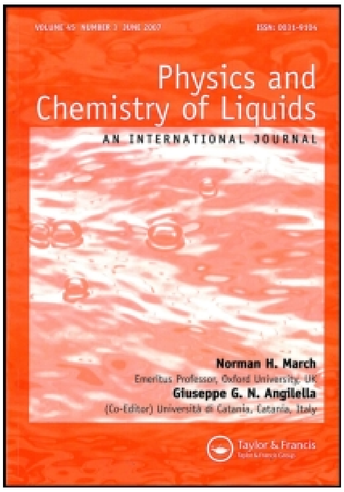

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Effect of Pressure on the Vapor-Liquid Equilibria of the System Methanol Ethyl 1,1-Dimethylethyl Ether

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EFFECT OF PRESSURE ON THE VAPOR–LIQUID EQUILIBRIA OF THE SYSTEM METHANOL + ETHYL 1,1-DIMETHYLETHYL ETHER

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Vapor–liquid equilibrium has been determined at 94 and 70 kPa for the binary system methanol + ethyl 1,1-dimethylethyl ether. The system deviates positively from ideal behavior and presents a minimum boiling azeotrope at 329 K with 57% mole methanol (94 kPa) and at 322 K with 52% mole methanol (70 kPa). The activity coefficients and boiling points of the solutions were correlated with the mole fraction by the Wohl, Wilson, UNIQUAC, NRTL and Wisniak-Tamir equations.

Keywords: Vapor–liquid equilibrium; Fuel oxygenating additive; Unleaded gasoline

INTRODUCTION

MTBE is the primary oxygenated compound currently used to reformulate gasolines. It meets the Clear Air Act requirement that reformulated gasolines used in certain air-polluted urban areas contain a minimum of 2% oxygen by mass. Nevertheless, it is being phased out because of evidence that it accumulates in surface and underground water. MTBE is not effectively removed by porous adsorbents or by air stripping, and bioremediation is not very effective. There is need to

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*Corresponding author. e-mail: wisniak@bgumail.bgu.ac.il investigate additional oxygenated mixtures that may have potential to comply with environmental legislation. Possible candidates may contain methanol, methyl acetate, 2,2′-oxybis[propane] (diisopropyl ether or DIPE), and 2-methyl-2-butanol (*tert*-amyl alcohol).

The only data available in the literature for the system investigated here are those of Clark *et al.* [1] at 293 and 323 K, using a static experimental method. The data of Clark *et al.*, were determined over a limited range of liquid phase concentration and did not include the concentration of the vapor phase.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures. The present work was undertaken to measure and to characterize the vapor–liquid equilibria (VLE) data for the binary system methanol + ETBE, for which complete data are not available.

EXPERIMENTAL SECTION

Purity of Materials

Methanol (99.9 mass%) was purchased from Aldrich and was used without further purification. ETBE (96.0 + mass%) was purchased from *TCI* (*Tokyo Chemical Industry Co. Ltd.*, Japan) and was purified to more than 99.7 + mass% by rectification in a 1-m height – 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm stainless steel spirals), working at a 1 : 100 reflux ratio. After this step, gas chromatography failed to show any significant impurity. 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 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, the solution is heated to its boiling point by a 250 W immersion heater (Cottrell pump). The vapor–liquid mixture flows through an extended contact line that guarantees an intense phase

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

Component (purity/mass %)	n_D	T_b/K
Methanol (99.9)	1.32656[a] /298.15 K 1.32562[b] /298.15 K	337.88[a] 337.85[b]
Ethyl 1,1-dimethylethyl ether (99.7+)	1.37594[a] /293.15 K 1.37564[c] /293.15 K	345.85[a] 345.86[d]

[a] Measured.
[b] TRC Tables [14].
[c] DIPPR (Daubert and Danner [3]).
[d] Krähenbühl and Gmehling [15].

