Vapor-Liquid Equilibria of Hydrocarbons and *tert*-Amyl Methyl Ether

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The *P-T-x-y* data for *tert*-amyl methyl ether (TAME) separately with 2,2,4-trimethylpentane (TMP), methylcyclohexane (MCHX), and toluene were obtained at three temperatures, 293, 311, and 333 K. The vapor-liquid equilibria of a five-component mixture (TAME + TMP + 1-heptene + MCHX + toluene) at the same temperatures were measured as well. The data reported have been succesfully described using a Peng-Robinson equation of state with van der Waals one-fluid mixing rules.

Introduction

tert-Amyl methyl ether (TAME) is an oxygenated compound considered as a possible additive to gasoline because of its antiknock effect and expected pollution-reducing capabilities. As a part of the work on reformulated gasoline the American Petroleum Institute has commissioned the vapor-liquid equilibrium (VLE) measurements on mixtures of hydrocarbons with TAME.

In this work vapor-liquid equilibrium measurements are reported for binary mixtures of TAME separately with 2,2,4-trimethylpentane (TMP), methylcyclohexane (MCHX), and toluene at 293, 311, and 333 K, and at the same three temperatures for TAME with a model gasoline mixture consisting of 2,2,4-trimethylpentane + 1-heptene + methylcyclohexane + toluene.

We find that these data are easily correlated using the van der Waals one-fluid mixing rules and a modification of the Peng-Robinson (1) cubic equation of state by Stryjek and Vera (2) which gives the correct pure component vapor pressures.

Experimental Measurements

Materials. High-purity TAME was prepared from a product available from the Aldrich Chemical Co., which had a purity of about 97 mass %, by drying over molecular sieves (type 4A) for 30 h, and then by fractional distillation using a 100-theoretical plate column at a reflux ratio of approximately 30:1. From gas chromatographic analysis (with FID and TCD dectectors) we found the resulting purity to be approximately 99.8 mass %.

Other chemicals used in this study and their suppliers and purities in mass percent are listed in Table 1. The purities were checked by gas chromatography in all cases.

Apparatus and Procedure. A Stage-Muller double recirculation still was used to measure the vapor pressure of TAME and *P-T-x-y* data. This dynamic still and its method of operation have been described previously (3). This equipment is useful for obtaining vapor-liquid equilibrium data below atmospheric pressure and temperatures above 288 K. Pressure was measured using a Wallace-Tiernan precision mercury manometer with an accuracy of 0.02 kPa. Temperature was measured using a Rosemount high-precision platinum resistance thermometer and Fluke multimeter. The accuracy of the temperature reading was about 0.01 K. The

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Table 1. Chemicals Used

chemical	supplier	purity/%
2,2,4-trimethylpentane	Aldrich	99.9
1-heptene	Aldrich	99.6
methylcyclohexane	Aldrich	99.7
toluene	Aldrich	99.8

Table 2. Coefficients of the Antoine Equation, Standard Deviation in Pressure, and the Normal Boiling Point of TAME

antoine constants				T_b/K	
A	B	C	δ/kPa	this work	ref 4
6.095 435	1273.145	225.033	0.008	359.42	359.26

Table 3. Vapor-Liquid Equilibrium Data for the TAME (1) + 2,2,4-Trimethylpentane (2) System at Temperature T and Pressure P, Where x_1 and y_1 Are the Liquid- and Vapor-Phase Mole Fractions of TAME, Respectively

T = 293.15 K			T = 311.15 K			T = 333.15 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
5.14	0.000	0.000	11.88	0.000	0.000	28.58	0.000	0.000
5.37	0.053	0.075	12.25	0.045	0.068	29.37	0.042	0.066
5.66	0.134	0.176	12.94	0.124	0.179	30.57	0.106	0.158
5.84	0.181	0.243	13.50	0.198	0.277	31.69	0.169	0.245
6.10	0.257	0.330	14.14	0.288	0.375	32.81	0.238	0.327
6.32	0.326	0.402	14.56	0.346	0.445	34.20	0.327	0.430
6.52	0.386	0.471	14.91	0.404	0.501	35.33	0.405	0.506
6.59	0.414	0.492	15.13	0.442	0.539	36.56	0.494	0.587
6.76	0.470	0.548	15.28	0.459	0.556	36.75	0.505	0.597
6.93	0.535	0.605	15.52	0.522	0.609	37.82	0.586	0.669
7.17	0.640	0.693	16.03	0.595	0.674	38.88	0.669	0.738
7.25	0.679	0.724	16.53	0.688	0.753	40.06	0.768	0.819
7.48	0.775	0.805	16.92	0.764	0.815	41.04	0.856	0.888
7.68	0.869	0.884	17.38	0.860	0.890	41.87	0.934	0.948
7.79	0.926	0.936	17.68	0.923	0.939	42.33	0.978	0.983
7.89	0.978	0.981	17.90	0.975	0.981	42.55	1.000	1.000
7.94	1.000	1.000	18.04	1.000	1.000			

