Vapor–Liquid Equilibria for the System Benzene–Thiophene–Methanol

Jaime O. Triday* and Patricio Rodriguez

Departamento de Procesos Químicos, Universidad Têcnica Federico Santa Maria, Valparaíso 110-V, Chile

Isothermal vapor pressure data over the whole range of composition were obtained for the system benzene–thiophene–methanol. Data were taken at temperatures of 35, 40, and 45 °C by using a static equilibrium cell. The systems benzene–methanol and thiophene–methanol are highly nonideal, while the system benzene–thiophene shows a very small deviation from ideality. The models suggested by Wilson and by Renon and Prausnitz (NRTL) and the modified equation of Abrams and Prausnitz (UNIQUAC) were used in the reduction of data. Physical parameters of these equations obtained from the binary data were used to predict the ternary system. The Wilson equation gives the best fit for the binary as well as the ternary data. Also, this equation gives the best prediction for the ternary system.

Introduction

Vapor–liquid phase equilibria measurements continue to be of major importance in thermodynamics, not only for their direct use in process design but also for their importance in the testing and extension of fluid mixture theories.

The models suggested by Wilson (*1*) and by Renon and Prausnitz (NRTL) (*2*) and the modified equation of Abrams and Prausnitz (UNIQUAC) (*3*, 4) can be easily extended to multicomponent mixtures without any additional assumptions beyond those for binary mixtures.

The aim of this work was to test the extension of these well-known models for the ternary system benzene–thiophene–methanol at 35, 40, and 45 °C. Also, isothermic data for this ternary system were not found in the literature (*5*).

The binary systems benzene–methanol and thiophene–methanol have been already measured by using the same experimental method at the same temperatures (*6*, *7*).

Experimental Section

***Chemicals*.** Benzene was Merck analytical-grade reagent used without further purification. The certified minimum purity of this chemical was 99.7%. Thiophene and methanol were also Merck reagents and were redistilled in a high-efficiency packed column. Physical properties of the chemicals are shown in Tables I and II along with literature values.

***Vapor Pressure Measurements*.** The vapor pressures of the systems were measured at constant temperature as a function of composition by using a static equilibrium cell. The apparatus, which is described in detail by Vera (*8*), is shown schematically in Figure 1. Briefly the major items were a large-diameter mercury manometer, measuring the difference in pressure between the reference high vacuum and measuring manifold systems, and a thermostatic bath containing the vapor pressure cell assembly. The latter consisted of a mercury null manometer connected to the static cell. Stirring of the contents of the cell was achieved with a small PTFE-coated magnet activated by a magnetic stirrer motor sited under the bath. The mercury levels were read by using an Eberbach cathetometer.

Table I. Physical Properties of the Pure Compounds at 20 °C

	density, g cm^{-3}		refractive index	
	obsd	lit.	obsd	lit.
benzene	0.8790	0.87901^a	1.5011	1.50108^a
thiophene	1.0581	1.05887^a	1.5290	1.5287^a
methanol	0.7911	0.79131^a	1.3290	1.32840^a

^{a} Reference *12*.

Table II. Vapor Pressures of the Pure Compounds

	P, mmHg					
	35 °C		40 °C		45 °C	
	obsd	lit.	obsd	lit.	obsd	lit.
benzene	148.0	148.30^a	182.3	182.77^a	223.2	223.50^a
thiophene	126.5	125.50^a	156.4	155.46^a	192.3	191.04^a
methanol	209.5	209.59^a	265.5	265.76^a	333.5	334.17^a

^{a} Reference *13*.

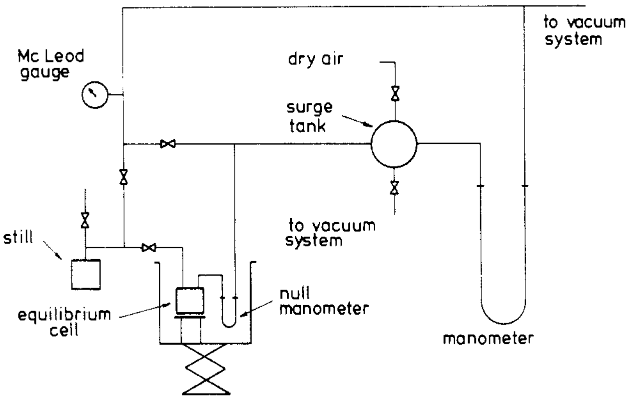

Figure 1. Schematic view of the apparatus.

