

**Phase Equilibrium Properties of Binary and Ternary Mixtures Containing Dibutyl Ether, Cyclohexane and Heptane or 1-Hexene at T=313.15 K.**

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# Phase Equilibrium Properties of Binary and Ternary Mixtures Containing Dibutyl Ether, Cyclohexane and Heptane or 1-Hexene at T=313.15 K.

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## Abstract

New experimental isothermal  $P,x,y$  data for the ternary systems dibutyl ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene and for the binary systems dibutyl ether + 1-hexene and dibutyl ether + heptane at 313.15 K are reported. 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 ternaries. Wilson, NRTL and UNIQUAC models have been applied successfully to both of the binary and the ternary mixtures presented here.

KEYWORDS: VLE data, dibutyl ether, heptane, 1-hexene, cyclohexane, ternary system.

## Introduction

Due to the environmental regulations placed by the Clean Air Act of 1990 on automobile emissions, refineries worldwide have increased continuously their use of alcohol and ether based oxygenates in gasoline blending. IUPAC has sponsored three international workshops on vapor-liquid equilibria and related properties in binary and ternary mixtures of ethers,

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3 alkanes, and alkanols with the objective of developing a set of recommended values. A  
4 comprehensive review of the thermophysical property measurements of these mixtures are  
5 presented by Marsh et al. in reference<sup>1</sup>. Our group has contributed to this research program on  
6 the thermodynamic characterization of ternary mixtures as the simplest multicomponent system,  
7 containing oxygenated additives (ethers and alcohols) and different type of hydrocarbons  
8 (paraffins, cycloparaffins, aromatics, olefins) in order to better understand and model these  
9 reformulated gasolines<sup>2-6</sup>. Methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-  
10 amyl methyl ether (TAME), diisopropyl ether (DIPE) and dibutyl ether (DBE) have been  
11 chosen as representative ethers and some of them have been used widely as commercial fuel  
12 additives.  
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23 An appropriate gasoline blending requires finding a balance between the combustion  
24 performance and the volatility of the involved fuel mixtures. Key parameters in the  
25 formulation and storage of commercial gasoline are the distillation curve, which affects the  
26 evolution of fuel's combustion, together with the Reid's vapour pressure (RVP) which is  
27 widely used as a volatility indicator. Both the distillation curve and RVP depend directly on  
28 the vapour-liquid equilibrium (VLE) behaviour of fuel mixtures.  
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34 In this work, experimental isothermal  $P,x,y$  data are reported for the ternary systems dibutyl  
35 ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene and for the binary  
36 systems dibutyl ether + 1-hexene and dibutyl ether + heptane at 313.15 K. Results of the  
37 remaining binary systems involved, dibutyl ether + cyclohexane<sup>6</sup>, cyclohexane + heptane<sup>7</sup> and  
38 cyclohexane + 1-hexene<sup>7</sup> have been previously published.  
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## 45 Experimental Section

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49 **Materials.** All the chemicals used were purchased from Fluka Chemie AG and were of the  
50 highest purity available, chromatography quality reagents (of the series puriss. p.a.) with a  
51 stated purity > 99.5 % (GC) for dibutyl ether, cyclohexane and heptane and > 98 % (GC) for  
52 1-hexene. Only dibutyl ether was additionally distilled in a packed column. The first and last  
53 portions of the distillate were discarded and the intermediate fraction distilling at constant  
54 temperature was collected; the purity was improved up to 99.7 % (GC). All reagents were  
55 thoroughly degassed. The purity of the products after degassing was checked by gas  
56 chromatography, and the values were > 99.8 % (GC) for all the compounds.  
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3 In Table 1, the vapour pressures of the pure constituents measured in this work are compared  
4 with those reported in the literature as a check for complete degassing.  
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9 **Apparatus and procedure.** A static VLE apparatus, consisting of an isothermal total pressure  
10 cell, has been employed for measuring the vapor-liquid equilibrium of binary and ternary  
11 mixtures. The apparatus and measuring technique are based on that by Van Ness and  
12 coworkers<sup>8,9</sup>, and whose performance has been described detailed in previous papers<sup>10,11</sup>.  
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17 The total uncertainties of the equilibrium properties directly measured are: injected volume  
18  $\pm 0.03$  mL, temperature  $\pm 0.01$  K, total pressure  $\pm 5$  Pa and liquid phase mole fraction  $\pm 0.001$ .  
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23 Experimental values of total vapour pressure for the binary mixtures were obtained in two  
24 overlapping runs starting from opposite ends of the composition range. For the ternary  
25 mixture, data were obtained by addition of a pure species to a mixture of the other two at a  
26 fixed temperature. Six runs (dilution lines) were made starting from the corresponding binary  
27 system at mole fractions close to 0.3 or 0.7 and adding the third pure component up to a mole  
28 fraction of 0.5.  
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### 33 34 35 Experimental Results and Correlations

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38 The use of the static VLE measurement allows a condition of true thermodynamic equilibrium  
39 to be established. As a consequence of Duhem's theorem, sampling of the phases is not  
40 necessary. Given a set of isothermal pressure and total composition data, thermodynamics  
41 allows calculation of the coexisting liquid and vapour phases. Thus, the equilibrium vapour  
42 does not need to be sampled for analysis and the data are thermodynamically consistent "per  
43 se"<sup>12</sup>. Data reduction for the binary and ternary mixtures was done by Barker's<sup>13</sup> method  
44 according to well established procedures<sup>14,15</sup>. The non-ideality of the vapour phase was taken  
45 into account with the virial equation of state, truncated after the second term. The pure  
46 component and interaction second virial coefficients ( $B_{ij}$ ) were calculated by the Hayden and  
47 O'Connell method<sup>16</sup> using the parameters given by Dymond and Smith<sup>17</sup> and they appear in  
48 Table 1.  
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60 Experimental data of the total vapour pressure and the corresponding composition of the  
liquid and vapour phases for the binary systems dibutyl ether + heptane and dibutyl ether + 1-

hexene at 313.15 K are presented in Table 2. The remaining binary systems involve in the ternaries, dibutyl ether + cyclohexane<sup>6</sup>, cyclohexane + heptane<sup>7</sup> and cyclohexane + 1-hexene<sup>7</sup> have been previously published.

