Prediction of Phase Equilibria for Binary and Ternary Mixtures Involving *tert*-Butyl Methyl Ether and *tert*-Amyl Methyl Ether

Baudilio Coto

ESCET, Universidad Rey Juan Carlos, E-28933 Móstoles, Madrid, Spain

Concepción Pando and Juan A. R. Renuncio*

Departamento de Química Física I, Universidad Complutense, E-28040 Madrid, Spain

Vapor–liquid equilibrium (VLE) and excess enthalpy (H^E) data of binary and ternary mixtures involving 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether or MTBE) or 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME) and alkanes, olefins, benzene, and alcohols have been studied using the UNIQUAC model, the original UNIFAC group contribution model, and the modified UNIFAC models of Lyngby and Dortmund. Values for the binary parameters required in the UNIQUAC model are obtained from binary VLE or H^E data. Binary VLE data are predicted using the UNIQUAC equation with parameters obtained from H^E data and the UNIFAC and modified UNIFAC models. Ternary VLE data are predicted using the UNIQUAC equation with parameters obtained from binary H^E or VLE data and the UNIFAC and modified UNIFAC models. Accurate ternary data are obtained using the UNIQUAC equation with parameters determined from binary VLE data. The modified UNIFAC (Dortmund) model is shown to provide good predictions of binary and ternary VLE data and can be recommended for those cases in which the related binary VLE data are not available.

Branched ethers are being used as additives in lead-free gasoline alone or with other ethers or alcohols. The thermodynamic properties of binary and ternary mixtures formed by hydrocarbons, ethers, and alcohols are essential in the design of chemical processes involving these oxygenating agents. Numerous investigations on vapor–liquid equilibrium (VLE) and excess enthalpy (H^E) data for these mixtures have been carried out during the past few years, and a review paper has been recently published by Marsh et al.[1] Nevertheless, data for some binary mixtures are still scarce, and for most ternary mixtures only one property, either VLE or H^E, is available. The aim of this paper is to examine the feasibility of predicting VLE data for ternary mixtures using four well-known thermodynamic models: the UNIQUAC model,[2] the UNIFAC group contribution model,[3,4] the modified UNIFAC model (Lyngby version),[5] and the modified UNIFAC model (Dortmund version).[6,7] We will refer to these three UNIFAC models as UNIFAC, modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund), respectively. Ternary VLE data for the most widely used branched ethers, 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether or MTBE) and 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME), have been considered. Values for the binary parameters required in the UNIQUAC model are obtained from binary VLE or H^E data. The prediction of binary VLE data from H^E data using the UNIQUAC model is also examined. Among previous attempts to predict VLE data for these kinds of mixtures, we should mention those of Pividal et al.[8] and Soave et al.[9] for binary systems and that of Vetere et al.[10] for a ternary system and the related binaries.

Correlation of Binary Data

The correlation of binary data has been carried out using the UNIQUAC equation. Table 1 lists the components of the binary and ternary systems studied and the values for the pure-component parameters r and q. The Roman numbers assigned to each component are used to describe the values obtained for the binary parameters in this paper, given as Supporting Information. Linear alkanes are represented by hexane, heptane, and octane; cyclic alkanes by cyclohexane; olefins by 1-butene, 1-hexene, and 1-heptene; aromatic hydrocarbons by benzene; and alcohols by methanol and ethanol. The binary and ternary systems studied are listed in Table 2, and each system is assigned a number. Because our aim is the prediction of phase equilibria, the ternary systems considered are those for which VLE data are available. The first component of the 13 ternary systems studied is a branched ether. The second and third components are alkanes, olefins, benzene, methanol, and ethanol. These ternary systems are a good representation of the different kinds of mixtures involved in the processes related to oxygenating agents. The binary systems studied are those required to obtain parameters for phase equilibria prediction and may not have a branched ether as a component. The systems are classified according to the UNIFAC groups involved in their components. Class 1 (group CH_2) includes binary systems consisting of two alkanes and class 2 (groups CH_2 and CH_2O) includes binary and ternary systems consisting of a branched ether and alkanes. Class 3 (groups CH_2, C=C, and CH_2O) includes binary and ternary systems consisting of an olefin + a branched ether and/or an alkane. Class 4 (groups CH_2, ACH, and CH_2O) includes systems similar to those of class 3 but the olefin is replaced by benzene. Class 5 includes systems consisting of an olefin + benzene and/or a branched ether (groups CH_2, C=C, ACH, and CH_2O).

* To whom correspondence should be addressed. Phone: 34 91394-4120. Fax: 34 91394-4135. E-mail: renuncio@eucmax.sim.ucm.es.

