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Isobaric Vapor-Liquid Equilibria and Densities for the System Ethyl 1,1-Dimethylethyl Ether + 2-Propanol

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ISOBARIC VAPOR–LIQUID EQUILIBRIA AND DENSITIES FOR THE SYSTEM ETHYL 1,1-DIMETHYLETHYL ETHER + 2-PROPANOL

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Vapor–liquid equilibrium (VLE) data at 50, 75, and 94 kPa have been determined for the binary system ethyl 1,1-dimethylethyl ether + 2-propanol, in the temperature range 323–344 K. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. Excess volumes have been also determined from density measurements at 298.15 K. The system exhibits positive deviation from ideal behavior and azeotropic behavior in the range of experimental pressures. The excess volume of the system is negative over the whole mole fraction range. The activity coefficients and boiling points of the solutions were well correlated with the mole fraction by the Wohl, Wilson, UNIQUAC, NRTL equations and predicted by the UNIFAC group contribution method. Excess volume data were correlated using the Redlich–Kister expansion.

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

INTRODUCTION

The Clean Air Act Amendments of 1990 required oil companies to add oxygen-rich compounds to gasolines sold in regions not meeting established air quality standards. Gasoline additives available to oil

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companies included ethanol, methanol, and synthetic ethers such as methyl 1,1-dimethylethyl ether (MTBE), ethyl 1,1-dimethylethyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE). MTBE was the preferred option because it has a high octane rating, blends easily with gasoline, and helps dilute the gasoline content of potentially toxic aromatic hydrocarbons. However, reports of water contamination and potential health concerns have prompted to take steps to ban the sale of MTBE-containing gasolines. There is still need to investigate the phase equilibrium and toxicological properties of oxygenated mixtures in order to find an optimum that may comply with the environmental legislation. Mixtures of ethers with alcohols appear frequently in the industrial production of ethers for gasoline blending and, in recent years, they have been considered for producing reformulated gasolines. In addition, vapour–liquid equilibrium (VLE) data of ethers and alcohols are also important to dehydrate alcohols by means of azeotropic distillation technologies.

From a theoretical viewpoint, the VLE behavior of mixtures of ethers with alcohols is difficult to predict, since their physical properties depend on complex patterns of association effects [1]. In a recent publication [2], we have presented VLE and density data for MTBE + 2-propanol, whose physical behavior may be explained in terms of competitive self and cross-association regimes. To the best of our knowledge, no VLE data have been reported for the system ETBE + 2-propanol. It has been well established that VLE data of oxygenated mixtures are important for predicting the vapor phase concentration that would be in equilibrium with hydrocarbon mixtures [3]. The present work was undertaken to measure isobaric VLE data and densities for the title system.

EXPERIMENTAL SECTION

Purity of Materials

ETBE (96.0 + mass%) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan) and 2-propanol (99.9 mass%) was purchased from Merck. Then, ETBE was further purified to more than 99.7 + mass% by rectification in a 1-m height–30 mm diameter

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 (293.15 K)		Density $1 \text{ g} \times \text{cm}^{-3}$ (298.15 K)		T_b (101.3 kPa)/K	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
ETBE (99.7+)	1.37594 ^a	1.37564 ^b	0.73635 ^a	0.73513 ^b	345.85 ^a	345.86 ^c
2-propanol (99.9+)	1.37731 ^a	1.3772 ^d	0.78131 ^a	0.78126 ^e	355.40 ^a	355.39 ^f

^aMeasured; ^bDIPPR [12]; ^cKrähenbühl and Gmehling [19]; ^dBallard and van Winkle [20]; ^eRiddick *et al.* [21]; ^fAmbrose and Sprake [22].

Normschliffgerätee Bau adiabatic distillation column (packed with 3×3 mm stainless steel spirals), working at a 1 : 100 reflux ratio. 2-propanol was dried using 3A molecular sieves. After these steps, gas chromatography failed to show any significant impurity. The properties and purity of the pure components, as determined by GLC, 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. 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 to 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 Systemtechnik S1224 digital temperature meter, and a Pt 100 Ω probe calibrated at the Swedish Statens Provningsanstält. 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 $1.0 \mu\text{L}$ 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. 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. At least three analyses were made of each sample. Concentration measurements were accurate to better than ± 0.001 in mole fraction.

