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Vapor–Liquid Equilibria of Binary Mixtures with Ethyl *tert*-Butyl Ether

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In this work *P–T–x–y* vapor–liquid equilibria were obtained for ethyl *tert*-butyl ether (ETBE) + toluene at temperatures of 273.15, 311.15, and 333.15 K and for 2-methylbutane (isopentane) + ETBE at temperatures of 293.15 and 303.15 K. These mixtures are found to be almost ideal, and the reported data are well described using a Peng–Robinson equation of state, modified by Stryjek and Vera with the van der Waals one-fluid mixing rule.

Introduction

Ethyl *tert*-butyl ether (ETBE) and several other oxygenated chemicals are being considered as possible gasoline additives because of their antiknock and expected pollution-reducing properties. In order to develop calculational models for gasoline reformulation, accurate vapor–liquid equilibrium (VLE) data are needed. In this work vapor–liquid equilibrium measurements are reported for the binary mixture of ETBE + toluene at 273.15, 311.15, and 333.15 K and for 2-methylbutane (isopentane) + ETBE at temperatures of 293.15 and 303.15 K.

We find that the mixtures are nearly ideal and that the experimental data are easily correlated using either activity coefficient models or, as we show here, the Peng–Robinson equation of state (*1*), as modified by Stryjek and Vera (*2*) to give the correct pure component vapor pressures, and the van der Waals one-fluid mixing rule.

Experimental Measurements

Materials. All chemicals used had a purity of more than 99.9% as was verified by gas chromatographic analysis with an FID detector. The 2-methylbutane and ETBE were dried and distilled to achieve these purities, the toluene delivered by the supplier had a purity of 99.9% and was used as received. The ETBE was obtained from Lancaster Synthesis Inc., while the toluene and 2-methylbutane came from Aldrich Chemical Co., as shown in Table 1.

Apparatus and Procedere. A Stage-Muller double recirculation still was used to measure the pure component vapor pressures and the *P–T–x–y* data. This dynamic still and its method of operation have been described previously (*3*). This equipment is useful for obtaining data below and around atmospheric pressure, and at temperatures above 288 K. Pressure was measured using a Wallace-Tiernan precision mercury manometer with an accuracy of 0.02 kPa and an uncertainity of ±0.05 kPa. Temperature was measured using a Rosemont high-precision platinium resistance thermometer and a Fluke multimeter. The accuracy of the temperature was about 0.01 K with an uncertainity of ±0.02 K. Before these measurements were made, the accuracy of the equipment was tested and calibrated by measuring the vapor pressure of ultrapure heptane.

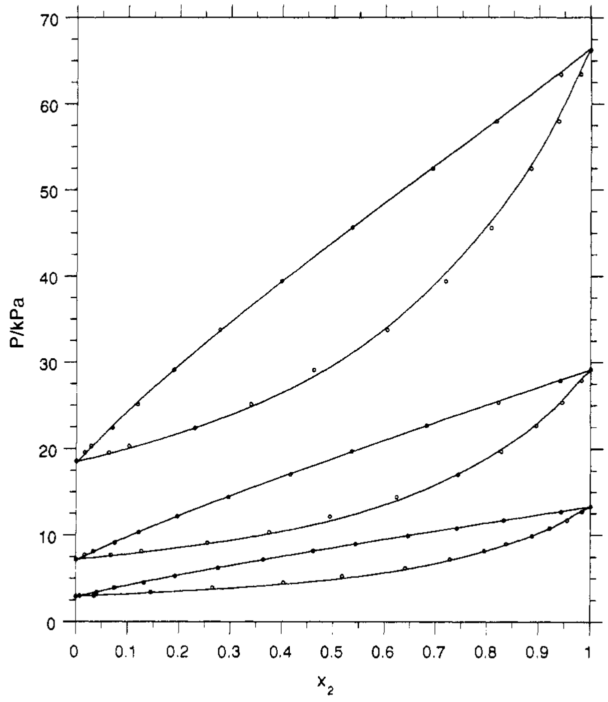

Figure 1. Experimental VLE data (points) and correlations (lines) for toluene (1) + ethyl *tert*-butyl ether (2) at temperatures of 293.15, 311.15, and 333.15 K.

Table 1. Chemicals Used and their Supplier and Purity

chemical	registry no.	supplier	purity used in measurements/%
toluene	108-88-3	Aldrich	99.9
ethyl *tert*-butyl ether	637-92-3	Lancaster	>99.9
2-methylbutane	78-78-4	Aldrich	99.9

A Hewlett-Packard 5890 Series II gas chromatograph equipped with an FID detector and a capillary column (HP5, cross-linked 5% phenyl methyl silicon, 50 m × 0.32 mm × 0.52 mm film thickness) was used for analyzing samples. The gas chromatograph operating conditions used in the analysis are listed in Table 2.