estimated uncertainities in the equilibrium temperature and pressure are ±0.02 K and ±0.05 kPa, respectively.

The binary VLE measurements were made at 293, 311, and 333 K over the whole concentration range of TAME, while multicomponent VLE were measured at concentrations of TAME from 0 to 40 mol %. The gravimetrically prepared feed composition of the four-component hydrocarbon mixture, in mole fraction, was 0.3998, 0.1137, 0.1030, and 0.3835 of TMP, 1-heptene, MCHX, and toluene, respectively, which corresponds to 48, 12, 10, and 30 vol %.

Table 4. Vapor–Liquid Equilibrium Data for the TAME (1) + Methylcyclohexane (2) System at Temperature T and Pressure P, Where x_1 and y_1 Are the Liquid- and Vapor-Phase Mole Fractions of TAME, Respectively

T = 293.15 K			T = 311.15 K			T = 333.15 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
4.86	0.000	0.000	11.21	0.000	0.000	27.04	0.000	0.000
4.96	0.023	0.042	11.65	0.041	0.071	27.99	0.042	0.072
5.08	0.057	0.091	12.26	0.103	0.168	28.22	0.053	0.087
5.21	0.080	0.131	12.76	0.162	0.252	29.65	0.121	0.192
5.33	0.109	0.178	13.26	0.220	0.321	30.85	0.180	0.272
5.48	0.136	0.224	13.64	0.267	0.376	31.98	0.241	0.345
5.58	0.159	0.252	14.28	0.352	0.472	33.18	0.310	0.422
5.66	0.185	0.291	14.75	0.420	0.534	34.34	0.381	0.496
5.78	0.213	0.329	15.07	0.473	0.583	35.01	0.424	0.537
5.88	0.243	0.367	15.73	0.575	0.670	35.45	0.449	0.561
6.07	0.289	0.412	16.20	0.656	0.737	36.52	0.525	0.625
6.26	0.343	0.473	16.69	0.744	0.804	37.71	0.609	0.698
6.37	0.377	0.512	17.08	0.812	0.857	38.88	0.696	0.768
6.44	0.403	0.528	17.45	0.884	0.911	40.05	0.788	0.839
6.63	0.475	0.596	17.83	0.962	0.970	41.24	0.886	0.914
6.83	0.573	0.642	18.04	1.000	1.000	42.12	0.963	0.972
6.95	0.574	0.680				42.55	1.000	1.000
7.40	0.751	0.816						
7.55	0.818	0.864						
7.76	0.909	0.932						
7.88	0.967	0.975						
7.94	1.000	1.000						

Table 5. Vapor–Liquid Equilibrium Data for the TAME (1) + Toluene (2) System at Temperature T and Pressure P, Where x_1 and y_1 Are the Liquid- and Vapor-Phase Mole Fractions of TAME, Respectively

T = 293.15 K			T = 311.15 K			T = 333.15 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
2.91	0.000	0.000	7.20	0.000	0.000	18.50	0.000	0.000
2.94	0.007	0.019	7.42	0.019	0.043	19.22	0.025	0.060
3.11	0.033	0.095	8.06	0.066	0.152	20.67	0.076	0.169
3.63	0.121	0.281	8.88	0.136	0.271	22.43	0.138	0.274
3.98	0.187	0.384	9.59	0.194	0.369	24.42	0.217	0.385
4.40	0.264	0.499	10.44	0.271	0.475	26.48	0.299	0.494
4.76	0.343	0.579	11.40	0.356	0.563	28.53	0.381	0.586
5.06	0.407	0.646	12.17	0.429	0.631	29.94	0.435	0.648
5.35	0.458	0.696	12.32	0.438	0.644	31.25	0.497	0.696
5.71	0.523	0.735	12.97	0.499	0.696	32.51	0.556	0.744
6.06	0.604	0.787	13.65	0.568	0.745	34.18	0.626	0.795
6.55	0.698	0.852	14.39	0.640	0.798	35.88	0.697	0.840
7.00	0.796	0.903	15.14	0.712	0.843	37.43	0.769	0.880
7.38	0.882	0.945	16.23	0.820	0.907	39.27	0.852	0.926
7.74	0.955	0.980	17.25	0.923	0.962	41.22	0.939	0.971
7.94	1.000	1.000	18.03	1.000	1.000	42.55	1.000	1.000