Table 1. Pure-Component UNIQUAC Structural Parameters

number	component	r	q
I	MTBE	4.0678	3.632
II	TAME	4.7422	4.172
III	cyclohexane	4.0464	3.240
IV	hexane	4.4998	3.856
V	heptane	5.1742	4.396
VI	octane	5.8486	4.936
VII	1-butene	2.9209	2.564
VIII	1-hexene	4.2697	3.644
IX	1-heptene	4.9441	4.184
X	benzene	3.1878	2.400
XI	ethanol	2.5755	2.588
XII	methanol	1.4311	1.432

Table 2. Binary and Ternary Systems Studied

class	group	system no.	components
1	CH$_2$	1	cyclohexane + heptane
		2	hexane + heptane
		3	hexane + octane
		4	heptane + octane
2	CH$_2$, CH$_2$O	5	MTBE + cyclohexane
		6	MTBE + hexane
		7	MTBE + heptane
		8	MTBE + octane
		9	TAME + cyclohexane
		10	TAME + hexane
		11	TAME + heptane
		12	TAME + octane
		13	MTBE + TAME
		14	MTBE + cyclohexane + heptane
		15	MTBE + hexane + heptane
		16	MTBE + hexane + octane
		17	MTBE + heptane + octane
3	CH$_2$, C=C, CH$_2$O	18	cyclohexane + 1-hexene
		19	MTBE + 1-butene
		20	MTBE + 1-hexene
		21	MTBE + 1-heptene
		22	TAME + 1-hexene
		23	TAME + 1-heptene
		24	MTBE + cyclohexane + 1-hexene
		25	TAME + cyclohexane + 1-hexene
4	CH$_2$, ACH, CH$_2$O	26	cyclohexane + benzene
		27	heptane + benzene
		28	MTBE + benzene
		29	TAME + benzene
		30	MTBE + cyclohexane + benzene
		31	MTBE + heptane + benzene
5	CH$_2$, C=C, ACH, CH$_2$O	32	1-hexene + benzene
		33	MTBE + 1-hexene + benzene
6	CH$_2$, OH, CH$_2$O	34	MTBE + ethanol
		35	TAME + ethanol
		36	octane + ethanol
		37	MTBE + octane + ethanol
7	CH$_2$, CH$_3$OH, CH$_2$O	38	MTBE + methanol
		39	TAME + methanol
		40	heptane + methanol
		41	MTBE + heptane + methanol
		42	TAME + heptane + methanol
8	CH$_2$, OH, CH$_3$OH, CH$_2$O	43	ethanol + methanol
		44	TAME + ethanol + methanol

Class 6 (groups CH$_2$, OH, and CH$_2$O) includes systems consisting of ethanol + a branched ether and/or an alkane. Class 7 (groups CH$_2$, CH$_3$OH, and CH$_2$O) includes systems similar to those of class 6 but the ethanol is replaced by methanol. Finally, class 8 (groups CH$_2$, OH, CH$_3$OH, and CH$_2$O) includes the binary system formed by methanol and ethanol and the ternary system formed by the two alcohols and TAME.

Table 3 lists the conditions and source of the sets of H^E data available for the binary systems and results

Table 3. Conditions and Source of Experimental H^E Data and Statistical Measures of Fits of H^E Data Using the UNIQUAC Equation

system no.	T/K	H^E_{max}/ (J mol^{-1})	UNIQUAC, σ_H (%)	data source
1A	298	250.0	4	11
1B	313	230.3	5	11
2	298	0.5	11	12
3	298	3.4	15	13
4	298	9.2	0	14
5	298	467.5	0.2	15
6	298	371.8	0.8	16
7A	298	383.2	2	17
7B	313	363.8	3	17
8	298	430.5	0.4	18
9	298	399.7	0.2	19
10	298	270.2	0.6	19
11A	298	294.8	4	20
11B	313	267.8	4	20
12A	298	319	3	20
12B	313	302.8	3	20
13	298	1.0	3	21
18	298	232.2	1.1	22
19A	293	68.5	46	23
19B	313	42.2	31	23
19C	333	18.6	37	23
20A	298	144.2	5	24
20B	308	143.4	4	24
21A	298	145.6	5	24
21B	308	155.6	4	24
22A	298	76.6	6	24
22B	308	64.1	6	24
23A	298	98.2	11	24
23B	308	69.6	15	24
26A	298	804.9	1.4	25
26B	303	778.7	3	26
27A	298	958.9	5	27
27B	308	861.0	6	27
28	298	135.2	2	28
29	298	211.4	1.9	19
32	298	533.6	5	22
34A	298	525.6	1.5	29
34B	298	513.6	1.7	18
35	298	561.6	3	29
36A	293	587.0	14	30
36B	308	708.0	13	30
38A	298	328.2	5	17
38B	313	378.2	4	17
38C	323	432.1	5	17
39A	298	390.1	7	29
39B	298	425.3	8	20
39C	313	453.5	7	20
40A	303	546.0	21	31
40B	318	798.0	19	31
43	298	4.7	3	32

for the correlation of these data using the UNIQUAC equation. The maximum values of the excess enthalpy, H_{ax}, and the percent ratio of the standard deviation between experimental and calculated H^E values and the maximum value of H^E, σ_H (%), are listed in Table 3. When two or three sets of H^E data are available for a system, the letters A−C are used to label them. For some systems such as cyclohexane + benzene, there are two or more sets of H^E data taken at the same temperature and providing similar H^E values. In such cases, only one set of H^E data is used in the correlation. For the sake of simplicity, the interaction parameters of the UNIQUAC model, A_{ij}, are assumed to be temperature independent. Values obtained for the parameters A_{ij} from the correlation of binary H^E data are reported in a table included as Supporting Information. For most systems H^E data were measured only at one tempera-