For density measurements, the samples were prepared by mass on an analytical balance (Chyo Balance Corp., Japan) with an accuracy of $\pm 10^{-4}$ g. Densities of the pure components and their mixtures were measured using a DMA 5000 densimeter (Anton Paar, Austria) with an accuracy of $5 \times 10^{-6} \text{ g} \times \text{cm}^{-3}$. The density determination is based on measuring the period of oscillation of a vibrating U-shaped tube filled with the liquid sample. The temperature of the apparatus thermostat was maintained constant to within ± 0.01 K.

RESULTS

Vapor–Liquid Equilibria

The equilibrium temperature T , liquid-phase x and vapor-phase y mole fraction measurements at $P = 50, 75,$ and 94 kPa are reported in Tables II–IV and in Figs. 1–4, together with the activity coefficients γ_i that were calculated from the following equation [4]:

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

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

TABLE II Experimental vapor-liquid equilibrium data for ETBE (1) + 2-Propanol (2) at 50.00 kPa

T/K	x_1	y_1	γ_1	γ_2
338.77	0.000	0.000		1.000
336.32	0.036	0.141	2.632	0.997
333.46	0.080	0.271	2.508	1.013
331.32	0.123	0.360	2.333	1.032
329.62	0.169	0.440	2.202	1.035
328.88	0.205	0.476	2.016	1.049
327.70	0.252	0.524	1.883	1.073
326.13	0.320	0.584	1.748	1.115
325.42	0.400	0.627	1.541	1.174
324.73	0.452	0.655	1.460	1.231
324.06	0.517	0.685	1.368	1.319
323.63	0.581	0.711	1.284	1.425
323.42	0.620	0.728	1.242	1.495
323.18	0.686	0.753	1.171	1.663
323.08	0.750	0.779	1.112	1.879
323.00	0.788	0.797	1.086	2.043
323.12	0.848	0.830	1.046	2.372
323.49	0.909	0.877	1.017	2.813
323.98	0.952	0.924	1.005	3.214
324.94	1.000	1.000	1.000	

TABLE III Experimental vapor-liquid equilibrium data for ETBE (1) + 2-propanol (2) at 75.00 kPa

T/K	x_1	y_1	γ_1	γ_2
348.06	0.000	0.000		1.000
345.26	0.037	0.131	2.669	1.017
343.18	0.082	0.249	2.445	1.009
341.40	0.122	0.334	2.334	1.012
339.58	0.170	0.411	2.187	1.027
339.01	0.204	0.438	1.979	1.048
335.97	0.338	0.559	1.687	1.136
335.48	0.404	0.594	1.525	1.188
335.14	0.457	0.622	1.428	1.234
334.23	0.513	0.654	1.379	1.314
334.04	0.580	0.679	1.275	1.426
333.96	0.618	0.695	1.228	1.495
333.79	0.686	0.727	1.164	1.641
333.78	0.748	0.755	1.109	1.836
333.75	0.790	0.777	1.081	2.008
334.01	0.852	0.816	1.044	2.323
334.57	0.910	0.867	1.019	2.689
335.23	0.952	0.919	1.009	2.978
336.55	1.000	1.000	1.000	

TABLE IV Experimental vapor–liquid equilibrium data for ETBE (1)+2-propanol (2) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_2
353.52	0.000	0.000		1.000
351.15	0.037	0.124	2.640	1.003
348.99	0.081	0.236	2.452	1.003
347.26	0.123	0.312	2.251	1.018
345.36	0.173	0.395	2.151	1.029
344.53	0.208	0.427	1.985	1.055
342.39	0.322	0.533	1.714	1.103
342.17	0.327	0.533	1.699	1.122
341.27	0.406	0.576	1.523	1.201
340.96	0.459	0.604	1.427	1.248
340.43	0.513	0.634	1.363	1.312
340.26	0.581	0.662	1.264	1.419
340.19	0.621	0.680	1.217	1.490
340.11	0.688	0.712	1.153	1.635
340.09	0.750	0.743	1.105	1.822
340.15	0.791	0.766	1.078	1.979
340.70	0.862	0.816	1.035	2.300
341.23	0.909	0.861	1.018	2.574
341.91	0.953	0.917	1.012	2.887
343.47	1.000	1.000	1.000	

