Isobaric Vapor-Liquid Equilibria and Densities for the Binary Systems Oxolane + Ethyl 1,1-Dimethylethyl Ether, Oxolane + 2-Propanol and Propan-2-One + Trichloromethane

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Vapor–liquid equilibrium data have been determined at 50 kPa for the binary systems oxolane (THF) + ethyl 1,1-dimethylethyl ether (ETBE) and oxolane + 2-propanol, and at 94 kPa for the system propan-2-one + trichloromethane. Excess volumes have also been determined from density measurements at 298.15 K. The systems oxolane + ethyl 1,1-dimethylethyl ether and oxolane + 2-propanol exhibit slight to moderate positive deviations from ideal behavior and no azeotrope is present. The system propan-2-one + trichloromethane exhibits negative deviations from ideal behavior and presents an azeotrope. The excess volumes of the system oxolane + ethyl 1,1-dimethylethyl ether are negative over the whole mole fraction range while those of the system oxolane + 2-propanol are positive. Excess volumes of the system propan-2-one + trichloromethane, change from negative to positive as the concentration of propan-2-one increases. The activity coefficients and boiling points of the solutions were correlated with the mole fraction by the Wohl, Wilson, UNIQUAC, and NRTL equations, and predicted by the UNIFAC group contribution method. Excess volume data were correlated using the Redlich–Kister expansion. The chemical association theory was applied for explaining the equilibrium behavior of the systems oxolane + 2-propanol and propan-2-one + trichloromethane.

Keywords: Vapor–liquid equilibrium; Excess volume; Ether; ETBE

INTRODUCTION

This work is part of our program to determine vapor–liquid equilibria (VLE) in systems formed by oxygenates (ethers and alcohols) and other organics, mainly gasoline components. Such a kind of mixtures appear frequently in the industrial production of ethers for gasoline blending and in recent years, they have been considered for producing reformulated gasolines. VLE data of ethers and alcohols are important

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for predicting the vapor phase concentration that would be in equilibrium with hydrocarbon mixtures and to dehydrate alcohols by means of azeotropic distillation technologies.

From a theoretical viewpoint, the vapor–liquid equilibrium of mixtures of ethers with alcohols is difficult to model since it depends on complex patterns of self- and cross-association. For this reason, this work gives a detailed treatment of the association effects present. The system propan-2-one + trichloromethane constitutes a well-known case of cross association; consequently, its measurement and treatment is a good opportunity for testing the reliability of our experimental methods and theoretical approach.

VLE data for the system THF (1) + ETBE (2) have been reported by Wisniak and Segura [1] at 94 kPa, found to show slight positive deviations from the Raoult's law and not to show azeotropy. The densities of this system have not been reported in the literature. VLE data for the mixture THF (1) + 2-propanol (3) have been reported at 94 kPa by Wisniak [2] and at 101 kPa by Shnitko *et al.* [3] and Yoshikawa *et al.* [4]. Sales *et al.* [5] have reported VLE and density data at 298.15 K. The experimental data show that the system THF (1) + 2-propanol (3) deviates positively from ideal behavior, exhibits positive excess volumes, and no azeotrope is present. According to Letcher and Govender [6], many mixtures of linear ethers + alcohols exhibit negative excess volumes; however, the experimental evidence suggests that cyclic ethers may present a different behavior. Many VLE data have been reported for the system propan-2-one (4) + trichloromethane (5). Isothermal VLE data have been reported by the Röeck and Schröeder [7] at (288.15, 293.15, 303.15, 308.15, 313.15, 323.15, 328.15) K, by Apelblat *et al.* [8] at (298.15, 308.15) K, by Tamir *et al.* [9,10] at (298.15, 308.15) K, by Kudryavtseva and Susarev [11] at (308.15, 318.15, 328.15) K and at 101 kPa, and by Mueller and Kearns [12] at (298.15, 308.15, 323.15) K. Data at atmospheric pressure have been also reported by Morachevskii and Leontev [13], by Schnelle and Canjar [14], and by Kogan and Deizenrot [15]. According to these references, the system propan-2-one (4) + trichloromethane (5) presents large negative deviations from ideal behavior and a negative azeotrope rich in chloroform. Campbell *et al.* [16] determined the excess volumes of the system propan-2-one (4) + chloroform (5) at 298.15 K and found that it was negative for concentrations of propan-2-one below 68-mole%, and positive afterwards. In addition, the curve of the excess volumes presented two stationary points, a negative minimum ($-0.152 \, \text{cm}^{-3} \, \text{mol}^{-1}$, at 32 mole% of propan-2-one) and a positive maximum ($0.05 \, \text{cm}^{-3} \, \text{mol}^{-1}$, at 86 mol%).

The present work was undertaken to measure isobaric VLE data for the systems THF + ETBE and THF + 2-propanol at 50 kPa and for the system propan-2-one + trichloromethane at 94 kPa. No VLE data have been reported previously for the quoted systems at the indicated pressures. In addition, the densities of all these are also reported at 298.15 K.