Table 4. VLE Data of Binary Mixtures Related to Ternary Mixtures Involving MTBE and TAME: Correlation Using the UNIQUAC Equation and Predictions Using the UNIQUAC Equation with Parameters Determined from H^E Data and the UNIFAC and Modified UNIFAC Models

	VLE data		UNIQUAC VLE param		UNIQUAC H^E param		UNIFAC		modified UNIFAC Lyngby		modified UNIFAC Dortmund		data source
no.	conditions	p_{max}/kPa	σ_{y_1}	σ_p (%)	σ_{y_1}	σ_p (%)	σ_{y_1}	σ_p (%)	σ_{y_1}	σ_p (%)	σ_{y_1}	σ_p (%)	
1a	298 K	13.0	0.0009	0.16	0.026	5	0.006	1.1	0.007	1.3	0.010	1.8	33
1b	313 K	24.6	0.0002	0.08	0.025	5	0.004	0.8	0.006	1.0	0.011	2	33
2	94 kPa	94.0	0.0019	0.7	0.007	1.4	0.007	1.4	0.006	1.3	0.006	1.3	34
3a	70 kPa	70.1	0.004	5	0.014	9	0.014	9	0.015	9	0.016	9	35
3b	101 kPa	101.3	0.009	1.8	0.008	6	0.008	6	0.009	6	0.010	6	35
4	94 kPa	94.0	0.004	0.6	0.004	1.1	0.004	1.2	0.004	1.2	0.004	1.1	36
5	313 K	59.9	0.0003	0.04	0.042	9	0.011	2	0.002	0.2	0.011	2	37
6	313 K	59.9	0.002	0.13	0.029	6	0.014	3	0.008	1.5	0.0013	0.3	33
7a	298 K	33.5	0.003	0.5	0.035	6	0.022	3	0.015	2	0.006	0.9	38
7b	308 K	49.8	0.003	0.3	0.026	5	0.014	2	0.008	1.6	0.0016	0.2	38
8	94 kPa	94.0	0.005	0.6	0.049	16	0.027	8	0.014	4	0.009	2	36
9	313 K	24.7	0.0009	0.04	0.034	10	0.010	3	0.0013	0.3	0.010	3	39
11a	298 K	10.0	0.005	0.5	0.018	4	0.013	3	0.007	1.7	0.005	0.5	38
11b	308 K	15.8	0.004	0.3	0.018	4	0.013	3	0.007	1.6	0.005	0.4	38
11c	313 K	19.6	0.002	0.4	0.020	5	0.014	3	0.008	2	0.002	0.6	39
12a	323 K	29.3	0.030	4	0.026	4	0.018	3	0.010	1.5	0.005	0.6	40
12b	423 K	500.4	0.006	1.2	0.017	3	0.011	1.9	0.004	1.6	0.004	1.9	40
13	101 kPa	101.3	0.007	0.3	0.008	0.7	0.008	0.7	0.007	0.6	0.007	0.6	41
18	313 K	45.0	0.0003	0.05	0.027	6	0.003	0.4	0.007	1.3	0.005	1.0	42
19a	293 K	241.3	0.039	3	0.0016	1.0	0.015	0.9	0.002	0.7	0.011	1.8	43
19b	313 K	442.9	0.015	2	0.0018	3	0.006	3	0.003	3	0.005	4	43
19c	333 K	737.6	0.025	3	0.015	4	0.003	3	0.014	4	0.027	5	43
19d	353 K	1168.4	0.020	3	0.021	6	0.011	5	0.020	5	0.036	7	43
20	94 kPa	94.0	0.003	0.5	0.0011	1.8	0.015	3	0.005	0.7	0.005	1.8	44
21a	293 K	27.1	0.024	0.7	0.041	1.6	0.047	2	0.033	0.4	0.024	1.0	45
21b	311 K	55.4	0.008	0.4	0.021	1.7	0.026	2	0.013	0.4	0.006	1.0	45
22	313 K	44.9	0.0004	0.08	0.004	0.9	0.013	3	0.004	1.0	0.004	0.8	39
26	313 K	27.5	0.0005	0.05	0.077	21	0.003	0.8	0.002	0.4	0.003	0.9	37
27	313 K	24.4	0.0006	0.08	0.077	21	0.0019	0.3	0.0006	0.2	0.002	0.6	46
28a	94 kPa	94.0	0.004	0.6	0.026	5	0.006	1.1	0.011	2	0.010	2	47
28b	313 K	59.9	0.0009	0.12	0.023	4	0.003	0.6	0.008	1.4	0.007	1.3	37
29	313 K	24.4	0.0002	0.04	0.026	7	0.003	0.8	0.003	0.8	0.006	1.5	39
32	313 K	45.0	0.0005	0.06	0.051	11	0.003	0.6	0.0009	0.3	0.0016	0.14	46
34	101 kPa	101.3	0.007	0.4	0.016	4	0.008	1.5	0.015	3	0.010	1.3	41
35a	323 K	38.7	0.006	0.9	0.024	5	0.013	2	0.024	4	0.010	1.1	48
35b	333 K	59.1	0.006	0.6	0.020	4	0.011	1.5	0.020	3	0.011	1.1	48
35c	333 K	60.0	0.010	1.3	0.021	3	0.010	0.3	0.017	1.9	0.007	1.4	49
36a	318 K	25.3	0.024	5	0.114	18	0.012	3	0.015	5	0.008	1.6	50
36b	328 K	40.6	0.029	4	0.122	17	0.020	3	0.021	4	0.003	1.5	50
38a	298 K	36.0	0.009	1.0	0.042	10	0.006	1.7	0.012	3	0.004	0.7	51
38b	318 K	80.3	0.007	0.3	0.043	10	0.005	1.8	0.011	2	0.005	0.4	51
38c	328 K	115.8	0.005	0.3	0.043	10	0.005	1.7	0.010	1.7	0.005	0.4	51
39a	298 K	19.5	0.009	1.2	0.061	14	0.010	2	0.015	3	0.010	1.0	52
39b	308 K	31.7	0.005	0.3	0.063	14	0.012	3	0.011	2	0.007	1.1	53
39c	328 K	75.6	0.010	0.6	0.059	14	0.011	2	0.011	2	0.011	2	53
40a	101 kPa	101.3	0.020	3	0.078	21	0.021	3	0.023	5	0.007	0.9	54
40b	101 kPa	101.3	0.020	4	0.118	25	0.030	6	0.020	5	0.007	0.7	55
43	101 kPa	101.3	0.011	0.5	0.013	4	0.017	3	0.013	1.7	0.010	1.2	56