Samples of the equilibrium phases were taken for GC analysis approximately 20 min after the still conditions had stabilized. A Hewlett-Packard 5890 Series II model gas chromatograph equipped with a FID detector and a capillary column (HP5, cross-linked 5% phenyl methyl silicone, 50 m × 0.32 mm × 0.52 mm film thickness) was used. Calibration was done by analyzing gravimetrically prepared mixtures. For the TAME + hydrocarbon binaries the relation between mass and area percent was found using standards over the whole concentration range. For the multicomponent mixtures the response factor method was used. The estimated uncertainity in the determined mole fractions is about ±0.002.

Results and Discussion

The Antoine equation constants obtained from the measured vapor pressures of TAME are listed in Table 2, together

$$\log(P/\text{kPa}) = A - \frac{B}{C + t/°C} \qquad (1)$$

with the TAME boiling point at 101.325 kPa. The vapor-

Table 6. Vapor–Liquid Equilibrium Data for the TAME (1) + TMP (2) + 1-Heptene (3) + MCHX (4) + Toluene (5) System at Temperature T and Pressure P, Where x_i and y_i Are the Liquid- and Vapor-Phase Mole Fractions

P/kPa		i = 1	i = 2	i = 3	i = 4	i = 5
		T = 293.15 K				
4.76	y_i	0.000	0.468	0.138	0.110	0.284
	x_i	0.000	0.396	0.111	0.103	0.390
4.96	y_i	0.081	0.429	0.125	0.102	0.264
	x_i	0.051	0.374	0.105	0.097	0.373
5.12	y_i	0.154	0.399	0.116	0.094	0.236
	x_i	0.098	0.356	0.100	0.092	0.354
5.26	y_i	0.226	0.368	0.107	0.086	0.213
	x_i	0.149	0.336	0.093	0.087	0.335
5.46	y_i	0.310	0.331	0.095	0.077	0.187
	x_i	0.211	0.313	0.086	0.080	0.311
5.70	y_i	0.399	0.290	0.081	0.067	0.163
	x_i	0.292	0.282	0.076	0.071	0.280
6.07	y_i	0.507	0.244	0.066	0.054	0.128
	x_i	0.381	0.247	0.066	0.061	0.245
		T = 311.15 K				
11.17	y_i	0.000	0.461	0.139	0.109	0.292
	x_i	0.000	0.400	0.113	0.103	0.384
11.45	y_i	0.054	0.437	0.131	0.103	0.275
	x_i	0.032	0.385	0.108	0.099	0.375
11.76	y_i	0.124	0.405	0.119	0.095	0.256
	x_i	0.081	0.364	0.101	0.094	0.359
12.14	y_i	0.206	0.365	0.106	0.086	0.236
	x_i	0.139	0.337	0.091	0.087	0.345
12.62	y_i	0.310	0.311	0.089	0.076	0.215
	x_i	0.217	0.297	0.079	0.078	0.329
13.13	y_i	0.403	0.268	0.078	0.067	0.184
	x_i	0.296	0.264	0.071	0.071	0.297
13.64	y_i	0.487	0.242	0.068	0.056	0.146
	x_i	0.374	0.247	0.065	0.062	0.252
		T = 333.15 K				
27.17	y_i	0.000	0.450	0.141	0.108	0.301
	x_i	0.000	0.389	0.109	0.103	0.399
27.77	y_i	0.054	0.428	0.133	0.102	0.283
	x_i	0.032	0.382	0.108	0.100	0.377
28.43	y_i	0.119	0.399	0.123	0.095	0.264
	x_i	0.076	0.364	0.102	0.095	0.364
29.27	y_i	0.202	0.363	0.110	0.086	0.239
	x_i	0.134	0.341	0.094	0.088	0.342
30.41	y_i	0.309	0.307	0.091	0.075	0.218
	x_i	0.214	0.302	0.082	0.079	0.322
31.48	y_i	0.396	0.273	0.081	0.065	0.185
	x_i	0.287	0.277	0.075	0.072	0.289
32.65	y_i	0.494	0.227	0.066	0.055	0.157
	x_i	0.371	0.235	0.062	0.063	0.268

