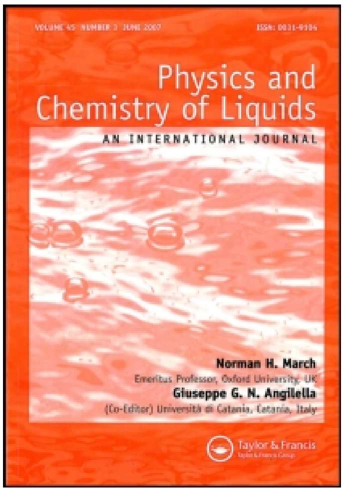

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ISOBARIC VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEMS ETHYL 1,1-DIMETHYLETHYL ETHER + 2,2,4-TRIMETHYLPENTANE AND + OCTANE

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Consistent vapor-liquid equilibrium data for the binary systems ethyl 1,1-dimethylethyl ether (ETBE) + 2,2,4-trimethylpentane and ethyl 1,1-dimethylethyl ether + octane at 94 kPa, including pure component vapor pressures of 2,2,4-trimethylpentane and octane, have been experimentally determined. The measured systems deviate slightly from ideal behavior, can be described as symmetric regular solutions and present no azeotropes. Boiling points were correlated using the Wisniak-Tamir equation.

Keywords: Vapor-liquid equilibrium; 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. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their

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octane rating and pollution-reducing capability. However, potential and documented contamination of water resources by MTBE has become a major public issue over the past few years, and restrictions in its use as additive are expectable. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment. The US Environmental Protection Agency (EPA) has classified it as a possible human carcinogen. Finally, it is reported to have an unpleasant taste and odor in water. In contrast, ethyl 1,1-dimethylethyl ether (ETBE) shows also good characteristics as gasoline additive including: high octane value, excellent distillation curve response, large reductions in carbon monoxide (CO) and hydrocarbon (HC) emissions but, in addition, it shows low volatility and low water solubility compared with MTBE. Few vapor–liquid equilibrium data have been published on binary systems of ETBE with hydrocarbons typically present in gasoline mixtures. Wisniak *et al.* [1] have already reported VLE data of the ternary system ETBE + heptane + octane at 94 kPa.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure to measure VLE data of the title binary systems at 94 kPa, for which no data have been previously published.

EXPERIMENTAL SECTION

Purity of Materials

Ethyl 1,1-dimethylethyl ether (96.0 + mass%) was purchased from TCI (Japan), 2,2,4-trimethylpentane (99.73 + mass%) and octane (99.80 mass%) were purchased from Aldrich. All the reagents were further purified to 99.9 + mass% by distillation using a 1 m high × 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm SS spirals) working at a 1:100 reflux ratio. At this concentration gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the

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 K)*		*T_b(101.3 kPa)/K*	
	exptl.	*lit.*	*exptl.*	*lit.*
ethyl 1,1-dimethylethyl ether (99.9 +)	1.37594[a]	1.37564[b]	345.85[a]	345.86[c]
2,2,4-trimethylpentane (99.92)	1.39162[a]	1.39145[d]	372.24[a]	372.386[e]
octane (99.9 +)	1.39783[a]	1.39750[d]	398.59[a]	398.830[d]

[a] Measured;
[b] DIPPR (Daubert and Danner [10]);
[c] Krähenbühl and Gmehling [11];
[d] TRC Tables, a-1490 [12];
[e] Willingham *et al.* [5].

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 602, manufactured by Fischer Labor - und Verfahrenstechnik (Germany), was used in the equilibrium determinations. General details of the experimental equipment and procedure appear in another publication [2]. The equilibrium temperature was measured with an accuracy of ±0.01 K using a Lauda thermometer, model R42/2, provided with a 4 mm diameter Pt-100 temperature sensor. The total pressure of the system is controlled by a vacuum pump capable of working at pressures down to 0.25 kPa. The pressure is measured by a Vac Probs pressure transducer with an accuracy of ±0.07 kPa; a 5-L Erlenmeyer flask connected between the separating chamber and the Vac Probs dampens the pressure variations to no more than 0.01 kPa. On the average the system reaches equilibrium conditions after 0.5-3 h of operation. Samples, taken by syringing 0.7 mL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics model SP 4290 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-3O, for the system ETBE + 2,2,4-trimethylpentane and 3 m long and 0.2 cm in diameter, packed with OV-17, for the system ETBE + octane. The column, injector, and detector temperatures were

