Isobaric Vapor-Liquid Equilibria in Ternary System Benzene-*n*-Heptane-Acetonitrile from Binary *t*-*x* Measurements

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Measurements of isobaric vapor-liquid equilibria for the system benzene-*n*-heptane-acetonitrile at 760 mm Hg are reported from temperature-liquid composition measurements of the constituent binaries. The three-parameter NRTL equation is used to predict the vapor-liquid equilibria of the said ternary system from binary data alone. The predicted results for the partially miscible *n*-heptane-acetonitrile binary and the ternary system show good agreement with the experimental data obtained by the authors. The ternary liquid-liquid equilibrium data at 25°C is predicted from a knowledge of binary NRTL parameters alone.

The generation of vapor-liquid equilibrium (VLE) data from temperature-liquid composition (*t*-*x*) measurements consists in the determination of bubble-point temperatures of a series of liquid mixtures of known composition at constant total pressure. The indirect method results in considerable reduction in experimental work and time, since the analysis of equilibrium vapor and liquid phases is not required to obtain the VLE data. The composition of the vapor phase is calculated indirectly from liquid-phase activity coefficients utilizing suitable thermodynamic expression for the liquid phase.

In the present investigation, vapor-liquid equilibrium data of the three constituent binaries are reported at 500, 600, 700, and 760 mm Hg pressures from the binary *t*-*x* measurements by a least-squares fit of the total pressure. The vapor-liquid equilibrium data at 760 mm Hg pressure for the ternary system benzene-*n*-heptane-acetonitrile are predicted solely from a knowledge of the properties of the constituent binary pairs using the nonrandom, two-liquid (NRTL) equation (*16*) for correlating the liquid-phase activity coefficients. To the authors' knowledge, the isobaric data for the two binary pairs of acetonitrile (1-3, 2-3 systems) and also for the ternary system benzene-*n*-heptane-acetonitrile have not been reported in the literature, although recently, isothermal data at 45°C have been published by Palmer and Smith (*12*) and Palmer et al. (*13*). Experimental measurements of VLE data (*t*-*x*-*y*) in the partially miscible *n*-heptane-acetonitrile binary and the benzene-*n*-heptane-acetonitrile ternary systems at 760 mm Hg have also been carried out and reported. The predicted results from the binary *t*-*x* measurements show good agreement with experimental data.

Experimental

Materials. Benzene and *n*-heptane obtained from Phillips Petroleum Co. were of 99.0 + mol % purity. These were used as such without any further purification. Acetonitrile obtained from Prolabo Rhone-Poulenc, France, was purified by fractional distillation in an Oldershaw column with a good reflux ratio by discarding the first 10% distillate and the last 10% residue. The important characteristics of three compounds given in Table I compare well with the literature values (*6*).

Apparatus. *Ebulliometer.* The apparatus used for measurement of bubble points of various liquid mixtures and at different total pressures was essentially the same as Cottrell's ebulliometer. With a vacuum pump the ebulliometer could be operated below atmospheric pressure. The total pressure of the system was controlled by a cartesian manostat with an accuracy of ±0.5 mm Hg pressure, the pressure being measured with a manometer coupled with a cathetometer. Mercury-in-glass thermometers were used to measure temperatures within ±0.05°C. The liquid mixtures were prepared by weighing appropriate amounts of the relevant binary components to cover the whole range of composition. The reliability in the composition measurements is estimated to be within ±0.001 mole fraction.

Equilibrium stills. For the *n*-heptane-acetonitrile partially miscible binary system, the special circulation type of still as described by Smith and Bonner (*17*) was used to obtain the VLE data. The still was slightly modified by providing a mechanical stirrer for thorough mixing of the two liquid phases. The equilibrium data for the ternary system benzene-*n*-heptane-acetonitrile in the miscible region were obtained with an improved Othmer still (*11*). The temperature measurements were made within ±0.1°C, with mercury-in-glass thermometers. The pressure in the stills was maintained at 760 mm Hg with the help of a cartesian manostat. The precision in the pressure measurements is estimated to be ±0.5 mm Hg.

Analyses. *Partially miscible binary system.* Since a large amount of liquid mixture (about 1 liter) was taken in the still, the withdrawal of about 1.5 ml of the condensed vapor phase after proper attainment of equilibrium did not affect the composition of the total liquid samples in the still. The composition of the liquid phase at equilibrium was thus taken to be that of the mixture originally charged to the still. The condensed vapor sample was collected in a finely graduated and jacketed receiver maintained at 20°C; its total volume, as well as that of the two individual phases, was noted at this temperature. The densities of the two liquid phases at 20°C were determined earlier by equilibrating the two components in a mixer settler. The compositions of the two liquid phases were calculated from the solubility curve. Subsequently, by a combination of component material balance and the density of each phase, the amount, and hence the concentration of each component in the vapor phase, was calculated.

Table I. Physical Properties of Chemicals Used

Components	Density, 20°C		Refractive index, 20°C		Normal boiling point, °C
	Exptl	Lit	Exptl	Lit	
Benzene	0.8789	0.87901	1.50105	1.50112	80.1
n-Heptane	0.6837	0.68376	1.38760	1.38764	98.4
Acetonitrile	0.7828	0.78300	1.34350	1.34360	81.6

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The VLE measurements were made in the region where the binary liquid mixture had one liquid phase at the equilibrium temperature. The vapor, however, on cooling and condensation, split into two liquid phases. The heteroazeotropic composition was determined by taking a series of partially miscible liquid systems, giving the same vapor composition which again on proper condensation gave two liquid phases. Care was taken so that the partially miscible liquid system in the still was thoroughly agitated to ascertain a uniform vapor-phase composition. The extremes of the bubble-point curve in the two-liquid phase region were established by determination of the binary solubility curve of the system.

