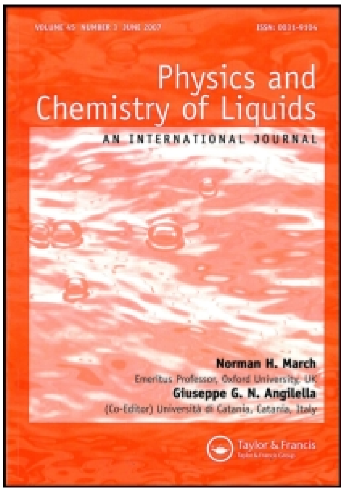

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Isobaric Vapor-Liquid Equilibria in the Systems Ethyl 1,1-Dimethylethyl Ether Hexane and Heptane

Ricardo Reich[a]; Marcela Cartes[a]; Hugo Segura[a]; Jaime Wisniak[b]
[a] Departamento de Ingenieria Quimica, Universidad de Conceptión, Concepción, Chile [b] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

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ISOBARIC VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS ETHYL 1,1-DIMETHYLETHYL ETHER + HEXANE AND + HEPTANE

RICARDO REICH[a,*], MARCELA CARTES[a], HUGO SEGURA[a] and JAIME WISNIAK[b,†]

[a]*Departamento de Ingeniería Quimica, Universidad de Concepción, P.O.B. 53-C, Concepción, Chile;*
[b]*Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105*

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Pure-component vapor pressure of ethyl 1,1-dimethylethyl ether and vapor-liquid equilibrium for the binary systems of ETBE with hexane and with heptane have been measured at 94 kPa. Both systems deviate slightly from ideal behavior, can be described as regular solutions and do no present an azeotrope. The activity coefficients and boiling points of the solutions were correlated with its composition by the Redlich-Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak-Tamir equations.

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

INTRODUCTION

Amendments of the U.S. Clean Air in 1990 have mandated that new gasoline formulations be sold in highly polluted areas of the country, with oxygenated gasolines being supplied particularly during the winter. Most of the oxygenates used in gasolines are alcohols or ethers that contain 1 to 6 carbons. These regulations have caused oxygenates like

*e-mail: rreich@udec.cl
†Corresponding author.

methyl 1,1-dimethylethyl ether (MTBE) and ethanol to play a significant role as octane improvers. MTBE has been used as a gasoline blending agent since 1979, although other oxygenates like ethyl 1,1-dimethylethyl ether (ETBE) and methyl 1,1-dimethylpropyl ether (TAME) are also being considered and used in lesser amounts. ETBE has some important advantages over MTBE like being chemically more similar to hydrocarbons and having a lower solubility in water and solubility of water in ETBE. The higher boiling point of ETBE allows incorporation of more light feedstocks in gasoline. In addition, ETBE has a Reid vapor pressure (Rvp) of 27.6 kPa, one half of that of MTBE, making it an attractive oxygenate for gasolines having a low vapor pressure. 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 alkanes are scarce, only limiting activity coefficients γ_i^∞ for ETBE with hexane at 333.15 K and for ETBE with heptane at 348.15 K have been measured by Delcros *et al.* [1], using the comparative ebulliometry technique. According to their results, the systems under consideration deviate slightly from ideal behavior, when concentrated in alkane, yielding γ_i^∞ in the range $1.10 \sim 1.11$. According to Delcros *et al.* their results compared very well with those predicted by the DISQUAC [2], [3] and the UNIFAC Dortmund group contribution [4] methods. The fact that the values of γ_i^∞ for of both components are very similar suggest that the behavior of the almost-ideal liquid phase can be represented by a symmetric regular or Porter model [5], although there is not enough experimental information to support this conclusion.

The present work was undertaken to measure vapor–liquid equilibrium (VLE) data for the title systems at 94 kPa, for which isobaric data are not available or are incomplete. It is part of our experimental program to determine the phase equilibria of oxygenates and main gasoline components.

