

# Vapor-Liquid Equilibria for the Methanol-Benzene and Methanol-Thiophene Systems

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The equilibrium still of Rogalski and Malanowski was modified to collect data for the methanol-benzene and methanol-thiophene systems. Two isothermal sets (318.15 and 323.15 K) and one isobaric set (60.03 kPa) of data are presented for the system containing thiophene. For this system, data have not been reported in the literature for the 323.15 K isotherm nor for any isobar. In addition, isothermal data at 318.15 K and isobaric data at 69.52 kPa are presented for the methanol-benzene system. The data presented for methanol-benzene agree with available literature data. However, data for approximately twice as many compositions in the dilute composition region as are available in the literature have been measured in this work. Data in this region are useful for extracting infinite dilution values for the activity coefficients.

## Introduction

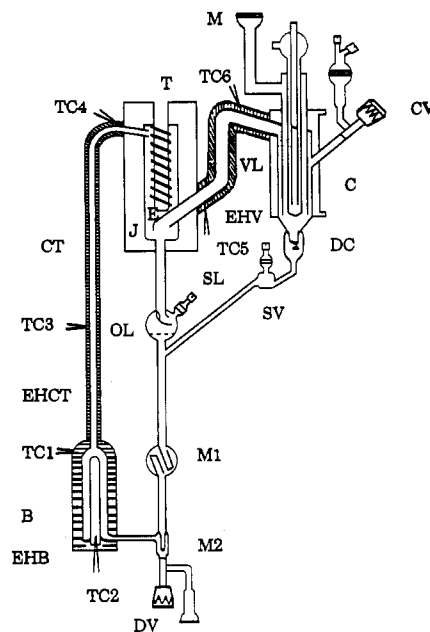
The availability of accurate vapor-liquid equilibrium data is of utmost importance in the design of separation processes. As new and improved reaction schemes lead to the production of new chemicals and new mixtures of known chemicals, there will be a continuing need for new phase equilibrium data. These data must be obtained either experimentally or by using existing predictive methods.

In this work, the equilibrium still design of Rogalski and Malanowski (1) was adapted with minor modifications. Both isothermal and isobaric data sets can be measured in this device. This apparatus can also be used to measure the vapor pressure for pure components. Two binary systems were studied. VLE data were taken for the methanol-benzene system for the 318.15 K isotherm and the 69.52-kPa isobar. For the methanol-thiophene system, the 318.15 and 323.15 K isotherms were studied as was the 60.03-kPa isobar. For the methanol-thiophene system, no data were available in the literature for the 323.15 K isotherm or for any isobar. Vapor pressure was also measured for all three pure components.

## Experimental Section

**Chemicals.** All chemicals used in this research were supplied by the Aldrich Chemical Co. and were used without further purification. Chemicals used were methanol with a stated purity of 99.9+%, HPLC grade, with the main impurity of less than 0.05% water, benzene with a stated purity of 99.9+%, HPLC grade, with less than 0.02% water, and thiophene with a stated purity of 99+%. The refractive index and normal boiling point of the pure components were measured to verify the stated purity of the chemicals.

**Apparatus.** The modified Malanowski still used in this work is shown schematically in Figure 1. The still, made primarily of Pyrex, was fabricated by the Glassblowing Section at the University of Missouri—Columbia. The fabrication techniques for construction of the activated boiler, B, the spiral thermometer well, T, and the drop counter, DC, are given by Swietoslawski (2) and Barr and Anhorn (3). In addition to the two mixing chambers in the original design of Malanowski, a third mixing device was used to ensure



**Figure 1.** Modified Malanowski still: B, boiler; CT, Cottrell tube; T, thermometer well; E, equilibrium chamber; J, vacuum jacket; C, double condenser; DC, drop counter; SL and SV, sampling ports; OL, liquid operating level; M1 and M2, mixers; CV, charging valve; DV, drain valve; EHB, IHB, EHCT, and EHV, electrical heaters; VL, vapor line; M, to vacuum or pressure system.

