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Vapor−Liquid Equilibria for the Binary Systems Isobutyl Alcohol + Toluene, + Isooctane, and + Methylcyclohexane at 101.3 kPa

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The vapor−liquid equilibrium at 101.3 kPa and at temperatures from 364 K to 384 K has been determined for binary systems of isobutyl alcohol with toluene, isooctane, and methylcyclohexane, using a recirculating still. All the systems show a minimum boiling temperature azeotrope. The results are thermodynamically consistent according to the point-to-point consistency test. The experimental data were correlated with the help of the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models.

Introduction

The present work represents a continuation of a series of experimental studies on vapor−liquid equilibria for binary systems containing oxygenated additives of reformulated gasoline: methyl isobutyl ether (MTBE), *tert*-amyl methyl ether (TAME), and alcohols (methanol, ethanol, *tert*-butyl alcohol (TBA), and isobutyl alcohol (IBA)). These oxygenated compounds have elevated octane numbers and little pollutant effect (Chang, 1994). The purpose of this work is to obtain VLE data of the binary mixtures of isobutyl alcohol with three hydrocarbons (toluene, methylcyclohexane, and isooctane (2,2,4-trimethylpentane)) which are representative compounds of the aromatic, naftenic, and paraffinic hydrocarbon main fractions of the gasoline pool.

For the binary systems IBA + isooctane and IBA + methylcyclohexane, no experimental vapor−liquid equilibrium data have been published up to now. However, we have found in the literature some experimental vapor−liquid equilibrium data for the binary system IBA + toluene. Most of them are isothermal data (Susarev et al., 1973; Lnenickova and Wichterle, 1977; Oracz, 1989), but we have found isobaric vapor−liquid equilibrium data too (Kireev, 1952). Recently, data for the binary system IBA + octane have been published (Hiaki et al., 1998). In this work, the results have been treated considering the nonideality of both liquid and vapor phases and the thermodynamic consistency of experimental data has been verified.

Experimental Section

Chemicals. The chemicals isobutyl alcohol (2-methyl-1-propanol) (>99.5%), methylcyclohexane (>99%), toluene (>99.8%), and isooctane (2,2,4-trimethylpentane) (>99.7%) were supplied by Aldrich. The purity of all chemicals was checked by gas chromatography (GC), and the results of these analyses showed that the impurities did not exceed 0.2 mass %. The pure components were degassed ultrasonically. The liquids were used without further purification. The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. The temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements were ±0.01 kg m^{-3} and ±0.0002, respectively. The experimental values of these properties and the boiling points of pure compounds are given in Table 1 along with the corresponding values found in the literature.

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

	ρ/kg•m^{-3}		n		T_b/K	
compound	exptl	lit.	exptl	lit.	exptl	lit.
IBA	797.83	798.30[b]	1.3937	1.3937[b]	381.1	380.9[b]
toluene	861.87	862.13[a]	1.4940	1.4942[a]	383.8	383.8[a]
isooctane	687.67	687.80[a]	1.3890	1.3890[a]	372.5	372.4[a]
methylcyclohexane	764.87	764.59[a]	1.4204	1.4206[a]	374.0	374.1[a]

[a] *TRC* (1996a). [b] *TRC* (1996b).

Table 2. Experimental Vapor Pressure $P_i°$, Antoine Coefficients A, B, and C, Standard Deviations (σ) of IBA, and Antoine Coefficients of Toluene, Isooctane, and Methylcyclohexane

T/K	$P°$/kPa	T/K	$P°$/kPa	T/K	$P°$/kPa
341.9	19.39	360.7	45.43	375.2	81.29
345.2	22.67	361.9	47.79	376.2	84.45
346.8	24.48	363.0	49.95	377.4	88.23
347.4	25.18	364.4	53.03	378.5	91.89
350.8	29.43	366.0	56.60	379.5	95.37
352.5	31.80	367.1	59.14	380.2	97.76
354.6	34.88	368.6	62.83	381.1	101.33
355.7	36.69	370.2	66.85	382.2	105.20
356.0	37.22	371.2	69.50	383.9	111.95
358.3	40.98	372.6	73.53	385.7	119.37
359.4	43.09	373.9	77.34	387.3	126.28

	A	B	C	σ^a
IBA	15.07065	3001.427	−93.9496	0.075
isooctane	13.80220	2999.098	−45.9600	
methylcyclohexane	13.64381	2891.014	−53.8124	
toluene	13.84529	2998.040	−58.7957	

[a] $\sigma = [\sum(P° - P_{calc}°)^2/(N - p)]^{1/2}$ where N is the number of points and p is the number of parameters.

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic recirculating still equipped with a Cottrell pump. This apparatus is a modified version of the Gillespie still described by Walas (1985). The still (Labodest model) manufactured by Fischer

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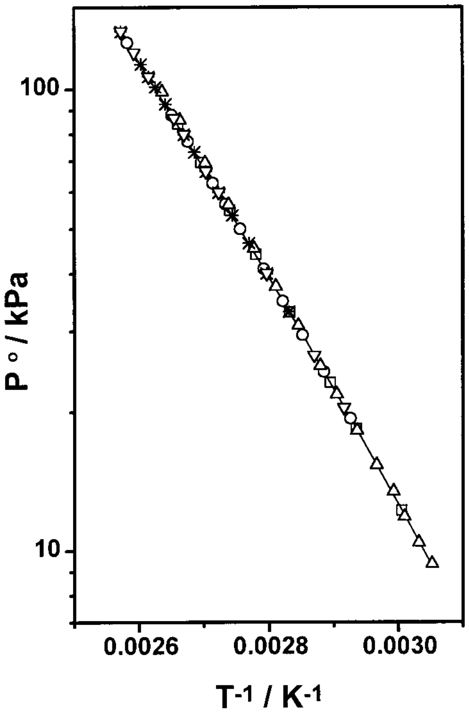

Figure 1. Vapor pressures $P°$ of isobutyl alcohol as a function of temperature: (○) our data; (□) Brown et al., 1969; (△) Suska et al., 1970; (∗) Biddiscombe et al., 1963; (▽) Ambrose and Sprake, 1970; (—) Antoine equation adjustment of our data.