1. EXPERIMENTAL SECTION

1.1. Purity of Materials

ETBE (96.0+mass%) was purchased from *TCI* (Japan) and was further purified to 99.9 + mass% by distillation in a 1-m high × 30 mm

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 (298.15)	T/K
Hexane (99.73)	1.3730[a]	341.84[a]
	1.37226[b]	341.89[c]
Ethyl 1,1-dimethylethyl ether (99.9+)	1.3730[a]	345.85[a]
	1.3729[d]	345.86[e]
Heptane (99.57)	1.3851[a]	371.54[a]
	1.38511[f]	371.57[g]

[a] Measured; [b] TRC Tables, fa-1010 [19]; [c] TRC Tables, k1440 [19]; [d] DIPPR [10]; [e] Krähenbühl and Gmehling [13]; [f] TRC Tables, fa-1460 [19]; [g] TRC Tables, k-1460 [19].

diameter Normschiffgerätebau adiabatic column (packed with 3 × 3 mm SS spirals) working at a 1:100 reflux ratio. Hexane (99.73 + mass%) and heptane (99.57 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.

1.2. Apparatus and Procedure

An all glass vapor-liquid-equilibrium apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used 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 publication [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 kPa are reported in Tables II and III and Figures 1 to 4,

TABLE II Experimental vapor–liquid equilibrium data for hexane (1)+ethyl 1,1-dimethylethyl ether (2) at 94 kpa

T/K	x_1	y_1	γ_1	γ_2
343.47	0.000	0.000	–	1.000
342.74	0.064	0.079	1.115	1.007
342.30	0.124	0.149	1.104	1.008
342.07	0.165	0.195	1.091	1.008
341.73	0.218	0.253	1.080	1.011
341.45	0.268	0.306	1.073	1.012
341.19	0.319	0.358	1.063	1.015
340.92	0.378	0.417	1.056	1.017
340.82	0.405	0.444	1.050	1.019
340.60	0.459	0.495	1.043	1.023
340.45	0.499	0.533	1.036	1.028
340.33	0.531	0.564	1.034	1.030
340.17	0.580	0.609	1.028	1.035
340.10	0.607	0.633	1.025	1.040
340.05	0.624	0.649	1.023	1.042
339.90	0.674	0.695	1.019	1.048
339.83	0.707	0.726	1.016	1.053
339.79	0.725	0.742	1.015	1.056
339.71	0.759	0.773	1.012	1.063
339.63	0.804	0.814	1.009	1.073
339.59	0.826	0.835	1.008	1.079
339.55	0.866	0,872	1.006	1.084
339.48	0.929	0.932	1.004	1.096
339.47	0.977	0.978	1.002	1.107
339.47	0.967	0.968	1.002	1.107
339.47	0.950	0.952	1.003	1.106
339.46	1.000	1.000	1.000	–

together with the activity coefficients γ_i that were calculated from the following ideal vapor phase relation [7]:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{1}$$

where T and P are the boiling point and the total pressure and P_i^0 is the pure component vapor pressure. In Eq. (1) no correction of the vapor and liquid phase fugacities have been considered because, in one hand, the low pressure makes this assumption reasonable and, on the other hand, the scarce physical information available for mixtures of ETBE does not allow a reliable estimation of the second virial coefficient. A similar discussion has been pointed out by Arce *et al.* [8] for TAME in their VLE atmospheric measurements of ether and alcohol

TABLE III Experimental vapor-liquid equilibrium data for ethyl 1,1-dimethylethyl ether (2) + heptane (3) at 94 kpa

T/K	x_2	y_2	γ_2	γ_3
369.02	0.000	0.000	–	1.000
366.43	0.059	0.129	1.121	1.000
365.01	0.085	0.182	1.126	1.010
364.19	0.114	0.237	1.119	0.997
360.99	0.199	0.370	1.098	1.006
359.42	0.249	0.436	1.082	1.009
358.02	0.295	0.492	1.073	1.012
356.65	0.340	0.544	1.070	1.015
355.42	0.385	0.591	1.063	1.018
353.09	0.483	0.683	1.050	1.013
352.43	0.519	0.710	1.038	1.016
351.58	0.559	0.739	1.028	1.026
350.67	0.604	0.769	1.017	1.045
348.61	0.700	0.835	1.016	1.053
347.69	0.749	0.866	1.012	1.061
346.54	0.813	0.902	1.008	1.075
345.69	0.858	0.928	1.008	1.079
344.90	0.905	0.952	1.006	1.100
343.95	0.959	0.980	1.006	1.119
343.47	1.000	1.000	1.000	–

