

# Thermodynamics of Fuels with a Biosynthetic Component. II. Vapor–Liquid Equilibrium Data for Binary and Ternary Mixtures Containing Ethyl 1,1-Dimethylethyl Ether, 1-Hexene, and Cyclohexane at $T = 313.15$ K

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Vapor–liquid equilibria, data containing ethyl 1,1-dimethylethyl ether (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) + 1-hexene + cyclohexane and the two binary systems involved containing the ether 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 a slight positive deviation from ideal behavior.

## Introduction

Due to the promotion of biofuels approved for transportation in Europe, there is an increasing interest in the use of ethyl 1,1-dimethylethyl ether, better known as ethyl *tert*-butyl ether or ETBE, as an additive for gasolines. It is synthesized from isobutylene and ethanol, which should be of vegetable origin (bioethanol).

Our group has been involved in the research of oxygenated additives for gasoline through a wide program concerning the thermodynamic characterization of ternary mixtures containing oxygenated additives (ethers and alcohols) and different types of hydrocarbons, as well as the application of these data to predict the behavior of different additives.<sup>1</sup>

We recently began a series of measurements of ternary and binary mixtures containing ethyl *tert*-butyl ether (ETBE),<sup>2</sup> and this paper is a continuation. Experimental isothermal  $p$ – $x$  data are reported for the ternary system ethyl 1,1-dimethylethyl ether (ETBE) + 1-hexene + cyclohexane and two of the binary systems involved measured at the temperature of 313.15 K; the third binary was measured in a previous paper.<sup>3</sup>

## Experimental Section

**Materials.** Ethyl 1,1-dimethylethyl ether, supplied by the La Coruña Refinery of REPSOL-YPF, was purified by rectification at atmospheric pressure to a purity  $> 0.997$  (by gas chromatography, GC). 1-Hexene and cyclohexane were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (pro analysis) with a stated purity  $> 0.98$  and  $> 0.995$  (by gas chromatography, GC), respectively. Their purities were also checked by gas chromatography and were found to be  $> 0.997$  (GC).

Before measurements, all the compounds were degassed by a modified distillation method, based on that suggested by Van Ness and Abbott,<sup>4</sup> and kept in glass balloons equipped with leak proof valves. The average experimental vapor pressures

**Table 1.** Average Experimental Vapor Pressures ( $p_i^{\text{sat}}$ ) for the Pure Compounds and Literature Values ( $p_i^{\text{sat}}$  (lit.)), Molar Volumes of Pure Liquids ( $V_i^L$ ), Second Virial Coefficients ( $B_{ij}$ ,  $B_j^E$ ) 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 ( $i = 1$ )	1-hexene ( $i = 2$ )	cyclohexane ( $i = 3$ )
$p_i^{\text{sat}}/(\text{kPa})$	31.637	44.962	24.639
$p_i^{\text{sat}}(\text{lit.})/(\text{kPa})$	31.629 <sup>a</sup>	44.979 <sup>e</sup>	24.626 <sup>c</sup>
	31.78 <sup>b</sup>	45.050 <sup>f</sup>	24.635 <sup>e</sup>
	31.546 <sup>c</sup>	45.030 <sup>g</sup>	24.634 <sup>f</sup>
	31.913 <sup>d</sup>		24.670 <sup>g</sup>
$V_i^L/(\text{cm}^3 \cdot \text{mol}^{-1})^f$	142	128	111
$B_{i1}/(\text{cm}^3 \cdot \text{mol}^{-1})^h$	−1772.2	−1619.7	−1644.5
$B_{i2}/(\text{cm}^3 \cdot \text{mol}^{-1})^h$	−1619.7	−1510.1	−1520.81
$B_{i3}/(\text{cm}^3 \cdot \text{mol}^{-1})^h$	−1644.5	−1520.81	−1554.6
$r_i^i$	4.7422	4.2697	4.0464
$q_i^i$	4.172	3.64	3.24

<sup>a</sup> Ref 2. <sup>b</sup> Ref 19. <sup>c</sup> Calculated from the Antoine equation using constants reported in ref 20. <sup>d</sup> Calculated from the Antoine equation using constants reported in ref 21. <sup>e</sup> Ref 3. <sup>f</sup> Calculated from the Antoine equation using constants reported in ref 22. <sup>g</sup> Calculated from the Antoine equation using constants reported in ref 23. Ref 10. <sup>h</sup> Calculated by ref 12 from ref 13. <sup>i</sup> Calculated from ref 24.

of the pure compounds are compared with those reported in the literature, and both are given in Table 1.

