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Isobaric vapour–liquid equilibrium of binary and ternary mixtures containing cyclohexane, *n*-hexane, 1,3-dioxolane and 1-butanol at 40.0 and 101.3 kPa

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Abstract

Isobaric vapour–liquid equilibrium (VLE) data for the binary mixture cyclohexane + 1-butanol and for the ternary system cyclohexane + 1,3-dioxolane + 1-butanol have been obtained with a recirculating still at 40.0 and 101.3 kPa. We also have determined isobaric VLE data at 101.3 kPa for the systems *n*-hexane+1,3-dioxolane and *n*-hexane+1,3-dioxolane+1-butanol. The experimental data for all the systems were checked for thermodynamic consistency using the method of Van Ness. Activity coefficients have been correlated with different equations (Wilson, van Laar, Margules, NRTL and UNIQUAC) giving satisfactory results. Predictions with the group contribution methods ASOG and UNIFAC were obtained and compared with the experimental data.

Keywords: VLE isobaric data; Ternary mixture; Alkane; 1,3-Dioxolane; 1-Butanol; ASOG; UNIFAC

1. Introduction

The design of separation process in industry requires a great knowledge of the behaviour of different systems in the phase equilibrium. This information is also very useful in the development of the group contribution methods, which are used in many cases while experimental data are not available.

In previous articles we have reported vapour–liquid equilibrium (VLE) data for the other constituent binary mixtures: *n*-hexane+1-butanol at 101.3 kPa [1], 1,3-dioxolane+1-butanol [2] and cyclohexane + 1,3-dioxolane [3] at both 40 and 101.3 kPa.

To contribute to increase the information about these kind of systems we present here the isobaric vapour–liquid equilibrium of the binary mixture cyclohexane + 1-butanol and for the ternary system cyclohexane + 1,3-dioxolane + 1-butanol at 40.0 and 101.3 kPa along with the VLE data at 101.3 kPa for the binary system *n*-hexane + 1,3-dioxolane and for the ternary mixture *n*-hexane + 1,3-dioxolane + 1-butanol. The VLE predictions using the group contribution methods ASOG and UNIFAC have also been included.

A survey of the literature shows that there are numerous studies for the system cyclohexane+1-butanol at isothermic conditions but only a few ones at isobaric conditions [4–7]. For the rest of the systems we have not found references in the literature.

2. Experimental apparatus and procedure

The liquids used were cyclohexane (>99.9%), *n*-hexane (>99%), 1,3-dioxolane (>99%) and 1-butanol (>99.8%) obtained from Aldrich. The purity of chemicals was checked by comparing the experimental densities at 298.15 K and the normal boiling points with those reported in [8,9], as they are listed in Table 1. We have also employed chromatographic methods to confirm the absence of other significant components, so they were used without any additional purification.

VLE data have been obtained with an all-glass dynamic recirculating still Fischer–Labodest model equipped with a Cottrell pump, a thermometer provided from Automatic System Laboratories, model F25, and a pressure transducter Druck PDCR 110/W. The experimental uncertainties in temperature and pressure are ±0.01 K and ±0.1 kPa, respectively.

Experimental procedure has been previously described [10]: when the equilibrium was reached, samples of liquid and vapour-condensed phase were taken and their densities (binary mixtures) analysed at 298.15 K with an Anton

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Nomenclature

A_{ij}	adjustable parameter for VLE correlation equations
B_{ii}	second virial coefficient of component i ($m^3\,mol^{-1}$)
B_{ij}	cross second virial coefficient ($m^3\,mol^{-1}$)
F	objective function
N	number of experimental data
p_i^0	vapour pressure of component i (Pa)
P	total pressure (Pa)
Q	reduced excess Gibbs free energy
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
T_i	normal boiling point of component i (K)
V_i^0	molar volume of component i ($m^3\,mol^{-1}$)
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapour phase

Greek letters

α_{ij}	non-randomness parameter in the NRTL equation
Δ	average deviation
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient of component i at infinite dilution
ρ	density ($kg\,m^{-3}$)

Subscript

i	component i

Superscripts

cal	calculated quantity
exp	experimental quantity

Paar DMA-58 vibrating tube densimeter. While for the ternary mixtures densities and speeds of sound of liquid and vapour-condensed phase have been analysed at 298.15 K with a density and sound analyser Anton Paar DSA-48. Before this, we have determined the density calibration curves at 298.15 K for binary systems and the composition dependence of density and speed of sound at the same temperature for the ternary systems. Experimental uncertainty in liquid and vapour mole fractions can be estimated in ±0.001.

Table 1
Densities of pure compounds at 298.15 K, normal boiling points and comparison with literature data

Compound	ρ ($kg\,m^{-3}$)		T_i (K)	
	Experimental	Literature	Experimental	Literature[a]
Cyclohexane	773.72	773.89[a]	353.92	353.88
n-Hexane	655.07	654.84[a]	341.88	341.89
1,3-Dioxolane	1058.62	1058.66[b]	348.55	348.8
1-Butanol	805.64	805.75[a]	390.97	390.87

[a] [8].
[b] [9].