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 return again to the immersion heater. The equilibrium temperature is measured with a Hart Scientific thermometer, model 1502, provided with a 4 mm diameter Pt-100 temperature sensor, with an accuracy of ± 0.005 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. A Vac Probs measures the pressure with an accuracy of ± 0.1 kPa. On the average the system reaches equilibrium conditions after 1–2 h operation. Samples, taken by syringing 0.7 inicroliter after the system had achieved equilibrium, were analyzed by gas chromatography on a DANI model GC1000 apparatus provided with a thermal conductivity detector and a Spectra Physics Model Chromjet SP 4400 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SP-2100. Column, injector and detector temperatures were (473.15, 493.15, 448.15) K, respectively. Very 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 fit had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ± 0.001 mole fraction.

RESULTS

The temperature T and liquid-phase x and vapor-phase y mole fraction measurements at $P = 94$ kPa are reported in Tables II and III

TABLE II Experimental vapor–liquid equilibrium data for methanol (1) + ETBE (2) at 94 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}/$ $cm^3\,mol^{-1}$	$-B_{22}/$ $cm^3\,mol^{-1}$	$-B_{12}/$ $cm^3\,mol^{-1}$
343.47	0.000	0.000		1.000	840	1343	1091
340.80	0.013	0.076	4.712	1.020	877	1372	1124
337.15	0.048	0.202	4.014	1.029	933	1414	1173
335.63	0.065	0.250	3.897	1.036	958	1432	1195
334.45	0.099	0.305	3.263	1.037	978	1446	1212
333.98	0.116	0.331	3.082	1.034	986	1452	1219
333.22	0.124	0.342	3.088	1.052	999	1461	1230
332.53	0.154	0.372	2.778	1.065	1012	1470	1241
332.28	0.170	0.392	2.679	1.060	1016	1473	1244
331.15	0.217	0.427	2.392	1.101	1037	1487	1262
330.04	0.323	0.473	1.865	1.217	1058	1502	1280
330.13	0.331	0.485	1.857	1.200	1056	1500	1278
329.81	0.400	0.509	1.635	1.289	1063	1505	1284
329.17	0.411	0.517	1.659	1.322	1075	1513	1294
329.01	0.545	0.563	1.371	1.558	1078	1515	1297
329.46	0.583	0.584	1.305	1.592	1069	1509	1289
329.21	0.653	0.605	1.221	1.831	1074	1512	1293
330.05	0.807	0.671	1.057	2.669	1058	1501	1280
330.80	0.857	0.718	1.032	3.005	1044	1492	1268
331.60	0.881	0.741	1.003	3.230	1029	1481	1255
332.15	0.912	0.802	1.026	3.264	1018	1474	1246
332.48	0.921	0.811	1.014	3.416	1013	1470	1241
332.85	0.930	0.833	1.015	3.397	1006	1466	1236
333.29	0.945	0.855	1.008	3.657	998	1460	1229
335.96	1.000	1.000	1.000		952	1428	1190

TABLE III Experimental vapor–liquid equilibrium data for methanol (1) + ETBE (2) at 70 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}/$ $cm^3\,mol^{-1}$	$-B_{22}/$ $cm^3\,mol^{-1}$	$-B_{12}/$ $cm^3\,mol^{-1}$
334.51	0.000	0.000		1.000	977	1445	1211
328.66	0.051	0.200	3.919	1.032	1085	1520	1303
326.32	0.091	0.287	3.473	1.045	1134	1551	1343
325.72	0.110	0.314	3.257	1.047	1147	1560	1353
324.29	0.176	0.381	2.619	1.075	1179	1580	1379
323.37	0.226	0.425	2.367	1.100	1200	1593	1396
322.35	0.387	0.473	1.608	1.322	1224	1608	1416
322.43	0.532	0.523	1.286	1.564	1222	1607	1414
322.35	0.574	0.543	1.245	1.648	1224	1608	1416
322.37	0.660	0.581	1.157	1.892	1224	1608	1416
322.51	0.704	0.601	1.115	2.058	1220	1605	1413
322.76	0.769	0.632	1.062	2.409	1214	1602	1408
323.65	0.844	0.692	1.019	2.886	1194	1589	1391
324.02	0.864	0.718	1.016	2.993	1185	1584	1384
324.77	0.897	0.776	1.023	3.071	1168	1573	1371
325.86	0.939	0.826	0.993	3.894	1144	1558	1351
326.29	0.951	0.854	0.997	3.934	1135	1552	1343
326.16	0.952	0.857	1.004	3.948	1137	1554	1345
328.74	1.000	1.000	1.000		1084	1519	1301

and Figures 1 to 4, together with the activity coefficients γ_i that were calculated from the following equation [2]:

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

where T and P are the boiling point and the total pressure, 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

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

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation (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

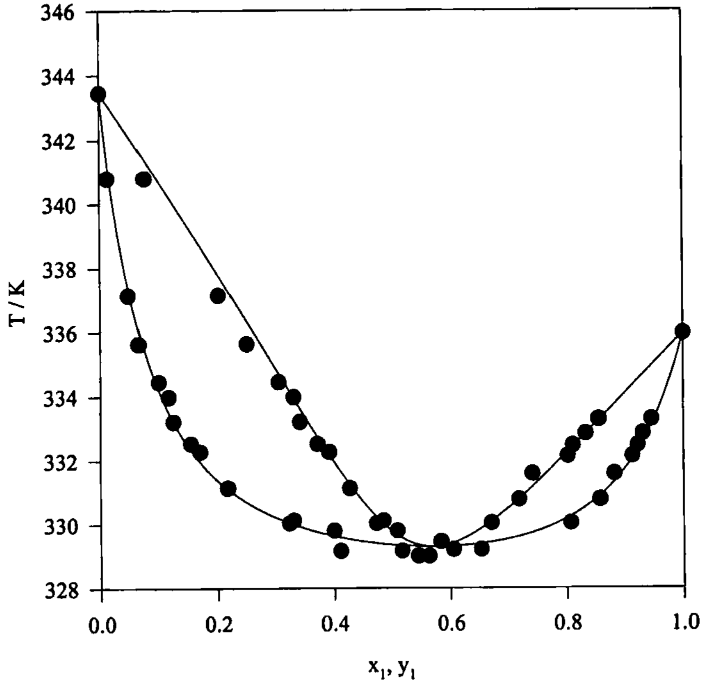

FIGURE 1 Boiling temperature diagram for the system methanol (1)+ETBE (2) at 94.00 kPa: (•) experimental, (—) predicted by Eq. (16).

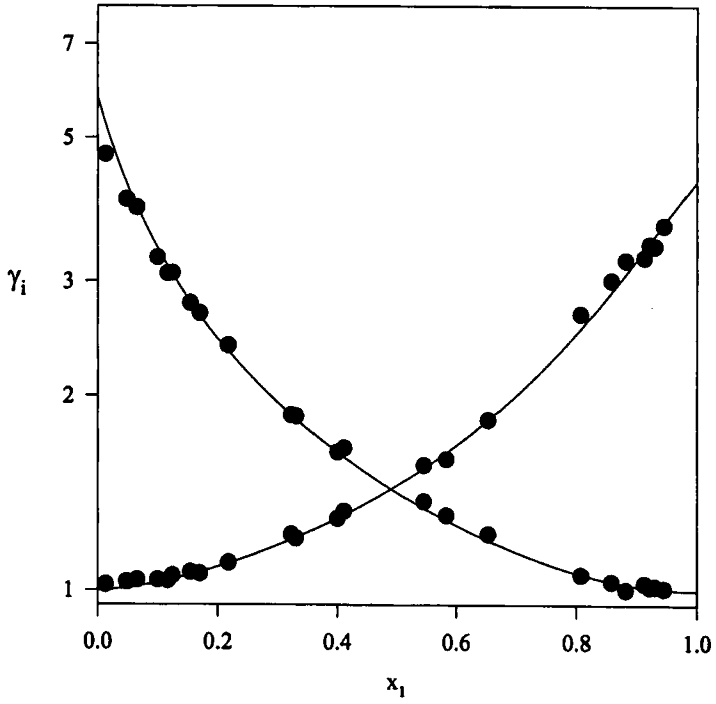

FIGURE 2 Activity coefficients for the system methanol (1) + ETBE (2) at 94.00 kPa: (●) γ_1^{exptl}, γ_2^{exptl}, (—) predicted by Eq. (16).

volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i^0 were calculated according to Antoine's equation:

$$\log(P_i^0/kPa) = A_i - \frac{B_i}{(T/K) - C_i} \qquad (3)$$

where Antoine's constants A_i, B_i, and C_i are reported in Table IV. The molar virial coefficients B_{ii} were taken from DIPPR (Daubert and Danner [3]) correlations. The cross second virial coefficient was estimated as

$$B_{ij} = \frac{B_{ii} + B_{jj}}{2} \qquad (4)$$

The last two terms in Eq. (1), particularly the second one that express the correction due to the non ideal behavior of the vapor phase,

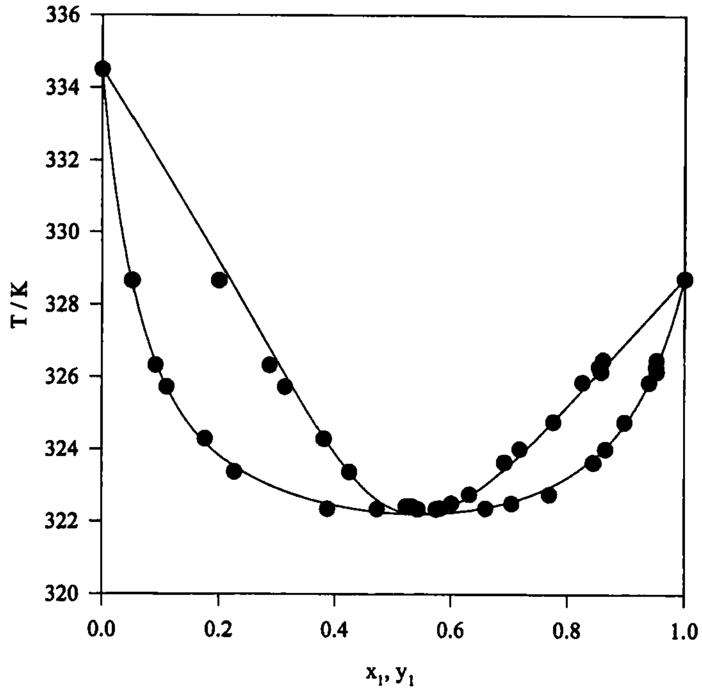

FIGURE 3 Boiling temperature diagram for the system methanol (1)+ETBE (2) at 70.00 kPa: (•) experimental, (—) predicted by Eq. (16).

contributed less than 2% to the activity coefficients; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables II to III and are estimated accurate to within ±2%. The results reported in these Tables indicate that the system methanol (1)+ETBE (2) deviates positively from ideal behavior and presents a minimum boiling azeotrope at 329 K with 57% mole methanol (94 kPa) and at 322 K with 52% mole methanol (70 kPa). The VLE data at 94 kPa, reported in Table II, were found to be thermodynamically consistent by the point-to-point method of Van Ness *et al.* [4] as modified by Fredenslund *et al.* [5] ($\Delta y < 0.01$). The VLE data at 70 kPa, reported in Table III, exceed slightly the consistency criteria, probably due to association effects that were not considered in the data treatment. Pertinent consistency statistics are presented in Table V.

