J. Chem. Eng. Data **1999,** *44,* 869−872

Vapor−Liquid Equilibria for the Binary Systems Isobutanol with *m*-Xylene, *o*-Xylene and *p*-Xylene at 101.3 kPa

M. T. Lores, J. de la Torre, M. C. Burguet, and J. B. Montón*

Departamento de Ingeniería Química, Facultad de Química, Universidad de Valencia,
46100 Burjassot, Valencia, Spain

Vapor−liquid equilibria were measured for binary systems of isobutanol with *m*-xylene, *o*-xylene, and *p*-xylene at 101.3 kPa using a recirculating still. The accuracy of experimental measurements was ±0.1 K in temperature, ±0.01 kPa in pressure, and ±0.001 in mole fraction. The results were determined to be thermodynamically consistent according to the point-to-point consistency and Wisniak tests. All the systems show moderate positive deviations from ideality. The data were correlated with five liquid-phase activity coefficient models (Margules, Van Laar, Wilson, NRTL, UNIQUAC).

Introduction

Experimental determinations of vapor−liquid equilibria (VLE) are indispensable for the design of distillation columns and the selection of solvents. Although these data can be estimated from available VLE models, experimental data are required to update and improve the data bank used to fit the model parameters.

Additionally, pollution has become one of the most important problems of our world. For this reason, gasoline and its composition have been largely studied by different branches of research. The composition of reformulated gasoline includes a large amount of oxygenated additives such as ethers and alcohols such as isobutanol that have a elevated octane number and little pollutant effect. Other components such as *m*-xylene, *o*-xylene, and *p*-xylene, which are aromatic hydrocarbons, also appear in gasoline, although as minor fractions.

In this paper, we report VLE data at constant pressure (101.3 kPa) for the binary systems isobutanol with *m*-xylene, *o*-xylene, and *p*-xylene. Only one paper published in the last 30 years has been found which concerns some of these systems. Oracz (1989) studied the system *p*-xylene with isobutanol at one temperature (313.15 K). Previously, Chiolan (1962) studied these three systems at 101.3 kPa and Garber (1962) studied the effect of pressure on the azeotropic compositions. Bonauguri (1951) presented only the experimental liquid- and vapor-phase concentrations at 100 kPa.

The results have been treated considering the non-ideality of both liquid and vapor phases, and the thermodynamic consistency of experimental data has been verified by the methods of Van Ness−Byer−Gibbs and Wisniak.

Experimental Section

Chemicals. The chemicals isobutanol (99.5%), *m*-xylene (99%), *o*-xylene (98%), and *p*-xylene (99%) were supplied by Aldrich. *o*-Xylene was purified by batch distillation in a Fisher SPALTROUHR columm HMS-500, controlled by a Fisher System D•301-C, but it was impossible to get a purity higher than 98.5 mass %. The final purity of all chemicals was checked by gas chromatography. The physical properties (densities, refractive indexes, and normal boiling points) of the three compounds are listed in Table 1 with literature values.

Table 1. Physical Properties of Chemicals: Densities ρ and Refractive Indexes η at 298.15 K and Normal Boiling Points T_b of Pure Compounds

	ρ/kg·m^{-3}		η		T_b/K	
compound	exptl	lit.	exptl	lit.	exptl	lit
isobutanol	797.83	798.30[a]	1.3937	1.3937[a]	381.15	380.90[a]
m-xylene	859.66	860.06[a]	1.4946	1.4946[b]	412.45	412.27[b]
o-xylene	875.49	875.58[a]	1.5029	1.5029[b]	417.55	417.58[b]
p-xylene	856.55	856.48[b]	1.4930	1.4932[b]	411.65	411.51[b]

[a] TRC (1996). [b] Daubert and Danner (1989).

Apparatus and Procedure. The apparatus used in this work is an all-glass, dynamic recirculating still equipped with a Cottrell pump, described by Walas (1985). The still (Labodest model), manufactured by Fisher Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also that contact between the phases and the sensor element is maintained. The equilibrium temperature was measured with a digital Fisher thermometer provided with a 2 mm diameter Pt-100 temperature sensor with an accuracy of ±0.1 K, and the pressure was measured with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated at the ice and steam points of distilled water. The manometer was calibrated with vapor pressure data of high-purity hexane (99.9 mass %).