EXPERIMENTAL SECTION

Purity of Materials

ETBE (96.0 + mass%) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan) and, then, it was purified to more than 99.7 + mass% by rectification in a 1 m height to 30 mm diameter Normschliffgerätebau adiabatic distillation column

(packed with 3×3 mm stainless steel spirals), working at a $1:100$ reflux ratio. Acetone $(99.9 + \text{mass}\%)$, chloroform $(99.9 + \text{mass}\%)$ and 2-propanol $(99.9 \text{ mass}\%)$ were purchased from Merck and were used without further purification. Before measurements, 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 Systemteknik S1224 digital temperature meter, and a Pt $100 \, \Omega$ 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 $1.0 \, \mu$L after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus and a Thermo Separation Products model SP4400 electronic integrator. For the case of the systems THF + ETBE and THF + 2-propanol, the column was 3 m long and 0.3 cm in diameter, packed with Carbowax. Column, injector and detector (thermal conductivity detector, TCD) temperatures were (333.15, 383.15, 473.15) K, respectively. For the system propan-2-one + trichloromethane, a 30 m capillary column, packed with

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

Component (purity/mass %)	n_D (293.15 K)		Density (g cm^{-3}) (298.15 K)		T_b (101.33 kPa) (K)	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
THF (99.9 +)	1.40751[a]	1.4072[b]	0.88229[a]	0.8823[f]	339.10[a]	339.08[i]
ETBE (99.7 +)	1.37594[a]	1.37564[c]	0.73553[a]	0.73513[c]	345.85[a]	345.86[j]
2-Propanol (99.9 +)	1.37731[a]	1.3772[d]	0.78094[a]	0.78126[g]	355.40[a]	355.39[k]
Propan-2-one (99.9 +)	1.35884[a]	1.3591[e]	0.78503[a]	0.7856[h]	329.25[a]	329.22[l]
Trichloromethane (99.9 +)	1.44617[a]	1.4476[e]	1.47884[a]	1.4828[c]	334.29[a]	334.35[m]

[a]Measured; [b]Kobe *et al.* [34]; [c]DIPPR [21]; [d]Ballard and van Winkle [35]; [e]The Merck Index [36]; [f]Ramkumar and Kudchadker [37]; [g]Riddick *et al.* [38]; [h]Dizechi and Marschall [39]; [i]Wu and Sandler [22]; [j]Krähenbühl and Gmehling [40]; [k]Ambrose and Sprake [41]; [l]Ambrose *et al.* [23]; [m]Boublik and Aim [24].

Supelcowax, was used. Column, injector and detector (flame ionization detector, FID) temperatures were $(373.15, 403.15, 423.15)$ K, respectively. Good separations were achieved for each system 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. Density of the pure components and their mixtures were measured using a DMA 5000 densimeter (Anton Paar, Austria) with an accuracy of 5×10^{-6} g 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 for the mixtures studied here are reported in Tables II–IV and in Figs. 1–6, together with the activity coefficients γ_i that were calculated from the following equation [17]:

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

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

T (K)	x_1	y_1	γ_1	γ_2
324.94	0.000	0.000		1.000
324.07	0.062	0.084	1.117	1.008
323.29	0.130	0.170	1.109	1.014
322.85	0.176	0.225	1.101	1.016
322.32	0.232	0.289	1.094	1.020
321.86	0.280	0.341	1.088	1.025
321.37	0.341	0.404	1.078	1.032
320.98	0.394	0.456	1.068	1.039
320.71	0.438	0.499	1.062	1.043
320.25	0.502	0.558	1.054	1.056
319.95	0.560	0.611	1.046	1.064
319.77	0.616	0.661	1.036	1.070
319.66	0.641	0.683	1.033	1.074
319.45	0.699	0.733	1.024	1.088
319.30	0.750	0.778	1.019	1.095
319.19	0.796	0.817	1.012	1.111
319.05	0.853	0.867	1.008	1.127
319.00	0.902	0.911	1.003	1.133
318.92	0.957	0.960	0.999	1.164
318.82	1.000	1.000	1.000	

TABLE III   Experimental vapor–liquid equilibrium data for THF (1) + 2-propanol (3) at 50.00 kPa

T (K)	x_1	y_1	γ_1	γ_3
338.77	0.000	0.000		1.000
337.45	0.040	0.096	1.246	1.001
335.98	0.084	0.191	1.243	1.003
334.15	0.143	0.305	1.235	1.004
332.55	0.195	0.389	1.221	1.013
331.51	0.233	0.446	1.213	1.014
330.09	0.283	0.515	1.212	1.016
328.90	0.331	0.567	1.189	1.029
327.71	0.380	0.616	1.174	1.045
326.56	0.431	0.661	1.158	1.060
325.60	0.480	0.700	1.138	1.079
324.65	0.532	0.736	1.118	1.105
323.66	0.585	0.771	1.103	1.137
322.93	0.636	0.800	1.081	1.174
322.20	0.699	0.835	1.054	1.218
321.98	0.719	0.846	1.046	1.232
321.35	0.768	0.873	1.034	1.276
320.70	0.824	0.904	1.023	1.313
320.18	0.872	0.930	1.014	1.349
318.82	1.000	1.000	1.000	

TABLE IV   Experimental vapor–liquid equilibrium data for propan-2-one (4) trichloromethane (5) at 94.00 kPa

T (K)	x_4	y_4	γ_4	γ_5	$-B_{44}$ (cm³ mol⁻¹)	$-B_{55}$ (cm³ mol⁻¹)	$-B_{45}$ (cm³ mol⁻¹)
332.01	0.000	0.000		1.000	1328	911	1364
332.47	0.042	0.024	0.475	1.003	1321	908	1356
333.16	0.102	0.065	0.518	1.002	1312	903	1344
333.66	0.151	0.107	0.567	0.996	1305	899	1336
334.05	0.183	0.138	0.595	0.986	1300	896	1330
334.58	0.234	0.190	0.630	0.972	1293	892	1321
334.94	0.274	0.238	0.666	0.953	1288	890	1315
335.15	0.321	0.297	0.704	0.934	1285	889	1312
335.22	0.350	0.345	0.749	0.907	1284	888	1311
335.13	0.390	0.400	0.781	0.888	1286	889	1312
335.00	0.417	0.433	0.794	0.882	1287	890	1314
334.88	0.441	0.471	0.820	0.861	1289	890	1316
334.83	0.451	0.482	0.822	0.860	1290	891	1317
334.42	0.507	0.560	0.861	0.824	1295	894	1324
333.90	0.560	0.629	0.891	0.792	1302	897	1332
333.27	0.609	0.691	0.919	0.758	1311	902	1342
332.70	0.647	0.739	0.943	0.723	1318	906	1352
331.81	0.706	0.800	0.964	0.685	1331	912	1367
331.05	0.755	0.845	0.977	0.653	1341	918	1380
330.40	0.794	0.876	0.984	0.635	1350	923	1391
329.60	0.843	0.912	0.992	0.608	1362	929	1405
328.85	0.889	0.943	0.998	0.571	1373	934	1419
328.06	0.939	0.972	1.000	0.524	1384	940	1433
327.07	1.000	1.000	1.000		1399	948	1452