Table 3 and Table 4 show VLE data of the ternary system dibutyl ether + cyclohexane + heptane and dibutyl ether + cyclohexane + 1-hexene at  $T=313.15$  K. They are adequately correlated by the Wohl equation<sup>18</sup>:

$$g_{123} = \frac{G^E}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad [1]$$

Here,  $G^E$  is the excess molar Gibbs energy and the parameters  $C_0$ ,  $C_1$  and  $C_2$  were found by regression of the ternary data. The parameters  $g_{ij}$  of the constituent binary systems were represented by the three parameters Margules equation<sup>19</sup>:

$$g_{ij} = \frac{G^E}{x_i x_j RT} = \left[ A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i - \lambda_{ij}x_j) \cdot x_i x_j + (\eta_{ji}x_i + \eta_{ij}x_j) \cdot x_i^2 x_j^2 \right] \quad [2]$$

Binary and ternary systems have been correlated using Wilson<sup>20</sup>, NRTL<sup>21</sup>, and UNIQUAC<sup>22</sup> models. Results of data correlation for binary systems are summarized in Table 5. For the ternary systems the results of the correlation are given in Tables 6 and 7. We have made also the prediction of the fluid phase equilibrium behaviour of the ternary system using the correlation parameters of the binary systems included in Table 5. These tables contain the root mean square of the differences between experimental and calculated pressures, rms  $\Delta P$ , and the maximum value of these pressures residuals,  $\max |\Delta P|$ , both indicators of the quality of the agreement with data.

Figure 1 shows a plot of  $(P-P_{exp})$  versus  $x_i$  for the binary systems presented here, where the pressure was calculated by Margules equation. It can be seen that both branches, necessary to cover the entire composition range, exhibit good agreement close to equimolar concentrations. Furthermore, all deviations are less than 0.1 % of the total pressure.

## Discussion

The binary systems presented of the work, dibutyl ether + heptane and dibutyl ether + 1-hexene show rather ideal behaviour respect to the Raoult's law. For binary system dibutyl ether + heptane we have found literature data at 363.15 K<sup>23</sup>, far away of the temperature of

