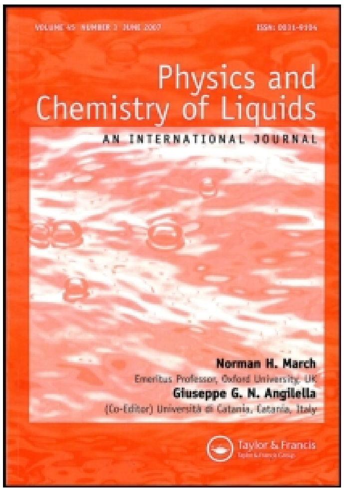

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Vapor-Liquid Equilibria in the Systems Ethyl 1,1-Dimethylethyl Ether Cyclohexane and Benzene at 94.00 kPa

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VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS ETHYL 1,1-DIMETHYLETHYL ETHER + CYCLOHEXANE AND + BENZENE AT 94.00 kPa

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Consistent vapor-liquid equilibria for the binary systems of ETBE with benzene and cyclohexane at 94.00 kPa have been measured. Both systems show slightly positive deviation from ideal behavior and do no present azeotropic behavior. The activity coefficients and boiling points of the solutions were correlated with its mole fractions by the Redlich-Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak -Tamir equations. The data were also compared with UNIFAC predictions.

Keywords: Vapor-liquid equilibrium; fuel oxygenating additive; aromatics; unleaded gasoline; ether; ETBE

0. INTRODUCTION

The last decade has seen a progressive substitution of lead and aromatics octane-enhancers by oxygenates, particularly light alkanols and ethers. The ethers used mostly, methyl 1,1-dimethylethyl ether (MTBE) and ethyl 1,1-dimethylethyl ether (ETBE) have gained particular favor because of their low Reid vapor pressure (Rvp) and the availability of the feedstock ethanol from renewable resources. MTBE is the primary

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*Corresponding author. e-mail: hsegura@diq.udec.cl oxygenated compound being used in reformulated gasolines, but it has the drawback of easily dissolving in water and difficulty to remove from the same. These factors have promoted research on the possible use of ethers of higher molecular weights, less harmful for the environment. ETBE has some important advantages over MTBE like being chemically more similar to hydrocarbons and having a lower solubility in water. The higher boiling point of ETBE allows incorporation of more light feedstocks in gasoline, specifically light cyclic alkanes that are also octane-enhancers. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures.

Vapor-liquid equilibrium data of ETBE in mixture with cyclic alkanes and aromatics are scarce. Particularly, no previously published data have been found for the binary systems considered in this work, which was undertaken to measure vapor-liquid equilibrium (VLE) data for the title systems at 94.00 kPa.

1. EXPERIMENTAL SECTION

1.1. Purity of Materials

Ethyl 1,1-dimethylethyl ether (96.0 + mass%) was purchased from *TCI* (Japan) and was further purified to 99.9 + mass% by distillation in a 1m high × 30 mm diameter Normschliffgerätebau adiabatic column (packed with 3 × 3 mm SS spirals) working at a 1:100 reflux ratio. Cyclohexane (99.73 + mass%) and benzene (99.9 + mass%) were purchased from Aldrich and used without further purification, after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table I. Appropriate precautions were taken when handling ETBE, in order to avoid peroxide formation, and benzene, a human carcinogen.

1.2. Apparatus and Procedure

An all glass vapor-liquid-equilibrium apparatus model 601 manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used

TABLE I Mole% GLC purities (mass%), refractive index n_D at Na D line, and normal boiling points t of pure components

Component (purity/mass %)	n_D (293.15)	T/K
ethyl 1,1-dimethylethyl ether (99.9+)	1.37594[a]	345.85[a]
	1.37564[b]	345.86[c]
benzene (99.9+)	1.50113[a]	353.20[a]
	1.50111[d]	353.21[d]
cyclohexane (99.73)	1.42659[a]	353.84[a]
	1.4261[e]	353.95[f]

[a] Measured.
[b] DIPPR (Daubert and Danner [4]).
[c] Krähenbühl and Gmehling [13].
[d] TRC Tables, a-3200 [14].
[e] Papanastasiou and Ziogas [15].
[f] Willingham *et al.* [6].

in the equilibrium determinations. Concentrations were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a *Tsp* model SP4400 electronic integrator. The experimental equipment and pertinent techniques have been described in a previous work [6]. The chromatographic column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector and detector temperatures were (323.15, 353.15, 473.15) K for both systems. Concentration measurements were accurate to better than ± 0.001 mole fraction.

