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Liquid−Liquid Equilibrium of MTBE + Ethanol + Water and MTBE + 1-Hexanol + Water over the Temperature Range of 288.15 to 308.15 K

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Liquid−liquid equilibrium data for methyl *tert*-butyl ether (MTBE) + ethanol + water and MTBE + 1-hexanol + water have been experimentally measured over the temperature range of 288.15 to 308.15 K. The equilibrium data of this work, in addition to the available MTBE-containing LLE data in the technical literature, are analyzed using UNIQUAC, NRTL, UNIFAC-LL, and UNIFAC-DMD models as programmed by the Aspen Plus simulator. On the basis of analyses of the experimental data of this work, UNIFAC-LLE and UNIFAC-DMD showed the best predictive performance for the mole fraction of the target species (MTBE) in both the organic and aqueous phases.

Introduction

For the last three decades, a group of chemicals commonly known as oxygenates have been used as fuel additives in motor gasoline.[1,2] Examples of such oxygenate compounds are methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE), di-propyl ether (DPE), and alcohols (e.g., ethyl alcohol, EtOH, and *tert*-butyl alcohol, TBA). MTBE is an industrial commodity that is mainly used as a fuel oxygenate to enrich the quality of gasoline as a replacement for tetraethyl lead, which is considered to be toxic and environmentally objectionable. It has been commercially used since 1973 in Italy and was adopted in the U.S. in 1990. Currently, Saudi Arabia and Europe are the main producers of MTBE after the U.S. banned its production because of environmental concerns. Following the detection of MTBE and other oxygenate contamination in ground and surface water,[3−5] many researchers started exploring different methods for the removal of such contaminants from water.[6,7] The extraction of MTBE using suitable solvents is of primary importance in this regard.

Thermophysical property measurements on mixtures containing MTBE and other oxygenates, including LLE, have been reviewed by Marsh et al.[8] and Domanska and Malanowski.[9] These reviews covered relevant material up to 1998. There are many experimental studies on LLE ternary systems containing MTBE.[10−15] Studies on binary LLE systems involving MTBE are very scarce. As a matter of fact, only one binary system for MTBE + water has been found in the literature.[10] Furthermore, a literature survey reveals the existence of three quaternary systems and only one five-component aqueous system including MTBE.[16−19] Moreover, six ternary systems covered liquid−liquid equilibria for organics containing nonpolar solvents and MTBE.[17,18,20]

In this study, LLE data for two ternary systems containing MTBE are reported. These systems are MTBE + ethanol + water and MTBE + 1-hexanol + water. The study covers a temperature range of 288.15 to 308.15 K under atmospheric pressure. Moreover, four predictive activity coefficient models are used in the analysis of the experimental data These models are UNIQUAC, NTRL, and two versions of UNIFAC, which differ only in the database for the group interaction parameters (i.e., UNIFAC-LL with group interaction parameters extracted from the LLE data bank and UNIFAC-DMD with group interaction parameters extracted from the Dortmund data bank[21]).

Experimental Section

MTBE used in this work was supplied by BDA (GBR TM) with a stated purity of 99% and water content of 0.05%. Ethanol was also supplied by BDA (AnalaR) with a stated purity of 99.8% and water content of 0.2%. 1-Hexanol was supplied by Fluka with a stated purity of 98% and water content of 0.005%. All materials were used as received without further purification.

The equilibrium experimental data were determined using a tightly closed, jacketed equilibrium cell with 100-cm^3 volume. The temperature was measured with a mercury-in-glass thermometer with a precision better than 0.1 K. The temperature in the jacket of the cell was kept constant by circulating water from a water bath (Julabo Labortechnik GMBH-Germany), which is equipped with a temperature controller (Julabo PC) capable of maintaining the temperature at a fixed value within ±0.1 K. Mixtures of known masses of the three species were introduced into the cell and stirred for 2 h and then left for 8 h to equilibrate and settle down into raffinate (aqueous phase) and extract (organic phase) layers under the same temperature.