mixtures. As shown by Figures 2 and 4, the mixtures under consideration in this work are almost ideal, so that activity coefficients become very sensitive to vapor phase corrections. In order to illustrate this important point, the activity coefficient plot of the system ETBE (2) + heptane (3) is shown Figure 5 when using the rigorous relation [7]:

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

In Eq. (2) V_i^L is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} the cross second virial coefficient and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{3}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation (2) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the

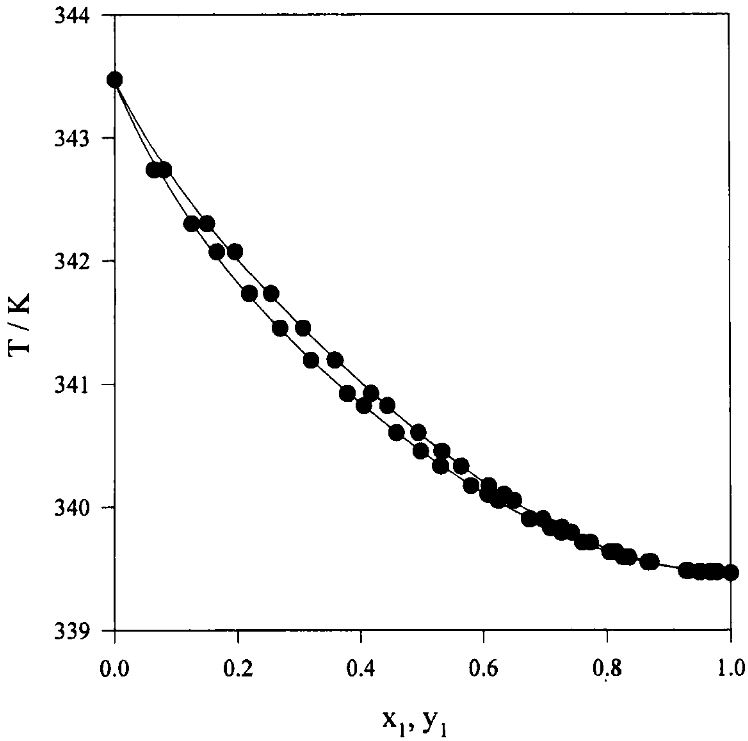

FIGURE 1 Boiling temperature diagram for the system hexane (1) + ethyl 1,1-dimethylethyl ether (2) at 94 kPa. Experimental data (•); smoothed with the zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (—).

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 [9] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. Physical properties of all components were taken from DIPPR [10], assuming that the dipolar moments of ETBE and MTBE are equal. The last two terms in Eq. (2), particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase, contributed less than 2% to the activity coefficients in the binary system heptane (2) + ETBE. Comparison of Figures 2 and 5, indicates the large sensitivity of the

