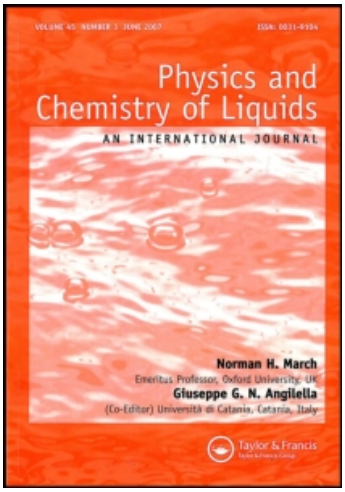

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Isobaric Vapour - Liquid Equilibrium for the Binary Systems Cycloalkane and Benzene with 1,3-Dioxolane

C. Lafuente[a]; A. M. Mainar[a]; P. Cea[a]; F. M. Royo[a]; J. S. Urieta[a]
[a] Departamento de Quimica Orgánica-Quimica Fisica, Facultad de Ciencias, Universidad de Zaragoza, Zaragoza, Spain

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ISOBARIC VAPOUR–LIQUID EQUILIBRIUM FOR THE BINARY SYSTEMS CYCLOALKANE AND BENZENE WITH 1,3-DIOXOLANE

C. LAFUENTE, A. M. MAINAR, P. CEA, F. M. ROYO and J. S. URIETA*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, Ciudad Universitaria, Zaragoza 50009, Spain

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Isobaric vapour–liquid equilibrium (VLE) is reported for the binary systems cyclopentane, cyclohexane, benzene with 1,3-dioxolane. All the systems show a minimum temperature azeotrope. The VLE results were thermodynamically consistent and correlated with six previously proposed equations.

Keywords: Isobaric vapour–liquid equilibrium; cycloalkane; benzene; 1,3-dioxolane

INTRODUCTION

In this paper, isobaric vapour–liquid equilibrium measurements for cyclopentane, cyclohexane and benzene with 1,3-dioxolane at 40.0 (except for cyclopentane because its low boiling temperature), 66.6 and 101.3 kPa are reported. This study is a continuation of our thermodynamic research on systems containing cyclic ethers with one or two oxygen atoms [1–3]. The only literature data available for these systems were isobaric vapour–liquid equilibrium for the mixture cyclohexane with 1,3-dioxolane at 101.3 kPa [4].

*Corresponding author.

The experimental results have been checked for the thermodynamic consistency, and the activity coefficients have been correlated with the models: Margules [5]; Van Laar [6]; Wilson [7]; NRTL [8]; and UNIQUAC [9]. Satisfactory predictions with the UNIFAC group contribution method [10] have been performed.

EXPERIMENTAL

The liquids used were: cyclopentane (better than 99 mol%) provided by Merck, cyclohexane and benzene (better than 99.9 mol%) and 1,3-dioxolane (better than 99.5 mol%) supplied by Aldrich. The purity of the materials was checked by GLC and was considered sufficient, so liquids were used without further purification. Table I shows the physical properties of the chemicals, densities at 298.15 K and normal boiling points appear together with the values from literature [11–14]. The vapour–liquid equilibrium measurements were carried out in a still (Labodest) manufactured by Fischer (Germany). It is an all-glass dynamic recirculating still, equipped with a Cottrell pump. The equilibrium temperatures were measured to an accuracy of ±0.01 K by means of a thermometer (model F25) from Automatic Systems Laboratories, and the pressure in the still was obtained with a pressure transducer Druck PDCR 110/W (pressure indicator DPI201) with an accuracy of ± 0.1 kPa. Composition of both phases, vapour and liquid, were determined by measuring their densities at 298.15 K with an Anton Paar DMA-58 vibrating tube densimeter that was previously calibrated at atmospheric pressure with doubly distilled water and dry air. Density-calibration curves used for these systems were taken from a previous paper [3]. The estimated error in the determination of both liquid and vapor phase mole fractions is ±0.0001.

TABLE I Physical properties (densities at $T = 298.15$ K and normal boiling points) of the pure compounds

	$\rho/g.cm^{-3}$		T_b/K	
Compound	*This paper*	*Lit.*	*This paper*	*Lit.* [12]
Cyclopentane	0.73969	0.7403 [11]	322.40	322.412
Cyclohexane	0.77387	0.77381 [13]	353.85	353.880
Benzene	0.87355	0.87360 [12]	353.20	353.244
1,3-Dioxolane	1.05880	1.05877 [14]	348.75	348.8

RESULTS AND DISCUSSION

Table II shows the vapour–liquid equilibrium data (T, x_1, and y_1) and the calculated activity coefficients at 40.0, 66.6 and 101.3 kPa. The systems present positive deviation from ideality and their $T - x_1 - y_1$ diagrams are represented in Figures 1–3.