Table 7. 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	vapor pressure ref
TAME	531.6	30.68	0.325	−0.0115	this work
2,2,4-trimethylpentane	544.	25.7	0.303	0.0354	5
1-heptene	537.3	28.3	0.358	−0.1473	6
methylcyclohexane	572.2	34.7	0.237	0.0405	5
toluene	591.8	41.06	0.263	0.0381	5

liquid equilibrium data obtained for the systems studied are presented in Tables 3–6. For the binary mixture the compositions of the liquid phase (x_1) and the vapor phase (y_1) are given in TAME mole fraction.

As is evident from the Tables 3–5 and Figures 1–3, these mixtures form nearly ideal mixtures. In fact, the maximum excess Gibbs free energy of mixing calculated from our experimental data for the TAME + TMP mixture is only 140, 106, and 92 J/mol at 293.15, 311.15, and 333.15 K, respectively. Similarly for the TAME + MCH mixture the values are 122, 126, and 116 J/mol, and for the TAME + toluene mixture the values are 114, 122, and 89 J/mol. With
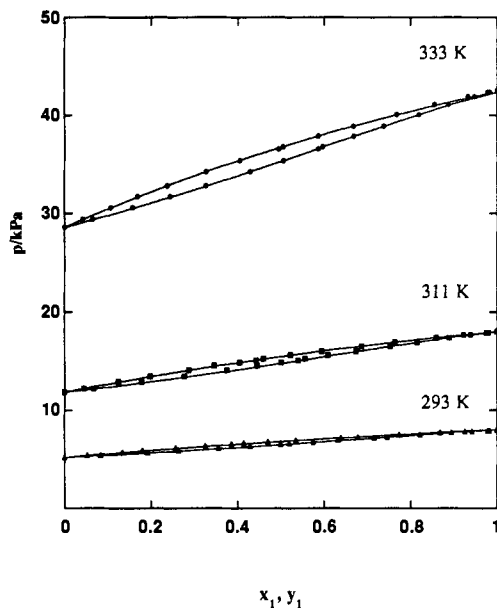
Figure 1. Vapor–liquid equilibrium data for TAME (1) + 2,2,4-trimethylpentane (2) at 293, 311, and 333 K: total pressure, P, as a function of the liquid-phase, x_1, and vapor-phase, y_1, mole fractions of TAME. Points are the experimental data, and the line is the equation of state correlation.
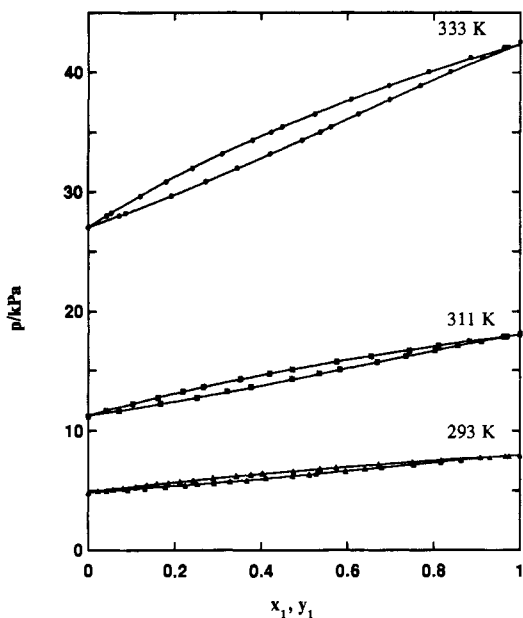

Figure 2. Vapor–liquid equilibrium data for TAME (1) + methylcyclohexane (2) at 293, 311, and 333 K: total pressure, P, as a function of the liquid-phase, x_1, and vapor-phase, y_1, mole fractions of TAME. Points are the experimental data, and the line is the equation of state correlation.

such small extents of nonideality, these mixtures are easily fit with any two-parameter activity coefficient model.