**Apparatus and Procedure.** A static VLE apparatus, consisting of an isothermal total pressure cell, was used to measure the vapor–liquid equilibrium of binary and ternary mixtures. The apparatus and measuring technique are based on that by Van Ness and co-workers,<sup>5,6</sup> and its performance was described in a previous paper.<sup>7</sup>

Three positive displacement pumps, of 100 mL capacity (Ruska, model 2200-801), were used to inject known volumes of pure degassed components into the cell. This was immersed in a high-precision water bath (Hart Scientific model 6020) assuring a temperature stability of  $\pm 0.5$  mK and thermostatted at  $T = 313.15$  K. The pump resolution was 0.01 mL, and the resulting uncertainty in the volume injected was  $\pm 0.03$  mL.

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The cell is a cylindrical stainless steel piece with a volume of about 180 mL and is provided with an externally operated magnetic stirrer. Initially, about 50 mL of one component was injected into the evacuated cell, and the vapor pressure was recorded. The second or third components were then injected in appropriate proportions to achieve a desired composition. The total mass injected was determined accurately from the volume differences corresponding to the initial and final positions of the pistons, the temperature of the injectors, and the densities for the injected components, allowing an uncertainty in the mole fraction of  $\pm 0.0005$ . The composition of the liquid phase was close to the overall composition but was corrected taking into account the vapor space of the cell and using the virial equation, whereas the composition of the vapor phase was calculated by data reduction.

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 mixtures, 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.

The temperature was measured by a calibrated platinum resistance thermometer (SDL model 5385/100) connected to an a.c. resistance bridge (ASL model F250) with a temperature resolution of 1 mK. The estimated uncertainty of the temperature measurement was  $\pm 10$  mK. The pressure was measured using a differential pressure cell provided with a null indicator (Ruska models 2413-705 and 2416-711, respectively). When atmospheric air balanced the vapor pressure of the cell, a Bourdon-fused quartz precision pressure gauge (Texas Instruments model 801) provided with a capsule indicated the pressure with an estimated uncertainty of  $\pm 5$  Pa for the 125 kPa range. Both temperature and pressure devices were calibrated using our own standards which are traceable to S.I. units. All the uncertainties were estimated using the recommended guide EA-4/02<sup>8</sup> with a coverage factor of 2 that corresponds to a coverage probability of approximately 95 %.

## Experimental Results and Correlations

Data reduction for the binary and ternary mixtures was done by Barker's method<sup>9</sup> according to well-established procedures.<sup>10,11</sup>

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<sup>12</sup> using the parameters given by Dymond and Smith<sup>13</sup> and summarized in Table 1.

Binary systems were correlated by the five-parameter Margules<sup>14</sup> equation

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

and  $A_{ij}$ ,  $A_{ji}$ ,  $\lambda_{ij}$ ,  $\lambda_{ji}$ , and  $\eta$  are the adjustable parameters of the model.

The ternary system was correlated by the three-parameter Wohl equation,<sup>15</sup> which also includes the parameters of the corresponding binary systems ( $g_{ij}$ ) previously obtained by eq