for the system THF (1) + ETBE (2) and THF (1) + 2-propanol (3). In Eq. (1) P is the total pressure and P_i^0 is the pure component vapor pressure. When activity coefficients are calculated according to 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
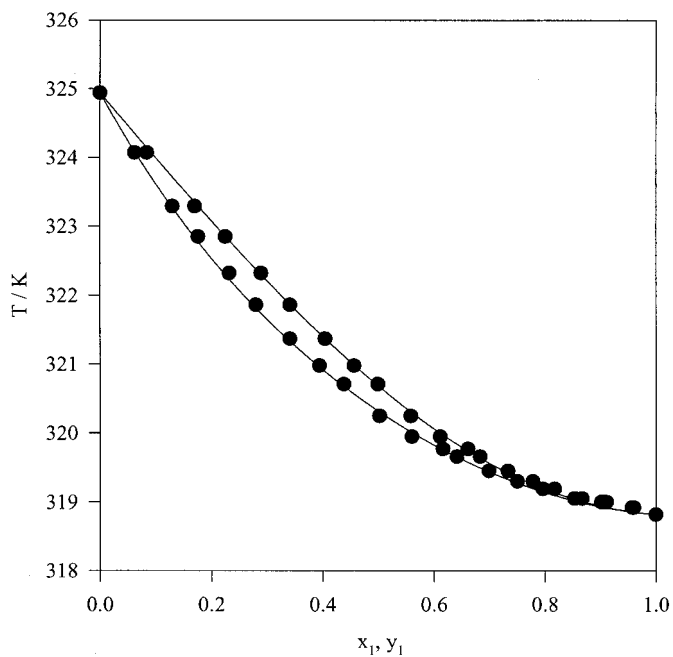
FIGURE 1 Boiling temperature diagram for the system THF (1) + ETBE (2) at 50 kPa. (●): Experimental data; (—): Smoothed by the Legendre polynomial that gives consistency to the data.
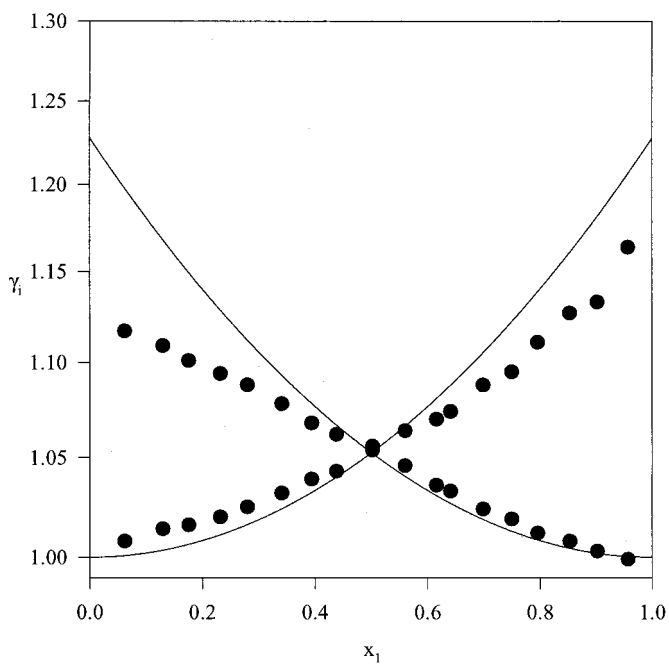

FIGURE 2 Activity coefficients for the system THF (1) + ETBE (2) at 50 kPa. (●): Experimental data; (—): Smoothed by the Legendre polynomial that gives consistency to the data.