Ternary system. The liquid and vapor samples were analyzed in duplicate with a Perkin-Elmer vapor fractometer equipped with a thermal conductivity detector and coupled to a Honeywell recorder. The column used to separate the components of the ternary system was of 2-meter length and 3 mm i.d. packed with 20% $\beta\beta'$-oxydipropionitrile supported on chromosorb P. The determinations were carried out at 80°C with nitrogen as the carrier gas. The accuracy of the analysis was checked by making several synthetic mixtures of known compositions. Quantitative calculations were done from peak areas after applying correction factors as reported by Dietr (*5*). The accuracy of composition measurements was within ±0.003 mole fraction for benzene and *n*-heptane, whereas for acetonitrile, it is estimated to be within ±0.005 mole fraction.

Correlating Equations for Calculation of NRTL Parameters and Other Quantities

From the basic thermodynamic equation of vapor-liquid equilibria

$$\phi_i y_i P = \gamma_i x_i f_i^{0L} \exp \frac{RT}{v_i^L P} \qquad (1)$$

the liquid-phase activity coefficient γ_i is given by the following expression:

$$\gamma_i = \frac{\phi_i y_i P}{x_i P_i^s \phi_i^s} \exp \frac{(P_i^s - P) v_i^L}{RT} \qquad (2)$$

since the reference (or standard state) fugacity

$$f_i^{0L} = P_i^s \phi_i^s \exp \frac{-v_i^L P_i^s}{RT}$$

In the present investigation, the liquid-phase activity coefficients are correlated by means of the NRTL (*16*) equation as follows:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad (3a)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \qquad (3b)$$

where $\tau_{12} = (g_{12} - g_{22})/RT$; $\tau_{21} = (g_{12} - g_{11})/RT$; $G_{12} = \exp(-\alpha_{12}\tau_{12})$; $G_{21} = \exp(-\alpha_{21}\tau_{21})$; and $\alpha_{12} = \alpha_{21}$.

The quantities $(g_{12} - g_{22})$, $(g_{12} - g_{11})$, and α_{12} are the three adjustable parameters of the NRTL equation. Now rearranging Equation 2, we obtain for a binary mixture:

$$P = \frac{\gamma_1 x_1 P_1^s \phi_1^s}{\phi_1} \exp \frac{(P - P_1^s) v_1^L}{RT} + \frac{\gamma_2 x_2 P_2^s \phi_2^s}{\phi_2} \exp \frac{(P - P_2^s) v_2^L}{RT} \qquad (4)$$

since $y_1 + y_2 = 1.0$.

After substituting Equation 3 into Equation 4, the total pressure P is a nonlinear function of the liquid composition, ϕ_i, P_i, Poynting correction, and the NRTL constants, viz., $(g_{12} - g_{22})$, $(g_{12} - g_{11})$, and α_{12}.

In Equation 4 the vapor-phase fugacity coefficients ϕ_i in the binary mixture are obtained from the relation (*15*):

$$\ln \phi_i = \frac{2}{v} (y_j B_{ij} + y_i B_{ii}) - \ln Z_{\text{mix}} \; (i, j = 1, 2) \qquad (5)$$

where compressibility factor Z and molar volume v are related by the second virial equation of state truncated after the second term:

$$Z_{\text{mix}} = \frac{Pv}{RT} = 1 + \frac{B_{\text{mix}}}{v} \qquad (6)$$

and B_{mix}, the mixture virial coefficient for a binary mixture is given exactly by

$$B_{\text{mix}} = y_i^2 B_{ii} + 2\, y_i y_j B_{ij} + y_j^2 B_{jj} \; (i, j = 1, 2) \qquad (7)$$

B_{ii} and B_{jj} are the pure component second virial coefficients and B_{ij} $(i \neq j)$ is the second virial cross coefficient for the pair ij.

The second virial coefficients for nonpolar components benzene and *n*-heptane were calculated by the correlation of Pitzer and Curl (*14*), whereas for the polar component acetonitrile, it was calculated from the correlation of O'Connell and Prausnitz (*10*). The cross coefficients B_{ij} $(i \neq j)$ were also estimated from correlating equations for pure components with suitable mixing rules (*10*) for various parameters. The pure component fugacity coefficients ϕ_i^s were calculated by the three-parameter corresponding states correlation of Lyckman et al. (*8*) for reduced temperatures higher than 0.56.

The various critical properties and other parameters required for estimating the second virial coefficients are available elsewhere (*15*). For calculating the Poynting correction in Equation 4, the liquid molar volumes available at three temperatures were fitted to a quadratic equation, and the resultant equation was used to estimate the liquid molar volumes at the desired temperatures (*15*). The pure component vapor pressures were calculated by using the Antoine equation with various constants reported by Dreishbach (*6*).

In the present case, each set of binary NRTL parameters was calculated according to the procedure suggested by Prausnitz et al. (*15*), which as defined in Equation 4 earlier, is similar in some respects to the one proposed by Barker (*2*).

The effect of temperature (*1*) on NRTL parameters was also taken into account. For a binary pair 1–2, it is given by (noting that $g_{21} = g_{12}$):

$$g_{21} - g_{11} = C_1 + D_1 (T - 273.15) \qquad (8a)$$

$$g_{12} - g_{22} = C_2 + D_2 (T - 273.15) \qquad (8b)$$

The constants C_1 and C_2 represent the values of NRTL parameters at 0°C, whereas D_1 and D_2 represent their dependence on temperatures.

