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Thermochimica Acta 373 (2001) 161–171

thermochimica
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Thermodynamics of mixtures containing ethers PART II Isothermal x–y data for the ternary system MTBE + methanol + 1-butanol and for two constituent binaries: DISQUAC predictions on VLE of ternary mixtures containing tertiary-alkyl ethers and organic solvents

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Received 6 December 2000; accepted 15 January 2001

Abstract

VLE data at 298.15 K (x–y measurements, where x and y are the mole fractions in liquid and vapor phase, respectively) for methanol or 1-butanol + methyl *tert*-butyl ether (MTBE) and for MTBE + methanol + 1-butanol systems are reported. These data and those available on literature on VLE at isothermal conditions for ternary systems containing tertiary-alkyl ethers (MTBE, *tert*-amyl methyl ether (TAME)) and organic solvents (hydrocarbons and 1-alkanols) are analyzed in terms of DISQUAC. The model correctly predicts VLE of this type of mixtures using binary parameters only, i.e. neglecting ternary interactions. Results are independent of the mixture considered.

Keywords: VLE; Ternary systems; Tertiary-alkyl ethers; 1-Alkanols; Binary parameters; Group contributions

1. Introduction

Tertiary-alkyl ethers have become important additives for gasoline because their influence to increase the octane number and to decrease the emission of carbon monoxide is combined with a similarity of properties (e.g. vapor pressures) compared to hydrocarbons. So, the use of, e.g. methyl *tert*-butyl ether (MTBE) pure or mixed with C_4 alkanols have been recommended as a high octane blending agent for motor gasoline [1,2].

The mentioned ethers are commonly obtained by means of the reduction between an unsaturated hydrocarbon and an alcohol. The final step is the separation process, e.g. a mixture of MTBE, methanol and non-reacted hydrocarbons is obtained in the synthesis of MTBE. The separation process starts with an azeotropic distillation, which separates the hydrocarbons from the mixture of MTBE and methanol, which is usually separated by means of another distillation.

So in order to correctly design the separation process and to optimize the operation conditions, the

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PII: S0040-6031(01)00457-9

thermodynamic study of mixtures containing alkanols and tertiary-alkyl ethers are of great importance.

From a theoretical point of view, mixtures of alkanols and oxaalkanes are of interest due to their complexity, consequence of the self-association of the alcohols, partially destroyed by the active molecules of ethers, and of the new intermolecular OH–O bonds created [3,4]. So, the treatment of this class of mixtures is a severe test for any theoretical model. An additional complication comes when it is necessary to account for isomeric effects, because the compounds involved are of technological importance. It is known that the different VLE behavior of binary solutions containing a given solvent and different isomers is often due to different vapor pressure of pure compounds and not to different activities. However, excess euthalpy H^E is much sensitive to molecular structure and is modified rather substantially when a component is replaced by an isomer in a given mixture. In terms of models based on the group contribution concept, this means that new groups must be defined.

In part I of this series [4], systems of tertiary-alkyl ethers (MTBE, *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE)) and alkanes, 1-alkanols and benzene have been successfully characterized by us in terms of DISQUAC [5,6], a purely physical model based on the rigid lattice theory developed by Guggenheim [7]. As in previous works on the ability of DISQUAC to represent H^E measurements of ternary mixtures [8–10], it was then shown that DISQUAC provides good predictions on H^E for systems containing one tertiary-alkyl ether and hydrocarbons and 1-alkanols using binary parameters only, i.e. neglecting ternary interactions [4]. As a continuation, we examine here the ability of DISQUAC to predict isothermal VLE of these type of solutions. The model usually represents accurately total pressure measurements at isothermal conditions of any type of ternary mixture [10–12]. Here, the study is not restricted to predictions on total pressures, but is also extended to those on vapor-phase compositions. At this end, we report *x*–*y* data at 298.15 K for MTBE + methanol + 1-butanol and for the two binaries MTBE + methanol, or MTBE + 1-butanol. The VLE of the methanol + MTBE mixture has been widely studied [13–20]. VLE measurements for methanol + 1-butanol are also available [21]. In exchange, the literature survey showed [22,23] that no data have been reported for MTBE + 1-butanol and for the ternary considered.

In order to develop a more complete comparison with data available in literature, and to extend the matrix of DISQUAC interaction parameters, we also report here interaction parameters for tertiary-alkyl ethers + toluene mixtures.

2. Theory

In the framework of DISQUAC, mixtures of tertiary-alkyl ethers with organic solvents are regarded as possessing three types of surfaces: (i) type a (aliphatic: CH_3, CH_2, CH, C, in ethers, *n*-alkanes, or 1-alcohols); (ii) type e (O, oxygen in tertiary-alkyl ethers); (iii) type s (s = b, C_6H_6 in benzene; s = c, cyclic, c-CH_2 in C_6H_{12}; s = h, hydroxyl, OH in 1-alkanols; s = p, C_6H_5 in toluene).

