}} - T_{\text{obsd}}|}{n}$$

where n is the number of experimental points and T is the equilibrium boiling temperature.

In addition, it became interesting to show how the Wilson parameters vary with the chemical nature of the components for the systems examined. The values of interaction energy, $\lambda_{12} - \lambda_{11}$, were found to be 621 ± 18 (*n*-decane (1)-*o*-toluidine (2)), 606 ± 2 (*n*-dodecane-*m*-xylidine), and -168 ± 3 cal/mol (pseudocumene-aniline), respectively. While the values of $\lambda_{12} - \lambda_{11}$ are of similar magnitude for the systems containing *n*-paraffins, there is an indication that would suggest a strong interaction between the NH_2 group and the methyl groups in the aniline-pseudocumene system.

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A New Total Pressure Vapor-Liquid Equilibrium Apparatus. The Ethanol + Aniline System at 313.15, 350.81, and 386.67 K

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A new multicell apparatus for the measurement of total pressure vapor-liquid equilibrium data is described. Fifteen cells provide thirteen mixture and two pure compound points on the P vs. x isotherm. Multiple freezing-evacuation-thawing cycles are used to degas the loaded cells. The number of isotherms measured with one loading of the cells is limited only by chemical stability; usually three are measured in a typical 5-day run (including loading, degassing, and isotherm measurements). The method of Mixon, Gumowski, and Carpenter is used to reduce the data. Data are reported on the ethanol + aniline system at 313.15, 350.81, and 386.67 K and the effect of the equation of state used is explored.

Introduction

The fact that any one of the four experimental variables (P , T , x_1 , and y_1) in binary vapor-liquid equilibrium (VLE) measurements can be calculated from the other three permits us to exclude from our experimental measurements that variable most subject to error. In high-temperature systems where chemical reaction rates are not negligible, the pressure may be the variable whose measurement is least reliable and it may be advisable to measure Txy data and calculate the equilibrium pressure. When chemical reactions are not a factor, the equilibrium vapor composition is usually most difficult to measure accurately and it is advisable to measure PTx (total pressure) data.

The PTx approach eliminates analyses of the phase compositions, thereby eliminating two of the major sources of error

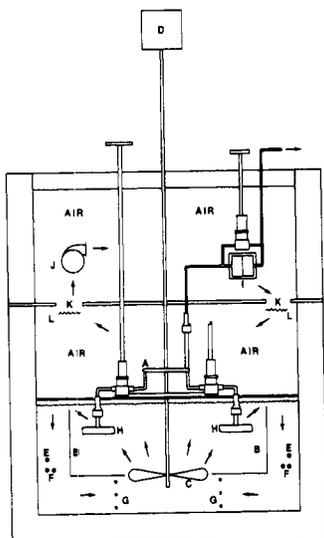


Figure 1. Schematic sketch of the PTx apparatus showing the liquid and air baths: A = manifold assembly; B = baffle tank; C = impeller; D = impeller motor; E = auxiliary heater; F = auxiliary cooling coils; G = control heater; H = cells; I = nulling transducer; J = air bath blower; K = openings for air flow; L = air bath heaters.

in VLE measurements and greatly reducing the cost of the measurements. However, the price which must be paid for those advantages is not negligible. All of the experimental information about the system is contained in the experimental P vs. x isotherm and subtle changes in the shape of that curve can cause large changes in the calculated y_i , γ_i , and G^E values. Consequently, the P , T , and x values must be measured at very high levels of accuracy, and there must be no degradation of those values during the data reduction, if the calculated variables are to be accurate. Also, the reduction of PTx data is more complicated than for $PTxy$ data and therefore more costly.

This paper describes a PTx apparatus which has been developed over the last 5 years. The techniques used provide some advantages in both accuracy and speed over the titration devices which have been used so effectively for total pressure measurements.

Experimental Technique

One design objective was the measurement of three P vs. x isotherms for a given binary system within 5 working days. That rate of data accumulation is not possible with the titration technique where one component is put into a cell and the second component is added in increments to change the composition. Only part of one isotherm can be obtained in each titration and six titrations, each requiring new batches of degassed liquids, are required to produce three isotherms. This consideration led to the use of multiple cells instead of a titration device.

Fifteen small cells (approximately 25 cm^3 each) are loaded with the two pure components and thirteen intermediate binary mixtures. The cells are loaded by adding the desired amounts of liquid to each cell and weighing after each addition. After loading, the 15 cells are attached via Cajon Ultra-Torr fittings (for glass cells) or Cajon VCO fittings (for metal cells) to 15 bellows valves mounted in a ring and connected to a common low-volume manifold. The liquids in the cells are degassed by successive freezing-evacuation-thawing cycles. After degassing, the manifold with the attached cells is placed in a temperature-controlled bath and connected to a pressure transducer. The P vs. x isotherm at the bath temperature is obtained by opening each cell in turn to the pressure transducer. Isotherms at other temperatures are obtained by repeating the cell pressure measurements at other bath temperatures. It is

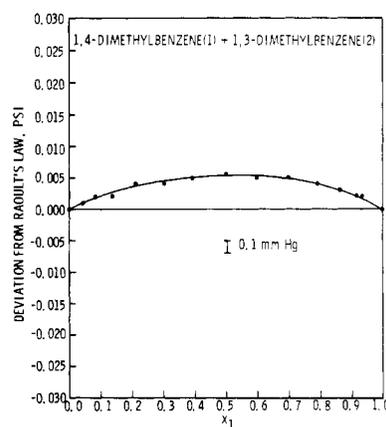


Figure 2. Deviation from Raoult's law for the 1,4-dimethylbenzene + 1,3-dimethylbenzene system.

sometimes possible to measure two isotherms in the same day.