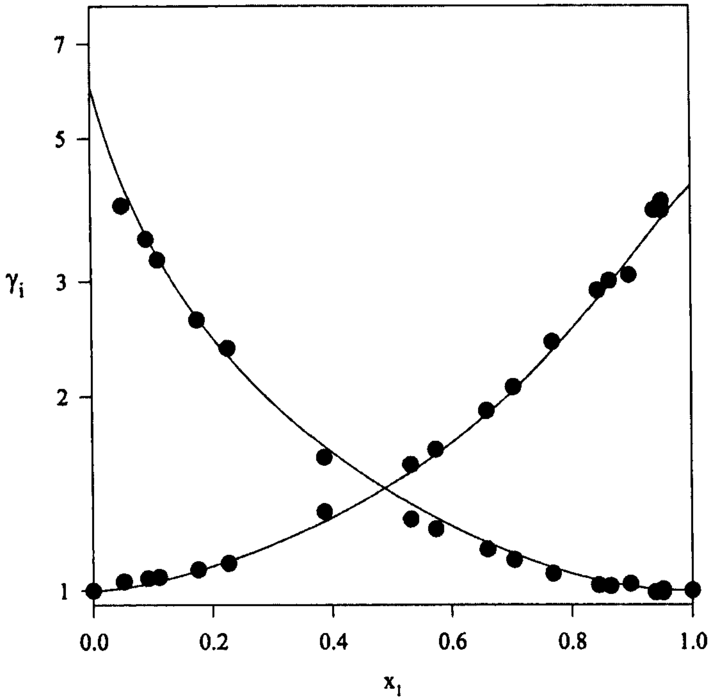

FIGURE 4 Activity coefficients for the system methanol (1) + ETBE (2) at 70.00 kPa: (●) $\gamma_1^{\mathrm{exptl}}$, $\gamma_2^{\mathrm{exptl}}$, (—) predicted by Eq. (16).

TABLE IV Antoine coefficients, Eq. (3)

Compound	A_i	B_i	C_i
Methanol[a]	7.02240	1474.080	44.020
ETBE[b]	5.96651	1151.730	55.060

[a] TRC Tables [14].
[b] Reich *et al.* [16].

TABLE V Consistency test statistics for the system methanol (1) + ETBE (2)

System	N_p[a]	$100 \times \Delta y$[b]	ΔP[c] */KPA*
94 kPa	3	0.88	0.56
70 kPa	3	1.22	0.28

[a] Number of parameters for the Legendre polynomial used in consistency.
[b] Average absolute deviation in vapor phase mole fractions $\Delta y = 1/N \sum_{i=1}^{N} |y_1^{\exp tl} - y_1^{\mathrm{calc}}|$ (N: number of data points).
[c] Average absolute deviation in pressure $\Delta P = 1/N \sum_{i=1}^{N} |p^{\exp tl} - y_1^{\mathrm{calc}}|$.

The activity coefficients were correlated with the Wohl, NRTL, Wilson, and UNIQUAC equations [6] and predicted by the UNIFAC group contribution method [5, 7]. The parameters of the Wohl, Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (*OF*):

$$OF = \sum_{i=1}^{N} \left(\left| P_i^{\mathrm{exp}\ tl} - P_i^{\mathrm{calc}} \right| / P_i^{\mathrm{exp}\ tl} + \left| y_i^{\mathrm{exp}\ tl} - y_i^{\mathrm{calc}} \right| \right)^2 \qquad (5)$$

and are reported in Table VI, together with the relative deviation of the vapor mole fraction. Inspection of the results given in Table VI shows that all four models gave a reasonable fit of the binary systems, the best fit corresponding to the Wilson correlation. The capability of predicting the vapor phase mole fraction was been used as the ranking factor. Table VI shows also that the UNIFAC model does not predict the VLE data of systems reported in this work.

Although the VLE data of the system were reasonable correlated at both pressures (exception being UNIFAC), none of the models considered was able to represent satisfactorily the experimental trend of activity coefficients on the liquid phase mole fraction. In fact, different deviation statistics in bubble and dew-point pressure calculations were obtained for the system in question, as shown in Table VI. In addition, as mentioned before, the VLE data at 70 kPa exceeded the consistency criteria. The probable reason for this is that association effects were not considered when correlating the VLE data.

As follows from the chemical theory [8] positive deviations from ideal behavior, as observed in the present system, may be explained in terms of dominant self-association of methanol. In addition, cross association between the components of the mixture may be expected for the functional groups of ether and alcohol. According to the theory of Nath and Bender [9, 10] it is possible to calculate the enthalpy of association and the equilibrium constant for pure liquids from saturation data. For the system in question, the results indicate that at 323.15 K the equilibrium association constants for methanol and ETBE are in the ratio 250 : 1. Consequently, self-association of ETBE may be neglected. According to Nath and Bender [10], when an associating molecule *A* (for example, methanol) forms linear polymers

