Thermodynamics of Fuels with a Biosynthetic Component: Vapor−Liquid Equilibrium Data for Binary and Ternary Mixtures Containing Ethyl 1,1-Dimethylethyl Ether, *n*-Heptane, and Toluene at $T = 313.15$ K

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New fluid phase equilibria data containing ETBE as an ether synthesized from ethanol of biological origin are presented giving isothermal $p-x-y$ data for the ternary system ethyl 1,1-dimethylethyl ether (ETBE) + *n*-heptane + toluene and the three binary systems involved at 313.15 K. A static technique consisting of an isothermal total pressure cell was used for the measurements. Data reduction by Barker's method provides correlations for G^{E}, using the Margules equation for the binary systems and the Wohl expansion for the ternary system. Wilson, NRTL, and UNIQUAC models have also been applied to both binary and ternary systems. The mixtures measured exhibit slight positive deviation from ideal behavior.

Introduction

Directive 2003/30/CE of the "Promotion and Use of Biofuels" was approved by the European Parliament and the European Council. This is the first time that a European directive regulates the minimum usage of renewable fuels in every member state. As a result of the application of the directive to local legislation, each member state must follow the European Union objectives, which require that by December 31, 2005, 2 % of fuel marketed for transportation be biofuels, gradually increasing to 6.76 % by December 31, 2010. Because of that bioethers and bioalcohols are used as blending agents for enhancing the octane number. These compounds also help fuels burn cleaner and more efficiently. Their effects are to make gasoline work harder, help engine last longer, and reduce air pollution. They also cause changes in the fuel properties. The development of renewable fuels needs both knowledge of new thermodynamic data and improvement of clean energy technologies.

Ethyl 1,1-dimethylethyl ether, better known as ethyl *tert*-butyl ether or ETBE, is synthesized from isobutylene and ethanol by using an acidic ion-exchange resin such as Amberlyst-15. This exothermic reaction is equilibrium limited in the industrial temperature range of (40 to 70) °C. The principal side reactions are dimerization of isobutylene and hydration of isobutylene. The former can be minimized by using excess ethanol, and the latter is neglected in this process analysis because it occurs only in the presence of water. The use of ethanol of vegetal origin in its manufacture process, increases the interest of ETBE or bio-ETBE as oxygenated additive.

Our group has been interested on the research of oxygenated additives of gasoline through a wide program on the thermodynamic characterization of ternary mixtures, as the simplest multicomponent system, containing oxygenated additives (ethers and alcohols) and different type of hydrocarbons (paraffins, cycloparaffins, aromatics, oleffins) in order to better understand and model these reformulated gasolines. Methyl *tert*-butyl ether (MTBE), *tert*-amylmethyl ether (TAME), and isopropyl ether or diisopropyl ether (DIPE) were chosen as representative ethers, and a comparison of the behavior of the different ethers was also published.[1]

Table 1. Experimental Vapor Pressures (p_i^{sat}) for the Pure Compounds Measured in This Work and Literature Values (p_i^{sat}(lit.)), Molar Volumes of Pure Liquids (V_i^{L}), Second Virial Coefficients (B_{ii}, B_{ij}) and van der Waals Molecular Volumes (r_i) and Surfaces (q_i) at $T = 313.15$ K Used for the Calculations

	ethyl 1,1-dimethylethyl ether ($i = 1$)	*n*-heptane ($i = 2$)	toluene ($i = 3$)
p_i^{sat}/(kPa)	31.629	12.319	7.884
p_i^{sat}(lit.)/(kPa)	31.78[a]	12.334[d]	7.894[d]
	31.527[b]	12.327[e]	7.887[e]
	31.913[c]	12.335[f]	7.895[f]
$V_i^{\text{L}}/(\text{cm}^3\cdot\text{mol}^{-1})$[g]	142	147	107
$B_{i1}/(\text{cm}^3\cdot\text{mol}^{-1})$[h]	−1772.2	−2078.9	−2189.0
$B_{i2}/(\text{cm}^3\cdot\text{mol}^{-1})$[h]	−2078.9	−2516.6	−2295.8
$B_{i3}/(\text{cm}^3\cdot\text{mol}^{-1})$[h]	−2189.0	−2295.8	−2105.7
r_i[i]	4.7422	5.17	3.9228
q_i[i]	4.172	4.4	2.968

[a] Ref 3. [b] Calculated from the Antoine equation using constants reported in ref 4. [c] Calculated from the Antoine equation using constants reported in ref 5. [d] Ref 6. [e] Ref 7. [f] Ref 8. [g] Ref 9. [h] Calculated by ref 10 from ref 11. [i] Calculated from ref 12.

