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# PHASE EQUILIBRIA IN THE SYSTEMS 1-HEXENE + HEPTANE AND 1-HEXENE + ETHYL 1,1-DIMETHYLETHYL ETHER + HEPTANE AT 94.00 kPa

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Consistent vapor-liquid equilibrium data at 94.00 kPa have been determined for the ternary system 1-hexene + ethyl 1,1-dimethylethyl ether + heptane and for its constituent binary 1-hexene + heptane, in the temperature range 334 to 369 K. According to the experimental results the ternary system 1-hexene + ethyl 1,1-dimethylethyl ether + heptane exhibits moderate positive deviations from ideal behavior. The binary system 1-hexene + heptane exhibits slight negative deviations from ideal behavior. None of the systems present an azeotrope. The vapor liquid equilibrium data have been correlated with the mole fraction using the Redlich-Kister, Wilson, NRTL, UNIQUAC, and Tamir relations. These models, in addition to UNIFAC, allow good prediction of the VLE properties of the ternary system from those of the pertinent binary systems.

**Keywords:** Vapor-Liquid equilibrium; Fuel oxygenating additive; Unleaded gasoline; Ether; ETBE

## INTRODUCTION

The use of reformulated gasoline is now required in those areas of the U.S. with the most severe ozone air pollution. To achieve this goal

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gasolines are modified by the addition of oxygenates such as MTBE or ethanol. These additives enhance combustion, reduce the emissions that cause ground level ozone problems, and reduce air toxic emissions. MTBE is the primary oxygenated compound being but it has the drawbacks of easily dissolving in water and of difficult removal from water. These drawbacks are behind the recent decision of the state of California to phase out its use within the next years. New additives such as ETBE are being investigated as possible replacements. ETBE shows good characteristics for unleaded gasoline formulation including low volatility, high-octane value, and low water solubility.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase concentration that would be in equilibrium with gasoline mixtures. Although aromatics such as benzene may be present in small concentrations in typical gasolines, they represent fundamental examples of mixtures of ethers with an aromatic compound. In addition, alkenes are unstable and are limited to low volume percentages, but they are used in gasoline blending to improve octane ratings.

Vapor-liquid equilibrium (VLE) data for the binary systems 1-hexene + ETBE and ETBE + heptane have been reported at 94 kPa by Segura *et al.* [1] and by Reich *et al.* [2]. These two binaries exhibit slight to moderate positive deviations from ideal behavior and do not present azeotropes. To the best of our knowledge, no VLE data have been reported for the binary system 1-hexene + heptane. The present work was undertaken to measure VLE data for the system 1-hexene + ETBE + heptane and for its constituent binary 1-hexene + heptane at 94 kPa, for which isobaric data have not been determined.

## EXPERIMENTAL SECTION

### Materials

ETBE (96.0+mass %) was purchased from TCI (*Tokyo Chemical Industry Co. Ltd.*, Japan) and 1-hexene (99.0 mass %) and heptane (99.6 mass %) were purchased from Aldrich. 1-hexene and ETBE were further purified to more than 99.7+mass % by rectification in a 1-m height – 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with  $3 \times 3$  mm stainless steel spirals), working at a

TABLE I Mole % 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 K)		$T_b(101.3 \text{ kPa})/K$	
	<i>exptl.</i>	<i>lit.</i>	<i>exptl.</i>	<i>lit.</i>
1-hexene (99.7 +)	1.38806 <sup>a</sup>	1.38788 <sup>b</sup>	336.61 <sup>a</sup>	336.635 <sup>b</sup>
ethyl 1,1-dimethylethyl ether (99.9 +)	1.37594 <sup>a</sup>	1.37564 <sup>c</sup>	345.85 <sup>a</sup>	345.86 <sup>d</sup>
heptane (99.6 +)	1.38818 <sup>a</sup>	1.38764 <sup>e</sup>	371.46 <sup>a</sup>	371.57 <sup>f</sup>

<sup>a</sup> Measured.

<sup>b</sup> TRC Tables a-2630 [15].

<sup>c</sup> DIPPR (Daubert and Danner [16]).