2.1. Assessment of geometrical parameters

When DISQUAC is applied, the total relative molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_{si}, of the compounds present in the mixture are usually calculated additively on the basis of the group volumes R_G and surfaces Q_G, recommended by Bondi [24]. As volume and surface units, the volume R_{CH_4} and surface Q_{CH_4} of methane are taken arbitrarily [25]. The geometrical parameters referred to in this work are given elsewhere [25–27].

2.2. Equations

The equations used to calculate G^E and H^E are the same as in other applications [26,27]. The interaction terms in the excess thermodynamic properties G^E, H^E and C_p^E contain a DIS and a QUAC contribution, which are calculated independently by the classical formulas and then simply added. The degree of non-randomness is thus expressed by the relative amounts of dispersive and quasichemical terms.

$$F^E = F^{E,COMB} + F_{int}^{E,DIS} + F_{int}^{E,QUAC} \tag{1}$$

where $F^E = G^E$, H^E or C_p^E. In Eq. (1), $F^{E,COMB}$ is only different to zero for $F^E = G^E$ (Flory–Huggins combinatorial term [25,28]).

Table 1
Interchange coefficients, dispersive $C^{\mathrm{DIS}}_{\mathrm{es},l}$ and quasichemical $C^{\mathrm{QUAC}}_{\mathrm{es},l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for contacts (e, s) (type s = h, OH in 1-alkanols; s = p, C_6H_5 in toluene; type e, O in tertiary-alkyl ethers)

System	$C^{\mathrm{DIS}}_{\mathrm{es},1}$	$C^{\mathrm{DIS}}_{\mathrm{es},2}$	$C^{\mathrm{DIS}}_{\mathrm{es},3}$	$C^{\mathrm{QUAC}}_{\mathrm{es},1}$	$C^{\mathrm{QUAC}}_{\mathrm{es},2}$	$C^{\mathrm{QUAC}}_{\mathrm{es},3}$
Tertiary-alkyl ethers + C_7H_8 (s = p)						
MTBE + C_7H_8	8.4	24.55	0.0	2.35	−0.5	0.0
TAME + C_7H_8	8.4	19.47	0.0	2.35	−0.5	0.0
ETBE + C_7H_8	8.4	14.5[a]	0.0	2.35	−0.5	0.0
Tertiary-alkyl ethers + 1-alkanols[b] (s = h)						
MTBE + MeOH	0.85	5.3	14.0	−0.2	6.3	−8.0
MTBE + EtOH	1.70[a]	13.0	14.0	−0.2	6.3	−8.0
MTBE + 1-PrOH	2.90[a]	20.8	14.0	−0.2	4.7	−8.0
MTBE + ≥1-BuOH	3.40	22.0[a]	14.0	−0.2	4.7	−8.0
TAME + MeOH	2.80	2.7	−4.0	−0.2	6.3	−8.0
TAME + EtOH	2.80	9.4	−4.0	−0.2	6.3	−8.0
TAME + 1-PrOH	2.80[a]	17.0	−4.0	−0.2	4.7	−8.0
TAME + ≥1-BuOH	2.80[a]	18.0	−4.0	−0.2	4.7	−8.0

[a] Estimated value.

[b] MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol.

For the QUAC part, as coordination number the reference value was chosen, i.e. $z = 4$. The temperature dependence of the interaction parameters g_{st}, h_{st} and c_{pst} has been expressed in terms of the DIS and QUAC interchange coefficients [27], $C^{\mathrm{DIS}}_{\mathrm{st},l}$ and $C^{\mathrm{QUAC}}_{\mathrm{st},l}$, where s, t = a, b, c, e, h, p and $l = 1$ (Gibbs energy: $C^{\mathrm{DIS/QUAC}}_{\mathrm{st},l} = g^{\mathrm{DIS/QUAC}}_{\mathrm{st}}(T_0)/RT_0$); $l=2$ (enthalpy: $C^{\mathrm{DIS/QUAC}}_{\mathrm{st},2} = h^{\mathrm{DIS/QUAC}}_{\mathrm{st}}(T_0)/RT_0$) and $l = 3$ (heat capacity: $C^{\mathrm{DIS/QUAC}}_{\mathrm{st},3} = c^{\mathrm{DIS/QUAC}}_{\mathrm{pst}}(T_0)/R$). $T_0 = 298.15$ K is the scaling temperature.

2.3. DISQUAC interaction parameters

Most of the interaction parameters used in this work are available in the literature [4,9,12,27,28]. In this work, interaction parameters for the e/p contacts have been obtained. The method applied in their estimation has been explained in detail elsewhere, and need not to be repeated here [4,28]. Table 1 lists the $C^{\mathrm{DIS/QUAC}}_{\mathrm{ep},l}$ ($l = 1, 2, 3$) interchange coefficients. As in other applications, mixtures of benzene or toluene and tertiary-alkyl ethers are characterized by the same QUAC parameters [29,30].