The ternary mixtures were sealed in a separate still for degassing. The air was removed by freezing the mixture with liquid nitrogen and opening the still to the vacuum system. Afterward, the mixture was melted under vigorous agitation by the magnetic stirrer. Degassing was considered complete when the vacuum gage located in the vacuum line did not detect any air at the time of opening the still with the frozen mixture. The mixture was transferred to the equilibrium cell by distilling from the still and condensing in the cell with liquid nitrogen. The cell was then gradually warmed and thermostated at the desired temperature. The small null manometer was balanced by bleeding dry air into its reference side through a needle valve. The mixture in the cell was under continuous agitation to assure uniform temperature and composition. After the vapor pressure measuring at three different temperatures, the sample was completely transferred from the equilibrium cell to the still previously evacuated and cooled with liquid nitrogen.

Ternary mixture compositions were determined by mixing

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* Address correspondence to this author at the Department of Chemical Engineering, University of California, Davis, CA 95616.

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Table III. Isothermal Vapor-Liquid Equilibrium Data for the Benzene (1)-Thiophene (2)-Methanol (3) System

				P, mmHg		
	x_1	x_2	x_3	35 °C	40 °C	45 °C
1	0.516	0.484	0.000	139.0	172.9	210.2
2	0.468	0.439	0.094	249.9	309.2	375.4
3	0.411	0.385	0.204	270.4	337.1	411.3
4	0.338	0.317	0.344	279.0	346.8	428.5
5	0.212	0.199	0.589	284.0	352.7	436.9
6	0.140	0.132	0.728	280.4	351.1	433.3
7	0.088	0.082	0.830	268.5	337.7	418.4
8	0.043	0.041	0.916	250.0	313.8	390.5
9	0.000	0.000	1.000	209.5	265.5	333.5
10	0.464	0.000	0.536	291.8	364.5	448.1
11	0.429	0.074	0.497	289.8	362.0	446.7
12	0.385	0.170	0.445	284.3	355.0	438.6
13	0.302	0.348	0.350	275.9	343.6	426.3
14	0.200	0.568	0.232	270.4	337.6	417.3
15	0.136	0.707	0.157	255.5	316.7	388.4
16	0.058	0.874	0.068	227.0	278.3	337.5
17	0.000	1.000	0.000	126.5	156.4	192.3
18	0.000	0.504	0.496	266.5	335.8	415.0
19	0.149	0.429	0.422	271.9	340.1	422.3
20	0.319	0.344	0.338	275.4	345.1	425.8
21	0.512	0.246	0.242	275.4	344.6	425.3
22	0.730	0.136	0.134	269.9	334.1	410.3
23	0.862	0.070	0.069	254.0	309.8	375.5
24	1.000	0.000	0.000	148.0	182.3	223.2

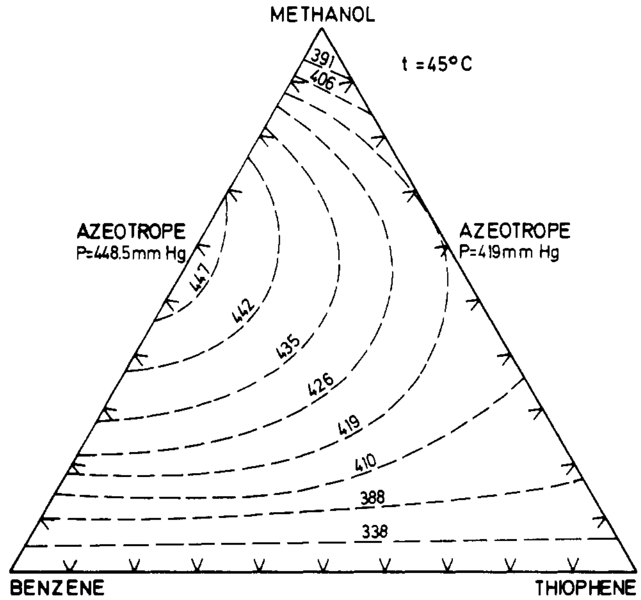

Figure 2. Vapor-Liquid equilibrium data for the system benzene (1)-thiophene (2)-methanol (3) at 45 °C.

known amount of pure compounds. The refractive indexes of the mixtures were measured before and after the vapor pressure measurement by using a Bausch and Lomb Abbe-3L refractometer at 20 °C. Refractive index measurements were taken in order to detect any change in composition during the vapor pressure measurements. When a change in the refractive index was detected, the experimental point was disregarded.