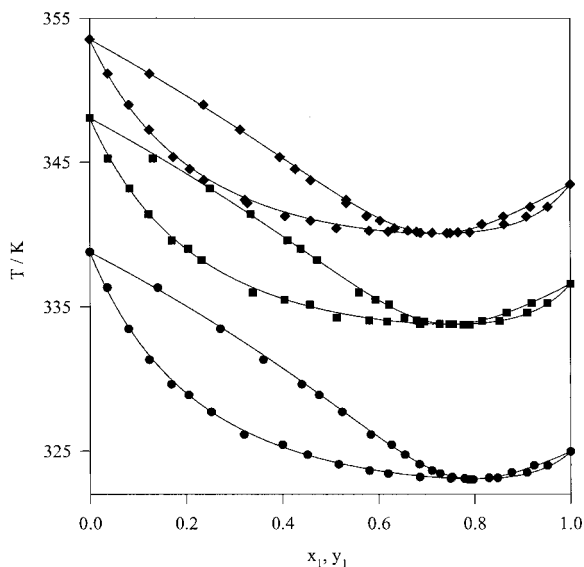


FIGURE 1 Boiling temperature diagram for the system ETBE (1)+2-propanol (2). Experimental data at (●) 50.00 kPa, (■) 75.00 kPa and (○) 94.00 kPa; (—) Smoothed by the Wilson model, with the parameters given in Table VIII.

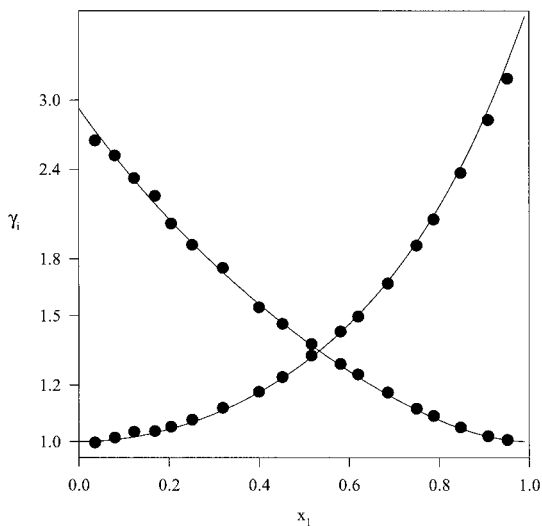


FIGURE 2 Activity coefficients for the system ETBE (1)+2-propanol (2) at 50.00 kPa. (●) experimental data; (—) smoothed by the Wilson model, with the parameters given in Table VIII.

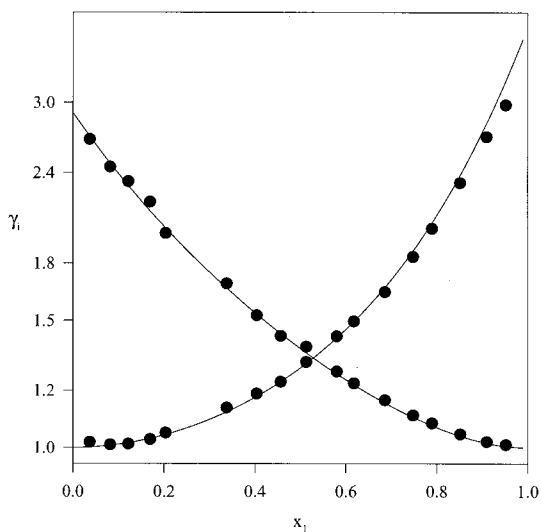


FIGURE 3 Activity coefficients for the system ETBE (1)+2-propanol (2) at 75.00 kPa. (●) experimental data; (—) smoothed by the Wilson model, with the parameters given in Table VIII.