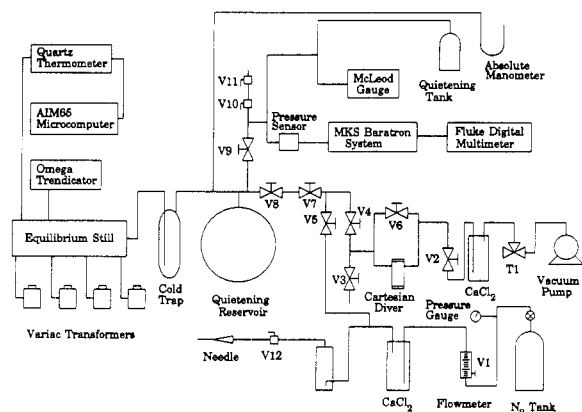
homogeneous composition of the condensed vapor in the condensate holdup volume, SV. A Teflon-coated micro stir bar (7 mm × 1.5 mm, available from Ace Glass, Inc.) placed in this vapor holdup volume was rotated by an external drive. The maximum volume of holdup in the vapor sampling port SV is 1.5 cm<sup>3</sup>.

The two sampling cells in the original design of Rogalski and Malanowski (1) were each fitted with a Viton O-ring seal and septum holder in place of the screw cap fitting. The liquid return line from the equilibrium chamber was extended into the bulb SL, and the tip of this extension was curved toward the sampling port. This extension was added in case thermal "bumping" occurred to prevent any contamination of the liquid sample by the vapor condensate.

A schematic diagram showing the complete experimental apparatus including all auxiliary equipment and connections

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**Figure 2.** Experimental apparatus including auxiliary equipment.

is shown in Figure 2. Every item downstream of the cold trap was used for control and measurement of pressure. A Cartesian Diver type absolute pressure control device (Cole Palmer type H) was located after the pressure manifold. This instrument controls pressure to  $\pm 0.013$  kPa.

The system pressure was measured directly using an MKS Baratron system consisting of a type 170M-6B range multiplier unit, interfaced to a type 170M-27B digital readout unit and a type 170M-36B selector. The pressure sensor, type 310-BHS1000, was capable of measuring absolute pressure in the range 0–133.32 kPa (0–1000 mmHg) and was interfaced to the range multiplier. The dc analog output of the range multiplier unit was monitored using a Fluke Model 8300A digital multimeter.

The MKS sensor was recalibrated by the manufacturer using an air dead weight gauge traceable to the National Bureau of Standards shortly before the experimental work began. A McLeod gauge was also inline to allow checking of the system zero. This gauge was manufactured by the Ace Glass Co. and has a range of 0–0.133 kPa (0–1 mmHg) and an accuracy of  $\pm 3\%$ . A Meriam absolute manometer was used to give a rough estimate of the system pressure. Temperature was measured with a Hewlett-Packard 2804 quartz thermometer coupled to an 1811A probe. The highest level of resolution for the quartz thermometer is 0.1 mK.

Compositions were determined by measurement of the refractive index. A Bausch and Lomb precision refractometer, model 33-45-03, series 945, was used for this determination, with the highest precision obtainable being  $\pm 0.00003$  refractive index unit. Gravimetrically prepared samples were used to provide calibration data. Traditionally, the refractive index is correlated as a function of liquid composition. An alternative is to correlate the composition dependence of the mixture refraction index using an  $n$ th-order polynomial expansion in liquid mole fraction. In this work, the experimental values of the mole fraction and refractive index of both binary systems were fitted using Legendre polynomials. A more detailed description of the experimental apparatus, auxiliary equipment, and calibration procedures is given by Toghiani (4).

## Results and Discussion

**Vapor Pressure Data.** Pure component vapor pressure data were measured in the present work. These data, measured in the modified Malanowski still, were correlated using Antoine's equation:

$$\log(P/\text{kPa}) = A - \frac{B}{(T/\text{K} + C)} \quad (1)$$

Data correlation was carried out using the Britt-Luecke generalized least-squares algorithm (5) which allows all

**Table 1.** Antoine Equation Constants

compound	A	B	C
methanol	7.210 86	1583.801	-33.3673
benzene	5.990 14	1187.685	-55.0713
thiophene	6.103 66	1259.054	-49.9150

