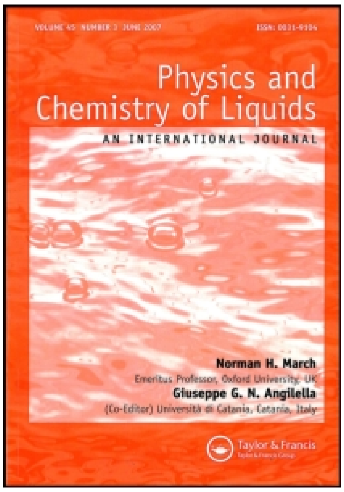

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Segura, Hugo , Lam, Elizabeth , Reich, Ricardo and Wisniak, Jaime(2001) 'Isobaric Phase Equilibria in the Binary Systems Ethyl 1,1-Dimethylethyl Ether 1-hexene and Cyclohexene at 94.00 kPa', Physics and Chemistry of Liquids, 39: 1, 43 — 54

To link to this Article: DOI: 10.1080/00319100108030325

URL: http://dx.doi.org/10.1080/00319100108030325

Phys. Chem. Liq., 2001, Vol. 39, pp. 43-54
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ISOBARIC PHASE EQUILIBRIA IN THE BINARY SYSTEMS ETHYL 1,1-DIMETHYLETHYL ETHER + 1-HEXENE AND + CYCLOHEXENE AT 94.00 kPa

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(Received 11 November 1999)

Consistent vapor-liquid equilibrium has been determined for the binary systems 1-hexene + ethyl 1,1-dimethylethyl ether (ETBE) and ethyl 1,1-dimethylethyl ether + cyclohexene at 94.00 kPa. The two systems present slight positive deviations from ideal behavior, can be considered to behave like regular solutions and do not present azeotropic behavior. Pure component vapor pressures are also reported for 1-hexene and cyclohexene. The phase equilibrium of the systems was correlated well by the Wilson, UNIQUAC, and NRTL models and reasonably predicted by the UNIFAC group contribution method. The boiling points of the binary systems were correlated with the Wisniak-Tamir equation.

Keywords: Vapor-liquid equilibrium; Fuel oxygenating additive; Ethers; ETBE

Ether based oxygenates are used for reducing toxic emissions from gasoline combustion, and its use is being stimulated by the official energy programs of many countries. 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

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pressure (Rvp) and the availability of the feedstock ethanol from renewable resources. Phase equilibria data of ether oxygenates and hydrocarbon mixtures are important, since the vapor phase concentration is a key quality index in gasoline blending. Scarce physical properties have been determined for mixtures that contain ETBE + alkenes and, according to a recent review by Marsh *et al.* [1], no VLE data has been presented for the two binaries reported here.

This work was undertaken to measure the VLE of the title systems and is part of our program to determine vapor–liquid equilibria (VLE) in systems formed by oxygenates and gasoline components.

EXPERIMENTAL SECTION

Purity of Materials

Ethyl 1,1-dimethylethyl ether (96 + mass %) was purchased from *TCI* (Japan). 1-Hexene (99 mass%) and cyclohexene (97 mass%) were purchased from *Aldrich*. All the reagents were purified to 99 + mass% by distillation using a 1 m high × 30 mm diameter Normschliff-gerätebau adiabatic distillation column (packed with 3 × 3 mm SS spirals) working at a 1 : 100 reflux ratio. 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.

Apparatus and Procedure

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

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

	n_D(293.15)		T_b(101.33 *kPa*)/*K*	
Component (*purity*/*mass*%)	*exptl*	*lit*	*exptl*	*lit*
1-Hexene (99.8 +)	1.38308[a]	1.3837[b]	336.60[a]	336.64[c]
Ethyl 1,1-dimethylethyl ether (99.9 +)	1.37594[a]	1.37564[d]	345.85[a]	345.86[e]
Cyclohexene (99.8 +)	1.44686[a]	1.4465[b]	356.07[a]	356.09[c]

[a] Measured; [b] CRC. [11]; [c] Boublik *et al.* [12]; [d] DIPPR (Daubert and Danner [13]); [e] Krähenbühl and Gmehling [14].