Samples from both layers were carefully taken and analyzed using a gas chromatograph (Chrompack CP 9001) with a flame ionization detector (FID). Chromatographic separation of the mixture constituents is achieved by a capillary column with a 50 m × 0.32 mm i.d., WCOT (wall-coated open-tube) fused silica coated with a 1.2-μm stationary film (CP-Sil 5 CB). The inlet pressure of the carrier nitrogen gas was set to 40 kPa, and the temperatures of both the detector and injector were set to 250 °C. For the MTBE + ethanol + water system, the oven temperature

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Table 1. Liquid−Liquid Equilibrium Studies of Systems Containing MTBE (1)

ID	substance 2	substance 3	substance 4	t/°C	data points	reference
I	water			0.0−60.0	9	10
II a	water	methanol		25	6	11
II b				25	6	12
II c				35	6	11
III a	water	ethanol		15	8	this work
III b				25	8	this work
III c				25	6	13
III d				25	8	12
III e				35	9	12
IV	water	propanol		25	6	12
V	water	2-propanol		25	6	12
VI	water	butanol		25	3	12
VII	water	2-butanol		25	3	12
VIII	water	2-methyl 1-propanol		25	3	12
IX	water	*tert*-butyl alcohol		25	6	12
X a	water	1-hexanol		15	6	this work
X b				25	6	this work
X c				35	7	this work
XI a	water	octanol		25	10	14
XI b				35	10	14
XII	water	2,2,4-TMP		25	17	15
XIII	water	toluene		25	13	15
XIV	water	tertrahydrofuran		25	10	10
XV	heptane	methanol		25	6	20
XVI	octane	methanol		25	7	20
XVII	nonane	methanol		25	6	20
XVIII	decane	methanol		25	8	20
XIX	methanol	2,2,4-TMP		25	8	18
XX	water	2,2,4-TMP	methanol	25	24	18
XXI	water	2,2,4-TMP	ethanol	25	25	17
XXII	water	methanol	toluene	25	25	16
XXIII a	water	reformate[a]		15	7	19
XXIII b				25	7	19
XXIII c				35	7	19
XXIII d				45	7	19

[a] Reformate consists of 5% cyclohexane (4), 35% 2,2,4-TMP (5), and 60% xylene (6).

Table 2. Experimental LLE Data of the MTBE (1) + Ethanol (2) + Water (3) System at 288.15 and 298.15 K

overall mole fractions			mole fractions in the upper (MTBE-rich) phase				mole fractions in the lower (water-rich) phase			
x_1	x_2	x_3	x_1	x_2	x_3	ρ/g·cm^{-3}	x_1	x_2	x_3	ρ/g·cm^{-3}
288.15 K										
0.1316	0	0.8684	0.9217	0.0000	0.0783	0.746	0.0120	0.0000	0.9880	0.979
0.1268	0.0254	0.8478	0.8812	0.0304	0.0884	0.742	0.0127	0.0231	0.9642	0.974
0.1250	0.0513	0.8237	0.8066	0.0744	0.1190	0.755	0.0137	0.0466	0.9397	0.967
0.1186	0.0950	0.7864	0.6108	0.1702	0.2190	0.770	0.0162	0.0786	0.9052	0.954
0.1132	0.1378	0.7490	0.3711	0.2184	0.4105	0.793	0.0223	0.1045	0.8732	0.898
0.1105	0.1579	0.7316	0.2657	0.2243	0.5101	0.806	0.0341	0.1224	0.8434	0.918
0.1071	0.1764	0.7165	0.1638	0.2009	0.6352	0.838	0.0582	0.1471	0.7947	0.936
0.1046	0.1954	0.6999	one layer							
298.15 K										
0.1317	0	0.8683	0.9259	0.0000	0.0741	0.7369	0.0078	0.0000	0.9922	0.987
0.1268	0.0251	0.8481	0.8723	0.0382	0.0894	0.7416	0.0093	0.0223	0.9683	0.974
0.1242	0.0504	0.8253	0.7983	0.0845	0.1171	0.7478	0.0104	0.0445	0.9451	0.967
0.1183	0.0954	0.7863	0.5997	0.1849	0.2155	0.7604	0.0140	0.0787	0.9073	0.954
0.1138	0.1381	0.7481	0.3564	0.2316	0.4120	0.7885	0.0204	0.1058	0.8738	0.934
0.1079	0.1743	0.7177	0.1982	0.2312	0.5706	0.8224	0.0394	0.1331	0.8274	0.910
0.1059	0.1927	0.7013	one layer							
0.1023	0.2083	0.6893	one layer							