On the other hand, the $C^{\mathrm{DIS}}_{\mathrm{eh},1}$ coefficient of the 1-alkanols (from ethanol) + TAME mixtures has been slightly modified in comparison with the value previously given [4] (Table 1).

3. Experimental

3.1. Materials

Methanol and 1-butanol used were from Merck. MTBE was kindly supplied by Petromec. Prior to purification, MTBE was stored over 0.4 nm molecular sieve (Fluka). MTBE and methanol were purified by fractional distillation at atmospheric pressure through a 25-plate laboratory column. The same procedure was applied to 1-butanol, but using 100-plate laboratory column. The final mole fraction purity as determined by GLC was >99.9% for the three compounds. Physical properties of pure compounds are listed in Table 2.

Table 2
Vapor pressures of pure compounds, P_i^0, molar volumes of pure liquids, V_i^{L}, and second virial coefficients (B_{ii}, B_{ij}) at 298.15 K used in Eq. (2) to obtain total pressures from the *x*–*y* data measured in this work

	MTBE	Methanol	1-Butanol
P_i^0 (kPa)	33.50[a]	16.92[b]	0.91[b]
V_i^{L} ($\mathrm{cm^3\,mol^{-1}}$)	119.92[a]	40.735[b]	91.991[b]
B_{ii} ($\mathrm{cm^3\,mol^{-1}}$)	−1527	−2809	−8237
B_{ij} (1, 2) ($\mathrm{cm^3\,mol^{-1}}$)	−955		
B_{ij} (1, 3) ($\mathrm{cm^3\,mol^{-1}}$)	−1684		
B_{ij} (2, 3) ($\mathrm{cm^3\,mol^{-1}}$)		−2860	

[a] Mentioned in [35].

[b] Mentioned in [36].

Table 3
VLE of the methanol(1) + MTBE(2) system at 298.15 K[a]

x_1	y_1		DISQUAC values		
	Experimental	DQ	P_{DQ} (kPa)	γ_1	γ_2
0.1482	0.1760	0.1684	35.88	4.11	1.02
0.3244	0.2603	0.2593	35.60	2.55	1.13
0.3763	0.2818	0.2812	35.29	2.28	1.18
0.5061	0.3308	0.3348	34.12	1.80	1.36
0.6140	0.3782	0.3837	32.67	1.52	1.58
0.6997	0.4187	0.4308	31.10	1.35	1.87
0.8044	0.5074	0.5105	28.36	1.18	2.45
0.8957	0.6350	0.6295	24.64	1.07	3.43

[a] Experimental mole fractions in vapor phase (y_1) and DISQUAC values (y_1, pressures, P_{DQ}, and activity coefficients) calculated with coefficients from Table 1.

Table 4
VLE of the 1-butanol(1) + MTBE(2) system at 298.15 K[a]

x_1	y_1		DISQUAC values		
	Experimental	DQ	P_{DQ} (kPa)	γ_1	γ_2
0.1221	0.0069	0.0076	30.45	2.04	1.03
0.2120	0.0086	0.0016	28.52	1.67	1.07
0.3117	0.0134	0.0157	26.39	1.43	1.13
0.4030	0.0189	0.0198	24.33	1.26	1.18
0.5019	0.0263	0.0251	21.87	1.16	1.27
0.6052	0.0292	0.0326	18.93	1.09	1.36
0.6960	0.0373	0.0427	15.91	1.06	1.51
0.7895	0.0536	0.0601	12.23	1.03	1.65

[a] Experimental mole fractions in vapor phase (y_1) and DISQUAC values (y_1, pressures, P_{DQ}, and activity coefficients) calculated with coefficients from Table 1.

Table 5
VLE of the MTBE(1) + methanol(2) + 1-butanol(3) system at 298.15 K[a]