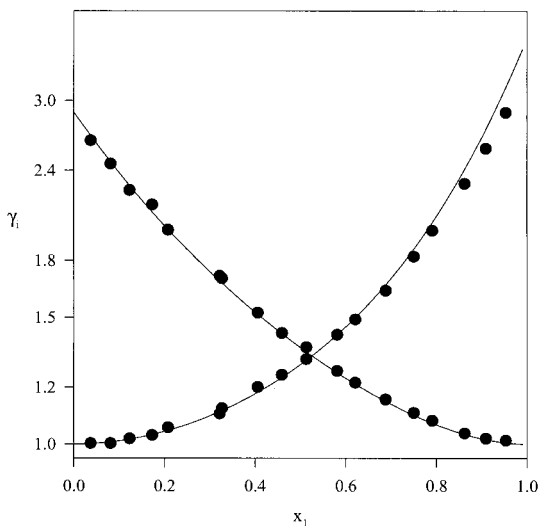


FIGURE 4 Activity coefficients for the system ETBE (1)+2-propanol (2) at 94.00 kPa. (●) experimental data; (—) smoothed by the Wilson model, with the parameters given in Table VIII.

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.* [5] and by Aucejo *et al.* [6], the scarce physical information available for mixtures of ETBE with alkanes does not allow a reliable estimation of second virial coefficients, thus introducing uncertainty in the estimation of vapor phase corrections. The temperature dependence of the pure component vapor pressure P_i^0 was calculated using the Antoine equation

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

where the Antoine constants A_i , B_i , and C_i are reported in Table V. The calculated activity coefficients are reported in Tables II–IV and are estimated accurate to within $\pm 2\%$. The results reported in these tables indicate that, for the range of pressures of the measurements, the system ETBE (1)+2-propanol (2) deviates positively from ideal

TABLE V Antoine coefficients, Eq. 2

Compound	A_i	B_i	C_i
ETBE ^a	5.96651	1151.7300	55.060
2-propanol ^b	6.90592	1382.0250	73.362

^aReich *et al.* [5]; ^bSegura *et al.* [2].

TABLE VI Estimated azeotropic coordinates for the system ETBE (1) + 2-Propanol (2)

Pressure	x_1^{Az}	T^{Az}/K
50	0.815	323.05
75	0.760	333.75
94	0.730	340.08

behavior and exhibits azeotropic behavior. The azeotropic concentrations of the measured binaries were estimated by fitting the function

$$f(x) = 100 \times \frac{y - x}{x} \quad (3)$$

where $f(x)$ is an empirical interpolating function and x, y have been taken from the experimental data. Azeotropic concentrations, as determined by solving $f(x) = 0$, are indicated in Table VI, from which it is concluded that the azeotrope impoverishes in ETBE as pressure (and/or temperature) increases. The trend of the azeotropic concentration is in good agreement with Wrewki's law [7], according to which with increasing temperature and pressure, a positive azeotrope becomes impoverished in the component which exhibits the lowest enthalpy of vaporization.

The VLE data reported in Tables II–IV, were found to be thermodynamically consistent by the point-to-point method of Van Ness *et al.* [8] as modified by Fredenslund *et al.* [9] ($\Delta y < 0.01$). In all cases, the consistency criteria was met by fitting the data to a three-parameter Legendre polynomial. Pertinent consistency statistics are presented in Table VII.

The VLE data were also correlated with the Wohl, NRTL, Wilson, and UNIQUAC equations [10] and predicted by the UNIFAC group

TABLE VII Consistency test statistics for the binary system ETBE (1) + 2-propanol (2)

Pressure level/kPa	N_p^a	$100 \times \Delta y^b$	ΔP^c /kPa
50.00	3	0.4	0.24
75.00	3	0.5	0.39
94.00	3	0.6	0.23

^aNumber of parameters for the Legendre polynomial used in consistency; ^bAverage absolute deviation in vapor phase mole fractions $\Delta y = 1/N \sum_{i=1}^N |y_i^{\text{exptl}} - y_i^{\text{calc}}|$ (N : number of data points);

