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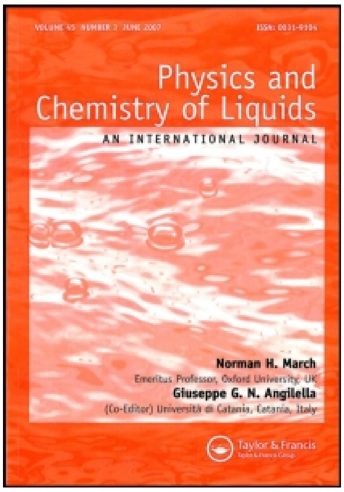

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Isobaric Vapour-Liquid Equilibrium of Ternary Mixtures Cyclohexane (or n -Hexane) Plus 1,3-Dioxolane Plus 2-Butanol at 40.0 and 101.3 kPa

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ISOBARIC VAPOUR–LIQUID EQUILIBRIUM OF TERNARY MIXTURES CYCLOHEXANE (OR *n*-HEXANE) PLUS 1,3-DIOXOLANE PLUS 2-BUTANOL AT 40.0 AND 101.3 kPa

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Isobaric vapour–liquid equilibrium (VLE) data for the mixtures cyclohexane + 2-butanol and cyclohexane + 1,3-dioxolane + 2-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 system *n*-hexane + 1,3-dioxolane + 2-butanol. The experimental data for all the binary and ternary mixtures 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 experimental data.

Keywords: VLE; Ternary mixture; Alkane; 1,3-dioxolane; 2-butanol

INTRODUCTION

The design of separation processes in industry requires a great knowledge of the behaviour of different systems in the phases 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.

Our research group has been studying during the last years thermodynamic and transport properties of different binary and ternary mixtures [1–5], being specially interested in interactions between different functional groups.

Recently we have been working with ternary mixtures [1,2] containing an alkane (cyclohexane or *n*-hexane) plus 1,3-dioxolane plus an isomer of butanol (1-butanol or 2-butanol). To contribute to increase the information about these systems we present here the isobaric vapour–liquid equilibrium (VLE) at 101.3 and 40.0 kPa for the binary mixture cyclohexane + 2-butanol and for the ternary system cyclohexane + 1,3-dioxolane + 2-butanol at 40.0 and 101.3 kPa. We also have obtained the VLE

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data at 101.3 kPa for the ternary mixture *n*-hexane + 1,3-dioxolane + 2-butanol. The VLE predictions using the group contribution methods ASOG and UNIFAC have also been included.

In previous articles we have reported VLE data for the other constituent binary mixtures: *n*-hexane + 2-butanol [3] and *n*-hexane + 1,3-dioxolane at 101.3 kPa [2b], and 1,3-dioxolane + 2-butanol [4] and cyclohexane + 1,3-dioxolane [5] at both work pressures (40.0 and 101.3 kPa).

EXPERIMENTAL

The liquids used were cyclohexane (better than 99.9 mol%), *n*-hexane, 1,3-dioxolane and 2-butanol (better than 99 mol%) 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 the literature [6,7], as they are listed in Table I. 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 [8]: 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 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.

RESULTS

VLE data for all the systems are presented in Tables II (binary mixture) and III (ternary mixtures) along with calculated activity coefficients. These coefficients, γ_i, have been

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

Compound	ρ/kg m^{-3}		T_b/K	
	This paper	*Lit.*	*This paper*	*Lit. [6]*
Cyclohexane	773.72	773.89 [6]	353.92	353.88
n-Hexane	655.07	654.84 [6]	341.88	341.89
1,3-Dioxolane	1058.62	1058.66 [7]	348.55	348.8
2-Butanol	802.20	802.41 [6]	372.78	372.66