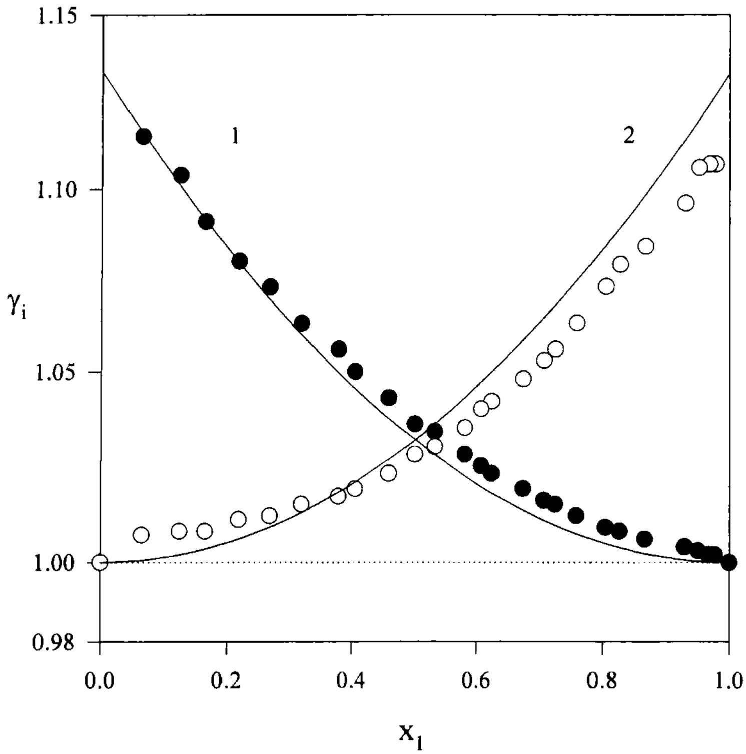

FIGURE 2 Activity coefficient plot for the system hexane(1) + ethyl 1,1-dimethylethyl ether (2) at 94 kPa. γ_{1exptl} (•); γ_{2exptl} (o); smoothed with a zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (—).

data to the correct prediction of the second virial coefficients, no reasonable fit of the activity coefficients is achieved when using Legendre polynomials of different degrees [11]. Similar conclusions were achieved when using correlations for the second virial coefficients other than that of Hayden and O'Connel, or when comparing data for the hexane (1) + ETBE (2) system reported here and the data for the 2-methylpentane + ETBE system at 101.3 kPa reported by Aucejo *et al.* [12]. The data treatment reported in this work is based in the ideal vapor phase relation given by Eq. (1), which yields a more reasonable behavior of activity coefficients.

The pure component vapor pressure P_i^0 of ETBE was determined experimentally as a function of the temperature, using the same

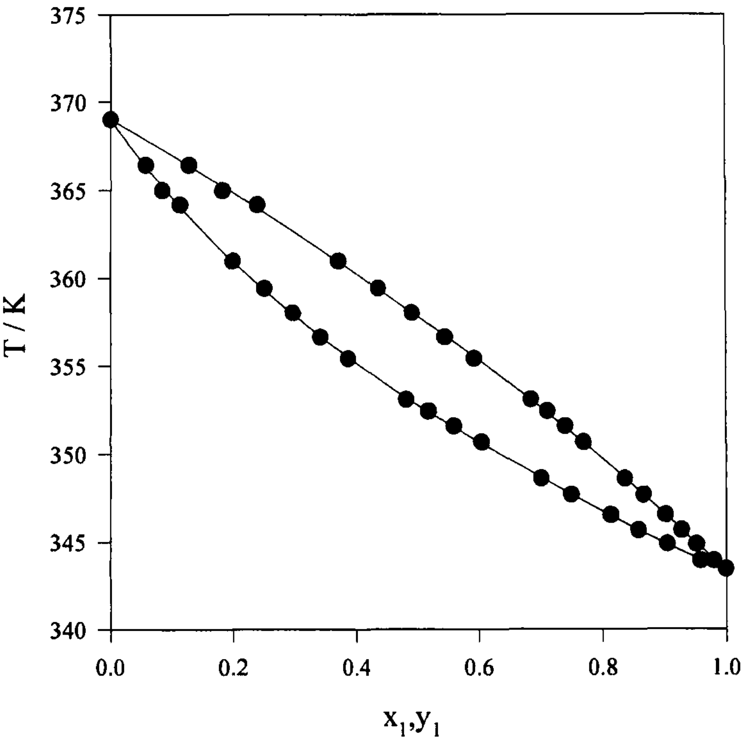

FIGURE 3 Boiling temperature diagram for the system ethyl 1, 1-dimethylethyl ether (2)+heptane (3) at 94 kPa. Experimental data (•); smoothed with the zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (—).

equipment as that for obtaining the VLE data, and the pertinent results appear in Table IV. The measured vapor pressures for ETBE were correlated using the Antoine equation:

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

A relation of the same algebraic structure was used for calculating the vapor pressures of hexane and heptane. The Antoine constants A_i, B_i, and C_i are reported in Table V. Figure 6 shows that our experimental results are in excellent agreement those of Krähenbühl and Gmehling [13], yielding an average percentual deviation of 0.4%. The calculated activity coefficients reported in Tables II and III and are estimated

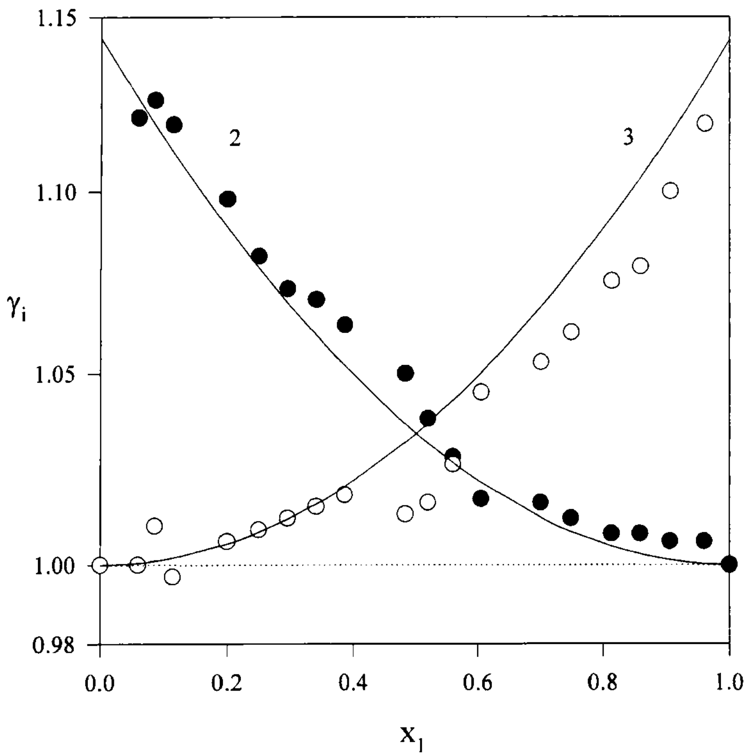

FIGURE 4 Activity coefficient plot for the system ethyl 1,1-dimethylethyl ether (2) + heptane (3) at 94 kPa. γ_{2exptl} (•); γ_{3exptl} (○); smoothed with a zeroth-order Legendre polynomial [symmetric regular model, Eq. (5)] (—).

accurate to within ± 3%. In addition, the results reported in these Tables indicate that both systems exhibit small positive deviations from ideal behavior and that no azeotrope is present.

The vapor-liquid equilibria data reported in Tables II and III were found to be thermodynamically consistent by the point-to-point method of Van Ness *et al.* [14] as modified by Fredenslund *et al.* [11]. Consistency criteria ($\Delta y \leq 10^{-2}$) was met using a zeroth-order Legendre polynomial, which is equivalent to the symmetric regular solution model given by