3. Results and discussion

Vapour–liquid equilibrium data for binary mixtures and ternary mixtures are presented in Tables 2 and 3

, respectively, along with calculated activity coefficients. These coefficients, γ_i, have been calculated taking into account the non-ideality of the vapour phase, by means of Eqs. (1) and (2).

Table 2
Experimental VLE data for the binary systems, cyclohexane (1)+1-butanol (2), at 40.0 and 101.3 kPa and *n*-hexane + 1,3-dioxolane at 101.3 kPa

T (K)	x_1	y_1	γ_1	γ_2
Cyclohexane + 1-butanol at $P = 40.0$ kPa				
361.52	0.023	0.228	3.182	0.989
355.62	0.051	0.419	3.121	0.994
349.04	0.094	0.587	2.887	1.004
342.71	0.138	0.712	2.906	1.003
338.85	0.195	0.771	2.524	1.040
335.44	0.246	0.822	2.389	1.032
333.96	0.294	0.830	2.122	1.140
331.94	0.359	0.864	1.939	1.121
330.10	0.417	0.883	1.818	1.174
328.42	0.533	0.901	1.540	1.362
327.62	0.593	0.912	1.442	1.454
326.63	0.733	0.920	1.219	2.133
326.11	0.840	0.936	1.103	2.934
325.95	0.868	0.939	1.077	3.421
325.81	0.938	0.952	1.015	5.779
Cyclohexane + 1-butanol at $P = 101.3$ kPa				
386.12	0.026	0.178	2.923	0.997
382.86	0.046	0.302	3.030	0.972
380.15	0.067	0.372	2.738	0.989
371.55	0.140	0.590	2.585	0.975
366.29	0.205	0.671	2.309	1.048
364.23	0.241	0.722	2.235	1.011
362.06	0.278	0.749	2.134	1.052
359.33	0.360	0.784	1.863	1.149
357.64	0.407	0.817	1.802	1.131
355.60	0.509	0.836	1.564	1.341
354.59	0.598	0.861	1.412	1.453
353.52	0.730	0.877	1.216	2.010
352.92	0.847	0.902	1.097	2.905
352.64	0.913	0.916	1.042	4.437
352.73	0.938	0.931	1.028	5.094
n-Hexane + 1,3-dioxolane at $P = 101.3$ kPa				
343.94	0.043	0.188	4.127	0.989
340.90	0.092	0.301	3.377	0.996
339.19	0.127	0.354	3.029	1.016
338.13	0.161	0.385	2.683	1.045
336.91	0.225	0.431	2.231	1.093
336.14	0.284	0.462	1.940	1.150
335.55	0.353	0.490	1.686	1.232
335.29	0.397	0.506	1.561	1.293
335.01	0.480	0.533	1.371	1.432
334.82	0.533	0.552	1.287	1.540
334.87	0.624	0.593	1.179	1.735
335.22	0.731	0.650	1.090	2.060
336.20	0.809	0.707	1.039	2.346
337.29	0.870	0.769	1.016	2.615
340.43	0.970	0.929	1.000	3.124

Table 3
Experimental VLE data of the ternary mixture cyclohexane (1) + 1,3-dioxolane (2) + 1-butanol (3) at 40.0 and 101.3 kPa and for the ternary mixture *n*-hexane (1) + 1,3-dioxolane (2) + 1-butanol (3) at 101.3 kPa