**Table 2. Total Pressure  $p$  for the Binary Systems Containing Ethyl 1,1-Dimethylethyl Ether 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)
Ethyl 1,1-Dimethylethyl Ether (1) + 1-Hexene (2)					
0.0000	0.0000	44.958	0.5008	0.4169	38.653
0.0521	0.0389	44.359	0.5477	0.4620	38.037
0.1001	0.0750	43.767	0.5516	0.4658	37.991
0.1494	0.1129	43.146	0.5998	0.5137	37.355
0.2007	0.1536	42.492	0.6491	0.5644	36.688
0.2515	0.1953	41.856	0.6997	0.6189	35.983
0.3004	0.2366	41.223	0.7501	0.6756	35.281
0.3503	0.2799	40.577	0.7989	0.7331	34.586
0.4006	0.3246	39.941	0.8499	0.7960	33.855
0.4478	0.3675	39.333	0.8991	0.8595	33.128
0.4496	0.3692	39.318	0.9451	0.9218	32.445
0.4955	0.4120	38.716	1.0000	1.0000	31.628
Ethyl 1,1-Dimethylethyl Ether (1) + Cyclohexane (3)					
0.0000	0.0000	24.639	0.5050	0.5613	29.441
0.0596	0.0887	25.453	0.5504	0.6019	29.694
0.0985	0.1410	25.937	0.5518	0.6032	29.721
0.1499	0.2051	26.525	0.5960	0.6424	29.969
0.2062	0.2695	27.106	0.6006	0.6464	29.979
0.2499	0.3166	27.521	0.6501	0.6900	30.235
0.3068	0.3749	28.008	0.6987	0.7325	30.480
0.3496	0.4169	28.363	0.7504	0.7778	30.723
0.4003	0.4652	28.729	0.8013	0.8225	30.935
0.4011	0.4660	28.744	0.8507	0.8661	31.124
0.4496	0.5109	29.084	0.9006	0.9106	31.306
0.4498	0.5111	29.073	0.9506	0.9554	31.465
0.5002	0.5570	29.392	1.0000	1.0000	31.624

1. Only parameters  $C_0$ ,  $C_1$ , and  $C_2$  were found by regression of the ternary data.

$$g_{123} = \frac{G^E}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1 x_1 + C_2 x_2) x_1 x_2 x_3 \quad (2)$$

Wilson,<sup>16</sup> NRTL,<sup>17</sup> and UNIQUAC<sup>18</sup> models have also been used for fitting both binary and ternary systems, whose expressions for the excess Gibbs energy are given by

$$\frac{G^E}{RT} = - \sum_i x_i \ln \left( \sum_j x_j A_{ij} \right) \quad (3)$$

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j A_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \quad (4)$$

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\varphi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\vartheta_i}{q_i} - \sum_i q_i x_i \ln \left( \sum_j \vartheta_j A_{ji} \right) \quad (5)$$

where  $G_{ji} = \exp(-\alpha_{ji} A_{ji})$ ;  $\vartheta_i = q_i x_i / \sum_j q_j x_j$ ;  $\varphi_i = r_i x_i / \sum_j r_j x_j$ ;  $z = 10$ ; and the adjustable parameters are  $A_{ij}$  and  $A_{ji}$ . The parameter  $\alpha_{ji}$  of the NRTL model has also been adjusted.

Tables 2 and 3 show the experimental values of total pressure and the calculated mole fractions of the liquid and vapor 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-

**Table 3. Total Pressure  $p$  for the Ternary System Ethyl 1,1-Dimethylethyl Ether (1) + 1-Hexene (2) + Cyclohexane (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**