**Table 2.** Vapor Liquid Equilibrium Data for Methanol (1)–Benzene (2)

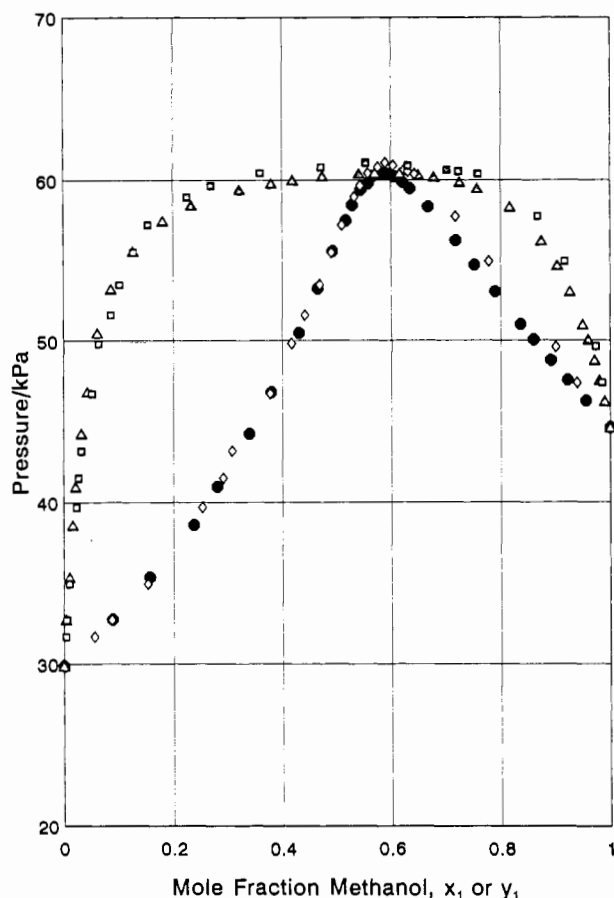
$T/\text{K} = 318.15$			$P/\text{kPa} = 69.52$		
$P/\text{kPa}$	$x_1$	$y_1$	$T/\text{K}$	$x_1$	$y_1$
29.894	0.0000	0.0000	341.39	0.0000	0.0000
32.744	0.0037	0.0882	340.72	0.0011	0.0274
35.358	0.0102	0.1567	339.75	0.0040	0.0576
38.587	0.0161	0.2364	336.89	0.0120	0.1504
40.962	0.0207	0.2794	334.34	0.0196	0.2236
44.231	0.0314	0.3391	332.89	0.0254	0.2698
46.832	0.0431	0.3794	330.84	0.0337	0.3257
50.488	0.0613	0.4306	329.23	0.0449	0.3650
53.224	0.0854	0.4642	328.07	0.0516	0.3951
55.571	0.1263	0.4921	327.04	0.0613	0.4201
57.454	0.1811	0.5171	325.94	0.0749	0.4463
58.427	0.2334	0.5288	324.92	0.0932	0.4694
59.402	0.3217	0.5450	324.01	0.1207	0.4950
59.802	0.3805	0.5538	323.02	0.1749	0.5177
60.015	0.4201	0.5590	322.38	0.2451	0.5363
60.242	0.4746	0.5673	321.92	0.3451	0.5540
60.416	0.5420	0.5783	321.65	0.4589	0.5692
60.443	0.5716	0.5821	321.54	0.5494	0.5839
60.416	0.6164	0.5908	321.53	0.5938	0.5923
60.350	0.6509	0.5990	321.54	0.6274	0.5993
60.215	0.6793	0.6067	321.58	0.6632	0.6087
59.868	0.7259	0.6216	321.65	0.7006	0.6198
59.482	0.7575	0.6346	321.84	0.7500	0.6382
58.321	0.8171	0.6681	322.20	0.8019	0.6651
56.213	0.8744	0.7181	322.82	0.8536	0.7046
54.692	0.9033	0.7525	323.67	0.8970	0.7532
53.037	0.9264	0.7896	324.23	0.9132	0.7825
51.009	0.9497	0.8368	325.12	0.9429	0.8296
50.048	0.9594	0.8599	325.83	0.9591	0.8669
48.767	0.9707	0.8916	326.53	0.9727	0.9035
47.540	0.9804	0.9222	327.20	0.9838	0.9385
46.232	0.9895	0.9558	327.55	0.9891	0.9568
44.608	1.0000	1.0000	328.37	1.0000	1.0000