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3 the work. For the binary system dibutyl ether + cyclohexane, we have found literature data at  
4 298.15 K<sup>24</sup>. We have not found literature data for the remaining binary and ternary systems  
5 involved in this work. All models used to fit the experimental data show very similar results  
6 for the binaries. The root mean square deviation of the pressure is 8 Pa and the maximum  
7 deviation is 17 Pa. Figure 2 is a  $P,x,y$  plot, where both binary subsystems are shown.  
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14 We have determined by Margules equation the excess molar Gibbs energy,  $G^E$ , for the five  
15 binary systems involved in the ternaries measured, as Figure 3 shows. We can see a varied  
16 behaviour of the mixtures: from a positive deviation from ideality in the mixtures of two  
17 hydrocarbons or dibutyl ether + heptane, to a negative deviation with negatives values of  $G^E$   
18 in the binary system dibutyl ether + 1-hexene, going through an alternative behaviour in  
19 function of the composition on the mixture dibutyl ether + cyclohexane. Maximum positive  
20 values of the excess Gibbs energy are for cyclohexane + 1-hexene, 81 J·mol<sup>-1</sup>, close to  
21 equimolar composition, 60 J·mol<sup>-1</sup> for dibutyl ether (1) + heptane (2) in  $x_1=0.44$  and 36.8  
22 J·mol<sup>-1</sup> in  $x_1=0.55$  in binary system cyclohexane (1) + heptane (2). The remaining binary  
23 systems, dibutyl ether + 1-hexene and dibutyl ether + cyclohexane shows very small values of  
24  $G^E$ , -13.8 J·mol<sup>-1</sup> and 5.1 J·mol<sup>-1</sup>, respectively.  
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35 Concerning the ternary systems, all models employed to correlate the data give very similar  
36 values. For the for the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3), root  
37 mean square pressure residuals is 43 Pa for NRTL model with a maximum deviation of 80 Pa.  
38 For dibutyl ether (1) + cyclohexane (2) + 1-hexene (3) root mean square pressure residuals is  
39 30 Pa for UNIQUAC model with a maximum deviation of 62 Pa.  
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46 Prediction of the ternary systems from Wilson, NRTL and UNIQUAC models present very good  
47 results. The maximum deviation in pressure is 127 Pa from NRTL model in the ternary system  
48 dibutyl ether (1) + cyclohexane (2) + heptane (3) and 165 Pa from UNIQUAC model for the  
49 ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3).  
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55 Graphical results for the ternary systems are in Figures 4 to 7. They show the isobar lines and an  
56 oblique view of the excess molar Gibbs energy surface, reduced by Wilson equation. The total  
57 equilibrium pressure is always increasing from the value of the vapour pressure of the less  
58 volatile compound (dibutyl ether) to the vapour pressure of the more volatile compound  
59 (cyclohexane in the first ternary system or 1-hexene in the second one). The behaviour of the  
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3 excess molar Gibbs energy is also increasing up to a maximum value which corresponds to  
4 the less ideal binary system (dibutyl ether + heptane in the first ternary system and  
5 cyclohexane + 1-hexene in the second one).  
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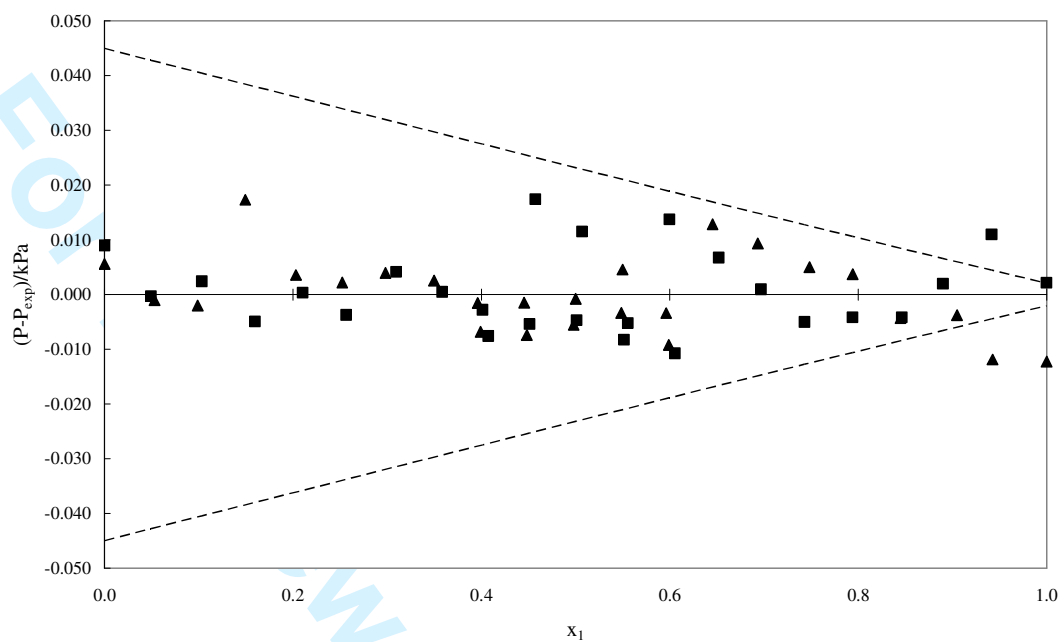
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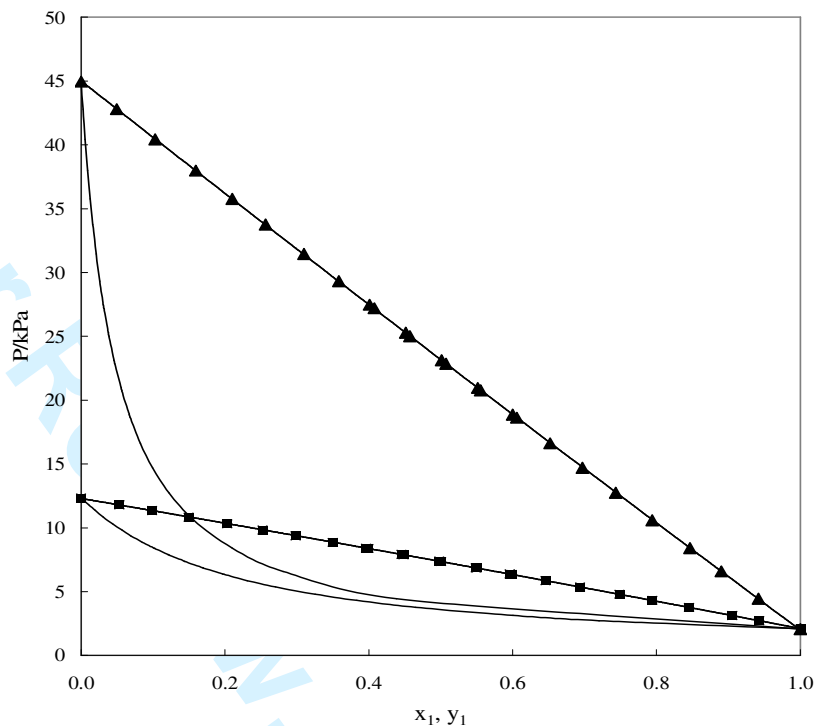
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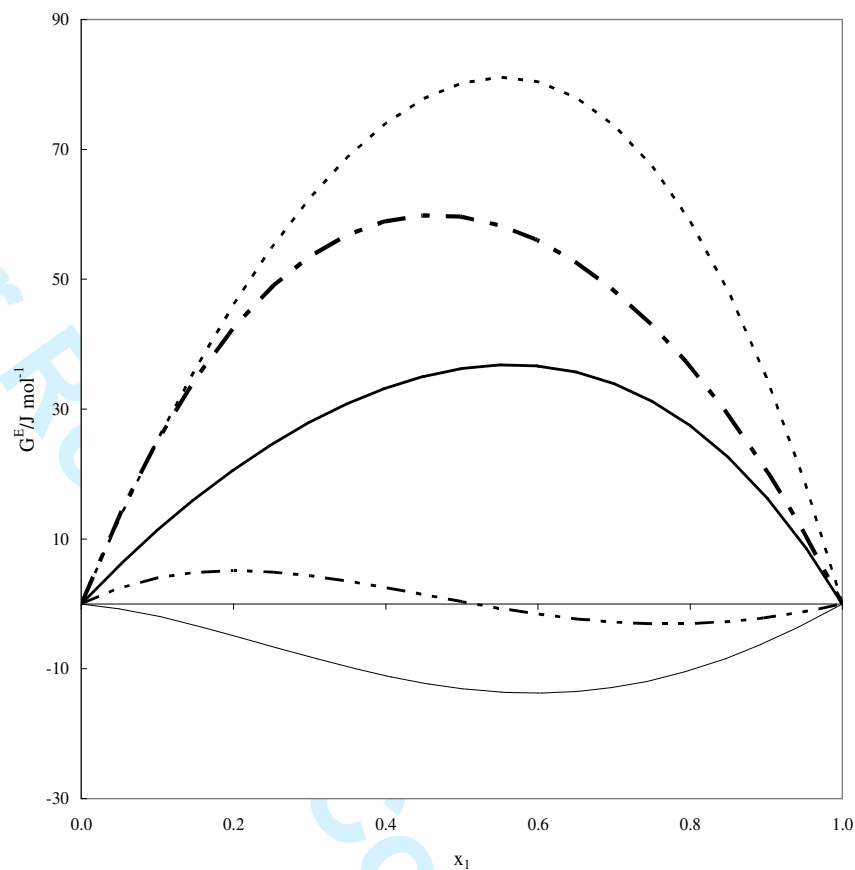