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
Cyclohexane + 1,3-dioxolane + 1-butanol at $P = 40.0$ kPa							
321.17	0.853	0.098	0.742	0.235	1.030	2.635	4.585
322.27	0.793	0.088	0.755	0.195	1.082	2.384	3.842
323.35	0.737	0.075	0.783	0.156	1.161	2.165	2.783
324.02	0.669	0.074	0.784	0.158	1.250	2.157	1.861
318.40	0.704	0.236	0.597	0.378	1.114	1.967	4.819
319.59	0.653	0.226	0.614	0.358	1.181	1.857	2.488
320.39	0.584	0.209	0.633	0.325	1.321	1.784	2.078
321.35	0.563	0.192	0.638	0.311	1.333	1.799	2.012
325.18	0.348	0.130	0.664	0.254	1.952	1.905	1.211
326.90	0.379	0.092	0.713	0.200	1.810	1.993	1.148
327.84	0.327	0.097	0.699	0.203	1.990	1.862	1.126
331.87	0.222	0.084	0.656	0.207	2.393	1.916	1.044
316.72	0.517	0.423	0.508	0.481	1.376	1.480	2.355
317.89	0.478	0.395	0.513	0.464	1.437	1.468	2.163
319.07	0.453	0.355	0.538	0.432	1.521	1.456	1.735
322.65	0.281	0.285	0.519	0.421	2.071	1.554	1.237
324.43	0.248	0.253	0.513	0.411	2.175	1.606	1.227
327.02	0.207	0.211	0.515	0.398	2.385	1.693	1.037
331.29	0.153	0.161	0.495	0.372	2.673	1.799	1.059
340.67	0.088	0.107	0.427	0.338	2.940	1.806	0.970
346.25	0.061	0.080	0.370	0.286	3.086	1.741	1.008
316.43	0.328	0.624	0.420	0.566	1.813	1.195	3.817
317.01	0.322	0.615	0.417	0.561	1.794	1.178	4.407
317.77	0.325	0.567	0.429	0.555	1.776	1.222	1.783
321.70	0.171	0.475	0.385	0.578	2.616	1.305	0.991
323.84	0.143	0.422	0.355	0.569	2.667	1.349	1.459
326.27	0.117	0.358	0.337	0.568	2.836	1.451	1.312
329.51	0.098	0.308	0.324	0.573	2.905	1.503	1.046
334.30	0.066	0.239	0.276	0.568	3.121	1.626	1.042
341.03	0.044	0.176	0.231	0.524	3.145	1.635	1.026
345.32	0.040	0.126	0.243	0.440	3.181	1.694	1.002
351.45	0.021	0.086	0.165	0.392	3.419	1.843	0.975
321.82	0.080	0.754	0.240	0.741	3.472	1.037	1.078
322.36	0.078	0.727	0.222	0.737	3.229	1.053	1.918
324.48	0.071	0.661	0.210	0.734	3.106	1.064	1.682
326.62	0.059	0.577	0.191	0.731	3.149	1.122	1.524
327.45	0.052	0.527	0.183	0.744	3.325	1.208	1.176
331.55	0.034	0.436	0.144	0.756	3.471	1.275	1.018
333.76	0.030	0.386	0.130	0.753	3.295	1.324	0.958
338.91	0.018	0.277	0.088	0.722	3.136	1.486	0.982
343.30	0.011	0.195	0.068	0.651	3.448	1.664	1.031
349.34	0.007	0.138	0.050	0.569	3.310	1.710	0.968
353.75	0.003	0.096	0.026	0.462	3.526	1.781	1.005
Cyclohexane + 1,3-dioxolane + 1-butanol at $P = 101.3$ kPa							
348.20	0.857	0.091	0.762	0.207	1.052	2.338	3.352
349.32	0.789	0.084	0.757	0.163	1.098	1.966	3.359
350.35	0.736	0.077	0.772	0.143	1.164	1.824	2.310
352.19	0.669	0.073	0.780	0.130	1.226	1.651	1.628
359.00	0.364	0.018	0.757	0.035	1.802	1.523	1.158
363.19	0.252	0.012	0.702	0.027	2.152	1.576	1.059
366.71	0.198	0.009	0.650	0.022	2.309	1.560	1.027
376.32	0.092	0.004	0.452	0.012	2.706	1.495	1.006
346.40	0.637	0.222	0.619	0.332	1.214	1.638	2.131
347.86	0.568	0.205	0.624	0.305	1.313	1.566	1.788
348.82	0.530	0.184	0.645	0.274	1.413	1.526	1.547
353.70	0.357	0.128	0.640	0.219	1.804	1.530	1.193
354.16	0.351	0.128	0.640	0.220	1.811	1.513	1.147
355.81	0.338	0.102	0.652	0.185	1.828	1.530	1.153
359.60	0.247	0.091	0.613	0.179	2.115	1.491	1.054
375.35	0.074	0.045	0.365	0.135	2.783	1.499	1.000

Table 3 (*Continued*)