<sup>d</sup> Krähenbühl and Gmehling [17].

<sup>e</sup> TRC Tables, fa-1460 [15].

<sup>f</sup> TRC Tables, k-1460 [15].

1:100 reflux ratio. After this step, gas chromatography failed to show any significant impurity. The properties and purity (as determined by gas liquid chromatography) 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 used in the equilibrium determinations. Concentrations 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 experimental equipment and pertinent techniques are described in detail in a previous work [2]. The overall accuracy in temperature and pressure measurements are estimated as  $\pm 0.02$  K and  $\pm 0.03$  kPa, respectively. 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, 383.15, 473.15) K for both systems. Concentration measurements were accurate to better than  $\pm 0.001$  mole fraction.

### RESULTS AND DISCUSSION

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

**TABLE II** Experimental vapor-liquid equilibrium data for the binary system 1-hexene (1) + heptane (3) at 94.00 kPa

$T/K$	$x_1$	$y_1$	$\gamma_1$	$\gamma_3$
368.94	0.000	0.000		1.000
365.72	0.059	0.149	1.004	0.998
363.49	0.102	0.242	1.001	0.997
361.06	0.155	0.337	0.984	1.000
359.12	0.195	0.407	0.997	0.998
357.32	0.237	0.470	0.995	0.997
355.67	0.278	0.523	0.988	1.001
353.64	0.328	0.585	0.991	1.000
351.24	0.394	0.653	0.989	1.003
349.88	0.431	0.689	0.990	1.004
347.90	0.490	0.740	0.991	1.003
346.07	0.545	0.787	1.001	0.979
344.38	0.600	0.821	0.997	0.997
343.19	0.641	0.847	0.999	0.987
341.75	0.692	0.875	0.999	0.991
340.50	0.740	0.898	0.997	0.996
339.36	0.783	0.919	0.998	0.992
337.89	0.844	0.944	0.997	1.001
336.73	0.891	0.963	0.999	0.989
335.54	0.944	0.982	0.998	0.993
334.59	0.986	0.996	0.999	1.018
334.27	1.000	1.000	1.000	

**TABLE III** Experimental vapor-liquid equilibrium data for the ternary system 1-hexene (1) + ETBE (2) + heptane (3) at 94.00 kPa

$T/K$	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$
336.76	0.829	0.095	0.896	0.078	0.998	1.022	0.995
337.46	0.792	0.106	0.874	0.089	0.997	1.022	1.027
338.15	0.798	0.054	0.900	0.047	0.996	1.031	1.002
338.31	0.693	0.202	0.787	0.174	0.998	1.019	1.037
339.36	0.578	0.312	0.680	0.277	1.001	1.012	1.053
340.11	0.681	0.112	0.816	0.103	0.996	1.027	1.007
340.29	0.480	0.406	0.581	0.373	1.001	1.017	1.046
341.03	0.580	0.210	0.715	0.200	0.996	1.029	1.021
341.10	0.381	0.509	0.475	0.478	1.006	1.015	1.046
342.00	0.291	0.599	0.373	0.578	1.007	1.011	1.069
342.05	0.484	0.299	0.614	0.293	0.994	1.023	1.036
342.74	0.583	0.111	0.756	0.112	0.994	1.039	1.010
342.76	0.382	0.413	0.498	0.412	0.998	1.020	1.036
343.29	0.184	0.700	0.246	0.700	1.008	1.005	1.075
343.84	0.288	0.497	0.389	0.511	1.000	1.017	1.053
344.12	0.096	0.790	0.132	0.812	1.014	1.008	1.091
344.13	0.469	0.208	0.634	0.220	0.993	1.035	1.014
344.55	0.384	0.312	0.527	0.333	0.994	1.030	1.021
344.70	0.047	0.845	0.066	0.881	1.018	1.003	1.073
345.18	0.183	0.592	0.258	0.634	1.003	1.014	1.042

TABLE III (Continued)