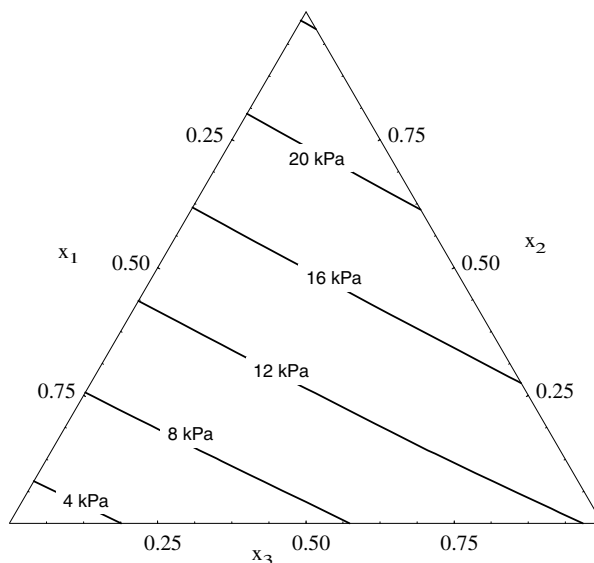
**Figure 1.** Pressure residuals,  $(P - P_{\text{exp}})$ , defined as differences between calculated and experimental pressures as a function of the liquid composition,  $x_1$ , for the binary systems: ■, dibutyl ether (1) + heptane (2); ▲, dibutyl ether (1) + 1-hexene (2); ---,  $\pm 0.1\%$   $P_{\text{exp}}$



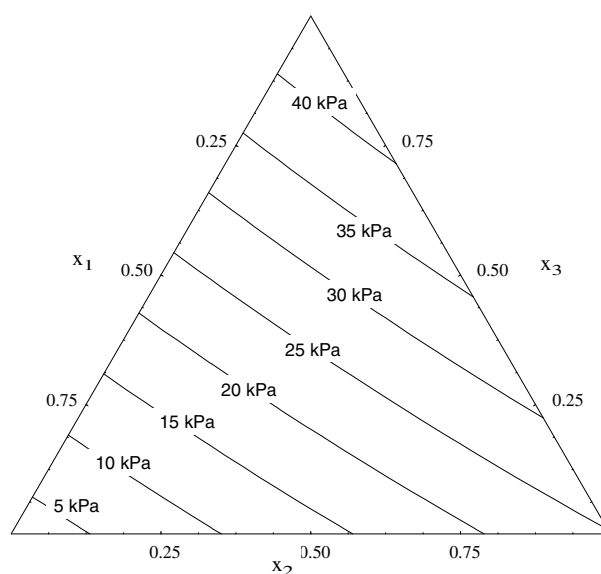
**Figure 2:** Total pressure,  $P$ , at  $T=313.15$  K of the binary systems as a function of the liquid,  $x_1$ , and vapour composition,  $y_1$ : ■, dibutyl ether (1) + heptane (2); ▲, dibutyl ether (1) + 1-hexene (2). Symbols represent the experimental points; lines are calculated from Margules equation.



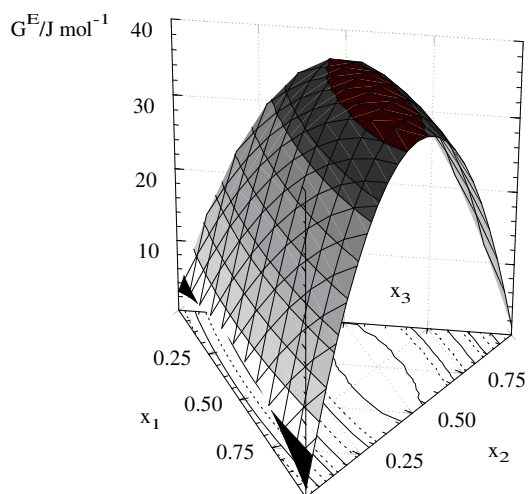
**Figure 3.** Excess Gibbs energy, calculated by Margules equation, for the five binary systems involved in the work, as a function of the liquid mole fraction,  $x_1$ : —, dibutyl ether (1) + 1-hexene (2); ---, dibutyl ether (1) + cyclohexane (2); — —, cyclohexane (1) + heptane (2); -·-, dibutyl ether (1) + heptane (2); ···, cyclohexane (1) + 1-hexene (2).