2. RESULTS AND DISCUSSIONS

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction at 94.00 kPa are reported in Tables II and III and Figures 1 to 4, together with the activity coefficients γ_i that, for the system ETBE (1) + benzene (2), were calculated according to the following relation [1]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \tag{1}$$

In Eq. (1), T and P are the boiling point and the total pressure, P_i^0 is the pure component vapor pressure, V_i^L is the molar liquid volume of

TABLE II Experimental vapor-liquid equilibrium data for ethyl 1, 1-dimethylethyl ether (1) + benzene (2) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$	$-B_{22}$ $/cm^3 \times mol^{-1}$	$-B_{12}$
350.76	0.000	0.000		1.000	1181	988	1069
350.20	0.043	0.060	1.130	1.000	1181	988	1069
349.64	0.083	0.112	1.111	1.003	1186	992	1074
349.42	0.109	0.144	1.100	1.002	1188	994	1075
349.11	0.134	0.176	1.101	1.003	1191	996	1078
348.57	0.181	0.231	1.086	1.007	1196	1000	1082
348.13	0.224	0.279	1.075	1.010	1200	1003	1086
347.79	0.262	0.318	1.057	1.016	1203	1006	1089
347.83	0.260	0.316	1.059	1.014	1203	1005	1088
347.74	0.271	0.326	1.053	1.017	1204	1006	1089
347.36	0.309	0.367	1.049	1.022	1207	1009	1092
346.93	0.360	0.416	1.037	1.030	1211	1012	1096
346.55	0.408	0.463	1.030	1.037	1215	1015	1099
346.17	0.456	0.512	1.031	1.039	1218	1018	1102
345.81	0.502	0.555	1.025	1.048	1222	1020	1105
345.56	0.542	0.592	1.022	1.052	1224	1022	1107
345.24	0.591	0.638	1.020	1.057	1227	1025	1110
344.93	0.646	0.688	1.016	1.063	1230	1027	1112
344.74	0.702	0.738	1.010	1.067	1232	1028	1114
344.48	0.752	0.783	1.008	1.071	1235	1030	1116
344.17	0.809	0.832	1.006	1.085	1238	1033	1119
343.95	0.856	0.873	1.005	1.093	1240	1035	1121
343.62	0.947	0.954	1.003	1.092	1242	1036	1122
343.47	1.000	1.000	1.000		1242	1036	1122

TABLE III Experimental vapor-liquid equilibrium data for ethyl 1,1-dimethylethyl ether (1) + cyclohexane (3) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_3
351.37	0.000	0.000		1.000
351.03	0.022	0.033	1.186	0.999
350.67	0.046	0.067	1.164	0.999
350.38	0.067	0.094	1.131	1.001
350.18	0.081	0.113	1.132	1.001
349.70	0.116	0.159	1.129	1.002
349.18	0.157	0.207	1.103	1.007
348.92	0.177	0.232	1.105	1.007
348.65	0.202	0.259	1.090	1.010
348.28	0.232	0.293	1.086	1.013
347.87	0.271	0.335	1.077	1.017
347.42	0.317	0.381	1.062	1.025
346.98	0.362	0.429	1.061	1.026
346.61	0.409	0.474	1.050	1.033
346.25	0.458	0.520	1.040	1.039
345.90	0.512	0.568	1.027	1.050
345.55	0.556	0.609	1.026	1.057
345.17	0.618	0.664	1.018	1.068
344.84	0.684	0.722	1.011	1.080
344.50	0.749	0.779	1.007	1.093
344.05	0.812	0.834	1.008	1.112
343.89	0.870	0.886	1.005	1.110
343.75	0.903	0.914	1.003	1.127
343.47	1.000	1.000	1.000	