measured variables, both dependent and independent, to possess error. Maximum likelihood estimates of the parameters  $A$ ,  $B$ , and  $C$  in the Antoine equation, determined using the Britt-Luecke regression technique, are given in Table 1. The standard deviations (the estimated error) for temperature and pressure were set at 0.02 K and 0.027 kPa in this regression.

**Vapor-Liquid Equilibrium Data.** Experimental data for the methanol–benzene and methanol–thiophene binary systems at 318.15 K are available in the literature. This isotherm was selected in the present work to provide a basis for comparison and a verification of the still operation.

Experimental data for the methanol–benzene system at 318.15 K obtained in the present work are given in Table 2. Data obtained by Strubl et al. (6) for the methanol (1)–benzene (2) system at 318.15 K are plotted in Figure 3 along with the experimental data measured in the present work. The data of Strubl and co-workers, published in the DECHEMA Data Series (7), were judged thermodynamically consistent, and this was verified in the present work.

From the dilute methanol region to the maximum azeotrope, the data obtained in the present work are in excellent agreement with those obtained by Strubl and co-workers. At higher concentrations of benzene, only a limited number of data points were reported in the literature. In the present work, approximately twice as many data points were obtained for this concentration range and are in good agreement with the literature data.



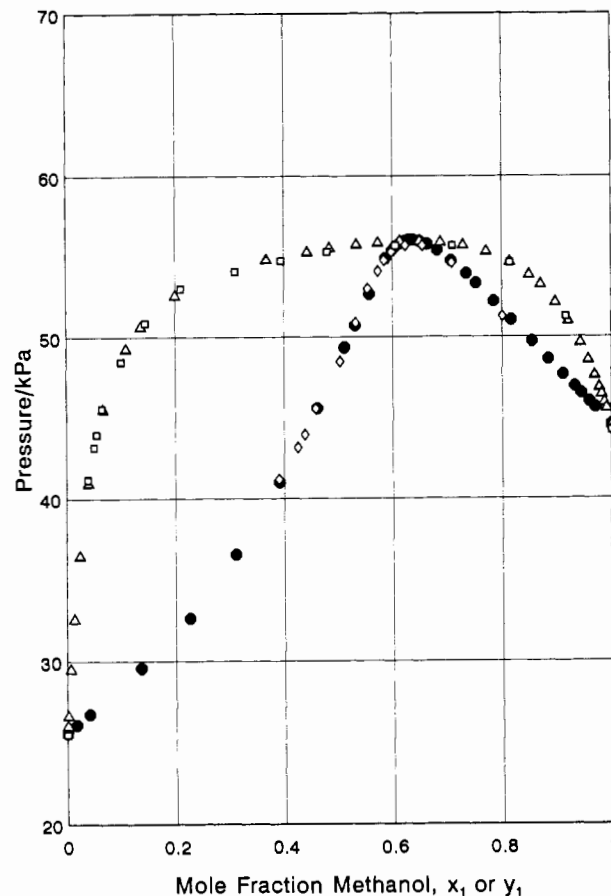
**Figure 3.** Vapor-liquid equilibrium data for methanol (1)-benzene (2) at 318.15 K:  $\square$ , Strubl et al.,  $P$ - $x_1$ ;  $\diamond$ , Strubl et al.,  $P$ - $y_1$ ;  $\Delta$ , present work,  $P$ - $x_1$ ;  $\bullet$ , present work,  $P$ - $y_1$ .

Experimental data for the methanol-thiophene system obtained in the present work are given in Table 3. For this system, the only data available in the literature at 318.15 K (8) are plotted in Figure 4 along with the experimental data obtained in this work. The literature data were taken using a static equilibrium cell, and vapor compositions were computed using the Wilson equation. The literature data set was also examined in the present work and was found to be thermodynamically consistent.