(323.15, 483.15, and 503.15) K for ETBE + 2,2,4-trimethylpentane and (388.15, 493.15, and 543.15) K for ETBE + octane. Very good separation was achieved under these conditions, and calibration analyses were carried out with synthetic mixtures 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. Concentration measurements were accurate to better than 0.001 mole fraction for ETBE + 2,2,4-trimethylpentane and 0.009 mole fraction for ETBE + octane.

RESULTS AND DISCUSSION

The temperature T, the liquid-phase x_i and vapor-phase y_i mole fraction at 94.00 kPa are reported in Figures 1 and 2 and in Tables II and III. Figures 3 and 4 show the activity coefficients γ_i that were calculated from the following equation [3]:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \qquad (1)$$

where P is the total pressure and P_i^0 is the pure component vapor pressure. The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The non-idealities of the vapor phase were not considered because the pressure is low, and the vapor phase can be considered ideal. In addition, as pointed out by Reich *et al.* [4], the estimation of second virial coefficients of ETBE in mixtures with hydrocarbons is not reliable. The pure component vapor pressure P_i^0 for ETBE was taken from the work of Reich *et al.* [4]. For 2,2,4-trimethylpentane and octane, pure component vapor pressures were determined experimentally, as a function of the temperature, using the same equipment as that for obtaining the VLE data, pertinent results appear in Table III. The measured vapor pressures were correlated using the Antoine equation:

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

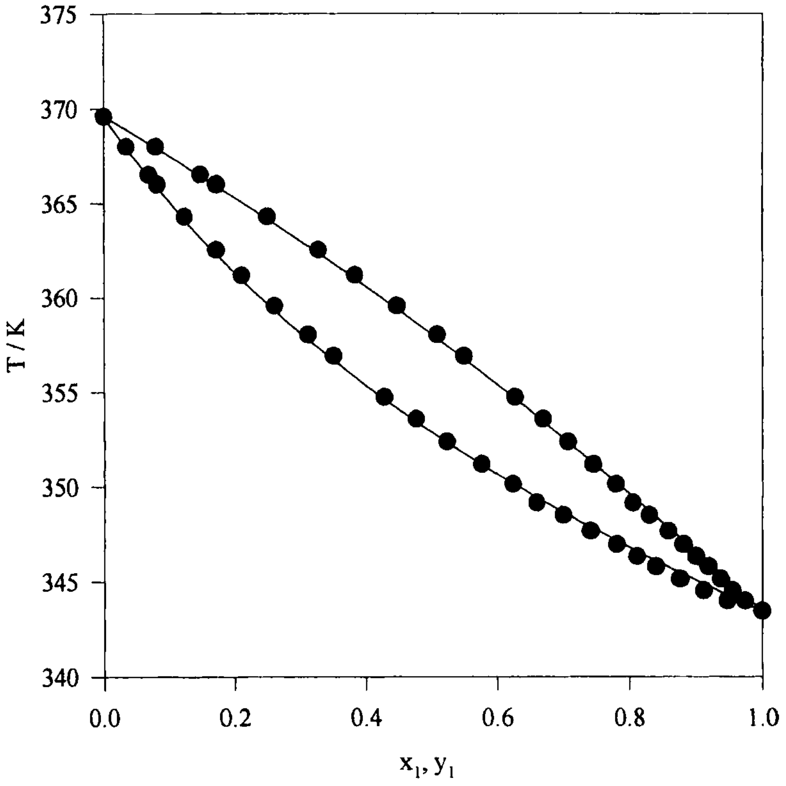

FIGURE 1 Experimental data for the system ETBE (1) + 2,2,4-trimethylpentane (2) at 94.00 kPa. Experimental data (•). Smoothed data using the regular model with the parameters given in Table VI, Eq. (3) (—).