FIGURE 3   Boiling temperature diagram for the system THF (1) + 2-propanol (3) at 50 kPa. (●): Experimental data; (—): Smoothed by the Legendre polynomial that gives consistency to the data.
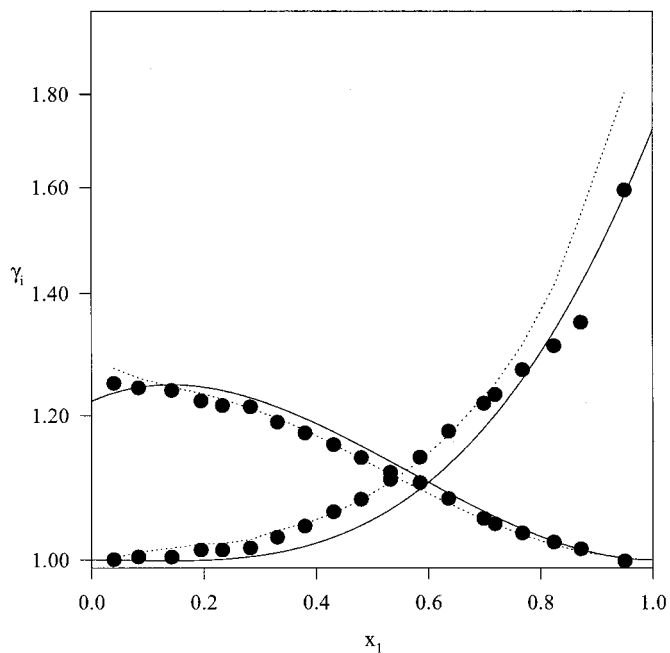
FIGURE 4   Activity coefficients for the system THF (1) + 2-propanol (3) at 50 kPa. (●): Experimental data; (—): Smoothed by 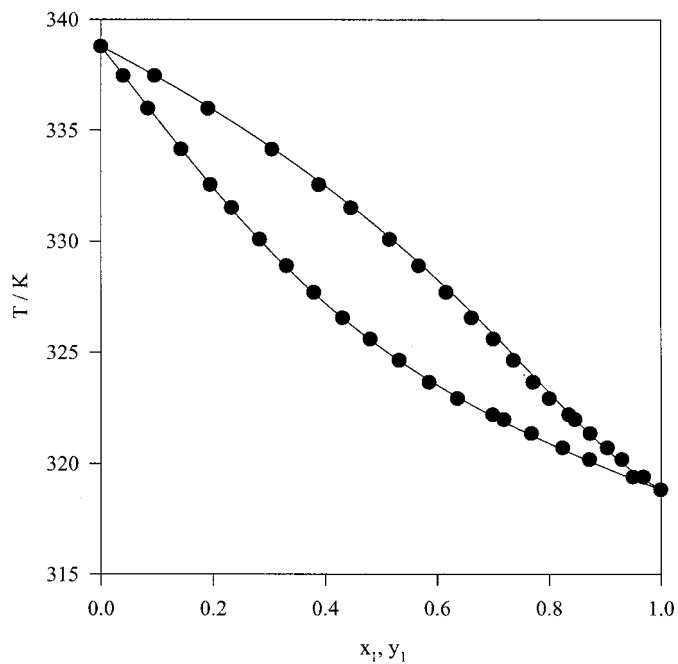the Legendre polynomial that gives consistency to the data; (···): Smoothed by the association model presented in Eqs. (9)–(20).

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FIGURE 5 Boiling temperature diagram for the system propan-2-one (4) + trichloromethane (5) at 94 kPa. (●): Experimental data; (—): Smoothed by the Legendre polynomial that gives consistency to the data.

FIGURE 6 Activity coefficients for the system propan-2-one (4) + trichloromethane (5) at 94 kPa. (●): Experimental data; (—): Smoothed by the Legendre polynomial that gives consistency to the data; (···): Smoothed by the association model presented in Eqs. (9)–(20).
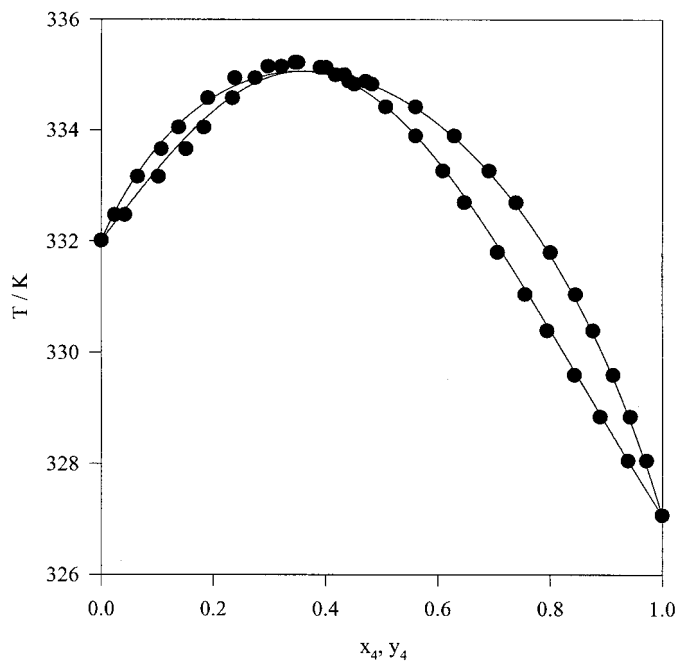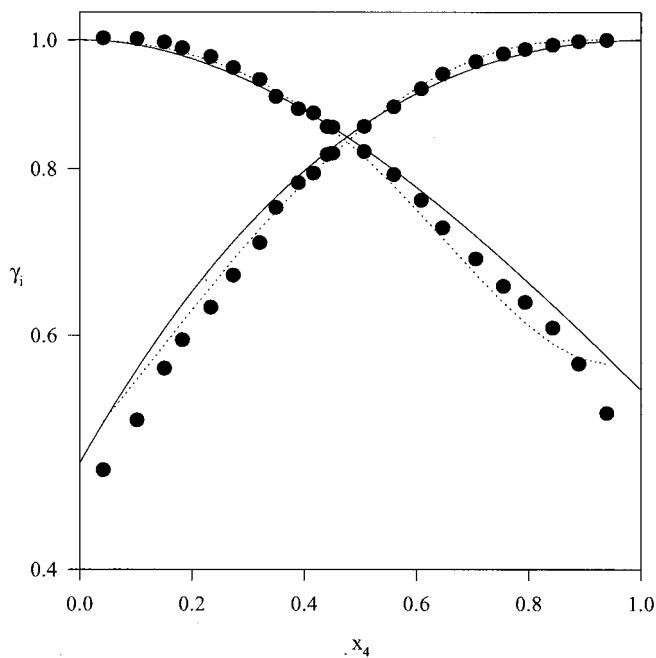
selected to calculate activity coefficients because the low pressure observed in the present VLE data makes these simplifications reasonable. In addition, and as discussed by Reich et al. [18] and by Aucejo et al. [19], the scarce physical information available for virial coefficients of mixtures of ETBE introduces uncertainty in the estimation of vapor phase corrections. Activity coefficients for the system propane-2-one $(4)+$ trichloromethane (5), were calculated according to [17]