The data obtained in the present work show excellent agreement with the literature data for the entire composition range. For both ends of the concentration range, the literature data were lacking. A number of experimental points in both dilute ends of the curve were taken in the present work.

Experimental data for the methanol-benzene binary system were also taken for the 69.52-kPa isobar, and these are listed in Table 2 and plotted in Figure 5. For the methanol-thiophene binary system, a second isotherm (323.15 K) was studied as was an isobar (60.03 kPa). These data are also given in Table 3. Data for the 323.15 K isotherm are plotted in Figure 6 and for the 60.03-kPa isobar in Figure 7.

Thermodynamic consistency of the experimental data was examined using the method of Fredenslund et al. (9). The minimum value in the vapor composition deviation should be less than 0.01 as specified by Fredenslund and his co-workers for the data set to be judged thermodynamically consistent. In this work, the vapor composition deviation was less than 0.01 when a third-order expansion was used to represent the experimental data for all three isotherms and the two isobars studied. Thus, all five data sets were shown to be thermodynamically consistent. For the three isotherms, a fifth-order expansion was necessary to observe the minimum vapor composition deviation. The minimum vapor compo-



**Figure 4.** Vapor-liquid equilibrium data for methanol (1)-thiophene (2) at 318.15 K:  $\square$ , Triday,  $P$ - $x_1$ ;  $\diamond$ , Triday,  $P$ - $y_1$ ;  $\Delta$ , present work,  $P$ - $x_1$ ;  $\bullet$ , present work,  $P$ - $y_1$ .

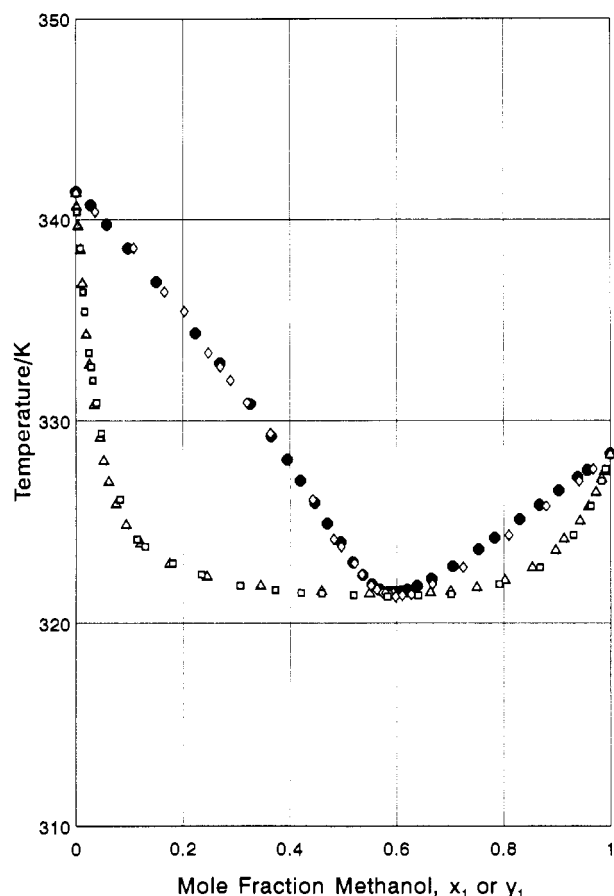
sition deviation was achieved for both isobars when a third-order expansion was used.

During the course of experimentation, some difficulty was encountered when the binary system methanol-thiophene was studied. Normal operation was observed from 0 mole fraction of thiophene up to the neighborhood of the azeotropic point. As the azeotrope was passed, bumping in the still was noted and foam formation in the liquid flowing from the equilibrium chamber was observed. Occasionally these problems could be alleviated by eliminating the temperature gradient along the Cottrell tube. This was achieved by adjusting the compensatory heat tape on the Cottrell tube and the heat tape on the outside of the boiler. The foaming action noted for the methanol-thiophene system was not observed for the methanol-benzene system.