x_1	x_2	y_1	y_2	DISQUAC values			
				P_{DQ} (kPa)	γ_1	γ_2	γ_3
0.1045	0.1108	0.6681	0.2036	9.42	1.92	1.11	1.00
0.1042	0.2026	0.5878	0.3440	11.26	2.01	1.10	1.00
0.1019	0.5016	0.4492	0.5163	17.08	2.31	1.06	1.01
0.1015	0.6939	0.3757	0.6118	20.75	2.51	1.03	1.05
0.1017	0.7647	0.3724	0.6214	22.09	2.63	1.02	1.07
0.2036	0.1126	0.7904	0.1636	14.43	1.73	1.14	1.02
0.2023	0.2079	0.7061	0.2495	16.47	1.79	1.13	1.02
0.2039	0.3040	0.6444	0.3281	18.64	1.85	1.11	1.02
0.2048	0.4976	0.6008	0.3813	22.81	1.97	1.09	1.02
0.2041	0.5989	0.5212	0.4642	24.85	2.03	1.07	1.03
0.3015	0.1198	0.8144	0.1548	18.62	1.57	1.02	1.05
0.3028	0.2139	0.7595	0.2256	20.85	1.61	1.02	1.05
0.3075	0.3037	0.7160	0.2674	23.08	1.65	1.16	1.05
0.3002	0.3962	0.7031	0.2814	24.86	1.69	1.15	1.04
0.3081	0.4880	0.6273	0.3671	27.16	1.71	1.14	1.05
0.4033	0.2056	0.7892	0.1930	24.22	1.45	1.25	1.10
0.4019	0.3896	0.7360	0.2544	28.45	1.50	1.23	1.09
0.4027	0.4897	0.6663	0.3321	30.69	1.52	1.22	1.09
0.4929	0.1171	0.8542	0.1299	24.77	1.32	1.36	1.17
0.5068	0.2112	0.7869	0.2049	27.55	1.32	1.36	1.17
0.4982	0.4022	0.6869	0.3064	31.91	1.36	1.34	1.15
0.5945	0.1197	0.8477	0.1451	27.60	1.22	1.51	1.27
0.5945	0.3024	0.7610	0.2355	32.46	1.24	1.50	1.25
0.6929	0.1080	0.8888	0.1099	29.82	1.14	1.74	1.42
0.6883	0.2067	0.8290	0.1649	32.64	1.15	1.72	1.40
0.7879	0.1054	0.8802	0.1175	32.26	1.08	2.07	1.65

[a] Experimental mole fractions in vapor phase (y_1, y_2) and DISQUAC values (pressures, P_{DQ}, and activity coefficients, γ_i) calculated with coefficients from Table 1.

3.2. Vapor–liquid measurements

Vapor–liquid equilibria were obtained by a saturation method based on the isothermal saturation of a flow of dry nitrogen passing through the liquid phase embedded in a packed column. The vapor phase is condensed in a liquid air trap and the condensate dissolved in a solvent adequate for gas chromatographic analysis. A more detailed description of the experimental equipment and operating procedure can be found in a previous paper [31].

The equilibrium temperature T was measured accurate to ±0.05 K with a certified PROTON mercury thermometer (model Ber-MAN) previously calibrated with a Hewlett-Packard model 2804A quartz thermometer.

The mole fraction of the liquid phase x_i is accurate to within ±0.0002. The composition of the vapor phase was determined by the use of a Hewlett-Packard model 5980 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard model 3390 electronic integrator. The column, 200 cm long with diameter 1/4 in., was packed with Carbowax 1500 and was operated isothermally within the range 80–130°C depending on the nature of the analyzed materials. The chromatograph was calibrated with synthetic mixtures. The mole fraction of the vapor phase y_i accurate to within ±0.0002 was calculated from the peak-area ratio of the samples.

3.3. Experimental results

For the methanol or 1-butanol + MTBE systems, the experimental x_1, y_1 measurements at 298.15 K are listed in Tables 3 and 4, respectively. Table 5 lists x_1, y_1 $(i = 1, 2)$ for the ternary MTBE(1) + methanol(2)+ 1-butanol(3). Along these tables, total pressures and activity coefficients of compounds, γ_i, calculated using DISQUAC are also listed. Total pressures were calculated from

$$P_{\mathrm{DQ}}\,(\mathrm{kPa}) = x_1\gamma_1P_1^0\exp\left(\frac{(-B_{11}-V_1^{\mathrm{L}})(P-P_1^0)-P\delta_{12}y_2^2}{RT}\right) + x_2\gamma_2P_2^0\exp\left(\frac{(-B_{12}-V_2^{\mathrm{L}})(P-P_2^0)-P\delta_{12}y_1^2}{RT}\right) \qquad (2)$$

where P_i^0 and V_i^{L} are, respectively, the vapor pressure and saturated liquid volume of pure compound i at temperature T, and B_{ijs} stand for the second virial coefficients ($\delta_{12} = 2B_{12} - B_{11} - B_{22}$) obtained by the method of Hayden–O'Connell [32] (Table 2).

The two binaries have been also correlated with a iterative procedure similar to the Barker's method, assuming a Redlich–Kister equation for G^{E}

$$\frac{G^{\mathrm{E}}}{RT} = x_1(1-x_1)\sum_{m=0}^{k}A_m(2x_1-1)^m \qquad (3)$$

Table 6
Coefficients A_m and absolute mean deviations, $\Delta(y_1)$ for the least-squares representation of G^{E}/RT by Eq. (3) of the two binaries measured in this work

Mixture[a]	A_0	A_1	$\Delta(y_1)$[b]
MeOH + MTBE	1.2097	−0.0805	0.0031
1-BuOH + MTBE	0.8520	−0.2871	0.0026

[a] MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol.

[b] See Eq. (5).