$T/K$	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$
345.78	0.288	0.394	0.410	0.435	0.995	1.025	1.033
345.95	0.094	0.685	0.137	0.752	1.012	1.015	1.056
346.01	0.094	0.683	0.137	0.753	1.014	1.017	1.037
346.20	0.463	0.115	0.666	0.131	0.993	1.040	1.007
346.66	0.379	0.215	0.553	0.247	0.994	1.039	1.011
346.99	0.185	0.498	0.272	0.567	0.992	1.018	1.035
347.81	0.283	0.300	0.429	0.358	0.997	1.039	1.010
347.93	0.048	0.660	0.073	0.771	1.005	1.015	1.046
347.96	0.094	0.581	0.144	0.684	1.007	1.023	1.037
348.75	0.188	0.401	0.292	0.488	0.995	1.032	1.020
349.18	0.374	0.111	0.585	0.140	0.990	1.055	1.003
350.10	0.092	0.481	0.149	0.611	1.000	1.034	1.022
350.13	0.279	0.202	0.452	0.263	0.998	1.057	0.999
350.80	0.189	0.307	0.313	0.403	0.995	1.044	1.007
351.87	0.048	0.472	0.083	0.631	1.001	1.031	1.024
352.45	0.088	0.382	0.154	0.530	1.010	1.051	1.003
352.69	0.270	0.112	0.472	0.159	0.998	1.065	0.998
353.30	0.184	0.210	0.329	0.303	1.003	1.064	0.996
354.88	0.087	0.292	0.161	0.438	1.001	1.056	1.002
356.16	0.183	0.110	0.351	0.174	0.995	1.073	1.001
357.13	0.049	0.265	0.097	0.425	0.996	1.056	1.008
357.71	0.085	0.192	0.172	0.319	1.004	1.080	0.997
360.69	0.082	0.103	0.180	0.189	1.006	1.097	0.997
364.27	0.042	0.056	0.105	0.117	1.032	1.126	0.995

and in Figure 1, together with the activity coefficients  $\gamma_i$  that were calculated from the following equation [3]:

$$\gamma_i = \frac{Py_i}{P_i^0 x_i} \quad (1)$$

where  $P$  is the total pressure and  $P_i^0$  is the pure component vapor pressure. In Eq. (1) the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid phase fugacity is neglected. Equation (1) was selected to calculate activity coefficients because the low pressures observed in the present VLE data makes these simplifications reasonable. In addition, and as discussed by Reich *et al.* [2] and by Aucejo *et al.* [4], the scarce physical information available for mixtures of ETBE with hydrocarbons does not allow a reliable estimation of second virial coefficients, thus introducing uncertainty in the estimation of vapor phase corrections.

Pure component vapor pressures for 1-hexene and ETBE were taken from the works of Segura *et al.* [1] and Reich *et al.* [2], respectively.

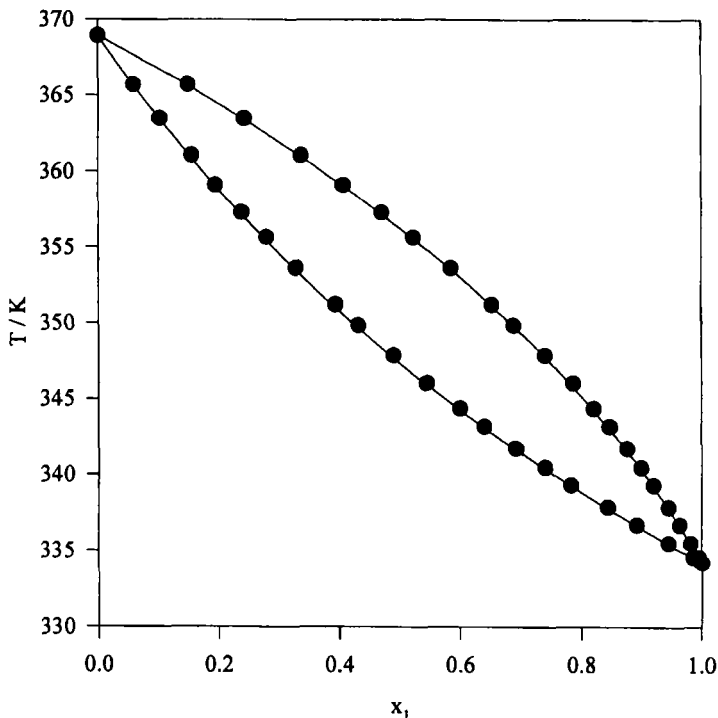


FIGURE 1 Experimental data for the system 1-hexene (1) + heptane (3) at 94.00 kPa: (●), experimental data reported in this work; (—) smoothed data using the regular model, Eq. (3), with the  $A$  parameter given in Table VI.