Since the equations available to use for finding various quantities are nonlinear and involve an iterative procedure, the proper solution was obtained in a CDC 6400 digital computer. The program starts with some estimates of NRTL parameters initially, and the activity coefficients are calculated at the reference pressure of the standard state fugacity. The total pressure P is evaluated by Equation 4 presented earlier. The NRTL parameters are obtained by a least-squares fit on total pressure which consists in minimizing the sum of squares of relative deviation in pressure for all data points. A comparison is then made between calculated and experimental pressure P so that:

$$\Sigma\left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right)^2$$

is minimum.

The NRTL parameters obtained above are then used to calculate the excess Gibbs free energy (G^E) for the binary mixture from the following expression:

$$\frac{G^E}{RT} = x_1x_2\,[\tau_{21}G_{21}/(x_1 + x_2G_{21}) + \tau_{12}G_{12}/(x_2 + x_1G_{12})] \tag{9}$$

The vapor composition is calculated from Equation 2 given earlier, since all the quantities are now known.

Binary NRTL parameters. Based on the above calculations, the values of temperature dependent binary NRTL parameters are reported in Table II. The "nonrandomness" parameter α_{12} was, however, assumed to be independent of temperature.

Results and Discussion

Binary VLE data. The *y-x* data for the system benzene(1)-*n*-heptane(2) are given in Table III along with liquid-phase activity coefficients, calculated total pressures, and G^E values. The standard deviation ($\sigma = \sqrt{\Sigma x_i - \bar{x}_i/N}$, where $\bar{x}_i$ is the arithmetic mean of all data points, and N is the number of such points) in calculated pressures in the range of 500–760 mm Hg varies from 0.6 to 2.4 mm. The average deviation of calculated pressures from experimental values as calculated from

$$\overline{\Delta P_i} = \frac{\sum_{i}^{N} |\Delta P_i| i}{N}$$

varies from 0.5 to 1.9 mm. The predicted vapor compositions at 760 mm Hg pressure compare very well in Figure 1 with the experimental data of Myers (*9*).

Table II. Binary NRTL Parameters[a] in Ternary System Benzene(1)–*n*-Heptane(2)–Acetonitrile(3)

Binary system	C_1	D_1	C_2	D_2	α_{ij}
Benzene(1)–*n*-heptane(2)	687.5	0.00	−203.7	−1.39	0.300
Benzene(1)–acetonitrile(3)	442.2	0.00	234.7	1.33	0.400
n-Heptane(2)–acetonitrile(3)	1683.3	−7.79	1689.9	−2.82	0.397

where $g_{ji} - g_{ii} = C_1 + D_1\,(T - 273.15)$

$g_{ij} - g_{jj} = C_2 + D_2\,(T - 273.15)$

[a] C_1 and C_2 are the NRTL parameters of the corresponding binaries, and D_1 and D_2 show their temperature dependence.

Table IV gives VLE data for the benzene(1)-acetonitrile(3) system. The maximum average deviation of calculated pressures from experimental values is 4.6 mm. This binary system forms a minimum boiling azeotrope at 72.9°C with $x_1 = y_1 = 0.51$. The predicted values of vapor compositions are compared in Figure 2 with the experimental data of Boeuve (*4*), and the agreement is generally good. The maximum percent deviation in *y* given by $(y_{\text{exptl}} - y_{\text{calcd}}) \times 100/y_{\text{exptl}}$ is about 2%. The activity coefficient data are plotted in Figure 3 as a function of liquid composition at 760 mm Hg pressure.

The VLE data at different total pressures for the partially miscible system *n*-heptane(2)-acetonitrile(3) are reported in Table V along with calculated pressures. The average deviation in calculated pressures varies from 4.2 to 5.4 mm, whereas the maximum standard deviation is 6.2 mm.

The calculated *t-x-y* curve for the system is shown in Figure 4 along with the experimental data obtained in the equilibrium still in the present investigation. The system forms a heteroazeotrope with $x_1 = 0.129$ and 0.755. The heteroazeotropic temperature of 69.4°C (experimental) and the corresponding vapor composition $y_1 = 0.355$ are in agreement with the data of Bishop and Denton (*3*). The maximum percent deviation between y_1 (experimental) and y_1 (calculated), viz., $\Delta y_1 \times 100/y_1$ exptl is 0.5%. The data in Figure 4 show that there is good agreement between the experimental vapor-phase compositions and that obtained through *t-x* measurements with the NRTL equation, thus establishing the thermodynamic consistency of the experimental data. Such a consistency test has also been applied by Palmer and Smith (*12*) for this system under isothermal conditions. The NRTL equa-

Table III. Vapor-Liquid Equilibrium Data for Benzene(1)–*n*-Heptane(2) System from *P-t-x* Measurements

Liquid molar composition, x_1	Calcd vapor composition, y_1	Activity coefficients γ_1	γ_2	*P* exptl, mm	*P* calcd, mm	*t* exptl, °C	G^E, J mol⁻¹
0.1	0.188	1.250	1.002	760	755.5	94.5	17.3
0.3	0.458	1.185	1.018	760	761.9	89.0	45.7
0.5	0.640	1.114	1.067	760	762.1	85.0	61.3
0.7	0.782	1.049	1.175	760	759.6	82.2	57.8
0.9	0.918	1.007	1.400	760	759.2	80.5	27.8
0.1	0.190	1.256	1.002	700	697.4	91.8	17.6
0.3	0.460	1.189	1.019	700	700.9	86.2	46.4
0.5	0.642	1.116	1.068	700	700.3	82.2	62.1
0.7	0.782	1.050	1.179	700	699.4	79.5	58.6
0.9	0.918	1.007	1.141	700	698.3	77.8	28.2
0.1	0.194	1.268	1.002	600	600.1	86.8	18.0
0.3	0.465	1.197	1.019	600	601.5	81.2	47.5
0.5	0.645	1.121	1.071	600	599.8	77.2	64.0
0.7	0.784	1.052	1.186	600	600.6	74.6	60.0
0.9	0.918	1.007	1.429	600	599.7	73.0	28.9
0.1	0.198	1.282	1.002	500	499.2	81.0	18.5
0.3	0.471	1.208	1.020	500	500.5	75.4	48.9
0.5	0.650	1.127	1.074	500	499.4	71.5	65.4
0.7	0.786	1.055	1.195	500	499.7	69.0	61.6
0.9	0.918	1.007	1.451	500	498.8	67.4	29.6

tion, therefore, correlates the data for this partially miscible binary system very satisfactorily. Figure 5 shows how the activity coefficient data at 760 mm Hg pressure compare with the data of Palmer et al. (*13*) at 45°C based on theoretical considerations of conformal solution equations.