The data were correlated using the Peng–Robinson cubic equation of state (1) as modified by Stryjek and Vera (2) to obtain the correct pure component vapor pressures. This form of the Peng–Robinson equation is

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

with

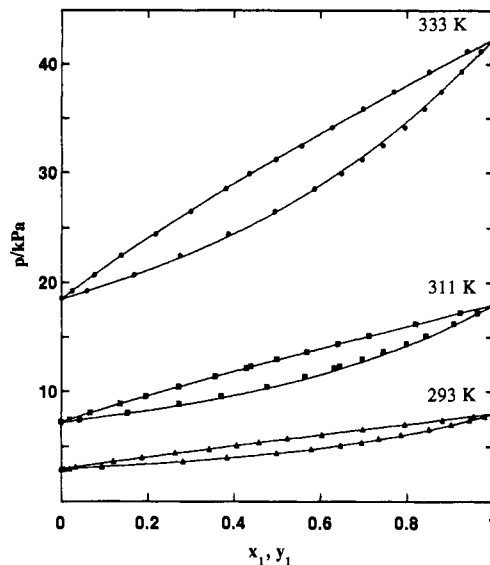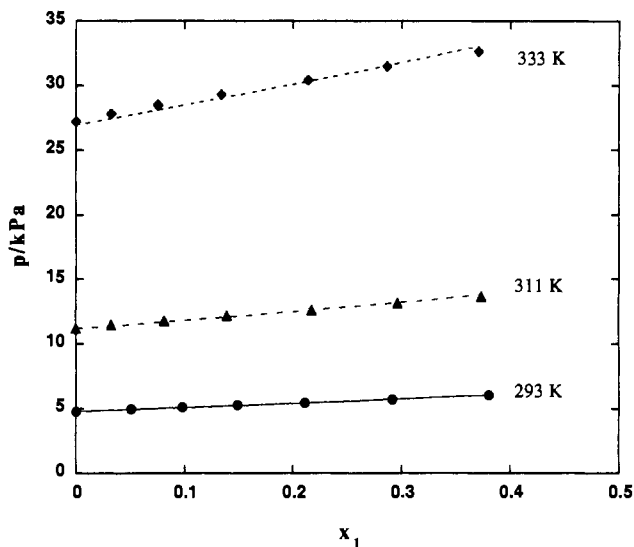$$a = 0.457235(RT_c)^2 \alpha / P_c \tag{3}$$

Figure 3. Vapor–liquid equilibrium data for TAME (1) + toluene (2) at 293, 311, and 333 K: total pressure, P, as a function of the liquid-phase, x_1, and vapor-phase, y_1, mole fractions of TAME. Points are the experimental data, and the line is the equation of state correlation.

Figure 4. Vapor–liquid equilibrium of the TAME (1) + four-component mixture at 293, 311, and 333 K: total pressure, P, as a function of the liquid-phase mole fraction, x_1, of TAME. Points are the experimental data, and the lines are the equation of state predictions based on binary mixture data.

$$b \; 0.077796RT_c / P_c \tag{4}$$

$$\alpha = [1 + \kappa(1 - T_R^{0.5})]^2 \tag{5}$$

and

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R) \tag{6}$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{7}$$