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

where 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

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{3}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation (2) is valid from low to 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 volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell [20] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. Physical properties were taken from DIPPR [21] and the predicted values of the virial coefficients for the system propan-2-one $(4)+$ trichloromethane (5) are presented in Table IV. The last two terms in Eq. (2), particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 2% to activity coefficients. In general, their influence was important only at very dilute concentrations. The pure component vapor pressures P_i^0 for THF, propan-2-one and trichloromethane were determined experimentally in the same still used for VLE determinations and results are presented in Table V. The temperature dependence of the pure component vapor pressure P_i^0 was calculated using the Antoine equation

$$\log(P_i^0) = A_i - \frac{B_i}{T - C_i} \tag{4}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table VI. The experimental vapor pressures were fitted with an average percentage deviation [MADP] of 0.05% for THF, 0.01% for propane-2-one and 0.02% for trichloromethane. In addition, the parameters presented in Table VI predict very well the experimental vapor pressures reported by Wu and Sandler [22] for THF [$MADP = 0.18\%$], by Ambrose et al. [23] for propan-2-one [$MADP = 0.23\%$], and by Boublik and Aim [24] for trichloromethane [$MADP = 0.34\%$], as shown in Fig. 7. The calculated activity coefficients are reported in Tables II–IV and are estimated accurate to

TABLE V   Experimental vapor pressures for THF, propan-2-one, and trichloromethane

THF		Propan-2-one		Trichloromethane	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
309.50	34.80	291.69	23.09	301.48	30.23
0312.91	39.83	297.09	29.34	306.11	36.53
315.98	44.87	301.05	34.75	309.28	41.41
318.83	50.00	304.10	39.45	312.62	47.10
321.66	55.54	308.22	46.59	315.49	52.52
324.28	61.17	311.31	52.64	318.48	58.65
327.06	67.53	314.47	59.43	321.19	64.70
329.33	73.05	317.00	65.39	323.49	70.20
331.58	78.94	319.28	71.15	325.75	75.98
333.42	84.03	321.48	77.11	328.15	82.56
335.18	89.10	323.50	82.89	330.23	88.59
336.80	94.00	325.50	88.96	332.01	94.00
339.10	101.33	327.07	94.00	334.30	101.33
		329.25	101.33		

TABLE VI   Antoine coefficient, Eq. (4)

Compound	A_i	B_i	C_i
THF[a]	5.95216	1109.6259	57.926
ETBE[b]	5.96651	1151.7300	55.060
2-Propanol[c]	6.90592	1382.0250	73.362
Propan-2-one[a]	6.28837	1233.5183	41.221
Trichloromethane[a]	6.14848	1207.7341	42.757

[a]Calculated from the vapor pressure data presented in Table V; [b]Reich *et al*. [8]; [c]Segura *et al*. [42].

within $\pm 2\%$. The results reported in these Tables indicate that, for the range of pressures of the measurements:

- the systems THF (1) + ETBE (2) and THF(1) + 2-propanol (3) deviate positively from ideal behavior and no azeotrope is present.
- the system propan-2-one (4) + trichloromethane (5) deviates negatively from ideal behavior and exhibits azeotropic behavior.

The azeotropic concentration of the system propan-2-one (4) + trichloromethane (5) was estimated by fitting the function

$$f(x) = 100 \times \frac{y-x}{x} \tag{5}$$

where $f(x)$ is an empirical interpolating function and x, y have been taken from the experimental data. The coordinates of the azeotrope, as determined by solving $f(x) = 0$, are indicated in Table VII. The VLE data determined for the system propan-2-one (4) + trichloromethane (5) are in good agreement with the data reported previously in [7–15].

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*. [25] as modified by Fredenslund *et al*. [26] ($\Delta y < 0.01$). Pertinent consistency details and statistics are presented in Table VIII.
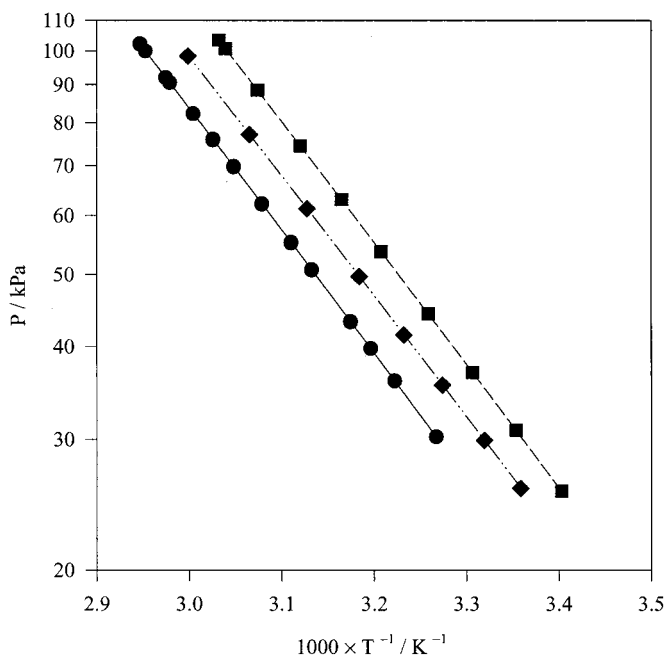
FIGURE 7 Comparison of correlated vapor pressures with other references. ($\bullet$): Experimental data reported by Wu and Sandler [22] for THF; ($\blacklozenge$): Experimental data reported by Ambrose *et al.* [23] for propan-2-one; ($\blacksquare$): Experimental data reported by Boublik and Aim [24] for trichloromethane. Predicted by Eq. (4) and parameters given in Table VI for THF (—), for propan-2-one ($-\cdots-$) and for trichloromethane ($--$).