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Table 2. Conditions Used for Gas Chromatographic Analysis

	T/K			flow/(mL s^{-1})				
	injector	detector	oven	total	septum	column	air	hydrogen
ETBE + toluene	413	423	333	3.50	0.05	0.025	5.52	0.61
2-methylbutane + ETBE	373	393	328	3.46	0.46	0.026	5.29	0.62

Table 3. Vapor–Liquid Equilibrium Data for Toluene (1) + Ethyl *tert*-Butyl Ether (2): Temperature T, Pressure P, and Mole Fraction of the Liquid (x_2) and Vapor (y_2) Phases

T = 293.15 K			T = 311.15 K			T = 333.15 K		
P/kPa	x_2	y_2	P/kPa	x_2	y_2	P/kPa	x_2	y_2
2.887	0.0000	0.0000	7.192	0.0000	0.0000	18.559	0.0000	0.0000
2.990	0.0078	0.0355	7.682	0.0167	0.0682	19.564	0.0165	0.0635
3.403	0.0403	0.1450	8.114	0.0334	0.1271	20.349	0.0289	0.1030
3.885	0.0752	0.2655	9.105	0.0757	0.2550	22.410	0.0702	0.2303
4.504	0.1316	0.4037	10.317	0.1214	0.3755	25.118	0.1187	0.3394
5.267	0.1922	0.5183	12.176	0.1955	0.4936	29.102	0.1883	0.4611
6.197	0.2754	0.6404	14.421	0.2957	0.6237	33.768	0.2785	0.6050
7.198	0.3637	0.7282	17.046	0.4167	0.7437	39.437	0.3992	0.7188
8.183	0.4609	0.7948	19.708	0.5362	0.8277	45.611	0.5361	0.8067
9.001	0.5444	0.8372	22.697	0.6822	0.8949	52.496	0.6920	0.8835
9.927	0.6469	0.8874	25.387	0.8216	0.9453	57.989	0.8160	0.9364
10.813	0.7416	0.9215	27.883	0.9413	0.9825	63.442	0.9405	0.9795
11.708	0.8322	0.9551	29.211	1.0000	1.0000	66.305	1.0000	1.0000
12.700	0.9439	0.9840						
13.301	1.0000	1.0000						

Table 4. Vapor–Liquid Equilibrium Data for Ethyl *tert*-Butyl Ether (1) + 2-Methylbutane (2): Temperature T, Pressure P, and Mole Fraction of the Liquid (x_2) and Vapor (y_2) Phases

T = 293.15 K			T = 303.15 K		
P/kPa	x_2	y_2	P/kPa	x_2	y_2
13.252	0.0000	0.0000	20.877	0.0000	0.0000
14.490	0.0160	0.0864	23.197	0.0224	0.1078
16.440	0.0423	0.2017	26.670	0.0547	0.2380
20.015	0.0843	0.3561	31.887	0.1043	0.3908
24.260	0.1500	0.4910	38.690	0.1829	0.5274
28.260	0.2062	0.5792	45.345	0.2497	0.6240
33.183	0.2688	0.6851	52.052	0.3291	0.7161
38.196	0.3619	0.7568	58.469	0.3976	0.7630
43.930	0.4516	0.8095	65.558	0.4840	0.8181
48.790	0.5421	0.8597	72.922	0.5729	0.8687
54.585	0.6278	0.8979	79.717	0.6563	0.9012
60.330	0.7252	0.9291	87.770	0.7470	0.9314
66.105	0.8185	0.9596	94.005	0.8260	0.9541
71.855	0.9173	0.9824	101.173	0.9099	0.9784
76.859	1.0000	1.0000	109.154	1.0000	1.0000

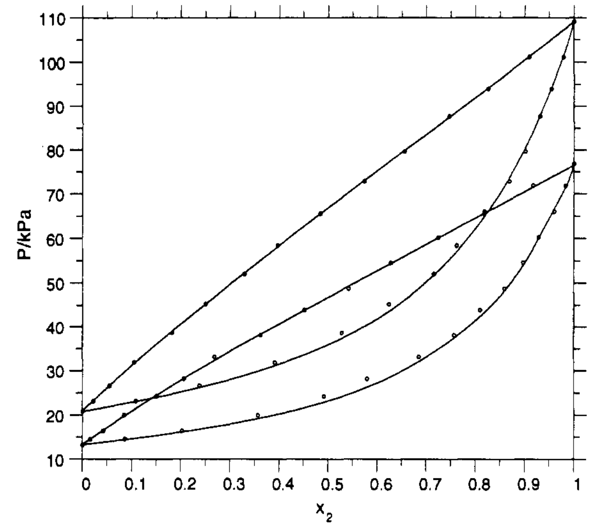

Figure 2. Experimental VLE data (points) and correlations (lines) for ethyl *tert*-butyl ether (1) + 2-methylbutane (2) at temperatures of 293.15 and 303.15 K.