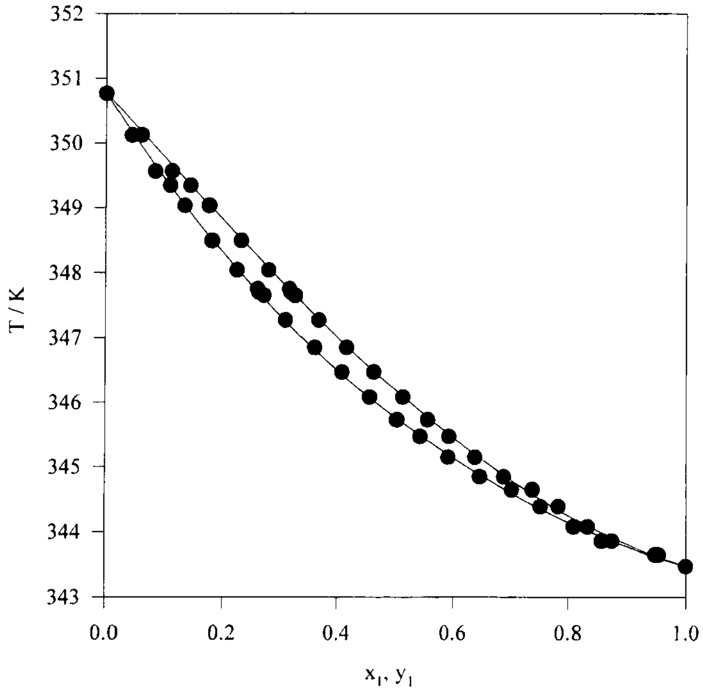

FIGURE 1 Boiling temperature diagram for the system ethyl 1,1-dimethylethyl ether (1) + benzene (2) at 94.00 kPa. Experimental data (●); smoothed with the zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (–).

component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} the cross second virial coefficient and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (1) is valid at low and moderate pressures, when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell [2] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. Liquid volumes were calculated according

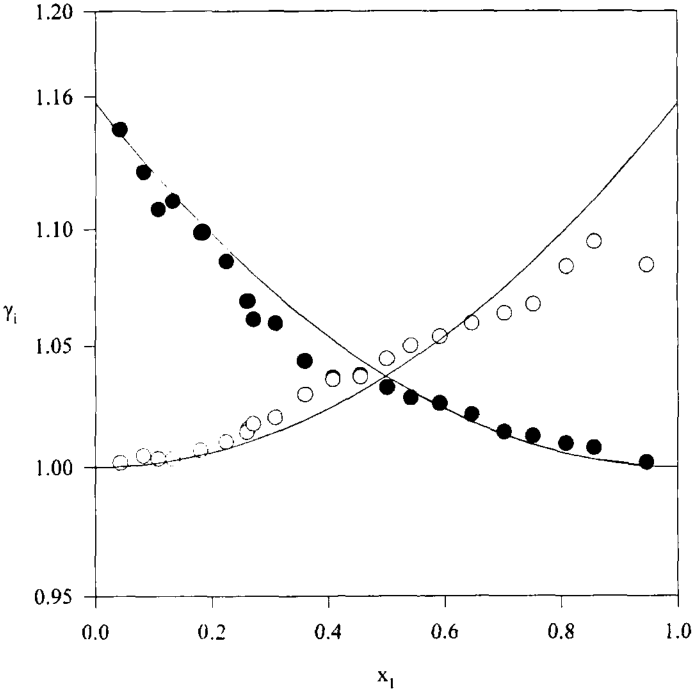

FIGURE 2 Activity coefficient plot for the system ethyl 1,1-dimethylethyl ether (1) + benzene (2) at 94.00 kPa. $\gamma_{1\text{exptl}}$ (•); $\gamma_{2\text{exptl}}$ (o); smoothed with a zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (–).

to the Rackett equation [3]. Physical properties of all components were taken from DIPPR (Daubert and Danner [4]), assuming that the dipolar moments of ETBE and methyl 1,1-dimethylethyl ether (MTBE) are equal. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase, contributed less than 0.4% to the activity coefficients in the binary of ETBE (1) + benzene (2).

For the system ETBE (1) + cyclohexane (3), activity coefficients were calculated from the following relation [1]:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{3}$$