TABLE II Experimental VLE data for the binary system, cyclohexane + 2-butanol, at 40.0 and 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
$P = 40.0$ kPa				
347.55	0.015	0.107	3.462	0.999
342.30	0.062	0.317	2.924	1.018
338.05	0.109	0.470	2.830	1.016
336.00	0.147	0.533	2.547	1.033
332.40	0.207	0.629	2.411	1.055
331.12	0.249	0.656	2.185	1.103
329.16	0.316	0.705	1.981	1.149
327.17	0.440	0.750	1.624	1.320
326.18	0.510	0.772	1.495	1.450
325.79	0.558	0.780	1.400	1.584
325.20	0.635	0.803	1.294	1.774
324.77	0.718	0.817	1.182	2.183
324.40	0.806	0.841	1.099	2.813
324.38	0.866	0.852	1.037	3.796
325.09	0.948	0.934	1.012	4.203
$P = 101.3$ kPa				
370.73	0.015	0.076	3.190	1.005
366.13	0.059	0.233	2.808	1.035
363.73	0.106	0.357	2.554	1.000
360.60	0.152	0.446	2.427	1.026
358.41	0.197	0.516	2.304	1.033
356.59	0.246	0.559	2.106	1.078
355.04	0.314	0.615	1.898	1.103
353.86	0.428	0.660	1.546	1.227
352.95	0.516	0.692	1.381	1.365
352.57	0.560	0.708	1.317	1.446
351.95	0.635	0.733	1.225	1.637
351.63	0.716	0.755	1.129	1.957
351.42	0.811	0.797	1.059	2.460
351.67	0.864	0.830	1.027	2.834
352.43	0.948	0.928	1.023	3.046

calculated taking into account the non-ideality of the vapour phase, by means of the equations:

- Binary system

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

- Ternary systems

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

being:

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{3}$$

where x_i and y_i are the liquid and vapour phase mole fractions of component i in the mixture, P is the total pressure, p_i^0 is the pure component vapour pressure, B_{ii} is

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

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
Cyclohexane + 1,3-dioxolane + 2-butanol at $P = 40.0$ kPa							
322.11	0.771	0.072	0.740	0.156	1.098	2.500	2.567
323.05	0.673	0.060	0.744	0.123	1.221	2.351	1.832
324.07	0.581	0.051	0.732	0.101	1.342	2.258	1.579
325.45	0.462	0.049	0.720	0.083	1.579	1.882	1.301
327.78	0.349	0.040	0.688	0.061	1.839	1.620	1.173
329.71	0.273	0.034	0.645	0.061	2.061	1.821	1.095
332.62	0.189	0.023	0.586	0.045	2.448	1.872	1.043
336.22	0.128	0.016	0.511	0.032	2.795	1.755	0.995
339.34	0.089	0.010	0.414	0.024	2.942	1.979	1.001
318.07	0.685	0.220	0.586	0.356	1.138	2.079	2.973
319.11	0.639	0.206	0.611	0.317	1.222	1.922	2.131
320.91	0.559	0.173	0.625	0.274	1.337	1.889	1.562
322.65	0.467	0.137	0.633	0.219	1.520	1.862	1.406
324.54	0.417	0.118	0.638	0.196	1.602	1.821	1.211
326.56	0.304	0.088	0.614	0.144	1.967	1.779	1.212
316.38	0.520	0.423	0.493	0.485	1.345	1.527	2.074
317.56	0.479	0.383	0.493	0.450	1.396	1.530	2.072
319.13	0.416	0.326	0.520	0.396	1.597	1.518	1.492
321.12	0.358	0.273	0.521	0.355	1.726	1.549	1.377
324.88	0.236	0.205	0.511	0.305	2.239	1.596	1.097
328.26	0.166	0.158	0.468	0.268	2.586	1.686	1.088
331.59	0.131	0.130	0.434	0.239	2.709	1.670	1.038
335.79	0.083	0.098	0.358	0.213	3.062	1.776	0.997
338.37	0.058	0.074	0.289	0.172	3.251	1.843	1.044
316.11	0.305	0.663	0.398	0.578	1.871	1.172	4.098
317.25	0.286	0.618	0.404	0.556	1.939	1.165	2.130
318.45	0.264	0.559	0.401	0.536	1.992	1.199	1.698
320.07	0.230	0.494	0.394	0.509	2.113	1.232	1.529
322.09	0.169	0.413	0.379	0.501	2.567	1.353	1.116
326.25	0.116	0.338	0.333	0.475	2.827	1.381	1.090
329.53	0.085	0.269	0.300	0.447	3.098	1.483	1.022
333.12	0.059	0.216	0.251	0.413	3.302	1.549	1.007
335.23	0.046	0.179	0.216	0.373	3.396	1.626	1.038
339.46	0.031	0.136	0.172	0.312	3.494	1.614	0.989
318.27	0.126	0.859	0.284	0.707	2.977	1.001	2.897
318.76	0.132	0.792	0.295	0.675	2.898	1.026	1.852
319.28	0.139	0.719	0.306	0.644	2.799	1.066	1.604
320.76	0.125	0.648	0.293	0.628	2.819	1.101	1.458
321.84	0.117	0.565	0.293	0.609	2.894	1.184	1.215
325.01	0.093	0.470	0.260	0.576	2.879	1.224	1.244
329.16	0.049	0.386	0.183	0.590	3.321	1.321	1.070
331.85	0.040	0.310	0.170	0.550	3.445	1.419	0.999
Cyclohexane + 1,3-dioxolane + 2-butanol at $P = 101.3$ kPa							
347.92	0.868	0.093	0.740	0.211	1.017	2.383	3.329
348.32	0.793	0.083	0.717	0.164	1.066	2.131	2.498
349.12	0.713	0.074	0.693	0.137	1.118	2.002	2.006
350.08	0.617	0.063	0.673	0.107	1.220	1.831	1.658
350.47	0.518	0.055	0.650	0.088	1.387	1.745	1.455
352.52	0.461	0.059	0.630	0.091	1.423	1.578	1.264
356.81	0.241	0.018	0.536	0.030	2.049	1.598	1.068
358.67	0.164	0.012	0.450	0.021	2.400	1.639	1.086
361.95	0.117	0.008	0.385	0.015	2.630	1.608	1.020
343.81	0.696	0.228	0.587	0.359	1.141	1.893	2.259
345.13	0.635	0.208	0.584	0.310	1.194	1.760	2.023
347.39	0.563	0.183	0.585	0.263	1.259	1.611	1.622
349.01	0.484	0.154	0.578	0.225	1.379	1.589	1.375
350.87	0.377	0.122	0.565	0.177	1.638	1.533	1.201