Recently, we have started a series of measurements of ternary and binary mixtures containing ethyl *tert*-butyl ether (ETBE). In this paper, experimental isothermal $P-x$ data are reported for the ternary system ethyl 1,1-dimethylethyl ether (ETBE) + *n*-heptane + toluene and the three binary systems involved. All of them have been measured at the temperature of 313.15 K.

Experimental Section

Materials. Heptane and toluene used were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss. p.a.) with a purity >0.995 and >0.997 (by gas chromatography, GC) respectively. Their purities were also checked by GC and were found to be >0.997.

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Table 2. Total Pressure p for the Binary Systems at $T = 313.15$ K and at Various Compositions of the Liquid Phase x_1 and the Calculated Composition of the Vapor Phase y_1 Using the Five-Parameter Margules Equation

x_1	y_1	p/(kPa)	x_1	y_1	p/(kPa)	x_1	y_1	p/(kPa)	x_1	y_1	p/(kPa)
Ethyl 1,1-Dimethylethyl Ether (1) + n-Heptane (2)											
0.0000	0.0000	12.318	0.3491	0.5875	19.999	0.5482	0.7508	23.744	0.7996	0.9007	28.165
0.0525	0.1399	13.602	0.3983	0.6336	20.947	0.5489	0.7513	23.773	0.8489	0.9263	29.000
0.1294	0.2987	15.376	0.3996	0.6348	20.981	0.5976	0.7838	24.640	0.9001	0.9521	29.883
0.1707	0.3677	16.294	0.4481	0.6760	21.896	0.5991	0.7847	24.675	0.9472	0.9751	30.695
0.1988	0.4098	16.904	0.4487	0.6765	21.921	0.6488	0.8158	25.540	1.0000	1.0000	31.620
0.2489	0.4767	17.969	0.4985	0.7152	22.836	0.6988	0.8453	26.419			
0.2997	0.5362	19.014	0.4989	0.7155	22.862	0.7492	0.8735	27.300			
n-Heptane (1) + Toluene (2)											
0.0000	0.0000	7.879	0.2863	0.4227	10.216	0.4998	0.6012	11.166	0.7986	0.8293	12.022
0.0386	0.0882	8.322	0.3313	0.4639	10.452	0.5273	0.6223	11.269	0.8485	0.8691	12.119
0.0776	0.1620	8.717	0.3783	0.5043	10.673	0.5491	0.6389	11.342	0.8966	0.9086	12.200
0.1173	0.2257	9.070	0.4032	0.5249	10.778	0.5995	0.6770	11.510	0.9520	0.9563	12.275
0.1581	0.2821	9.395	0.4267	0.5439	10.885	0.6496	0.7148	11.660	1.0000	1.0000	12.326
0.1986	0.3314	9.682	0.4496	0.5621	10.974	0.6999	0.7530	11.794			
0.2412	0.3780	9.951	0.4757	0.5825	11.078	0.7499	0.7913	11.913			
Ethyl 1,1-Dimethylethyl Ether (1) + Toluene (2)											
0.0000	0.0000	7.902	0.3490	0.6869	16.906	0.5493	0.8242	21.509	0.7997	0.9346	27.108
0.0566	0.2144	9.495	0.3993	0.7280	18.074	0.5503	0.8247	21.553	0.8493	0.9522	28.222
0.1033	0.3402	10.754	0.4010	0.7293	18.113	0.5990	0.8499	22.629	0.9017	0.9696	29.398
0.1544	0.4449	12.115	0.4492	0.7637	19.230	0.5998	0.8503	22.665	0.9508	0.9852	30.514
0.2003	0.5194	13.278	0.4514	0.7652	19.277	0.6494	0.8737	23.750	1.0000	1.0000	31.626
0.2494	0.5847	14.506	0.4991	0.7955	20.369	0.6995	0.8955	24.875			
0.2994	0.6401	15.725	0.5027	0.7976	20.449	0.7496	0.9158	25.994			