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
342.76	0.527	0.430	0.495	0.491	1.313	1.393	2.386
344.71	0.476	0.395	0.506	0.458	1.399	1.334	1.858
346.15	0.448	0.350	0.521	0.424	1.464	1.337	1.690
350.84	0.286	0.288	0.490	0.410	1.875	1.363	1.167
353.38	0.257	0.251	0.490	0.379	1.937	1.344	1.178
354.75	0.230	0.222	0.495	0.358	2.102	1.382	1.115
361.60	0.153	0.158	0.456	0.322	2.404	1.436	0.992
375.41	0.051	0.072	0.263	0.230	2.905	1.570	1.016
343.22	0.317	0.634	0.387	0.584	1.683	1.109	4.243
344.16	0.324	0.587	0.405	0.569	1.674	1.130	2.000
349.91	0.181	0.473	0.357	0.564	2.219	1.162	1.187
351.61	0.159	0.428	0.346	0.560	2.329	1.210	1.093
354.49	0.122	0.357	0.320	0.550	2.583	1.308	1.051
358.55	0.097	0.296	0.295	0.525	2.670	1.338	1.042
369.10	0.047	0.178	0.206	0.452	2.898	1.430	0.995
371.82	0.042	0.132	0.198	0.380	2.907	1.523	1.033
378.95	0.019	0.080	0.117	0.277	3.181	1.536	1.033
346.91	0.086	0.815	0.193	0.782	2.766	1.016	1.515
347.87	0.088	0.727	0.205	0.747	2.788	1.058	1.487
352.94	0.059	0.571	0.169	0.742	2.952	1.140	1.088
356.12	0.048	0.516	0.145	0.735	2.842	1.134	1.078
358.55	0.037	0.444	0.129	0.719	3.063	1.200	1.030
361.30	0.026	0.369	0.096	0.701	3.006	1.300	1.048
364.49	0.023	0.302	0.092	0.650	2.987	1.350	1.043
370.50	0.014	0.205	0.065	0.553	2.962	1.443	1.043
375.69	0.010	0.159	0.043	0.485	2.407	1.425	0.988
381.45	0.003	0.093	0.021	0.341	3.406	1.500	0.988
n-Hexane + 1,3-dioxolane + 1-butanol at $P = 101.3$ kPa							
339.10	0.870	0.087	0.817	0.151	1.021	2.447	6.537
340.25	0.775	0.076	0.826	0.125	1.119	2.252	2.725
341.10	0.691	0.064	0.844	0.097	1.250	2.029	1.912
342.02	0.617	0.056	0.845	0.086	1.364	2.004	1.600
344.37	0.459	0.040	0.843	0.060	1.706	1.836	1.308
346.38	0.371	0.033	0.832	0.052	1.966	1.819	1.193
350.33	0.278	0.025	0.809	0.046	2.280	1.884	1.058
354.53	0.203	0.019	0.765	0.033	2.630	1.587	1.089
368.00	0.094	0.011	0.587	0.029	3.076	1.656	1.011
337.33	0.682	0.221	0.686	0.274	1.155	1.863	3.969
339.32	0.591	0.193	0.716	0.238	1.309	1.734	1.851
341.23	0.491	0.161	0.736	0.201	1.529	1.659	1.428
343.47	0.384	0.129	0.747	0.171	1.856	1.647	1.189
346.65	0.284	0.100	0.731	0.146	2.239	1.662	1.208
350.72	0.229	0.083	0.718	0.138	2.430	1.665	1.045
357.16	0.154	0.058	0.655	0.114	2.765	1.648	1.094
362.53	0.111	0.043	0.606	0.106	3.085	1.772	1.007
370.01	0.070	0.030	0.490	0.084	3.283	1.653	1.028
336.19	0.478	0.426	0.577	0.406	1.437	1.469	1.810
338.30	0.424	0.383	0.597	0.371	1.570	1.395	1.519
340.36	0.350	0.331	0.597	0.342	1.786	1.404	1.577
342.62	0.286	0.280	0.609	0.314	2.084	1.419	1.307
345.35	0.233	0.237	0.608	0.300	2.357	1.468	1.119
348.27	0.193	0.202	0.592	0.288	2.548	1.515	1.112
354.18	0.141	0.156	0.564	0.265	2.819	1.513	1.037
360.39	0.099	0.119	0.523	0.243	3.155	1.520	0.970
364.82	0.077	0.096	0.456	0.224	3.158	1.547	1.039
371.45	0.048	0.065	0.367	0.183	3.463	1.569	1.041
379.76	0.022	0.038	0.218	0.135	3.697	1.595	1.025
337.14	0.293	0.635	0.485	0.505	1.914	1.179	1.352
339.01	0.260	0.581	0.488	0.483	2.049	1.162	1.613
341.26	0.217	0.516	0.489	0.473	2.298	1.189	1.123
343.58	0.183	0.454	0.477	0.462	2.481	1.228	1.182
345.87	0.154	0.401	0.460	0.454	2.659	1.275	1.216
351.64	0.099	0.315	0.409	0.459	3.123	1.370	1.079

Table 3 (*Continued*)

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
358.94	0.072	0.225	0.376	0.421	3.241	1.419	0.997
365.88	0.045	0.159	0.302	0.384	3.486	1.513	1.014
372.45	0.032	0.116	0.246	0.344	3.401	1.554	0.949
378.92	0.015	0.069	0.150	0.243	3.804	1.579	1.019
343.53	0.079	0.803	0.277	0.693	3.347	1.027	1.796
344.96	0.074	0.758	0.273	0.693	3.377	1.037	1.333
356.48	0.033	0.442	0.176	0.679	3.537	1.218	1.064
360.22	0.024	0.364	0.145	0.665	3.630	1.297	1.015
364.59	0.017	0.286	0.116	0.628	3.664	1.378	0.998
369.30	0.011	0.221	0.085	0.562	3.691	1.407	1.029
374.47	0.007	0.154	0.061	0.470	3.676	1.481	1.019
379.47	0.005	0.102	0.048	0.353	3.607	1.493	1.011

