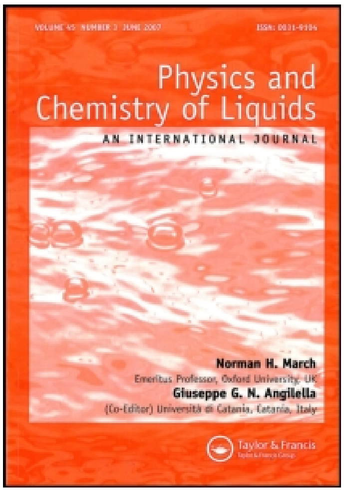

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Isobaric Vapour-Liquid Equilibrium of Some Cyclic Ethers with Bromobenzene at Several Pressures

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ISOBARIC VAPOUR–LIQUID EQUILIBRIUM OF SOME CYCLIC ETHERS WITH BROMOBENZENE AT SEVERAL PRESSURES

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A dynamic recirculating still was employed to study the isobaric vapour–liquid equilibrium (VLE) at 40.0 and 101.3 kPa for the binary systems tetrahydrofuran, tetrahydropyran, 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran with bromobenzene. The experimental data were tested for thermodynamic consistency and correlated with the Wilson, NRTL and UNIQUAC equations. Predictions with the UNIFAC method were also obtained.

Keywords: Isobaric VLE; Cyclic ethers; Bromobenzene

INTRODUCTION

In previous papers from our laboratory we have reported isobaric vapour–liquid equilibrium (VLE) measurements for some cyclic ethers with chlorobenzene [1] or chlorocyclohexane [2]. Following these studies we present here experimental data of the isobaric VLE for the mixtures of a cyclic ether (tetrahydrofuran, tetrahydropyran, 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran) with

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bromobenzene at 40.0 and 101.3 kPa. As far as we know, these systems have not been investigated.

For each mixture, the VLE results have been checked for thermodynamic consistency and the activity coefficients have been correlated with the following models: Wilson [3], NRTL [4] and UNIQUAC [5].

Apart from this experimental work we have verified the accuracy in the prediction of vapour–liquid equilibrium of the UNIFAC method [6].

EXPERIMENTAL

The liquids used were tetrahydrofuran (better than 99.5 mol%), tetrahydropyran, 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran (better than 99 mol%) obtained from Aldrich together with bromobenzene (better than 99.5 mol%) provided by Fluka. The purities of the materials were checked by gas chromatography and they were used without further purification. The comparison of measured physical properties of the chemicals, densities and normal boiling points, with literature values [7–11] are shown in Table I.

The still used to measure VLE data was an all-glass dynamic recirculating one, equipped with a Cottrell pump. It is a commercial unit (Labodest model) built in Germany by Fischer. 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 measured with a pressure transducer Druck PDCR 110/W (pressure indicator DPI201) with an accuracy of ± 0.1 kPa. Compositions of both phases vapour and liquid were determined by measuring their densities at 298.15 K with an Anton Paar

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

Compound	$\rho/\mathrm{g\,cm^{-3}}$		T_b/K	
	This paper	*Lit.*	*This paper*	*Lit.*
Tetrahydrofuran	0.88209	0.88197 [7]	339.12	339.115 [11]
Tetrahydropyran	0.87915	0.87196 [8]	361.17	361 [10]
2-Methyl-tetrahydrofuran	0.84990	0.84882 [9]	352.94	353.1 [10]
2,5-Dimethyl-tetrahydrofuran	0.82527	—	365.08	365.65 [11]
Bromobenzene	1.48818	1.48820 [10]	429.01	429.058 [10]

DMA-58 vibrating tube densimeter that was previously calibrated at atmospheric pressure with doubly distilled water and dry air. Prior to this, density-calibration curves for these systems were obtained [12], the estimated error in the determination of both liquid and vapour phase mole fractions is ±0.0001.

RESULTS

The VLE data (T, x_1, and y_1) together with calculated activity coefficients at 40.0 and 101.3 kPa, are gathered in Table II and the temperature–composition diagrams are represented in Figs. 1–4.

The activity coefficients γ_1 were calculated, taking into account the non-ideality of the vapour phase, from the following equations:

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

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

where x_i, and y_i are the liquid and vapour phase compositions, P is the total pressure, p_i° are the vapour-pressures of the pure compounds, B_{ii} are the second virial coefficients, B_{ij} are the cross second virial coefficients and V_i° are the molar volumes of the saturated liquids. The correction for the non-ideality of the vapour phase, represented by the exponential term in Eq. (1), was important only at very dilute concentrations.