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

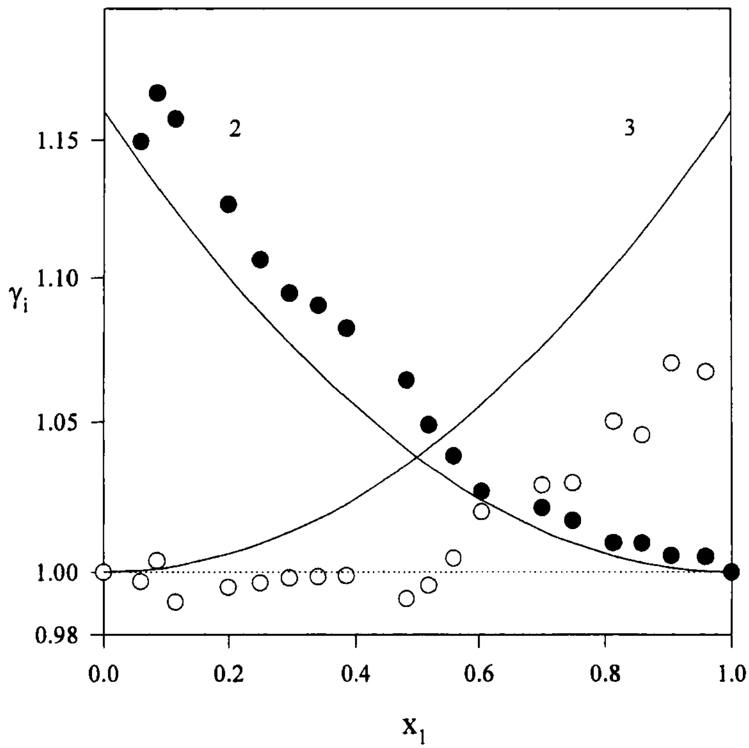

FIGURE 5 Activity coefficient plot for the system ethyl 1,1-dimethylethyl ether (2) + heptane (3) at 94 kPa including vapor phase correction. $\gamma_{2\text{exptl}}$ (•); $\gamma_{3\text{exptl}}$ (○); smoothed with a zeroth-order Legendre polynomial which gives consistency to the data [Eq. (5)] (—).

The pertinent consistency statistics are shown in Table VI. As can be seen in Figures 2 and 4, activity coefficients are well correlated by Eq. (5), which gives a consistent correlation of the data. In addition, the extrapolated limiting activity coefficients of ETBE are in fair agreement with the values of $\gamma_2^\infty = 1.11$ for the system hexane (1) + ETBE (2) at 333.15 K and $\gamma_2^\infty = 1.10$ for the system ETBE (2) + heptane (3) at 348.15 K, as measured by Delcros *et al.* [1]. Previously mentioned considerations allow to conclude that both systems considered in this work behave like regular solutions.

The activity coefficients were correlated with the Redlich-Kister, Wohl, Wilson, NRTL and UNIQUAC equations [15] and compared

TABLE IV Experimental vapor pressure data for ethyl 1,1-dimethylethyl ether

T/K	P/kPa
307.05	24.915
309.84	27.945
312.39	30.965
314.72	33.955
316.91	36.965
320.23	41.955
323.32	47.055
325.98	52.045
328.59	57.055
331.04	62.135
333.29	67.125
335.42	72.135
337.36	77.155
339.29	82.185
341.12	87.205
342.86	92.205
344.53	97.225
345.85	101.325

TABLE V Antoine coefficients, Eq. (4)

Compound	A_i	B_i	C_i
Hexane[a]	6.00091	1171.170	48.740
Ethyl 1,1-dimethylethyl ether[b]	5.96651	1151.728	55.062
Heptane[c]	6.02167	1264.900	56.610

[a] TRC Tables, k-1440 [19]; [b] Measured in this work; [c] TRC Tables, k-1460 [19].

with those of the modified UNIFAC group contribution method [16]. The following expression was used for the Redlich-Kister [17] 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 VII.A together with the pertinent statistics. It is seen that the Redlich-Kister model gives a good 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