(Continued)

TABLE III Continued

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
353.76	0.239	0.082	0.502	0.130	2.110	1.606	1.120
356.23	0.186	0.064	0.460	0.104	2.316	1.562	1.085
358.92	0.138	0.049	0.401	0.087	2.523	1.606	1.055
363.50	0.077	0.030	0.290	0.060	2.886	1.627	1.020
342.02	0.497	0.421	0.476	0.475	1.370	1.433	2.063
343.78	0.450	0.383	0.475	0.433	1.429	1.377	1.755
346.54	0.386	0.323	0.480	0.385	1.547	1.349	1.306
347.71	0.347	0.276	0.477	0.336	1.650	1.359	1.326
351.85	0.219	0.208	0.436	0.285	2.114	1.386	1.090
353.84	0.170	0.165	0.403	0.240	2.376	1.427	1.106
358.54	0.098	0.128	0.310	0.220	2.776	1.497	1.034
360.50	0.054	0.082	0.220	0.158	3.387	1.671	1.134
363.88	0.042	0.064	0.176	0.128	3.178	1.589	1.076
342.31	0.302	0.644	0.379	0.595	1.780	1.148	1.642
343.98	0.279	0.579	0.380	0.555	1.833	1.140	1.447
346.66	0.253	0.486	0.380	0.502	1.862	1.144	1.268
349.16	0.195	0.402	0.356	0.461	2.099	1.197	1.142
351.90	0.146	0.327	0.330	0.420	2.397	1.254	1.061
356.86	0.076	0.252	0.230	0.388	2.784	1.329	1.036
362.05	0.034	0.197	0.129	0.355	3.023	1.361	0.996
344.15	0.145	0.821	0.261	0.721	2.413	1.020	1.664
345.34	0.130	0.715	0.250	0.676	2.484	1.069	1.422
348.84	0.118	0.609	0.245	0.630	2.412	1.055	1.169
351.33	0.091	0.504	0.220	0.590	2.608	1.120	1.076
353.17	0.085	0.409	0.221	0.530	2.658	1.192	1.044
356.74	0.057	0.320	0.176	0.475	2.850	1.253	1.026
361.06	0.015	0.242	0.060	0.431	3.274	1.359	1.057
363.24	0.012	0.198	0.050	0.379	3.215	1.395	1.024
365.95	0.008	0.130	0.038	0.265	3.409	1.440	1.034
367.59	0.004	0.085	0.020	0.185	3.437	1.524	1.049
n-Hexane + 1,3-dioxolane + 2-butanol at $P = 101.3\,\mathrm{kPa}$							
337.34	0.880	0.107	0.783	0.204	1.021	2.829	4.280
339.69	0.695	0.092	0.766	0.110	1.177	1.781	2.229
341.85	0.512	0.053	0.762	0.060	1.490	1.631	1.418
344.43	0.373	0.046	0.725	0.050	1.803	1.473	1.194
346.86	0.294	0.038	0.683	0.052	2.008	1.739	1.099
350.82	0.197	0.030	0.608	0.040	2.385	1.546	1.063
353.48	0.151	0.023	0.549	0.038	2.611	1.794	1.045
357.12	0.111	0.017	0.486	0.029	2.850	1.682	1.001
361.36	0.073	0.010	0.385	0.021	3.072	1.859	0.986
336.54	0.723	0.238	0.670	0.310	1.090	1.993	2.282
338.59	0.626	0.214	0.670	0.250	1.182	1.732	2.018
341.63	0.407	0.124	0.688	0.134	1.703	1.551	1.329
343.61	0.345	0.109	0.667	0.121	1.837	1.517	1.243
346.05	0.262	0.090	0.638	0.113	2.155	1.607	1.103