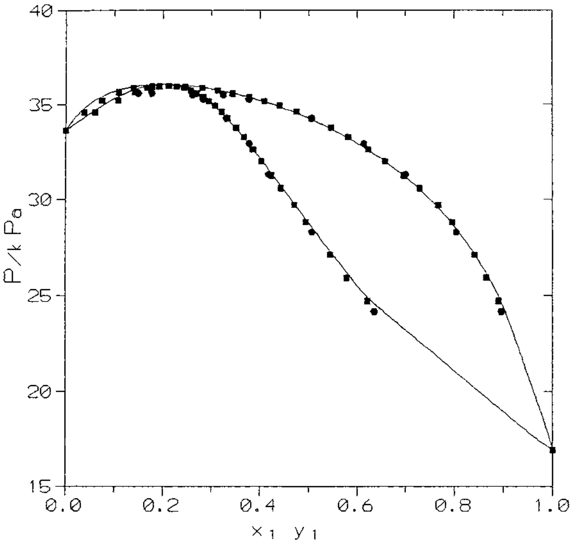

Fig. 1. VLE at 298.15 K for the methanol(1) + MTBE(2) system. Solid lines, DISQUAC calculations; points, experimental results; (■), [17] (y values calculated from P–x measurements); (●), this work (P values calculated from x–y measurements with coefficients of Table 6).

with the coefficients determined by regression through minimization of the sum of deviations in the vapor-phase composition (all points equally weighted). Coefficients are given in Table 6.

Our data of the methanol + MTBE system compare well with literature values, as it is shown in Fig. 1. The coordinates of the characteristic azeotrope of this mixture are: $x_{1az} = 0.217$; $P_{az} = 35.77$ kPa, in good agreement with published values: $x_{1az} = 0.205$; $P_{az} = 36.00$ kPa [17]; $x_{1az} = 0.196$; $P_{az} = 35.27$ kPa [14].

4. Discussion

DISQUAC results on VLE for ternary systems containing tertiary-alkyl ethers and for the binaries

Table 7
R.S.D., $\sigma_r(P)$, defined by Eq. (4) for the ternary and binary systems considered in this work[a]

System	T (K)	N	$\sigma_r(P)$		G^E (J mol^{-1})		Reference
			Experimental	DQ	Experimental	DQ	
MTBE + n-C_7 + C_6H_{12}	313.15	72		0.007			[37]
MTBE + n-C_7	313.15	24	0.0006	0.009	157	134	[38]
MTBE + C_6H_{12}	313.15	24	0.0006	0.004	209	220	[39]
C_6H_{12} + n-C_7	313.15	23	0.0006	0.0006	354	342	[37]
MTBE + n-C_7 + C_6H_6	313.15	71		0.033			[40]
MTBE + C_6H_6	313.15	21	0.0005	0.003	94	87	[39]
C_6H_6 + n-C_7	313.15	23	0.0003	0.004	330	322	[40]
MTBE + C_6H_{12} + C_6H_6	313.15	72		0.022			[39]
C_6H_{12} + C_6H_6	313.15	22	0.0002	0.003	301	311	[39]
MeOH + MTBE + n-C_7	313.15	67		0.010			[20]
MeOH + MTBE	313.15	23	0.001	0.006	782	769	[20]
MeOH + n-C_7	313.15	18	0.006	0.063	725[b]	692	[20]
MeOH + TAME + n-C_7	313.15	63		0.028			[41]
MeOH + TAME	313.15	21	0.001	0.003	894	888	[41]
MeOH + n-C_7	313.15	20	0.002	0.062	721[b]	692	[41]
TAME + n-C_7	313.15	21	0.002	0.004	126	125	[41]
MeOH + TAME + n-C_7	313.15	63		0.029			[42]
MeOH + TAME	313.15	25	0.001	0.009	909	888	[42]
TAME + n-C_7	313.15	23	0.0001	0.003	119	125	[43]
MeOH + TAME + i-C_8	313.15	64		0.012			[41]
MeOH + i-C_8	313.15	20	0.009	0.029	722[b]	690	[41]
TAME + i-C_8	313.15	21	0.0008	0.006	114	121	[41]
EtOH + TAME + C_7H_8	333.15	21		0.008			[44]
EtOH + TAME	333.15	10	0.001	0.014	816	774	[45]
EtOH + C_7H_8	333.15	13	0.002	0.008	1203	1208	[46]
TAME + C_7H_8	333.15	14	0.002	0.004	88	98	[47]
MeOH +1-BuOH + MTBE	298.15						
MeOH + 1-BuOH	298.15	21	0.003	0.004	85	94	[21]
MeOH + MTBE	298.15	26	0.002	0.004	746	746	[17]
MeOH + EtOH + TAME	333.15	21		0.006			[45]
MeOH + EtOH	303.15	22	0.0007	0.005	−7	4	[48]
MeOH + TAME	328.15	19	0.001	0.004	909	909	[49]

[a] For the binary mixtures a comparison between experimental and calculated (DQ) G^E, at equimolar composition and temperature T (K), is also listed. N is the number of data points for each system (MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol).

