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Vapor–Liquid Equilibria of Hydrocarbons and Fuel Oxygenates. 2

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Vapor–liquid equilibrium data for methyl *tert*-butyl ether (MTBE) + 1-heptene, MTBE + four-component gasoline prototype, ethanol + four-component gasoline prototype, and separately MTBE and ethanol with the Auto/Oil Air Quality Improvement Research Gasoline Blend A are reported. Small additions of MTBE have a very small effect on the total equilibrium pressure of this gasoline blend, and at most temperatures will decrease this pressure. In contrast, small additions of ethanol to this gasoline blend result in a significant increase in the equilibrium pressure at all temperatures. Analysis shows that the vapor–liquid equilibrium data for the MTBE-containing systems are easily correlated using a modified Peng–Robinson equation of state with conventional van der Waals one-fluid mixing rules. Data for mixtures containing ethanol cannot be accurately correlated in this way.

Introduction

As a result of environmental concerns and the Clean Air Act oxygenated compounds, such as ethers and alcohols, are being added to gasolines because of their octane-enhancing and expected pollution-reducing capabilities. To obtain data on the phase behavior of both model and real oxygenate–gasoline mixtures to develop gasoline reformulations, the American Petroleum Institute has commissioned the vapor–liquid equilibrium measurements on mixtures of hydrocarbons separately with methyl *tert*-butyl ether (MTBE) and ethanol.

In this work vapor–liquid equilibrium measurements are reported for (1) binary mixtures of 1-heptene and MTBE at 293, 311, and 333 K; (2) MTBE and a toluene + methylcyclohexane + 2,2,4-trimethylpentane + 1-heptene mixture at 266, 288, 298, 311, and 333 K; (3) ethanol and the toluene + methylcyclohexane + 2,2,4-trimethylpentane + 1-heptene mixture at 266, 288, 298, 311, and 333 K; (4) MTBE and the Auto/Oil Air Quality Improvement Research Gasoline Blend A (which will be referred to as the gasoline blend from here on) at 266, 293, 311, and 333 K; and (5) ethanol and this gasoline blend at the same four temperatures.

An equation of state analysis of some of the data are also reported. It is observed that the MTBE mixtures are easily described using a modified Peng–Robinson equation of state and a single binary interaction parameter between MTBE and all the hydrocarbons. However, because of the nonideality of the ethanol + hydrocarbon mixtures, this system is poorly described with this cubic equation of state with one binary interaction parameter.

Experimental Measurements

In this work P–T–x–y data were collected in a dynamic Stage–Muller still, and P–T–x data were measured in glass or stainless steel static cells, depending on the mixture and the conditions under investigation. The dynamic still, which has been described previously (*1, 2*), was used for the 1-heptene + MTBE binary mixture, and for the four-component (toluene, methylcyclohexane, 2,2,4-trimethylpentane, and 1-heptene) mixtures separately with MTBE and ethanol at pressures below atmospheric, and temperatures above 288 K. The static cells were used for all measurements involving the Auto/Oil Air Quality Improvement Research Gasoline Blend since it was desirable to maintain the liquid composition at the feed composition. Two different static cells were used to obtain the P–T–x data. For subatmospheric pressures the glass cell shown in Figure 1 was used. This unit allows adjustment of the composition of the cell contents by injections through its septum-protected injection port. For pressures above atmospheric, the stainless steel static cell of Chai Kao et al. (*3*) was used. These units are described briefly below. Several samples were run in both cells, and as seen below, the results using these two different units agreed quite well.

At 266 and 288 K the glass static cell was used for all mixtures since it was not possible to accurately control pressures in the dynamic still at the low pressures (4–8 kPa at 288 K and 1–3 kPa at 266 K) of these measurements.

Materials. The chemicals used in this study, their suppliers, and purities are listed below. Since all chemicals were of high purity, they were used as received.

chemical	supplier	purity
2,2,4-trimethylpentane	Aldrich	99.9%
1-heptene	Sigma	99.6%
methylcyclohexane	Aldrich	99+%
toluene	Fisher	99.9%
ethanol	Quantum	200 proof
MTBE	Aldrich	99+%
n-heptane	Aldrich	99.5%

A detailed compositional analysis of Auto/Oil Air Quality Research Blend A, prepared by the Phillips Petroleum Co., is given by Gerry et al. (*4*), where it is referred to as blend RF-A. (Note that there can be slight variations in composition each time this mixture is reblended.)

a. Stage–Muller Dynamic Still. Pressure in the Stage–Muller dynamic still was measured using either a Wallace–Tiernan precision mercury manometer with an accuracy of 0.02 kPa or, when the pressure was too low to be measured accurately with the mercury manometer, with a calibrated MKS Baratron low-pressure transducer (model 128A, maximum range of 10 kPa) with an estimated accuracy of 0.01 kPa. Temperature was measured using a Rosemount high-precision platinum resistance thermometer and Fluke multimeter. The estimated accuracy of the temperature readings is about 0.01 K. The accuracies of the temperature and pressure measurements were checked by measuring the vapor pressure of high-purity *n*-heptane and comparing the results with published data; excellent agreement was obtained.