Table 3. Total Pressure p for the Ternary System Ethyl 1,1-Dimethylethyl Ether (1) + n-Heptane (2) + Toluene (3) at $T = 313.15$ K and at Various Compositions of the Liquid x_1, x_2 and the Vapor Phases y_1, y_2 Calculated Using the Wohl Expansion

x_1	x_2	y_1	y_2	p/kPa	x_1	x_2	y_1	y_2	p/kPa	x_1	x_2	y_1	y_2	p/kPa
1.0000	0.0000	1.0000	0.0000	31.640	0.0000	0.0000	0.0000	0.0000	7.875	0.0000	1.0000	0.0000	1.0000	12.315
0.7281	0.2719	0.8618	0.1382	26.935	0.3133	0.0000	0.6540	0.0000	16.054	0.0000	0.6999	0.0000	0.7528	11.783
0.7101	0.2652	0.8537	0.1374	26.487	0.3051	0.0263	0.6335	0.0278	16.024	0.0291	0.6795	0.0787	0.6944	12.426
0.6932	0.2589	0.8459	0.1366	26.064	0.2980	0.0488	0.6168	0.0507	15.996	0.0507	0.6644	0.1316	0.6552	12.907
0.6579	0.2457	0.8292	0.1350	25.187	0.2826	0.0980	0.5820	0.0986	15.919	0.1005	0.6296	0.2391	0.5753	13.991
0.6204	0.2317	0.8107	0.1331	24.267	0.2670	0.1480	0.5490	0.1445	15.831	0.1504	0.5947	0.3306	0.5073	15.067
0.5851	0.2185	0.7925	0.1312	23.402	0.2516	0.1970	0.5183	0.1877	15.729	0.1996	0.5602	0.4082	0.4495	16.102
0.5500	0.2054	0.7735	0.1292	22.540	0.2361	0.2465	0.4886	0.2301	15.615	0.2496	0.5253	0.4769	0.3982	17.144
0.5138	0.1918	0.7528	0.1270	21.661	0.2203	0.2972	0.4590	0.2726	15.490	0.2997	0.4901	0.5377	0.3528	18.167
0.4773	0.1782	0.7307	0.1245	20.773	0.2050	0.3459	0.4313	0.3132	15.358	0.3489	0.4557	0.5906	0.3131	19.159
0.4409	0.1646	0.7072	0.1218	19.875	0.1893	0.3963	0.4029	0.3551	15.209	0.3994	0.4204	0.6394	0.2765	20.165
0.4047	0.1511	0.6820	0.1188	18.996	0.1730	0.4482	0.3738	0.3988	15.053	0.4496	0.3853	0.6833	0.2434	21.155
0.3684	0.1375	0.6548	0.1154	18.101	0.1579	0.4964	0.3467	0.4399	14.885	0.4990	0.3507	0.7227	0.2136	22.120
0.0000	1.0000	0.0000	1.0000	12.318	1.0000	0.0000	1.0000	0.0000	31.628	0.0000	0.0000	0.0000	0.0000	7.880
0.3268	0.6732	0.5651	0.4349	19.556	0.6985	0.0000	0.8951	0.0000	24.850	0.0000	0.2984	0.0000	0.4338	10.271
0.3180	0.6551	0.5553	0.4304	19.269	0.6786	0.0284	0.8787	0.0176	24.556	0.0278	0.2902	0.0842	0.3964	10.896
0.3101	0.6389	0.5466	0.4262	19.021	0.6612	0.0534	0.8643	0.0332	24.291	0.0515	0.2831	0.1485	0.3679	11.442
0.2931	0.6037	0.5274	0.4170	18.471	0.6267	0.1027	0.8359	0.0639	23.764	0.1011	0.2683	0.2641	0.3168	12.557
0.2764	0.5694	0.5085	0.4077	17.947	0.5916	0.1530	0.8069	0.0954	23.222	0.1506	0.2535	0.3598	0.2746	13.656
0.2599	0.5354	0.4895	0.3981	17.424	0.5572	0.2023	0.7784	0.1265	22.686	0.2003	0.2387	0.4410	0.2389	14.747
0.2435	0.5016	0.4703	0.3881	16.909	0.5222	0.2524	0.7490	0.1588	22.141	0.2493	0.2240	0.5096	0.2088	15.818
0.2271	0.4676	0.4506	0.3775	16.388	0.5157	0.2618	0.7434	0.1649	22.037	0.2991	0.2092	0.5702	0.1824	16.892
0.2103	0.4331	0.4302	0.3662	15.856	0.4551	0.3486	0.6905	0.2233	21.081	0.3489	0.1943	0.6235	0.1592	17.950
0.1939	0.3993	0.4095	0.3543	15.340	0.4179	0.4018	0.6565	0.2610	20.484	0.3988	0.1794	0.6707	0.1388	19.017
0.1777	0.3659	0.3885	0.3417	14.814	0.3833	0.4513	0.6233	0.2979	19.911	0.4488	0.1645	0.7131	0.1205	20.074
0.1612	0.3319	0.3662	0.3279	14.282	0.3485	0.5012	0.5882	0.3371	19.326	0.4985	0.1497	0.7510	0.1042	21.122

