J. Chem. Eng. Data **2001,** *46,* 683−685

Vapor−Liquid Equilibria for the Ternary Ethanol + *tert*-Amyl Methyl Ether + Methylcyclohexane System at 333.15 K

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Vapor−liquid equilibrium (VLE) data were measured for the ternary system ethanol + *tert*-amyl methyl ether + methylcyclohexane at 333.15 K by using a Boublik vapor−liquid recirculation still. The experimental results are compared with those predicted from the PRSV equation of state with the modified Huron−Vidal first-order (MHV1) and corrected Huron−Vidal (CHV) mixing rules. Good agreement was obtained.

Introduction

Some alkyl ethers are used as gasoline additives, owing to their octane-enhancing and pollution-reducing properties. As part of vapor−liquid equilibrium (VLE) studies of nonideal liquid mixtures containing *tert*-amyl methyl ether (TAME), we report here ternary VLE data for ethanol + TAME + methylcyclohexane at 333.15 K.

The experimental results are compared with those predicted from a modification of the Peng−Robinson equation of state by Stryjek and Vera[1−3] (PRSV) coupled with the modified Huron−Vidal[4] first-order (MHV1) and corrected Huron−Vidal[5] (CHV) mixing rules. The VLE data for the three binary systems constituting the ternary system have been reported in the literature: ethanol + TAME at 333.15 K by Ohta et al.,[6] ethanol + methylcyclohexane at 328.15 K by Gmehling and Onken,[7] and TAME + methylcyclohexane at 333.15 K by Antosik and Sandler.[8]

Experimental Section

Ethanol (super special grade, mass fraction > 0.998) and methylcyclohexane (spectro-grade, mass fraction > 0.99) were supplied by Wako Pure Chemical Industries Ltd. and were used without further purification. TAME (Aldrich Chemical Co., mass fraction = 0.97) was purified by a fractional distillation column (Sibata Scientific Technology Ltd., HP-9000B) after drying over molecular sieves (type 4A).

The densities of these compounds used for the experimental work, measured with a densimeter (Anton Paar DMA-58), agreed well with the literature values, as shown in Table 1.

Table 1. Densities of Compounds Used in This Work

compound	T/K	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} lit.
ethanol	298.15	0.784 92	0.784 93[a]
TAME	293.15	0.771 01	0.770 74[b]
methylcyclohexane	298.15	0.765 30	0.765 06[a]

[a] Riddick et al.[9] [b] Cervenkova and Boublik.[10]

Table 2. Experimental Vapor−Liquid Equilibrium Data for the Ethanol (1) + TAME (2) + Methylcyclohexane (3) System at 333.15 K

no.	x_1	x_2	y_1	y_2	P/kPa
1	0.754	0.193	0.662	0.231	60.17
2	0.586	0.328	0.582	0.320	60.32
3	0.744	0.134	0.675	0.153	61.13
4	0.598	0.227	0.585	0.225	61.46
5	0.402	0.399	0.508	0.332	60.08
6	0.374	0.514	0.475	0.431	60.25
7	0.414	0.288	0.546	0.229	60.92
8	0.228	0.650	0.393	0.522	56.70
9	0.154	0.219	0.475	0.169	56.64
10	0.147	0.120	0.516	0.089	57.05
11	0.557	0.081	0.600	0.072	61.90
12	0.195	0.325	0.461	0.249	57.68
13	0.816	0.064	0.690	0.085	60.18
14	0.241	0.524	0.436	0.408	57.80
15	0.587	0.173	0.597	0.161	61.48
16	0.714	0.074	0.645	0.080	62.06
17	0.419	0.091	0.589	0.069	61.98
18	0.813	0.119	0.690	0.173	58.88
19	0.170	0.452	0.410	0.356	56.06
20	0.114	0.762	0.264	0.654	51.45

Table 3. Equation of State Parameters of the Pure Compounds

compound	T_c/K	P_c/MPa	ω	κ_1
ethanol[a]	513.92	6.148	0.644 39	−0.033 74
TAME[b]	531.6	3.068	0.325	−0.011 5
methylcyclohexane[c]	572.12	3.471	0.236 37	0.048 59

[a] Stryjek and Vera.[1] [b] Antosik and Sandler.[8] [c] Proust and Vera.[3]

The VLE data at 333.15 K were measured using a Boublik vapor−liquid recirculating still. The details on the still have been described previously.[11] The temperature was measured by using a quartz thermometer (Tokyo Denpa, DMT-610). The pressure in the still was adjusted with a vacuum controller (Sibata Scientific Technology Ltd.,V-301) until a temperature of 333.15 K was maintained. Composition determinations of the vapor- and liquid-phase samples for the system were performed by using a gas chromatograph (Shimadzu GC-8A) connected to an electronic integrator (Shimadzu C-R6A). The experimental uncertainties of the measured variables were as follows: liquid and vapor

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10.1021/je000266l CCC: $20.00

Table 4. Binary Parameters of the Modified UNIQUAC Equation and Root-Mean-Square Deviations

system (1 + 2)	T/K	no. of data points	mixing rule	parameters a_{12}/K	a_{21}/K	root-mean-square deviations δP/kPa	δT/K	δx	δy	ref
ethanol + TAME	333.15	10	MHV1	−183.53	779.22	0.129	0.04	0.0010	0.0079	6
			CHV	−155.28	877.80	0.100	0.03	0.0012	0.0066	6
ethanol + methylcyclohexane	328.15	8	MHV1	−124.07	1313.15	0.083	0.02	0.0005	0.0046	7
			CHV	−53.51	2153.56	0.371	0.11	0.0015	0.0090	7
TAME + methylcyclohexane	333.15	15	MHV1	−118.02	142.03	0.079	0.01	0.0004	0.0031	8
			CHV	−101.55	121.51	0.079	0.02	0.0004	0.0032	8