#### Maximum Likelihood Analysis of Experimental Data.

The five sets of experimental data were subjected to maximum likelihood analysis following Prausnitz et al. (10). Regression on the entire data set,  $P$ - $T$ - $x$ - $y$ , was performed using three different liquid-phase activity models: the UNIQUAC (11, 12), Wilson (13), and NRTL (14) models. The parameter  $\alpha$  of the NRTL model was specified to be 0.47. For the UNIQUAC equation, the pure component parameters for methanol, benzene, and thiophene were available in the DECHEMA Chemical Data Series, edited by Gmehling and Onken (7). The  $(r_i, q_i)$  pairs were (1.43, 1.43), (3.19, 2.4), and (2.86, 2.14) for methanol, benzene, and thiophene, respectively.

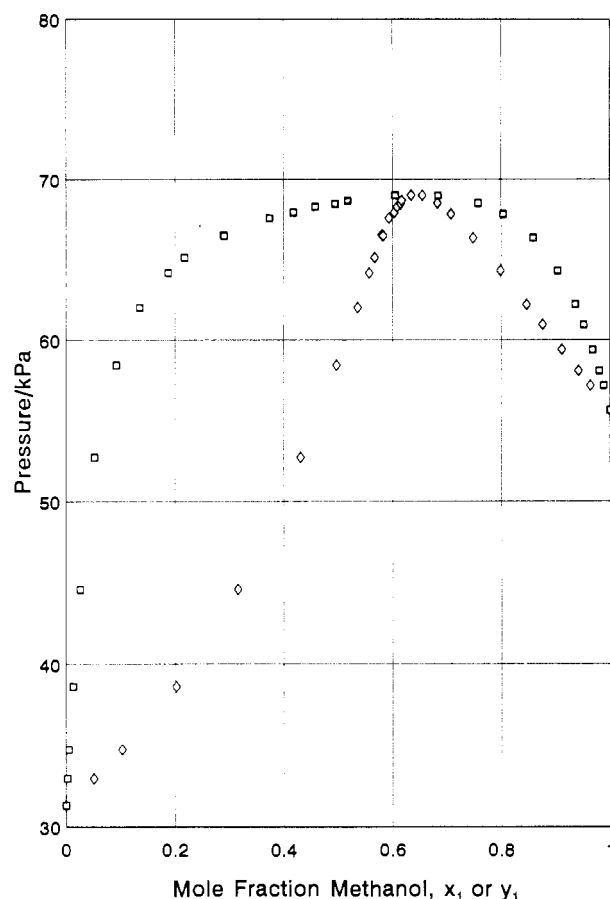
Parameters are given in Table 4 for the three activity coefficient models. The positive deviations are sufficiently large in these binary systems, and both binary systems exhibit minimum-boiling/maximum-pressure azeotropes. For isothermal data sets, analysis of the goodness of fit indicated



**Figure 5.** Vapor-liquid equilibrium data for methanol (1)-benzene (2) at 69.52 kPa:  $\square$ , Strubl et al.,  $P$ - $x_1$ ;  $\diamond$ , Strubl et al.,  $P$ - $y_1$ ;  $\triangle$ , present work,  $P$ - $x_1$ ;  $\bullet$ , present work,  $P$ - $x_1$ .