TABLE VII Estimated azeotropic coordinates for the system propan-2-one (4) + trichloromethane (5) at 94 kPa

x_4^{Az}	T^{Az} (K)
0.374	335.16

The VLE data were also correlated with the Wohl, NRTL, Wilson, and UNIQUAC equations [27], and predicted by the UNIFAC group contribution method [26,28]. The parameters of these models were obtained by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^{N} (|P_i^{\exp tl} - P_i^{calc}|/P_i^{\exp tl} + |y_i^{\exp tl} - y_i^{calc}|)^2 \qquad (6)$$

and are reported in Table IX, together with the relative deviation of the vapor phase mole fraction. Inspection of the results given in Table IX indicates that all four models gave a similar fit of the binary systems, the best fit corresponding to the Wohl model. The capability of predicting simultaneously the vapor phase mole fraction and the equilibrium pressure has been used as the ranking factor. Table IX shows also that the UNIFAC model [28] is not accurate for predicting the VLE data of the system THF(1) + 2-propanol (3).

TABLE VIII Consistency test statistics for the binary systems determined in this work

System	N_p^{a}	$100 \times \Delta y^{b}$	ΔP^{c} (kPa)
1 + 2	1	0.5	0.08
1 + 3	3	0.6	0.10
4 + 5	2	0.6	0.26

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

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

Model	P (kPa)	A_{12}	A_{21}	α_{12}	Bubble-point pressures		Dew-point pressures	
					ΔP (%)[f]	$100 \times \Delta y_i$	ΔP (%)	$100 \times \Delta x_i$
Wohl	1 + 2	0.184	0.191	0.667[e]	0.17	0.4	0.24	0.4
	1 + 3	0.266	0.440	0.262[e]	0.25	0.4	0.51	0.6
	4 + 5	−0.716	−0.471	0.597[e]	0.36	0.4	0.39	0.4
NRTL[a]	1 + 2	259.41	256.60	0.300	0.20	0.4	0.26	0.4
	1 + 3	2868.80	−1237.20	0.355	0.36	0.4	0.56	0.5
	4 + 5	−1921.49	223.30	0.300	0.41	0.6	0.24	0.6
Wilson[a,b]	1 + 2	1957.66	−1439.30		0.24	0.3	0.24	0.3
	1 + 3	−488.33	4463.51		0.42	0.4	0.58	0.5
	4 + 5	525.87	−2226.83		0.42	0.6	0.24	0.6
UNIQUAC[a,c]	1 + 2	−517.77	759.41		0.30	0.3	0.33	0.3
	1 + 3	1480.19	−869.23		0.41	0.4	0.59	0.5
	4 + 5	−1331.02	912.03		0.43	0.6	0.26	0.6
UNIFAC[d]	1 + 2				0.23	0.4	0.28	0.4
	1 + 3				5.68	2.0	4.50	2.2
	4 + 5				1.06	0.4	0.95	0.3

[a]Parameters in J mol^{-1}; [b]liquid volumes have been estimated from the Rackett equation [33]; [c]molecular parameters are those calculated from UNIFAC [26]; [d]calculations based on original UNIFAC [26,28]; [e]"q" parameter for the Wohl's model; [f]$\Delta P = 100/N \sum_{i}^{N} |P_i^{exptl} - P_i^{calc}|/P_i^{exptl}$.

Excess Volume Data

The density ρ measurements at $T = 298.15\,\text{K}$ are reported in Tables X–XII, together with the excess volumes V^E that were calculated from

$$V^E = \frac{1}{\rho} \sum_{i=1}^{2} x_i M_i - \sum_{i=1}^{2} x_i \frac{M_i}{\rho_i} \qquad (7)$$

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 DIPPR [21]. The calculated excess volumes reported in Tables X–XII and Fig. 8 are estimated accuate to within $\pm 10^{-3}\,\text{cm}^3\,\text{mol}^{-1}$. The experimental results may be summarized as follows:

- the excess volumes of the system THF (1) + ETBE (2) are negative.
- the excess volumes of the system THF (1) + 2-propanal (3) are positive, confirming the results obtained by Sales *et al.* [5].

TABLE X Densities and excess volumes for the binary system THF (1) + ETBE (2) at 298.15 K

x_1	ρ (g cm^{-3})	$10^3 \times V^E$ (cm^3 mol^{-1})
0.0444	0.73980	−67
0.0794	0.74324	−113
0.1219	0.74760	−174
0.1567	0.75119	−208
0.1979	0.75562	−249
0.2496	0.76133	−291
0.2873	0.76563	−315
0.3569	0.77398	−356
0.3860	0.77759	−365
0.4490	0.78577	−387
0.5088	0.79395	−395
0.5486	0.79961	−390
0.6064	0.80828	−384
0.6489	0.81496	−371
0.6901	0.82167	−352
0.7627	0.83415	−299
0.7930	0.83969	−281
0.8557	0.85160	−211
0.9056	0.86166	−149
0.9409	0.86914	−99

TABLE XI Densities and excess volumes for the binary system THF (1) + 2-propanol (3) at 298.15 K

x_1	ρ (g cm^{-3})	$10^3 \times V^E$ (cm^3 mol^{-1})
0.0468	0.78573	23
0.0883	0.78988	50
0.1340	0.79451	72
0.1919	0.80032	100
0.2383	0.80500	118
0.3076	0.81195	142
0.3629	0.81746	162
0.4023	0.82140	171
0.4534	0.82652	181
0.5038	0.83157	187
0.5428	0.83544	192
0.6016	0.84129	196
0.6601	0.84707	201
0.7056	0.85161	197
0.7277	0.85382	194
0.7314	0.85418	194
0.7804	0.85928	167
0.8428	0.86565	140
0.8835	0.86978	123
0.8988	0.87143	107
0.9058	0.87218	99
0.9433	0.87610	70

- the sign of excess volumes of the system propan-2-one (4) + trichloromethane (5) changes from negative to positive as the concentration of propan-2-one increases. The experimental results are in excellent agreement with the data reported by Campbell *et al.* [16].