349.22	0.195	0.072	0.580	0.092	2.404	1.530	1.119
352.16	0.148	0.059	0.531	0.088	2.672	1.650	1.061
355.36	0.110	0.046	0.460	0.077	2.853	1.716	1.061
359.55	0.076	0.034	0.381	0.060	3.060	1.624	1.027
363.16	0.053	0.024	0.295	0.049	3.095	1.711	1.009
334.67	0.527	0.465	0.563	0.435	1.333	1.512	1.219
337.18	0.434	0.383	0.579	0.348	1.539	1.401	1.722
340.10	0.359	0.330	0.578	0.303	1.699	1.313	1.439
342.34	0.301	0.278	0.573	0.274	1.878	1.329	1.233
345.04	0.230	0.230	0.543	0.250	2.151	1.374	1.152
348.52	0.172	0.186	0.515	0.223	2.469	1.382	1.052
351.33	0.129	0.151	0.452	0.205	2.670	1.475	1.089
355.60	0.091	0.123	0.383	0.189	2.853	1.490	1.043
338.14	0.266	0.581	0.471	0.467	1.984	1.180	1.674

(Continued)

TABLE III Continued

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
340.74	0.222	0.529	0.474	0.435	2.211	1.118	1.336
343.33	0.175	0.459	0.444	0.417	2.432	1.153	1.234
346.20	0.134	0.390	0.401	0.393	2.638	1.193	1.236
348.97	0.118	0.334	0.390	0.369	2.691	1.208	1.113
353.01	0.076	0.258	0.311	0.343	2.977	1.317	1.108
358.50	0.043	0.191	0.226	0.313	3.298	1.401	1.026
360.27	0.032	0.157	0.176	0.280	3.295	1.479	1.066
365.10	0.014	0.105	0.089	0.217	3.366	1.532	1.039
344.11	0.065	0.776	0.247	0.685	3.565	1.040	1.345
346.49	0.056	0.690	0.226	0.658	3.532	1.050	1.292
349.60	0.042	0.584	0.182	0.625	3.470	1.083	1.274
354.48	0.023	0.485	0.112	0.610	3.406	1.102	1.136
356.78	0.017	0.390	0.086	0.550	3.325	1.176	1.123
359.23	0.010	0.318	0.063	0.501	3.880	1.241	1.076
361.74	0.005	0.256	0.027	0.449	3.115	1.307	1.065
364.08	0.004	0.198	0.023	0.380	3.124	1.367	1.027
366.14	0.001	0.143	0.007	0.300	3.611	1.454	1.028

TABLE IV Coefficients of the Antoine equation in kPa and °C

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
2-Butanol[a]	6.35457	1171.891	169.955

[a] Ref. [6]; Ref. [27].

the second virial coefficient of the pure gas, B_{ij} is 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 the p_i^0. The constants used are presented in Table IV. The second virial coefficients, B_{ii}, have been estimated using the Redlich–Kwong equation [9] for the 1,3-dioxolane, while for the rest of components the equations of the TRC tables [10] were used. The cross second virial coefficients, B_{ij}, have been calculated by means of the Amdur–Mason equation [11]. The molar volumes, V_i^0, were estimated with the Yens and Woods method [12].