The vapor pressure of heptane was 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. Vapor pressures were correlated using the Antoine equation:

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

where the Antoine constants  $A_i$ ,  $B_i$ , and  $C_i$  are reported in Table V. The vapor pressure data of heptane were correlated by Eq. (2) with an absolute percentual deviation (MADP) of 0.01%. The parameters presented in Table V for heptane predict very well the experimental data reported by Forziati *et al.* [5] (MADP = 0.34%), as confirmed by Figure 2.

TABLE IV Experimental vapor pressure data for heptane

$T/K$	$P/kPa$
329.91	24.77
334.70	29.75
339.04	34.95
343.12	40.48
346.79	46.02
350.29	51.88
353.15	57.11
355.94	62.59
358.52	68.04
360.83	73.21
363.07	78.56
365.13	83.73
367.21	89.21
368.94	94.01
371.46	101.33

TABLE V Antoine coefficients, Eq. (2)

compound	$A_i$	$B_i$	$C_i$
1-hexene <sup>a</sup>	6.06006	1189.666	43.18
ETBE <sup>b</sup>	5.96651	1151.730	55.06
heptane <sup>c</sup>	6.15883	1343.977	47.85

<sup>a</sup> Segura *et al.* [1].

<sup>b</sup> Reich *et al.* [2].

<sup>c</sup> Calculated from the vapor pressure data presented in Table IV.

The activity coefficients presented in Tables II and III are estimated accurate to within  $\pm 2\%$ . It is seen that the binary system 1-hexene + heptane exhibits slight negative deviations from ideal behavior and that no azeotrope is present. The ternary system 1-hexene + ETBE + heptane exhibits moderate positive deviations from ideal behavior and no azeotrope is present.

The VLE data reported in Table II for the binary system 1-hexene (1) + heptane (3) were found to be thermodynamically consistent by the point-to-point test of Van Ness *et al.* [6], as modified by Fredenslund *et al.* [7]. Consistency criteria ( $\Delta y \leq 0.01$ ) was met using a one parameter Legendre polynomial, which reduces the functionality of the excess Gibbs energy  $G^E$  to the following relation

$$G^E = Ax_1x_2 \quad (3)$$



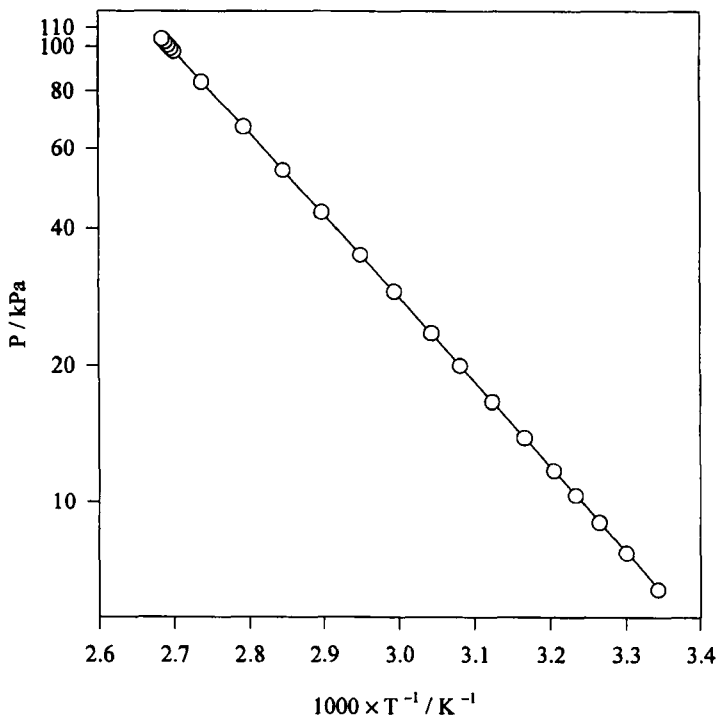


FIGURE 2 Comparison of correlated vapor pressures with other references: (o) experimental data reported by Forziati *et al.* [5] for heptane; (—) predicted by Eq. (2) and parameters in Table V for heptane.