ture, 298.15 K, or at two temperatures, either 298.15 and 313.15 K or 298.15 and 308.15 K, thus covering a 10−15 K temperature range. H^E data for the MTBE + 1-butene and MTBE + methanol systems cover a larger temperature range. Most of the systems studied exhibit moderately endothermic excess enthalpies over the whole mole fraction range. The methanol + ether systems exhibit slightly exothermic excess entalpies in the alcohol-rich region. H^E correlations are accurate in most cases. Higher values of σ_H are obtained when the excess enthalpy values are very small (hexane + heptane and hexane + octane) or when H_{ax} values change appreciably with temperature (MTBE + 1-butene, TAME + 1-heptene, octane + ethanol, and heptane + methanol). The latter also presents phase splitting. Obviously, temperature-independent parameters are not adequate to describe these sets of H^E data.

Table 4 lists the conditions, maximum value of the vapor pressure, p_{max}, and source of binary VLE data and results for the correlation of these data using the UNIQUAC model. A selection of literature data is necessary when the number of sets of data available for a system is very high. In these cases, the sets selected are those taken at conditions of temperature and pressure similar to those of ternary data. The letters a−d are used to label the sets of isobaric or isothermal VLE data considered for each system. The interaction parameters of the UNIQUAC model, A_{ij}, were assumed to be temperature independent. The standard deviation σ_{y_1} between experimental and calculated values of the first-component vapor composition, y_1, and the percent ratio of the standard deviation between experimental and calculated vapor pressures and p_{max}, σ_p (%), are also listed in the fourth and fifth columns of Table 4. A_{ij}
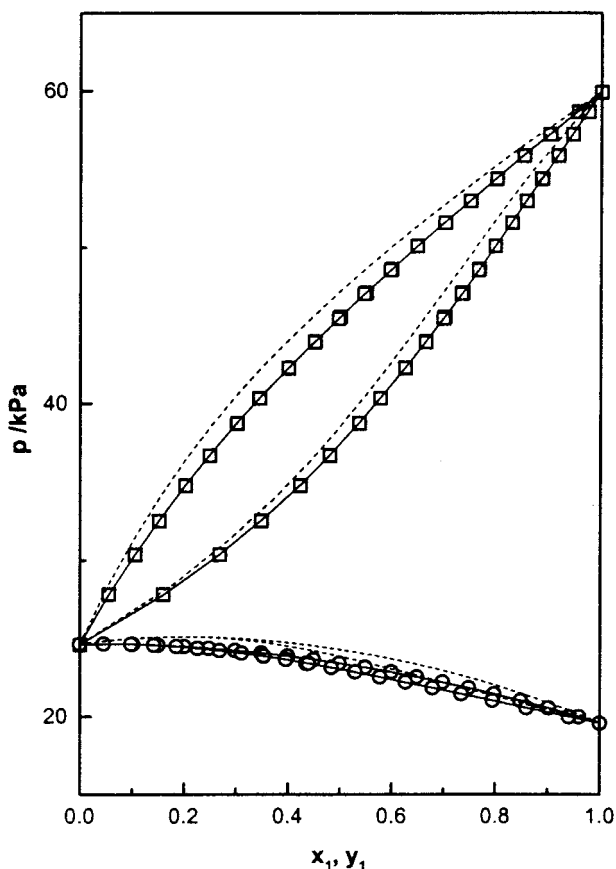
Figure 1. VLE data at 313.15 K for the following: □, MTBE + cyclohexane;[37] ○, TAME + cyclohexane;[39] —, correlations using the UNIQUAC equation and predictions using the modified UNIFAC (Lyngby) model; – - –, predictions using the modified UNIFAC (Dortmund) model.