Prediction of ternary VLE data. In the present investigation, the ternary VLE data for the system benzene(1)–*n*-heptane(2)–acetonitrile(3) were predicted solely from a knowledge of the properties of the corresponding binaries. The binary NRTL parameters (Table II) obtained earlier from a least-squares fit of the total pressure are then used in Equation 10 (which is a ternary form of the Renon-Prausnitz equation) to calculate the activity coefficients of the said ternary system as a function of liquid composition and equilibrium temperature at 760 mm Hg pressure:

$$\ln \gamma_i = \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{3} G_{li} x_l} + \sum_{j=1}^{3} \frac{x_j G_{ij}}{\left(\sum_{l=1}^{3} G_{lj} x_l\right)} \times \left[\tau_{ij} - \frac{\left(\sum_{r=1}^{3} x_r \tau_{rj} G_{rj}\right)}{\left(\sum_{l=1}^{3} G_{lj} x_l\right)} \right] \qquad (10)$$

where $G_{kk} = 1$ and $\tau_{kk} = 0$.

Since the calculations of ternary vapor-liquid equilibria from binary data involve highly nonlinear equations and are necessarily iterative, the proper solution of all quantities was obtained in a CDC 6400 digital computer. In the present work, ternary liquid compositions at 760 mm

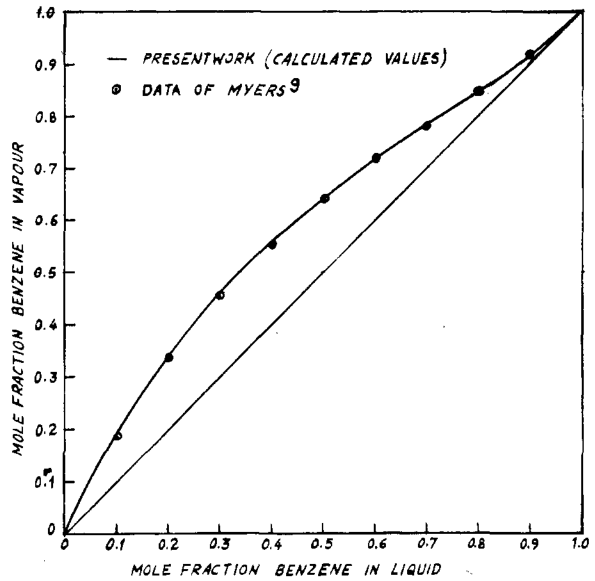

Figure 1. Vapor-liquid equilibrium data for system benzene(1)–*n*-heptane(2) at 760 mm Hg pressure

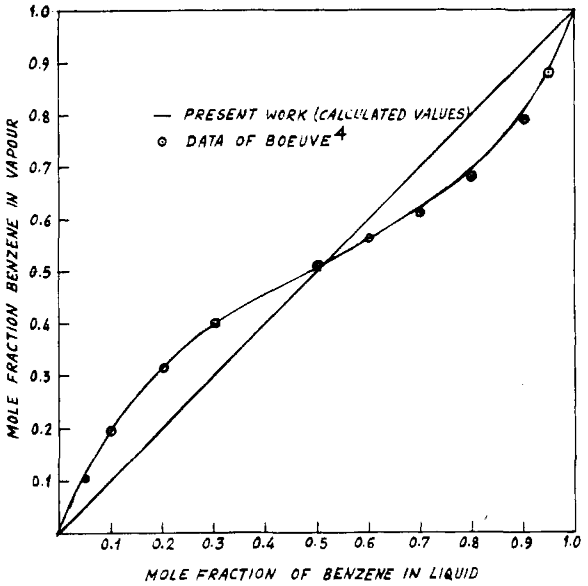

Figure 2. Vapor-liquid equilibrium data for system benzene(1)–acetontrile(3) at 760 mm Hg

Table IV. Vapor-Liquid Equilibrium Data for Benzene(1)–Acetonitrile(3) System from P-t-x Measurements

Liquid molar composition, x_1	Calcd vapor composition, y_1	Activity coefficients		P exptl, mm	P calcd, mm	t exptl, °C	G^E, J mol^{-1}
		γ_1	γ_2				
0.1	0.196	2.211	1.010	760	754.5	77.1	61.3
0.3	0.396	1.630	1.090	760	765.5	74.1	142.8
0.5	0.513	1.292	1.273	760	763.1	73.1	171.4
0.7	0.625	1.101	1.621	760	760.4	73.5	146.1
0.9	0.812	1.011	2.275	760	756.2	76.2	64.0
0.1	0.197	2.214	1.010	700	695.3	74.6	60.9
0.3	0.397	1.632	1.090	700	705.9	71.6	142.1
0.5	0.514	1.294	1.274	700	703.4	70.6	170.5
0.7	0.625	1.101	1.622	700	701.2	71.0	145.4
0.9	0.811	1.011	2.280	700	696.3	73.6	63.8
0.1	0.199	2.220	0.010	600	594.0	69.8	60.3
0.3	0.399	1.636	1.090	600	603.8	66.9	140.7
0.5	0.515	1.296	1.274	600	601.3	65.9	168.9
0.7	0.625	1.102	1.626	600	600.0	66.3	144.2
0.9	0.810	1.011	2.292	600	597.3	68.9	63.3
0.1	0.200	2.227	1.010	500	494.7	64.4	59.5
0.3	0.401	1.641	1.090	500	501.5	61.5	139.0
0.5	0.516	1.298	1.275	500	500.9	60.6	167.2
0.7	0.625	1.103	1.629	500	498.5	60.9	142.3
0.9	0.809	1.012	2.305	500	496.6	63.4	62.8