For the binary system benzene-thiophene the compositions were determined from a calibration plot of index of refraction vs. composition at 20 °C.

Considering the accuracy in the index of refraction measurement of ±0.0004, sample compositions were estimated to be accurate within ±0.001 mole fraction.

In addition, the effect of the accuracy in temperature of ±0.10 °C and a maximum error of 0.5 mmHg in measuring the pressure give experimental vapor pressures better than ±1.0 mmHg at each temperature.

Table IV. Isothermal Vapor-Liquid Equilibrium Data for the Benzene (1)-Thiophene (2) System

		P, mmHg		
	x_1	35 °C	40 °C	45 °C
1	0.000	126.5	156.4	192.3
2	0.064	128.5	158.4	195.3
3	0.134	131.5	161.9	197.8
4	0.266	134.5	166.4	203.3
5	0.330	135.5	168.3	205.3
6	0.392	136.5	169.4	207.2
7	0.455	137.5	171.4	209.2
8	0.519	139.0	172.5	210.7
9	0.595	140.5	174.5	212.7
10	0.651	142.0	175.5	214.2
11	0.728	143.5	177.4	216.3
12	0.795	145.0	178.4	218.4
13	0.860	146.5	179.3	219.7
14	0.921	147.5	180.8	221.2
15	1.000	148.0	182.3	223.2

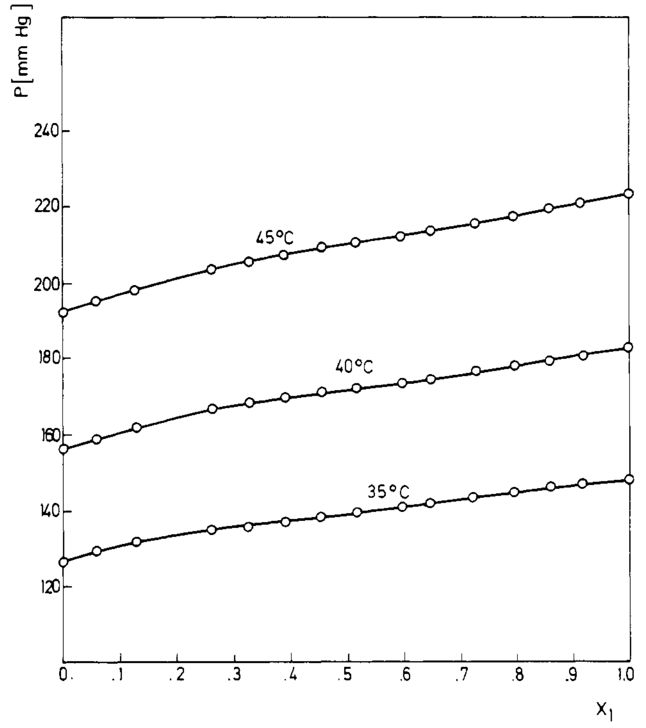

Figure 3. Vapor-liquid equilibrium data for the system benzene (1)-thiophene (2).

Results and Discussion

The vapor-liquid equilibrium data for the ternary system benzene-thiophene-methanol at 35, 40, and 45 °C are reported in Table III.

Figure 2 shows the data for the ternary system at 45 °C. The system does not exhibit a ternary azeotrope, having a maximum pressure at the binary azeotrope for the benzene-methanol system.

The vapor-liquid equilibrium data for the binary system benzene-thiophene are reported in Table IV and are shown in Figure 3. This system shows a very small deviation form ideality.

The experimental data were correlated by the Wilson (*1*), NRTL (*2*), and modified UNIQUAC (*3*, *4*) equations.