- Binary systems:

$$\gamma_i = \frac{y_i P}{x_i p_i^0} \exp\left[\frac{(B_{ii} - V_i^0)(P - p_i^0) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \quad (1)$$

- Ternary systems:

$$\gamma_i = \frac{y_i P}{x_i p_i^0} \exp\left[\frac{(B_{ii} - V_i^0)(P - p_i^0)}{RT} + \frac{P}{2RT}\sum_1^3\sum_1^3 y_j y_k (2\delta_{ji} - \delta_{jk})\right] \quad (2)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (3)$$

In the above equations, x_i and y_i are the liquid and vapour phase mole fractions of component i in the mixture, P the total pressure, p_i^0 the pure component vapour pressure, B_{ii} the second virial coefficient of the pure gas, B_{ij} the cross second virial coefficient, and V_i^0 is the molar volume of the pure liquid component.

The Antoine equation has been used for calculating p_i^0. The constants used are presented in Table 4. The second virial coefficient, B_{ii}, has been estimated using the Redlich–Kwong equation [12] for the 1,3-dioxolane, while for the rest of the components the equations of the TRC tables [13] were used. The cross second virial coefficient, B_{ij}, has been calculated by means of the Amdur–Mason equation [14]. The molar volume, V_i^0, was estimated with the Yen and Woods method [15].

Table 4
Coefficients of the Antoine equation

Compound	A	B	C
Cyclohexane[a]	5.93002	1182.77	220.618
n-Hexane[a]	6.00091	1171.170	224.408
1,3-Dioxolane[b]	6.23172	1236.70	217.235
1-Butanol[a]	6.54743	1338.769	177.042

[a] [8].
[b] [11].

The thermodynamic consistency of the experimental binary data has been checked by means of the test of Van Ness modified by Fredenslund et al. [16] and extended to multicomponent mixtures employing the equation proposed by Prausnitz et al. [17]:

$$\ln \gamma_i = Q + \left(\frac{\partial Q}{\partial x_i}\right)_{T,P,x_j \neq i} - \sum_{j=1}^{k-1} x_j \left(\frac{\partial Q}{\partial x_j}\right)_{T,P,x_i \neq j} \quad (4)$$

where k is the number of components in the mixture and Q is the reduced excess Gibbs free energy, $Q = G^E/RT$. We have used a Cibulka equation in order to determine the relationship between Q and the liquid phase composition:

$$Q = \sum_{i=1}^{k}\sum_{j=i+1}^{k} x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p + x_1 x_2 (1 - x_1 - x_2)(B_1 + B_2 x_1 + B_3 x_2) \quad (5)$$

According to this consistency test, the experimental data are considered thermodynamically consistent if the average deviation for the vapour phase composition (Δy) is less than 0.01. Applied to our mixtures we obtain satisfactory results, as it can be seen in Table 5.

Table 5
Results of the thermodynamic consistency test

	P (kPa)	ΔP[a] (kPa)	Δy[a]
Binary systems			
Cyclohexane + 1-butanol	40.0	0.3	0.0047
	101.3	0.9	0.0053
n-Hexane + 1,3-dioxolane	101.3	0.5	0.0015
Ternary systems			
Cyclohexane + 1,3-dioxolane + 1-butanol	40.0	0.6	0.006
	101.3	1.3	0.004
n-Hexane + 1,3-dioxolane + 1-butanol	101.3	1.9	0.006

[a] Average deviations.

Table 6
Coefficients and standard deviation (σ) in the correlation of boiling points by the Tamir–Wisniak equations

	P (kPa)	C_0	C_1	C_2	C_3	σ	A	B	C
Binary systems									
Cyclohexane + 1,3-dioxolane[a]	40.0	−35.99	−2.56	−35.85	−2.91	0.35			
	101.3	−38.53	−3.45	−34.26	−6.82	0.22			
Cyclohexane + 1-butanol	40.0	−69.14	50.82	−54.10	39.21	0.33			
	101.3	−65.56	41.96	−37.82	4.47	0.22			
1,3-Dioxolane + 1-butanol[b]	40.0	−50.71	40.46	−19.75	12.95	0.29			
	101.3	−39.48	27.83	−8.19	−1.96	0.16			
n-Hexane + 1,3-dioxolane	101.3	−40.67	6.31	−37.88	23.52	0.18			
n-Hexane + 1-butanol[c]	101.3	−83.05	66.46	−80.64	57.12	0.30			
Ternary systems									
Cyclohexane + 1,3-dioxolane + 1-butanol		40.0				0.64	−1.16	81.39	20.92
		101.3				0.53	10.69	84.58	22.09
n-Hexane + 1,3-dioxolane + 1-butanol		101.3				0.49	−48.25	124.22	43.86

[a] [3].
[b] [2].
[c] [1].