TABLE XII   Densities and excess volumes for the binary system propan-2-one (4) + trichloromethane (5) at $298.15\,K$

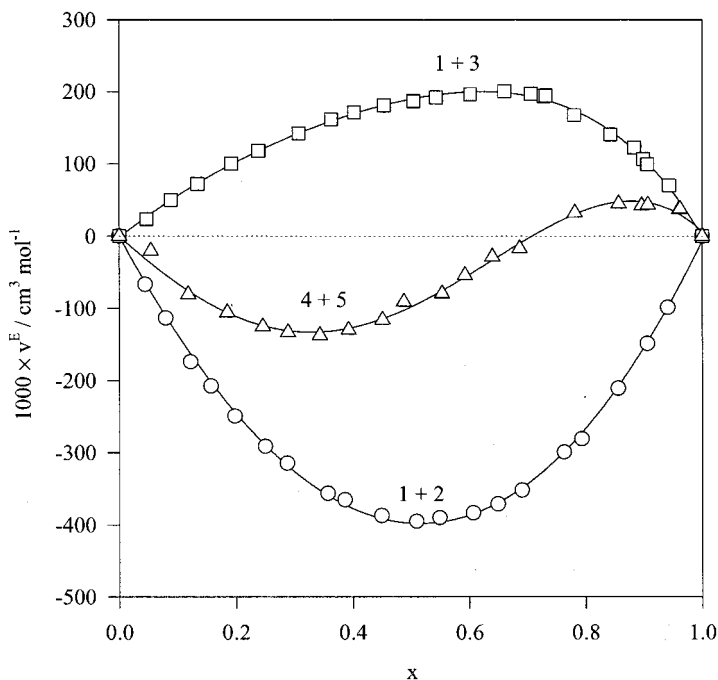| x_4	ρ $(g\,cm^{-3})$	$10^3 \times V^E$ $(cm^3\,mol^{-1})$
0.0542	1.44458	-21
0.1180	1.40448	-81
0.1851	1.36108	-106
0.2456	1.32148	-125
0.2889	1.29277	-133
0.3432	1.25637	-138
0.3926	1.22276	-130
0.4508	1.18273	-116
0.4875	1.15706	-91
0.5531	1.11126	-80
0.5924	1.08332	-54
0.6397	1.04953	-29
0.6865	1.01602	-17
0.7814	0.94687	32
0.8569	0.89141	45
0.8961	0.86246	42
0.9069	0.85445	44
0.9605	0.81442	37
0.9620	0.81327	38

FIGURE 8   Excess volumes for the binary systems measured in this work at $298.15\,K$. ($\bigcirc$): Experimental data for THF (1) + ETBE (2); ($\square$): Experimental data for THF (1) + 2-propanol (3); ($\triangle$): Experimental data for propan-2-one (4) + trichloromethane (5); (—): Smoothed by a Redlich–Kister expansion with the parameters shown in Table XIII.

TABLE XIII Coefficients in correlation of excess volumes, Eq. (8). Maximum, average and standard deviation, stdev.

| System	c_0[a]	c_1[a]	c_2[a]	c_3[a]	Max dev	Avg dev $(10^3\,cm^3\,mol^{-1})$	Stdev
1 + 2	-1.574	-1.042×10^{-1}	-1.304×10^{-1}	–	6	2	2
1 + 3	7.593×10^{-1}	3.141×10^{-1}	2.232×10^{-1}	6.140×10^{-2}	7	3	2
4 + 5	-3.946×10^{-1}	7.816×10^{-1}	4.625×10^{-1}	-2.108×10^{-2}	16	5	5

[a]parameters in $cm^3\,mol^{-1}$.

The excess volume data were correlated using a three-parameter Redlich–Kister expansion [29].

$$V^E = x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \quad (i < j) \qquad (8)$$

where the C_k parameters, together with the correlation statistics, are reported in Table XIII.

An Association Approach to the Data

In this section we consider an association approach for treating the VLE data of the systems THF (1) + 2-propanol (3) and propan-2-one (4) + chloroform (5). The effect of specific association interactions may be observed in the trend of the excess volumes (see Fig. 8), as well as by the fact that standard models give a poor correlation of the activity coefficients of the system THF (1) + 2-propanol (3) (see Fig. 4). According to the chemical theory [30], positive deviations from ideal behavior, as those observed in the system THF (1) + 2-propanol (3), may be explained in terms of dominant self-association of the alcohol. Cross association between the components induces negative deviation from ideal behavior and may be expected for the functional groups of ether and alcohol. In addition, the system propan-2-one (4) + chloroform (5) constitutes an example of a mixture where the negative deviations may be explained in terms of dominant cross-association. According to Nath and Bender's theory [31] it is possible to predict that the equilibrium self-association constants for 2-propanol and THF at 323.15 K, are in the ratio 46 : 8. Consequently, the self-association of THF is weak and may be neglected. In the treatment that follows, it is also assumed that self-association of propan-2-one or trichloromethane may be neglected. According to the association theory of Nath and Bender [32], when a molecule A self-associates according to the following scheme

$$A_1 + A_{i-1} \Leftrightarrow A_i$$
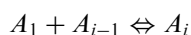
and cross-associates with an nonassociating molecule B according to

$$B_1 + A_i \Leftrightarrow A_i B$$
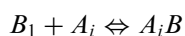
the chemical contribution to activity coefficients is given by the following relations

$$\ln \gamma_A^{\mathrm{chem}} = \ln\left(\frac{\phi_{A_1}}{x_A \phi_{A_1}^0}\right) - \frac{v_A}{v_{AB}} + \frac{v_A}{v_A^0} \tag{9}$$

$$\ln \gamma_B^{\mathrm{chem}} = \ln\left(\frac{\phi_{0B}}{x_B}\right) + 1 - \frac{v_B}{v_{AB}} \tag{10}$$