pressure are known, besides the binary parameters for calculations of liquid-phase activity coefficients. The program starts with some initial estimates of equilibrium temperature while setting vapor-phase fugacity coefficients, ϕ_i equal to unity. The initial values of vapor compositions are obtained by finding $\sum_{i=1}^{3} y_i = \sum_{i=1}^{3} f_i^L/P$, where f_i^L is given by the right-hand side of Equation 1. With these first estimates of the vapor compositions thus obtained, the vapor-phase fugacity coefficients, ϕ_i are then calculated, and second estimates of vapor compositions obtained by computing $\sum_{i=1}^{3} y_i = \sum_{i=1}^{3} f_i^L/\phi_i P$. This procedure is repeated until Σy_i no longer changes. Depending upon the value of Σy_i, the entire set of calculations is now repeated with a new estimate of temperature, and this iterative procedure continues till Equation 11 is satisfied.

$$\sum_{i=1}^{3} y_i = \sum_{i=1}^{3} \gamma_i x_i f_i^{0L} \exp\frac{v_i^L P}{RT}/\phi_i P = 1.0 \qquad (11)$$

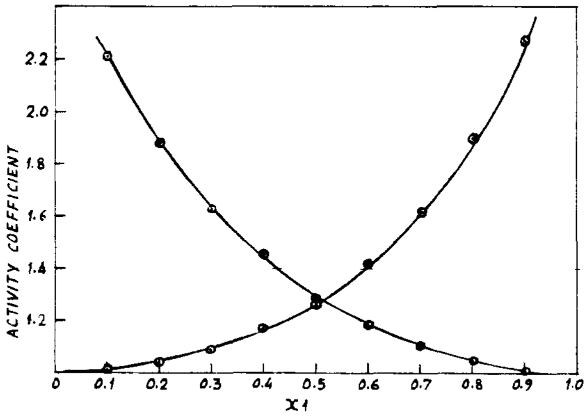

Figure 3. Activity coefficient data for system benzene(1)-acetonitrile(3) at 760 mm Hg

The results of these calculations, viz., vapor compositions, liquid-phase activity coefficients, and equilibrium temperature, are reported in Table VI. The conventional bubble-point and dew-point isotherms are shown in Figure 6, and the isoconcentration curves for the vapor compositions are plotted in Figure 7. These curves were plotted by interpolation and smoothing of the calculated results. The data in Table VI and Figure 6 do not indicate the occurrence of a ternary azeotrope, homogeneous or heterogeneous. The liquid curves are rather flat, whereas vapor curves are converging in the binary (1-3) heteroazeotrope region. The isoconcentration vapor curves in Figure 7 will be of use in ternary distillation calculations.

The calculated vapor-phase compositions of the said ternary system are compared in Table VII with the experimental data obtained in the equilibrium still in the miscible region. The values of activity coefficients and excess Gibbs free energy G^E (calculated from $G^E = RT \sum_{i=1}^{3} x_i \ln \gamma_i$) are also reported. The average deviations, without taking signs into account for the vapor compositions, are $\overline{\Delta y}_1 = 0.009$, $\overline{\Delta y}_2 = 0.005$, and $\overline{\Delta y}_3 = 0.019$; while for the temperature, it is 0.15°C. The calculated temperatures are those obtained from a knowledge of binary NRTL parameters using the experimental liquid composition values. The reliability of experimental vapor-liquid compositions is estimated to be within ±0.003 mole fraction for the

Table V. Vapor-Liquid Equilibrium Data for n-Heptane(2)-Acetonitrile(3) System from P-t-x Measurements

Liquid molar composition, x_2	Calcd vapor composition, y_2	Activity coefficients γ_1	γ_2	P exptl, mm	P calcd, mm	t exptl, °C	G^E, J mol^{-1}
0.025	0.182	15.173	1.003	760	755.7	75.2	796.9
0.050	0.271	12.439	1.012	760	757.7	72.2	713.6
0.075	0.317	10.218	1.027	760	756.8	70.5	638.0
0.129	0.357	6.974	1.074	760	765.5	69.5	530.1
0.755	0.353	1.174	3.827	760	762.6	69.5	314.2
0.850	0.389	1.067	5.536	760	769.0	71.9	433.3
0.900	0.445	1.013	6.839	760	756.1	74.6	519.6
0.950	0.591	1.007	8.164	760	771.6	82.9	612.9
0.025	0.178	15.182	1.004	700	699.8	72.8	791.6
0.050	0.268	12.448	1.014	700	705.2	69.9	709.3
0.075	0.315	10.226	1.032	700	701.2	68.1	633.1
0.115	0.346	7.564	1.062	700	697.1	66.8	527.1
0.780	0.348	1.152	4.232	700	694.0	66.8	339.1
0.850	0.395	1.071	5.542	700	703.4	68.9	430.5
0.900	0.454	1.016	6.845	700	694.7	71.6	515.4
0.950	0.602	1.010	8.172	700	695.0	79.0	606.5
0.025	0.175	15.196	1.004	600	598.1	67.9	761.3
0.050	0.265	12.462	1.015	600	604.6	65.1	699.6
0.075	0.313	10.240	1.034	600	601.5	63.4	625.6
0.097	0.334	8.245	1.051	600	597.7	62.5	553.0
0.816	0.338	1.112	4.752	600	593.7	62.5	378.2
0.900	0.463	1.020	6.862	600	598.9	66.5	508.6
0.950	0.608	1.012	8.183	600	592.2	73.2	596.9
0.025	0.172	16.101	1.005	500	498.5	62.3	784.2
0.050	0.263	12.470	1.016	500	503.5	59.6	688.5
0.075	0.310	10.248	1.035	500	499.3	57.9	614.9
0.082	0.325	9.012	1.040	500	497.0	57.5	577.6
0.848	0.327	1.078	5.563	500	497.8	57.5	418.4
0.900	0.468	1.023	6.880	500	513.3	61.4	501.7
0.950	0.613	1.014	8.196	500	494.5	66.9	586.6