The Antoine equation has been used for calculating the vapour pressures of the pure compounds and the corresponding constants are listed in Table III. Antoine's constants for tetrahydrofuran, 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran were taken from TRC tables [11], for bromobenzene were obtained from Riddick *et al.* [10], and those for tetrahydropyran were obtained from our own vapor pressure measurements. The second virial coefficients have been estimated using the Redlich–Kwong equation [13]. The cross second virial coefficients have been calculated by means of a suitable mixing rule [14]. The molar volumes were calculated using the Yen and Woods method [15].

TABLE II Experimental VLE data at the indicated pressure

T/K	x_1	y_1	γ_1	γ_2
Tetrahydrofuran + bromobenzene at 40.0 kPa				
393.34	0.0115	0.1192	0.988	0.986
388.98	0.0259	0.2284	0.926	1.007
381.72	0.0609	0.4235	0.863	0.990
376.37	0.0891	0.5379	0.852	0.983
355.88	0.2281	0.8193	0.869	0.969
346.24	0.3175	0.8920	0.901	0.971
338.62	0.4158	0.9436	0.922	0.823
330.89	0.5316	0.9693	0.955	0.795
324.96	0.6508	0.9824	0.971	0.811
318.22	0.8030	0.9929	1.015	0.813
315.12	0.9052	0.9975	1.016	0.698
313.50	0.9669	0.9992	1.014	0.697
Tetrahydrofuran + bromobenzene at 101.3 kPa				
420.91	0.0363	0.2229	0.848	1.001
414.67	0.0673	0.3720	0.857	0.990
409.79	0.0936	0.4713	0.857	0.983
402.01	0.1417	0.6064	0.852	0.969
389.63	0.2319	0.7700	0.862	0.927
381.09	0.3059	0.8449	0.873	0.915
372.93	0.3824	0.8976	0.904	0.899
364.52	0.4836	0.9354	0.926	0.921
358.01	0.5711	0.9625	0.962	0.825
353.71	0.6476	0.9743	0.969	0.815
346.62	0.7884	0.9891	0.995	0.769
340.55	0.9417	0.9979	1.013	0.697
Tetrahydropyran + Bromobenzene at 40.0 kPa				
395.09	0.0080	0.0413	0.853	1.012
393.73	0.0163	0.0823	0.861	1.020
392.77	0.0274	0.1356	0.863	1.001
387.58	0.0659	0.3041	0.912	0.990
381.11	0.1189	0.4741	0.927	0.983
376.97	0.1604	0.5594	0.903	0.995
368.98	0.2485	0.7055	0.914	0.987
361.78	0.3397	0.8073	0.940	0.961
353.55	0.4762	0.8860	0.945	0.988
347.69	0.5895	0.9324	0.968	0.950
339.77	0.7911	0.9779	0.988	0.857
334.96	0.9373	0.9952	1.006	0.769
Tetrahydropyran + bromobenzene at 101.3 kPa				
425.27	0.0238	0.1097	1.003	1.001
422.86	0.0423	0.1831	0.992	1.005
419.93	0.0655	0.2669	0.989	0.999
415.16	0.1062	0.3810	0.958	1.004
408.63	0.1629	0.5214	0.979	0.996
403.16	0.2215	0.6166	0.958	1.005
397.72	0.2863	0.6840	0.929	1.064
389.54	0.3972	0.7932	0.941	1.064

(Continued)