ETBE was supplied by La Coruña Refinery of REPSOL-YPF. It was purified by rectification at atmospheric pressure to a purity >0.997 (by GC). All the compounds were thoroughly degassed before measurements by a modified distillation method based on the one suggested by Van Ness and Abbott[2] and kept in glass balloons equipped with leak-proof valves. As a check for complete degassing, the vapor pressures of the pure constituents measured in this work were compared with those reported in the literature. The values are given in Table 1.

Apparatus and Procedure. A static VLE apparatus, consisting of an isothermal total pressure cell, has been employed for measuring the VLE equilibrium of binary and ternary mixtures. The apparatus and measuring technique are based on that by Van Ness and co-workers[13,14] and whose performance has been described in a previous paper.[15]

The equilibrium properties were measured directly. Their uncertainties are as follows: injected volume, ± 0.03 mL; temperature, ± 10 mK; and total pressure, ± 5 Pa. The overall mole fraction is determined accurately from the volumetric displacement of the pistons, the temperature of the injectors, and the densities for the pure components. This resulted in uncertainties in mole fraction of ± 0.0005. The composition of the liquid phase is close to the overall composition, but it is corrected taking into account the vapor space of the cell and using the virial equation.

Experimental values of total vapor pressure for the binary mixtures were obtained in two overlapping runs starting from opposite ends of the composition range. For the ternary mixture, data were obtained by addition of a pure species to a mixture of the other two at a fixed temperature. Six runs (dilution lines) were made starting from the corresponding binary system at mole fractions close to 0.3 or 0.7 and adding the third pure component up to a mole fraction of 0.5.

Experimental Results and Correlations

Data reduction for the binary and ternary mixtures was done by Barker's method[16] according to well-established procedures.[17,18] The nonideality of the vapor phase was taken into account with the virial equation of state, truncated after the second term. The pure component and interaction second virial coefficients (B_{ij}) were calculated by the Hayden and O'Connell method[10] using the parameters given by Dymond and Smith.[11] They are summarized in Table 1.

Binary systems have been correlated by the five-parameter Margules[19] equation:

$$g_{ij} = \frac{G_m^E}{RT} = \{A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda i_j x_j)x_i x_j + \eta x_i^2\, x_j^2\}x_i x_j \quad (1)$$

Parameters A_{ij}, A_{ji}, λ_{ij}, λ_{ji}, and η were obtained by regression of the binary data.