The activity coefficients of the components in the liquid phase, γ_i, were calculated, taking into account the non-ideality of the vapour phase, from the following equations:

TABLE II Experimental VLE data for the binary mixtures at the indicated pressure

T/K	x_1	y_1	γ_1	γ_2
	Cyclopentane + 1,3-Dioxolane at 66.6 kPa			
328.85	0.0348	0.2589	4.059	1.016
324.71	0.0735	0.3960	3.339	1.011
319.45	0.1442	0.5311	2.699	1.048
315.79	0.2144	0.6323	2.439	1.041
313.94	0.2922	0.6745	2.032	1.106
312.30	0.3995	0.7060	1.645	1.263
311.59	0.4750	0.7286	1.463	1.375
311.06	0.5700	0.7632	1.301	1.499
309.92	0.6990	0.7925	1.146	1.972
309.80	0.7723	0.8282	1.089	2.170
309.45	0.9252	0.9111	1.012	3.472
	Cyclopentane + 1,3-Dioxolane at 101.3 kPa			
339.31	0.0488	0.3024	3.750	1.002
336.52	0.0765	0.3803	3.255	1.012
328.89	0.2031	0.5908	2.382	1.025
326.01	0.2900	0.6280	1.936	1.167
324.99	0.3611	0.6747	1.724	1.180
323.26	0.5289	0.7311	1.346	1.416
322.45	0.5950	0.7423	1.247	1.630
322.07	0.6750	0.7678	1.150	1.858
321.76	0.7947	0.8298	1.067	2.183
321.54	0.9010	0.8878	1.014	3.011
	Cyclohexane + 1,3-Dioxolane at 40.0 kPa			
319.38	0.0604	0.1916	4.022	0.997
316.67	0.1792	0.3331	2.611	1.052
315.53	0.3052	0.4058	1.951	1.162
315.25	0.4139	0.4379	1.569	1.319
315.20	0.4674	0.4653	1.479	1.383
315.46	0.5973	0.5200	1.280	1.625
316.17	0.7139	0.5704	1.143	1.987
317.79	0.8159	0.6331	1.043	2.466
318.90	0.8766	0.7055	1.038	2.822
321.80	0.9477	0.8365	1.021	3.290

TABLE II (Continued)

T/K	x_1	y_1	γ_1	γ_2
	Cyclohexane + 1,3-Dioxolane at 66.6 kPa			
333.15	0.0598	0.1640	3.501	1.002
329.95	0.1809	0.3077	2.420	1.073
329.23	0.3085	0.3900	1.843	1.151
328.95	0.4138	0.4390	1.562	1.262
329.01	0.4694	0.4575	1.432	1.345
329.35	0.6018	0.5084	1.226	1.604
330.26	0.7166	0.5702	1.119	1.904
331.71	0.8191	0.6497	1.061	2.304
333.46	0.8770	0.7199	1.035	2.542
336.48	0.9432	0.8424	1.019	2.778
	Cyclohexane + 1,3-Dioxolane at 101.3 kPa			
344.47	0.0843	0.1854	2.919	1.019
342.46	0.1833	0.3092	2.381	1.037
341.39	0.3106	0.3881	1.823	1.129
341.28	0.4188	0.4331	1.514	1.246
341.45	0.4701	0.4583	1.420	1.298
341.87	0.6051	0.5156	1.224	1.536
343.26	0.7381	0.5929	1.105	1.856
344.50	0.8066	0.6391	1.048	2.138
346.47	0.8814	0.7299	1.031	2.444
349.21	0.9392	0.8316	1.015	2.717
	Benzene + 1,3-Dioxolane at 40.0 kPa			
323.07	0.0299	0.0316	1.172	0.997
322.99	0.0857	0.0893	1.159	0.998
322.91	0.1326	0.1344	1.131	1.003
322.89	0.1868	0.1872	1.118	1.006
322.92	0.2552	0.2508	1.095	1.011
323.00	0.3541	0.3407	1.069	1.023
323.20	0.5019	0.4795	1.053	1.039
323.38	0.5863	0.5575	1.041	1.056
323.65	0.6716	0.6408	1.034	1.068
324.11	0.8005	0.7692	1.024	1.110
324.66	0.9037	0.8826	1.020	1.145
	Benzene + 1,3-Dioxolane at 66.6 kPa			
336.46	0.0299	0.0312	1.185	0.999
336.40	0.0852	0.0879	1.173	0.999
336.38	0.1298	0.1312	1.150	1.001
336.36	0.1853	0.1839	1.130	1.005
336.43	0.2527	0.2464	1.107	1.010
336.55	0.3479	0.3326	1.081	1.020
336.90	0.4997	0.4691	1.049	1.045
337.20	0.5900	0.5530	1.036	1.062
337.56	0.6760	0.6384	1.032	1.074
338.21	0.8021	0.7665	1.021	1.110
338.89	0.9043	0.8817	1.019	1.136