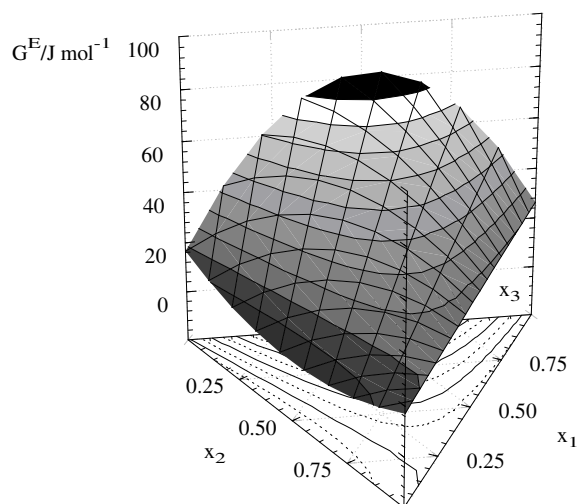
**Figure 4.** Isobar lines,  $P/\text{kPa}$ , as a function of the ternary liquid composition,  $x_i$ , for the VLE at  $T=313.15$  K of the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3), reduced by Wilson equation.



**Figure 5.** Isobar lines,  $P/\text{kPa}$ , as a function of the ternary liquid composition,  $x_i$ , for the VLE at  $T=313.15$  K of the ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3), reduced by Wilson equation.



**Figure 6.** Excess molar Gibbs energy surface, reduced by Wilson equation, for the ternary system dibutyl ether (1) + cyclohexane (2) + heptane (3) at  $T=313.15$  K.



**Figure 7.** Excess molar Gibbs energy surface, reduced by Wilson equation, for the ternary system dibutyl ether (1) + cyclohexane (2) + 1-hexene (3) at  $T=313.15$  K.

Table 1. Average Values of Experimental Vapour Pressures,  $P_i^{\text{sat}}$ , for the Pure Compounds Measured in this Work and Literature Values,  $P_i^{\text{sat}}$  (lit.), Molar Volumes of Pure liquids,  $V_i^{\text{L}}$ , 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 Reduction of the Systems.

	Dibutyl ether (i=1)	Cyclohexane (i=2)	Heptane (i=3)	1-Hexene(i=4)
$P_i^{\text{sat}}$ /kPa	2.068	24.623	12.337	44.964
$P_i^{\text{sat}}$ (lit.) /kPa	2.163 <sup>a</sup>	24.643 <sup>a</sup>	12.336 <sup>a</sup>	45.055 <sup>a</sup>
		24.634 <sup>b</sup>	12.335 <sup>b</sup>	45.050 <sup>b</sup>
		24.630 <sup>c</sup>	12.348 <sup>c</sup>	44.989 <sup>c</sup>
		24.635 <sup>d</sup>	12.331 <sup>d</sup>	44.979 <sup>d</sup>
		24.650 <sup>e</sup>	12.351 <sup>e</sup>	44.932 <sup>e</sup>
$V_i^{\text{L}}$ /( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) <sup>f</sup>	173	134	150	129
$B_{i1}$ / ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) <sup>g</sup>	-4372	-2537	-3263	-2455
$B_{i2}$ / ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) <sup>g</sup>	-2537	-1565	-1982	-1525
$B_{i3}$ / ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) <sup>g</sup>	-3263	-1982	-2521	
$B_{i4}$ / ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) <sup>g</sup>	-2455	-1525		-1522
$r_i^{\text{h}}$	5.5709	4.2816	4.4275	3.8132
$q_i^{\text{h}}$	6.9116	5.181	5.6621	4.7867

a) Calculated from Antoine equation using constants reported in ref 25 ; b) Calculated from Antoine equation using constants reported in ref 26; c) ref 27; d) ref 28; e) ref 3; f) ref 29; g) Calculated by Hayden et al.<sup>16</sup> from Dymond et al.<sup>17</sup> h) ref 30



**Table 2.** Total Pressure,  $P$ , for Dibutyl ether (1) + Heptane (2) and Dibutyl Ether (1) + 1-Hexene (2) at  $T=313.15$  K and at Various Compositions of the Liquid Phase,  $x_1$ , and the Calculated Composition of the Vapour Phase,  $y_{1,calc}$ . Using Three-Parameter Margules Equation.

Dibutyl Ether (1) + Heptane (2)						Dibutyl Ether (1) + 1-Hexene (2)					
$x_1$	$y_{1,calc}$	P/kPa	$x_1$	$y_{1,calc}$	P/kPa	$x_1$	$y_{1,calc}$	P/kPa	$x_1$	$y_{1,calc}$	P/kPa
0.000	0.000	0.000	0.448	0.122	7.891	0.0000	0.0000	44.955	0.5070	0.0468	22.864
0.000	0.000	0.000	0.498	0.143	7.3880	0.0494	0.0025	42.795	0.5513	0.0555	20.969
0.000	0.000	12.331	0.500	0.144	7.361	0.1032	0.0055	40.440	0.5556	0.0564	20.780
0.053	0.010	11.806	0.550	0.170	6.851	0.1597	0.0090	37.984	0.5997	0.0669	18.862
0.099	0.020	11.350	0.596	0.197	6.386	0.2103	0.0126	35.776	0.6055	0.0680	18.632
0.149	0.031	10.830	0.645	0.231	5.862	0.2566	0.0162	33.764	0.6519	0.0824	16.624
0.203	0.044	10.314	0.693	0.270	5.367	0.3096	0.0209	31.452	0.6968	0.0994	14.713
0.252	0.057	9.830	0.748	0.325	4.798	0.3584	0.0259	29.330	0.7431	0.1221	12.750
0.298	0.070	9.374	0.794	0.383	4.313	0.4012	0.0310	27.472	0.7939	0.1566	10.603
0.350	0.085	8.865	0.845	0.465	3.779	0.4076	0.0318	27.202	0.8462	0.2099	8.410
0.396	0.101	8.407	0.905	0.601	3.128	0.4513	0.0378	25.298	0.8900	0.2812	6.585
0.399	0.103	8.381	0.943	0.721	2.723	0.4572	0.0386	25.022	0.9416	0.4384	4.446
0.445	0.120	7.914	1.000	1.000	2.080	0.5010	0.0457	23.140	1.0000	1.0000	2.066