Figure 1 shows a schematic side view of the manifold mounted in the PTx bath. The cells are in the bath liquid but the manifold is in the air bath which is kept about 5 K warmer than the liquid to prevent condensation in the valves, manifold, pressure transducer, and connecting lines.

Measurement of Variables

The precision levels which have been achieved in the measurement of the P , T , and x variables are illustrated in Figure 2. 1,4-Dimethylbenzene + 1,3-dimethylbenzene differed by less than 10 mmHg in their vapor pressures at the temperature of the data, and the maximum deviation from Raoult's law is only about 0.25 mmHg. The scatter of less than ± 0.03 mmHg in the data points is necessary for a sufficiently accurate definition of the P vs. x isotherm. The uncertainties in the measured T , P , and x values which contribute to the scatter are as follows.

Temperature. The liquid bath temperature can be maintained indefinitely within ± 0.003 K of the set temperature. The temperature-controlled region is the volume within the thin baffle tank (item B) shown in Figure 1. That baffle tank has a diameter of 38 cm and is about 13 cm deep. The liquid stirrer (C) is positioned in a hole in the bottom of the baffle tank and impels the liquid up past the cells and then down the annular space around the baffle tank. An auxiliary heater (E) and a cooling coil (F) are positioned in the annular space. The control heater (G) is positioned close to the impeller and the sensing probe for the controller is positioned just above the impeller. A Tronac Model PTC-40 temperature controller is used. The Tronac control heater (G) is a 0.25-in. o.d. thin-wall stainless-steel tube with a thin silicone rubber liner. A cooling stream, kept about 10 K below the bath temperature by an auxiliary thermostated bath, flows through the heater. The silicone liner provides a heat transfer resistance between the cooling stream and the heater surface.

Platinum resistance thermometers and a Doric DS-100-T5 microvoltmeter with a TSU-10-RTD interfacing unit are used to measure the various temperatures of interest. The thermometer used to measure the liquid bath temperature in the vicinity of the cells is calibrated periodically against a Rosemount Model 162CE platinum thermometer. The calibration of that local standard was performed by Rosemount using the IPTS-1968. A Leeds and Northrup Model 8069-B Type G-2 Mueller bridge with thermostated temperature control is used for the resistance measurements.

The Doric temperature readout shows only two decimal places. Variations in the bath temperature smaller than ± 0.01 are monitored on a strip-chart recorder which receives its signal from a Tronac Model 120 temperature bridge. Sensitivity to

± 0.0005 K can be achieved. The bridge probe is located next to the cells in the bath. The strip chart record verifies that the temperature remains within ± 0.003 K of the set point throughout the experiment.

The experimental cell temperatures recorded are always within ± 0.02 K of the temperature scale as defined by the local Rosemount standard and are probably within ± 0.03 K of the true temperature.

Pressure. A Datametrix Model 531 pressure transducer is used for the nulling device (item I in Figure 1) in the air bath. The pressure of the equilibrium vapor on one side of the diaphragm is balanced with nitrogen gas on the other side to produce a null. The pressure of the nitrogen is measured with a Datametrix Model 572 transducer mounted outside the apparatus. The readout for both transducers is a Datametrix Model 1174 electronic manometer which has a resolution of 0.0001 below 4, 0.001 below 40, 0.01 below 400, etc. The 531 (nulling transducer) reads out millimeters of mercury while the 572 reads out pounds per square inch.

The Datametrix transducers are capacitance devices and the reading of the 531 (nulling device) will change with the dielectric constant of the equilibrium vapor. Also, as with any mechanical or electrical device, the zero will shift with pressure and temperature. Hence, it is necessary to check the zero of the 531 after each cell pressure measurement; that is accomplished by opening the bypass valve briefly (see Figure 1). Another valve (not shown) is closed first to make sure none of the nitrogen molecules can diffuse down into the cell manifold. The zero check ensures that the nitrogen pressure and the equilibrium vapor pressure are truly equal when the 1174 readout is zero. The possible error in the nulling operation is less than ± 5 in the last of the five digits displayed by the electronic manometer.