used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a 250 W immersion heater. The vapor – liquid mixture flows through an extended contact line (Cottrell pump) that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still has been determined with a Systemteknik S1224 digital temperature meter, and a Pt 100 Ω probe calibrated at the Swedish Statens Provningsanstält on the IPTS-68. The accuracy is estimated as ± 0.02 K. The total pressure of the system is controlled by a vacuum pump capable of work under vacuum up to 0.25 kPa. The pressure has been measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22 mm diameter precision tubing with cathetometer reading), the overall accuracy is estimated as ± 0.03 kPa. On the average the system reaches equilibrium conditions after 2 – 3 h operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a *Thermo Separation Products* model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector and detector temperatures were (323.15, 383.15, 473.15) K respectively, for both systems. Good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. At least three analyses were made of each composition. Concentration measurements were accurate to better than ± 0.001 mole fraction.

RESULTS

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94.00$ kPa are reported in Tables II and III and Figures 1 – 4, together with the activity coefficients γ_i

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

T/K	x_2	y_2	γ_2	γ_3
343.47	0.000	0.000		1.000
342.51	0.073	0.098	1.026	1.004
342.02	0.118	0.154	1.025	1.004
341.35	0.181	0.231	1.022	1.005
340.84	0.230	0.288	1.020	1.005
340.37	0.277	0.342	1.018	1.006
339.86	0.326	0.396	1.017	1.007
339.38	0.377	0.450	1.015	1.007
338.93	0.427	0.502	1.014	1.007
338.54	0.467	0.542	1.013	1.008
338.08	0.519	0.592	1.010	1.010
337.63	0.571	0.642	1.009	1.011
337.21	0.622	0.689	1.009	1.009
336.85	0.665	0.727	1.006	1.013
336.42	0.718	0.773	1.005	1.015
336.00	0.772	0.818	1.002	1.020
335.67	0.814	0.853	1.002	1.018
335.24	0.868	0.897	1.002	1.018
334.89	0.914	0.934	1.001	1.020
334.53	0.964	0.973	1.000	1.029
334.27	1.000	1.000	1.000	

TABLE III Experimental vapor–liquid equilibrium data for ethyl 1,1-dimethylethyl ether (2) + cyclohexene (3) at 94.00 kPa

T/K	x_2	y_2	γ_2	γ_3
353.59	0.000	0.000		1.000
353.00	0.038	0.056	1.098	0.999
352.24	0.087	0.124	1.087	1.000
351.40	0.147	0.199	1.058	1.005
351.11	0.168	0.226	1.061	1.004
350.49	0.213	0.280	1.057	1.007
350.01	0.252	0.323	1.045	1.011
349.42	0.298	0.374	1.042	1.015
348.85	0.349	0.427	1.034	1.020
348.38	0.391	0.470	1.031	1.023
347.66	0.448	0.527	1.031	1.031
347.30	0.497	0.572	1.020	1.035
346.75	0.551	0.622	1.018	1.042
346.38	0.582	0.651	1.020	1.046
345.95	0.669	0.726	1.003	1.052
345.43	0.726	0.775	1.003	1.061
345.07	0.776	0.817	1.001	1.068
344.71	0.817	0.852	1.003	1.069
344.36	0.869	0.894	1.000	1.082
344.01	0.913	0.930	1.001	1.088
343.71	0.958	0.966	1.001	1.106
343.47	1.000	1.000	1.000	