**Table 3.** Total pressure, P, for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + Heptane (3) at  $T=313.15$  K, and at Various Compositions of the Liquid,  $x_1$ ,  $x_2$ , and the Vapour Phases  $y_{1,calc}$ ,  $y_{2,calc}$ , Calculated Using Wohl Expansion.

$x_1$	$x_2$	$y_{1,calc}$	$y_{2,calc}$	P/kPa
1.0000	0.0000	1.0000	0.0000	2.045
0.6902	0.0000	0.2668	0.0000	5.352
0.6663	0.0346	0.2313	0.1354	6.016
0.6477	0.0615	0.2080	0.2237	6.546
0.6172	0.1057	0.1761	0.3442	7.410
0.5852	0.1522	0.1492	0.4455	8.313
0.5533	0.1983	0.1274	0.5272	9.214
0.5137	0.2556	0.1055	0.6090	10.341
0.4824	0.3011	0.0912	0.6622	11.226
0.4508	0.3468	0.0789	0.7077	12.115
0.4153	0.3983	0.0672	0.7513	13.118
0.3808	0.4482	0.0574	0.7874	14.086
0.3465	0.4980	0.0489	0.8187	15.055
1.0000	0.0000	1.0000	0.0000	2.062
0.3064	0.0000	0.0720	0.0000	9.249
0.2940	0.0403	0.0647	0.0973	9.893
0.2882	0.0595	0.0615	0.1400	10.197
0.2725	0.1106	0.0538	0.2440	11.018
0.2583	0.1571	0.0477	0.3275	11.759
0.2450	0.2006	0.0426	0.3971	12.457
0.2294	0.2512	0.0374	0.4692	13.253
0.2134	0.3035	0.0326	0.5351	14.083
0.1990	0.3504	0.0289	0.5878	14.818
0.1842	0.3987	0.0254	0.6367	15.597
0.1680	0.4517	0.0220	0.6849	16.387
0.1522	0.5033	0.0190	0.7272	17.184
1.0000	0.0000	1.0000	0.0000	2.035
0.2975	0.7025	0.0355	0.9645	17.902
0.2899	0.6847	0.0348	0.9466	17.786
0.2809	0.6634	0.0339	0.9251	17.639
0.2662	0.6287	0.0325	0.8896	17.390
0.2525	0.5963	0.0312	0.8558	17.166
0.2374	0.5607	0.0298	0.8179	16.907
0.2221	0.5246	0.0284	0.7785	16.645
0.2064	0.4877	0.0268	0.7368	16.364
0.1920	0.4535	0.0254	0.6970	16.107
0.1773	0.4190	0.0239	0.6554	15.837
0.1624	0.3839	0.0224	0.6118	15.565
0.1475	0.3486	0.0208	0.5662	15.290

$x_1$	$x_2$	$y_{1,calc}$	$y_{2,calc}$	P/kPa
0.0000	1.0000	0.0000	1.0000	24.621
0.6878	0.3122	0.1578	0.8422	9.095
0.6700	0.3041	0.1523	0.8118	9.122
0.6465	0.2935	0.1452	0.7725	9.241
0.6077	0.2758	0.1339	0.7100	9.456
0.5799	0.2633	0.1261	0.6671	9.599
0.5408	0.2455	0.1155	0.6087	9.809
0.5044	0.2290	0.1061	0.5567	9.998
0.4718	0.2143	0.0979	0.5119	10.161
0.4348	0.1975	0.0889	0.4628	10.467
0.4001	0.1817	0.0808	0.4187	10.508
0.3656	0.1661	0.0730	0.3764	10.672
0.3326	0.1511	0.0657	0.3373	10.831
0.0000	0.0000	0.0000	0.0000	12.326
0.0000	0.6836	0.0000	0.8078	20.986
0.0271	0.6651	0.0029	0.8055	20.449
0.0489	0.6501	0.0053	0.8036	20.041
0.1016	0.6141	0.0115	0.7986	19.017
0.1482	0.5823	0.0175	0.7937	18.128
0.1991	0.5475	0.0247	0.7878	17.152
0.2506	0.5123	0.0329	0.7812	16.166
0.2968	0.4808	0.0411	0.7744	15.281
0.3476	0.4460	0.0512	0.7660	14.310
0.3960	0.4129	0.0623	0.7570	13.392
0.4468	0.3782	0.0756	0.7460	12.429
0.4967	0.3441	0.0907	0.7335	11.483
0.0000	1.0000	0.0000	1.0000	24.615
0.0000	0.2808	0.0000	0.4420	16.040
0.0258	0.2736	0.0036	0.4394	15.652
0.0473	0.2675	0.0068	0.4373	15.341
0.0867	0.2565	0.0128	0.4333	14.763
0.1335	0.2434	0.0206	0.4283	14.089
0.1743	0.2319	0.0279	0.4237	13.506
0.2228	0.2183	0.0374	0.4180	12.812
0.2685	0.2055	0.0473	0.4123	12.164
0.3158	0.1922	0.0586	0.4061	11.493
0.3611	0.1795	0.0706	0.3996	10.863
0.4103	0.1657	0.0853	0.3920	10.180
0.4634	0.1507	0.1035	0.3829	9.444

**Table 4.** Total pressure, P, for the Ternary System Dibutyl Ether (1) + Cyclohexane (2) + 1-Hexene (3) at  $T=313.15$  K, and at Various Compositions of the Liquid,  $x_1$ ,  $x_2$ , and the Vapour Phases  $y_{1,calc}$ ,  $y_{2,calc}$ , Calculated Using Wohl Expansion.