Here κ_1 is an adjustable parameter specific to each component; it is obtained by fitting the low-pressure region of the vapor–liquid saturation curve. The values of the critical parameters we used and the κ_1 parameters obtained in the fitting procedure, along with the sources of the vapor pressure data
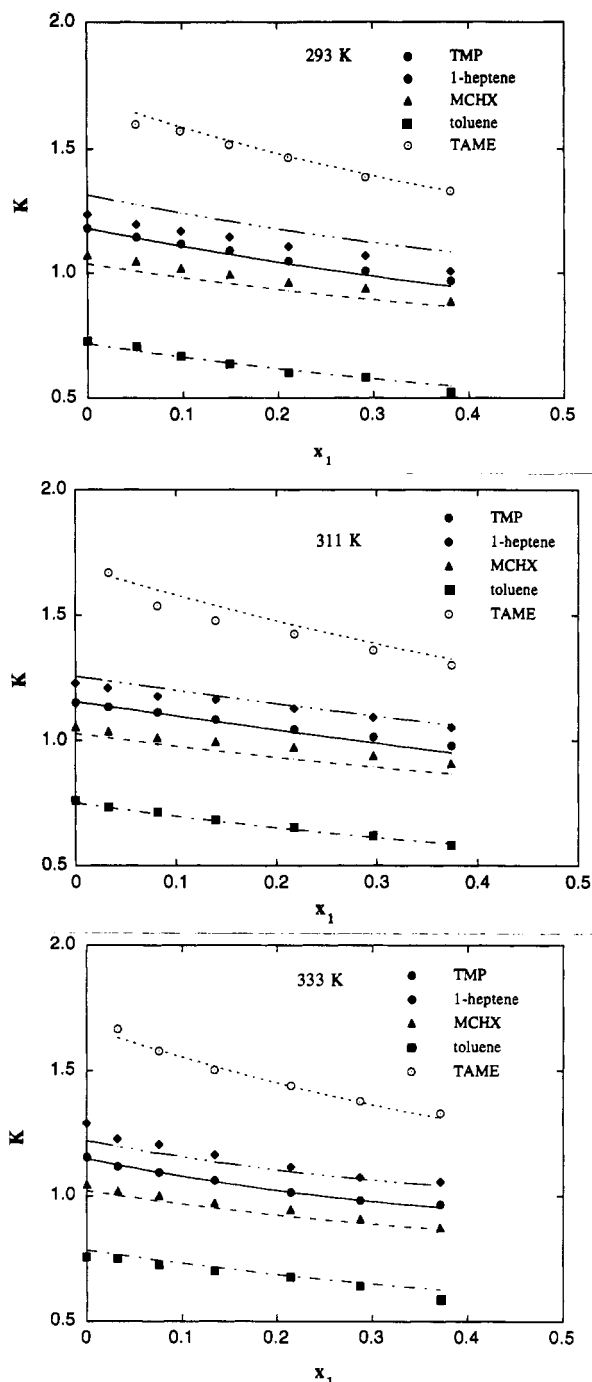
Figure 5. Vapor–liquid equilibrium of the TAME (1) + four-component mixture at (a, top) 293, (b, middle) 311, and (c, bottom) 333 K: distribution ratio $K = y_i/x_i$ as a function of the liquid-phase mole fraction, x_1, of TAME. Points are the experimental data, and the lines are the equation of state predictions based on binary mixture data.

for all components, are given in Table 7.

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

$$b = \sum x_i b_i \quad a = \sum \sum x_i x_j a_{ij} \quad \text{and}$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \quad (8)$$

optimum values of the binary parameter k_{12} were found by minimizing the error between the calculated and measured

Table 8. Binary Parameters of the Equation of State for Studied Systems: Temperature T, Binary Parameter k_{12}, Average Deviation in Vapor-Phase Concentration AVY, and Average Deviation in Pressure AVP

system 1 + 2	T/K	k_{12}	AVY/ mole fract	AVP/ kPa
TAME + 2,2,4-trimethylpentane	293.15	0.004 97	0.007	0.031
	311.15	0.006 02	0.008	0.024
	333.15	0.007 61	0.002	0.065
TAME + methylcyclohexane	293.15	0.007 81	0.004	0.025
	311.15	0.008 81	0.010	0.030
	333.15	0.010 00	0.002	0.052
TAME + toluene	293.15	−0.007 92	0.005	0.026
	311.15	−0.005 24	0.013	0.026
	333.15	−0.003 35	0.006	0.085

VLE. The values of k_{12} obtained for the systems we have studied and the average errors in pressure and concentration of the vapor phase are reported in Table 8. The results of the calculations for the binary mixtures studied are shown in the Figures 1–3.

In the equation of state calculations for the TAME + four-hydrocarbon mixtures, k_{12} values obtained from binary data were used. For the system TAME + 1-heptene, values of k_{12} for the similar mixture of methyl *tert*-butyl ether + 1-heptene (7) have been used, since no binary data are available for this system. For the hydrocarbon + hydrocarbon binaries, the values of binary parameter k_{12} were taken equal to zero. As shown in Figure 4, a satisfactory description of the total pressure of the mixture as a function of TAME mole fraction was obtained. Also the K factors, defined as $K_i = y_i/x_i$, for this mixture are reasonably well predicted as can be seen in Figure 5. Only in the case of 1-heptene at 293 K does the prediction from the equation of state differ from the experimental results. In this case the calculated distribution factor values differ by about 6% from the experiment. However, as was mentioned above, the 1-heptene +TAME binary k_{12} parameter is approximate.

Conclusions

Vapor–liquid equilibrium data are reported for three binary mixtures and a five-component mixture formed from TAME and the hydrocarbons toluene, methylcyclohexane, 2,2,4-trimethylpentane, and 1-heptene. From these results we see that TAME forms only slightly nonideal mixtures with hydrocarbons. Correlation of these data with a cubic equation of state shows that such mixtures can be easily described using a modified Peng–Robinson equation of state with the conventional van der Waals mixing rules.

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