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

					Bubble-point pressures		*Dew-point pressures*	
Model	P/kPa	A_{12}	A_{21}	α_{12}	$\Delta P(\%)$[f]	$100 \times \Delta y_i$	$\Delta P(\%)$	$100 \times \Delta x_i$
Wohl	94.00	1.51	1.42	1.07[e]	1.00	0.9	1.20	1.4
	70.00	1.51	1.41	1.07[e]	0.89	1.0	1.14	1.6
NRTL[a]	94.00	1968.91	2658.54	0.30	0.97	0.8	0.62	1.3
	70.00	1893.43	2605.51	0.30	0.91	0.9	1.14	1.6
Wilson[a,b]	94.00	4618.79	600.72		0.80	0.7	0.98	0.9
	70.00	4728.30	392.98		0.64	1.0	0.94	1.4
UNIQUAC[a,c]	94.00	−696.23	4594.14		1.04	0.9	1.20	1.4
	70.00	−693.58	4509.34		1.01	0.9	1.14	1.5
UNIFAC[d]	94.00				5.90	2.4	4.42	2.2
	70.00				4.74	3.0	3.10	3.8

[a] Parameters in J × mol^{-1}.

[b] Liquid volumes have been approximated using the Rackett equation [12].

[c] Molecular parameters are those calculated from UNIFAC [7].

[d] Calculations based on original UNIFAC [7].

[e] "q" parameter for the Wohl's model.

[f] $\Delta P = 100/N \sum_i^N |P_i^{\mathrm{exptl}} - P_i^{\mathrm{calc}}|/P_i^{\mathrm{exptl}}$.

by successive chemical reactions expressed by

$$A_1 + A_{i-1} \Leftrightarrow A_i$$

for self-association, and by

$$B_1 + A_i \Leftrightarrow A_iB$$

for cross-association with a molecule B (here, ETBE), then the chemical contribution to activity coefficients is given by

$$\ln\gamma_A^{\mathrm{chem}} = \ln\left(\frac{\phi_{A_1}}{x_A\phi_{A_1}^0}\right) - \frac{v_A}{v_{AB}} + \frac{v_A}{v_A^0} \tag{6}$$

$$\ln\gamma_B^{\mathrm{chem}} = \ln\left(\frac{\phi_{0B}}{x_B}\right) + 1 - \frac{v_B}{v_{AB}} \tag{7}$$

where v_i is the apparent molar volume of component i; ϕ_{A1}, ϕ_{0B} are the volume fractions of the monomer A_1 and of the unreacted component B, respectively; and V_{AB} corresponds to the molar volume of the solution which, in turn, may be calculated from

$$\frac{1}{v_{AB}} = \frac{\phi_{A_1}}{v_A(1 - K_A\phi_{A_1})} + \frac{\phi_{0B}}{v_B}\left[\frac{1 - (K_A - K_{AB})\phi_{A_1}}{1 - K_A\phi_{A_1}}\right] \tag{8}$$

In addition, ϕ_{A1}^0 and v_A^0 are the volume fraction and the molar volume of pure component A present as the monomer, given as a function of the self association equilibrium constant K_A by

$$\phi_{A_1}^0 = [(2K_A + 1) - (1 + 4K_A)^{1/2}]/2K_A^2 \tag{9}$$

$$\frac{1}{v_A^0} = \frac{\phi_{A_1}^0}{v_A(1 - K_A\phi_{A_1}^0)} \tag{10}$$

ϕ_{A1}, ϕ_{0B} a can be calculated by solving simultaneously the following relations

$$\phi_A = [\phi_{A_1}/(1 - K_A\phi_{A_1})^2] \times [1 + K_{AB}\phi_{0B}v_A/v_B] \tag{11}$$

$$\phi_B = \phi_{0B}[1 - (K_A - K_{AB})\phi_{A_1}] \times [1 - K_A\phi_{A_1}]^{-1} \tag{12}$$

where ϕ_A and ϕ_B are apparent volume fractions defined as

$$\phi_i = \frac{x_i v_i}{x_A v_A + x_B v_B} \quad (i = A, B) \tag{13}$$

K_A and K_{AB} are equilibrium constants for self- and cross-association, respectively.