was set to 70 °C and kept isothermal. In the case of the MTBE + 1-hexanol + water system, the oven temperature was programmed as follows: the initial temperature was set to 100 °C for 4 min, followed by a constant heating rate of 20 °C/min until a final temperature of 180 °C is attained. The final temperature was kept for 3.5 min, and the cycle was repeated. 1-Butanol (40 g/100 mL of acetone) was prepared. 1-Butanol (2 mL) was added to 2 mL of the sample, and 21 mL of acetone was added to this mixture to give a total volume of 25 mL. 1-Butanol is used as the internal standard for the 1-hexanol determination, and acetone is used to prepare the internal standard because of its miscibility with both phases. Water analysis was performed using a thermal conductivity detector (TCD). The inlet carrier gas (hydrogen) was set to 20 kPa, and the temperature of both the detector and injector was set to 250 °C. The oven temperature was programmed as follows: the initial temperature was set to 70 °C for 2 min, followed by a constant heating rate of 20°C/min until a final temperature of 125 °C was attained. The final temperature was held for 1 min, and the cycle was repeated. Mixtures of known compositions of the reagents were used to calibrate the gas chromatograph. The reproducibility of the composition measurements is found to be better than 0.1%. The density of both phases was measured using a pycnometer and is reported in this paper.

Table 3. Experimental LLE Data of the MTBE (1) + 1-Hexanol (2) + Water (3) System at 288.15, 298.15, and 308.15 K

overall mole fractions			mole fractions in the upper (MTBE-rich) phase				mole fractions in the lower (water-rich) phase			
x_1	x_2	x_3	x_1	x_2	x_3	ρ/g·cm^{-3}	x_1	x_2	x_3	ρ/g·cm^{-3}
288.15 K										
0.1320	0	0.8679	0.9098	0.0000	0.0902	0.742	0.0156	0.0000	0.9844	0.976
0.1302	0.0119	0.8580	0.8105	0.0728	0.1167	0.760	0.0119	0.0002	0.9879	0.979
0.1273	0.0241	0.8486	0.7105	0.1386	0.1509	0.767	0.0106	0.0003	0.9891	0.985
0.1255	0.0472	0.8273	0.5844	0.2213	0.1943	0.776	0.0094	0.0006	0.9900	0.986
0.1232	0.0698	0.8070	0.3293	0.4424	0.2284	0.790	0.0084	0.0007	0.9909	0.986
0.1205	0.0900	0.7895	0.3810	0.3805	0.2385	0.795	0.0075	0.0007	0.9918	0.987
0.0501	0.1197	0.8302	0.1829	0.5010	0.3161	0.803	0.0038	0.0021	0.9941	0.989
0.0379	0.1200	0.8421	0.1518	0.5411	0.3071	0.802	0.0031	0.0020	0.9950	0.983
0.0254	0.1226	0.8520	0.1030	0.5860	0.3110	0.805	0.0022	0.0023	0.9955	0.985
0.0131	0.1244	0.8625	0.0572	0.6239	0.3188	0.803	0.0011	0.0021	0.9968	0.981
0	0.1244	0.8756	0	0.6720	0.3280	0.806	0	0.0026	0.9974	0.974
298.15 K										
0.1354	0	0.8646	0.9329	0.0000	0.0671	0.744	0.0087	0.0000	0.9913	0.985
0.1340	0.0103	0.8557	0.8329	0.0687	0.0984	0.750	0.0079	0.0002	0.9919	0.986
0.1327	0.0207	0.8466	0.7529	0.1226	0.1245	0.758	0.0072	0.0003	0.9926	0.986
0.1304	0.0401	0.8295	0.6361	0.2053	0.1586	0.767	0.0068	0.0004	0.9928	0.986
0.1274	0.0585	0.8140	0.5505	0.2630	0.1865	0.775	0.0060	0.0005	0.9936	0.987
0.1245	0.0766	0.7989	0.4764	0.3164	0.2072	0.782	0.0054	0.0005	0.9941	0.990
0.0504	0.1189	0.8306	0.1948	0.5066	0.2986	0.823	0.0023	0.0009	0.9969	0.998
0.0381	0.1220	0.8398	0.1462	0.5388	0.3150	0.821	0.0020	0.0009	0.9971	0.997
0.0261	0.1224	0.8514	0.1081	0.5851	0.3069	0.816	0.0014	0.0009	0.9978	0.996
0.0130	0.1249	0.8620	0.0576	0.6351	0.3073	0.812	0.0008	0.001	0.9983	0.998
0	0.1250	0.8750	0	0.6763	0.3237	0.807	0	0.0012	0.9988	1.00
308.15 K										
0.131098	0	0.8689	0.9180	0.0000	0.0820	0.736	0.0072	0.0000	0.9928	0.997
0.127502	0.0121	0.8604	0.7971	0.0860	0.1169	0.748	0.0065	0.0003	0.9932	0.994
0.126092	0.0241	0.8498	0.7161	0.1465	0.1373	0.761	0.0061	0.0003	0.9936	0.994
0.124799	0.0366	0.8387	0.6259	0.2049	0.1692	0.768	0.0054	0.0004	0.9942	0.995
0.123213	0.0467	0.8301	0.5832	0.2413	0.1755	0.773	0.0050	0.0004	0.9946	0.997
0.11988	0.0698	0.8103	0.4878	0.3110	0.2012	0.780	0.0045	0.0005	0.9950	0.995
0.1171	0.0910	0.7918	0.4270	0.3463	0.2267	0.785	0.0042	0.0007	0.9951	0.991
0.0498	0.1194	0.8307	0.1595	0.4426	0.3979	0.786	0.0021	0.0014	0.9965	0.975
0.0389	0.1233	0.8378	0.1330	0.4738	0.3933	0.792	0.0016	0.0011	0.9973	0.976
0.0249	0.1227	0.8523	0.0880	0.5155	0.3965	0.799	0.0012	0.0016	0.9972	0.978
0.0130	0.1242	0.8627	0.0494	0.5513	0.3993	0.804	0.0006	0.0018	0.9976	0.985
0	0.1241	0.8759	0	0.6039	0.3961	0.802	0	0.0023	0.9977	0.991