TABLE II (Continued)

T/K	x_1	y_1	γ_1	γ_2
	Benzene + 1,3-Dioxolane at 101.3 kPa			
348.58	0.0308	0.0312	1.169	0.999
348.56	0.0857	0.0861	1.160	0.999
348.57	0.1303	0.1293	1.145	1.000
348.61	0.1858	0.1820	1.129	1.003
348.70	0.2532	0.2400	1.089	1.013
348.89	0.3484	0.3285	1.077	1.019
348.38	0.4997	0.4648	1.046	1.042
349.75	0.5905	0.5497	1.035	1.058
350.23	0.6813	0.6423	1.033	1.064
350.85	0.7848	0.7404	1.014	1.121
351.82	0.9057	0.8820	1.016	1.128

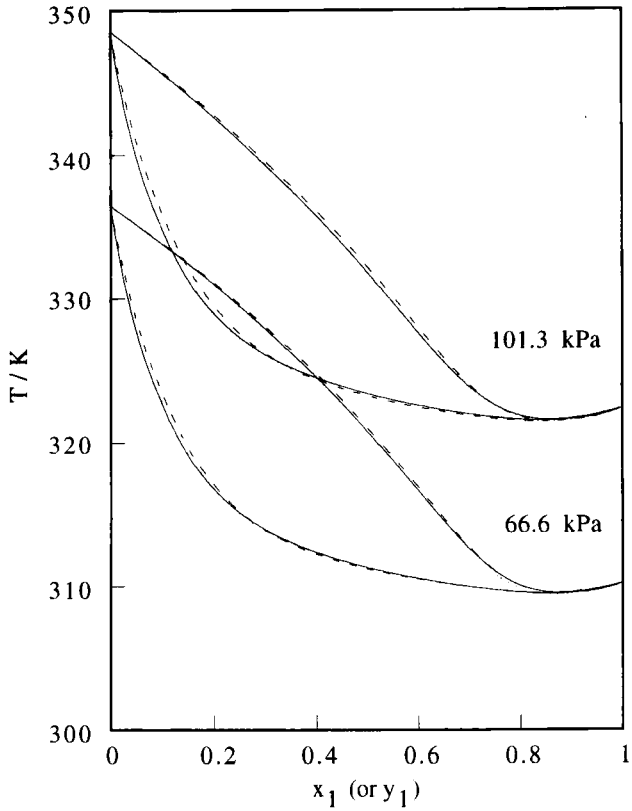

FIGURE 1 $T - x_1 - y_1$ diagrams for cyclopentane (1) + 1,3-dioxolane (2) at 66.6 and 101.3 kPa, (——) Wilson equation; (– – – – –) UNIFAC method.