For multicomponent systems these models give the following equations for the molar excess Gibbs energy, g^E:

Wilson

$$g^E/RT = -\sum_i^N x_i \ln \left(\sum_j^N x_j \Lambda_{ij}\right) \tag{1}$$

where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{2}$$

λ_{ij} is the binary energy interaction parameter for the i–j pair; V_i is the liquid molar volume of the component i.

NRTL

$$\frac{g^E}{RT} = \sum_i^N x_i \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} \tag{3}$$

where

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \tag{4}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{5}$$

g_{ij} is the binary energy interaction parameter for the i–j pair; α_{ij} is the nonrandomness parameter for the mixture ij.

The α_{ij} parameters were fixed according with recommendations given by Renon (*2*).

UNIQUAC

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \tag{6}$$

$$\frac{g^E}{RT}(\text{combinatorial}) = \sum_i^N x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2}\sum_i^N q_i x_i \ln \frac{\theta_i}{\Phi_i} \tag{7}$$

$$\frac{g^E}{RT}(\text{residual}) = -\sum_i^N q'_i x_i \ln \left(\sum_j^N \theta'_j \tau_{ji}\right) \tag{8}$$

where the coordination number, z, is set equal to 10 and the segment fraction, Φ_i, and the area fractions θ_i and θ'_i are given by

$$\Phi_i = x_i r_i / \sum_j^N x_j r_j \tag{9}$$

$$\theta_i = x_i q_i / \sum_j^N x_j q_j \tag{10}$$

$$\theta'_i = x_i q'_i / \sum_j^N x_j q'_j \tag{11}$$

The parameters r, q, and q' are pure-component molecular structure constants depending on the molecular size and the external surface area.

$$\tau_{ij} = \exp[-(u_{ij} - u_{jj})/RT] \tag{12}$$

where u_{ij} is the binary energy parameter for the i–j pair; when $q_i = q'_i$, eq 6 reduces to the original UNIQUAC of Abrams and Prausnitz (*3*).

Table V. Critical Properties and Parameters Characterizing Vapor-Phase Nonideality

	P_c,[a] atm	T_c,[a] K	V_c,[a] cm^3 g-mol^{-1}	ω[a]	a_t[b]	b_t[b]
benzene	48.3	562.1	259	0.212	0.0000	0.0000
thiophene	56.2	579.4	219	0.200	0.0000	0.0000
methanol	79.9	512.6	118	0.559	0.0878	0.0560

[a] Reference *13*. [b] Reference *10*.

Table VI. Parameters for the System Benzene (1)–Thiophene (2)

	35 °C	40 °C	45 °C
	Wilson		
$\lambda_{12} - \lambda_{11}$[a]	249.8	319.3	247.7
$\lambda_{12} - \lambda_{22}$[a]	−68.2	−82.4	−69.5
$\sigma_p(\%)$[b]	0.40	0.27	0.22
	NRTL (α_{12} = 0.30)		
$g_{12} - g_{22}$[a]	265.7	264.9	309.2
$g_{12} - g_{11}$[a]	−121.3	−75.7	−165.3
$\sigma_p(\%)$[b]	0.40	0.32	0.26
	UNIQUAC		
$u_{12} - u_{22}$[a]	489.6	502.1	514.7
$u_{21} - u_{11}$[a]	−384.1	−374.9	−407.1
$\sigma_p(\%)$[b]	0.45	0.35	0.29

[a] Units: J/mol. [b] $\sigma_p(\%) = 100\{[\sum_k^{NEX}((p - p^*)/p)_k^2]/(NEX - NP)\}^{1/2}$.

Table VII. Parameters for the System Benzene (1)–Methanol (3)

	35 °C	40 °C	45 °C
	Wilson		
$\lambda_{13} - \lambda_{11}$[a]	753.2	870.3	845.2
$\lambda_{13} - \lambda_{33}$[a]	7418.6	7167.2	6857.9
$\sigma_p(\%)$[b]	0.26	0.33	0.33
	NRTL (α_{13} = 0.47)		
$g_{13} - g_{33}$[a]	5033.6	4820.2	4531.5
$g_{13} - g_{11}$[a]	2970.8	3079.6	3046.1
$\sigma_p(\%)$[b]	0.38	0.41	0.43
	UNIQUAC		
$u_{13} - u_{33}$[a]	7866.3	7585.9	7268.0
$u_{31} - u_{11}$[a]	−472.8	−443.5	−464.4
$\sigma_p(\%)$[b]	0.33	0.39	0.40

[a] Units: J/mol. [b] $\sigma_p(\%) = 100\{[\sum_k^{NEX}((p - p^*)/p)_k^2]/(NEX - NP)\}^{1/2}$.