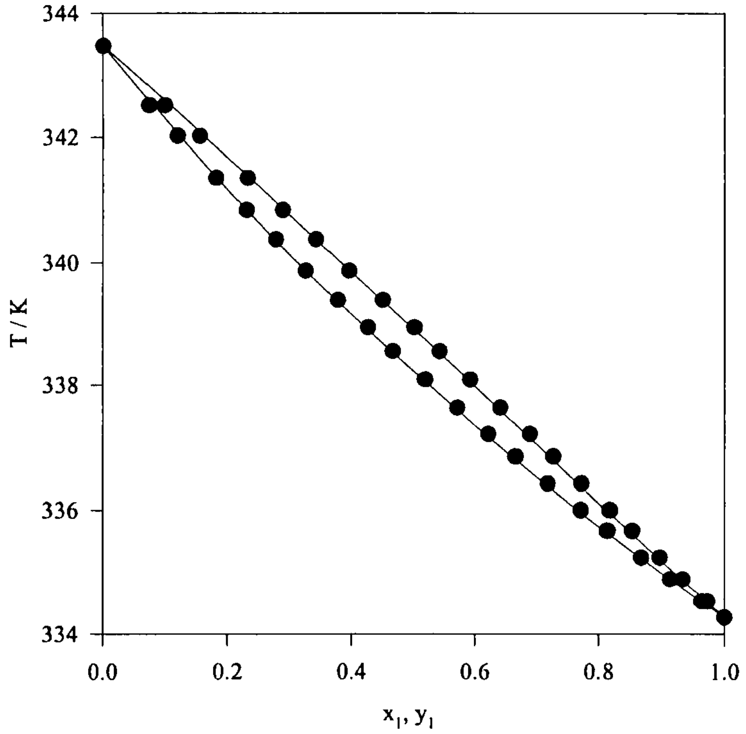

FIGURE 1 Experimental data for the system 1-hexene (1) + ETBE (2) at 94.00 kPa. Experimental data (●). Smoothed data using the regular model, Eq. (3), with the *A* parameter given in Table VI (—).

that were calculated from the following equation [2]

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

In Eq. (1) 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 [3]. Equation (1) is a good approximation at low pressures for non associating mixtures. The pure component vapor pressures P_i^0 of 1-hexene and cyclohexene were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table IV. The measured vapor pressures were

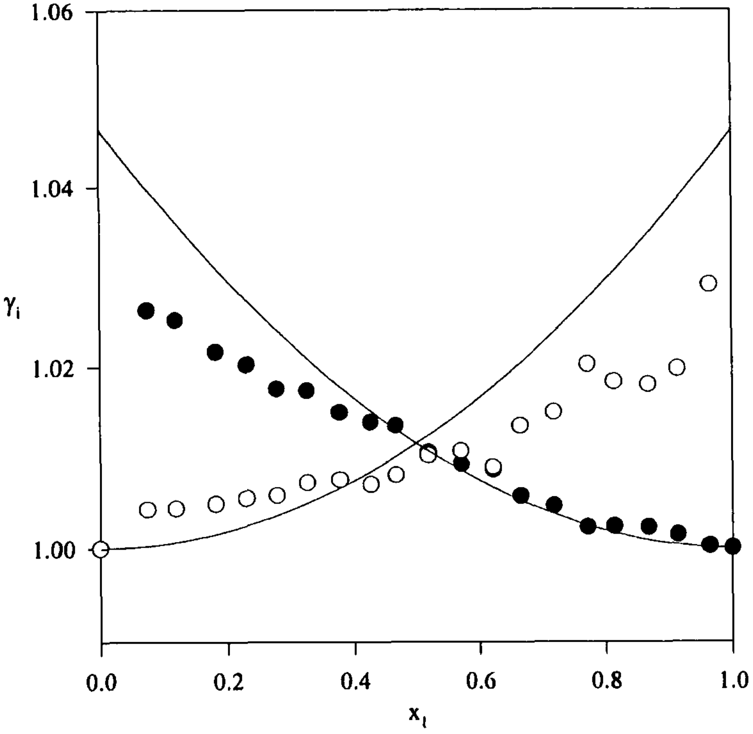

FIGURE 2 Activity coefficient plot of the system 1-hexene (1) + ETBE (2) at 94.00 kPa. Experimental data (●, ○). Smoothed data using the regular model, Eq. (3), with the *A* parameter given in Table VI (—).

correlated using the Antoine equation:

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/K) - C_i} \tag{2}$$

where the Antoine constants A_i, B_i and C_i are reported in Table V. Figure 5 shows that our experimental vapor pressure results are in excellent agreement with the data reported by Camin *et al.* [4] for 1-hexene and the data of Forziati *et al.* [5] for cyclohexene, with an average percentile deviation of 0.1 and 0.2% respectively. The pure component vapor pressure P_i^0 for ETBE was calculated from Eq. (2) using the parameters given by Reich *et al.* [3]. The calculated activity coefficients are reported in Tables II and III and are estimated accurate