Equation (3) is equivalent to the symmetric Porter equation [8]. Table VI presents the value of parameter  $A$  and the pertinent deviations. The statistics show that Eq. (3) gives a very good fit of the data.

TABLE VI Deviation statistics for the binary system 1-hexene (1) + heptane (3), as predicted from Raoult's Law

$A^a$	$100 \times \Delta y^b$	$\Delta P^c / kPa$
-0.017	0.1	0.1

<sup>a</sup> Parameter for the Legendre polynomial in Eq. (3).

<sup>b</sup> Average absolute deviation in vapor phase mole fractions  $\Delta y = 1/N \sum_{i=1}^N |y_i^{exp} - y_i^{calc}|$  ( $N$ : number of data points).

<sup>c</sup> Average absolute deviation in pressure  $\Delta P = 1/N \sum_{i=1}^N |p_i^{exp} - p_i^{calc}|$ .

In addition, the residual plot presented in Figure 3 shows a reasonable distribution of residuals.

The vapor-liquid equilibrium data reported in Table III for the ternary system 1-hexene + ETBE (1) + heptane (3) were found to be thermodynamically consistent by the McDermott – Ellis method [9], as modified by Wisniak and Tamir [10]. According to these references, two experimental points *a* and *b* are considered thermodynamically consistent if the following condition is fulfilled

$$D < D_{\max} \tag{4}$$

where the local deviation *D* is given by

$$D = \sum_{i=1}^N (x_{ia} - x_{ib}) \times (\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{5}$$

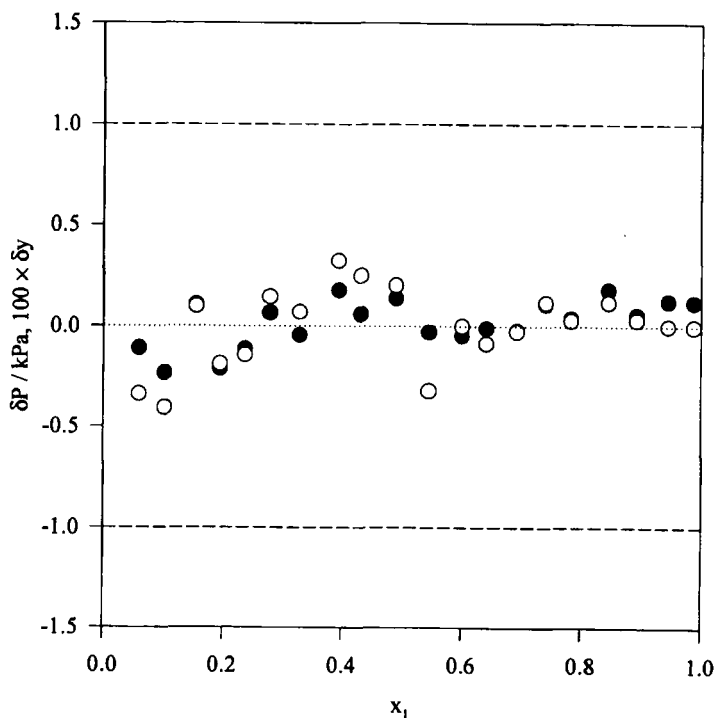


FIGURE 3 Residuals of consistency analysis for the system 1-hexene (1) + heptane (3) at 94.00 kPa: (o), vapor phase mole fraction residuals  $100 \times \delta y$ ; (●) vapor pressure residuals  $\delta P/kPa$ .