The technique used for data fitting was basically that described by Prausnitz (*9*). Vapor-phase nonidealities were determined from the virial equation truncated after the second term. The second virial coefficients were calculated from the generalized correlations presented by Tsonopoulous (*10*). The critical properties and other parameters required for estimating the second virial coefficients by the correlation of Tsonopoulous are listed in Table V.

The physical parameters were obtained by minimizing the objective function

$$S^2 = 100 \sum_i^{NEX} \left(\frac{P - P^*}{P}\right)^2 = \text{minimum} \tag{13}$$

where P and P^* are respectively the experimental and calculated values of the total vapor pressure and NEX is the total number of experimental points.

The secant method for simultaneous nonlinear equations was used for solving the objective function (*11*).

All the regression analyses were carried out by using double precision arithmetic upon a DEC-2020 computer.

The resulting binary interaction parameters obtained from the binary data are listed in Tables VI–VIII together with the estimated variance of the fit, $\sigma_p(\%)$.

$$\sigma_p(\%) = 100\left\{\left[\sum_i^{NEX}\left(\frac{P - P^*}{P}\right)^2\right]/(\text{NEX} - \text{NP})\right\}^{1/2} \tag{14}$$

where NP is the number of parameters to be fitted.

Table VIII. Parameters for the System Thiophene (2)-Methanol (3)

	35 °C	40 °C	45 °C
	Wilson		
$\lambda_{23} - \lambda_{22}$[a]	631.8	631.8	652.7
$\lambda_{23} - \lambda_{33}$[a]	7912.3	7661.3	7422.8
$\sigma_p(\%)$[b]	0.76	0.69	0.41
	NRTL ($\alpha_{23} = 0.47$)		
$g_{23} - g_{33}$[a]	5481.3	5318.1	5154.9
$g_{23} - g_{22}$[a]	2627.7	2615.1	2627.1
$\sigma_p(\%)$[b]	0.82	0.86	0.51
	UNIQUAC		
$u_{23} - u_{33}$	8456.3	8180.1	7908.1
$u_{32} - u_{22}$	−493.7	−510.5	−510.5
$\sigma_p(\%)$	0.77	0.70	0.43

[a] Units: J/mol. [b] $\sigma_p(\%) = 100\{[\sum_k^{\mathrm{NEX}}((p - p^*)/p)_k^2]/(\mathrm{NEX} - \mathrm{NP})\}^{1/2}$.

Table IX. Prediction of the VLE for the System Benzene (1)-Thiophene (2)-Methanol (3)

	$\sigma_p(\%)$[a]		
	Wilson	NRTL[b]	UNIQUAC
35 °C	1.21	1.49	1.44
40 °C	1.07	1.26	1.31
45 °C	1.32	1.34	1.64

[a] $\sigma_p(\%) = 100\{[\sum_i^{\mathrm{NEX}}((p - p^*)/p)_i^2]/(\mathrm{NEX} - \mathrm{NP})\}^{1/2}$. [b] $\alpha_{12} = 0.30$; $\alpha_{13} = \alpha_{23} = 0.47$.

Table X. Fit of the VLE Data for the System Benzene (1)-Thiophene (2)-Methanol (3)

	$\sigma_p(\%)$[a]		
	Wilson	NRTL[b]	UNIQUAC
35 °C	0.58	0.79	0.65
40 °C	0.50	0.66	0.58
45 °C	0.56	0.66	0.64

[a] $\sigma_p(\%) = 100\{[\sum_i^{\mathrm{NEX}}((p - p^*)/p)_i^2]/(\mathrm{NEX} - \mathrm{NP})\}^{1/2}$. [b] $\alpha_{12} = 0.30$; $\alpha_{13} = \alpha_{23} = 0.47$.