The ternary system has been correlated by the three-parameter Wohl equation,[20] which also includes the parameters of the corresponding binary systems (g_{ij}) previously obtained by eq 1. Only parameters C_0, C_1, and C_2 were found by regression of the ternary data:

$$g_{123} = \frac{G^E}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad (2)$$

Also the Wilson,[21] NRTL,[22] and UNIQUAC[23] models have been used for fitting both binary and ternary systems, whose expressions for the excess Gibbs energy are given by the following:

$$\frac{G^E}{RT} = -\sum_i x_i \ln(\sum_j x_j A_{ij}) \quad (4)$$

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j A_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k} \quad (5)$$

$$\frac{G^E}{RT} = \sum_i x_i \ln\frac{\varphi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln\frac{\vartheta_i}{q_i} - \sum_i q_i x_i \ln(\sum_j \vartheta_j A_{ji}) \quad (6)$$

where $G_{ji} = \exp(-\alpha_{ji}A_{ji})$, $\vartheta_i = q_ix_i/\sum_j q_jx_j$, $\varphi_i = r_ix_i/\sum_j r_jx_j$, and $z = 10$. The adjustable parameters are A_{ij} and A_{ji}. The parameter α_{ji} of the NRTL model has also been adjusted.

Tables 2 and 3 show experimental values of total pressure and the calculated mole fractions of the liquid and vapor phases for the binary systems and the ternary system, respectively. The composition of the vapor phase was calculated by using the Margules equation for the binary systems and the Wohl expansion for the ternary system.

Results of data correlation for the binary systems are summarized in Table 4. For the ternary system, the results of the correlation are given in Table 5. Both tables contain the adjustable parameter values of the different models, the root mean square (rms) of the difference between the experimental and the calculated pressures (rms Δp), and the maximum value of this difference (max $|\Delta p|$).

Table 4. Parameters of the Models Used for the Binary Subsystems of Ternary System Ethyl 1,1-Dimethylethyl Ether (1) + *n*-Heptane (2) + Toluene (3) at T = 313.15 K, together with the Root Mean Square Deviation of Pressure (rms Δp) and the Maximum Value of the Deviation (max $|\Delta p|$)[a]

	Margules	Wilson	NRTL	UNIQUAC
	Ethyl 1,1-Dimethylethyl Ether (1) + *n*-Heptane (2)			
A_{12}	0.1634	0.8812	110.2961	1.0772
A_{21}	0.1463	0.9554	0.1709	0.8902
λ_{12}	−0.0637			
λ_{21}	−0.1336			
η	−0.1931			
α_{12}			0.2299	
rms Δp/kPa	0.007	0.012	0.012	0.012
max $|\Delta p|$/kPa	0.016	0.028	0.028	0.028
	Ethyl 1,1-Dimethylethyl Ether (1) + Toluene (3)			
A_{13}	0.1620	0.7787	10.0402	1.1363
A_{31}	0.1375	1.0862	0.1643	0.8800
λ_{13}	−0.0269			
λ_{31}	−0.0218			
η	−0.0930			
α_{13}			1.0804	
rms Δp/kPa	0.009	0.009	0.009	0.012
max $|\Delta p|$/kPa	0.020	0.020	0.021	0.029
	n-Heptane (2) + Toluene (3)			
A_{23}	0.4847	0.5797	−2.1790	0.8402
A_{32}	0.3776	1.0581	2.8731	1.0763
λ_{23}	0.0333			
λ_{32}	0.0839			
η	−0.0886			
α_{23}			0.043	
rms Δp/kPa	0.003	0.005	0.007	0.006
max $|\Delta p|$/kPa	0.007	0.009	0.012	0.010

[a] The Δp term is defined as the difference between the experimental and calculated pressure.