Compositional analysis was done by capillary gas chromatography. A Hewlett-Packard GC (model 5890) equipped with an FID detector and sample splitter was used with a Hewlett-Packard capillary column (HP5, cross-linked 5%

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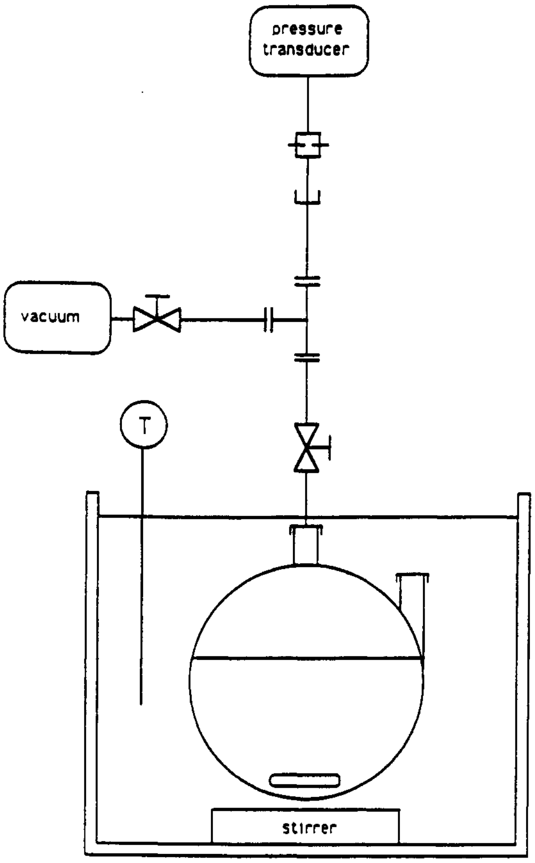

Figure 1. Schematic diagram of the glass static cell.

phenyl methyl silicone, 50 m × 0.32 mm × 0.52 μm film thickness). The gas chromatograph operating conditions used in the analysis are as follows: air flow rate, 260 mL/min; H_2 flow rate, 32 mL/min; He flow rate, 1.75 mL/min (80-kPa head pressure); vent, 213 mL/min; purge, 2 mL/min; injection temperature, 423 K; detector temperature, 433 K; column temperature, 305 K.

Calibration was done by injecting gravimetrically prepared samples. Calibration mixtures over the whole composition range were used for the MTBE + 1-heptene mixture, while the response factor method was used with carefully weighed pure components for the multicomponent mixtures. All samples were analyzed immediately after being removed from the still.

b. Glass Static Cell. At and below 293 K, the gasoline blends were studied using a glass static cell. This equipment, a schematic diagram of which is shown in Figure 1, consists of a glass cell of about 180 cm^3 volume equipped with an injection port, connected to a pressure transducer (MKS Model 128A). The transducer was temperature controlled at 373 K, and was connected to an MKS PDR-C-2C power supply and readout. The transducer to stainless steel tubing connection was made using a silver-plated stainless steel gasket. Leybold vacuum fittings were used for tubing unions, and the connection to the glass still was made with Swagelock fittings and nylon ferrules. The cell was placed in a thermostated water bath with temperature controlled to within 0.05 K. The temperature was monitored by a platinum thermometer with an estimated accuracy of 0.01 K.

Before each measurement, the chemicals were degassed in the glass cells by first freezing in liquid nitrogen and then evacuating the vapor space above the frozen solid for a short time. Next, the cell was warmed to room temperature, submerged in an ultrasonic water bath, and then refrozen. This freeze–thaw cycle was repeated three times. The composition of the liquid in the cell was determined gravimetrically, and oxygenate additions were made by weighed injections through the injection port.

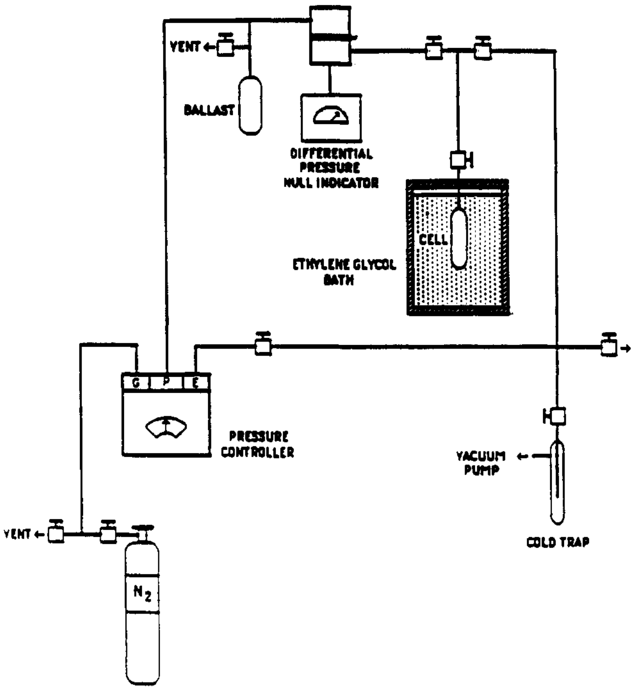

Figure 2. Schematic diagram of the stainless steel static cell.

c. Steel Static Cell. The measurements involving the research gasoline blend at temperatures higher than 293 K were made using the stainless steel static cell unit shown schematically in Figure 2. This unit consisted of a thermostated steel cell of 75 cm^3 volume and auxiliary thermostating, pressure monitoring, and vacuum units. The cell had a port at the bottom and a needle valve at the top for feed addition and for attaching the cell to the other units.