and the parameters A_i, B_i and C_i reported in Table IV. It should be pointed out that the vapor pressures determined in this work were correlated with an mean absolute deviation [MADP] of 0.05% for 2,2,4-trimethylpentane and 0.03% for octane by Eq. (2). In addition, the parameters presented in Table V predict very well the experimental vapor pressures reported by Willingam *et al.* [5] for 2,2,4-trimethylpentane [MADP = 0.30%] and by Wu *et al.* [6] for octane [MADP = 0.59%], as can be confirmed in Figure 5. The calculated actvity coefficients reported in Tables II and III are estimated accurate to within ±2% for the system ETBE (1) + 2,2,4-trimethylpentane (2)

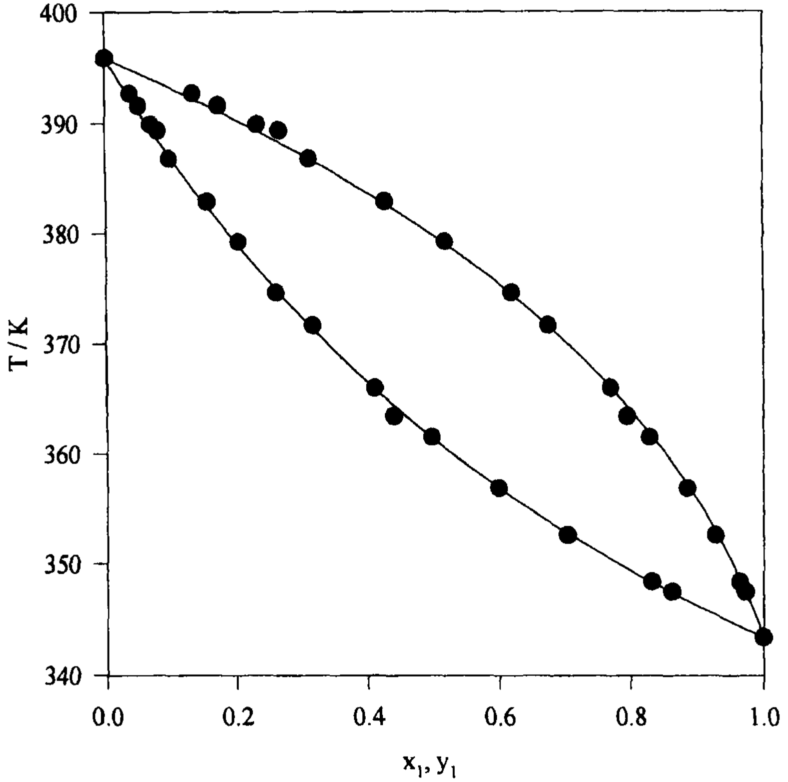

FIGURE 2 Experimental data for the system ETBE (1) + octane (3) at 94.00 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table III, Eq. (5) (—).

and ±4% for the system ETBE (1) + octane (3). The results reported in these Tables indicate that the measured systems exhibit moderate 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.* [7], as modified by Fredenslund *et al.* [8]. Consistency was achieved using a one parameter Legendre polynomial, or regular model, which reduces the functionality of the excess

TABLE II Experimental vapor-liquid equilibrium data for ETBE(1) + 2,2,4-trimethylpentane (2) at 94.00 kPa. (Ideal gas treatment for the vapor phase)

T/K	x_1	y_1	γ_1	γ_2
369.60	0.000	0.000		1.000
368.01	0.034	0.079	1.133	0.998
366.54	0.068	0.148	1.100	0.999
366.01	0.081	0.172	1.094	1.000
364.30	0.123	0.249	1.090	1.000
362.54	0.172	0.327	1.074	1.001
361.19	0.210	0.383	1.072	1.001
359.57	0.260	0.447	1.059	1.007
358.04	0.311	0.508	1.051	1.008
356.91	0.350	0.549	1.040	1.016
354.74	0.428	0.626	1.034	1.026
353.59	0.476	0.669	1.029	1.027
352.38	0.523	0.707	1.027	1.036
351.18	0.576	0.745	1.018	1.057
350.15	0.623	0.779	1.017	1.061
349.16	0.659	0.805	1.023	1.072
348.52	0.700	0.830	1.012	1.086
347.67	0.741	0.859	1.017	1.069
346.97	0.780	0.881	1.012	1.090
346.33	0.811	0.900	1.013	1.094
345.81	0.840	0.918	1.015	1.076
345.15	0.876	0.937	1.014	1.097
344.54	0.911	0.955	1.013	1.109
344.02	0.947	0.974	1.011	1.077
343.47	1.000	1.000	1.000	