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was turned on. The still was operated until equilibrium was reached. At this time, samples (3 μL) of liquid and condensed vapor were taken with special chromatographic syringes, until constant composition was observed; sampling did not disrupt operation of the still.

All the samples were analyzed using a Hewlett-Packard 5890 S-II gas chromatograph (GC) after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d. fused silica capillary column, Supelcowax 10. The GC

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* To whom correspondence should be addressed. E-mail: Juan.B.Monton@uv.es.

10.1021/je980275i CCC: $18.00

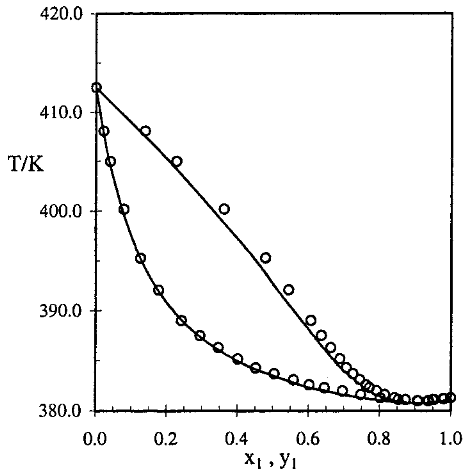

Figure 1. $T-x_1-y_1$ diagram for the system isobutanol (1) + *m*-xylene (2) at constant pressure, $P = 101.3$ kPa: ○, experimental; —, Margules model.

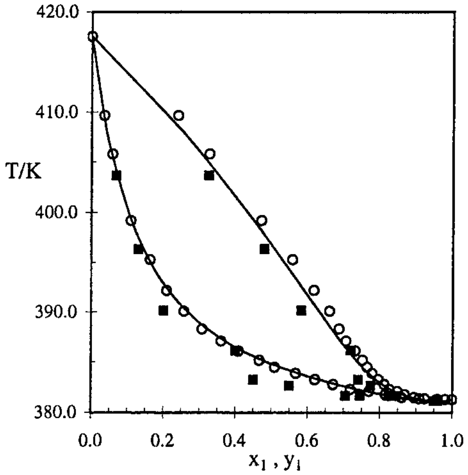

Figure 2. $T-x_1-y_1$ diagram for the system isobutanol (1) + *o*-xylene (2) at constant pressure, $P = 101.3$ kPa: ○, our experimental data; ■, Chiolan, I., et al., 1962; —, Margules model.

response peaks were integrated using a Hewlett-Packard 3396 integrator. The accuracy of the mole fraction was ±0.001. At least two analyses were performed for each liquid and each vapor sample.

Results and Discussion

Antoine constants for isobutanol were taken from Martinez-Soria et al. (1999), the constants for *m*-xylene and *p*-xylene were taken from Ambrose (1987), and the constants for *o*-xylene were taken from Forziati (1949).

VLE data (T, x_1, and y_1) along with the calculated activity coefficients at 101.3 kPa are presented in Tables 2−4 and Figures 1−3. Both systems isobutanol with *m*-xylene and *p*-xylene show a minimum boiling azeotrope, but there is no azeotrope in the system isobutanol with *o*-xylene. The composition and boiling temperature of the azeotropes are summarized in Table 5 together with literature values. Azeotropic compositions have been obtained, in all cases, by determining x_1 values that make zero the best polynomial fit of the function $(x_1 - y_1) = f(x_1)$. Azeotropic temperatures have been obtained from the best polynomial fit for $T = f(x_1)$, using the x_1 values previously determined.

The activity coefficients γ_i were calculated, taking into account the nonideality of the vapor phase, from the equation (Van Ness and Abbott, 1982)

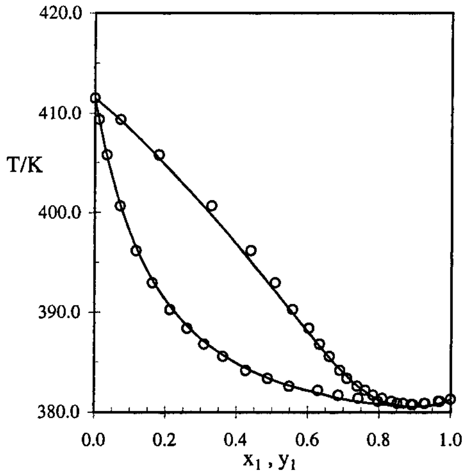

Figure 3. $T-x_1-y_1$ diagram for the system isobutanol (1) + *p*-xylene (2) at constant pressure, $P = 101.3$ kPa: ○, experimental; —, Margules model.