The boiling temperatures of binary and ternary systems were correlated by the following equations proposed by Tamir and Wisniak [13]:

$$T = \sum_{i=1}^{2} x_i T_i + x_1 x_2 \sum_{k=0}^{m} C_k (x_1 - x_2)^k \tag{4}$$

$$T = \sum_{i=1}^{3} x_i T_i + \sum_{i,j=1}^{3} \left[x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \right] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3)] \tag{5}$$

where T_i is the boiling temperature of pure component i (in K) and m is the number of binary parameters, C_k are the binary coefficients, 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

TABLE V Coefficients and standard deviation (σ) in the correlation of boiling points by the Tamir and Wisniak equations

	P/kPa	C_0	C_1	C_2	C_3	σ/K
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 + 2-butanol	40.0	– 45.51	26.44	– 32.85	11.70	0.17
	101.3	– 41.01	21.90	– 32.66	1.58	0.29
1,3-Dioxolane + 2-butanol[b]	40.0	– 25.96	13.41	– 4.51	8.13	0.16
	101.3	– 19.66	9.34	– 0.83	2.34	0.16
n-Hexane + 1,3-dioxolane[c]	101.3	– 40.67	6.31	– 37.88	23.52	0.18
n-Hexane + 2-butanol[d]	101.3	– 54.55	35.01	– 43.14	13.92	
Ternary systems		P/kPa	A	B	C	σ/K
Cyclohexane + 1,		40.0	– 7.93	66.83	20.69	0.41
3-dioxolane + 2-butanol		101.3	– 5.03	– 3.66	39.17	0.74
n-Hexane + 1,3-dioxolane + 2-butanol		101.3	– 35.82	77.27	81.70	0.54

[a] Ref. [5]; [b] Ref. [4]; [c] Ref. [2b]; [d] Ref. [3].

are presented in Table V. We have included in this table the parameters of the constituent binary mixtures which have already been published [2–5].

The activity coefficients of the binary mixtures, γ_i, were correlated with the Margules, Van Laar, Wilson, NRTL and UNIQUAC equations [14–18]. While for the ternary mixtures were fitted to the Wilson, NRTL and UNIQUAC equations. The α_{ij} parameters in the NRTL equation were 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:

$$F = \sum_{i=1}^{m} \left[\sum_{j=1}^{n} \left(\frac{\gamma_j^{\mathrm{exp}} - \gamma_j^{\mathrm{cal}}}{\gamma_j^{\mathrm{exp}}} \right)^2 \right]_i \tag{6}$$

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

The minimisation of F has been done with a non-linear regression procedure [19]. Parameters resulting of the fitting, 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 VI and the ternary parameters are presented in Table VII. In these tables we can observe that fitting results for each system with different equations show very similar deviations in temperature and composition of vapour phase.

The thermodynamic consistency of the experimental binary data has been checked by means of the test of Van Ness modified by Fredeslund *et al.* [20] and extended to multicomponent mixtures employing the equation proposed by Prausnitz *et al.* [21]:

$$\ln \gamma_i = Q + \left(\frac{\partial Q}{\partial x_i} \right)_{T,P,x_j \neq i} - \sum_{j=1}^{k-1} x_j \left(\frac{\partial Q}{\partial x_j} \right)_{T,P,x_i \neq j} \tag{7}$$

TABLE VI Correlation parameters, average deviations ΔT and Δy, and activity coefficients at infinite dilution, γ_i^∞, for the binary system cyclohexane + 2-butanol

Equation	A_{12}	A_{21}	ΔT/K	Δy	γ_1^∞	γ_2^∞
$P = 40.0$ kPa						
Margules	1.2322	1.6961	0.32	0.0100	3.43	5.45
Van Laar	1.2574	1.7238	0.29	0.0096	3.52	5.61
Wilson	1204.2868	4090.2759	0.33	0.0081	3.63	6.06
NRTL	3690.6742	1100.1283	0.29	0.0083	3.47	5.59
UNIQUAC	1721.5351	−239.5378	0.30	0.0085	3.48	5.55
$P = 101.3$ kPa						
Margules	1.1798	1.3542	0.30	0.0056	3.25	3.87
Van Laar	1.1865	1.3542	0.31	0.0059	3.28	3.87
Wilson	1437.8370	3151.0451	0.36	0.0083	3.33	4.00
NRTL	2602.5377	1616.4416	0.31	0.0067	3.24	3.86
UNIQUAC	1133.9831	108.2073	0.30	0.0065	3.23	3.83