$x_1$	$x_2$	$y_{1,calc}$	$y_{2,calc}$	P/kPa
0.0000	1.0000	0.0000	1.0000	24.613
0.3153	0.6847	0.0380	0.9620	17.552
0.3074	0.6677	0.0354	0.8998	18.293
0.2981	0.6474	0.0326	0.8330	19.170
0.2848	0.6186	0.0291	0.7492	20.469
0.2687	0.5836	0.0255	0.6612	21.983
0.2517	0.5467	0.0223	0.5815	23.545
0.2360	0.5126	0.0197	0.5168	24.963
0.2233	0.4852	0.0178	0.4699	26.101
0.2052	0.4458	0.0154	0.4094	27.712
0.1888	0.4102	0.0135	0.3601	29.142
0.1739	0.3780	0.0119	0.3195	30.428
0.1568	0.3407	0.0102	0.2763	31.901
0.0000	0.0000	0.0000	0.0000	44.949
0.3044	0.0000	0.0204	0.0000	31.725
0.2951	0.0306	0.0199	0.0255	31.585
0.2877	0.0550	0.0194	0.0460	31.480
0.2760	0.0934	0.0187	0.0784	31.291
0.2593	0.1481	0.0176	0.1249	31.016
0.2451	0.1948	0.0167	0.1650	30.791
0.2288	0.2483	0.0157	0.2115	30.503
0.2131	0.2997	0.0147	0.2566	30.223
0.2001	0.3425	0.0139	0.2945	29.986
0.1850	0.3919	0.0130	0.3388	29.695
0.1681	0.4475	0.0119	0.3894	29.354
0.1521	0.5000	0.0109	0.4381	29.006
0.0000	0.0000	0.0000	0.0000	44.951
0.0000	0.2893	0.0000	0.1927	39.776
0.0271	0.2815	0.0015	0.1922	38.715
0.0466	0.2758	0.0026	0.1917	37.963
0.1015	0.2600	0.0059	0.1905	35.827
0.1653	0.2415	0.0104	0.1891	33.361
0.2108	0.2283	0.0140	0.1880	31.593
0.2664	0.2122	0.0190	0.1867	29.434
0.3140	0.1984	0.0238	0.1854	27.602
0.3639	0.1840	0.0297	0.1840	25.680
0.4165	0.1687	0.0369	0.1823	23.659
0.4640	0.1550	0.0445	0.1806	21.834
0.5138	0.1406	0.0539	0.1786	19.936

$x_1$	$x_2$	$y_{1,calc}$	$y_{2,calc}$	P/kPa
1.0000	0.0000	1.0000	0.0000	2.055
0.6865	0.0000	0.0951	0.0000	15.144
0.6707	0.0231	0.0914	0.0377	15.402
0.6481	0.0560	0.0862	0.0894	15.785
0.6220	0.0941	0.0806	0.1463	16.183
0.5830	0.1509	0.0727	0.2259	16.805
0.5506	0.1980	0.0665	0.2876	17.310
0.5168	0.2472	0.0606	0.3482	17.838
0.4816	0.2985	0.0547	0.4076	18.373
0.4463	0.3499	0.0493	0.4638	18.905
0.4124	0.3992	0.0443	0.5148	19.412
0.3786	0.4484	0.0397	0.5630	19.903
0.3413	0.5028	0.0348	0.6137	20.438
1.0000	0.0000	1.0000	0.0000	2.050
0.7139	0.2861	0.1758	0.8242	8.512
0.6903	0.2766	0.1484	0.6989	9.716
0.6690	0.2681	0.1293	0.6108	10.794
0.6398	0.2564	0.1085	0.5150	12.308
0.6067	0.2431	0.0905	0.4316	14.020
0.5686	0.2279	0.0745	0.3573	15.945
0.5332	0.2137	0.0628	0.3026	17.776
0.4983	0.1997	0.0534	0.2584	19.566
0.4644	0.1862	0.0457	0.2224	21.294
0.4207	0.1687	0.0375	0.1836	23.541
0.3925	0.1574	0.0330	0.1620	24.926
0.3610	0.1448	0.0286	0.1407	26.600
0.0000	0.0000	0.0000	0.0000	44.955
0.0000	0.7058	0.0000	0.5606	31.628
0.0222	0.6901	0.0015	0.5603	31.011
0.0588	0.6642	0.0041	0.5597	29.807
0.0996	0.6354	0.0072	0.5589	28.576
0.1506	0.5994	0.0116	0.5575	27.046
0.2001	0.5644	0.0163	0.5557	25.519
0.2440	0.5335	0.0210	0.5538	24.164
0.3042	0.4910	0.0284	0.5506	22.373
0.3502	0.4585	0.0348	0.5476	20.991
0.3997	0.4236	0.0428	0.5437	19.469
0.4468	0.3903	0.0516	0.5392	18.107
0.4971	0.3548	0.0626	0.5335	16.599
1.0000	0.0000	1.0000	0.0000	2.055

**Table 5.** Summary of the Data Reduction Results for Binary Systems Dibutyl Ether (1) + Cyclohexane (2), Dibutyl Ether (1) + Heptane (3), Dibutyl Ether (1) + 1-Hexene (3), Cyclohexane (2) + Heptane (3) and Cyclohexane (2) + 1-Hexene (3) at  $T=313.15$  K.