$x_1$	$x_2$	$y_1$	$y_2$	$p/\text{kPa}$
1.0000	0.0000	1.0000	0.0000	31.653
0.6993	0.3007	0.6184	0.3816	36.005
0.6812	0.2929	0.6062	0.3732	35.803
0.6642	0.2856	0.5947	0.3654	35.603
0.6292	0.2705	0.5707	0.3494	35.195
0.5942	0.2555	0.5465	0.3335	34.763
0.5589	0.2403	0.5220	0.3175	34.328
0.5238	0.2252	0.4973	0.3016	33.875
0.4890	0.2103	0.4725	0.2857	33.418
0.4537	0.1951	0.4470	0.2695	32.946
0.4188	0.1801	0.4213	0.2532	32.458
0.3837	0.1650	0.3949	0.2366	31.958
0.3489	0.1501	0.3680	0.2197	31.439
0.0000	1.0000	0.0000	1.0000	44.965
0.2993	0.7007	0.2357	0.7643	41.281
0.2915	0.6824	0.2317	0.7506	40.928
0.2844	0.6657	0.2280	0.7378	40.601
0.2694	0.6307	0.2202	0.7107	39.894
0.2543	0.5952	0.2122	0.6827	39.164
0.2381	0.5575	0.2034	0.6524	38.388
0.2243	0.5251	0.1957	0.6258	37.715
0.2092	0.4898	0.1870	0.5961	36.970
0.1942	0.4546	0.1781	0.5659	36.222
0.1792	0.4196	0.1689	0.5350	35.471
0.1643	0.3847	0.1593	0.5033	34.713
0.1492	0.3495	0.1492	0.4700	33.930
0.0000	0.0000	0.0000	0.0000	24.653
0.2996	0.0000	0.3676	0.0000	27.999
0.2899	0.0324	0.3468	0.0539	28.639
0.2816	0.0599	0.3301	0.0972	29.149
0.2696	0.1002	0.3071	0.1572	29.895
0.2539	0.1524	0.2794	0.2295	30.852
0.2393	0.2014	0.2553	0.2928	31.725
0.2247	0.2502	0.2328	0.3522	32.585
0.2097	0.3000	0.2112	0.4095	33.452
0.1946	0.3507	0.1906	0.4647	34.331
0.1796	0.4005	0.1713	0.5165	35.176
0.1647	0.4505	0.1530	0.5662	36.021
0.1497	0.5003	0.1357	0.6135	36.855
1.0000	0.0000	1.0000	0.0000	31.644
0.6997	0.0000	0.7334	0.0000	30.539
0.6803	0.0277	0.7027	0.0416	30.980
0.6635	0.0518	0.6770	0.0766	31.349
0.6296	0.1001	0.6277	0.1435	32.091
0.5946	0.1501	0.5798	0.2089	32.853
0.5597	0.2001	0.5344	0.2708	33.601
0.5246	0.2502	0.4911	0.3300	34.353
0.4898	0.2999	0.4500	0.3862	35.092
0.4546	0.3502	0.4102	0.4407	35.828
0.4196	0.4003	0.3719	0.4930	36.549
0.3845	0.4505	0.3350	0.5436	37.275
0.3496	0.5004	0.2994	0.5921	37.992
0.0000	1.0000	0.0000	1.0000	44.962
0.0000	0.6992	0.0000	0.7988	39.501
0.0253	0.6816	0.0216	0.7812	39.338
0.0511	0.6635	0.0437	0.7632	39.180
0.1010	0.6286	0.0865	0.7282	38.865
0.1506	0.5940	0.1293	0.6933	38.534
0.1999	0.5595	0.1723	0.6583	38.208
0.2503	0.5243	0.2169	0.6222	37.856
0.3001	0.4894	0.2615	0.5862	37.504
0.3497	0.4548	0.3065	0.5501	37.143
0.3994	0.4200	0.3522	0.5135	36.776
0.4496	0.3850	0.3989	0.4761	36.398
0.4997	0.3499	0.4464	0.4383	36.006
0.0000	0.0000	0.0000	0.0000	24.627
0.0000	0.3126	0.0000	0.4594	31.985
0.0262	0.3044	0.0289	0.4448	32.053
0.0516	0.2965	0.0565	0.4308	32.121
0.1035	0.2803	0.1115	0.4033	32.253
0.1553	0.2641	0.1647	0.3770	32.372
0.2055	0.2484	0.2151	0.3525	32.475
0.2566	0.2325	0.2654	0.3282	32.520
0.3073	0.2166	0.3145	0.3049	32.565
0.3580	0.2008	0.3631	0.2821	32.592
0.4089	0.1849	0.4114	0.2596	32.608
0.4588	0.1693	0.4587	0.2378	32.608
0.5091	0.1536	0.5064	0.2161	32.591