Both the zero and the calibration of the 572 transducer (not shown in Figure 1) must be checked to ensure an accurate measurement of the cell pressure. The zero is checked for each cell measurement using a bypass valve similar to the one shown for the 531 (item I) in Figure 1. The accuracy of the transducer is checked periodically during an isotherm measurement using a Ruska Model 2465 dead weight gauge operating under an evacuated cover. The nitrogen pressure used to float the gauge piston (loaded with appropriate weights) is piped directly to the *PTx* apparatus where it can be measured by the 572 transducer. When the *P* vs. x_1 isotherm is steep, the transducer will be checked every second or third cell to adjust for the slight shift in the instrument calibration with pressure. The frequent checks against a dead weight gauge (which approaches the accuracy of a primary pressure standard) permit the accuracy of the experimental measurements to approach the resolution of the transducer readout. It is believed that the accuracy of the pressure measurements, including the possible error in the null, is $\pm(0.035\%$ of the reading + 0.02 mm + 2.5 in the last digit of the five-digit readout). The percentage errors at various pressure levels are then as follows: 0.10% at 1.0 psia, 0.11% at 4.0 psia, 0.06% at 10.0 psia, 0.10% at 40 psia, etc.

Liquid Mole Fractions. The liquid mole fractions are determined gravimetrically by weighing before and after each component addition. The analytical balance used has a resolution of 0.0001 g, and compensation is made for nitrogen and vapor displaced from the cells as liquids are added. After loading, the uncertainty in the cell mole fractions is within ± 0.00005 .

Care is taken to ensure that the component mole fractions are not affected by the cell evacuations which occur during degassing. A freezing medium cold enough to cool the components well below their freezing points (including any eutectics) is used to ensure very low vapor pressures. Visual verification that negligible amounts of the component masses are removed

is obtained by inspection of the vacuum pump trap. That trap is usually cooled with liquid nitrogen and an acceptable degassing run requires that the glass trap be "shiny" clean after all the degassing cycles have been completed.

Some changes in the cell mole fractions do occur during the pressure measurements. The magnitudes of those changes are minimized by using the following sequence in the cell pressure measurements for systems without an azeotrope. Cell 1 (less volatile pure compound) is measured first to ensure that its pressure corresponds closely enough to the known vapor pressure data for that compound. Cell 15 (more volatile component) is measured next after thorough evacuation of the manifold and transducer to remove all of the cell 1 component. After the cell 15 measurement, the manifold pressure is reduced to a few millimeters of mercury below the expected cell 14 pressure. When cell 14 is opened, some vapor flows out to bring the manifold pressure up to the cell 14 pressure but the amount is small compared to the mass of the liquid (from 15 to 20 cm³) in the cell. Enough vapor does flow out to push the vapor in the manifold far enough away to prevent any mixing with the material still in the cell.

As explained later under degassing, it is sometimes advisable to reduce further the residual gas (nitrogen) in the cells by removing some vapor from the cells after they have been mounted in the *PTx* bath. This process involves opening each cell individually to an evacuated manifold, an operation called "bumping the cell". Each cell has from 5 to 8 cm³ of vapor depending upon the type of cell being used. The two manifolds being used have volumes of 53.75 and 62.64 cm³ which include all the volume from the cell valve seat up to the 531 transducer diaphragm. The mass of vapor withdrawn from the cell to fill that space can be calculated but there is some uncertainty due to adsorption of some of the vapor molecules. However, experiments in which the calculated amounts withdrawn were checked against the change in the cell weights indicated that the uncertainty in the mole fractions can be kept below ± 0.0005 even when more than inconsequential amounts of vapor have been withdrawn from the cells.

The discussion above has focused on the cell mole fractions. The data reduction algorithm first corrects the cell mole fractions for any vapor removed during pressure measurement and then calculates the liquid mole fractions using the calculated *y* values. The difference between the cell mole fractions and liquid mole fractions can be significant (greater than 0.0001) even at pressures below atmospheric pressure.

Degassing Technique

Accurate VLE data require the reduction to a tolerable level of the contribution of impurity gases (such as nitrogen, oxygen, helium, etc.) to the system pressure. The tolerable level may be less than 0.1 mmHg (e.g., in very close boiling systems such as 1,4-dimethylbenzene + 1,3-dimethylbenzene) but in many cases useful data can be obtained if the contribution can be reduced below 0.5 mmHg.

In the *PTx* approach described in this paper, the cell liquids must be degassed in situ without changing the liquid mole fraction appreciably. That is done with successive freezing–evacuation–thawing cycles. After freezing (with liquid nitrogen, dry ice and acetone, or ice and water), the cells are evacuated to remove the gases above the solids. The manifold and cells are then swung over and lowered into an oven where they are heated above the highest freezing temperature to release gas trapped when the liquids were frozen. After the impurity gases have achieved a new equilibrium distribution between vapor and liquid in each cell, the cell contents are quickly frozen again and the cycle repeated. The procedure is terminated when the residual pressure (measured when the cell is opened to a Hastings VT-5 vacuum gauge with the vacuum line valve closed)

is less than 10 μ of mercury in each cell. Usually, seven to nine cycles are required with each cycle taking about 1 h.

Tests were run on ethanol, 1,2-dimethylbenzene, and normal pentane using the above procedure. The cell pressures measured in the *PTx* bath at about 40 °C were essentially independent of the number of degassing cycles after about five cycles. The residual nitrogen pressure in millimeters of mercury, the true compound vapor pressure in millimeters of mercury, and the percent error caused by the nitrogen pressure were as follows for the ethanol, 1,2-dimethylbenzene, and *n*-pentane, respectively: 0.35/134.26/0.26%, 0.13/15.52/0.8%, and 0.40/867.1/0.046%. The "true" vapor pressures were obtained by completely degassing the liquids by removing small amounts of vapor until no further change occurred in the vapor pressure of the remaining liquid. The cell pressure used to calculate the initial residual gas pressure was measured by opening the cell to a manifold whose pressure was only a few millimeters of mercury below the cell pressure; i.e., very little vapor was withdrawn from the cell.