[b] Non-miscible system; value at $x = 0.1$.

Table 8
Absolute mean deviations, defined by Eq. (5) of mole fractions in vapor phase, y_i ($i = 1, 2$), for some of the ternary and binary systems considered in this work[a]

System[b]	T (K)	N	$\Delta(y_1)$		$\Delta(y_2)$		Reference
			Experimental	DQ	Experimental	DQ	
MeOH + TAME + n-C_7	313.15	63		0.013		0.011	[41]
MeOH + TAME	313.15	21	0.003	0.014			[41]
MeOH + n-C_7	313.15	20	0.002	0.035			[41]
TAME + n-C_7	313.15	21	0.01	0.007			[41]
MeOH + TAME + i-C_8	313.15	64		0.007		0.006	[41]
MeOH + i-C_8	313.15	20	0.004	0.008			[41]
TAME + i-C_8	313.15	21	0.003	0.011			[41]
EtOH + TAME + C_7H_8	333.15	21		0.009		0.011	[44]
EtOH + TAME	333.15	10	0.007	0.008			[45]
TAME + C_7H_8	333.15	14	0.002	0.008			[47]
MTBE + MeOH + 1-BuOH	298.15	26		0.019		0.018	This work
MeOH + 1-BuOH	298.15	21	0.0003	0.003			[21]
MeOH + MTBE	298.15	8	0.003	0.005			This work
1-BuOH + MTBE	298.15	8	0.003	0.003			This work
MeOH + EtOH + TAME	333.15	21		0.013		0.008	[45]
MeOH + TAME	323.15	27	0.004	0.004			[50]

[a] N is the number of data points for each system.

[b] MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol.

involved are given along Tables 7–9. Figs. 1–4 plot this comparison for some selected binary systems. Fig. 5 shows DISQUAC results together with the experimental data for H^E of the TAME + toluene mixture.

For the sake of clarity, Table 7 includes standard relative deviations for pressure defined as

$$\sigma_r(P) = \left\{ \frac{1}{N} \sum \left(\frac{P_{\exp} - P_{\text{calc}}}{P_{\exp}} \right)^2 \right\}^{1/2} \tag{4}$$

Table 9
Comparison of experimental coordinates of azeotropes: temperature (T^{az}); mole fraction (x_1^{az}) and pressure (P^{az}) for some binary mixtures considered in this work with DISQUAC results calculated using the coefficients from Table 1 and from literature[a]

System	T^{az} (K)	x_1^{az}		P^{az} (kPa)		Reference
		Experimental	Calculated	Experimental	Calculated	
C_6H_{12} + C_6H_6	313.15	0.497	0.483	27.52	27.6	[39]
MeOH + n-C_7	313.15	0.732	0.737	45.76	44.64	[20]
MeOH + i-C_8	313.15	0.724	0.727	46.53	46.69	[41]
MeOH + MTBE	298.15	0.205	0.201	36.0	36.1	[17]
		0.217		35.77		This work
	325.00	0.695	0.695	103.15	103.24	[15]
	363.54	0.458	0.532	354.60	358.25	[18]
	403.42	0.412	0.384	1000.0	1001.3	[51]
MeOH + TAME	288.15	0.681	0.695	11.58	11.59	[49]
	313.15	0.739	0.740	40.56	40.64	[41]
	328.15	0.763	0.769	75.68	76.07	[49]
	363.10	0.818	0.825	272.81	275.05	[18]
EtOH + TAME	333.15	0.531	0.548	60.15	59.28	[45]

[a] MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol.

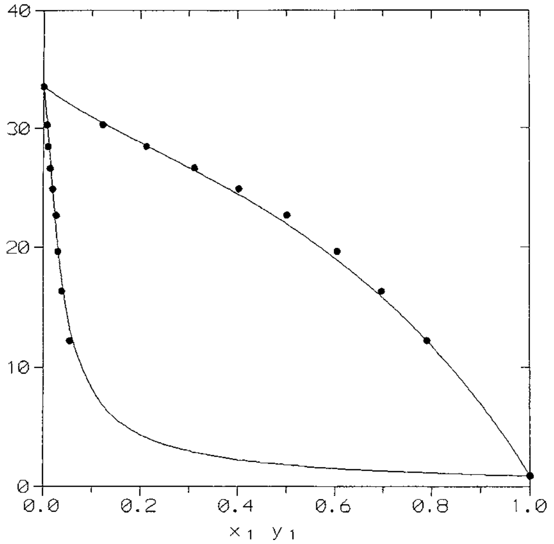

Fig. 2. VLE at 298.15 K for the 1-butanol(1) + MTBE(2) system. Solid lines, DISQUAC calculations; points, experimental results (this work; P values calculated from x–y measurements with coefficients of Table 6).