Results and Discussion

A summary of citations of LLE studies of binary and multicomponent systems involving MTBE, including this work, is given in Table 1. The cited literature data span a temperature range of 0 to 60 °C in 31 isothermal data sets with more than 240 experimental data points. Because major industrial applications of LLE are desired at low temperature, most of the studies were performed at 25 °C with very few performed at 35 °C. Studies at higher temperatures are very infrequent. Table 1 shows only one experimental investigation at 60 °C and another at 45 °C.

The experimental liquid−liquid equilibrium data for the two systems under study are shown in Tables 2 and 3. Experimental data from this work, in addition to two data sets found in the literature,[12,13] for the ternary system MTBE + ethanol + water at 298.15 K are also displayed in a triangular diagram shown in Figure 1. It is clearly revealed that the experimental data of this work are in very good agreement with those in the literature. Figure 2 shows the LLE data of the MTBE + 1-hexanol + water system at 288.15, 298.15, and 308.15 K. It is clear from the data shown in Figures 1 and 2 (and also Tables 2 and 3) that MTBE has a much higher affinity toward alcohol than toward water. The lower phase is almost free of MTBE and 1-hexanol. This impliesthat washing out trace contamination of MTBE in water using heavy alcohols is feasible.

The experimental data of this work, in addition to the available LLE data for systems containing MTBE, have been used to test the LLE predictive capability of some liquid-phase models. The models used in this study are UNIQUAC, NRTL, and two versions of UNIFAC (i.e., UNIFAC-LL (with group interaction parameters extracted from LLE data bank) and UNIFAC-DMD (with group interaction parameters extracted from the Dortmund data bank)[21]). All models were used as programmed in the Aspen Plus simulator.[21] The availability of a rich data bank of the required interaction parameters for these models employed by many simulators such as Aspen Plus provides, on one side, a good means of testing for the cross consistency of the emerging experimental LLE data[22] (i.e., agreement between different data sets when treated by the same model, which uses the same interaction parameters for the different data sets). On the other side, experimental LLE data for systems containing species of very limited solubility, such as the systems under experimental study in this work, represent a tough test for predictive models. A table[24] (not presented in this paper) reveals the average absolute relative deviations (AARD) of the compositions (mole fractions) obtained from UNIQUAC, NRTL, UNIFAC-LL, and UNIFAC-DMD models (in the predictive mode). The AARD is

$$\mathrm{AARD} = \frac{1}{N}\sum\left|\frac{x_i^{\mathrm{exptl}} - x_i^{\mathrm{pred}}}{x_i^{\mathrm{exptl}}}\right|$$

Table 4 presents the coefficients that were retrieved from Aspen Plus for the following equations that were used to calculate the binary interaction parameters for the NRTL and UNIQUAC models.