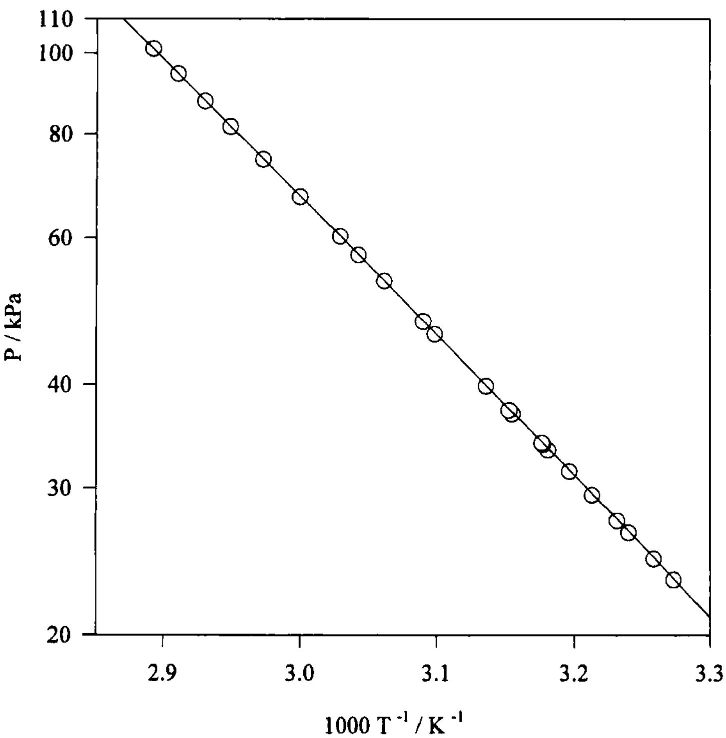

FIGURE 6 Vapor pressures for ethyl 1,1-dimethylethyl ether. Experimental data of Krähenbühl and Gmehling [13] (o). Correlation of the experimental data measured in this work, according to Eq. (4) and the parameters shown in Table V (—).

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

System	$100 \times \Delta y^{a}$	$\Delta P^{b}/kPa$	A^{c}	$\gamma_2^{\infty d}$
1 + 2	0.18	0.17	0.125	1.133
2 + 3	0.29	0.21	0.134	1.144

[a] Average absolute deviation in vapor phase composition $\Delta y = 1/N \sum_i^N |y_i^{\mathrm{exptal}} - y_i^{\mathrm{calc}}|$. N: number of data points; [b] Average percentual deviation in bubble pressure $\Delta P = 1/N \sum_i^N |P_i^{\mathrm{exptal}} - P_i^{\mathrm{calc}}|$; [c] Parameter in Eq. (5). [d] Limiting activity coefficient of ETBE, predicted by Eq. (5).

minimizing the following objective function (OF):

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

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

System	*B*	*C*	*Bubble-point pressures*		*Dew-point pressures*	
			$\Delta P^a/\%$	$100\times\Delta y^b$	$\Delta P^b/\%$	$100\times\Delta x^a$
Hexane (1) + ETBE (2)	0.125	0.000	0.46	0.11	0.46	0.11
ETBE (2) + heptane (3)	0.134	0.000	0.60	0.32	0.42	0.39

B. Other Models[d]

Model	*System*	A_{ij}	A_{ji}	q_i/q_j	α_{ij}	*Bubble-point pressures*		*Dew-point pressures*	
	$i+j$	$J\times mol^{-1}$	$J\times mol^{-1}$			$\Delta P^a/\%$	$100\times\Delta y^b$	$\Delta P^a/\%$	$100\times\Delta y^b$
Wohl	1 + 2	0.1330	0.1404	0.9080		0.26	0.18	0.27	0.18
	2 + 3	0.1268	0.1963	0.6512		0.37	0.22	0.42	0.30
[d]Wilson	1 + 2	33.11[c]	371.25[c]			0.28	0.17	0.29	0.17
	2 + 3	−594.04[c]	1266.91[c]			0.38	0.22	0.42	0.31
NRTL	1 + 2	275.14[c]	79.86[c]		0.3	0.12	0.20	0.12	0.22
	2 + 3	776.74[c]	−331.17[c]		0.3	0.29	0.19	0.38	0.24
[e]UNIQUAC	1 + 2	−744.49[c]	972.11[c]			0.20	0.30	0.20	0.30
	2 + 3	646.86[c]	−489.27[c]			0.25	0.30	0.40	0.40
[f]UNIFAC	1 + 2					2.79	1.28	2.64	1.31
	2 + 3					2.96	1.32	2.79	1.44

[a] Average percentual deviation in bubble pressure $\Delta P = 100/N\sum_i^N |P_i^{exptal} - P_i^{calc}|/P_i^{exptal}$ (N: number of data points);
[b] Average absolute deviation in vapor phase composition;
[c] Parameters in J/mol;
[d] Liquid volumes have been estimated from the Rackett equation [20];
[e] Volume and surface parameters calculated from UNIFAC [16];
[f] Original UNIFAC version [16].