Figure 2. VLE data for the MTBE + methanol system:[51] □, 298.15 K; ○, 318.15 K; △, 328.15 K; —, correlations using the UNIQUAC equation and predictions using the modified UNIFAC (Dortmund) model; - – -, predictions using the UNIFAC model.

values obtained from VLE data are given in a table included as Supporting Information. VLE correlations are very accurate in most cases. The higher values of σ_{y_1} or σ_p observed in some cases could be related to the considerable temperature interval covered by the several sets of VLE data available for a system. This is the case of the TAME + octane and MTBE + 1-butene systems. Figure 1 shows results obtained at 313.15 K for the MTBE + cyclohexane and TAME + cyclohexane systems, and Figure 2 shows results obtained for the MTBE + methanol system at 298.15, 318.15, and 328.15 K.

Prediction of Binary VLE Data

The prediction of binary VLE data has been attempted following four procedures: the UNIQUAC equation with parameters obtained from H^E data, the UNIFAC model, and the modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund) models. For each procedure, Table 4 lists the standard deviations between experimental and calculated vapor compositions, σ_{y_1}, and the percent ratio of the standard deviation between experimental and calculated vapor pressures and the maximum value of this magnitude, σ_p (%). Because results from VLE data correlation are also included in this table, a comparison of predictions and correlations can be readily made. The UNIFAC model and the modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund) models are shown to be always more adequate than the UNIQUAC equation with parameters
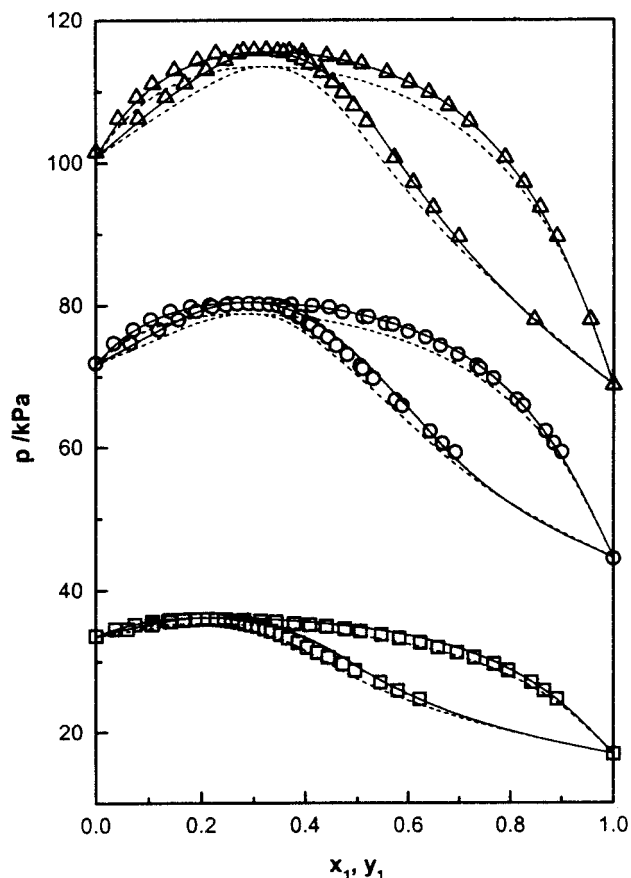
obtained from H^E data. Results obtained for class 2 systems using this prediction procedure are similar to those previously reported for 21 binary systems consisting of an alkane and a polyether or a monoether different from MTBE or TAME (Coto et al.[57]). The three UNIFAC models predict with similar accuracy the data for systems of classes 1, 4, and 5. For most systems of classes 2 and 6 and for all systems of classes 7 and 8, the modified UNIFAC (Dortmund) model is preferred. No clear conclusions can be established for systems of class 3 (MTBE or TAME + olefin). Relatively high values of σ_{y_1} or σ_p are obtained in the UNIQUAC model correlation for systems of this group. Nevertheless, considering simultaneously all sets of binary VLE data, the modified UNIFAC (Dortmund) model may be recommended for VLE predictions. Most values of σ_{y_1} range from 0.002 to 0.016, and most values of σ_p are less than 4%.