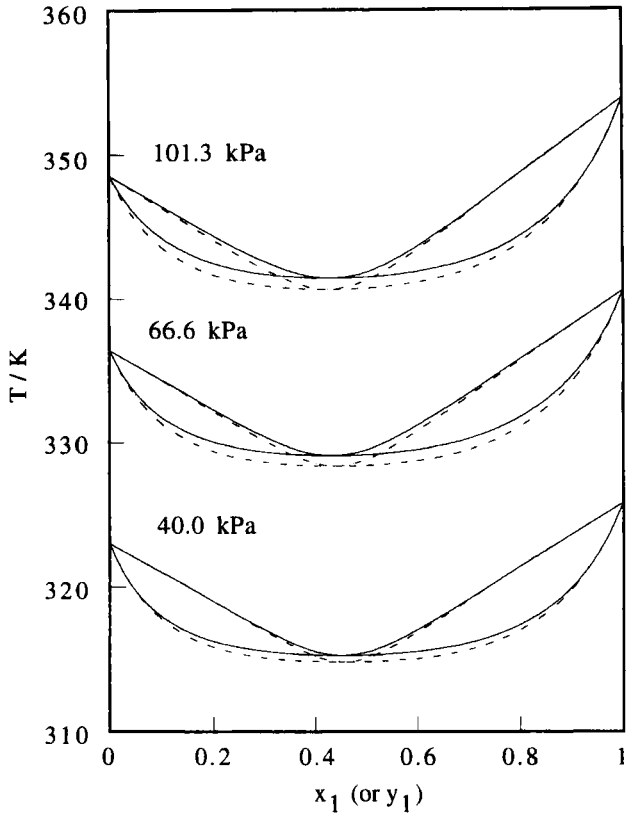

FIGURE 2 $T-x_1-y_1$ diagrams for cyclohexane (1) + 1,3-dioxolane (2) at 40.0, 66.6 and 101.3 kPa, (——) Wilson equation; (– – – – –) UNIFAC method.

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

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

where x_i and y_i are the liquid and vapour phase compositions, P, the total pressure, p_i^0, the vapour pressures of the pure compounds calculated by using the Antoine's equation whose constants are given in Table III, B_{ii}, are the second virial coefficients, B_{ij}, are the second

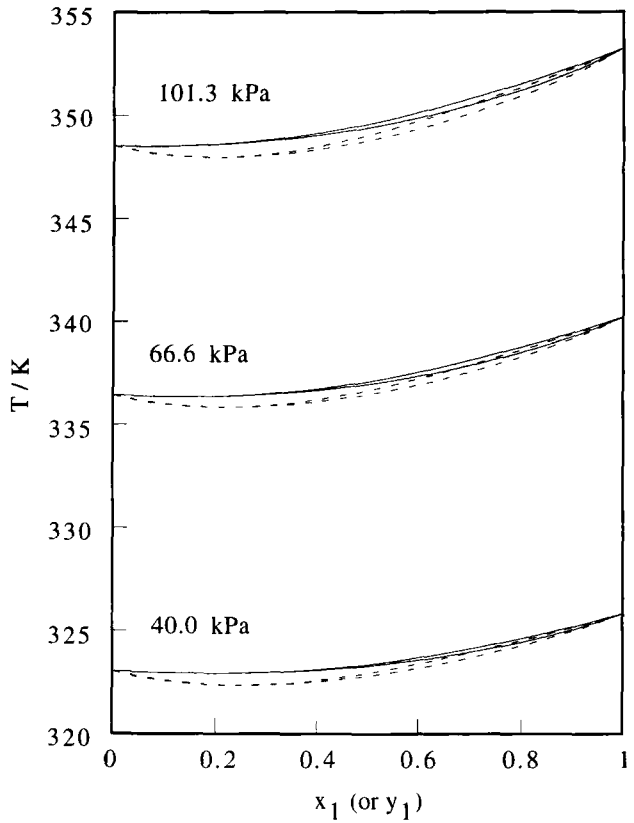

FIGURE 3 $T - x_1 - y_1$ diagrams for benzene (1) + 1,3-dioxolane (2) at 40.0, 66.6 and 101.3 kPa, (——) Wilson equation; (– – – – –) UNIFAC method.

TABLE III Constants of Antoine's equation for vapour pressures of the pure compounds (pressure in kPa, temperature in °C)

Compound	*A*	*B*	*C*
Cyclopentane [12]	6.04584	1142.30	233.463
Cyclohexane [12]	5.96407	1200.31	222.504
Benzene [13]	6.03055	1211.033	220.79
1,3-Dioxolane [17]	6.23182	1236.70	217.235

cross virial coefficients calculated through the Amdur-Mason equation [15] and, V_i^0, are the molar volumes of the saturated liquids calculated using the Yen and Woods method [16].

Antoine's constants for cyclopentane and cyclohexane were obtained from Riddick *et al.* [12], for benzene were taken from TRC-tables [13] and for 1,3-dioxolane from Wu and Sandler [17]. The second virial coefficients for cyclopentane, cyclohexane, and benzene were obtained from TRC-tables [13] and for 1,3-dioxolane was estimated by the Redlich-Kwong equation [18].