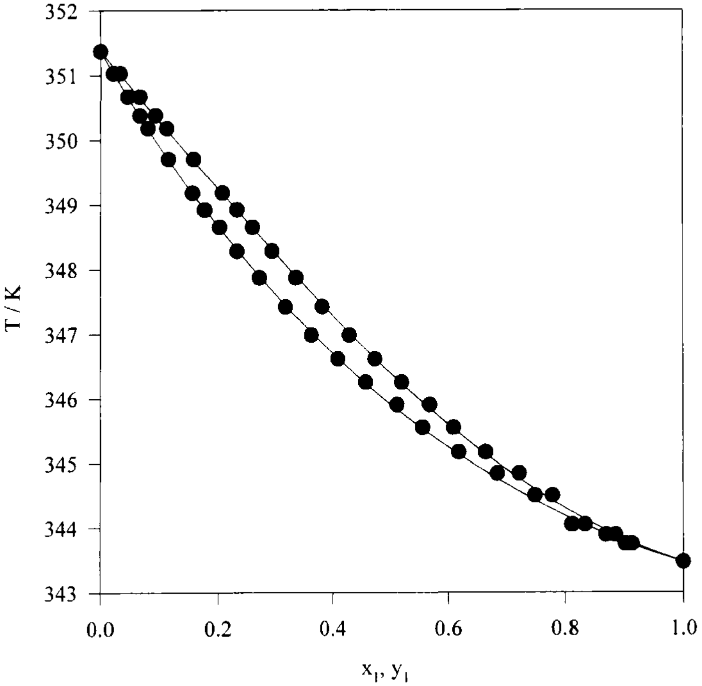

FIGURE 3 Boiling temperature diagram for the system ethyl 1,1-dimethylethyl ether (1) + cyclohexane (3) at 94.00 kPa. Experimental data (•); smoothed with the zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (–).

In Eq. (3) no correction of the vapor and liquid phase fugacities have been considered because the scarce physical information available for mixtures of ETBE and hydrocarbons does not allow a reliable estimation of the second virial coefficient [5]. Equation (3) is a good approximation at low pressures for non-associating mixtures. The pure component vapor pressure P_i^0 of cyclohexane was determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data, and the pertinent results appear in Table IV. The measured vapor pressures for cyclohexane were correlated using the Antoine equation:

$$\log(P_i^0/kPa) = A_i - \frac{B_i}{(T/K) - C_i} \tag{4}$$

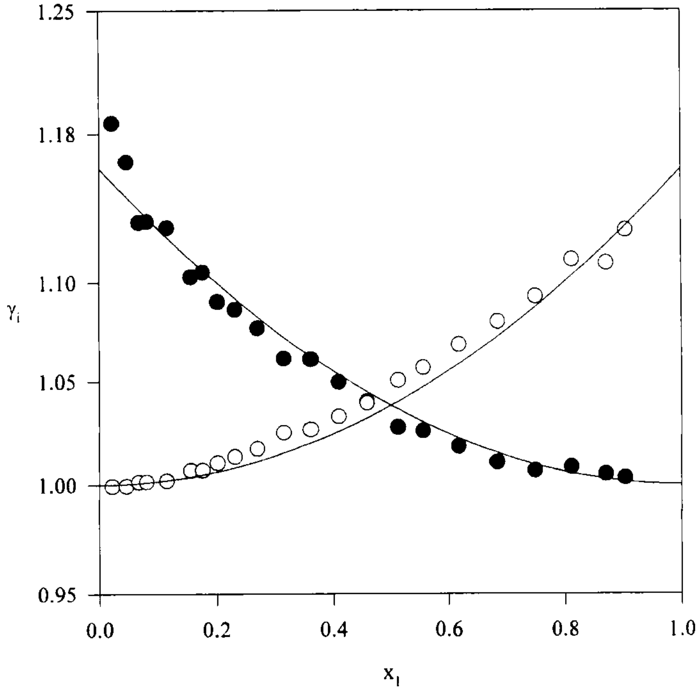

FIGURE 4 Activity coefficient plot for the system ethyl 1,1-dimethylethyl ether (1) + cyclohexane (3) at 94.00 kPa. $\gamma_{1\text{exptl}}$ (•); $\gamma_{3\text{exptl}}$ (○); smoothed with a zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (–).

TABLE IV Experimental vapor pressure data for cyclohexane

T/K	*P/kPa*
316.06	27.63
320.21	32.44
323.69	36.95
327.15	41.95
330.30	46.96
333.20	51.96
335.90	57.02
338.36	61.96
340.66	66.88
342.85	71.82
344.99	76.94
347.00	82.02
348.88	87.04
350.72	92.13
352.42	97.06
353.84	101.33

The Antoine equation was used also for calculating the vapor pressures of ETBE and benzene. The Antoine constants A_i, B_i, and C_i are reported in Table V. Figure 5 shows that the experimental results are in fair agreement those of Willingham *et al.* [6], yielding an average percentual deviation of 0.6%.