Opening the cells only once to a completely evacuated manifold (53.75 cm³) changed the numbers given above to the following values: 0.04/134.26/0.03%, 0.05/15.52/0.32%, 0.00/867.1/0.00%. Completing the degassing in this fashion is necessary for very close-boiling binaries where 0.2 or 0.3 mmHg represents an important fraction of the difference between the two pure compound vapor pressures. For many systems, residual gas pressures of 0.2 or 0.4 mmHg will be tolerable.

For some chemicals, traces of water in the cells will give the appearance of inadequate degassing. Water is not removed by the degassing technique described above and must be scrupulously eliminated from the liquids and the cells before degassing. An effective way to dry the liquids is by direct contact with 4A molecular sieves for several days followed by distillation (under vacuum) to produce a dust-free product. The first and last portions of the distillate are discarded, and the middle portion is loaded into the cells. The cells are baked at 150–200 °C in a vacuum oven for at least 24 h before loading. The O-rings used are also baked in the vacuum oven for 2 or 3 days at the highest tolerable temperature. After drying and distillation, the chemicals are kept under dry nitrogen and all additions to the cells are made under a nitrogen blanket in a glovebox. When traces of water are not present, the degassing technique has been effective for all nonreactive compounds used.

Manifold and Cells

A manifold plus the attached (empty) cells will typically take about 72 h to reach 100 μ of pressure while hanging in air after being pumped down to 2 or 3 μ pressure for a few hours. Most of that rise is probably due to desorption rather than leakage from the outside. That degree of tightness is essential for the degassing technique to work and to permit the measurement of successive isotherms.

Two manifolds are used, with one being cleaned and baked-out while the other is in service. Both are stainless steel with welded connections. One manifold uses Nupro SS-4BK valves (rated at 1000 psi at 250 °C) and the other uses Nupro SS-4TG valves (2000 psi at 300 °C). The "manifold" is a 3-in. diameter circle of heavy-walled 0.25-in. tubing (0.094 in. i.d.). The valves are connected to the manifold with short lengths of the 0.25-in. tubing. The Cajon fittings to which the cells are attached are fastened to the other side of the valves with the same size tubing bent at right angles as shown in Figure 1. The part of the Cajon fittings attached to the valve has been modified to accept either glass cells or metal cells.

Both types of valves have removable bellows to permit changing the valve tips. Kel-F bellows gaskets are used for low-temperature work, and stainless-steel O-rings are used at

high temperatures. Three types of valve inserts (stem tips) are used: Kel-F at low temperatures (below 80 or 90 °C), copper for higher temperatures, and Vespel for temperatures above the Kel-F range when the chemicals attack copper. The entire experimental technique requires a very high level of performance by the valves, and the items described routinely perform as required.

Three types of cells are available for use depending upon the pressure level. Pyrex glass cells can be used in the 0–1.0 atm range. Two sets of stainless steel cells are available for higher pressure runs, one set for the 0–20 atm range and the other for the 0–100 atm range. The glass and the lower pressure steel cells are designed to minimize the height of the liquid in the cell; they have large diameters (about 5 cm) and body heights of about 1.9 cm, with stems 5–6 cm long to connect them to the manifold. The 100-atm cells have bodies 2.5 cm in diameter and 5.5 cm high, with connecting stems 5 cm long.

Originally, 12 cells were used but ten mixture points often did not adequately define the *P* vs. *x*₁ isotherm. The definition provided by 13 mixture points is sometimes marginal and there undoubtedly will be systems where two runs (26 mixture points) will be necessary for an adequate definition of the isotherm. When that is necessary, one major advantage over the titration devices will be lost.

Experimental Limitations

The standard operating procedure is to load the cells on Monday and start the degassing, finish the degassing on Tuesday and transfer the manifold and cells to the *PTx* bath, and then measure isotherms at three different temperatures on Wednesday, Thursday, and Friday. The bath temperature is changed overnight from one isotherm temperature to the next. Usually the top of the *PTx* bath is raised as soon as an isotherm is finished so that the cells can be kept at room temperature overnight.

The most severe limitation on the experimental technique is the length of time at temperature. Both compounds must be very stable if the pressure changes in the cells due to reaction products are to remain negligible over a 3-day period. For example, aromatic isomer systems at their normal boiling points are usually not stable enough, presumably because of the disproportionation reactions. It was not possible to measure accurate data for the C₈ aromatic isomer binary systems at their normal boiling points (about 135 °C). Ethylbenzene was the most reactive of the C₈ isomers but enough reaction also occurred in the 1,4-dimethylbenzene + 1,3-dimethylbenzene system at considerably lower temperatures to create serious doubts about the accuracy of the isotherm shown in Figure 2. The cell pressures were not completely independent of time and it was necessary to "bump" each cell a few times to achieve a "hard" pressure reading. Presumably the bumping removed the benzene and toluene being formed but left the heavier reaction products in the cell. In repeated measurements (with bumping) of the pure compound cells, the cell compositions definitely became "heavier" as the measurements were repeated, and it was necessary to increase the bath temperature about 0.0025 °C/h to keep the endpoint cells at their original pressures. Such changes are not negligible in such a close-boiling system and, despite the smoothness of the data in Figure 2, it is not at all certain that the isotherm shown there is an accurate representation of that system.