The bath into which the cell was placed controlled temperature to within 0.05 K. Temperatures were measured with mercury thermometers capable of being read to 0.01 K. The pressure measurements were made using a Ruska null detector connected to a Heise pressure controller. It is estimated that the pressure measurements are precise to about 0.2 kPa.

All chemicals used in the experiments were degassed in the steel cells. In each case the cell and its contents were submerged into liquid nitrogen for about 10 min, and then, while keeping the cell in liquid nitrogen, the space above the chemicals was evacuated for about 10 min, by which time the pressure was reduced to about 0.4 Pa. The valve to the vacuum line was then closed, the chemicals thawed to 311 K, and the freeze–evacuation procedure repeated. Total pressure measurements of the cell contents showed that the degassing was complete at the end of the third cycle. In the case of the gasoline blend, it was found that the total pressure obtained after degassing, 65.29 kPa (9.47 psia) at 311 K (100 °F), was in agreement with the Reid vapor pressure reported by the Phillips Petroleum Co. for the sample provided.

As a test, pure *n*-butane (the lightest component in the gasoline blend) was also degassed by the same procedure in order to make sure that the butane in the gasoline blend was not lost. The weight loss of the pure butane sample following this degassing was negligible, confirming that the light ends of the gasoline blend were not lost in the degassing.

The measurement procedure was as follows. For the defined component mixtures, degassed chemicals were transferred from the degassing cell to the measurement cell by gravity, and the mass fraction of each component was

Table I. Vapor–Liquid Equilibrium Data for the 1-Heptene (1) + MTBE (2) System at Temperature T: Vapor Pressure, P, Liquid-Phase, x_2, and Vapor-Phase, y_2, Mole Fractions of MTBE

$T = 333.15$ K			$T = 311.15$ K			$T = 293.15$ K		
P/kPa	x_2	y_2	P/kPa	x_2	y_2	P/kPa	x_2	y_2
118.29	1.000	1.000	55.45	1.000	1.000	27.11	1.000	1.000
114.96	0.991	0.957	53.94	0.990	0.963	26.70	0.996	0.981
111.52	0.975	0.913	51.77	0.970	0.900	26.13	0.987	0.952
107.65	0.958	0.868	49.29	0.947	0.837	25.21	0.975	0.904
107.34		0.863	46.76	0.925	0.772	24.23	0.960	0.855
105.70	0.948	0.843	44.31	0.898	0.711	23.35	0.945	0.808
104.13	0.941	0.823	42.27	0.875	0.656	22.12	0.925	0.743
101.54	0.926	0.791	39.92	0.846	0.599	20.76	0.897	0.670
98.80	0.909	0.758	39.89	0.849	0.599	19.19	0.849	0.596
95.22	0.889	0.711	37.76	0.822	0.550	17.56	0.819	0.512
91.62	0.866	0.668	34.93	0.779	0.478	16.13	0.775	0.447
87.45	0.841	0.617	32.00	0.728	0.406	14.70	0.720	0.385
83.99	0.819	0.575	29.39	0.680	0.348	13.12	0.659	0.307
80.83	0.791	0.536	26.69	0.611	0.283	10.94	0.533	0.216
77.35	0.766	0.495	24.53	0.549	0.226	10.08	0.464	0.175
75.66	0.747	0.471	21.80	0.457	0.173	8.87	0.349	0.120
71.60	0.713	0.425	19.19	0.346	0.116	8.09	0.281	0.090
66.61	0.664	0.360	17.79	0.273	0.084	7.26	0.164	0.051
46.23	0.605	0.308	15.12	0.108	0.032	5.79	0.000	0.000
56.59	0.539	0.246	13.64	0.000	0.000			
51.92	0.469	0.202						
46.65	0.368	0.143						
42.72	0.277	0.097						
39.22	0.188	0.061						
35.64	0.081	0.025						
33.25	0.000	0.000						

established by weighing the cell before and after each transfer. Once the desired composition was reached, the cell was placed into the constant-temperature bath and attached to the manifold. Successive pressure readings were taken with intermittent shaking of the cell. Usually the pressure stabilized within 20 min. Once a stable pressure had been recorded, the bath temperature was changed to the next temperature of interest. In this way data were obtained for fixed compositions at several temperatures. The same general procedure was followed for the gasoline blend, except that only the gasoline blend and oxygenates had to be weighed into the cells.

In three cases measurements were repeated with the glass static cell described below in order to check both sets of measurements. The total pressures measured agreed to within a few percent, which is very good agreement considering that different equipment was used, and that the temperatures and compositions did not exactly coincide.

Experimental Data

The data collected are reported in two different formats. The complete (P–T–x–y) isothermal vapor–liquid equilibrium (VLE) data obtained with the dynamic still are reported in Tables I–III in mole fractions. The static cell P–T–x data in Tables IV–VII are reported in mass fractions since compositions were prepared gravimetrically.