TABLE III Experimental vapor-liquid equilibrium data for ETBE (1) + octane (3) at 94.00 kPa. (Ideal gas treatment for the vapor phase)

T/K	x_1	y_1	γ_1	γ_3
395.91	0.000	0.000		1.000
392.75	0.038	0.135	0.929	0.984
391.63	0.051	0.173	0.910	0.985
389.93	0.070	0.233	0.929	0.980
389.35	0.081	0.267	0.933	0.964
386.77	0.098	0.311	0.956	0.997
382.88	0.155	0.427	0.912	0.995
379.23	0.203	0.518	0.925	0.994
374.61	0.260	0.619	0.972	0.980
371.67	0.315	0.675	0.945	0.994
366.01	0.410	0.769	0.963	0.992
363.46	0.439	0.795	0.998	1.011
361.55	0.497	0.829	0.970	1.005
356.89	0.599	0.885	0.982	1.002
352.62	0.704	0.928	0.994	0.994
348.45	0.832	0.965	0.992	0.998
347.54	0.862	0.973	0.993	0.971
343.47	1.000	1.000	1.000	

Gibbs energy G^E to the following symmetric relation

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

The parameter A in Eq. (3), together with the pertinent statistics required by the Fredenslund's test, are shown in Table VI for the different systems considered in this work. From Table VI it is concluded the proposed model gives a reasonable fit of the data. In addition, the data satisfy consistency criteria.

The variation of activity coefficients with composition for the system ETBE (1) + 2,2,4-trimethylpentane (2) appears in Figure 3. Inspection of this figure shows a symmetric trend of the experimental activity

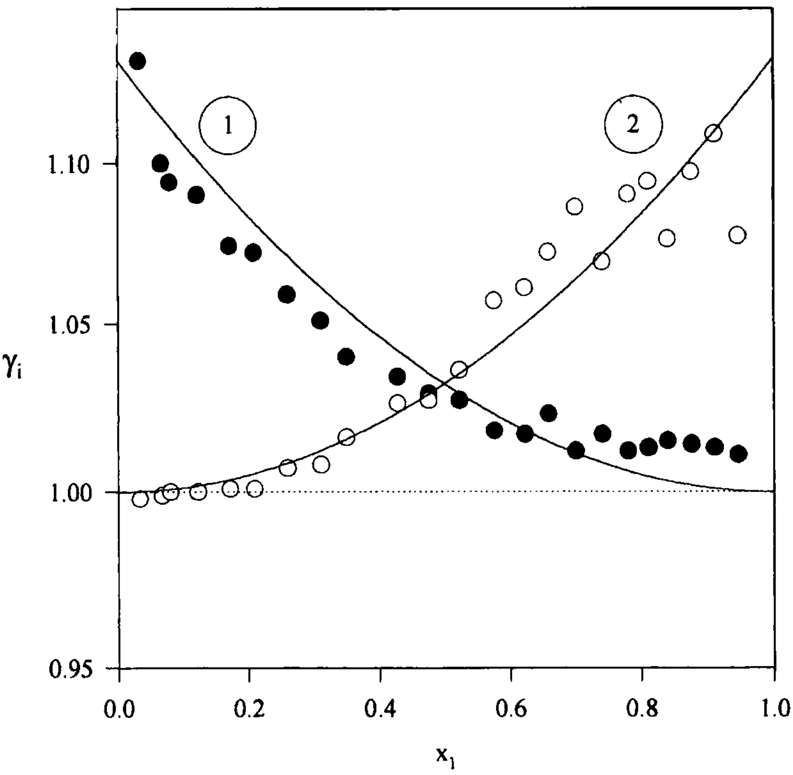

FIGURE 3 Activity coefficient plot of the system ETBE (1) + 2,2,4-trimethylpentane (2) at 94.00 kPa, calculated from experimental data. Experimental data (○, ●). Smoothed data using the regular model with the parameters given in Table VI, Eq. (3) (—).