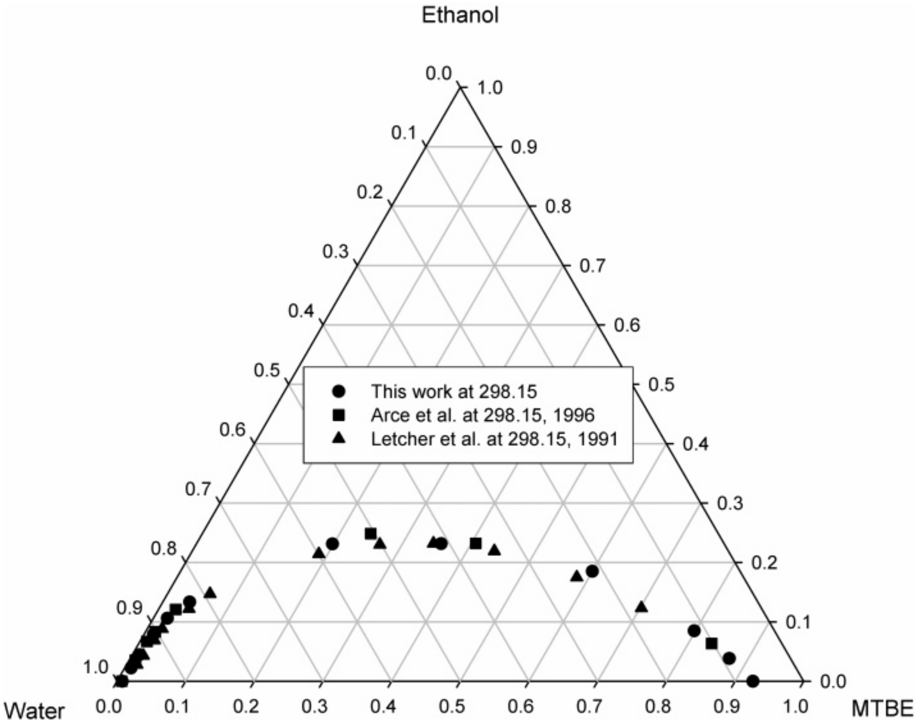


Figure 1. Experimental LLE data equilibrium compositions of the ternary system MTBE + ethanol + water at 298.15 K.