The chemical reaction problem is not unique to this apparatus or even to static apparatuses in general. Circulating VLE devices, even if they continuously distill off the light reaction products, will still experience the buildup of heavier products. An admittedly extreme example (the 1,4-dimethylbenzene + 1,3-dimethylbenzene system) has been used here to illustrate the fact that the reaction problem will be recognized only if the

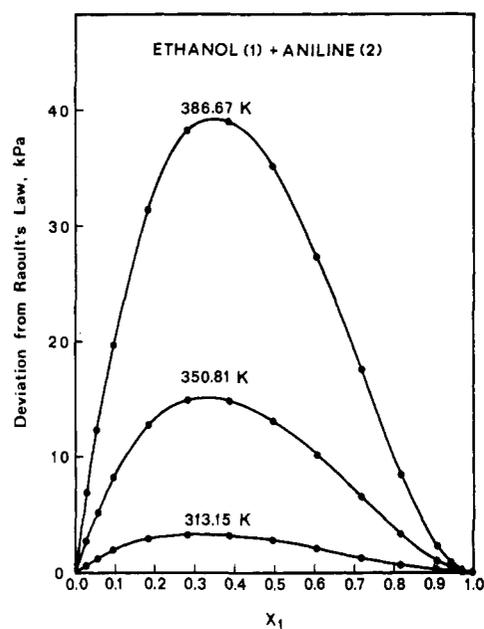


Figure 3. Deviations from Raoult's law for the ethanol (1) + aniline (2) system at 313.15, 350.81, and 386.67 K.

measuring devices are sensitive enough to "see" the effect of the reactions.

Another limitation to the apparatus and technique being described is the buildup of pressure (about 30 μ /day for evacuated cells) due to leakage and desorption. Over the 3-day period from the last degassing cycle to the end of the third isotherm, the pressure buildup might reach about 0.1 mmHg for a low-pressure system. If that error is nonnegligible for the system being studied, it is necessary to "bump" the cells on the third day to remove the extra pressure.

Experimental Data

Experimental data on the ethanol + aniline system are presented as an example of data taken on the PTx apparatus. Figure 3 shows the deviations from Raoult's law at each of the three temperatures. The experimental P vs. x_1 values are tabulated in Table I.

Sources and Purities of Chemicals. The absolute ethanol used was produced by U.S. Industrial Chemicals Co. and was found by gas-liquid chromatography to be approximately 99.98% pure. The aniline was purchased from Aldrich Chemical Co. (lot no. AB111867) and had a stated purity of 99.9+%. It was dried by distillation over molecular sieves (4A) and then distilled again with the first 20 and last 50 cm^3 being discarded. The middle portion was loaded immediately into the cells under a dry nitrogen blanket. No impurities could be detected at the 0.1% level by gas-liquid chromatography.

Data Reduction. The Mixon-Gumowski-Carpenter (2) method was used to reduce the data to γ and γ_i values, some of which are shown in Table II. That procedure requires evenly spaced x_1 values, and an increment of 0.025 was used. Evenly spaced P values were obtained from a least-squares cubic spline fit of the data with equal weights being assigned to all points. The method of Mixon et al. reproduces the input P values through at least four digits, hence any degradation of the experimental P - x data will occur in the production of the evenly spaced values. Comparison of the smoothed (spline) P values with the experimental values is made in Table I. The largest differences between the experimental and smoothed P values at 313.15, 350.81, and 386.67 K are 0.018, 0.02, and 0.2 kPa, respectively, values which are within the possible experimental error. Consequently, it can be concluded that there is no significant

Table I

Experimental P vs. x_1 Values at 313.15 K and a Comparison with the Smoothed P Values

x_1	pressure, kPa		difference	
	exptl	spline	kPa	%
0.0000	0.248	0.248	0.001	0.000
0.0264	1.405	1.403	-0.002	-0.142
0.0550	2.498	2.505	+0.007	+0.280
0.0936	3.853	3.844	-0.009	-0.234
0.1818	6.370	6.376	+0.006	+0.094
0.2792	8.507	8.504	-0.003	-0.035
0.3867	10.332	10.333	+0.001	+0.010
0.4953	11.804	11.805	+0.001	+0.008
0.6056	13.068	13.065	-0.003	-0.023
0.7188	14.265	14.271	+0.006	+0.042
0.8184	15.389	15.380	-0.009	-0.058
0.9080	16.507	16.513	+0.006	+0.036
0.9471	17.065	17.068	+0.003	+0.018
0.9722	17.457	17.542	-0.005	-0.029
1.0000	17.935	17.917 ^a	-0.018	-0.100