Analysis of the Data Using a Cubic Equation of State

An attempt was made to analyze some of the data using a modification of the Peng–Robinson (*5*) cubic equation of state. Since MTBE and ethanol are not well described by the generalized correlations for the parameters in cubic equations of state, the modification proposed by Stryjek and Vera (*6*), which was referred to as PRSV here, was chosen to obtain the correct pure component vapor pressures. The Peng–Robinson equation is

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \tag{1}$$

with $a = 0.457235(RT_c)^2\alpha/P_c$, $b = 0.077796RT_c/P_c$, and

$$\alpha = [1 + \kappa(1 - T_R^{0.5})]^2 \tag{2}$$

Stryjek and Vera modified the κ function of the Peng–Robinson equation of state as follows:

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R) \tag{3}$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{4}$$

and κ_1 is an adjustable parameter specific to each component which is fit in the low-pressure region of its saturation curve. Values we used for the critical properties and the κ_1 parameter are given in Table VIII.

For the binary systems considered in this study the conventional van der Waals mixing rules were used:

$$b = \sum x_i b_i \tag{5}$$

and

$$a = \sum\sum x_i x_j a_{ij} \tag{6}$$

with

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \tag{7}$$

With the reported critical properties and κ_1 values, the binary k_{ij} parameters for the 1-heptene + MTBE system were obtained by fitting data measured here. In this calculation optimum values of k_{ij} were found by minimizing the error between the measured and calculated pressures. The k_{ij} values obtained were 0.008 at 293.15 K, 0.010 at 311.15 K, and 0.012 at 333.15 K. Figure 3 shows very good agreement between the measured VLE data (points) and the correlations (lines) using the equation of state at 311 K. Similar results were obtained at other isotherms.

For the MTBE + four-component mixture first an equation of state description of MTBE-free mixtures of the four hydrocarbons was developed. From available data for the

Table II. Vapor–Liquid Equilibrium Data for the Toluene (1) + Methylcyclohexane (2) + 2,2,4-Trimethylpentane (3) + 1-Heptene (4) + MTBE (5) System at Temperature T: Vapor Pressure, P, Liquid-Phase, x_i, and Vapor-Phase, y_i, Mole Fractions

P/kPa		$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
T = 333.15 K						
27.52	y_i	0.267	0.108	0.472	0.153	0.000
(27.5[a])	x_i	0.335	0.107	0.430	0.128	0.000
31.43	y_i	0.229	0.093	0.405	0.131	0.143
	x_i	0.323	0.102	0.412	0.122	0.041
39.68	y_i	0.189	0.078	0.335	0.108	0.290
	x_i	0.306	0.097	0.388	0.115	0.094
44.16	y_i	0.148	0.061	0.261	0.085	0.445
	x_i	0.283	0.089	0.356	0.105	0.168
52.15	y_i	0.115	0.048	0.205	0.066	0.567
	x_i	0.252	0.079	0.318	0.094	0.256
60.38	y_i	0.088	0.037	0.157	0.051	0.667
	x_i	0.223	0.070	0.280	0.083	0.344
67.72	y_i	0.072	0.030	0.126	0.041	0.731
	x_i	0.200	0.062	0.248	0.074	0.417
T = 311.15 K						
11.03	y_i	0.294	0.113	0.450	0.144	0.000
(11.1[a])	x_i	0.387	0.107	0.388	0.117	0.000
13.65	y_i	0.230	0.089	0.350	0.112	0.217
	x_i	0.368	0.102	0.366	0.110	0.054
16.93	y_i	0.175	0.066	0.270	0.086	0.401
	x_i	0.342	0.094	0.339	0.102	0.123
21.50	y_i	0.126	0.050	0.192	0.061	0.571
	x_i	0.310	0.084	0.303	0.091	0.212
25.78	y_i	0.092	0.036	0.140	0.044	0.688
	x_i	0.272	0.073	0.263	0.079	0.314
29.91	y_i	0.071	0.029	0.109	0.034	0.758
	x_i	0.234	0.063	0.227	0.068	0.408
T = 298.15 K						
6.00	x_i	0.284	0.115	0.458	0.144	0.000
(6.20[a])	y_i	0.382	0.108	0.392	0.118	0.000
7.54	y_i	0.221	0.090	0.355	0.112	0.223
	x_i	0.364	0.103	0.371	0.112	0.049
9.50	y_i	0.165	0.068	0.269	0.084	0.414
	x_i	0.339	0.095	0.344	0.104	0.118
11.82	y_i	0.128	0.053	0.208	0.065	0.545
	x_i	0.310	0.087	0.313	0.095	0.196
14.52	y_i	0.092	0.039	0.153	0.048	0.668
	x_i	0.276	0.077	0.278	0.084	0.285
17.13	y_i	0.074	0.032	0.122	0.038	0.733
	x_i	0.248	0.069	0.249	0.075	0.359

[a] Calculated from the equation of state.

toluene + methylcyclohexane and 1-heptene + toluene binary mixtures (7), the interaction parameters for these binaries were found to be 0.02 and 0.01, respectively, for temperatures above 293 K. For temperatures in the range from 293 to 333 K it was assumed that all other hydrocarbon–hydrocarbon binary interaction parameters are zero, and a satisfactory representation of the four-component hydrocarbon system was obtained.