TABLE VII Correlation parameters and average deviations, ΔT and Δy, for the ternary systems cyclohexane + 1,3-dioxolane + 2-butanol and *n*-hexane + 1,3-dioxolane + 2-butanol

Equation	*ij*	A_{ij}	A_{ji}	ΔT/K	Δy
Cyclohexane + 1,3-dioxolane + 2-butanol at 40.0 kPa					
Wilson	12	1663.5710	3119.3486	0.28	0.005
	13	1186.5540	4078.2256		
	23	391.4256	2652.5588		
NRTL	12	1919.0850	2426.6023	0.31	0.007
	13	3159.7100	1523.8591		
	23	1033.5391	1115.8535		
UNIQUAC	12	1799.0637	83.0172	0.34	0.006
	13	1685.6758	−194.2658		
	23	1102.2725	−55.7445		
Cyclohexane + 1,3-dioxolane + 2-butanol at 101.3 kPa					
Wilson	12	866.3358	3324.6538	0.54	0.004
	13	1435.4771	3473.6597		
	23	1621.6637	24.9743		
NRTL	12	1063.7271	2926.1016	0.53	0.004
	13	2859.3438	1612.4143		
	23	932.8461	747.2672		
UNIQUAC	12	1620.0825	68.3848	0.53	0.004
	13	1095.0652	193.9310		
	23	−541.4427	1386.0425		
n-Hexane + 1,3-dioxolane + 2-butanol at 101.3 kPa					
Wilson	12	1910.1829	3580.0093	0.50	0.005
	13	587.3557	5321.3145		
	23	4372.7300	−1955.3994		
NRTL	12	1231.9128	3298.4766	0.55	0.006
	13	3238.0005	1397.7527		
	23	969.7779	563.6241		
UNIQUAC	12	2051.9004	−46.1939	0.55	0.006
	13	2.006.8169	−404.3394		
	23	−1494.3413	2969.0400		

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 determinate the relationship between Q and the liquid phase composition:

$$Q = \sum_{i=1}^{k} \sum_{j=i+1}^{k} x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p + x_1 x_2 (1 - x_1 - x_2)(B_1 + B_2 x_1 + B_3 x_2) \tag{8}$$

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 VIII.

We have chosen the Wilson equation to plot the VLE data (T, x_1, y_1) of the binary mixture cyclohexane + 2-butanol in Fig. 1. We have found one reference for this system at 101.3 kPa [22] with a very similar results. In Fig. 1 it can be observed that

TABLE VIII Results of the thermodynamic consistency test. Average deviations ΔP and Δy

	P/kPa	ΔP/kPa	Δy
Binary system			
Cyclohexane + 2-butanol	40.0	0.5	0.0089
	101.3	1.2	0.0041
Ternary system			
Cyclohexane + 1,3-dioxolane + 2-butanol	40.0	0.5	0.005
	101.3	2.0	0.003
n-Hexane + 1,3-dioxolane + 2-butanol	101.3	1.8	0.006

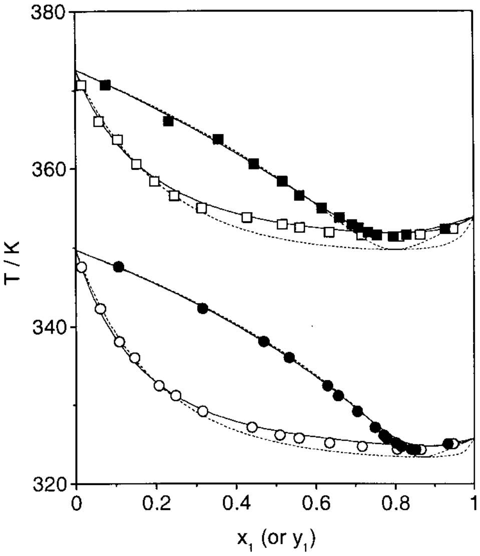

FIGURE 1 $T - x_1 - y_1$ for the binary mixture cyclohexane + 2-butanol: (○, ●) exptl. data at 40.0 kPa; (□, ■) exptl. data at 101.3 kPa; Wilson equation (continuous lines) and UNIFAC predictions (dashed lines).