Figures 1 and 2 show some typical results obtained. VLE data for MTBE + cyclohexane and TAME + cyclohexane are shown in Figure 1 together with correlations provided by the UNIQUAC equation and predictions obtained from the modified UNIFAC (Dortmund) and modified UNIFAC (Lyngby) models. VLE data for MTBE + methanol are shown in Figure 2 together with correlations provided by the UNIQUAC equation and predictions provided by the UNIFAC and the modified UNIFAC (Dortmund) models.
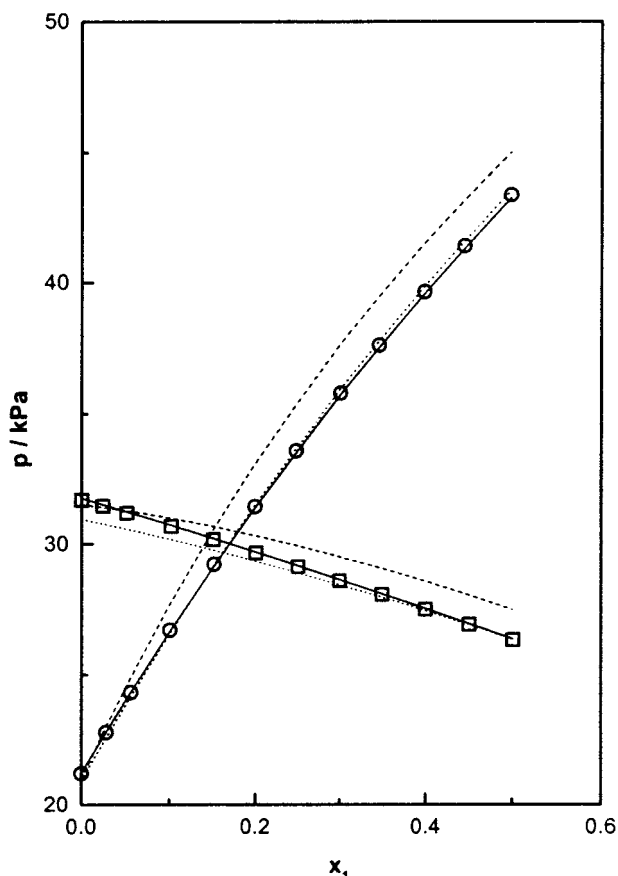
Prediction of Ternary VLE Data

Table 5 lists the conditions, the maximum value of the vapor pressure, results of ternary VLE data predic-

Table 5. Prediction of VLE Data for Ternary Mixtures Involving MTBE and TAME by Means of the UNIQUAC Equation and the UNIFAC and Modified UNIFAC Models