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*
Hexane(1) + ethyl 1,1-dimethylethyl ether (2)	−3.85	0.97	−1.05	0.05	0.02	0.004
Ethyl 1,1-dimethylethyl ether (2) + heptane (3)	−13.41	5.73	−2.94	0.21	0.77	0.022

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

and are reported in Table VII.B, together with the pertinent statistics of VLE interpolation. Inspection of the results given in Table VII.B shows that all the models fitted well both systems, the best fit corresponding to the NRTL model for the hexane + ETBE system and ETBE + heptane system. The UNIFAC group contribution method [16] yields a fair prediction of the VLE data and shows the largest deviations, when compared to the other models.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir [18]:

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

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 $cm^3 \times mol^{-1}$
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. (3) $cm^3 \times mol^{-1}$
γ = activity coefficient

Superscripts

∞ = at infinite dilution
E = excess property
L = pertaining to the liquid phase

Subscripts

i, j = component i, j respectively

References

[1] Delcros, S., Grolier, J.-P. E., Dohnal, V. and Fenclová, D. (1995). *Chem. Engng. Sci.*, **50**, 2957.
[2] Kehiaian, H. V. (1983). *Fluid Phase Equilibria*, **13**, 243.
[3] Kehiaian, H. V. (1985). *Pure Applied Chem.*, **57**, 15.
[4] Weidlich, U. and Gmehling, J. (1987). *Ind. Eng. Chem. Res.*, **26**, 1372.
[5] Prigogine, I. (1957). *The Molecular Theory of Solutions* (North-Holland. Amsterdam Pub. Co.: Netherlands), pp. 53–58.

[6] Reich, R., Cartes, M., Wisniak, J. and Segura, H. (1998). *J. Chem. Eng. Data*, **43**, 299.
[7] Van Ness, H. C. and Abbott, M. M. (1982). *Classical Thermodynamics of Nonelectrolyte Solutions* (McGraw-Hill Book Co., New York, USA).
[8] Arce, A., Martinez-Ageitos, J. and Soto, A. (1996). *J. Chem. Eng. Data*, **41**, 718.
[9] Hayden, J. and O'Connell, J. (1975). *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209.
[10] Daubert, T. E. and Danner, R. P. (1989). *Physical and Thermodynamics Properties of Pure Chemicals. Data Compilation* (Taylor and Francis. Bristol, PA. England).
[11] Fredenslund, Aa., Gmehling, J. and Rasmussen, P. (1977). *Vapor–Liquid Equilibria Using UNIFAC. A Group Contribution Method* (Elsevier, Amsterdam, Netherlands), pp. 68–74.
[12] Aucejo, A., Loras, S., Muñoz, R., Reich, R. and Segura, H. (1998). *J. Chem. Eng. Data*, Accepted for publication.
[13] Krähenbühl, M. A. and Gmehling, J. (1994). *J. Chem. Eng. Data*, **39**, 759.
[14] Van Ness, H. C., Byer, S. M. and Gibbs, R. E. (1973). *AIChE J.*, **19**, 238.
[15] Walas, S. M. (1985). *Phase Equilibria in Chemical Engineering* (Butterworth Publishers, Boston. USA).
[16] Hansen, H. K., Rasmussen, P., Fredenslund, Aa., Schiller, M. and Gmehling, J. (1991). *Ind. Eng. Chem. Res.*, **30**, 2355.
[17] Redlich, O. and Kister, A. T. (1948). *Ind. Eng. Chem.*, **40**, 345.
[18] Wisniak, J. and Tamir, A. (1976). *Chem. Engng. Sci.*, **31**, 631.
[19] TRC-Thermodynamic Tables-Non-Hydrocarbons. Thermodynamics Research Center. (The Texas A & M University System, College Station, Texas Loose-leaf data sheets, extant 1974).
[20] Rackett, H. G. (1970). *J. Chem. Eng. Data*, **15**, 514.