The boiling temperatures of binary and ternary systems were correlated by the following equations proposed by Tamir and Wisniak [18]:

$$T = \sum_{i=1}^{2} x_i T_i + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \quad (6)$$

$$T = \sum_{i=1}^{3} x_i T_i + \sum_{i,j=1}^{3} \left[x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \right] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3)] \quad (7)$$

where T_i is the boiling temperature of pure component i (K), m the number of binary parameters, C_k the binary coefficient, and A, B and C are the ternary parameters. All these parameters obtained by the least squares method, along with the standard deviations between experimental and calculated boiling temperatures are presented in Table 6. We have included in this table the parameters of the constituent binary mixtures which have already been published [1–3].

The activity coefficients of the binary mixtures, γ_i, were correlated with the Margules, van Laar, Wilson, NRTL and UNIQUAC equations [19–23], while for the ternary mixtures were fitted to the Wilson, NRTL and UNIQUAC equations.

Table 7
Correlation parameters, average deviations ΔT and Δy, and activity coefficients at infinite dilution, γ_i^∞, for the binary systems cyclohexane + 1-butanol and *n*-hexane + 1,3-dioxolane

Equation	A_{12}	A_{21}	ΔT (K)	Δy	γ_1^∞	γ_2^∞
Cyclohexane + 1-butanol at $P = 40.0$ kPa						
Margules	1.1460[a]	1.9014[a]	0.42	0.0073	3.15	6.69
van Laar	1.1768[a]	2.0921[a]	0.33	0.0061	3.24	8.10
Wilson	564.1032[b]	6329.9522[b]	0.25	0.0051	3.33	11.97
NRTL	5264.9959[b]	385.1990[b]	0.35	0.0072	3.17	8.00
UNIQUAC	2728.7085[b]	−771.5987[b]	0.34	0.0068	3.20	8.40
Cyclohexane + 1-butanol at $P = 101.3$ kPa						
Margules	1.0578	1.8520	0.50	0.0078	2.88	6.37
van Laar	1.1002	2.0283	0.22	0.0059	3.00	7.60
Wilson	394.2109	6498.4314	0.23	0.0059	3.09	9.98
NRTL	5752.4913	146.5947	0.22	0.0066	2.96	7.42
UNIQUAC	3007.7152	−928.3162	0.21	0.0062	3.00	7.75
n-Hexane + 1,3-dioxolane at $P = 101.3$ kPa						
Margules	1.5447	1.1663	0.15	0.0035	4.69	3.21
van Laar	1.5718	1.1827	0.15	0.0022	4.82	3.26
Wilson	1788.9594	3216.3424	0.14	0.0024	5.10	3.38
NRTL	838.9685	3721.2216	0.16	0.0023	4.71	3.25
UNIQUAC	1781.1570	−8.5440	0.16	0.0024	4.74	3.23

[a] These values are dimensionless.
[b] These values are in J/mol.

As recommended by Renon and Prausnitz [22] the mixture non-randomness parameter α_{ij} in the NRTL equation was taken equal to 0.3 for all the systems. The estimation of the corresponding parameters is based on the minimisation of the following objective function:

$$F = \sum_{i=1}^{m} \left[\sum_{j=1}^{n} \left(\frac{\gamma_j^{\exp} - \gamma_j^{\mathrm{cal}}}{\gamma_j^{\exp}} \right)^2 \right]_i \quad (8)$$

where m is the number of experimental data and n is the number of components in the mixture.

The minimisation of F has been done with a non-linear regression procedure [24]. Parameters resulting of the fitting A_{ij} (see definitions in [25]) along with the average deviations in temperature (ΔT) and composition of vapour phase (Δy) and activity coefficients at infinite dilution for binary mixtures are gathered in Table 7 and the ternary parameters are presented in Table 8. In these tables we can observe that the more important differences in correlation results between the different equations appear in activity coefficients at infinite dilution of the 1-butanol in the binary system cyclohexane + 1-butanol at both pressures. While fitting results for the other binary mixture and the three ternary systems are much more similar with all the equations.

Table 8
Correlation parameters and average deviations, ΔT and Δy, for the ternary systems cyclohexane + 1,3-dioxolane + 1-butanol and *n*-hexane + 1,3-dioxolane + 1-butanol