At lower temperatures, where small solution nonidealities become more important, a better prediction of the VLE behavior of the MTBE-free hydrocarbon mixtures required use of interaction parameters for the various binaries. Good results were obtained using the same value of k_{ij} for all hydrocarbon binaries, including toluene + methylcyclohexane and 1-heptene + toluene: 0.015 at 266 K and 0.01 at 288 K. The estimates of the total pressure of the MTBE-free mixtures of the four hydrocarbons as a function of temperature obtained by this approach are given as footnotes in Tables II and IV. Next, for mixtures of hydrocarbons with MTBE, it was assumed that all MTBE–hydrocarbon binary interaction parameters were the same and a single parameter was optimized using the total pressure data. The binary interaction parameter $k_{\mathrm{MTBE-HC}}$ found in this way was 0 at 298 K and above, 0.022 at 288 K, and 0.030 at 266 K.

Table III. Vapor–Liquid Equilibrium Data for the Toluene (1) + Methylcyclohexane (2) + 2,2,4-Trimethylpentane (3) + 1-Heptene (4) + Ethanol (5) System at Temperature T: Vapor Pressure, P, Liquid-Phase, x_i, and Vapor-Phase, y_i, Mole Fractions

P/kPa		$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
T = 333.15 K						
27.09	y_i	0.298	0.112	0.445	0.145	0.000
	x_i	0.382	0.108	0.392	0.119	0.000
55.42	y_i	0.179	0.072	0.290	0.093	0.366
	x_i	0.361	0.102	0.371	0.112	0.055
58.23	y_i	0.170	0.068	0.272	0.086	0.404
	x_i	0.335	0.094	0.341	0.103	0.127
59.74	y_i	0.152	0.066	0.263	0.083	0.436
	x_i	0.296	0.083	0.301	0.091	0.229
60.40	y_i	0.145	0.065	0.261	0.081	0.443
	x_i	0.266	0.074	0.268	0.081	0.311
60.70	y_i	0.138	0.063	0.257	0.079	0.463
	x_i	0.239	0.067	0.235	0.071	0.389
T = 311.15 K						
11.05	y_i	0.297	0.113	0.448	0.142	0.000
	x_i	0.384	0.108	0.391	0.118	0.000
21.82	y_i	0.190	0.077	0.305	0.097	0.332
	x_i	0.359	0.101	0.368	0.111	0.060
22.40	y_i	0.177	0.074	0.295	0.092	0.362
	x_i	0.333	0.093	0.338	0.102	0.133
22.51	y_i	0.168	0.072	0.290	0.090	0.380
	x_i	0.307	0.085	0.305	0.092	0.212
22.74	y_i	0.160	0.071	0.287	0.088	0.396
	x_i	0.276	0.076	0.275	0.083	0.290
22.86	y_i	0.158	0.070	0.285	0.087	0.400
	x_i	0.247	0.068	0.244	0.074	0.367
T = 298.15 K						
6.03	y_i	0.286	0.114	0.456	0.144	0.000
	x_i	0.383	0.108	0.391	0.119	0.000
11.66	y_i	0.193	0.081	0.321	0.100	0.306
	x_i	0.359	0.101	0.367	0.112	0.061
11.72	y_i	0.178	0.076	0.304	0.094	0.348
	x_i	0.338	0.094	0.340	0.103	0.124
11.79	y_i	0.173	0.076	0.303	0.094	0.354
	x_i	0.311	0.087	0.314	0.095	0.194
11.84	y_i	0.172	0.076	0.303	0.093	0.357
	x_i	0.186	0.079	0.284	0.086	0.266
11.85	y_i	0.160	0.073	0.298	0.090	0.380
	x_i	0.253	0.067	0.251	0.076	0.349
T = 288.15 K						
3.54	y_i	0.281	0.115	0.460	0.143	0.000
	x_i	0.385	0.107	0.390	0.118	0.000
6.19	y_i	0.201	0.084	0.333	0.103	0.280
	x_i	0.365	0.103	0.373	0.113	0.047
6.44	y_i	0.188	0.080	0.318	0.097	0.317
	x_i	0.337	0.094	0.342	0.103	0.124
6.56	y_i	0.177	0.079	0.318	0.096	0.331
	x_i	0.307	0.085	0.308	0.093	0.207
6.59	y_i	0.167	0.077	0.316	0.095	0.345
	x_i	0.275	0.077	0.274	0.083	0.291
6.64	y_i	0.167	0.077	0.316	0.094	0.346
	x_i	0.246	0.067	0.240	0.073	0.376

The results of our measurements and the correlations of the MTBE + four-component mixtures using this approach are presented in Figures 4 and 5 at 333 K. Similar results were obtained at other temperatures. For temperatures at 298 K and above for which the dynamic still was used, the compositions of both phases and the total pressures were measured, so that for these cases the pressure and the K factor, $K = y_i/x_i$, for each species are presented as a function of the MTBE mole fraction. While pressures are slightly underestimated as a function of MTBE concentration, K factors are well predicted by the equation of state at all temperatures.