Experimental P vs. x_1 Values at 350.81 K and a Comparison with the Smoothed P Values

x_1	pressure, kPa		difference	
	exptl	smooth	kPa	%
0.0000	2.16	2.17	+0.01	+0.463
0.0265	7.47	7.47	0.00	0.000
0.0551	12.76	12.78	+0.02	+0.157
0.0937	19.41	19.39	-0.02	-0.103
0.1822	32.44	32.45	+0.01	+0.031
0.2797	44.11	44.10	-0.01	-0.023
0.3869	54.53	54.55	+0.02	+0.037
0.4954	63.32	63.30	-0.02	-0.032
0.6056	70.97	70.98	+0.01	+0.014
0.7189	78.221	78.229	+0.008	+0.010
0.8185	84.619	84.603	-0.016	-0.019
0.9080	90.969	90.976	+0.007	+0.008
0.9472	94.093	94.108	+0.015	+0.016
0.9722	96.278	96.263	-0.015	-0.016
1.0000	98.823	98.824	+0.001	-0.001

Experimental P vs. x_1 Values at 386.67 K and a Comparison with the Smoothed P Values

x_1	pressure, kPa		difference	
	exptl	smooth	kPa	%
0.0000	10.5	10.5	0.0	0.000
0.0263	26.2	26.2	0.0	0.000
0.0548	41.9	42.1	+0.2	+0.477
0.0929	62.4	62.2	-0.2	-0.321
0.1815	104.2	104.4	+0.2	+0.192
0.2788	144.1	144.0	-0.1	-0.069
0.3858	181.3	181.3	0.0	0.000
0.4954	214.3	214.3	0.0	0.000
0.6057	243.9	243.9	0.0	0.000
0.7186	272.5	272.5	0.0	0.000
0.8181	297.3	297.3	0.0	0.000
0.9078	321.4	321.4	0.0	0.000
0.9470	333.1	333.1	0.0	0.000
0.9721	341.1	341.1	0.0	0.000
1.0000	350.3	350.3	0.0	0.000

^a The spline value of 17.936 kPa resulted in a maximum in the γ_2 curve. This substituted value gave a more regularly shaped curve.

degradation of the experimental data in the data reduction procedures used.

The equations used to calculate the γ_i and G^E values were

$$\gamma_i = \frac{y_i P_{i,p}}{x_i P_i' \phi_{i,p}'} \left[\exp \frac{V_i'(P - P_i')}{RT} \right]^{-1}$$

and

$$G^E = RT \sum_i x_i \ln \gamma_i$$

Table II

Smoothed P vs. x_1 Values at 313.15 K and the y_1 , γ_1 , and G^E Values Calculated Using the Virial Equation through the Second Coefficient ^a											
x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹	x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹
0.00	0.248	0.0000	2.6654	1.0000	0.00	0.55	12.450	0.9877	1.2536	1.3188	647.80
0.05	2.320	0.8975	2.3543	1.0030	118.90	0.60	13.005	0.9889	1.2012	1.3972	634.71
0.10	4.053	0.9437	2.1593	1.0099	223.60	0.65	13.540	0.9900	1.1552	1.4912	608.32
0.15	5.541	0.9605	2.0006	1.0210	316.84	0.70	14.070	0.9911	1.1154	1.6039	568.13
0.20	6.818	0.9692	1.8610	1.0368	398.72	0.75	14.607	0.9923	1.0816	1.7398	513.62
0.25	7.923	0.9746	1.7380	1.0576	469.13	0.80	15.166	0.9935	1.0536	1.9047	444.23
0.30	8.893	0.9783	1.6306	1.0835	528.06	0.85	15.761	0.9948	1.0313	2.1071	359.29
0.35	9.757	0.9810	1.5366	1.1149	575.56	0.90	16.404	0.9962	1.0147	2.3616	257.98
0.40	10.530	0.9832	1.4534	1.1528	611.55	0.95	17.110	0.9979	1.0038	2.7042	138.93
0.45	11.227	0.9849	1.3791	1.1984	635.81	1.00	17.917	1.0000	1.0000	3.1173	0.00
0.50	11.863	0.9864	1.3127	1.2532	648.02						

Smoothed P vs. x_1 Values at 350.81 K and the y_1 , γ_1 , and G^E Values Calculated Using the Virial Equation through the Second Coefficient ^a											
x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹	x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹
0.00	2.17	0.0000	2.2065	1.0000	0.00	0.55	67.22	0.9800	1.2268	1.2593	630.51
0.05	11.86	0.8239	2.0441	1.0019	109.53	0.60	70.60	0.9821	1.1822	1.3241	620.40
0.10	20.42	0.9014	1.9192	1.0070	208.48	0.65	73.858	0.9841	1.1424	1.4019	597.29
0.15	28.02	0.9308	1.8078	1.0157	297.58	0.70	77.036	0.9860	1.1072	1.4961	560.52
0.20	34.78	0.9464	1.7065	1.0282	376.60	0.75	80.185	0.9878	1.0764	1.6120	509.26
0.25	40.81	0.9561	1.6148	1.0448	445.31	0.80	83.386	0.9898	1.0502	1.7554	442.47
0.30	46.25	0.9628	1.5325	1.0657	503.55	0.85	86.743	0.9918	1.0290	1.9326	359.17
0.35	51.19	0.9678	1.4587	1.0914	551.22	0.90	90.362	0.9941	1.0133	2.1527	258.40
0.40	55.69	0.9718	1.3920	1.1225	588.10	0.95	94.347	0.9968	1.0035	2.4305	139.15
0.45	59.82	0.9749	1.3314	1.1601	613.88	1.00	98.824	1.0000	1.0000	2.7844	0.00
0.50	63.65	0.9776	1.2764	1.2052	628.17						