two hydrocarbons and ±0.005 mole fraction for acetonitrile. With these experimental limitations, the agreement between calculated and experimental vapor composition is considered to be good. The predicted values of temperatures are also in good agreement with the experimental values except at one or two points.

Although Palmer et al. (*13*) observed that the NRTL parameters obtained by fitting G^E data did not give a satisfactory prediction of ternary VLE data for the present system at 45°C compared to that obtained from the conformal solution equation, in the present case, however, the NRTL parameters obtained for each binary system by fitting total pressure data gave a good prediction of ternary VLE data for the same system at 760 mm Hg pressure. The better prediction in our case is due to good precision in the *p-t-x* measurements and also to taking into account the temperature dependence of the two adjustable parameters.

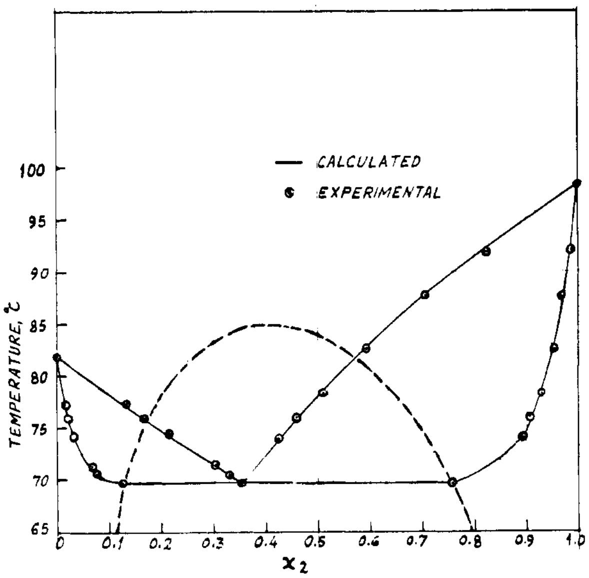

Figure 4. Comparison of calculated and experimental vapor-liquid equilibrium data for *n*-heptane(2)-acetonitrile(3) system at 760 mm Hg. Dotted lines show solubility curve

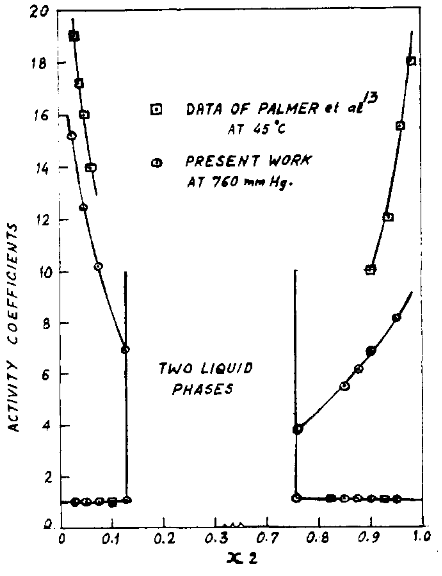

Figure 5. Activity coefficient data for system *n*-heptane(2)-acetonitrile(3) at 760 mm Hg

Prediction of ternary solubility envelope. The binary NRTL parameters obtained from vapor-liquid equilibrium measurements were used to predict the ternary liquid-liquid equilibria (tie-line data) for the benzene-*n*-heptane-acetonitrile system. The parameters were corrected to 25°C, and liquid-phase activity coefficients were calculated with the help of Equation 10. The liquid-liquid phase boundary and tie-line data were established by searching for the compositions at which the activities of each component were uniform.

The prediction of the ternary solubility envelope at 25°C is shown in Figure 8 and is compared with the experimental data at the same temperature obtained by the authors. Except near the plait point where such predictions are susceptible to errors to a small change in activities, the agreement is fairly satisfactory (within 3 mol %). The available data of Hartwig et al. (*7*) also show fairly good agreement with the predicted values obtained

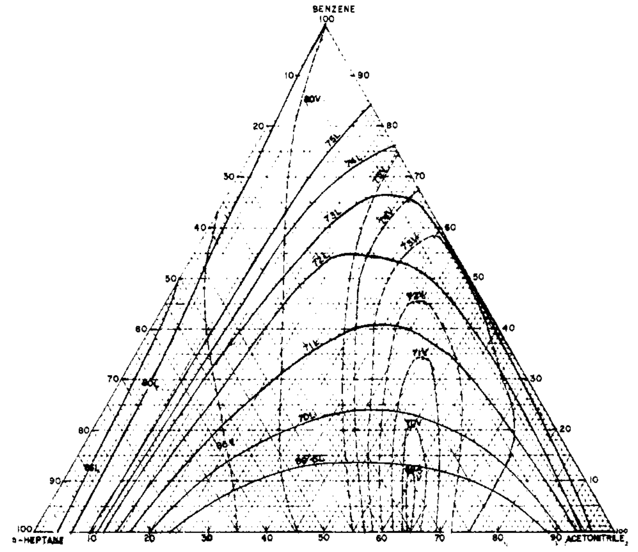

Figure 6. Liquid and vapor isotherms for ternary benzene-*n*-heptane-acetonitrile system at 760 mm Hg pressure