Dibutyl Ether (1) + Cyclohexane (2) <sup>a</sup>	Margules	Wilson	NRTL	UNIQUAC
$A_{12}$	0.0223	0.5078	-0.6506	1.2931
$A_{21}$	-0.0104	1.6517	0.8126	0.7403
$\lambda_{12}=\lambda_{21}$	0.0218			
$\alpha_{12}$			0.3	
rms $\Delta P/kPa$	0.007	0.006	0.007	0.006
Max $ \Delta P /kPa$	0.014	0.014	0.010	0.014
Dibutyl Ether (1) + Heptane (3)	Margules	Wilson	NRTL	UNIQUAC
$A_{13}$	0.1129	0.7047	-0.3452	1.0770
$A_{31}$	0.0889	1.2426	0.4895	0.9100
$\lambda_{13}=\lambda_{31}$	0.0372			
$\alpha_{13}$			0.3	
rms $\Delta P/kPa$	0.007	0.008	0.008	0.008
Max $ \Delta P /kPa$	0.017	0.017	0.017	0.017
Dibutyl Ether (1) + 1-Hexene (3)	Margules	Wilson	NRTL	UNIQUAC
$A_{13}$	-0.0032	0.5056	-0.6537	1.2272
$A_{31}$	-0.0250	1.6829	0.7904	0.7878
$\lambda_{13}=\lambda_{31}$	0.0222			
$\alpha_{13}$		0.3		
rms $\Delta P/kPa$	0.008	0.007	0.008	0.007
Max $ \Delta P /kPa$	0.018	0.015	0.018	0.015
Cyclohexane (2) + Heptane (3) <sup>b</sup>	Margules	Wilson	NRTL	UNIQUAC
$A_{23}$	0.0480	1.3540	0.5794	0.8642
$A_{32}$	0.0745	0.6528	-0.4439	1.1304
$\lambda_{23}=\lambda_{32}$	0.0236			
$\alpha_{23}$			0.3	
rms $\Delta P/kPa$	0.009	0.009	0.009	0.009
Max $ \Delta P /kPa$	0.017	0.017	0.018	0.017
Cyclohexane (2) + 1-Hexene (3) <sup>b</sup>	Margules	Wilson	NRTL	UNIQUAC
$A_{23}$	0.1055	1.3048	0.6202	0.7273
$A_{32}$	0.1568	0.6316	-0.4135	1.2853
$\lambda_{23}=\lambda_{32}$	0.0315			
$\alpha_{23}$			0.3	
rms $\Delta P/kPa$	0.014	0.014	0.015	0.014
Max $ \Delta P /kPa$	0.032	0.033	0.033	0.033

a) Experimental data published in ref 6; b) Experimental data published in ref 7

**Table 6.** Summary of the Data Reduction Results Obtained for the Ternary System  
Dibutyl Ether (1) + Cyclohexane (2) + Heptane (3) at  $T=313.5$  K

<i>Correlation</i>	Wohl	Wilson	NRTL	UNIQUAC
$C_0$	-0.0715			
$C_1$	-0.0347			
$C_2$	-0.2282			
$A_{12}$		-0.7079	0.4728	1.3167
$A_{21}$		0.9223	1.6971	0.7203
$A_{13}$		0.1857	1.0646	0.8538
$A_{31}$		-0.1117	0.8783	1.1452
$A_{23}$		0.7042	1.4498	0.6961
$A_{32}$		-0.5202	0.5772	1.3519
$\alpha_{12}$				
$\alpha_{13}$				
$\alpha_{23}$				
rms $\Delta P$ /kPa	0.044	0.042	0.043	0.043
Max $ \Delta P $ /kPa	0.094	0.082	0.080	0.080
<i>Prediction</i>		Wilson	NRTL	UNIQUAC
rms $\Delta P$ /kPa		0.059	0.060	0.053
Max $ \Delta P $ /kPa		0.122	0.127	0.100
Max $ \Delta P $ /P <sub>exp</sub>		0.016	0.016	0.016

**Table 7.** Summary of the Data Reduction Results Obtained for the Ternary System  
Dibutyl Ether (1) + Cyclohexane (2) + 1-Hexene (3) at  $T=313.5$  K

<i>Correlation</i>	Wohl	Wilson	NRTL	UNIQUAC
$C_0$	-0.0090			
$C_1$	0.0860			
$C_2$	0.0410			
$A_{12}$		0.5257	-0.6734	1.3446
$A_{21}$		1.6018	0.8723	0.6998
$A_{13}$		1.0981	-0.6564	1.1583
$A_{31}$		0.9209	0.7954	0.8444
$A_{23}$		1.2814	0.6144	0.7178
$A_{32}$		0.6457	-0.4072	1.3016
$\alpha_{12}$			0.3	
$\alpha_{13}$			0.3	
$\alpha_{23}$			0.3	
rms $\Delta P$ /kPa	0.028	0.034	0.029	0.030
Max $ \Delta P $ /kPa	0.065	0.103	0.063	0.062
<i>Prediction</i>		Wilson	NRTL	UNIQUAC
rms $\Delta P$ /kPa		0.048	0.046	0.072
Max $ \Delta P $ /kPa		0.116	0.111	0.165
Max $ \Delta P /P_{\text{exp}}$		0.009	0.009	0.009



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