Equation	*ij*	A_{ij}	A_{ji}	ΔT (K)	Δy
Cyclohexane + 1,3-dioxolane + 1-butanol at 40.0 kPa					
Wilson	12	1437.9124	3659.7583	0.56	0.010
	13	238.7424	10674.0967		
	23	1857.0105	482.5190		
NRTL	12	1591.3994	2678.0547	0.45	0.007
	13	5368.0879	617.5519		
	23	1422.4998	992.8501		
UNIQUAC	12	1254.7439	505.7956	0.51	0.008
	13	2657.6680	−686.9653		
	23	1262.0513	−162.6295		
Cyclohexane + 1,3-dioxolane + 1-butanol at 101.3 kPa					
Wilson	12	1221.3320	2728.2788	0.45	0.006
	13	648.2503	5101.4277		
	23	159.5993	2397.0752		
NRTL	12	1435.8020	2392.8743	0.48	0.006
	13	4572.7666	713.0212		
	23	927.8273	831.5840		
UNIQUAC	12	1613.5835	21.3056	0.39	0.005
	13	2313.2500	−589.6110		
	23	1071.8336	−202.5556		
n-Hexane + 1,3-dioxolane + 1-butanol at 101.3 kPa					
Wilson	12	1174.3831	4109.3467	0.46	0.007
	13	153.5058	8444.2559		
	23	1595.5479	216.0244		
NRTL	12	1289.7380	3410.1040	0.32	0.006
	13	5378.6455	863.4644		
	23	1205.6902	677.5863		
UNIQUAC	12	1700.5527	228.5577	0.46	0.006
	13	3198.7336	−929.110		
	23	201.3244	612.3384		

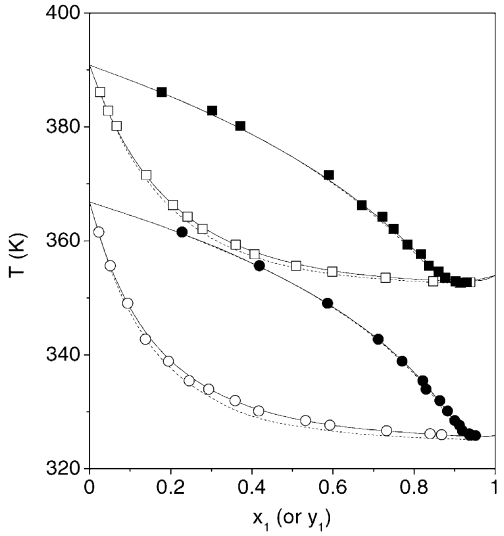

Fig. 1. T–x_1–y_1 for the binary mixture cyclohexane (1) + 1-butanol (2): experimental at 40.0 kPa (○, ●) and 101.3 kPa (□, ■); Wilson equation (continuous lines); UNIFAC predictions (dashed lines).

We have chosen the Wilson equation to plot the vapour–liquid equilibrium data (T, x_1, y_1) of the binary mixtures in Figs. 1 and 2, where it can be observed that the two systems show azeotropic behaviour. The calculated compositions of the azeotropic points are as follows:

- cyclohexane + 1-butanol at 40.0 kPa ($x_{1\mathrm{az}} = 0.965$ at $T_{\mathrm{az}} = 325.6$ K);
- cyclohexane + 1-butanol at 101.3 kPa ($x_{1\mathrm{az}} = 0.919$ at $T_{\mathrm{az}} = 352.9$ K) which is near the same experimental

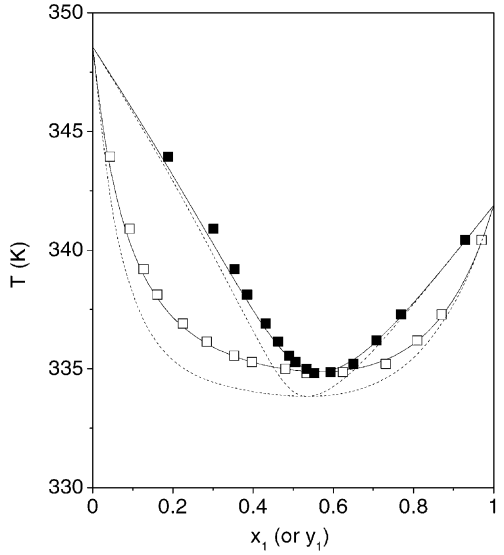

Fig. 2. T–x_1–y_1 for the binary mixture *n*-hexane (1) + 1,3-dioxolane (2): experimental at 101.3 kPa (□, ■); Wilson equation (continuous lines); UNIFAC predictions (dashed lines).