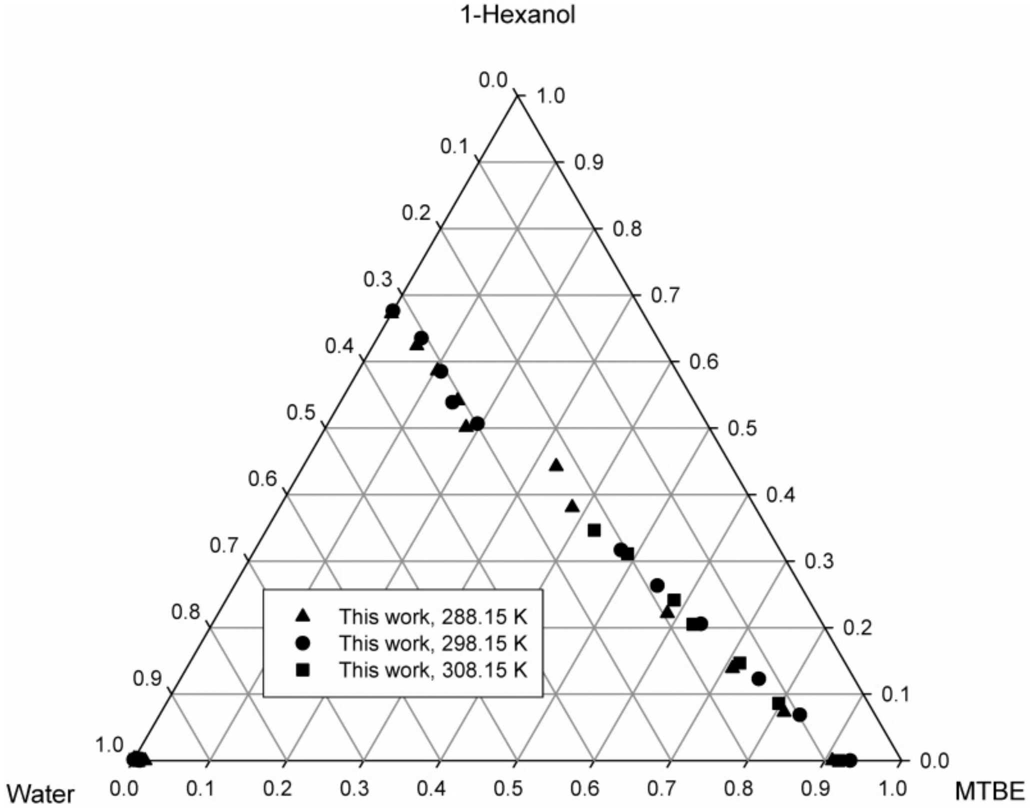


Figure 2. Experimental LLE data equilibrium compositions of the ternary system MTBE + 1-hexanol + water at 288.15, 298.15, and 308.15 K.

NRTL

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

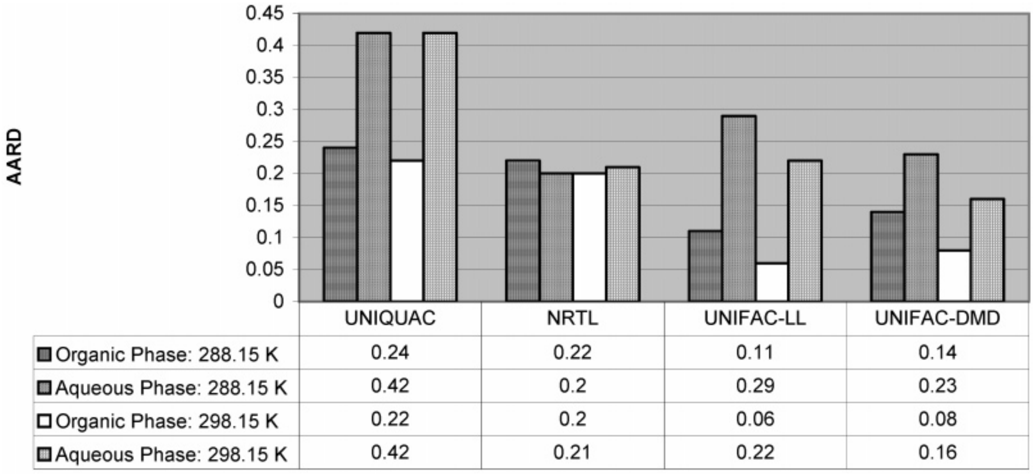
$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij}\ln T + f_{ij}T$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15)$$

UNIQUAC

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij}\ln T + d_{ij}T$$

For the five LLE data sets of the MTBE + ethanol + water system in this work, UNIFAC-based models outperform the other two models. This is made more evident in



	UNIQUAC	NRTL	UNIFAC-LL	UNIFAC-DMD
▦ Organic Phase: 288.15 K	0.24	0.22	0.11	0.14
▦ Aqueous Phase: 288.15 K	0.42	0.2	0.29	0.23
□ Organic Phase: 298.15 K	0.22	0.2	0.06	0.08
▦ Aqueous Phase: 298.15 K	0.42	0.21	0.22	0.16

Figure 3. Absolute average relative deviations in the mole fraction of MTBE in the organic and aqueous phases for the MTBE + water + ethanol system as predicted by different models.

Table 4. NRTL and UNIQUAC Coefficients of the Equations for Binary Interaction Parameters

component *i*		MTBE	ethanol	ethanol	1-hexanol
component *j*		water	1-hexanol	water	water
NRTL a_{ij}					
	a_{ji}	0	−0.0677	−0.8009	0
	bij	0	0.2856	3.4578	0
	b_{ji}	686.1436	60.464	246.18	216.6345
	cij	1106.9764	−123.4329	−586.0809	1636.1768
	dij	0.3	0.3	0.3	0.3
	eij	0	0	0	0
	e_{ji}	0	0	0	0
	fij	0	0	0	0
	f_{ji}	0	0	0	0
		0	0	0	0
UNIQUAC					
	aij	0	0.774	2.0046	0
	a_{ji}	0	−1.1734	−2.4936	0
	bij	−748.6477	−220.2272	−728.9705	−287.9751
	b_{ji}	−4.367	311.6534	756.9477	−69.4038
	cij	0	0	0	0
	c_{ji}	0	0	0	0
	dij	0	0	0	0
	d_{ji}	0	0	0	0
	eij	0	0	0	0
	e_{ji}	0	0	0	0

	structure parameters for the UNIQUAC equation			
	MTBE	ethanol	water	1-hexanol
Q	3.632	1.972	1.4	4.132
Q1	3.632	1.972	1.4	4.132
R	4.0679	2.10547	0.92	4.803