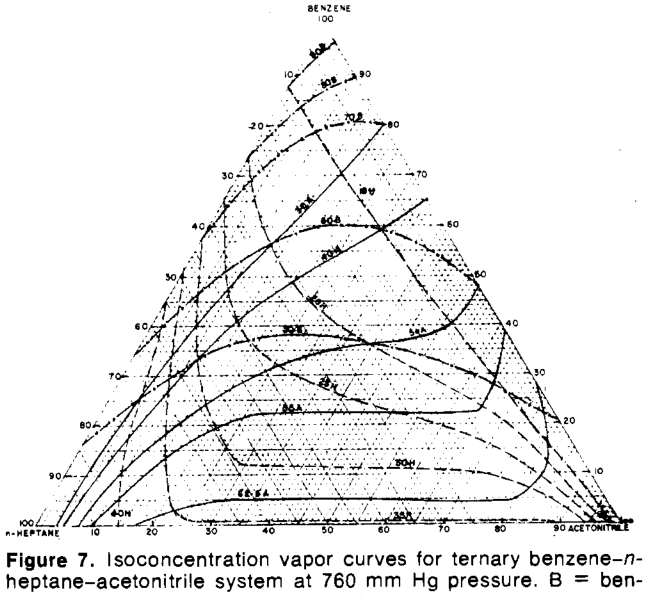

Figure 7. Isoconcentration vapor curves for ternary benzene-*n*-heptane-acetonitrile system at 760 mm Hg pressure. B = benzene, H = *n*-heptane, A = acetonitrile

above. The prediction of the ternary solubility envelope at 25°C for the present ternary system from binary NRTL parameters alone has, however, been somewhat superior to that obtained by Palmer et al. (13) for the same system at 45°C based on the parameters of the conformal solution equation.

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Table VI. Vapor-Liquid Equilibrium Data for Ternary Benzene(1)–*n*-Heptane(2)–Acetonitrile(3) System at 760 mm Hg Pressure

Liquid molar composition			Vapor molar composition			Activity coefficients			
x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3	Temp, °C
0.1	0.1	0.8	0.121	0.262	0.617	1.682	6.378	1.0901	70.2
0.1	0.2	0.7	0.100	0.300	0.600	1.419	3.747	1.239	69.5
0.1	0.3	0.6	0.089	0.307	0.604	1.272	2.559	1.458	69.5
0.1	0.4	0.5	0.083	0.308	0.609	1.182	1.930	1.768	69.4
0.1	0.5	0.4	0.079	0.310	0.611	1.275	1.554	2.218	69.3
0.1	0.6	0.3	0.078	0.316	0.606	1.102	1.311	2.913	69.6
0.1	0.7	0.2	0.082	0.336	0.582	1.109	1.494	4.062	70.7
0.1	0.8	0.1	0.099	0.409	0.492	1.162	1.046	6.016	75.2
0.2	0.1	0.7	0.218	0.205	0.557	1.491	4.918	1.156	70.6
0.2	0.2	0.6	0.185	0.250	0.565	1.292	3.064	1.347	69.9
0.2	0.3	0.5	0.169	0.265	0.565	1.180	2.174	1.625	69.8
0.2	0.4	0.4	0.160	0.273	0.567	1.116	1.683	2.031	69.9
0.2	0.5	0.3	0.157	0.284	0.559	1.087	1.384	2.649	70.2
0.2	0.6	0.2	0.163	0.306	0.531	1.091	1.1911	3.646	71.3
0.2	0.7	0.1	0.195	0.369	0.436	1.136	1.069	5.306	75.4
0.3	0.1	0.6	0.298	0.164	0.538	1.341	3.883	1.248	70.9
0.3	0.2	0.5	0.264	0.211	0.525	1.191	2.546	1.493	70.4
0.3	0.3	0.4	0.243	0.232	0.525	1.110	1.870	1.855	70.4
0.3	0.4	0.3	0.237	0.249	0.514	1.073	1.485	2.402	70.7
0.3	0.5	0.2	0.246	0.272	0.482	1.071	1.248	3.268	71.8
0.3	0.6	0.1	0.287	0.328	0.385	1.108	1.099	4.688	75.6
0.4	0.1	0.5	0.367	0.144	0.489	1.224	3.131	1.374	71.2
0.4	0.2	0.4	0.332	0.182	0.486	1.114	2.149	1.693	70.9
0.4	0.3	0.3	0.319	0.209	0.472	1.062	1.630	2.174	71.2
0.4	0.4	0.2	0.327	0.236	0.437	1.051	1.328	2.926	72.3
0.4	0.5	0.1	0.375	0.285	0.340	1.080	1.143	4.144	75.6
0.5	0.1	0.4	0.434	0.112	0.454	1.135	2.575	1.547	71.7
0.5	0.2	0.3	0.406	0.161	0.433	1.060	1.842	1.966	71.8
0.5	0.3	0.2	0.409	0.196	0.395	1.036	1.440	2.619	72.8
0.5	0.4	0.1	0.459	0.241	0.300	1.054	1.204	3.665	75.7
0.6	0.1	0.3	0.504	0.096	0.400	1.071	2.157	1.782	72.5
0.6	0.2	0.2	0.495	1.473	0.358	1.027	1.602	2.346	73.2
0.6	0.3	0.1	0.540	0.194	0.266	1.041	1.290	3.244	75.8
0.7	0.1	0.2	0.589	0.086	0.325	1.028	1.838	2.105	73.7
0.7	0.2	0.1	0.622	0.143	0.255	1.014	1.414	2.875	75.8
0.8	0.1	0.1	0.710	0.081	0.209	1.006	1.592	2.553	76.0