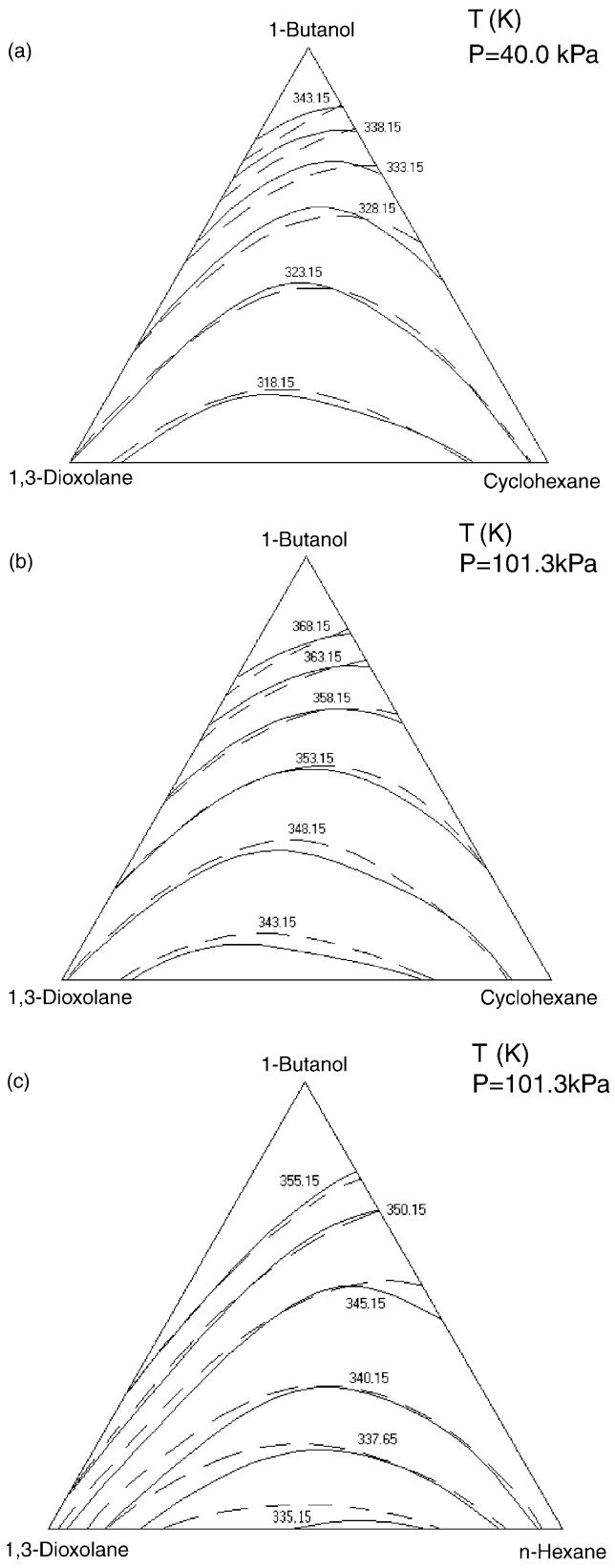

Fig. 3. Isotherms in liquid phase of the isobaric VLE: correlated with Tamir–Wisniak equation (continuous lines) and predicted with UNIFAC model (dashed lines): (a) cyclohexane + 1,3-dioxolane + 1-butanol at 40.0 kPa; (b) cyclohexane + 1,3-dioxolane + 1-butanol at 101.3 kPa; (c) *n*-hexane + 1,3-dioxolane + 1-butanol at 101.3 kPa.

Table 9
VLE predictions with the group contribution methods ASOG and UNIFAC, average deviations ΔT and Δy

	ASOG			UNIFAC	
	P (kPa)	ΔT^a (K)	Δy^a	ΔT^a (K)	Δy^a
Binary systems					
Cyclohexane + 1-butanol	40.0	0.41	0.0063	0.72	0.0066
	101.3	0.72	0.0137	0.45	0.0063
n-Hexane + 1,3-dioxolane	101.3	9.20	0.1270	1.26	0.0182
Ternary systems					
Cyclohexane + 1,3-dioxolane + 1-butanol	40.0	6.96	0.0746	0.88	0.0186
	101.3	5.91	0.0499	0.75	0.0118
n-Hexane + 1,3-dioxolane + 1-butanol	101.3	10.14	0.0441	0.80	0.0119

[a] Average deviations.

azeotropic point ($x_{1az} = 0.917$ at $T_{az} = 352.7$ K) determined by Chen et al. [7];

- *n*-hexane + 1,3-dioxolane at 101.3 kPa ($x_{1az} = 0.568$ at $T_{az} = 352.9$ K).

The isotherms for the ternary systems calculated with the Tamir–Wisniak equation are represented in Fig. 3. To search the azeotropic temperature and composition of the ternary systems we have used the Wang et al. method [26] as it is described in, giving that our ternary systems does not exhibit azeotropic behaviour.

The binary and ternary mixtures analysed show positive deviations from ideality with activity coefficients bigger than the unit for all the systems. The behaviour of the mixtures has been analysed in terms of the existing molecular interactions in previous papers [1–3], being confirmed now our precedent conclusions by the experimental results reported here.

4. Predictions

Modified UNIFAC and ASOG methods, with parameters proposed by Gmehling et al. [27,28] and Tochigi et al. [29], respectively, have been employed to predict the VLE data of the binary and ternary systems studied. The average deviations between experimental and calculated temperature (ΔT) and composition of vapour phase (Δy) appear in Table 9. In general, we can observe that UNIFAC predictions are satisfactory for all the systems. UNIFAC predictions are especially better than ASOG for the ternary mixtures analysed. We have plotted the UNIFAC predictions for each system in Figs. 1–3 along with the experimental results.

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