TABLE II Continued

T/K	x_1	y_1	γ_1	γ_2
383.36	0.4943	0.8687	0.965	0.985
376.70	0.6192	0.9277	0.977	0.902
370.09	0.7581	0.9635	0.991	0.905
364.67	0.8903	0.9876	1.007	0.905
2-Methyl-tetrahydrofuran + bromobenzene at 40.0 kPa				
391.28	0.0272	0.1603	0.872	1.019
387.28	0.0505	0.3052	0.982	0.982
383.56	0.0723	0.3788	0.931	1.016
375.19	0.1322	0.5886	0.974	0.957
367.88	0.1908	0.6882	0.957	1.010
363.31	0.2412	0.7511	0.936	1.019
352.02	0.3748	0.8736	0.972	0.977
345.25	0.4769	0.9223	0.994	0.950
339.36	0.6017	0.9529	0.985	0.976
331.20	0.8031	0.9845	1.007	0.941
329.02	0.8631	0.9904	1.018	0.928
326.75	0.9564	0.9969	1.004	1.049
2-Methyl-tetrahydrofuran + bromobenzene at 101.3 kPa				
425.99	0.0189	0.1127	1.084	0.982
420.86	0.0488	0.2505	1.027	0.979
416.03	0.0799	0.3461	0.951	1.006
410.43	0.1192	0.4635	0.954	1.008
405.57	0.1593	0.5401	0.919	1.041
394.59	0.2577	0.7210	0.962	0.994
383.05	0.3928	0.8400	0.963	1.010
373.07	0.5366	0.9201	0.991	0.930
368.00	0.6285	0.9470	0.996	0.923
364.65	0.6969	0.9633	1.001	0.887
359.60	0.8122	0.9810	1.007	0.897
355.86	0.9152	0.9932	1.008	0.822
2,5-Dimethyl-tetrahydrofuran + bromobenzene at 40.0 kPa				
391.86	0.0275	0.1465	1.101	1.017
388.16	0.0527	0.2629	1.124	1.015
385.09	0.0755	0.3442	1.106	1.023
381.41	0.1044	0.4466	1.135	1.007
377.10	0.1430	0.5402	1.118	1.013
370.56	0.2103	0.6628	1.107	1.016
361.60	0.3260	0.8012	1.106	0.978
357.65	0.4043	0.8514	1.063	0.963
349.53	0.5612	0.9122	1.049	1.070
346.18	0.6488	0.9384	1.038	1.078
341.17	0.8051	0.9716	1.020	1.110
339.29	0.8682	0.9808	1.017	1.205
2,5-Dimethyl-tetrahydrofuran + bromobenzene at 101.3 kPa				
425.04	0.0268	0.1359	1.317	0.988
421.12	0.0551	0.2403	1.219	0.992
417.68	0.0772	0.3029	1.172	1.023

(Continued)

TABLE II Continued

T/K	x_1	y_1	γ_1	γ_2
413.71	0.1109	0.4164	1.212	0.991
408.28	0.1602	0.5188	1.167	1.008
403.04	0.2145	0.6217	1.166	0.987
394.79	0.3185	0.7355	1.114	1.020
388.34	0.4358	0.8356	1.073	0.939
383.01	0.5323	0.8810	1.053	0.976
378.33	0.6302	0.9161	1.039	1.019
371.27	0.8110	0.9670	1.023	1.003
368.65	0.8895	0.9791	1.014	1.194
367.66	0.9217	0.9857	1.012	1.196

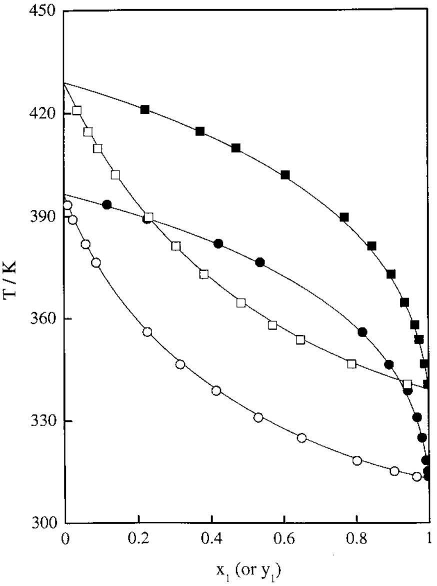

FIGURE 1 $T-x_1-y_1$ diagram for tetrahydrofuran + bromobenzene: (○, ●) exptl. data at 40.0 kPa; (□, ■) exptl. data at 101.3 kPa; (—) Wilson equation.

The thermodynamic consistency of the experimental results was checked using the Van Ness method [16], described by Fredenslund *et al.* [17], using a third order Legendre polynomial for the excess free energies. All the experimental data are consistent (average deviations in y smaller than 0.01), the results are shown in Table IV.