VLE data			UNIQUAC VLE param			UNIQUAC H^E param.			UNIFAC			modified UNIFAC (Lyngby)			modified UNIFAC (Dortmund)			data source
no.	conditions	p_{max}/kPa	σ_{y_1}	σ_{y_2}	σ_p (%)	σ_{y_1}	σ_{y_2}	σ_p (%)	σ_{y_1}	σ_{y_2}	σ (%)	σ_{y_1}	σ_{y_2}	σ_p (%)	σ_{y_1}	σ_{y_2}	σ_p (%)	
14	313 K	59.9	0.002	0.002	0.2	0.026	0.022	8	0.020	0.014	3	0.010	0.008	0.8	0.007	0.009	1.6	42
15	94 kPa	94.0	0.008	0.009	1.6	0.035	0.033	7	0.020	0.022	3	0.011	0.016	1.1	0.007	0.012	1.7	34
16	94 kPa	94.0	0.024	0.028	3	0.047	0.040	12	0.027	0.026	6	0.018	0.019	3	0.011	0.014	1.7	58
17	94 kPa	94.0	0.009	0.008	2	0.046	0.037	13	0.029	0.025	7	0.018	0.018	4	0.012	0.014	2	59
24	313 K	59.9	0.002	0.003	0.2	0.018	0.021	7	0.017	0.009	3	0.006	0.006	0.6	0.005	0.007	1.2	42
25	313 K	45.0	0.0005	0.0003	0.07	0.014	0.028	6	0.010	0.006	2	0.004	0.004	0.6	0.004	0.010	1.0	39
30	313 K	59.9	0.002	0.0011	0.15	0.032	0.040	10	0.008	0.005	1.0	0.006	0.004	0.8	0.007	0.005	1.0	37
31	313 K	59.9	0.003	0.002	0.3	0.035	0.028	7	0.011	0.004	1.2	0.006	0.004	0.8	0.007	0.004	0.9	46
33	313 K	59.9	0.006	0.005	0.7	0.021	0.020	6	0.008	0.010	2	0.005	0.008	0.7	0.007	0.004	1.4	46
37	101 kPa	101.3	0.018	0.008	2	0.074	0.017	6	0.010	0.005	4	0.015	0.005	4	0.015	0.005	4	60
41	313 K	66.3	0.008	0.007	1.0	0.071	0.013	9	0.008	0.011	1.9	0.007	0.007	4	0.003	0.003	0.6	61
42	313 K	45.6	0.007	0.010	1.8	0.060	0.039	18	0.012	0.015	2.8	0.006	0.007	4	0.003	0.005	0.9	62
44	333 K	88.8	0.014	0.008	2.0	0.033	0.021	7	0.016	0.013	1.0	0.018	0.016	1.9	0.012	0.010	0.8	39
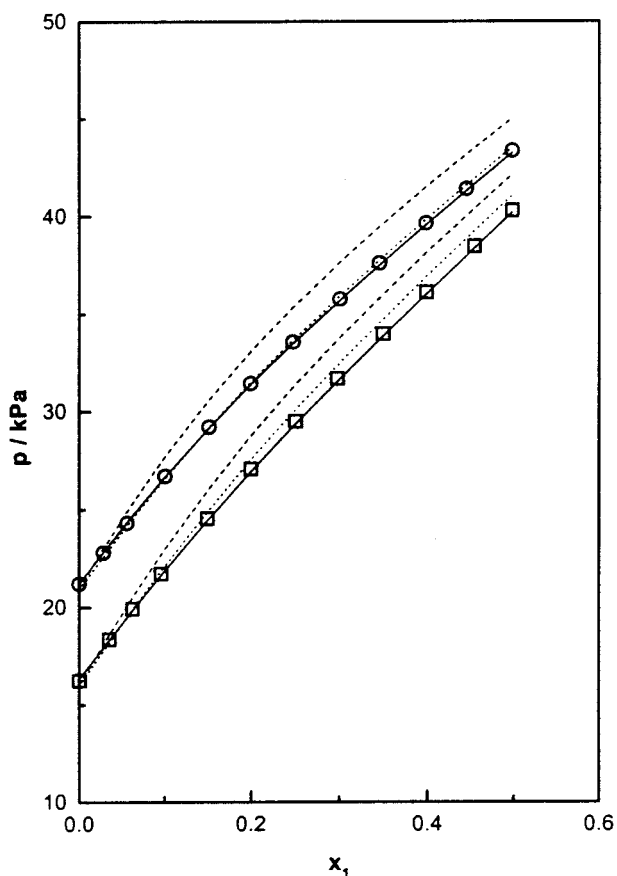
Figure 3. Vapor pressure versus liquid composition x_1 plots for the MTBE + cyclohexane + heptane system at 313.15 K:[42] □, x_3/x_2 = 2.3; ○, x_3/x_2 = 0.4; predictions from the UNIQUAC, (—), UNIFAC (- - -), and modified UNIFAC (Lyngby) (···) models.

Figure 4. Vapor pressure versus liquid composition x_1 plots at 313.15 K and x_3/x_2 = 0.4: ○, MTBE + cyclohexane + 1-hexene;[42] □, TAME + cyclohexane + 1-hexene;[39] predictions from the UNIQUAC (—), UNIFAC (- - -), and modified UNIFAC (Lyngby) (···) models.

tions, and the source of ternary VLE data. Four sets of data are isobaric, and nine sets are isothermal. Predictions are carried out using the UNIQUAC equation with parameters obtained from H^E or VLE data, the UNIFAC model, and the modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund) models. For each procedure, Table 5 lists the standard deviations between experimental and calculated vapor compositions of components 1 and 2, σ_{y_1} and σ_{y_2}, and the percent ratio of the standard deviation between experimental and calculated vapor pressures and the maximum value of this magnitude, σ_p (%). Accurate ternary data are obtained using the UNIQUAC equation with parameters deter-

mined from binary VLE data. As could be expected, ternary data predicted using the UNIQUAC equation with parameters obtained from binary H^E data are much less accurate than those predicted using any of the UNIFAC models. Best predictions are obtained by means of the modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund) models.