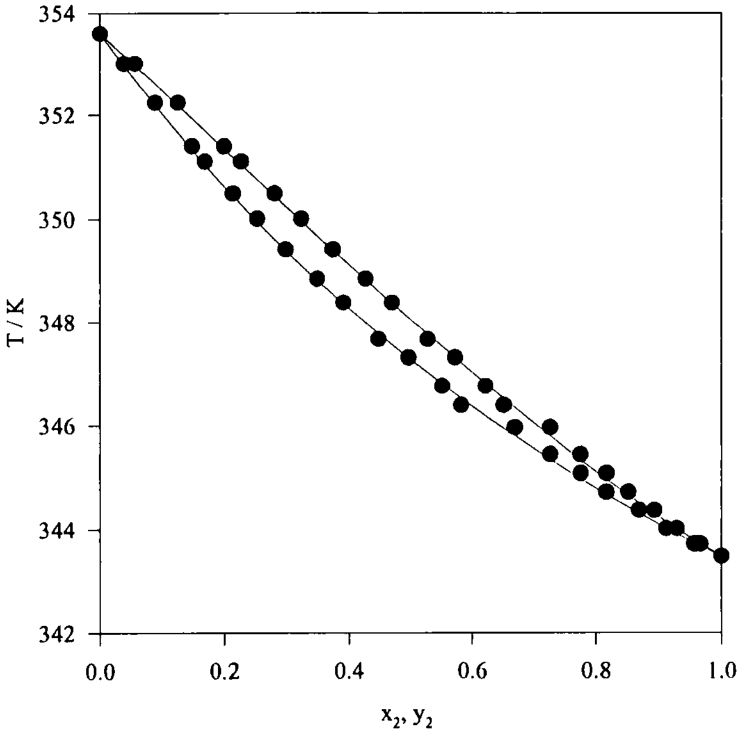

FIGURE 3 Experimental data for the system ETBE (2) + cyclohexene (3) at 94.00 kPa. Experimental data (●). Smoothed data using the regular model, Eq. (3), with the *A* parameter given in Table VI (—).

to within ± 3%. The results reported in these tables indicate that the binary systems show small 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.* [6] as modified by Fredenslund *et al.* [7]. For the two sets of data, Fredenslund's test consistency criteria was met using a one parameter Legendre polynomial, or symmetric model, which reduces the functionality of the excess Gibbs energy G^E to the following relation

$$G^E = Ax_1x_2 \tag{3}$$

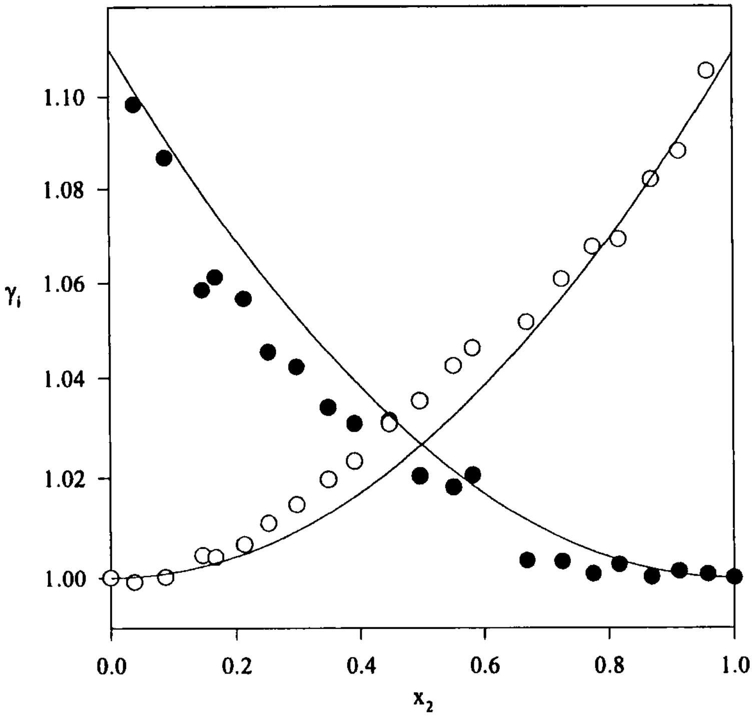

FIGURE 4 Activity coefficient plot of the system ETBE (2) + cyclohexene (3) at 94.00 kPa. Experimental data (•, ○). Smoothed data using the regular model, Eq. (3), with the *A* parameter given in Table VI (—).