Table 8 lists the absolute mean deviation of mole fractions in vapor phase defined as

$$\Delta(y_1) = \frac{1}{N}\sum |y_{1\mathrm{exp}} - y_{1\mathrm{calc}}| \qquad (5)$$

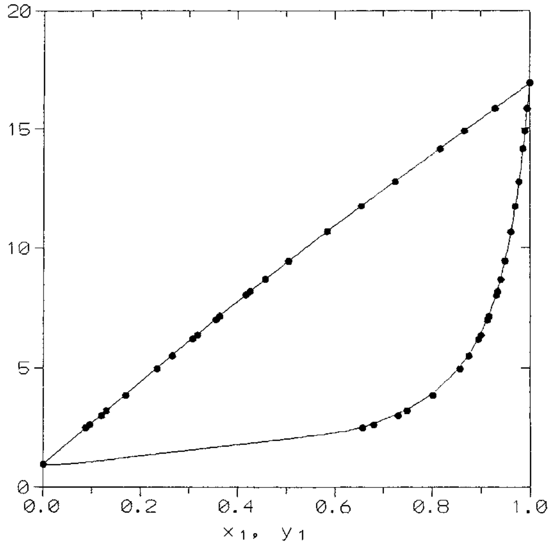

Fig. 3. VLE at 298.15 K for the methanol(1) + 1-butanol(2) system. Solid lines, DISQUAC results; points, experimental values [21].

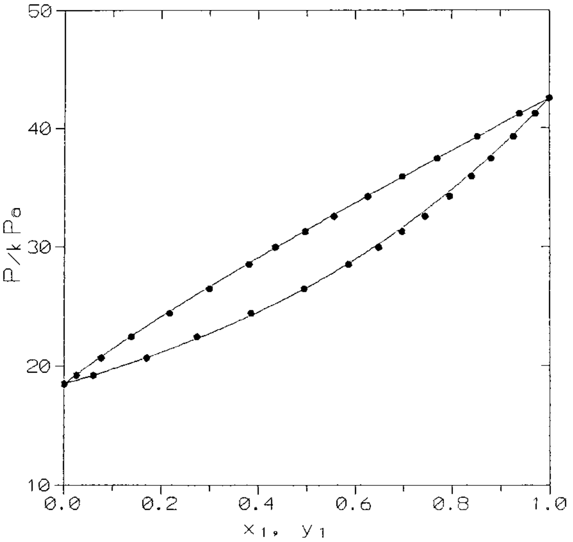

Fig. 4. VLE at 333.15 K for the TAME(1) + toluene(2) system. Solid lines, DISQUAC calculations; points, experimental results [47].

In Eqs. (4) and (5), N is the number of data points of each system. DISQUAC represents rather accurately VLE of the studied ternary systems using only information from the constituent binaries. Note the good

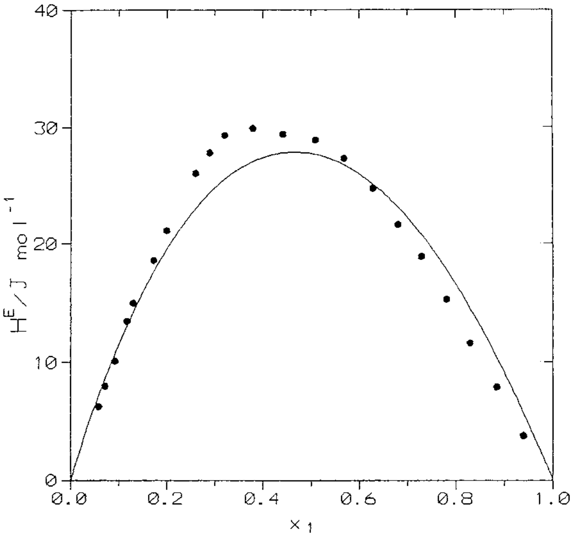

Fig. 5. H^E at 298.15 K for the TAME(1) + toluene(2) mixture. Solid line, DISQUAC calculation; points, experimental results [52].

results for azeotropic coordinates over a wide range of temperature (Table 9).

Five of the ternary systems considered here have been analyzed by Coto et al., in terms of different models [33]. The DORTMUND version of UNIFAC [34] gives an average standard relative deviation of pressure, $\overline{\sigma_r}(P) = \sum \sigma_r(P)$/number of systems, equal to 0.010. DISQUAC yields $\overline{\sigma_r}(P) = 0.015$. DISQUAC improves VLE results of binary systems containing tertiary-alkyl ethers and alkanols, and of course, those on magnitudes which are strongly dependent on the molecular structure, H^E and C_p^E [3,4]. Previous calculations show that DISQUAC predictions on H^E of ternary systems of the class examined in the present