Table 2. Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the System Isobutanol (1) + *m*-Xylene (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
412.5	0	0		
408.1	0.0223	0.1392	2.6593	0.9868
405.0	0.0411	0.2274	2.5832	0.9810
400.2	0.0792	0.3620	2.4600	0.9623
395.3	0.1270	0.4785	2.3574	0.9532
392.1	0.1781	0.5441	2.1170	0.9712
389.0	0.2425	0.6074	1.9190	0.9950
387.5	0.2951	0.6369	1.7379	1.0345
386.3	0.3471	0.6632	1.6015	1.0747
385.2	0.4017	0.6893	1.4927	1.1186
384.3	0.4523	0.7077	1.4033	1.1820
383.7	0.5045	0.7259	1.3171	1.2481
383.1	0.5587	0.7455	1.2469	1.3257
382.6	0.6026	0.7624	1.2027	1.3962
382.3	0.6458	0.7722	1.1485	1.5161
382.0	0.6968	0.7926	1.1040	1.6275
381.6	0.7477	0.8153	1.0729	1.7645
381.3	0.8030	0.8431	1.0440	1.9375
381.1	0.8538	0.8733	1.0242	2.1209
381.0	0.9068	0.9093	1.0075	2.3918
381.0	0.9391	0.9369	1.0023	2.5472
381.1	0.9539	0.9501	0.9973	2.6480
381.2	0.9822	0.9795	0.9949	2.8202
381.2	1.0000	1.0000		

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and x_i and y_i are the liquid- and vapor-phase compositions, T and P are the boiling point and the total pressure, $P_i^\circ$are the vapor pressures of pure compounds, B_{ii} are the second virial coefficients of pure gases, B_{ij} are the cross second virial coefficients, and V_i^{L} are the molar volumes of the saturated liquids. The last two terms in eq 1, particularly the second one which expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 3% to the activity coefficients; in general, its influence was important only at very dilute concentrations. The molar virial coefficients B_{ii} and B_{ij} were estimated by means of the Pitzer and Curl equations (1957) with the corrections proposed by Tsonopoulos (1974). The critical properties of both components and the molar volumes of the saturated liquids were taken from DIPPR (Daubert and Danner, 1989). Figures 4−6 show the

Table 3. Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i, for the System Isobutanol (1) + *o*-Xylene (2) at 101.3 KPa

T/K	x_1	y_1	γ_1	γ_2
417.6	0	0		
409.7	0.0353	0.2398	2.7689	0.9672
405.8	0.0580	0.3275	2.5713	0.9730
399.2	0.1098	0.4720	2.3844	0.9709
395.3	0.1635	0.5578	2.1348	0.9679
392.2	0.2099	0.6175	2.0317	0.9707
390.1	0.2579	0.6609	1.8935	0.9756
388.3	0.3081	0.6878	1.7502	1.0170
387.1	0.3606	0.7067	1.5994	1.0721
386.1	0.4091	0.7319	1.5094	1.0937
385.2	0.4671	0.7523	1.4009	1.1517
384.5	0.5097	0.7655	1.3376	1.2113
383.9	0.5678	0.7794	1.2479	1.3170
383.3	0.6214	0.7960	1.1888	1.4165
382.8	0.6711	0.8125	1.1430	1.5222
382.3	0.7194	0.8272	1.1045	1.6702
382.1	0.7706	0.8495	1.0661	1.7912
381.8	0.8158	0.8693	1.0413	1.9562
381.5	0.8610	0.8960	1.0276	2.0815
381.4	0.9093	0.9246	1.0076	2.3204
381.3	0.9572	0.9603	0.9976	2.5987
381.3	0.9811	0.9817	0.9949	2.7188
381.2	1.0000	1.0000		