With the exception of the MTBE + hexane + octane system, values of σ_{y_1} and σ_{y_2} ranging from 0.0003 to 0.018 are obtained using the UNIQUAC equation with parameters determined from VLE data. For systems formed by MTBE or TAME and two hydrocarbons
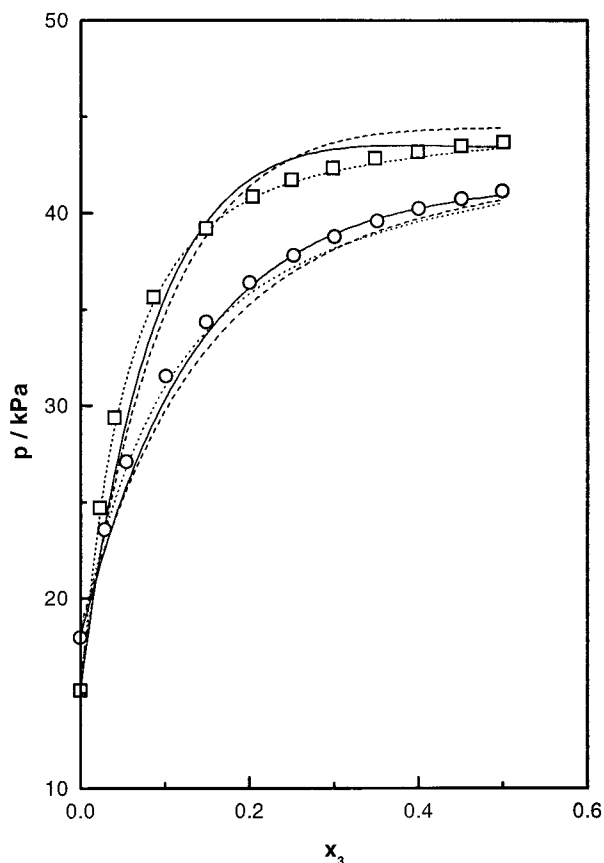
Figure 5. Vapor pressure versus liquid composition x_3 plots at 313.15 K for the TAME + heptane + methanol system:[62] $\bigcirc$, x_2/x_1 = 0.4; $\square$, x_2/x_1 = 2.3; predictions from the UNIQUAC (—), UNIFAC (- - -), and modified UNIFAC (Dortmund) ($\cdots$) models.

(classes 2−5), values of σ_{y_1} and σ_{y_2} obtained using the UNIQUAC equation are slightly lower than those corresponding to the modified UNIFAC (Lyngby) and modified UNIFAC (Dortmund) models. For systems involving MTBE or TAME and alcohols (classes 6−8), values of σ_{y_1} and σ_{y_2} obtained using the UNIQUAC equation are of magnitude similar to those corresponding to the modified UNIFAC (Lyngby) model and higher than those corresponding to the modified UNIFAC (Dortmund) model. Similar trends are observed for deviations in pressure. Figure 3 shows vapor pressure versus liquid composition x_1 plots obtained at 313.15 K for the MTBE + cyclohexane + heptane system at two fixed values of the ratio x_3/x_2 using the UNIQUAC, UNIFAC, and modified UNIFAC (Lyngby) models. Figure 4 shows similar plots obtained for the MTBE + cyclohexane + 1-hexene and TAME + cyclohexane + 1-hexene systems at 313.15 K. Figure 5 shows vapor pressure versus liquid composition x_3 plots obtained for the TAME + heptane + methanol system at 313.15 K and two fixed values of the ratio x_2/x_1 using the UNIQUAC, UNIFAC, and modified UNIFAC (Dortmund) models. The plots shown in Figures 3−5 are typical of the results obtained and also point out that the UNIQUAC equation with parameters determined from VLE data is preferred for systems involving MTBE or TAME and hydrocarbons, while for systems involving MTBE or TAME and an alcohol, the modified UNIFAC (Dortmund) model leads to better results. Consequently, this model may be recommended to estimate the VLE data for ternary and binary mixtures involving MTBE or TAME when binary VLE data are lacking.

Nomenclature

Latin Letters

A_{ij} = UNIQUAC model interaction parameters
H = enthalpy
J = joule
kPa = 10^3 Pa
K = Kelvin
p = vapor pressure
q = UNIQUAC structural parameter
r = UNIQUAC structural parameter
T = temperature
V = volume
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Symbols

σ_H (%) = percent ratio of the standard deviation between experimental and calculated excess enthalpy values and the maximum value of this magnitude
σ_p (%) = percent ratio of the standard deviation between experimental and calculated vapor pressures and the maximum value of this magnitude
σ_{y_1} = standard deviation between experimental and calculated vapor compositions of component 1
σ_{y_2} = standard deviation between experimental and calculated vapor compositions of component 2

Superscript

E = excess property

Subscripts

i, j = components of binary systems
H = excess enthalpy
max = maximum
p = vapor pressure
y_1, y_2 = vapor compositions of components 1 and 2 of binary and ternary systems
1, 2, 3 = first, second, and third components of a system

Abbreviations

MTBE = 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether)
TAME = 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether)
VLE = vapor−liquid equilibrium

Supporting Information Available: Tables of interaction A_{ij}/K parameters for the UNIQUAC equation determined from binary H^E and VLE data. This information is available free of charge via the Internet at http://pubs.acs.org.

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