Smoothed P vs. x_1 Values at 386.67 K and the y_1 , γ_1 , and G^E Values Calculated Using the Virial Equation through the Second Coefficient ^a											
x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹	x_1	P , kPa	y_1	γ_1	γ_2	G^E , J mol ⁻¹
0.00	10.5	0.0000	1.9223	1.0000	0.0	0.55	229.3	0.9706	1.1873	1.2071	575.8
0.05	39.5	0.7415	1.7908	1.0017	98.9	0.60	242.5	0.9740	1.1515	1.2581	567.4
0.10	65.8	0.8497	1.7024	1.0058	187.7	0.65	255.3	0.9771	1.1196	1.3186	547.2
0.15	90.1	0.8937	1.6247	1.0125	268.0	0.70	267.9	0.9801	1.0910	1.3914	514.6
0.20	112.4	0.9176	1.5530	1.0223	339.7	0.75	280.3	0.9829	1.0654	1.4814	468.7
0.25	132.9	0.9328	1.4867	1.0353	402.4	0.80	292.7	0.9858	1.0432	1.5931	408.3
0.30	151.9	0.9434	1.4259	1.0519	456.0	0.85	305.6	0.9888	1.0251	1.7307	332.3
0.35	169.5	0.9513	1.3699	1.0724	500.1	0.90	319.2	0.9921	1.0116	1.8996	239.7
0.40	185.8	0.9578	1.3182	1.0974	534.6	0.95	334.0	0.9957	1.0032	2.1062	129.4
0.45	201.1	0.9626	1.2706	1.1277	559.0	1.00	350.3	1.0000	1.0000	2.4103	0.0
0.50	215.6	0.9669	1.2269	1.1640	572.8						

^a The virial coefficients were obtained using the Tsonopoulos correlation.

Table III. Effect of Assumed Equation of State on Calculated Properties

x_1	virial through B											
	ideal gas			Redlich-Kwong			Pitzer-Curl			O'Connell-Prausnitz		
	γ_1	γ_2	G^E ^a	γ_1	γ_2	G^E ^a	γ_1	γ_2	G^E ^a	γ_1	γ_2	G^E ^a
At $T = 313.15$ K; $P = 0.248$ – 17.917 kPa												
0.0	2.6296	1.0000	0.00	2.6390	1.0000	0.00	2.6495	1.0000	0.00	2.6598	1.0000	0.00
0.2	1.8459	1.0363	393.36	1.8499	1.0364	394.80	1.8543	1.0366	396.34	1.8588	1.0367	397.89
0.5	1.3070	1.2500	639.06	1.3086	1.2508	641.49	1.3102	1.2517	644.07	1.3120	1.2526	646.72
0.8	1.0516	1.8903	436.38	1.0522	1.8942	438.55	1.0527	1.8983	440.80	1.0534	1.9025	443.20
1.0	1.0000	2.9694	0.00	1.0000	3.0115	0.00	1.0000	3.0533	0.00	1.0000	3.1019	0.00
At $T = 350.81$ K; $P = 2.10$ – 98.823 kPa												
0.0	2.1367	1.0000	0.00	2.1678	1.0000	0.00	2.1920	1.0000	0.00	2.2162	1.0000	0.00
0.2	1.6717	1.0270	361.83	1.6874	1.0275	368.52	1.6994	1.0279	373.59	1.7117	1.0283	378.68
0.5	1.2627	1.1975	603.10	1.2691	1.2009	614.57	1.2738	1.2036	623.20	1.2790	1.2061	632.13
0.8	1.0456	1.7218	421.07	1.0478	1.7370	431.08	1.0494	1.7485	438.47	1.0513	1.7602	446.53
1.0	1.0000	2.4932	0.00	1.0000	2.6310	0.00	1.0000	2.7351	0.00	1.0000	2.8623	0.00
At $T = 386.67$ K; $P = 10.5$ – 350.3 kPa												
0.0	1.8063	1.0000	0.0	1.8785	1.0000	0.0	1.9209	1.0000	0.0	1.9592	1.0000	0.0
0.2	1.4887	1.0201	307.1	1.5291	1.0215	327.7	1.5527	1.0222	339.4	1.5746	1.0228	350.0
0.5	1.1993	1.1494	515.9	1.2171	1.1584	552.1	1.2272	1.1636	572.8	1.2373	1.1681	592.0
0.8	1.0341	1.5298	359.5	1.0402	1.5693	391.1	1.0436	1.5926	408.9	1.0472	1.6139	426.4
1.0	1.0000	1.9349	0.0	1.0000	2.2455	0.0	1.0000	2.4336	0.0	1.0000	2.6546	0.0

^a Units in J mol⁻¹.