Table 4. Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i, for the System Isobutanol (1) + *p*-Xylene (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
411.7	0	0		
409.4	0.0122	0.0723	2.4384	1.0012
405.8	0.0339	0.1806	2.5128	0.9870
400.7	0.0719	0.3288	2.4666	0.9863
396.2	0.1170	0.4391	2.3343	0.9855
393.0	0.1629	0.5079	2.1061	0.9827
390.3	0.2122	0.5568	1.9267	1.0148
388.4	0.2610	0.6025	1.8043	1.0265
386.8	0.3089	0.6328	1.6887	1.0639
385.6	0.3621	0.6604	1.5649	1.1058
384.2	0.4261	0.6902	1.4576	1.1702
383.4	0.4876	0.7103	1.3581	1.2466
382.6	0.5480	0.7386	1.2812	1.3173
382.2	0.6284	0.7610	1.1671	1.4836
381.7	0.6856	0.7831	1.1201	1.6163
381.4	0.7416	0.8089	1.0809	1.7484
381.1	0.7972	0.8355	1.0494	1.9367
380.9	0.8509	0.8677	1.0283	2.1309
380.8	0.8899	0.8947	1.0173	2.3053
380.9	0.9291	0.9265	1.0054	2.4931
381.1	0.9703	0.9660	0.9968	2.7364
381.2	1.0000	1.0000		

Table 5. Composition (y_{az}) and Boiling Temperature (T_{az}) of the Azeotropic Mixtures (P = 101.3 kPa)

	exptl		lit.		
system	y_{az}	T_{az}/K	y_{az}	T_{az}/K	ref
IBA + *m*-xylene	0.933	380.9	0.93	380.35	Garber, 1962
IBA + *o*-xylene					
IBA + *p*-xylene	0.915	380.8	0.92	380.25	Garber, 1962

activity coefficients γ_i calculated from eq 1 and those calculated from the Margules model.

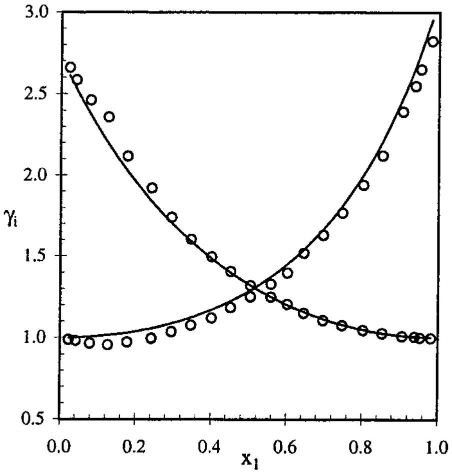

Figure 4. Activity coefficient plots for the system isobutanol (1) + *m*-xylene (2): ○, experimental; —, Margules model.

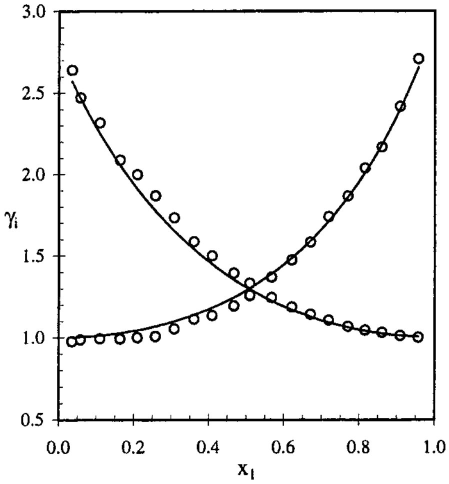

Figure 5. Activity coefficient plots for the system isobutanol (1) + *o*-xylene (2): ○, experimental; —, Margules model.