**Table 3.** Vapor-Liquid Equilibrium Data for Methanol (1)-Thiophene (2)

$T/K = 318.15$			$T/K = 323.15$			$P/\text{kPa} = 60.03$		
$P/\text{kPa}$	$x_1$	$y_1$	$P/\text{kPa}$	$x_1$	$y_1$	$T/K$	$x_1$	$y_1$
25.693	0.0000	0.0000	31.312	0.0000	0.0000	341.01	0.0000	0.0000
26.129	0.0008	0.0171	32.957	0.0022	0.0506	339.97	0.0034	0.0366
26.755	0.0018	0.0407	34.745	0.0050	0.1026	338.37	0.0067	0.0908
29.596	0.0067	0.1357	38.627	0.0129	0.2019	335.83	0.0139	0.1760
32.677	0.0137	0.2259	44.591	0.0261	0.3154	331.69	0.0279	0.3001
36.560	0.0238	0.3110	52.744	0.0526	0.4311	323.93	0.0901	0.4953
41.015	0.0393	0.3907	58.441	0.0919	0.4972	322.17	0.1448	0.5366
45.592	0.0668	0.4608	62.004	0.1357	0.5360	321.25	0.2089	0.5621
49.355	0.1089	0.5111	64.179	0.1879	0.5570	320.67	0.2856	0.5790
50.716	0.1362	0.5310	65.127	0.2179	0.5676	320.33	0.3609	0.5888
52.664	0.1998	0.5575	66.473	0.2901	0.5815	320.11	0.4289	0.5993
54.865	0.3682	0.5876	66.527	0.2895	0.5830	319.97	0.4924	0.6097
55.358	0.4434	0.5999	67.568	0.3743	0.5948	319.86	0.5610	0.6221
55.599	0.4841	0.6058	67.928	0.4185	0.6032	319.81	0.6153	0.6330
55.799	0.5344	0.6144	68.276	0.4583	0.6086	319.81	0.6531	0.6424
55.919	0.5739	0.6211	68.462	0.4948	0.6149	319.85	0.7002	0.6563
55.999	0.6144	0.6298	68.662	0.5183	0.6175	319.79	0.6310	0.6366
56.013	0.6503	0.6387	68.996	0.6050	0.6345	319.80	0.6667	0.6458
55.946	0.6885	0.6494	68.982	0.6843	0.6550	319.84	0.7046	0.6573
55.759	0.7293	0.6638	68.502	0.7578	0.6829	319.94	0.7462	0.6738
55.385	0.7718	0.6824	67.821	0.8038	0.7075	320.10	0.7826	0.6918
54.731	0.8146	0.7078	66.353	0.8587	0.7485	320.35	0.8186	0.7136
53.917	0.8498	0.7343	64.312	0.9042	0.7988	320.74	0.8564	0.7441
53.330	0.8698	0.7525	62.218	0.9362	0.8463	321.19	0.8867	0.7748
52.222	0.8977	0.7852	60.936	0.9518	0.8758	321.82	0.9174	0.8154
51.062	0.9213	0.8172	59.402	0.9681	0.9113	322.34	0.9377	0.8482
49.728	0.9428	0.8544	58.094	0.9803	0.9420	322.78	0.9519	0.8751
48.647	0.9578	0.8842	57.174	0.9880	0.9635	323.32	0.9667	0.9068
47.687	0.9695	0.9114	55.639	1.0000	1.0000	323.84	0.9787	0.9378
46.939	0.9776	0.9327				324.32	0.9893	0.9663
46.526	0.9820	0.9442				324.91	1.0000	1.0000
46.006	0.9870	0.9595						
45.646	0.9908	0.9706						
44.608	1.0000	1.0000						



**Figure 6.** Vapor-liquid equilibrium data for methanol (1)-thiophene (2) at 323.15 K:  $\square$ , present work,  $P$ - $x_1$ ;  $\diamond$ , present work,  $P$ - $y_1$ .

**Table 4.** Activity Model Parameters: Wilson, NRTL, and UNIQUAC Models<sup>a</sup>

data set				estimated variance of fit
Methanol (1)-Benzene (2)				
Wilson	318.15 K	$\Delta\lambda_{12} = 7886.17$	$\Delta\lambda_{21} = 644.36$	0.98
Wilson	69.52 kPa	$\Delta\lambda_{12} = 7567.74$	$\Delta\lambda_{21} = 700.26$	2.85
NRTL	318.15 K	$\Delta g_{12} = 3038.17$	$\Delta g_{21} = 5160.49$	5.63
NRTL	69.52 kPa	$\Delta g_{12} = 3061.56$	$\Delta g_{21} = 4952.86$	3.30
UNIQUAC	318.15 K	$\Delta u_{12} = -518.32$	$\Delta u_{21} = 8353.02$	0.75
UNIQUAC	69.52 kPa	$\Delta u_{12} = -506.81$	$\Delta u_{21} = 7963.12$	2.93
Methanol (1)-Thiophene (2)				
Wilson	318.15 K	$\Delta\lambda_{12} = 7299.60$	$\Delta\lambda_{21} = 754.87$	0.59
Wilson	323.15 K	$\Delta\lambda_{12} = 7173.23$	$\Delta\lambda_{21} = 786.71$	1.27
Wilson	60.03 kPa	$\Delta\lambda_{12} = 7113.14$	$\Delta\lambda_{21} = 797.21$	1.76
NRTL	318.15 K	$\Delta g_{12} = 2818.86$	$\Delta g_{21} = 4898.05$	3.17
NRTL	323.15 K	$\Delta g_{12} = 2819.49$	$\Delta g_{21} = 4822.73$	2.76
NRTL	60.03 kPa	$\Delta g_{12} = 2843.01$	$\Delta g_{21} = 4745.36$	1.39
UNIQUAC	318.15 K	$\Delta u_{12} = -463.17$	$\Delta u_{21} = 7688.71$	0.41
UNIQUAC	323.15 K	$\Delta u_{12} = -467.98$	$\Delta u_{21} = 7566.02$	1.07
UNIQUAC	60.03 kPa	$\Delta u_{12} = -449.66$	$\Delta u_{21} = 7437.06$	1.48