and  $N$  is the number of components. The maximum deviation  $D_{\max}$  is given by

$$\begin{aligned}
 D_{\max} = & \sum_{i=1}^N (x_{ia} + x_{ib}) \left( \frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x \\
 & + \sum_{i=1}^N (x_{ia} + x_{ib}) \frac{\Delta P}{P} + 2 \sum_{i=1}^N |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x \\
 & + \sum_{i=1}^N (x_{ia} + x_{ib}) B_j \{ (T_a + C_j)^{-2} + (T_b + C_j)^{-2} \} \Delta T \quad (6)
 \end{aligned}$$

The errors in the measurements  $\Delta x$ ,  $\Delta P$  and  $\Delta T$  were as previously indicated. The first term in Eq. (6) was the dominant one. For the experimental points reported here  $D$  never exceeded 0.018 while the smallest value of  $D_{\max}$  was 0.022.

The activity coefficients for the ternary system were correlated with the Redlich-Kister expansion [11]

$$\begin{aligned}
 \frac{G^E}{RT} = & \sum_{i=1}^3 \sum_{j>i}^3 x_i x_j [b_{ij} + c_{ij}(x_i - x_j) \\
 & + d_{ij}(x_i - x_j)^2] + x_1 x_2 x_3 [C + D_1 x_1 + D_2 x_2] \quad (7)
 \end{aligned}$$

where  $b_{ij}$ ,  $c_{ij}$  and  $d_{ij}$  are the constants for the pertinent  $ij$  binary, and  $C$ ,  $D_1$ , and  $D_2$  are ternary constants. All the constants in Eq. (7) are assumed to be independent of the temperature. Data and constants for the binary system 1-hexene (1) + ETBE (2) and ETBE (2) + heptane (3) have been calculated from the data reported by Segura *et al.* [1] and Reich *et al.* [2]. The Redlich-Kister coefficients for the binaries 1-hexene (1) + heptane (3) and the values of the constants  $C$ ,  $D_1$ , and  $D_2$  for the ternary mixture, were obtained by a Simplex optimization technique; the results are shown in Table VII. Analysis of the correlation indicated that the ternary constants  $C$ ,  $D_1$ , and  $D_2$  were not statistically significant, suggesting that the ternary data can be predicted directly from the binary systems. In fact, activity coefficients and equilibrium vapor pressures of the ternary system were predicted very well by the Redlich-Kister equation when using only the binary constants, as shown in Table VII, where  $C$ ,  $D_1$ , and  $D_2$  are zero. Equilibrium vapor pressures and VLE mole fractions were also well predicted for the ternary system using the NRTL, Wilson, and UNIQUAC models [12]) but somewhat worse by the UNIFAC model [7,13] using

TABLE VII Constants for the Redlich-Kister Model, fit, correlation and prediction Statistics

Binary data						
System	$b_{ij} \times 10^1$	$c_{ij}, d_{ij}$	$rmsd^a \times 10^2$	%dev <sup>b</sup>	max%dev <sup>c</sup>	
1-hexene (1) + ETBE (2) <sup>d</sup>	0.45	0.00	0.9	0.5	3.6	
1-hexene (1) + heptane (3)	-0.17	0.00	0.7	0.5	2.3	
ETBE (2) + heptane (3) <sup>e</sup>	1.34	0.00	1.0	0.8	2.3	

Ternary data					
rmsd	$\gamma_1/\gamma_2$		$\gamma_1/\gamma_3$		
	max % dev	% dev	rmsd	max % dev	% dev
$2 \times 10^{-2}$	4.7	1.8	$2 \times 10^2$	5.4	1.8

VLE correlations and predictions						
System	Bubble-point pressures			Dew-point pressures		
	$\Delta P/\%$ <sup>f</sup>	$100 \times \Delta y_1^g$	$100 \times \Delta y_2$	$\Delta P/\%$	$100 \times \Delta x_1$	$100 \times \Delta x_2$
1 + 2 <sup>d</sup>	0.09	0.1	0.1	0.12	0.1	0.1
1 + 3	0.11	0.1	-	0.10	0.2	-
2 + 3 <sup>e</sup>	0.60	-	0.3	0.42	-	0.4
1 + 2 + 3 <sup>h</sup>	0.24	0.2	0.2	0.29	0.2	0.2

<sup>a</sup> Root mean square deviation in activity coefficients  $\{\sum_i^N (\gamma_i^{exp} - \gamma_i^{calc})^2 / N\}^{0.5}$  ( $N$ : number of data points).