The thermodynamic consistency of the experimental results was checked using the Van Ness [19] method, described by Fredenslund *et al.* [20] using a third-order Legendre polynomial for the excess free energies. According to this test, experimental data are considered consistent if the average deviation in y (Δy) is smaller than 0.01. All systems satisfy this condition, as one can see in Table IV.

The activity coefficients were correlated through the Margules, Van Laar, Wilson, NRTL and UNIQUAC equations. Estimation of parameters for all equations was based on minimization, using a non-linear regression procedure [21], of an objective function F in terms of experimental and calculated γ_i values. The function F [22] for a binary system can be stated as:

$$F = \sum_{i=1}^{i=N} \left[\left(\frac{\gamma_1^{exp} - \gamma_1^{cal}}{\gamma_1^{exp}} \right)^2 + \left(\frac{\gamma_2^{exp} - \gamma_2^{cal}}{\gamma_2^{exp}} \right)^2 \right]_i \qquad (3)$$

where N is the number of experimental data. The parameters A_{12} and A_{21}, see definitions in Gmehling *et al.* [23], along with the average deviation in $T(\Delta T)$, the average deviation in $y(\Delta y)$, and the activity coefficients at infinite dilution are listed in Table V. The average

TABLE IV Results of the thermodynamic consistency test. Average deviation in P (ΔP), and average deviation in $y(\Delta y)$

System	*P/kPa*	*ΔP/kPa*	*Δy*
Cyclopentane + 1,3-Dioxolane	66.6	0.6	0.0065
	101.3	0.7	0.0066
Cyclohexane + 1,3-Dioxolane	40.0	0.3	0.0070
	66.6	0.6	0.0076
	101.3	0.5	0.0081
Benzene + 1,3-Dioxolane	40.0	0.2	0.0013
	66.6	0.2	0.0017
	101.3	0.3	0.0021

TABLE V Correlation parameters, average deviation in $T(\Delta T)$, average deviation in $y(\Delta y)$, and activity coefficients at infinite dilution γ_i^∞

Equation	A_{12}	A_{21}	$\Delta T/K$	Δy	γ_1^∞	γ_2^∞
			Cyclopentane + 1,3-Dioxolane at 66.6 kPa			
Margules	1.4179[a]	1.4027[a]	0.22	0.0074	4.13	4.07
Van Laar	1.4183[a]	1.4021[a]	0.22	0.0074	4.13	4.06
Wilson	1661.6258[b]	3018.1386[b]	0.21	0.0071	4.21	4.39
NRTL	1828.2055[b]	2363.9303[b]	0.22	0.0081	3.99	4.09
UNIQUAC	1437.6933[b]	347.0980[b]	0.23	0.0080	3.99	4.08
			Cyclopentane + 1,3-Dioxolane at 101.3 kPa			
Margules	1.4117	1.2924	0.18	0.0072	4.10	3.64
Van Laar	1.4160	1.2918	0.18	0.0072	4.12	3.64
Wilson	1885.2390	2750.7780	0.15	0.0068	4.18	3.89
NRTL	1446.9623	2755.3635	0.18	0.0084	3.98	3.65
UNIQUAC	1194.4388	541.5279	0.18	0.0084	3.98	3.63
			Cyclohexane + 1,3-Dioxolane at 40.0 kPa			
Margules	1.5342	1.2941	0.13	0.0080	4.64	3.65
Van Laar	1.5513	1.2968	0.13	0.0078	4.72	3.66
Wilson	1870.2593	2955.7212	0.13	0.0066	5.05	3.77
NRTL	1355.7019	2974.9141	0.13	0.0075	4.67	3.63
UNIQUAC	1597.7915	169.9619	0.14	0.0076	4.66	3.59
			Cyclohexane + 1,3-Dioxolane at 66.6 kPa			
Margules	1.4132	1.1529	0.21	0.0081	4.11	3.17
Van Laar	1.4254	1.1622	0.21	0.0080	4.16	3.20
Wilson	1702.7266	2750.7379	0.22	0.0069	4.34	3.25
NRTL	1091.0514	2983.4200	0.19	0.0077	4.11	3.17
UNIQUAC	1507.3782	157.3782	0.18	0.0075	4.11	3.14
			Cyclohexane + 1,3-Dioxolane at 101.3 kPa			
Margules	1.2758	1.1398	0.16	0.0092	3.58	3.13
Van Laar	1.2793	1.1428	0.15	0.0092	3.59	3.14
Wilson	1223.1459	2988.1022	0.13	0.0088	3.71	3.17
NRTL	1430.4711	2440.5335	0.15	0.0088	3.55	3.10
UNIQUAC	1800.8913	− 100.7589	0.16	0.0086	3.55	3.08
			Benzene + 1,3-Dioxolane at 40.0 kPa			
Margules	0.1639	0.1740	0.11	0.0020	1.18	1.19
Van Laar	0.1636	0.1748	0.11	0.0020	1.18	1.19
Wilson	− 616.4923	1088.5842	0.11	0.0020	1.18	1.19
NRTL	544.2982	− 72.7033	0.11	0.0020	1.18	1.19
UNIQUAC	787.6297	− 541.5082	0.11	0.0020	1.18	1.19
			Benzene + 1,3-Dioxolane at 66.6 kPa			
Margules	0.1836	0.1663	0.11	0.0021	1.20	1.18
Van Laar	0.1840	0.1667	0.11	0.0021	1.20	1.18
Wilson	− 170.2600	684.6414	0.11	0.0020	1.20	1.18
NRTL	− 159.1769	675.6198	0.11	0.0021	1.20	1.18
UNIQUAC	302.0781	− 115.9282	0.11	0.0021	1.20	1.18