TABLE IV Experimental vapor pressures for 1-hexene and cyclohexene

1-*Hexene*		*Cyclohexene*	
T/K	*P/kPa*	*T/K*	*P/kPa*
336.60	101.33	356.07	101.33
334.27	94.01	353.60	94.00
332.60	89.00	349.97	84.10
330.83	83.97	347.94	78.90
329.00	78.99	345.91	73.93
327.05	73.98	343.53	68.45
324.98	68.94	340.99	62.93
322.62	63.49	338.61	58.06
320.06	58.00	335.91	52.96
317.54	52.97	333.07	47.98
314.85	47.98	329.96	42.97
311.63	42.52	326.49	37.87
308.36	37.49	322.67	32.86
304.69	32.43	317.98	27.46
300.54	27.36	312.49	22.06

TABLE V Antoine coefficients, Eq. (2)

Compound	A_i	B_i	C_i
1-Hexene[a]	6.06006	1189.666	43.18
Ethyl 1,1-dimethylethyl ether[b]	5.96651	1151.730	55.06
Cyclohexene[a]	6.00690	1227.513	49.28

[a] Fitted from the data presented in Table IV;
[b] Reich *et al.* [3].

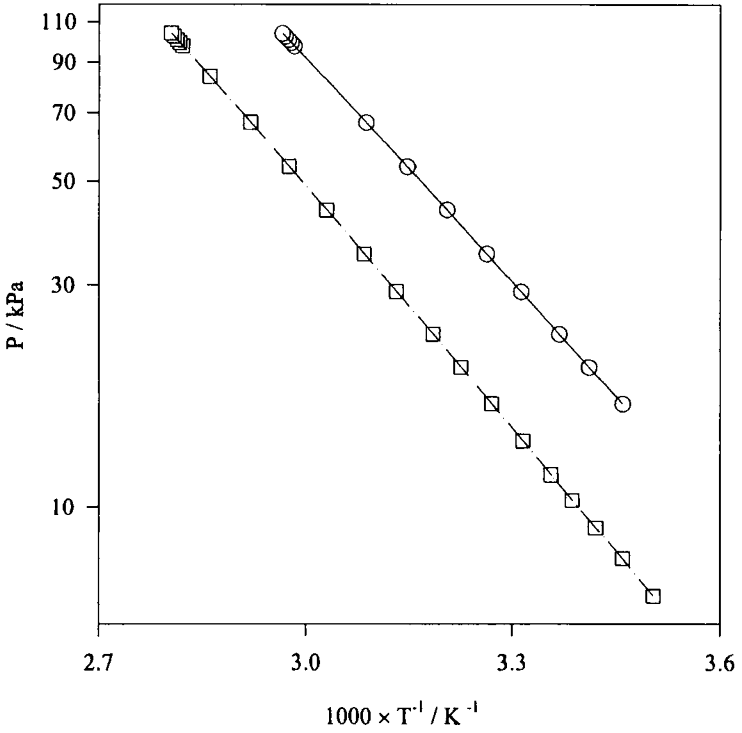

FIGURE 5 Pure component vapor pressures. Experimental data of Camin and Rossini *et al.* [4] for 1-hexene (o). Correlation of the experimental data measured in this work, according to Eq. (3) and the parameters shown in Table V (—) for 1-hexene. Experimental data of Forziati *et al.* [5] for cyclohexene (□). Correlation of the experimental data measured in this work, according to Eq. (3) and the parameters shown in Table V (– • –) for cyclohexene.

Pertinent statistics, besides the parameter A in Eq. (3) for each binary system, are presented in Table VI. Table VI and Figures 1–4 show that Eq. (3) gives a fair representation of the data of the systems and,

TABLE VI Consistency test statistics for the binary systems 1-hexene (1) + ETBE (2) and ETBE (2) + cyclohexene (3)

System	A[a]	$100 \times \Delta y$[b]	ΔP[c]$/kPa$
1+2	0.045	0.13	0.09
2+3	0.104	0.21	0.17

[a] Zeroth order Legendre polynomial (or Porter model) parameter in Eq. (3).