The calculated activity coefficients reported in Tables II and III and are estimated accurate to within ±3 % for the system ETBE (1)+

TABLE V Antoine coefficients, Eq. (4)

Compound	A_i	B_i	C_i
ethyl 1,1-dimethylethyl ether[a]	5.96651	1151.73	55.06
benzene[b]	6.08817	1243.26	48.64
cyclohexane[c]	6.06903	1259.10	43.97

[a] Reich *et al.* [5].
[b] Reich *et al.* [16].
[c] Measured in this work.

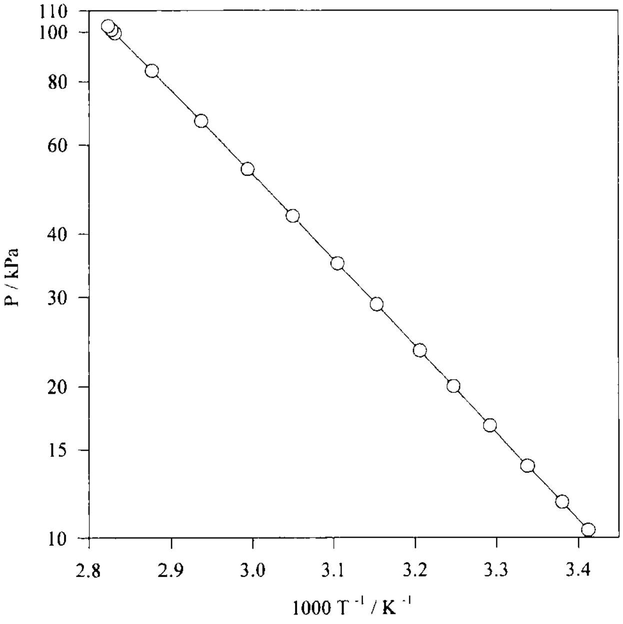

FIGURE 5 Experimental vapor pressures for cyclohexane. Experimental data of Willingham *et al.* (o). Correlation of the experimental data measured in this work, according to Eq. (4) and the parameters given in Table V (–).

benzene (2) and ±2% for the system ETBE (1) + cyclohexane (2). In addition, the results reported in these Tables indicate that both systems exhibit slight positive deviations from ideal behavior and that no azeotrope is present.

The vapor-liquid equilibrium data reported in Tables II and III were found to be thermodynamically consistent by the point-to-point method of Van Ness *et al.* [7], as modified by Fredenslund *et al.* [8]. Consistency criteria ($\Delta y \leq 10^{-2}$) was met using a zeroth-order Legendre polynomial, which is equivalent to the symmetric solution model given by

$$\frac{G^E}{RT} = Ax_1x_2 \tag{5}$$

The pertinent consistency statistics are shown in Table VI. As can be seen in Figures 2 and 4, activity coefficients are quantitatively represented by Eq. (5) that, in addition, gives a consistent correlation of the data.

The activity coefficients were correlated also with the Redlich-Kister, Wohl, Wilson, NRTL, and UNIQUAC equations [9] and compared with those of the modified UNIFAC group contribution method [10]. The following expression was used for the Redlich-Kister [11] expansion

$$\ln(\gamma_i/\gamma_j) = B(x_j - x_i) + C(6x_ix_j - 1) \tag{6}$$

The values of the constants B and C were determined by multilinear regression and appear in Table VIIA together with the pertinent statistics. It is seen that the Redlich-Kister model gives a good

TABLE VI Consistency statistics for a zero-th order Legendre polynomial

System	$100 \times \Delta y^{a}$	$\Delta P^{b}/KPA$	A^{c}
1+2	0.27	0.10	0.146
1+3	0.19	0.12	0.149

[a] Average absolute deviation in vapor phase mole fraction $\Delta y = 1/N \sum_i^N |y_i^{\text{exptal}} - y_i^{\text{calc}}|$. N : number of data points.

[b] Average percentual deviation in bubble pressure $\Delta P = 1/N \sum_i^N |P_i^{\text{exptal}} - P_i^{\text{calc}}|$.