coefficients which, in dilution ranges, are approximate equivalent for both components in each binary system. In addition, from the figure under consideration, it is clear that activity coefficients exhibit intersection about the composition $x_1 = 0.5$, and are reasonably represented by Eq. (3). Thus, according to the present experimental data, and its pertinent consistency test, it is concluded that the system ETBE (1) + 2,2,4-trimethylpentane (2) can be satisfactorily explained by a regular solution behavior (or Porter equation), showing a slightly positive deviation from ideal behavior. The activity coefficient plot for the system ETBE (1) + octane (3) appears in Figure 4, where a larger

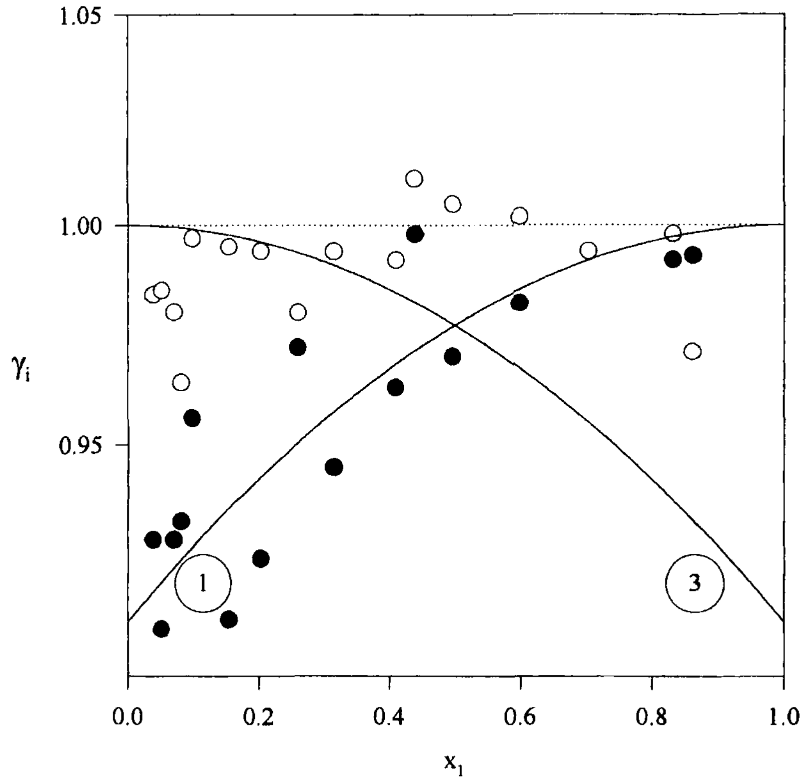

FIGURE 4 Activity coefficient plot of the system ETBE (1) + octane (3) at 94.00 kPa, calculated from experimental data. Experimental data (○, ●). Smoothed data using the regular model with the parameters given in Table VI, Eq. (3) (—).

TABLE IV Experimental vapor pressures determined for pure species

2,2,4-trimethylpentane		*Octane*	
T/K	*P/kPa*	*T/K*	*P/kPa*
317.09	15.32	341.29	14.81
321.81	18.56	345.49	17.49
325.36	21.35	349.51	20.45
328.96	24.61	352.16	22.60
332.55	28.11	355.00	25.11
335.58	31.42	360.07	30.18
339.10	35.59	364.64	35.44
342.67	40.29	368.25	40.05
346.22	45.46	371.56	44.73
349.61	50.85	375.27	50.40
352.20	55.33	378.10	55.18
355.05	60.63	380.94	60.28
357.53	65.51	383.69	65.67
360.09	70.87	385.94	70.28
362.21	75.55	388.25	75.30
364.32	80.52	390.62	80.71
366.57	86.07	392.59	85.47
368.60	91.30	394.50	90.30
370.70	97.01	396.45	95.46
372.24	101.33	397.88	99.34
		398.59	101.33

experimental noise is observed due to limitations of the Fischer VLE still for systems which exhibit large boiling temperature differences. According to Figure 4 the system ETBE(1) + octane(3) exhibits slightly negative deviation from ideal behavior and, as can be seen in Table VI, it may be satisfactorily represented by a Porter equation.