Table 6. Thermodynamic Consistency Tests

	Van Ness-Byer−Gibbs		Wisniak		
system	MAD(*y*)	MAD(*P*)/kPa	*L*	*W*	*D*
IBA + *m*-xylene	0.0049	0.241	8.42	8.53	0.65
IBA + *o*-xylene	0.0075	0.256	10.03	10.17	0.69
IBA + *p*-xylene	0.0051	0.216	8.33	8.75	2.46

The thermodynamic consistency of the results was tested by the point-to-point test of Van Ness−Byer−Gibbs (1973), described by Fredenslund et al. (1977), and the *L*−*W* method of Wisniak (1993). For the Van Ness method, a four-parameter Legendre polynomial was used for the excess Gibbs free energy. According to this test, the experimental data are consistent if the average deviation in *y* (Δy) is smaller than 0.01. The *L*−*W* method of Wisniak requires the evaluation of the integrals *L* and *W* as described in the paper by Wisniak (1993). Values of the deviation *D* defined as

$$D = 100\cdot\frac{|L - W|}{L + W} \tag{2}$$

which are less than 5 indicate thermodynamic consistency. All the experimental data are thermodynamically consistent according to both methods, as shown in Table 6.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (Gmehling and Onken, 1977). For the purpose of fitting the binary parameters, a nonlinear optimization method was used to minimize the objective function

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

Table 7. Correlation Parameters for the Activity Coefficients, the Activity Coefficients at Infinite Dilution γ_i^∞, and the Mean Absolute Deviations MAD(y) and MAD(T)

model	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(y)	MAD(T)/K
			IBA (1) + m-xylene (2) System				
Margules	0.9990[a]	1.12658[a]		2.715 45	3.085 08	0.0089	0.269
Van Laar	1.0032[a]	1.12720[a]		2.727 06	3.086 99	0.0089	0.265
Wilson	2669.12[b]	1363.92[b]		2.973 76	3.217 52	0.0104	0.239
NRTL	2711.86[b]	1346.56[b]	0.533[a]	2.667 91	3.416 08	0.0113	0.282
UNIQUAC	705.48[b]	293.08[b]		2.679 17	3.433 90	0.0103	0.337
			IBA (1) + o-xylene (2) System				
Margules	1.0069[a]	1.11016[a]		2.737 13	3.034 86	0.0144	0.184
Van Laar	0.0103[a]	1.11044[a]		2.746 37	3.035 69	0.0153	0.188
Wilson	2445.465[b]	1232.298[b]		2.733 23	2.934 86	0.0183	0.509
NRTL	2745.10[b]	1319.09[b]	0.421[a]	2.810 21	3.491 81	0.0150	0.295
UNIQUAC	654.47[b]	274.54[b]		2.527 27	3.176 16	0.0132	0.386
			IBA (1) + p-xylene (2) System				
Margules	0.9598[a]	1.14139[a]		2.611 28	3.131 10	0.0061	0.185
Van Laar	0.9407[a]	1.14885[a]		2.561 84	3.154 55	0.0067	0.139
Wilson	1988.66[b]	2037.09[b]		2.621 67	3.491 23	0.0092	0.224
NRTL	2804.29[b]	1204.65[b]	0.476[a]	2.650 66	3.444 12	0.0080	0.165
UNIQUAC	471.46[b]	498.93[b]		2.711 28	3.231 10	0.0070	0.112

[a] Dimensionless. [b] $J \cdot mol^{-1}$

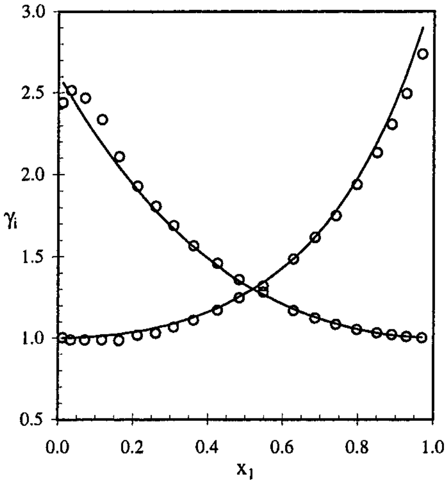

Figure 6. Activity coefficient plots for the system isobutanol (1) + p-xylene (2): ○, experimental; —, Margules model.

where N is the number of experimental data. The adjustable parameters A_{12}, A_{21}, and α_{12} obtained for the different correlation equations, the mean absolute deviation, and the activity coefficients at infinite dilution γ_i^∞ are given in Table 7.

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Received for review November 10, 1998. Accepted May 4, 1999. This work was financed by CICYT, Spain (Project No. PB96-0788).

JE980275I