the mixture shows azeotropic behaviour at both pressures. The calculated compositions of the azeotropic points are:

- cyclohexane + 2-butanol at 40.0 kPa $x_{1az} = 0.881$, at $T_{az} = 324.8$ K.
- cyclohexane + 2-butanol at 101.3 kPa $x_{1az} = 0.800$, at $T_{az} = 351.9$ K which is near the azeotropic point ($x_{1az} = 0.809$ at $T_{az} = 350.12$ K) determined by Feng *et al.* [22].

Three-dimensional surfaces of the liquid and vapour phases of the ternary mixtures calculated with the Wilson equation are plotted in Fig. 2 and isotherms for the same 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 as it is described in [23], 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. In our previous papers

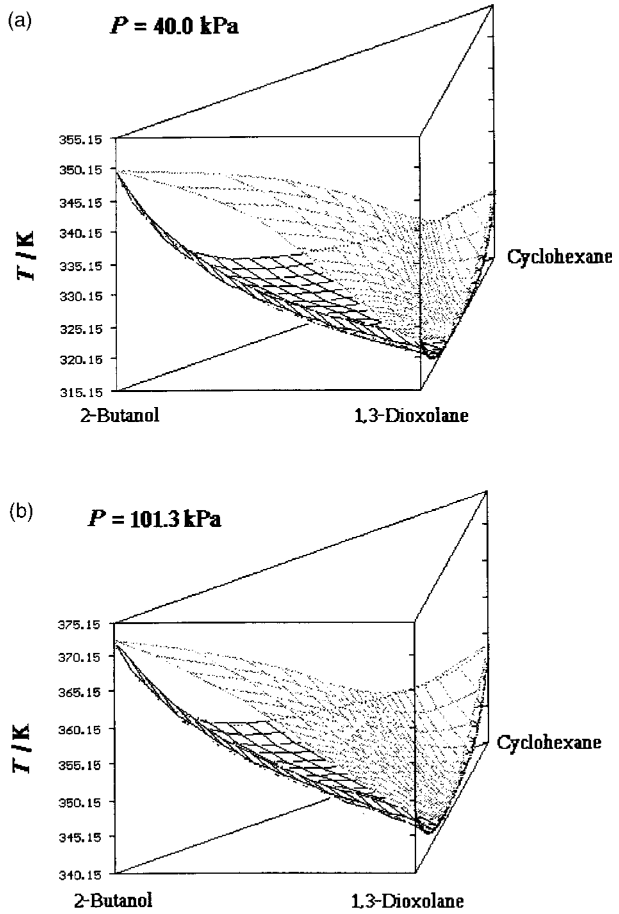

FIGURE 2 Three-dimensional surfaces of the vapour and liquid phases of the isobaric VLC correlated with Wilson equation: (a) Ternary system cyclohexane + 1,3-dioxolane + 2-butanol at 40.0 kPa; (b) Ternary system cyclohexane + 1,3-dioxolane + 2-butanol at 101.3 kPa; (c) Ternary system *n*-hexane + 1,3-dioxolane + 2-butanol at 101.3 kPa.

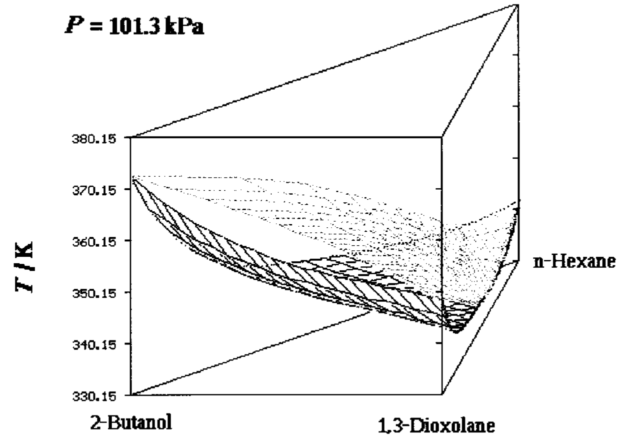

FIGURE 2 Continued.