Table VII. Calculated and Experimental VLE Data for Ternary Benzene(1)–*n*-Heptane(2)–Acetonitrile(3) System at 760 mm Hg

Liquid molar composition			Vapor molar composition														
			Calcd			Exptl						Activity coefficients			Temp, °C		G^E, J mol^{-1}
x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	Δy_1	Δy_2	Δy_3	γ_1	γ_2	γ_3	Calcd	Exptl	
0.907	0.053	0.040	0.859	0.046	0.095	0.859	0.046	0.095	0.000	0.000	0.000	1.001	1.562	2.741	78.3	78.4	45.0
0.881	0.051	0.068	0.809	0.044	0.147	0.807	0.044	0.149	−0.002	0.000	+0.002	1.003	1.629	2.576	77.2	77.3	64.1
0.783	0.100	0.117	0.685	0.081	0.234	0.686	0.082	0.232	+0.001	+0.001	−0.002	1.009	1.628	2.468	75.6	75.5	111.5
0.679	0.189	0.132	0.585	0.136	0.279	0.587	0.140	0.273	+0.002	+0.004	−0.006	1.015	1.487	2.651	74.8	74.6	118.9
0.654	0.259	0.087	0.595	0.175	0.230	0.589	0.177	0.234	−0.006	+0.002	+0.004	1.024	1.553	2.443	76.4	76.3	129.6
0.609	0.208	0.183	0.506	0.150	0.344	0.498	0.150	0.352	−0.008	0.000	+0.008	1.024	1.553	2.443	73.45	73.4	185.2
0.531	0.394	0.075	0.511	0.244	0.245	0.488	0.224	0.288	−0.023	−0.020	+0.043	1.057	1.182	3.861	77.0	76.4	136.5
0.508	0.319	0.173	0.423	0.202	0.375	0.410	0.196	0.394	−0.013	−0.006	+0.019	1.035	1.372	2.832	73.25	73.1	205.8
0.499	0.380	0.121	0.441	0.229	0.330	0.428	0.218	0.354	−0.013	−0.011	+0.024	1.047	1.244	3.403	74.7	74.4	181.8
0.478	0.363	0.158	0.405	0.220	0.375	0.395	0.214	0.391	−0.010	−0.006	+0.016	1.042	1.244	3.403	73.5	73.3	201.8
0.475	0.359	0.166	0.398	0.219	0.383	0.388	0.211	0.401	−0.010	−0.008	+0.018	1.042	1.321	3.002	73.3	73.2	207.4
0.447	0.303	0.250	0.358	0.203	0.439	0.339	0.208	0.453	−0.019	+0.005	+0.014	1.047	1.525	2.384	71.8	71.7	249.2

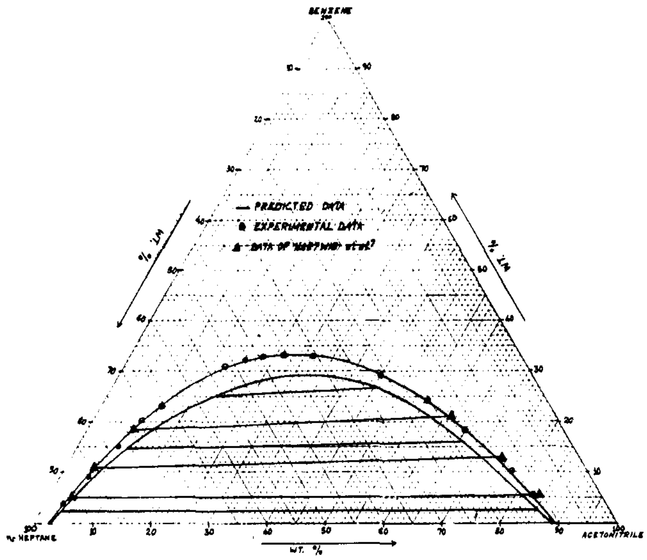

Figure 8. Prediction of liquid-liquid equilibria at 25°C for ternary system benzene(1)-*n*-heptane(2)-acetonitrile(3)

Nomenclature

B_{ij} = second virial coefficient, $cm^3 \ mol^{-1}$
B_{ij} = second virial cross coefficient
C_1, C_2, D_1, D_2 = NRTL parameters as defined in Equation 8
f_i^L = liquid-phase fugacity of component i at system temperature and pressure
f_i^{0L} = reference (or standard state) fugacity of pure liquid i at temperature T adjusted to zero pressure
G^E = excess Gibbs free energy, $J \ mol^{-1}$
G_{ij} = parameter of NRTL equation
P = total pressure of the system, mm Hg
P_i^s = saturation vapor pressure of pure liquid i at equilibrium temperature T
R = gas constant, $J \ K^{-1} \ mol^{-1}$
T = equilibrium temperature, degrees Kelvin
x = liquid-phase mole fraction
y = vapor-phase mole fraction
v = molar volume of vapor mixture, ml/mol
v_i^L = liquid molar volume of pure component i at temperature T, ml/mol
Z = compressibility factor

Greek Letters

α_{ij} = "nonrandomness" parameter of NRTL equation
γ_i = liquid-phase activity coefficient of component i at temperature T adjusted to zero pressure
ϕ_i = vapor-phase fugacity coefficient of component i in the mixture
ϕ_i^s = fugacity coefficient of pure saturated vapor at temperature T and pressure P_i^s
τ_{ij} = parameter of NRTL equation

Subscripts

1 = benzene
2 = *n*-heptane
3 = acetonitrile
i, j, k, l, r = running variables

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