The Wilson equation gives the best fit for the binary systems at each temperature. With these parameters, the ternary system was predicted and compared to the experimental data. Table IX shows the estimated variance for the predictions by Wilson, NRTL, and UNIQUAC models. These variances are larger than those obtained when binary data were fitted. This lack of fit indicates that predictions obtained by the Wilson, NRTL, and UNIQUAC equations do not represent the ternary system as well as the binaries. Even though, the predictions still represent a good agreement with the experimental data. Again, the Wilson equation gives the best prediction for the ternary system.

Furthermore, binary parameters were also obtained from the ternary data by using the same procedure already described. The obtained variances of the fit are shown in Table X and the resulting parameters are reported in Table XI. These variances compared well with those obtained when binary data are fitted. And once again, the Wilson equation gives the best fit for the ternary data.

Table XI. Parameters[a] for the System Benzene (1)-Thiophene (2)-Methanol (3)

	35 °C	40 °C	45 °C
	Wilson		
$\lambda_{12} - \lambda_{11}$	251.3	314.0	245.6
$\lambda_{12} - \lambda_{22}$	−61.8	−81.9	−66.7
$\lambda_{13} - \lambda_{11}$	610.9	627.6	573.2
$\lambda_{13} - \lambda_{33}$	7941.6	7732.4	7611.1
$\lambda_{23} - \lambda_{22}$	732.2	811.7	861.9
$\lambda_{23} - \lambda_{33}$	7238.7	7037.8	6816.1
	NRTL[b]		
$g_{12} - g_{22}$	257.9	259.6	310.6
$g_{12} - g_{11}$	−120.4	−79.8	−171.6
$g_{13} - g_{33}$	5167.5	5046.1	4970.8
$g_{13} - g_{11}$	2941.5	2941.5	2874.5
$g_{23} - g_{33}$	4975.0	4841.1	4665.4
$g_{23} - g_{22}$	2610.9	2682.1	2732.3
	UNIQUAC		
$u_{12} - u_{22}$	493.4	520.1	509.7
$u_{12} - u_{11}$	−381.6	−381.4	−409.8
$u_{13} - u_{33}$	8644.6	8330.7	8201.0
$u_{13} - u_{11}$	−522.3	−543.9	−577.4
$u_{23} - u_{33}$	7640.3	7506.4	7217.7
$u_{23} - u_{22}$	−431.0	−443.5	−426.8

[a] All values in J/mol. [b] $\alpha_{12} = 0.3$; $\alpha_{13} = \alpha_{23} = 0.47$.

Glossary

g^E	excess Gibbs energy, J/mol
g_{ij}	NRTL binary parameter for the i-j pair interaction, J/mol
G_{ij}	defined by eq 5
N	number of components
NEX	total experimental points
NP	number of parameters
P	pressure, mmHg
q_i	molecular-geometric area parameter for the pure component i
q'_i	molecular-interaction area parameter for the pure component i
r_i	molecular volume parameter for the pure component i
R	gas constant, J mol^{-1} K^{-1}
S^2	objective function defined by eq 13
T	absolute temperature, K
u_{ij}	UNIQUAC binary parameter for the i-j pair interaction, J/mol
v_i	liquid molar volume for the component i, cm^3 mol^{-1}
x_i	liquid mole fraction for the component i
y_i	vapor mole fraction for the component i
z	coordination number

Greek Letters

α_{ij}	NRTL nonrandomness parameter
λ_{ij}	Wilson binary parameter for the i-j pair interaction, J/mol
Λ_{ij}	defined by eq 2
τ_{ij}	defined by eq 4 and 12
Φ_i	volume fraction defined by eq 9
θ_i	area fraction defined by eq 10
θ'_i	area fraction defined by eq 11
$\sigma_p(\%)$	estimated variance of the fit defined by eq 14

Registry No. Benzene, 71-43-2; thiophene, 110-02-1; methanol, 67-56-1.

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Vapor-Liquid Equilibria in Toluene + *m*-Xylene, Toluene + *n*-Decane, and *n*-Decane + *m*-Xylene Mixtures

Bert Willman and Amyn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Isothermal vapor-liquid equilibria at three temperatures between 373.5 and 394.3 K were measured for the binary systems toluene + *m*-xylene, toluene + *n*-decane, and *n*-decane + *m*-xylene by using a recirculating still. The data reported were found to be thermodynamically consistent and were correlated with four well-known activity coefficient models. The maximum likelihood method was used to estimate the parameters of the models.