<sup>b</sup> Average percentage deviation in activity coefficients.

<sup>c</sup> Maximum percentage deviation in activity coefficients.

<sup>d</sup> Calculated from the data of Segura *et al.* [1].

<sup>e</sup> Calculated from the data of Reich *et al.* [2].

<sup>f</sup> Average percentage deviation in pressure.

<sup>g</sup> Average absolute deviation in mole fraction  $\Delta y = 1/N \sum_i^N |y_i^{exp} - y_i^{calc}|$ .

<sup>h</sup> Prediction from binary parameters.

parameters previously fitted to the binaries. Table VIII reports results of the pertinent bubble-point pressure and dew-point pressure calculations, together with statistics and parameters. From these results it can be concluded again that the binary contributions allow a good prediction of the ternary system.

The boiling points of the systems were correlated by the equation proposed by Tamir [14]

$$\begin{aligned}
 T/K = & \sum_{i=1}^3 x_i T_i^0 + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \dots] \\
 & + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \dots] \\
 & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \dots] \quad (8)
 \end{aligned}$$

TABLE VIII Parameters, correlation and prediction statistics for different  $G^E$  models

Model	$ij$	$a_{ij}$	$J \cdot \text{mol}^{-1}$	$a_{ij}$	$J \cdot \text{mol}^{-1}$	$\alpha_{ij}$	Bubble-point pressures			Dew-point pressures		
							$\Delta P/\%^f$	$100 \times \Delta y_1^g$	$100 \times \Delta y_2$	$\Delta P/\%$	$100 \times \Delta x_1$	$100 \times \Delta x_2$
NRTL	1+2 <sup>d</sup>	-1139.22	1433.47	0.3	0.05	0.1	0.1	0.05	0.1	0.1	0.1	
	1+3	13.72	-59.91	0.3	0.10	0.1	-	0.10	0.2	0.2	-	
	2+3 <sup>e</sup>	776.74	-331.17	0.3	0.29	-	0.2	0.38	-	-	0.2	
	1+2+3 <sup>h</sup>				0.17	0.3	0.2	0.25	0.2	0.2	0.2	
Wilson <sup>a</sup>	1+2 <sup>d</sup>	-78.13	208.22		0.12	0.1	0.1	0.13	0.1	0.1	0.1	
	1+3	-57.73	47.60		0.10	0.1	-	0.10	0.2	-	-	
	2+3 <sup>e</sup>	-287.73	792.40		0.32	-	0.2	0.38	-	-	0.2	
	1+2+3 <sup>h</sup>				0.21	0.3	0.2	0.29	0.2	0.2	0.2	
UNIQUAC <sup>b</sup>	1+2 <sup>d</sup>	-146.16	175.08		0.11	0.1	0.1	0.12	0.1	0.1	0.1	
	1+3	45.86	-43.73		0.10	0.1	-	0.10	0.2	-	-	
	2+3 <sup>e</sup>	765.01	-596.38		0.33	-	0.2	0.38	-	-	0.2	
	1+2+3 <sup>h</sup>				0.17	0.3	0.2	0.22	0.2	0.2	0.2	
UNIQUAC <sup>c</sup>	1+2+3 <sup>h</sup>				4.41	0.9	1.4	4.19	0.6	1.4		

<sup>a</sup> Liquid volumes have been estimated from the Rackett equation [18].

<sup>b</sup> Molecular parameters are those calculated from UNIFAC [13].

<sup>c</sup> Calculations based on original UNIFAC [7, 13].

<sup>d</sup> Calculated from the data of Segura *et al.* [1].

<sup>e</sup> Calculated from the data of Reich *et al.* [2].