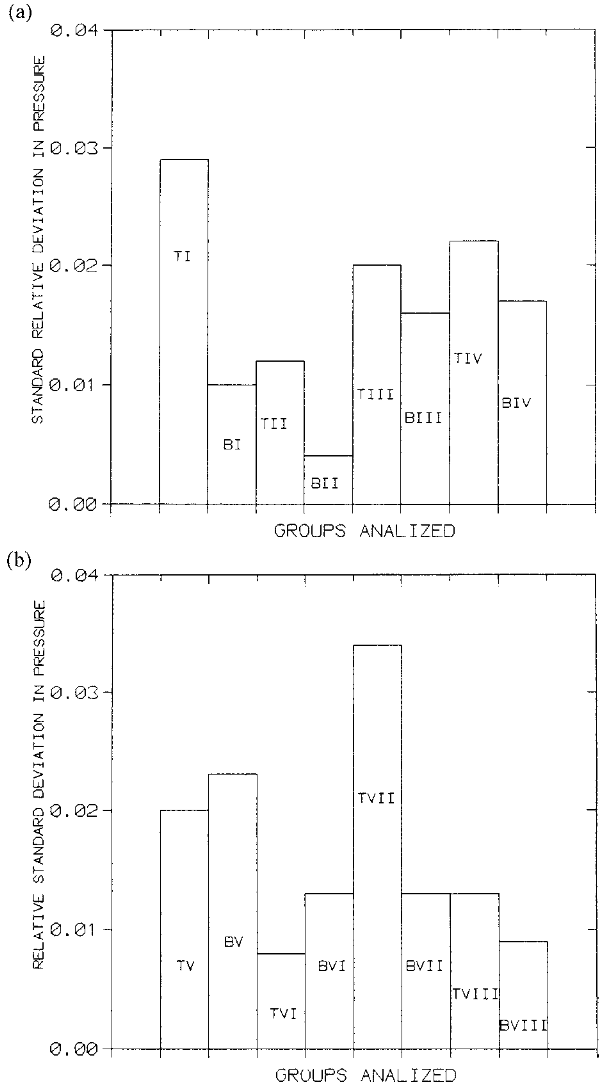

Fig. 6. Average standard relative deviations in pressure for ternary (T) and binary (B) systems analyzed ([4], this work): (a) TI, mixtures containing only hydrocarbons or CCl_4; TII, systems formed by one polar compound (not self-associated) and hydrocarbons or CCl_4; TIII, mixtures of one alcohol and two hydrocarbons or CCl_4; TIV, mixtures involving one alcohol, one polar compound and one hydrocarbon (or CCl_4) and (b) TV, solutions with two alcohols and one hydrocarbon or CCl_4; TVI, systems of two alcohols and one polar compound; TVII, mixtures containing one alcohol, one polar compound and one self-associated component (particularly $CHCl_3$); TVIII, solutions with two polar compounds and one self-associated component (particularly $CHCl_3$).

work are also improved. In exchange, VLE of mixtures including tertiary-alkyl ethers and *n*-alkanes are slightly better represented by UNIFAC, probably due to the empirical combinatorial term used in this model is more suitable, particularly for those systems with components very different in size [4].

In a previous work, we examined carefully the ability of the model to represent total pressure measurements at isothermal conditions of a large variety of ternary systems (55 mixtures, classified depending on the nature of the mixture compounds). Here, $\overline{\sigma_r}(P)$ are represented in Fig. 6. In view of these results, one can conclude that DISQUAC predictions are essentially independent of the ternary mixture considered. This is supported, because only a few of the binary systems tested were correlated to obtain interaction parameters which were later used to predict VLE of the related ternary. It can explain the somewhat large value of $\overline{\sigma_r}(P)$ for group I (mixtures with only hydrocarbons or CCl_4). Note that $\overline{\sigma_r}(P)$ for the related binaries is higher than for those of group II (solutions with a polar compound, not self-associated, and hydrocarbons or CCl_4). This probably indicates that the weight of the combinatorial term is more important for mixtures of group I. We also observe a somewhat large $\overline{\sigma_r}(P)$ value for group VII (essentially methanol + $CHCl_3$+ *n*-alkanone systems). This reveals that the interaction parameters of methanol or *n*-alkanone + $CHCl_3$ systems are not enough optimized, because $CHCl_3$ is considered, in the framework of DISQUAC, as a heterogeneous molecule. In terms of UNIFAC, $CHCl_3$ is assumed to be a homogeneous molecule and is defined as a main group [34].

5. Conclusions

VLE data (*x*–*y* measurements) at 298.15 K for methanol or 1-butanol + MTBE and for MTBE+ methanol + 1-butanol systems have been reported. DISQUAC correctly predicts VLE of ternary systems using binary parameters only. Results are independent of the mixture considered.

Acknowledgements

This work was supported by the Programa Sectorial de Promoción General del Conocimiento de la SEUI y D del MEC (Spain), Project No. PB97-0488 and by the Consejería de Educación y Cultura de la Junta de Castilla y León (Spain), under the Project VA54/98. N.R. acknowledges the grant received from the "Programa Nacional de Formación del Profesorado Universitario y Personal Investigador" de la SEUI y D del MEC. Authors gratefully acknowledge the MTBE supplied by Petromec.

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