Only total pressure data were collected in the measurements of MTBE + four-component system at 288.15 and 266.15 K. For these cases pressure as a function of the mass fraction of MTBE in the mixture was reported. The results obtained

Table IV. Vapor-Liquid Equilibrium Data for the MTBE (1) + Methylcyclohexane (2) + 1-Heptene (3) + 2,2,4-Trimethylpentane (4) + Toluene (5) System at Temperature *T*: Vapor Pressure, *P*, Liquid-Phase Mass Fractions, x_i

P/kPa	$x_i = 1$	$x_i = 2$	$x_i = 3$	$x_i = 4$	$x_i = 5$
T = 285.15 K					
3.92[a]	0.000	0.109	0.118	0.435	0.339
4.48	0.017	0.106	0.116	0.427	0.334
5.19	0.033	0.104	0.114	0.420	0.328
5.61	0.049	0.103	0.112	0.414	0.323
5.95	0.064	0.107	0.111	0.407	0.317
6.22	0.076	0.100	0.109	0.402	0.313
6.50	0.090	0.098	0.108	0.395	0.309
6.74	0.104	0.097	0.106	0.390	0.304
7.03	0.117	0.095	0.104	0.384	0.299
7.34	0.130	0.094	0.103	0.378	0.295
7.62	0.142	0.093	0.101	0.373	0.291
7.80	0.150	0.092	0.100	0.370	0.288
8.05	0.162	0.090	0.099	0.364	0.284
8.37	0.174	0.089	0.098	0.359	0.280
T = 266.15 K					
1.18[a]	0.000	0.106	0.128	0.429	0.336
1.53	0.017	0.105	0.126	0.422	0.330
1.69	0.033	0.103	0.124	0.415	0.325
1.85	0.048	0.101	0.122	0.409	0.320
1.97	0.063	0.100	0.120	0.402	0.315
2.06	0.074	0.098	0.119	0.398	0.311
2.16	0.088	0.097	0.117	0.391	0.306
2.25	0.102	0.096	0.115	0.386	0.302
2.36	0.115	0.094	0.114	0.380	0.297
2.45	0.128	0.093	0.112	0.374	0.293
2.57	0.141	0.091	0.110	0.369	0.288
2.62	0.148	0.091	0.109	0.366	0.286
2.72	0.160	0.089	0.108	0.361	0.282
2.81	0.172	0.088	0.106	0.356	0.278

[a] Calculated from the equation of state.

Table V. Vapor-Liquid Equilibrium Data for the Ethanol (1) + Methylcyclohexane (2) + 1-Heptene (3) + 2,2,4-Trimethylpentane (4) + Toluene (5) System at 265.63 K: Vapor Pressure, *P*, Liquid-Phase Mass Fractions, x_i (Measured in Glass Cell)

P/kPa	$x_i = 1$	$x_i = 2$	$x_i = 3$	$x_i = 4$	$x_i = 5$
1.19	0.000	0.101	0.113	0.443	0.343
1.65	0.017	0.099	0.111	0.436	0.339
1.71	0.034	0.098	0.109	0.428	0.331
1.74	0.053	0.096	0.107	0.420	0.324
1.76	0.069	0.094	0.105	0.413	0.319
1.77	0.084	0.093	0.103	0.406	0.314
1.78	0.099	0.091	0.101	0.400	0.309
1.79	0.106	0.090	0.101	0.397	0.306
1.80	0.120	0.089	0.099	0.390	0.301
1.80	0.134	0.088	0.097	0.384	0.297
1.81	0.147	0.086	0.096	0.378	0.292

for the 288.15 K isotherm are given in Figure 6. Similar trends were observed for the 266.15 K isotherm. Also indicated in this figure are the estimates of the total pressure computed using the PRSV equation of state with a single optimized interaction parameter for MTBE + hydrocarbon binaries, and with $k_{ij} = 0$. It is seen that even though the numerical value of k_{ij} is small, the contribution from this correction is significant. (For all these calculations it was assumed that the amount of material evaporated in the equilibrium cell is negligibly small, and bubble point calculations were performed using the composition of the charge to the cell as the liquid composition. Because of the low pressures involved and the small fractional vaporization of less than 0.1%, this assumption is a good one.)

Table VI. Vapor-Liquid Equilibrium Data for the MTBE (1) + Gasoline Research Blend System at Temperature *T*: Vapor Pressure, *P*, Liquid-Phase Mass Fraction, x_1, of MTBE

P/kPa	x_1	P/kPa	x_1	P/kPa	x_1
T = 333.15 K (Measured in Steel Cell)					
116.34	0.0000	119.59	0.0769	120.21	0.1377
T = 311.15 K (Measured in Steel Cell)					
65.31	0.0000	64.90	0.0769	64.76	0.1377
T = 293.15 K (Measured in Glass Cell Unless Otherwise Indicated)					
37.84	0.0000	37.49	0.0706	37.29	0.1317
37.24[a]	0.0000[a]	37.48	0.0745	37.25	0.1424
37.75	0.0141	37.03[a]	0.0769[a]	37.20	0.1527
37.71	0.0278	37.43	0.0866	37.19	0.1628
37.65	0.0410	37.44	0.0983	37.21	0.1727
37.59	0.0540	37.39	0.1097		
37.52	0.0665	37.35	0.1208		
T = 266.15 K (Measured in Glass Cell Unless Otherwise Indicated)					
14.71	0.0000	14.53	0.0744	14.40	0.1294
14.64	0.0166	14.21[a]	0.0769[a]	14.39	0.1420
14.61	0.0331	14.49	0.0887	14.36	0.1543
14.60	0.0489	14.45	0.1026	14.33	0.1666
14.56	0.0640	14.41	0.1163	14.32	0.1785

[a] Measured in steel cell.