Introduction

As part of a continuing study of phase equilibria involving coal chemicals, isothermal vapor-liquid equilibria (VLE) were measured for the binary systems toluene + *m*-xylene, toluene + *n*-decane, and *n*-decane + *m*-xylene at three temperatures between 373.5 and 394.3 K.

Experimental Section

The VLE still that was used in this work was an all-glass Stage-Muller recirculating still described recently by Gutsche and Knapp (*1*). The prominent features of the still are shown in Figure 1 and a schematic of the whole apparatus is given in Figure 2. The important features of the still are the magnetic sampling valves, the Cottrell pump, and the silver-plated vacuum jacket. The valves allow sampling of the equilibrium phases without disrupting the operation of the still. The vacuum jacket surrounds the equilibrium chamber and prevents partial condensation of the vapor separating from the liquid at the exit from the Cottrell pump. Heating of the fluid mixture was achieved with a heating mantle while a magnetic stirrer was used to mix the contents of the boiling flask. The temperature outside the equilibrium chamber was maintained approximately 1 K lower than the equilibrium temperature by means of a thermostated heating jacket.

The temperature was measured by a thermometer calibrated by the National Bureau of Standards and graduated in increments of 0.2 K. Pressure was measured by a mercury manometer graduated in 0.13 kPa increments. An electronic pressure regulator (constructed by Fischer of West Germany) positioned between the still and a vacuum pump maintained the pressure constant to 0.068 kPa. All experiments were carried out under an inert atmosphere of nitrogen (Matheson Co., purity > 99.99%) to minimize contact with moisture and to accurately control the pressure.

Table I. Physical Properties of Pure Compounds

property	this work	lit.[a]	Δ,[c] %
	m-Xylene		
n_d(293 K)	1.4930	1.4972	0.28
nbp,[d] K	412.1[b]	412.3	0.07
	n-Decane		
n_d(293 K)	1.4080	1.4102	0.16
nbp, K	447.0[b]	447.3	0.06
	Toluene		
n_d(293 K)	1.4904	1.4961	0.38
nbp, K	383.9	383.9	0.01
	Benzene		
n_d(293 K)	1.4960	1.5011	0.34
nbp, K	353.4	353.3	0.01

[a] Literature values taken from ref *12*. [b] Extrapolated from data in 373-393 K range. [c] Δ = 100(measured property - literature property)/(literature property). [d] nbp is the normal boiling point.

Table II. Constants of Eq 1 for Pure Compounds

compd	*A*	*B*	*C*
m-xylene	15.4744	4305.195	-15.437
n-decane	14.8129	3864.601	-65.932
toluene	15.175	3946.675	-9.824

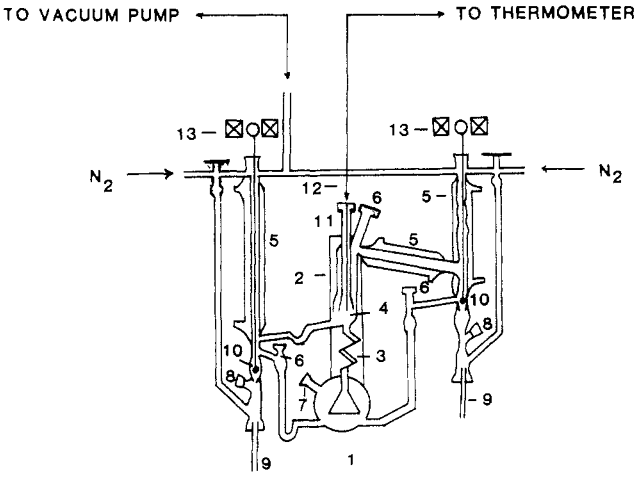

Figure 1. Sketch of Stage-Muller still used in this work: (1) boiling flask, (2) vacuum jacket, (3) Cottrell pump, (4) equilibrium chamber, (5) condensers, (6) injection ports, (7) filling spout and thermometer well, (8) Teflon valves, (9) sample tubes, (10) glass ball valves, (11) equilibrium thermometer well, (12) equilibrium thermometer, (13) solenoid devices (actuates 10).

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