<sup>f</sup> Average percentage deviation in pressure  $\Delta P = 100/N \sum_{i=1}^N |P_i^{\text{exp}} - P_i^{\text{calc}}| / P_i^{\text{exp}}$  (N: number of data points).

<sup>g</sup> Average absolute deviation in mole fraction  $\Delta y = 1/N \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{calc}}|$ .

<sup>h</sup> Ternary prediction from binary parameters.

where the coefficients  $A_{ij}$ ,  $B_{ij}$ , and  $C_{ij}$  are multicomponent parameters determined directly from the data. The various constants of Eq. (8) are reported in Table IX, together with information regarding the quality of the correlation. In addition, Figure 4 shows the isotherms of the

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

$ij$	$A_{ij}$	$B_{ij}$	$C_{ij}$	$max\ dev/K^a$	$avg\ dev/K^b$	$rmsd^c$
1+2	-1.708	0.437	1.338			
1+3	-15.369	4.353	-3.820	0.16	0.04	0.06
2+3	-12.951	3.964	-3.743			

<sup>a</sup> Maximum deviations.

<sup>b</sup> Average deviations.

<sup>c</sup> rmsd (T/K): Root mean square deviation,  $\{\sum(T_{expd} - T_{calc})^2/N\}^{0.5}$ .

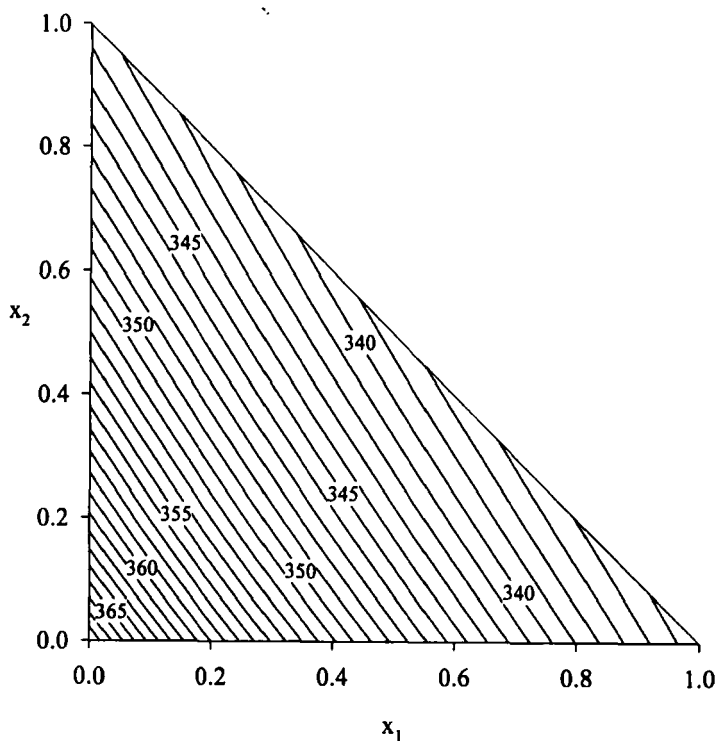


FIGURE 4 Isotherms for the ternary system 1-hexene (1) + ETBE (2) + heptane (3): (—) smoothed with Eq. (8) and the coefficients given in Table IX.

ternary system as calculated from Eq. (8). Inspection of Figure 4 reveals that no stationary point appears in boiling temperature, indicating that the ternary system is not azeotropic.

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### **LIST OF SYMBOLS**

$A_i$	Antoine's equation parameter, Eq. (2)
$B_i$	Antoine's equation parameter, Eq. (2)
$C_i$	Antoine's equation parameter, Eq. (2); parameter 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 $\text{J} \cdot \text{mol} \cdot \text{K}^{-1}$
$T$	absolute temperature K
$x, y$	mole fractions of the liquid and vapor phases

### ***Greek***

$\gamma$	activity coefficient
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### ***Superscripts***

$E$	excess property
$L$	pertaining to the liquid phase

### ***Subscripts***

$i, j$	component $i, j$ respectively
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