Table VII. Vapor-Liquid Equilibrium Data for the Ethanol (1) + Gasoline Research Blend System at Temperature *T*: Vapor Pressure, *P*, Liquid-Phase Mass Fraction, x_1, of Ethanol

P/kPa	x_1	P/kPa	x_1	P/kPa	x_1
T = 333.15 K (Measured in Steel Cell)					
116.34	0.0000	138.62	0.0463	140.28	0.1033
T = 311.15 K (Measured in Steel Cell)					
65.31	0.0000	71.59	0.0463	71.10	0.1033
T = 293.15 K (Measured in Glass Cell)					
37.67	0.0000	40.20	0.0501	40.36	0.0970
39.49	0.0090	40.27	0.0583	40.36	0.1004
39.83	0.0179	40.33	0.0663	40.37	0.1074
40.01	0.0265	40.27	0.0741	40.39	0.1149
40.11	0.0351	40.35	0.0818	40.40	0.1219
40.16	0.0435	40.36	0.0895		
T = 266.03 K (Measured in Glass Cell)					
14.88	0.0000	15.29	0.0618	15.52	0.1102
15.12	0.0128	15.29	0.0730	15.56	0.1203
15.16	0.0252	15.35	0.0839	15.60	0.1301
15.21	0.0372	15.40	0.0945		
15.28	0.0505	15.45	0.0999		

Table VIII. Equation of State Parameters: Critical Temperature, T_c, Critical Pressure, P_c, Acentric Factor, ω, and κ_1

substance	T_c/K	P_c/bar	ω	κ_1
2,2,4-trimethylpentane	544.0	25.70	0.303	0.0474
1-heptene	537.3	28.30	0.358	−0.1255
methylcyclohexane	572.2	34.70	0.236	0.0598
toluene	591.8	41.06	0.263	0.0331
ethanol	513.9	61.48	0.644	−0.0337
MTBE	496.4	33.70	0.269	0.0528

Previous studies (*8*) of this group have indicated that the phase behavior of the MTBE + hydrocarbon mixtures is significantly different from that of the ethanol + hydrocarbon mixtures, and that only the former can be correlated with a cubic equation of state and the simple mixing rule used here. One reason for this difference is the self-association of the alcohol. In the earlier measurements of infinite dilution activity coefficients for such mixtures (*8*), it was found that while MTBE forms only slightly nonideal mixtures with hydrocarbons (infinite dilution activity coefficients in the range from 0.94 to 1.41), the ethanol + hydrocarbon mixtures are very nonideal (infinite dilution activity coefficients range from 9.8 to 39.9). Such large solution nonidealities are not well described by a cubic equation of state and the van der Waals one-fluid mixing rules with a single binary interaction parameter. This is illustrated in Figure 7 which displays the

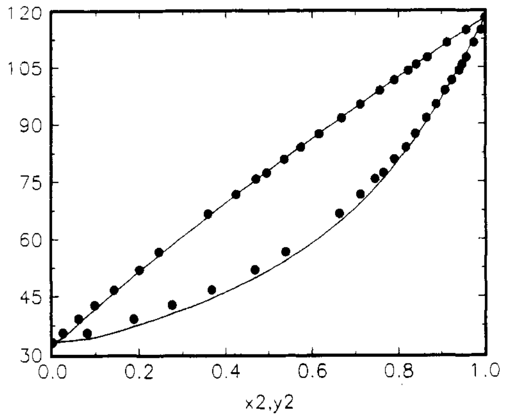

Figure 3. Vapor–liquid equilibrium data for the 1-heptene (1) + MTBE (2) system at 333 K: vapor pressure, P, as a function of the liquid-phase, x_2, or vapor-phase, y_2, mole fraction of MTBE. Points are the experimental data, and the line is the equation of state correlation.

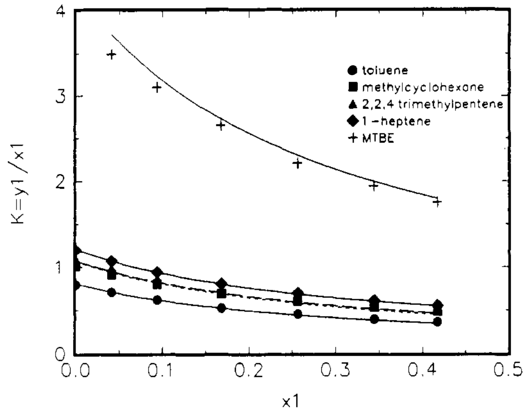

Figure 4. Vapor–liquid equilibrium of the MBTE (1) + four-coordinate mixture at 333 K: $K = y_1/x_1$ as a function of the liquid-phase mole fraction, x_1, of MTBE. Points are the experimental data, and the lines are the equation of state correlations.