**Table 4. Parameters of the Models Used for Two of the Binary Subsystems of the Ternary System Ethyl 1,1-Dimethylethyl Ether (1) + 1-Hexene (2) + Cyclohexane (3) at  $T = 313.15$  K together with the Root Mean Square Deviation of Pressure (rms  $\Delta p$ ) and the Maximum Value of the Deviation (max  $|\Delta p|$ )<sup>a</sup>**

	Margules	Wilson	NRTL	UNIQUAC
Ethyl 1,1-Dimethylethyl Ether (1) + 1-Hexene (2)				
$A_{12}$	0.0584	1.1426	-0.3264	0.8073
$A_{21}$	0.0369	0.8292	0.3263	1.2030
$\lambda_{12}$	0.1827			
$\lambda_{21}$	0.0299			
$\eta$	0.3095			
$\alpha_{12}$			-0.3731	
rms $\Delta p/\text{kPa}$	0.005	0.017	0.014	0.017
max $ \Delta p /\text{kPa}$	0.009	0.032	0.032	0.033
Ethyl 1,1-Dimethylethyl Ether (1) + Cyclohexane (3)				
$A_{13}$	0.2163	0.6149	-0.3597	1.3227
$A_{31}$	0.1465	1.2640	0.6243	0.6882
$\lambda_{13}$	-0.0153			
$\lambda_{31}$	-0.0164			
$\eta$	-0.0875			
$\alpha_{13}$			0.3268	
rms $\Delta p/\text{kPa}$	0.007	0.007	0.007	0.007
max $ \Delta p /\text{kPa}$	0.016	0.012	0.012	0.012

<sup>a</sup> The  $\Delta p$  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) + 1-Hexene (2) + Cyclohexane (3) at  $T = 313.15$  K together with the Root Mean Square Deviation of Pressure (rms  $\Delta p$ ) and the Maximum Value of the Deviation (max  $|\Delta p|$ )<sup>a</sup>**

	Wilson	NRTL	UNIQUAC	Wohl
$A_{12}$	1.0264	-0.3164	0.8229	$C_0 = 0.3317$
$A_{21}$	0.9315	0.2669	1.1835	$C_1 = 0.1086$
$A_{13}$	0.6341	0.0827	1.1303	$C_2 = -0.0651$
$A_{31}$	1.2234	0.1827	0.8466	
$A_{23}$	0.6083	-1.5595	1.3423	
$A_{32}$	1.3392	1.8654	0.6855	
$\alpha_{12}$		-1.0846		
$\alpha_{13}$		4.2546		
$\alpha_{23}$		0.0637		
rms $\Delta p/\text{kPa}$	0.033	0.029	0.031	0.033
max $ \Delta p /\text{kPa}$	0.092	0.088	0.087	0.079

<sup>a</sup> The  $\Delta p$  Term is Defined as the Difference Between the Experimental and Calculated Pressure.

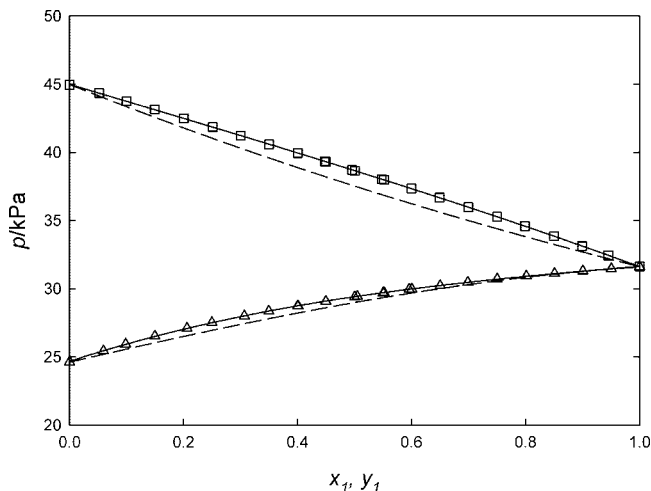
mean-square of the difference between the experimental and the calculated pressures (rms  $\Delta p$ ), and the maximum value of this difference (max  $|\Delta p|$ ).