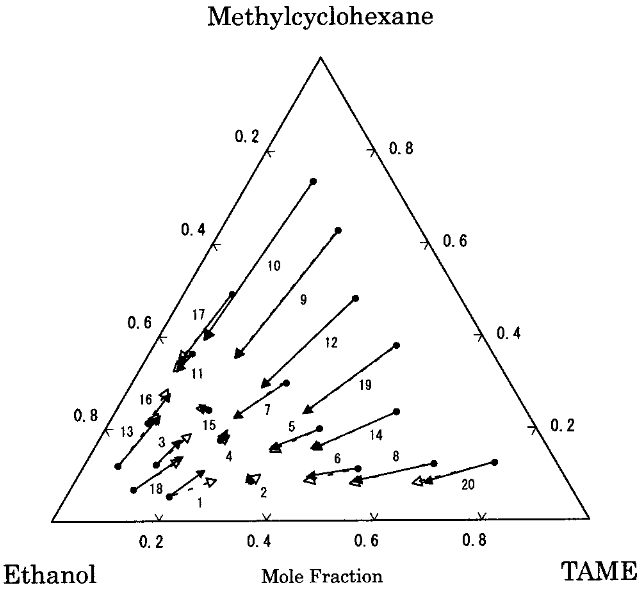

Figure 1. Equilibrium tie lines: (●) liquid mole fraction; (solid right triangle) experimental vapor mole fraction; (open right triangle) calculated vapor mole fraction; (—) experimental; (- - -) calculated from the PRSV equation of state with the MHV1 mixing rule.

Table 5. Comparison of Prediction of Ternary VLE Data for the Ethanol (1) + TAME (2) + Methylcyclohexane (3) System at 333.15 K with MHV1 and CHV Mixing Rules

mixing rule	vapor mole fraction δy_1	δy_2	δy_3	pressure δP/kPa	$\delta P/P$ (%)
	Mean Deviations				
MHV1	0.0064	0.0055	0.0051	0.640	1.08
CHV	0.0073	0.0058	0.0055	0.547	0.93
	Root-Mean-Square Deviations				
MHV1	0.0090	0.0090	0.0072	0.747	1.27
CHV	0.0094	0.0084	0.0075	0.667	1.16

compositions, 0.002 mole fraction; pressure, 0.02 kPa; temperature, 0.05 K.

Results and Discussion

The experimental ternary VLE data for ethanol + TAME + methylcyclohexane are presented in Table 2, and the equilibrium tie lines connecting the liquid and vapor mole fractions are given in Figure 1. Recently developed equation of state mixing rules based on excess Gibbs free energy models have proved to be very useful in correlating and predicting low- and high-pressure VLE data of nonideal mixtures.

In this work, the PRSV equation of state was utilized to represent the VLE data. The equation retains the cubic term in the volume form of the Peng–Robinson[12] equation; namely

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

with

$$a = (0.457235 R^2 T_c^2 / P_c) F(T) \qquad (2)$$

$$b = 0.077796 R T_c / P_c \qquad (3)$$

where

$$F(T) = \{1 + \kappa(1 - T_R^{0.5})\}^2 \qquad (4)$$

In the PRSV equation, the κ parameter is expressed by

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R) \qquad (5)$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \qquad (6)$$

and κ_1 is a constant specific to each pure component. Table 3 shows the values of T_c, P_c, ω, and κ_1 used in this work.

For mixtures, the following MHV1 and CHV mixing rules were investigated for the evaluation of the parameters a and b in eqs 1 and 2.

The MHV1 mixing rule is given by

$$\alpha = \sum_i x_i \alpha_i + (1/q_1)\{(G^E/RT) + \sum_i x_i \ln(b/b_i)\} \qquad (7)$$

$$b = \sum_i x_i b_i \qquad (8)$$

where the parameter a is replaced by the dimensionless parameter $\alpha = a/bRT$, and q_1 is a constant depending on the equation of state. The value of $q_1 = -0.53$ is recommended by Michelsen for the equation.

The CHV mixing rule is given by

$$\alpha = \sum_i x_i \alpha_i + (1/C^*)\{(G^E/RT) + (1 - \delta)\sum_i x_i \ln(b/b_i)\} \qquad (9)$$

where C^* is a constant depending on the equation of state equal to −0.6232, and δ is an empirical parameter. We have used the same value $\delta = 0.36$ as shown by Orbey and Sandler.[5] The b parameter of the mixtures is calculated from eq 8.

In the two mixing rules, the modified UNIQUAC[13] equation was employed to represent G^E.

Optimum binary parameters were obtained from the VLE data reduction for the three binary systems constituting the ternary system by using a computer program based on the maximum likelihood principle as described by Anderson and Prausnitz.[14]

The estimated standard deviations of the measured variables were taken from the literature.[15] Table 4 gives the binary parameters obtained from the modified UNIQUAC equation, and the root-mean-square deviations between the experimental and calculated values for the MHV1 and CHV mixing rules. These binary parameters were used to predict ternary VLE data for the present system without the use of adjustable ternary parameters.

Ternary calculations were performed using the bubble-point pressure calculation suggested by Anderson and Prausnitz.[14] The predicted results agree well with the experimental values as shown in Table 5. The table also indicates that the MHV1 and CHV mixing rules based on the modified UNIQUAC G^E model have similar predictive ability for the ternary system.

Acknowledgment

The authors are grateful to H. Todoriki for the computer work and to Y. Murato for the experimental work.

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Received for review August 9, 2000. Accepted February 8, 2001.

JE000266L