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. In Eqs. (9) and (10) V_{AB} corresponds to the molar volume of the solution which, in turn, may be calculated from

$$\frac{1}{v_{AB}} = \frac{\phi_{A_1}}{v_A(1 - K_A \phi_{A_1})} + \frac{\phi_{0B}}{v_B}\left[\frac{1 - (K_A - K_{AB})\phi_{A_1}}{1 - K_A \phi_{A_1}}\right] \tag{11}$$

where 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 function of the self association equilibrium constant K_A as

$$\phi_{A_1}^0 = \left[(2K_A + 1) - (1 + 4K_A)^{1/2}\right]/2K_A^2 \tag{12}$$

$$\frac{1}{v_A^0} = \frac{\phi_{A_1}^0}{v_A(1 - K_A \phi_{A_1}^0)} \tag{13}$$

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

$$\phi_A = \left[\phi_{A_1}/(1 - K_A \phi_{A_1})^2\right] \times [1 + K_{AB}\phi_{0B}v_A/v_B] \tag{14}$$

$$\phi_B = \phi_{0B}\left[1 - (K_A - K_{AB})\phi_{A_1}\right] \times \left[1 - K_A \phi_{A_1}\right]^{-1} \tag{15}$$

where ϕ_A and ϕ_B are apparent volume fractions defined as

$$\phi_i = \frac{x_i v_i}{x_A v_A + x_B v_B} \quad (i = A, B) \tag{16}$$

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

$$K_i = K_i^{323K} \exp\left[-\frac{h_i}{R}\left(\frac{1}{T} - \frac{1}{323.15}\right)\right] \quad (i = A, AB) \tag{17}$$

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 [31] provides a predictive scheme for calculating association enthalpies and equilibrium constants for pure fluids that self-associate. For the case of the system THF (1) + 2-propanol (3), we consider that only the alcohol self-associates. In the treatment of the system propan-2-one (4) + trichloromethane (5) self-association is neglected for each pure component (the chemical association regime is obtained from Eqs. (9) to (17) by letting $K_A = 0$ and $h_A = 0$). When cross-association is present in both mixtures, it is necessary to calculate the enthalpy and the normalized equilibrium constant from VLE data. Once activity coefficients have been calculated from Eqs. (9) to (17), the chemical contribution to the excess energy is evaluated as

$$\left(\frac{G^E}{RT}\right)^{\mathrm{chem}} = x_A \ln \gamma_A^{\mathrm{chem}} + x_B \ln \gamma_B^{\mathrm{chem}} \tag{18}$$

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

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)^{\mathrm{phys}} + \left(\frac{G^E}{RT}\right)^{\mathrm{chem}} \tag{19}$$

The physical contribution to the excess energy is calculated from the van Laar's method

$$\left(\frac{G^E}{RT}\right)^{\mathrm{phys}} = \frac{A_{ij} A_{ji} x_i x_j}{A_{ij} x_i + A_{ji} x_j} \tag{20}$$

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. (20). Additional parameters are

TABLE XIV(A) Data treatment for the systems THF (1) + 2-propanol (3) and propan-2-one (4) + trichloromethane (5), using the association approach, Eq. (19). Model parameters

System ($i+j$)	K_j^{323K}	h_j (J mol^{-1})	K_{ij}^{323K}	h_{ij} (J mol^{-1})	A_{ij}	A_{ji}
1 + 3	46.4[a]	−16936[a]	38.7[b]	−5777[b]	1.0208[b]	1.2364[b]
4 + 5	–	–	3.3[b]	−15871[b]	0.4679[b]	0.9038[b]

[a]calculated according to the approach of Nath and Bender [31] from saturation data; [b]calculated from the experimental data presented in Tables III and IV.

TABLE XIV(B) Data treatment for the systems THF (1) + 2-propanol (3) and propan-2-one (4) + trichloromethane (5), using the association approach, Eq. (19). Model correlation statistics

System ($i+j$)	Bubble-point pressures		Dew-point pressures	
	$\Delta P(\%)$	$100 \times \Delta y_4$	$\Delta P(\%)$	$100 \times \Delta x_i$
1 + 3	0.17	0.2	0.33	0.3
4 + 5	0.31	0.3	0.33	0.3

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 presented in Tables III and IV, using the objective function given by Eq. (6). Pure fluid volumes have been estimated from the Rackett equation [33] and pure component physical data have been taken from DIPPR [21]. Pertinent parameters and statistics are reported in Table XIV, from and show an excellent correlation of the data. Figures 4 and 6 show that the association approach yields a better representation of mid-range concentration activity coefficients.

NOMENCLATURE

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 ($cm^3\,mol^{-1}$)
$B_{ij} =$ cross second virial coefficient ($cm^3\,mol^{-1}$)
$C_i =$ Antoine's equation parameter, Eq. (4)
$c_k =$ Redlich–Kister parameter, Eq. (8)
$G^E =$ excess Gibbs energy ($J\,mol^{-1}$)
$h =$ association enthalpy ($J\,mol^{-1}$)
$K =$ association constant
$P =$ absolute pressure (kPa)
$P^0 =$ pure component vapor pressure (kPa)
$R =$ universal gas constant ($J\,mol\,K^{-1}$)
$T =$ absolute temperature (K)
$V =$ volume ($cm^3\,mol^{-1}$)
$x, y =$ mole fractions of the liquid and vapor phases

Greek

$\delta_{ij} =$ parameter defined in Eq. (3) ($cm^3\,mol^{-1}$)
$\gamma =$ activity coefficient
$\rho =$ density ($g\,cm^{-3}$)
$\phi =$ 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

Acknowledgment

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