## Discussion

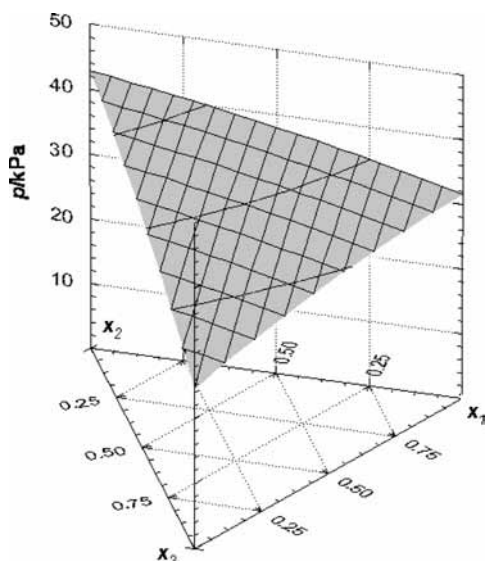
The binary systems are plotted in Figure 1. The ETBE + 1-hexene system shows a near ideal behavior, and the other binary containing the ether ETBE + cyclohexene exhibits a slight positive deviation from ideality. Neither presents an azeotrope. These systems have not been found in the literature measured with the same conditions for comparison.

All the models used to fit the experimental data give very good results for the correlation. The root-mean-square deviations of the pressure are 7 Pa for ETBE + cyclohexane for all the models, and the values for ETBE + 1-hexene range between (5 and 17) Pa. The maximum values of the deviations for both systems vary from (9 to 33) Pa.

The ternary system ethyl 1,1-dimethylethyl ether (ETBE) + 1-hexene + cyclohexane is also well correlated by all the models. The root-mean-square pressure ranges between 29 Pa, using the NRTL model, and 33 Pa for the Wilson and UNIQUAC models, while the maximum value of the absolute



**Figure 1.** Total vapor pressure at 313.15 K for binary systems as a function of the liquid,  $x_1$ , and vapor compositions,  $y_1$ :  $\square$ , ETBE (1) + 1-hexene (2);  $\triangle$ , ETBE (1) + cyclohexane (2). Symbols represent the experimental points. Lines are calculated with the Margules equation.

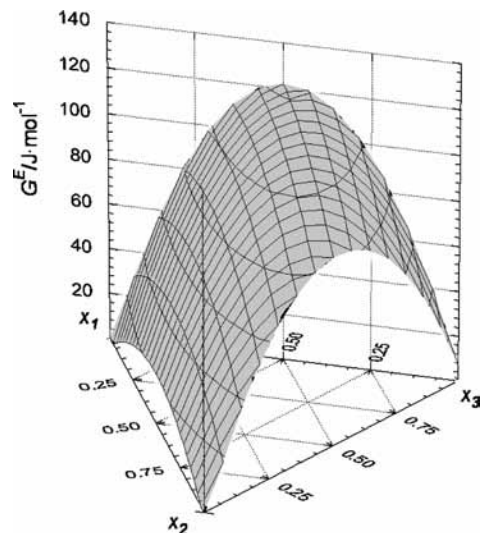


**Figure 2.** Oblique view of the pressure surface reduced by the Wohl expansion for the ternary system ETBE (1) + 1-hexene (2) + cyclohexane (3) at  $T = 313.15$  K.

deviation in pressure ranges between 79 Pa, for the Wohl expansion, and 92 Pa, for the Wilson model. Figures 2 and 3 show the oblique view of the pressure and the excess Gibbs energy surface, respectively. Both were calculated by the Wohl expansion.

The pressure surface gently increases from the value of the vapor pressure of the less volatile compound (cyclohexane) to the vapor pressure of the more volatile compound (1-hexene). The ternary system also exhibits 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 (ETBE + cyclohexane), around  $118 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction of ETBE of 0.45.

Finally, the comparison of this ternary system with that previously measured, using MTBE as the ether,<sup>3</sup> shows a quite similar qualitative behavior in pressure and excess Gibbs energy, and the quantitative differences are due to the values of the vapor pressure of the ethers, which is lower for ETBE.



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

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