The activity coefficients were correlated with the Wilson, NRTL and UNIQUAC equations. Estimation of the parameters for all the

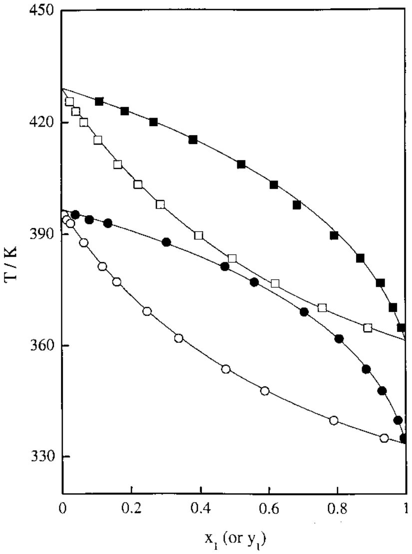

FIGURE 2 $T-x_1-y_1$ diagram for tetrahydropyran + bromobenzene: (○, ●) exptl. data at 40.0 kPa; (□, ■) exptl. data at 101.3 kPa; (—) Wilson equation.

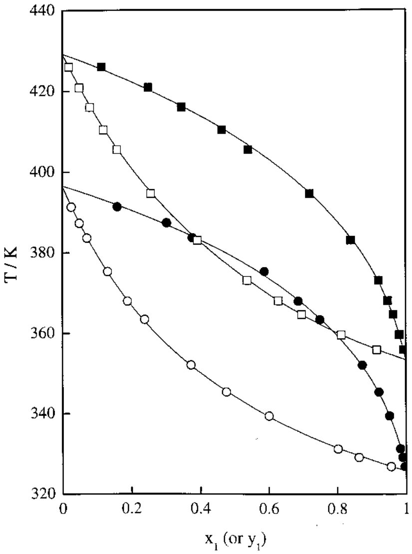

FIGURE 3 $T-x_1-y_1$ diagram for 2-methyl-tetrahydrofuran + bromobenzene: (○, ●) exptl. data at 40.0 kPa; (□, ■) exptl. data at 101.3 kPa; (—) Wilson equation.

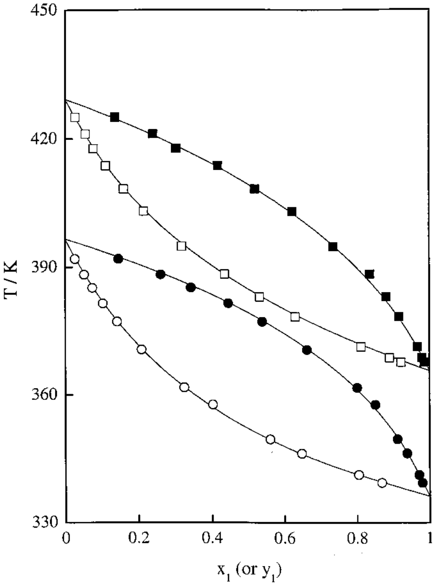

FIGURE 4 $T-x_1-y_1$ diagram for 2,5-dimethyl-tetrahydrofuran + bromobenzene: (○, ●) exptl. data at 40.0 kPa; (□, ■) exptl. data at 101.3 kPa; (—) Wilson equation.

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

Compound	*A*	*B*	*C*
Tetrahydrofuran	6.12142	1203.11	226.355
Tetrahydropyran	5.85520	1131.93	205.83
2-Methyl-tetrahydrofuran	5.95009	1175.51	217.802
2,5-Dimethyl-tetrahydrofuran	5.69272	1099.53	205.719
Bromobenzene	6.37912	1688.4	230

equations was based on minimization, using a non-linear regression procedure [18], of an objective function F in terms of experimental and calculated γ_i values. The function F for a binary system [19] can be stated as:

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

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

System	P/kPa	ΔP/kPa	Δy
Tetrahydrofuran + bromobenzene	40.0	1.1	0.0073
	101.3	1.7	0.0095
Tetrahydropyran + bromobenzene	40.0	0.4	0.0032
	101.3	1.2	0.0038
2-Methyl-tetrahydrofuran + bromobenzene	40.0	0.3	0.0056
	101.3	2.1	0.0052
2,5-Dimethyl-tetrahydrofuran + bromobenzene	40.0	0.3	0.0030
	101.3	1.0	0.0081

where N is the number of experimental data. These adjustable parameters, A_{12} and A_{21}, along with the average deviation in $T(\Delta T)$, the average deviation in y (Δy) and the activity coefficients at infinite dilution are listed in Table V. The average deviation in temperature is less than 0.5 degree and in vapor composition is less than 0.01, so all the equations correlate the activity coefficients quite well.