Table 5. Parameters of the Models Used for the Ternary System Ethyl 1,1-Dimethylethyl Ether (1) + *n*-Heptane (2) + Toluene (3) at T = 313.15 K, together with the Root Mean Square Deviation of Pressure (rms Δp) and the Maximum Value of the Deviation (max $|\Delta p|$)[a]

	Wilson	NRTL	UNIQUAC	Wohl
A_{12}	0.9032	0.0603	1.0113	C_0 = 0.7228
A_{21}	0.9326	0.1133	0.9519	C_1 = 0.0418
A_{13}	0.7748	−0.1385	0.8251	C_2 = −0.0697
A_{31}	1.0885	0.3065	1.2000	
A_{23}	0.5808	−0.1046	0.7922	
A_{32}	1.0596	0.5919	1.1330	
α_{12}		0.7475		
α_{13}		0.3175		
α_{23}		0.4305		
rms Δp/kPa	0.008	0.006	0.010	0.009
max $|\Delta p|$/kPa	0.019	0.016	0.023	0.019

[a] The Δp term is defined as the difference between the experimental and calculated pressure.

Discussion

The three binary systems measured exhibit a slight positive deviation from ideality, and they do not exhibit an azeotrope. The $p-x-y$ plot of the binary systems is shown in Figure 1.

The five-parameter Margules equation leads to the best correlation results for the binary systems measured. The rms deviations of the pressure are 7 Pa for (ETBE + *n*-heptane), 9 Pa for (ETBE + toluene), and 3 Pa for (*n*-heptane + toluene). The maximum values of the deviations are 16, 20, and 7 Pa, respectively. The other models also give quite good values of the rms deviations.

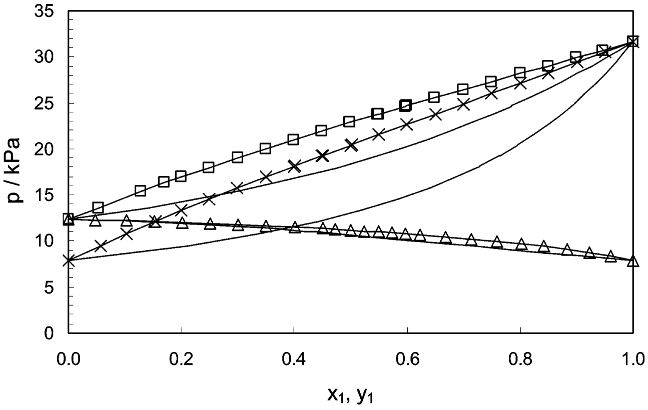

Figure 1. Total vapor pressure at 313.15 K for binary systems as a function of the liquid, x_1, and vapor compositions, y_1: □, ETBE (1) + heptane (2); ×, ETBE (1) + toluene (2); △, toluene (1) + heptane (2). Symbols represent the experimental points. Lines are calculated with Margules equation.

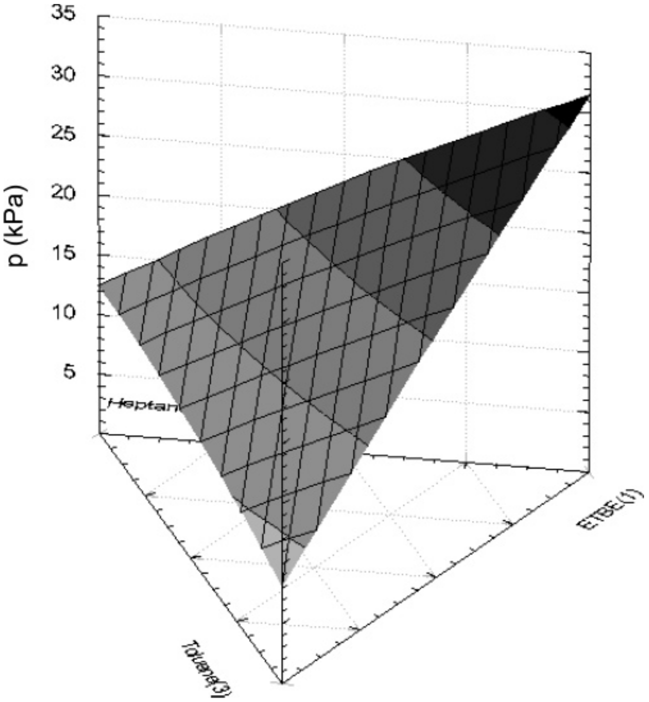

Figure 2. Oblique view of the pressure surface reduced by Wohl expansion for the ternary system ETBE (1) + heptane (2) + toluene (3) at T = 313.15 K.