According to the approach of Nath and Bender [9] these constants depend on the temperature, as follows

$$K_i = K_i^{323K} \exp\left[-\frac{h_i}{R}\left(\frac{1}{T/K} - \frac{1}{323.15}\right)\right] \quad (i = A, AB) \tag{14}$$

where h_i is the association enthalpy and K_i^{323K} corresponds to the equilibrium association constant, normalized to 323.15 K. The approach of Nath and Bender provides a predictive scheme for calculating association enthalpies and equilibrium constants for pure fluids that self-associate. For cross-association, both the enthalpy and the normalized equilibrium constant must be calculated from VLE data. Once activity coefficients have been calculated from Eqs. (6) to (14), the chemical contribution to the excess energy may be evaluated as

$$\left(\frac{G^E}{RT}\right)^{\text{chem}} = x_A \ln\gamma_A^{\text{chem}} + x_B \ln\gamma_B^{\text{chem}} \tag{15}$$

The excess Gibbs energy, including physical contributions, is given by

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)^{\text{phys}} + \left(\frac{G^E}{RT}\right)^{\text{chem}} \tag{16}$$

According to DIPPR[3], the critical volumes of methanol and ETBE are in the ratio 1 : 4, indicating that physical effects may yield an important contribution to the excess energy. The intrinsic excess model associated to the van der Waals equation of state, which is able to take into account size effects in phase equilibria [11], is van Laar's equation

$$\left(\frac{G^E}{RT}\right)^{\text{phys}} = \frac{A_{ij} A_{ji} x_i x_j}{A_{ij} x_i + A_{ji} x_j}. \tag{17}$$

Equation (17) has been used for modeling the physical contribution in Eq. (16). The association model proposed here depends on four parameters and on the pure (apparent) fluid volumes, v_A and v_B. Two parameters A_{ij}, A_{ji} are needed for modeling the physical contribution to the excess energy in Eq. (17). Additional parameters are the cross association enthalpy h_{AB} and the normalized equilibrium constant K_{AB}^{323K}. All these parameters have been calculated from the experimental VLE data given in Tables II and III, using the objective function indicated in Eq. (5). Pure-fluid volumes have been approximated using Rackett's equation [12] and pure-component physical data have been taken from DIPPR [3]. The corresponding parameters and statistics are reported in Table VII, from which we can conclude that consideration of association effects yields a better correlation of the data. The order of magnitude of the calculated association constants given in Table VII indicates that self-association of methanol is dominant over cross-association. In addition, Figures 2 and 4 shows a good representation of the activity coefficients.

The boiling points of the solutions were correlated with its composition by the equation proposed by Wisniak and Tamir [13]:

$$T/K = x_iT_i^0 + x_jT_j^0 + x_ix_j\sum_{k=0}^{m} C_k(x_i - x_j)^k \quad [j < i] \tag{18}$$

The various constants of Eq. (18) appear in Table VIII, which also contains information indicating the degree of goodness of the correlation.

TABLE VII Data treatment for the system methanol (1) + ETBE (2) using the association approach in Eq. (16). Model parameters and correlation statistics

I. *Parameters*

K_1^{323K}	$h_1/J mol^{-1}$	K_12^{323K}	$h_{12}/J mol^{-1}$	A_{12}	A_{21}
250.90[a]	−19917[a]	39.022[b]	−15797[b]	0.2282[b]	0.5561[b]

II. *Correlation statistics*

	Bubble-point pressures		*Dew-point pressures*	
P/kPa	$\Delta P(\%)$	$100 \times \Delta y$	$\Delta P(\%)$	$100 \times \Delta x$
94.00	0.77	0.6	0.94	0.7
70.00	0.55	1.0	0.85	1.5

[a] Calculated according to the approach of Nath and Bender [9] from saturation data.

[b] Calculated from the experimental data presented in Tables II and III.

TABLE VIII Coefficients and statistics in the correlation of boiling points, Eq. (18)

P/kPa	C_0	C_1	C_2	C_3	*Max dev/K*	*Avrg dev/K*	*Std dev/K*
94.00	−40.5908	5.4804	−49.8706	30.4495	1.08	0.35	0.32
70.00	−35.7009	8.3126	−49.7705	21.5279	0.75	0.28	0.20

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. (9)
G^E	excess Gibbs energy $J \times mol^{-1}$
h	association enthalpy $J \times mol^{-1}$
K	association constant
P	absolute pressure kPa
P^0	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	mole fractions of the liquid and vapor phases

Greek

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

Superscripts

E	excess property
L	pertaining to the liquid phase
0	reference state (pure component)

chem	chemical contribution
phys	physical contribution

Subscripts

i,j	component *i, j* respectively

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