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

Model	P/kPa	A_{12}	A_{21}	α_{12}	Bubble-point pressures		Dew-point pressures	
					$\Delta P(\%)^f$	$100 \times \Delta y_i$	$\Delta P(\%)$	$100 \times \Delta x_i$
Wohl	50.00	1.022	1.343	0.761 ^e	0.59	0.3	0.59	0.6
	75.00	1.025	1.303	0.761 ^e	0.51	0.5	0.47	0.7
	94.00	1.025	1.257	0.761 ^e	0.35	0.5	0.40	0.7
NRTL ^a	50.00	2779.85	1077.73	0.432	0.50	0.3	0.45	0.6
	75.00	2678.42	1175.82	0.432	0.49	0.4	0.42	0.7
	94.00	2572.56	1257.37	0.432	0.32	0.5	0.34	0.7
Wilson ^{a,b}	50.00	-570.35	4571.39		0.48	0.3	0.44	0.4
	75.00	-488.33	4463.51		0.46	0.4	0.39	0.6
	94.00	-444.98	4394.37		0.40	0.4	0.35	0.6
UNIQUAC ^{a,c}	50.00	2.065.32	-776.50		0.54	0.4	0.52	0.6
	75.00	2016.43	-744.84		0.49	0.5	0.44	0.8
	94.00	1946.77	-705.35		0.33	0.5	0.35	0.7
UNIFAC ^d	50.00				3.84	1.2	3.01	1.5
	75.00				3.82	1.2	3.10	1.3
	94.00				3.71	1.2	3.00	1.3

^aParameters in $\text{J} \times \text{mol}^{-1}$; ^bliquid volumes have been estimated from the Rackett equation [18]; ^cmolecular parameters are those calculated from UNIFAC [11]; ^dcalculations based on original UNIFAC [9,11]; ^e“q” parameter for the Wohl’s model; ^f $\Delta P = 100/N \sum_{i=1}^N |P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$.

contribution method [9,11]. The parameters of these models were obtained by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^N \left(\left| P_i^{\text{exptl}} - P_i^{\text{calc}} \right| / P_i^{\text{exptl}} + \left| y_i^{\text{exptl}} - y_i^{\text{calc}} \right| \right)^2 \quad (4)$$

and are reported in Table VIII, together with the relative deviation of the vapor phase mole fraction. Inspection of the results given in Table VIII shows that all four models gave a reasonable fit of the binary systems, the best fit corresponding to the Wilson model. The capability of predicting simultaneously the vapor phase mole fraction and the equilibrium pressure has been used as the ranking factor. Table VIII shows also that the UNIFAC model [11] does not predict accurately the VLE data of the system reported in this work.

Excess Volume Data

The density ρ measurements at $T = 298.15$ K are reported in Table IX, together with the excess volumes V^E that were calculated from the following equation

$$V^E = \frac{1}{\rho} \sum_{i=1}^2 x_i M_i - \sum_{i=1}^2 x_i \frac{M_i}{\rho_i} \quad (5)$$

where ρ is the density of the mixture, ρ_i the density of the pure components, and M_i is the molecular weight. M_i values were taken from

TABLE IX Densities and excess volumes for the binary system ETBE (1) + 2-propanol (2) at 298.15 K

x_1	$\rho/\text{g} \times \text{cm}^{-3}$	$10^3 \times V^E/\text{cm}^3 \times \text{mol}^{-1}$
0.0393	0.77898	-77
0.1061	0.77495	-169
0.1541	0.77229	-235
0.1852	0.77051	-261
0.2479	0.76715	-314
0.2942	0.76466	-330
0.3525	0.76183	-362
0.3995	0.75952	-366
0.4574	0.75684	-370
0.5091	0.75458	-370
0.5630	0.75235	-368
0.5671	0.75222	-373
0.6850	0.74760	-338
0.7327	0.74585	-317
0.7941	0.74370	-288
0.8071	0.74319	-270
0.8758	0.74080	-208
0.9614	0.73781	-89

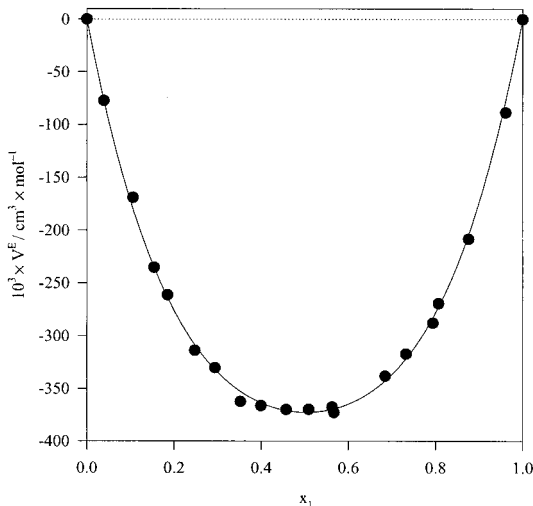


FIGURE 5 Excess volume for the system ETBE (1) + 2-propanol (2) at 298.15 K. (●) experimental data; (—) smoothed by a Redlich–Kister expansion with the parameters shown in Table X.