[c] Parameter in Eq. (5).

representation of the data both the systems, with the largest deviations occurring at the dilute end of the components. The parameters of the Wohl, Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^{N} 100 \times \left(\left| \frac{P_i^{\text{exptl}} - P_i^{\text{calc}}}{P_i^{\text{exptl}}} \right| + \left| y_i^{\text{exptl}} - y_i^{\text{calc}} \right| \right) \tag{7}$$

and are reported in Table VIIB, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table VIIB shows that all the models fitted well both systems, the best fit corresponding to the Wilson model for the ETBE + benzene and to the UNIQUAC

TABLE VIIA Parameters and deviations between experimental and calculated values for different G^e models Redlich-Kister, Eq. (6)

System	*B*	*C*	*Bubble-point pressures* $\Delta P^b/\%$	$100 \times \Delta y^a$	*Dew-point pressures* $\Delta P^b/\%$	$100 \times \Delta x^a$
ETBE (1) + benzene (2)	0.146	0.000	0.11	0.27	0.10	0.27
ETBE (1) + cyclohexane (3)	0.149	0.000	0.12	0.19	0.15	0.19

TABLE VIIB Other models

Model	*System* $i+j$	A_{ij}	A_{ji}	q_i/q_j	α_{ij}	*Bubble-point pressures* $\Delta P^a/\%$	$100 \times \Delta y^a$	*Dew-point pressures* $\Delta P^a/\%$	$100 \times \Delta y^a$
Wohl	1 + 2	0.158	0.117	1.312		0.21	0.15	0.21	0.15
	1 + 3	0.171	0.133	1.217		0.14	0.12	0.14	0.11
Wilson[d,c]	1 + 2	242.52	269.36			0.19	0.15	0.19	0.16
	1 + 3	263.49	268.22			0.13	0.11	0.14	0.10
NRTL[c]	1 + 2	92.84	314.46		0.3	0.14	0.22	0.18	0.22
	1 + 3	219.19	225.30		0.3	0.10	0.19	0.12	0.19
UNIQUAC[e,c]	1 + 2	835.77	−668.93			0.21	0.15	0.21	0.15
	1 + 3	−43.04	−254.23			0.09	0.07	0.09	0.07
UNIFAC[f,c]	1 + 2					1.38	0.35	1.33	0.34
	1 + 3					0.70	0.37	0.62	0.35

[a] Average percentual deviation in bubble pressure $\Delta P = 100/N \sum_i^N |P_i^{\text{exptal}} - P_i^{\text{calc}}|/P_i^{\text{exptal}}$ (N: number of data points);

[b] Average absolute deviation in vapor phase mole fraction;

[c] Parameters in J/mol;

[d] Liquid volumes have been estimated from the Rackett equation [3];

[e] Volume and surface parameters calculated from UNIFAC [10];

[f] Original UNIFAC version [10].

TABLE VIII Coefficients in correlation of boiling points, Eq. (8), average deviation and root mean square deviations in temperature, rmsd

System	C_0	C_1	C_2	*max dev*[a]*/K*	*avg dev*[b]*/K*	*rmsd*[c]*/K*
ethyl 1,1-dimethylethyl ether (1) + benzene (2)	− 5.02659	0.98503	0.00000	0.07	0.02	0.03
ethyl 1,1-dimethylethyl ether (2) + cyclohexane (3)	− 5.99687	1.80353	0.00000	0.16	0.02	0.17

[a] Maximum deviation.
[b] Average deviation.
[c] Root mean square deviation.

model for the system and ETBE + cyclohexane. The UNIFAC group contribution method [10] fairly predicts the VLE data and showing the largest deviations, as compared to the other models.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir [12]:

$$T/K = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{8}$$

In this equation T_i^0/K is the boiling point of the pure component i and m are the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of Eq. (8) are reported in Table VIII, which also contains information indicating the degree of goodness of the correlation.

Acknowledgment

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LIST OF SYMBOLS

A_i	Antoine's equation parameter, Eq. (4)
B_i	Antoine's equation parameter, Eq. (4)
B_{ii}	pure component second virial coefficient $\mathrm{cm}^3 \times \mathrm{mol}^{-1}$

B_{ij}	cross second virial coefficient $cm^3 \times mol^{-1}$
C_i	Antoine's equation parameter, Eq. (4); parameters in Eq. (8)
G^E	excess Gibbs energy J/mol
P	absolute pressure kPa
P^o	pure component vapor pressure kPa
R	universal gas constant $J \times mol \times K^{-1}$
T	absolute temperature K
V	volume $cm^3 \times mol^{-1}$
x, y	compositions of the liquid and vapor phases

Greek

δ_{ij}	parameter defined in Eq. (2) $cm^3 \times mol^{-1}$
γ	activity coefficient

Superscripts

E	excess property
L	pertaining to the liquid phase

Subscripts

i,j	component i, j respectively

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