The boiling point temperatures of each system at 94.00 kPa were well correlated with its composition by the equation proposed by Wisniak and Tamir [9]:

$$T/K = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{4}$$

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. (4) are reported in Table VII, which also contains information indicating the degree of goodness of the correlation.

TABLE V Antoine coefficients, Eq. (2)

Compound	A_i	B_i	C_i
ethyl 1,1-dimethylethyl ether[a]	5.966510	1151.7280	55.0620
2,2,4-trimethylpentane[b]	5.883433	1224.4559	56.4700
octane[b]	6.051411	1354.1065	63.8882

[a] Reich *et al.* [4];

[b] Antoine's parameters were calculated from the experimental data in Table IV.

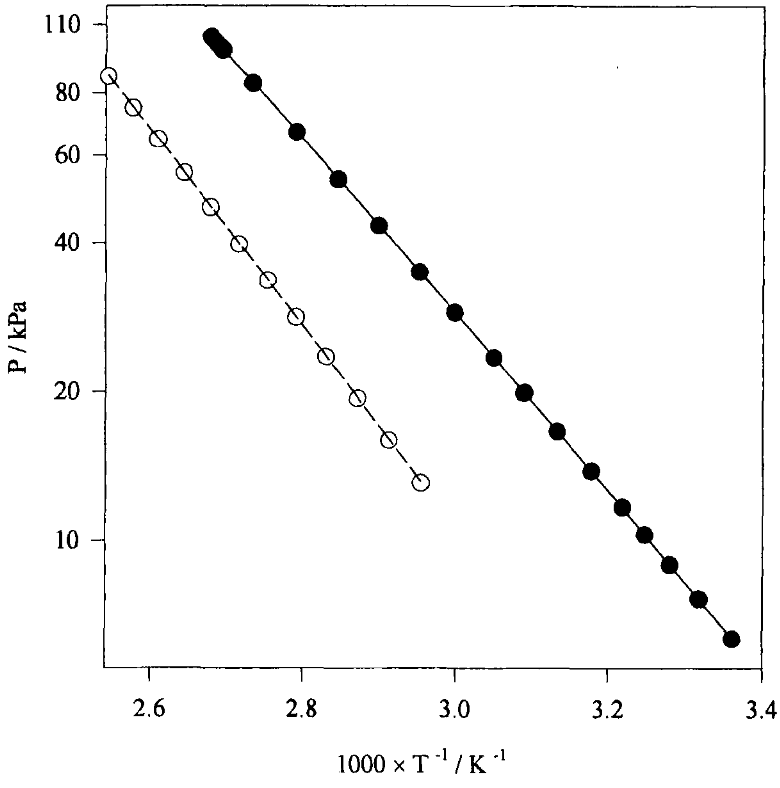

FIGURE 5 Comparison of correlated vapor pressures with other references. Experimental data reported by Willingham *et al.* [5] for 2,2,4-trimethylpentane (●). Experimental data reported by Wu *et al.* [6] for octane (○). Predicted by Eq. (2) and parameters in Table V for 2,2,4-trimethylpentane (—) and for octane (- -).

TABLE VI Consistency test for the various experimental systems considered in VLE measurements

System	A^a	$100 \times MADy_1{}^b$	$MADP^c/KPA$
1 + 2	0.125	0.09	0.54
1 + 3	−0.093	0.40	0.91

[a] Zeroth order Legendre polynomial (or Porter model) parameter in Eq. (3);
[b] Average absolute deviation in vapor phase composition;
[c] Average absolute deviation in pressure.

TABLE VII Coefficients in correlation of boiling points, Eq. (3). Average deviation, standard deviation and maximum deviation in temperature

System	C_0	C_1	C_2	$avg.dev./K^a$	σ/K^b	$max.dev./K^c$
1 + 2	−14.24876	3.34452	−4.16458	0.04	0.04	0.16
1 + 3	−37.21399	4.39369	5.36763	0.42	0.35	1.07

[a] Average deviation;
[b] Standard deviation;
[c] Maximum deviation.

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