Figure 3, which shows AARD values for the target species (MTBE) in both phases in a bar chart. The same Figure shows that NRTL is the most stable model as reflected in its response to changes in temperature and phase (i.e., it gives comparable results for AARD values for MTBE in both phases at two different temperatures). In view of the very limited solubility of MTBE in the aqueous phase, it becomes important to mention that AARD values of MTBE in the aqueous phase are expected to have a much higher uncertainty than those in the organic phase. This leaves us with the conclusion that the predictive capability of UNIFAC-LL and UNIFAC-DMD exceeds other models' predictive capability. As shown in Figure 3, the worst prediction is made by the UNIQUAC model. These results could be interpreted in terms of the fact that the interaction parameters used by UNIFAC-LL are all extracted from LLE data, which makes their predictive capability far better than that of UNIQUAC or NRTL, whose parameters are mainly derived by regressing VLE data rather than LLE data. Overall, however, UNIFAC-LL is again the preeminent model among all. It is not to be concluded, however, that UNIFAC-LL is always preferred over other models in its predictive capability for LLE. For example, it shows the poorest performance when the ternary LLE data of ref 16 are analyzed using these different models. It is, therefore, a questionable task to base judgments solely on such models. There is always no better alternative to a careful, cautious, and considerate experimental plan. Generally, the errors are high because the prediction accuracy of the data is very sensitive to small errors in the activity coefficients.[23]

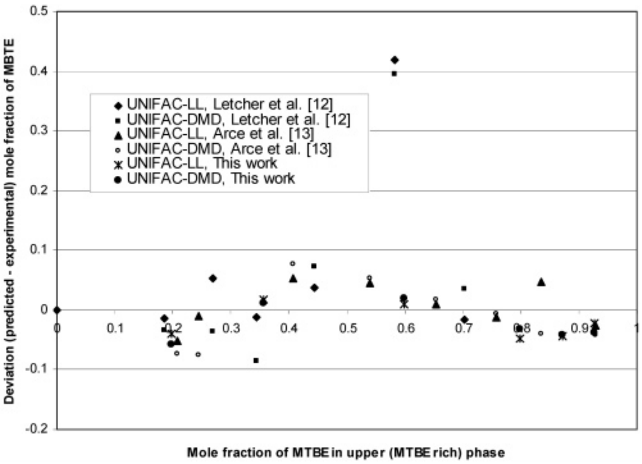


Figure 4. Absolute average relative deviations in the mole fraction of MTBE in the organic and aqueous phases for the MTBE + water + 1-hexanol system as predicted by different models.

Independent of the quality of the predictions, the deviation between experimental and predicted values can be used as a comparison tool between different data sets from different sources. Figure 4 demonstrates the deviations in the mole fraction of MTBE in the upper (organic) phase as predicted by the best two predictive models, namely, UNIFAC-LL and UNIFAC_DMD as depicted in Figure 3 for the MTBE + ethanol + water system at 298.15 K versus the mole fraction of MTBE in the upper (MBTE-rich) phase. Two sets of data from two sources in the literature[12,13] and one set from this work were used. It is clearly shown in this Figure that all three sets of data are comparable, and the data set from this work reveals the relative minimum deviation in comparisons with the two data sets from the literature.[12,13]

Conclusions

LLE data for MTBE + ethanol + water and MTBE + 1-hexanol + water were produced in the temperature range of 288.15 to 308.15 K. The equilibrium data of this work, in addition to the available MTBE-containing LLE data in the technical literature, are analyzed using four models in the predictive mode as programmed by the Aspen Plus simulator. The models used in this work are UNIQUAC, NRTL, UNIFAC-LL, and UNIFAC-DMD. Data from this work for the system MTBE + ethanol + water agrees well with data for the same system found in the literature. Models based on UNIFAC in general and UNIFAC-LL in particular showed the best predictive performance for the mole fraction of the target species (MTBE) in both the organic and aqueous phases. No sharp conclusion could be drawn as to the behavior of NRTL and UNIQUAC. Overall, however, it is not advisable to employ UNIQUAC and NRTL in the prediction of LLE. If no alternative exists, this must be done with a great deal of caution.

Acknowledgment

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