[b] Average absolute deviation in vapor phase mole fractions $\Delta y = 1/N \sum_{i=1}^{N} |y_1^{\text{exptl}} - y_1^{\text{calc}}|$ (N: number of data points).

[c] Average absolute deviation in pressure $\Delta P = 1/N \sum_{i=1}^{N} |P^{\text{exptl}} - P^{\text{calc}}|$.

that according to it, the three binaries may be assumed to behave like symmetric regular solutions.

The activity coefficients of the systems were correlated well with the NRTL, Wilson, and UNIQUAC equations [8]. Pertinent parameters were obtained by minimizing the following objective function (OF)

$$OF = 100 \times \left(\sum_{i=1}^{N} \left| y_{1,i}^{\text{exptl}} - y_{1,i}^{\text{calc}} \right| + \left| \frac{P_i^{\text{exptl}} - P_i^{\text{calc}}}{P_i^{\text{exptl}}} \right| \right) \tag{4}$$

and are reported in Table VII, together with the relative deviation of equilibrium pressures and mole fractions. Inspection of the results given in Table VII shows that these models fitted the binaries reasonable well, the NRTL model being the best. The capability for correlating equilibrium properties has been used as the ranking factor. Table VII also includes the prediction based on the UNIFAC group contribution method (Fredenslund *et al.* [7], Hansen *et al.* [9]), which results less accurate than the other models.

The boiling points of the two binaries were correlated by the equation proposed by Wisniak and Tamir [10]

$$T/K = x_i T_i^0 + x_j T_j^0 + x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \tag{5}$$

In this equation T_i^0/K is the boiling point of the pure component i at the operating pressure and m is the number of terms in the series expansion of $(x_i - x_j)$. The various constants of Eq. (5) are reported in Table VIII, which also contains information indicating the degree of goodness of the correlation.

TABLE VII Parameters and prediction statistics for different G^E models

					Bubble-point pressures			*Dew-point pressures*		
Model	*ij*	A_{ij}	A_{ji}	α_{ij}	$\Delta P(\%)^a$	$100 \times \Delta y_1$	$100 \times \Delta y_2$	$\Delta P(\%)$	$100 \times \Delta x_1$	$100 \times \Delta x_2$
NRTL[a]	1–2	−1139.22	1433.47	0.30	0.05	0.1	0.1	0.05	0.1	0.1
	2–3	−1166.02	1656.74	0.30	0.21	0.1	–	0.21	0.1	–
Wilson[a,b]	1–2	−78.13	208.22		0.12	0.1	0.1	0.13	0.1	0.1
	2–3	330.43	133.82		0.21	0.1	–	0.21	0.1	–
UNIQUAC[a,c]	1–2	−146.16	175.08		0.11	0.1	0.1	0.12	0.1	0.1
	2–3	−205.27	236.19		0.20	0.1	–	0.20	0.1	–
UNIFAC[d]	1–2				3.44	1.3	1.3	3.24	1.4	1.4
	2–3				3.00	1.2	–	2.76	1.2	–

[a] Parameters in J mol^{-1}; [b] Liquid volumes have been estimated from the Rackett equation [15]; [c] Molecular parameters are those calculated from UNIFAC; [d] Calculations based on original UNIFAC (Fredenslund *et al.* [7]; Hansen *et al.* [9]); [e] $\Delta P = 100/N \sum_i^N |P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$.

TABLE VIII Coefficients and statistics in correlation of boiling points, Eq. (5)

System	C_0	C_1	C_2	*Avrg dev/K*	*Max dev/K*	*Std dev/K*
1+2	−2.436	0.785	−0.502	0.01	0.05	0.01
2+3	−5.139	1.349	0.911	0.04	0.14	0.04

Acknowledgment

Graciela Galindo helped in the experimental part. This work was partially financed by FONDECYT, Chile, project No. 1990402. E. Lam was sponsored by CONICYT, Chile.

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