DIPPR [12]. The calculated excess volumes reported in Table IX are estimated accurate to within $\pm 10^{-3} \text{ cm}^3 \times \text{mol}^{-1}$. Table IX and Fig. 5 indicate that the excess volumes of the system ETBE (1) + 2-propanol (2) are negative, behavior that may be explained in terms of cross association between components, as expected for specific interactions between the polar alkanol and the aprotic aliphatic ether.

The excess volume data have been correlated using a three parameter Redlich–Kister expansion [13]

$$V^E = x_1 x_2 \sum_{k=0}^m c_k (x_1 - x_2)^k \quad (6)$$

where the c_k parameters, together with the correlation statistics, are reported in Table X.

An Association Approach to the Data

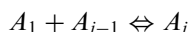
As follows from the chemical theory [14], positive deviations from ideal behavior, as observed in the present VLE data, may be explained

TABLE X Coefficients in correlation of excess volumes, Eq. 6. ETBE (1) + 2-propanol (2) at 298.15 K. Maximum, average and standard deviation, stdev

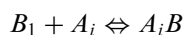
c_0^d	c_1^d	c_2^d	c_3^d	<i>Max dev</i>	<i>Avg dev</i>	<i>St dev</i>
$10^3 \times \text{cm}^3 \times \text{mol}^{-1}$						
-1.486	-9.103×10^{-2}	-6.926×10^{-1}	3.069×10^{-1}	5.9	2.8	1.9

^dParameters in $\text{cm}^3 \times \text{mol}^{-1}$.

in terms of dominant self association of 2-propanol. In addition, cross association between the components of the mixture may be expected for the functional groups of ether and alcohol. According to the association theory of Nath and Bender [15], it is possible to predict that the equilibrium association constants for 2-propanol and ETBE, at 323.15 K, are in the ratio 47:1. Consequently, the self-association of ETBE may be neglected. From the association theory of Nath and Bender for mixtures [16], when a molecule A (for example, 2-propanol) self-associates according to the following scheme



and cross-associates with a non-associating molecule B (in this case, ETBE) according to



the chemical contribution to activity coefficients is given by the following relations

$$\ln \gamma_A^{\text{chem}} = \ln \left(\frac{\phi_{A_1}}{x_A \phi_{A_1}^0} \right) - \frac{v_A}{v_{AB}} + \frac{v_A}{v_A^0} \quad (7)$$

$$\ln \gamma_B^{\text{chem}} = \ln \left(\frac{\phi_{0B}}{x_B} \right) + 1 - \frac{v_B}{v_{AB}} \quad (8)$$

where v_i is the apparent molar volume of component i ; ϕ_{A_1} , ϕ_{0B} are the volume fraction of the monomer A_1 and of the unreacted component

B , respectively. In Eqs. 7 and 8 v_{AB} corresponds to the molar volume of the solution which, in turn may be calculated from

$$\frac{1}{v_{AB}} = \frac{\phi_{A_1}}{v_A(1 - K_A\phi_{A_1})} + \frac{\phi_{0B}}{v_B} \left[\frac{1 - (K_A - K_{AB})\phi_{A_1}}{1 - K_A\phi_{A_1}} \right] \quad (9)$$

where $\phi_{A_1}^0$ and v_A^0 are the volume fraction and the molar volume of pure component A present as the monomer, given as function of the self association equilibrium constant K_A as

$$\phi_{A_1}^0 = [(2K_A + 1) - (1 + 4K_A)^{1/2}]/2K_A^2 \quad (10)$$

$$\frac{1}{v_A^0} = \frac{\phi_{A_1}^0}{v_A(1 - K_A\phi_{A_1}^0)} \quad (11)$$

ϕ_{A_1} , ϕ_{0B} can be calculated by solving simultaneously the following relations

$$\phi_A = [\phi_{A_1}/(1 - K_A\phi_{A_1})^2] \times [1 + K_{AB}\phi_{0B}v_A/v_B] \quad (12)$$

$$\phi_B = \phi_{0B}[1 - (K_A - K_{AB})\phi_{A_1}] \times [1 - K_A\phi_{A_1}]^{-1} \quad (13)$$

where ϕ_A and ϕ_B are apparent volume fractions defined as

$$\phi_i = \frac{x_i v_i}{x_A v_A + x_B v_B} \quad (i = A, B) \quad (14)$$

K_A and K_{AB} are equilibrium constants for self and cross association, respectively, and in the approach of Nath and Bender, they depend on temperature as follows

$$K_i = K_i^{323K} \exp \left[-\frac{h_i}{R} \left(\frac{1}{T/K} - \frac{1}{323.15} \right) \right] \quad (i = A, AB) \quad (15)$$