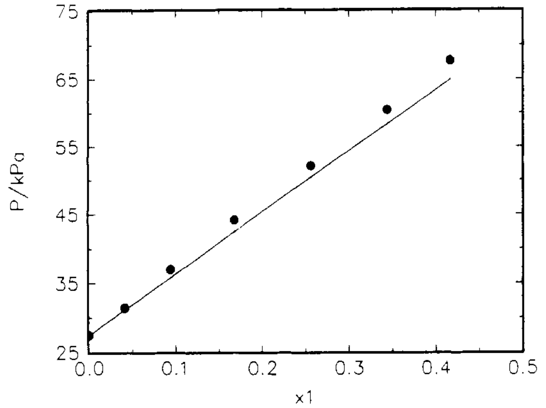

Figure 5. Vapor–liquid equilibrium of MTBE (1) + four-component mixture at 333 K: vapor pressure, P, as a function of the liquid-phase mole fraction, x_1, of MTBE. Points are the experimental data, and the line is the equation of state correlation.

experimental total pressure data (points) for the ethanol + four-component gasoline prototype at 266 K together with the best equation of state correlation using the van der Waals one-fluid mixing rules with a single binary interaction parameter (line). Similar results were observed for this system at other temperatures. A further analysis of our data using equations of state will be reported elsewhere.

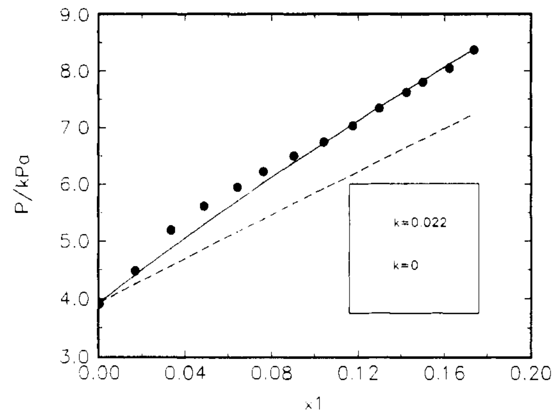

Figure 6. Vapor–liquid equilibrium of the MTBE (1) + four-component mixture at 288 K: Vapor pressure, P, as a function of the liquid-phase mass fraction, x_1, of MTBE. Points are the experimental data, and the lines are the equation of state correlations.

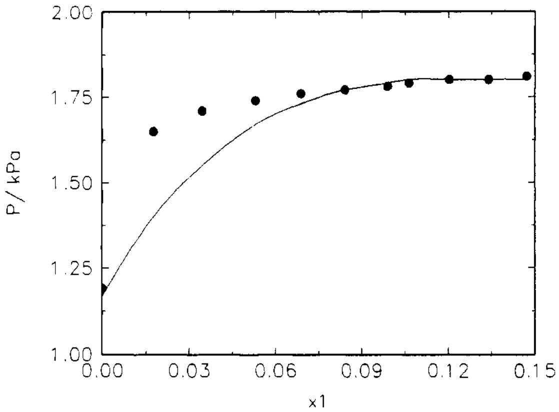

Figure 7. Vapor–liquid equilibrium of ethanol (1) + four-component mixture at 266 K: vapor pressure, P, as a function of liquid-phase mass fraction, x, of ethanol. Points are the experimental data, and the line is the equation of state correlation.

Conclusions

Vapor–liquid equilibrium data were reported for the systems of MTBE + 1-heptene, MTBE + four-component gasoline prototype, ethanol + four-component gasoline prototype, and separately MTBE and ethanol with Auto/Oil Air Quality Improvement Research Gasoline Blend A.

An interesting conclusion drawn from data measured in this work is that small additions of MTBE have a very small effect on the total equilibrium pressure (and consequently the Reid vapor pressure) of the research gasoline blend studied here, and at most temperatures will decrease this pressure. This is due to the already high vapor pressure of this gasoline blend, and the fact that the gasoline blend and MTBE have similar vapor pressures and form almost ideal mixtures. However, small additions of ethanol to this gasoline blend result in first a significant increase in the equilibrium pressure and then an essentially flat total pressure versus ethanol concentration curve at all temperatures. This is due to the strongly nonideal behavior of ethanol + hydrocarbon mixtures.

The analysis of data with cubic equations of state shows that the vapor–liquid equilibrium data for the MTBE-containing systems are easily correlated using a modified Peng–Robinson equation of state with conventional van der Waals one-fluid mixing rules. However, data for the ethanol-containing systems cannot be successfully correlated in this way.

Literature Cited

(1) Eng, R.; Sandler, S. I. *J. Chem. Eng. Data* **1984**, *29*, 156.
(2) Shealy, G. S.; Sandler, S. I. *J. Chem. Eng. Data* **1985**, *30*, 455.
(3) Chai Kao, C. P.; Pozo de Fernandez, M. E. and Paulaitis, M. E. *ACS Symp. Ser.*, to be published.
(4) Gerry, F. S.; Schubert, A. J.; McNally, M. J.; Pahl, R. H. *SAE Tech. Pap. Ser.* **1992**, Jan, No. 920324.
(5) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(6) Stryjek, R.; Vera, J. H. *Can. J. Chem. Eng.* **1986**, *64*, 323.
(7) Plura, J.; Matous, J.; Novak, J. P.; Sobr, J. *Collect. Czech. Chem. Commun.* **1979**, *44*, 38.
(8) Pividal, K. A.; Sterner, C.; Sandler, S. I.; Orbey, H. *Fluid Phase Equilib.* **1992**, *72*, 227.

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