<sup>a</sup> All energy parameters in units of J/mol.

that all three activity coefficient models performed at approximately the same level, with the UNIQUAC providing a marginally better fit than the Wilson, which was slightly better than the NRTL in representing liquid phase behavior.

## Conclusions

Vapor pressure data for the pure components methanol, benzene, and thiophene were measured for pressures up to atmospheric. Experimental results agreed well with available data in the literature. The Antoine equation accurately

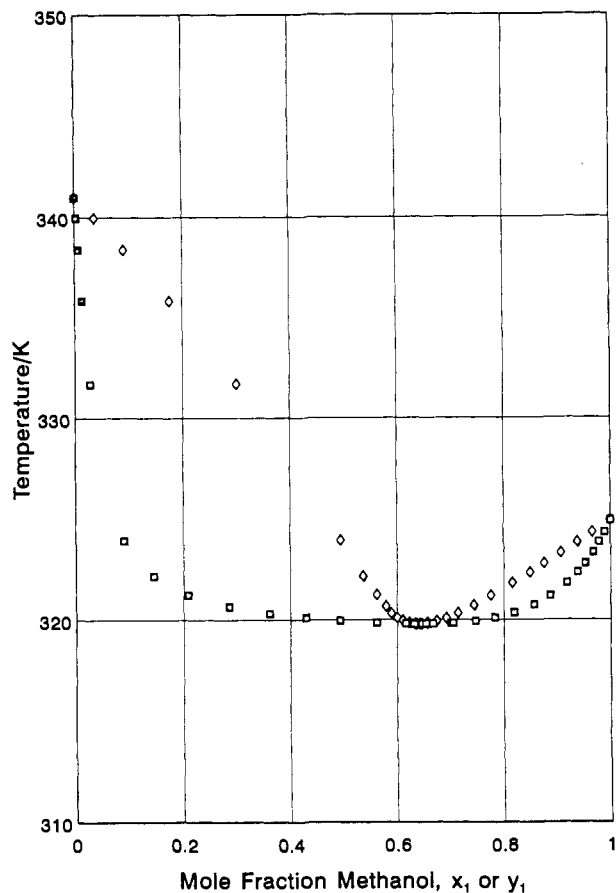


Figure 7. Vapor-liquid equilibrium data for methanol (1)-thiophene (2) at 60.03 kPa:  $\square$ , present work,  $P-x_1$ ;  $\diamond$ , present work,  $P-y_1$ .

represented the experimental data, and parameters were determined.

Vapor-liquid equilibrium data were obtained for two binary systems. Comparison with available literature data for both

systems verified that the equilibrium still was functioning properly. For the system methanol-benzene, the 318.15 K isotherm and the 69.52-kPa isobar were studied, and for the system methanol-thiophene, the 318.15 and 323.15 K isotherms and the 60.03-kPa isobar were studied.

Obtained VLE data were subjected to thermodynamic consistency tests, and all five data sets were found to be thermodynamically consistent using the technique of Fredenslund et al. (9). Maximum likelihood analysis of the obtained VLE data using the UNIQUAC, Wilson, and NRTL activity models for the liquid phase yielded expected results.

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