Gravimetrically prepared samples of 0.3-μL size were analyzed over the entire concentration range for each of these binary mixtures to calibrate the gas chromatograph. Estimated uncertainity in the mole fractions is about ±0.002. The binary VLE measurements were made over the entire mole fraction range. Samples of the equilibrium phases were taken approximately after 30 min when conditions in the still had been stabilized, and three analyses were done on each sample.

Results and Discussion

The vapor–liquid equilibrium data obtained for the systems studied are presented in Tables 3 and 4. The compositions of the liquid phase (x_2) and of the vapor phase (y_2) are given in mole fraction of ETBE for the ETBE + toluene system and in mole fraction of 2-methylbutane for the 2-methylbutane + ETBE system. The vapor pressure of 2-methylbutane at 303.15 K was computed using the equation and constants given in ref 4 because the vapor pressure was out of the range of our equipment. At lower temperatures, the measured vapor pressure for this component was in excellent agreement with that reported in that reference.

From the data reported in the tables and figures, it is evident that both ETBE mixtures are nearly ideal. Indeed, the maximum values of the activity coefficients computed from our data are 1.19 for ETBE and 1.10 for 2-methylbutane in their mixtures, and 1.14 for ETBE and 1.26 for toluene in the binary mixtures of those components. The vapor–liquid equilibrium data for these mixtures are easily fit with a two-parameter activity coefficient model.

The binary VLE data were correlated using the Peng–Robinson equation of state as modified by Stryjek and Vera (*2*) to produce the correct pure component vapor pressure. This form of the Peng–Robinson equation is as follows:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \qquad (1)$$

with

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

and

Table 5. Properties and Equation of State Parameters of the Pure Substances Used for the Calculation: Molecular Weight M, Boiling Point T_b, Critical Temperature T_c, Critical Pressure P_c, Acentric Factor ω, and κ_1[a]

substance	M/(g mol^{-1})	T_b/K	T_c/K	P_c/kPa	ω	κ_1
2-methylbutane	72.15	300.99	460.43	3381	0.227 46	0.0217
tert-butyl ethyl ether	102.18	345.95	514	3040	0.295 67	0.0978
toluene	92.141	383.78	591.8	4104	0.262 12	0.0416

[a] With the exception of the parameter κ_1 which was computed here, parameters were obtained from refs 2 and 4.

$$\alpha = [1 + \kappa(1 - T_r^{0.5})]^2 \qquad \kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r)$$

$$T_r = T/T_c \tag{3}$$

where

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

Here κ_1 is an adjustable parameter specific to each component, which is obtained by fitting the low-pressure pure component vapor pressure. The value of κ_1 and the critical properties of each component used in our calculations are given in Table 5.

The van der Waals one-fluid mixing rule was used to correlate the data for the binary systems we studied, since the mixtures are almost ideal. The equations for this mixing rule are

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{5}$$

and

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{6}$$

We also use the standard combining rules

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \quad \text{with} \quad k_{ii} = 0$$

$$\text{and} \quad b_{ij} = (1/2)(b_{ii} + b_{ij}) \tag{7}$$

The results of the correlation are given in Table 6, together with the average error as the difference between measured and calculated pressures and compositions. We see from this table that the data can be correlated to a high degree of accuracy using this model. Figures 1 and 2 show the experimental data and calculated curves for all measured temperatures for each system.

Table 6. Binary Parameter of the van der Waals One-Fluid Mixing Rule for the Systems Studied: T is Temperature, k_{12} is the Binary Interaction Parameter, ADP is the Average Deviation in Pressure, and ADY is the Average Deviation in Vapor-Phase Mole Fraction

system 1 + 2	T/K	k_{12}	ADP/kPa	ADY
(1) ethyl *tert*-butyl ether	293.15	−0.0234	0.50	0.014
(2) toluene	311.15	−0.025	0.50	0.004
	333.15	−0.009	0.50	0.005
(1) 2-methylbutane	293.15	0.007	0.68	0.008
(2) ethyl *tert*-butyl ether	303.15	−0.007	0.74	0.005

Conclusion

Vapor–liquid equilibrium data are reported for two binary ethyl *tert*-butyl ether + hydrocarbon mixtures. As we can see, these systems are nearly ideal and the experimental data we obtained are easily correlated by the described equation of state with the van der Waals one-fluid mixing rule.

Registry numbers in this paper were supplied by the author.

Literature Cited

(1) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(2) Stryjek, R.; Vera, J. H. *Can J. Chem. Eng.* **1986**, *64*, 323.
(3) Shealy, G. S.; Sandler, S. I. *J. Chem. Eng. Data* **1985**, *30*, 455.
(4) STN International, The Scientific & Technical Network, Columbus, OH 43210, 1993.

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