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 [15] provides a predictive scheme for calculating enthalpies and equilibrium constants for pure fluids that self-associate. In the case of cross association, both enthalpy and the normalized

equilibrium constant must be calculated from VLE data. Once activity coefficients have been calculated from Eqs. 7 to 15, the chemical contribution to the excess energy may be evaluated as

$$\left(\frac{G^E}{RT}\right)^{\text{chem}} = x_A \ln \gamma_A^{\text{chem}} + x_B \ln \gamma_B^{\text{chem}} \quad (16)$$

while the excess Gibbs energy, including physical contributions, is given by

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)^{\text{phys}} + \left(\frac{G^E}{RT}\right)^{\text{chem}} \quad (17)$$

According to DIPPR [12], the critical volumes of 2-propanol and ETBE are in the ratio 1:2, indicating that molecular size may effect the excess energy of the system. 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, is van Laar's equation [17]

$$\left(\frac{G^E}{RT}\right)^{\text{phys}} = \frac{A_{ij}A_{ji}x_i x_j}{A_{ij}x_i + A_{ji}x_j} \quad (18)$$

Equation 18 has been used for modeling the physical contribution in Eq. 17. The association model proposed here depends on four parameters and on 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. 18. Additional parameters are the cross association enthalpy h_{AB} and the normalized equilibrium constant $K_{AB}^{323\text{K}}$. All these previous parameters have been calculated from the experimental VLE data presented in Tables II and IV, using the objective function indicated in Eq. 4. Pure fluid volumes have been estimated from the equation proposed by Rackett [18] and pure component physical data have been taken DIPPR [12]. Pertinent parameters and statistics are reported in Table XI, from which it is possible to conclude an excellent correlation of the data.

TABLE XI Data treatment for the system ETBE (1)+2-propanol (2) using the association approach in Eq. 17. Model parameters and correlation statistics

I. Parameters

$K_2^{323\text{K}}$	$h_2/\text{J mol}^{-1}$	$K_{12}^{323\text{K}}$	$h_{12}/\text{J mol}^{-1}$	A_{12}	A_{21}
46.4 ^a	-16936 ^a	10.236 ^b	-11560 ^b	0.3898 ^b	0.3411 ^b

II. Correlation statistics

P/kPa	Bubble-point pressures		Dew-point pressures	
	$\Delta P(\%)$	$100 \times \Delta y_i$	$\Delta P(\%)$	$100 \times \Delta y_i$
50.00	0.53	0.2	0.49	0.3
75.00	0.53	0.3	0.43	0.4
94.00	0.47	0.4	0.40	0.5

^aCalculated according to the approach of Nath and Bender [15] from saturation data;

^bcalculated from the experimental data presented in Tables II-IV.

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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

Ck = Redlich Kister parameter, Eq. 6, $\text{cm}^3 \times \text{mol}^{-1}$

G^E = excess Gibbs energy, $\text{J} \times \text{mol}^{-1}$

h = association enthalpy, $\text{J} \times \text{mol}^{-1}$

K = association constant

P = absolute pressure, kPa

P^o = pure component vapor pressure, kPa

R = universal gas constant, $\text{J} \times \text{mol} \times \text{K}^{-1}$

T = absolute temperature, K

V = volume, $\text{cm}^3 \times \text{mol}^{-1}$

x, y = mole fractions of the liquid and vapor phases

Greek

γ = activity coefficient

ρ = density, $\text{g} \times \text{cm}^{-3}$

ϕ = volume fraction

Superscripts

E = excess property

L = pertaining to the liquid phase

0 = reference state (pure component)

$^{\text{chem}}$ = chemical contribution

$^{\text{phys}}$ = physical contribution

Subscripts

i, j = component i, j respectively

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