TABLE V (Continued)

Equation	A_{12}	A_{21}	$\Delta T/K$	Δy	γ_1^∞	γ_2^∞
Benzene + 1,3-Dioxolane at 101.3 kPa						
Margules	0.1714	0.1626	0.10	0.0020	1.19	1.18
Van Laar	0.1715	0.1628	0.10	0.0020	1.19	1.18
Wilson	−333.4584	832.8869	0.10	0.0020	1.19	1.18
NRTL	41.9082	454.7258	0.10	0.0020	1.19	1.18
UNIQUAC	477.2761	−278.2846	0.10	0.0020	1.19	1.18

[a] Dimensionless.
[b] Joules per mole.

deviation in temperature is less than 0.3 K and in vapour composition is less than 0.01, so all the equations correlated the activity coefficients quite well.

All the systems show minimum temperature azeotropes. Information about composition and boiling temperature of the azeotropes is included in Table VI. The temperature and composition that we have obtained for the azeotrope in the system cyclohexane with 1,3-dioxolane at 101.3 kPa ($x_{1(az)} = 0.429$, $T_{(az)} = 341.4$ K) are in good agreement with the value reported by Wisniak *et al.* [4] ($x_{1(az)} = 0.43$, $T_{(az)} = 341.04$ K).

In this work the UNIFAC method was used to predict the vapour–liquid equilibrium of the studied systems. For all systems the temperature and vapour–phase composition obtained experimentally were compared with the theoretical ones. In Figures 1–3 the predicted $T - x_1 - y_1$ diagrams are represented. The average deviations are given

TABLE VI Experimental compositions ($x_{1(az)}$) and boiling temperatures ($T_{(az)}$) of the azeotropes

System	*P/kPa*	$x_{1(az)}$	$T_{(az)}/K$
Cyclopentane + 1,3-Dioxolane	66.6	0.869	309.4
	101.3	0.855	321.5
Cyclohexane + 1,3-Dioxolane	40.0	0.450	315.3
	66.6	0.431	329.1
	101.3	0.429	341.4
Benzene + 1,3-Dioxolane	40.0	0.195	322.9
	66.6	0.148	336.3
	101.3	0.081	348.5

TABLE VII UNIFAC predictions, average deviation in $T(\Delta T)$, and average deviation in $y(\Delta y)$

System	*P/kPa*	$\Delta T/K$	Δy
Cyclopentane + 1,3-Dioxolane	66.6	0.18	0.0048
	101.3	0.27	0.0067
Cyclohexane + 1,3-Dioxolane	40.0	0.34	0.0076
	66.6	0.60	0.0101
	101.3	0.61	0.0096
Benzene + 1,3-Dioxolane	40.0	0.35	0.0065
	66.6	0.37	0.0057
	101.3	0.46	0.0063

in Table VII, these values indicate that the UNIFAC method give satisfactory predictions for the binary systems considered in this paper.

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