The systems present a behaviour near to ideality at both pressures, showing slightly negative deviations for tetrahydrofuran and slightly positive deviations for 2,5-dimethyltetrahydrofuran. The specific interactions between the components (Br–O and π(aromatic ring)–O) are practically compensated by the breaking of the dipole–dipole interactions in the pure liquids. This behaviour is very similar to that observed for the systems with chlorobenzene.

VLE Predictions

We have used the UNIFAC method to predict the VLE of the systems with tetrahydrofuran and tetrahydropyran, for systems containing 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran the UNIFAC method cannot be applied because the necessary van de Walls parameters are not available.

Table VI shows the average deviation in temperature and vapour-phase composition obtained applying the UNIFAC method. As one can see in this table the predictions are unsatisfactory, specially for the mixture tetrahydrofuran with bromobenzene. These predictions are worse than those reported in a previous paper [1] for the mixture

TABLE V Correlation parameters, average deviations ΔT and Δy, and activity coefficients at infinite dilution γ_i^∞

Equation	A_{12}^a	A_{21}^a	$\Delta T/\mathrm{K}$	Δy	γ_1^∞	γ_2^∞
Tetrahydrofuran + bromobenzene at 40.0 kPa						
Wilson	−2396.4940	4552.1503	0.44	0.0068	0.84	0.79
NRTL	5137.0377	−3834.5732	0.39	0.0069	0.83	0.73
UNIQUAC	549.7386	−1000.4572	0.48	0.0047	0.87	0.65
Tetrahydrofuran + bromobenzene at 101.3 kPa						
Wilson	−622.5851	−117.2710	0.48	0.0091	0.79	0.67
NRTL	6334.0827	−4467.3310	0.26	0.0066	0.81	0.74
UNIQUAC	−23.1249	−603.3423	0.40	0.0076	0.81	0.67
Tetrahydropyran + bromobenzene at 40.0 kPa						
Wilson	−2060.8034	2504.8174	0.28	0.0042	0.88	0.75
NRTL	2810.2538	−2645.3664	0.27	0.0043	0.87	0.77
UNIQUAC	514.4120	−895.6522	0.28	0.0043	0.88	0.75
Tetrahydropyran + bromobenzene at 101.3 kPa						
Wilson	−2205.1798	3188.5321	0.38	0.0074	0.93	0.90
NRTL	2729.2343	−2431.2668	0.38	0.0075	0.93	0.88
UNIQUAC	2764.5386	−2237.9089	0.18	0.0043	1.00	0.77
2-Methyl-tetrahydrofuran + bromobenzene at 40.0 kPa						
Wilson	693.1807	−826.9402	0.20	0.0056	0.94	0.93
NRTL	−791.8399	642.1297	0.20	0.0056	0.94	0.93
UNIQUAC	−960.5121	749.3557	0.25	0.0059	0.93	0.96
2-Methyl-tetrahydrofuran + bromobenzene at 101.3 kPa						
Wilson	−2732.3844	4634.5046	0.23	0.0059	0.93	0.98
NRTL	3486.0379	−2872.2729	0.32	0.0065	0.93	0.88
UNIQUAC	3490.8515	−2508.8106	0.38	0.0061	1.03	0.83
2,5-Dimethyl-tetrahydrofuran + bromobenzene at 40.0 kPa						
Wilson	−1943.1815	3335.7584	0.23	0.0035	1.14	1.37
NRTL	3758.6371	−2272.8399	0.27	0.0031	1.13	1.36
UNIQUAC	−480.9168	410.3225	0.34	0.0043	1.16	1.15
2,5-Dimethyl-tetrahydrofuran + bromobenzene at 101.3 kPa						
Wilson	1394.2541	−460.2868	0.36	0.0081	1.25	1.17
NRTL	−1349.6238	2290.3544	0.35	0.0078	1.24	1.17
UNIQUAC	3745.4006	−2381.3194	0.39	0.0047	1.23	1.44

[a] Joules per mole.

TABLE VI UNIFAC VLE predictions, average deviations ΔT and Δy

System	P/kPa	$\Delta T/\mathrm{K}$	Δy
Tetrahydrofuran + bromobenzene	40.0	1.82	0.0118
	101.3	2.34	0.0140
Tetrahydropyran + bromobenzene	40.0	1.56	0.0131
	101.3	0.83	0.0064

tetrahydrofuran and tetrahydropyran with chlorobenzene. This fact can be explained taking into account that UNIFAC has an only group for the bromine atom while presents seven different groups containing the chlorine one. Consequently, the lack of specialization of the bromine group leads to a poorer performance of the method.

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