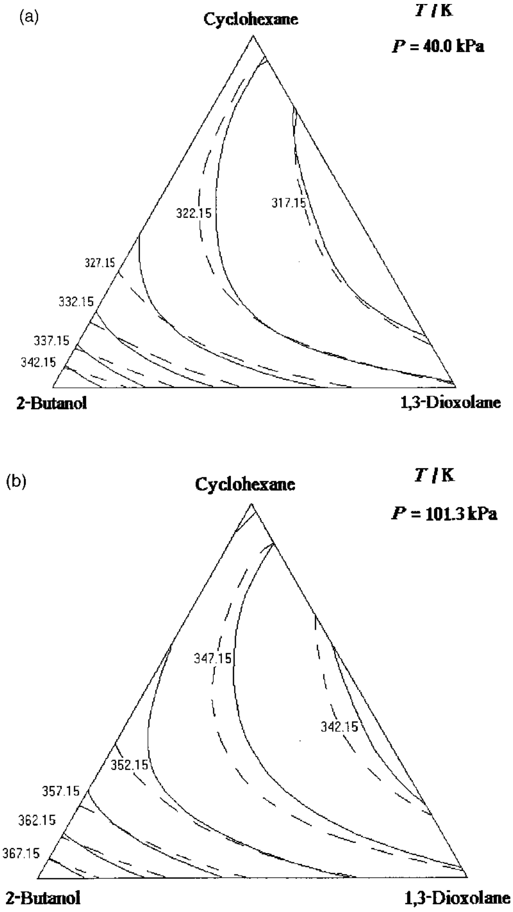

FIGURE 3 Isotherms in liquid phase of the isobaric VLE: correlated with Tamir–Wisniak equation (continuous lines) and predicted with UNIFAC model (dashed lines): (a) Ternary system cyclohexane + 1,3-dioxolane + 2-butanol at 40.0 kPa; (b) Ternary system cyclohexane + 1,3-dioxolane + 2-butanol at 101.3 kPa; (c) Ternary system *n*-hexane + 1,3-dioxolane + 2-butanol at 101.3 kPa.

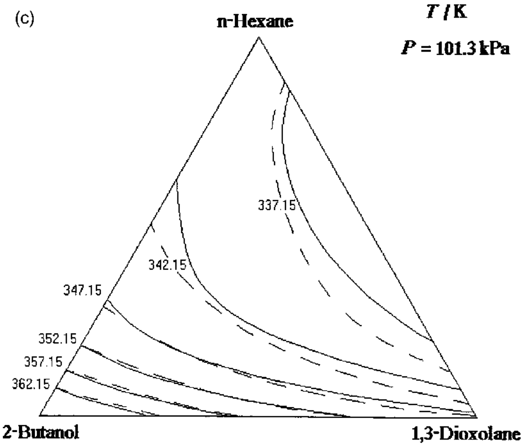

FIGURE 3 Continued.

TABLE IX VLE predictions with the group contribution methods ASOG and UNIFAC, average deviations ΔT and Δy

		ASOG		*UNIFAC*	
	P/kPa	ΔT/K	Δy	ΔT/K	Δy
Binary system					
Cyclohexane + 2-butanol	40.0	1.20	0.0244	0.70	0.0195
	101.3	1.39	0.0182	1.11	0.0176
Ternary system					
Cyclohexane + 1,3-dioxolane + 2-butanol	40.0	4.67	0.0600	0.56	0.0113
	101.3	4.20	0.0467	0.91	0.0085
n-Hexane + 1,3-dioxolane + 2-butanol	101.3	4.85	0.0449	0.69	0.0077

with this kind of mixtures [1,2] we have explained this behaviour in terms of molecular interactions.

VLE Predictions

Modified UNIFAC and ASOG methods, with parameters proposed by Gmehling *et al.* [24,25] and Tochigi *et al.* [26], 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 IX. In this table we can realise that ASOG predictions for the binary system are as good as UNIFAC calculations while for the ternary systems ASOG results are not at all acceptable. We have plotted UNIFAC predicted values along with experimental results in Figs. 1 and 3.

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