The binary system toluene + heptane was also measured by Góral,[6] and there is some agreement between both sets of data. Using the parameters of Table 4, the rms pressure deviation of the data from the literature is 27 Pa with a maximum deviation of 32 Pa. The correlation of these data using our programs gives a rms pressure deviation of 9 Pa and a maximum deviation of 16 Pa.

On the other hand, the binary system ETBE + *n*-heptane was measured by Del Rio et al.[4] at the temperatures of 298.15 K, 328.15 K, and 363.15 K. These data were used to calculate the temperature dependence of the interaction parameters for the UNIQUAC model. We have compared our experimental results with those obtained using the parameters of the literature: the rms deviation of the pressure is 77 Pa. It proves the agreement of the data and the fitting of the model.

The third binary system studied (ETBE + toluene) was measured by Steinhagen and Sandler[24] at different temperatures (273.15 K, 311.15 L, and 333.15 K) and also by Oh and Park[25] at 313.15 K. They have used a different method to measure the vapor liquid equilibria. They have calculated the total pressure, and their values are higher than ours. They have also compared their data with the prediction of UNIFAC model, and the same deviation was observed. The rms pressure deviation of their data is 488 Pa with a maximum deviation of 987 Pa, which are both much higher than our results.

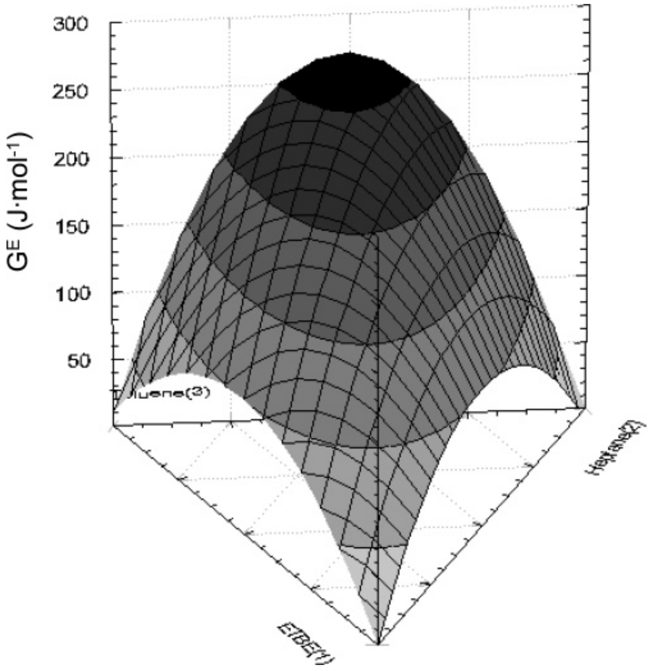

Figure 3. Oblique view of the excess Gibbs energy surface reduced by Wohl expansion for the ternary system ETBE (1) + heptane (2) + toluene (3) at T = 313.15 K.

The data for the ternary system ETBE + *n*-heptane + toluene are also well-correlated by all the models. The rms pressure ranges between 6 Pa using the NRTL model and 10 Pa for the UNIQUAC model, with a maximum value of the absolute deviation in pressure of 23 Pa for the UNIQUAC model, 16 Pa for the NRTL model, and 19 Pa for the other models. Figures 2 and 3 show graphical results for the ternary system. They show the oblique view of the pressure and of the excess Gibbs energy surface, respectively. Both were calculated by the Wohl expansion.

The pressure surface increases softly from the value of the saturation pressure of less volatile compound (toluene) to the saturation pressure of more volatile compound (ETBE). The ternary system also shows a positive deviation from ideality, and the molar excess Gibbs energy increases up to a maximum value, which corresponds to the less ideal binary system (heptane + toluene). The maximum value for G_m^E is around 271 J·mol^{-1} at a mole fraction of heptane of 0.45.

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