The standard state for each component was the pure liquid at the mixture temperature and pressure. The fugacity coefficients were predicted with the virial equation of state truncated after the second coefficient. The B_{11} , B_{12} , and B_{22} values used for

the Table II values were obtained from the Tsonopoulos correlation (δ). Experimental data were available for B_{11} (ethanol) but not for B_{12} and B_{22} . The Tsonopoulos predictions for B_{11} agreed well enough with the better sets of experimental data

Table IV. Comparison of Pure Component Vapor Pressures with Literature Values

T, K	vapor pressure, kPa			
	ethanol		aniline	
	this work	lit.	this work	lit.
313.15	17.935	17.895	0.248	0.246
350.81	98.923	98.764	2.16	2.11
386.67	350.3	351.4	10.5	10.4

for B_{11} (1).

Effect of Equation of State. Data reduction was performed with three different equations of state (ideal gas, unmodified Redlich-Kwong (5), and the truncated virial equation) to demonstrate the effect of the equation of state on the calculated properties. Three different correlations (Pitzer-Curl (3), O'Connell-Prasnitz (4), and Tsonopoulos) were used to predict the B_{ij} and B_j values. (Toluene was used as the homomorph for aniline in the O'Connell-Prasnitz correlation.) Table III plus Table II show how the calculated γ_1 , γ_2 , and G^E values varied with the equation of state used.

Despite being at relatively low pressures, and despite the fact that the fugacity coefficients appear as a ratio in the equation for γ_i , the departures from the ideal gas model are sufficient to have a nonnegligible effect on the γ_i and G^E values calculated. Presumably, the virial equation is more accurate than the unmodified Redlich-Kwong for these data, and the O'Connell-Prasnitz and Tsonopoulos correlations should give better B_{ij} and B_j values than the Pitzer-Curl equation. However, there is no easy way of identifying that set of results which is most accurate. All sets are consistent with the Gibbs-Duhem equation and it is not likely that the Gibbs-Helmholtz test (consistency between G^E and H^E values) would be sensitive enough to discriminate between the various sets.

Vapor Pressure Checks. The two most important points measured on any VLE device are the pure component vapor pressures. If good values of those vapor pressures have been established by previous workers, comparisons to those values

provide information on the purities and the stabilities of the chemicals used and on the accuracies of the temperature and pressure measurements.

The comparisons for the two components are shown in Table IV. The literature values given there were obtained from fits of selected values. The selection process involved plotting all known literature values in residual (deviation from a simple fitting equation) form to emphasize the scatter and identify obviously incorrect points, and then making repeated fits with a reliable equation to obtain smaller and smaller root-mean-squared deviation values as large deviation points were eliminated. The final ethanol fits utilized original experimental data points from 29 literature documents (the data from all the others were rejected) and two different four-term equations were used to fit the following two ranges: 233–411 K and 343–516 K.

Only nine literature documents reporting aniline vapor pressure data were available, and of these, five were used to provide the literature values in Table IV. The fit of the literature data was made with a four-term equation over the range 267.3–393.2 K.

Chemical Stabilities. Ethanol is very stable over the temperature range covered and was still perfectly clear at the end of the experiment. Aniline, as normally produced, has impurities that will cause it to turn reddish brown when exposed to air or light. However, the aniline removed from the cells after the last isotherm was clear, indicating that no significant reactions had occurred.

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Densities of AlCl_3 -Rich, Molten AlCl_3 -LiCl Mixtures

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Densities of seven aluminum chloride-lithium chloride mixtures containing 50–75 mol % aluminum chloride were measured by a dilatometric procedure from 148 to 270 °C. An empirical equation was obtained which expresses density as a function of composition and temperature with an overall root-mean-square error of 0.06 %.

As part of an investigation aimed at employing AlCl_3 -based electrolytes in high-energy density batteries, accurate densities of AlCl_3 -rich binary AlCl_3 -LiCl mixtures were required in order to compute equivalent conductivities, kinematic viscosities, and molar volumes. We required densities at more composition values and over more extended temperature ranges than were available from the chemical literature (7, 9).

Experimental Section

All operations associated with sample preparation were performed in a nitrogen-filled glovebox (Vacuum/Atmospheres Co., Model HE-43-8 Dri Lab) having a moisture content of less than 2 ppm. The samples were made by mixing accurately weighed amounts of purified, solid lithium tetrachloroaluminate with purified, solid aluminum chloride. The AlCl_3 was purified by the method of Giner and Holleck (5), which involves digesting a mixture of AlCl_3 -NaCl-KCl (molar ratio 9.8:1.0:1.5) with Mg turnings at ca. 130 °C and then evaporating the AlCl_3 at ca. 215 °C. The lithium tetrachloroaluminate was prepared by fusing at approximately 170 °C an excess of Mallinckrodt Analytical Reagent Grade LiCl, which had been vacuum-dried at 120 °C, with Fluka *puriss* AlCl_3 (Fe content < 0.008%). The tetra-