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 IBA (1) + Toluene (2) at 101.3 KPa

T/K	x_1	y_1	γ_1	γ_2
383.8	0	0		
383.0	0.0106	0.0363	3.222	0.995
380.3	0.0497	0.1414	2.942	0.995
378.6	0.0849	0.2090	2.700	0.998
376.9	0.1408	0.2822	2.335	1.012
375.8	0.2012	0.3328	2.004	1.044
374.9	0.2700	0.3766	1.746	1.096
374.6	0.3306	0.4128	1.581	1.136
374.3	0.3729	0.4356	1.495	1.176
374.2	0.4249	0.4585	1.385	1.234
374.1	0.4719	0.4796	1.309	1.295
374.2	0.5607	0.5225	1.196	1.424
374.3	0.6107	0.5492	1.150	1.513
374.5	0.6592	0.5780	1.113	1.609
375.0	0.7230	0.6203	1.069	1.756
375.5	0.7646	0.6481	1.037	1.888
376.1	0.8134	0.7010	1.032	1.989
377.0	0.8594	0.7548	1.018	2.111
378.1	0.9078	0.8213	1.008	2.276
379.0	0.9409	0.8719	1.000	2.481
380.0	0.9714	0.9363	1.004	2.477
381.1	1.000	1.000		

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 in contact with the sensor element. The equilibrium temperature was measured with a digital Fisher thermometer with an accuracy of ±0.1 K, and the pressure with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometer was calibrated using the vapor pressure data of high-purity hexane (Daubert and Danner, 1995).

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 IBA (1) + Isooctane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
372.5	0	0		
370.9	0.0143	0.0562	5.714	1.000
367.9	0.0546	0.1576	4.702	1.009
366.1	0.1055	0.2254	3.730	1.031
365.2	0.1768	0.2732	2.793	1.078
365.0	0.1912	0.2806	2.674	1.092
364.7	0.2630	0.3038	2.129	1.170
364.6	0.3293	0.3238	1.819	1.252
364.7	0.3660	0.3346	1.685	1.300
364.8	0.4376	0.3534	1.482	1.420
365.2	0.5179	0.3780	1.318	1.576
365.6	0.5899	0.4025	1.213	1.760
366.0	0.6195	0.4167	1.177	1.832
366.6	0.6743	0.4416	1.119	2.015
367.4	0.7273	0.4696	1.069	2.236
368.3	0.7697	0.5022	1.044	2.425
369.3	0.8057	0.5339	1.020	2.619
370.9	0.8521	0.5880	0.999	2.914
372.9	0.8938	0.6596	0.992	3.180
375.1	0.9313	0.7505	0.998	3.402
378.5	0.9730	0.8750	0.986	3.974
381.1	1.000	1.000		

Table 5. 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 IBA (1) + Methylcyclohexane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
374.0	0	0		
370.4	0.0368	0.1350	5.428	0.994
367.9	0.0866	0.2172	4.081	1.017
366.8	0.1356	0.2583	3.233	1.050
366.3	0.1885	0.2872	2.636	1.090
366.0	0.2354	0.3024	2.249	1.142
365.9	0.2874	0.3190	1.950	1.200
365.8	0.3410	0.3356	1.736	1.270
365.9	0.3932	0.3508	1.567	1.344
366.1	0.4474	0.3677	1.432	1.429
366.3	0.5070	0.3869	1.319	1.544
366.6	0.5538	0.3993	1.232	1.658
367.1	0.6144	0.4294	1.171	1.797
367.7	0.6620	0.4540	1.123	1.929
368.5	0.7093	0.4840	1.083	2.073
369.6	0.7603	0.5234	1.047	2.252
370.7	0.8041	0.5668	1.029	2.430
372.2	0.8473	0.6140	0.999	2.667
374.3	0.8960	0.6920	0.985	2.952
373.8	0.8823	0.6715	0.989	2.820
375.7	0.9241	0.7629	1.001	3.001
378.2	0.9634	0.8615	0.991	3.403
379.8	0.9834	0.9338	0.994	3.441
381.1	1.000	1.000		

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was turned on. The still was operating until equilibrium was reached. Equilibrium conditions were assumed when temperature and pressure remained constant for 30 min or longer. After this time, samples (1 μL) of liquid and condensed vapor were repeatedly taken with special chromatographic syringes, until constant composition was observed, without disruption of the operation.

All the samples were analyzed using a Hewlett-Packard 5890 S-II gas chromatograph after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used in conjunction with a 60 m, 0.2 mm i.d. fused silica capillary column, Supelcowax 10. The GC response peaks were integrated using a Hewlett-Packard 3396 integrator. The experimental error in these measurements was less than ±0.001 mole fraction.

Table 6. Composition (y_{az}) and Boiling Temperature (T_{az}) of the Azeotropic Mixtures

	exptl		lit.		
system	y_{az}	T_{az}/K	y_{az}	T_{az}/K	ref
IBA + toluene	0.4883	374.1	0.4839	373.2	Gmehling et al., 1994
IBA + isooctane	0.3189	364.6	0.3631	365.2	Gmehling et al., 1994
IBA + methylcyclohexane	0.3296	365.8	0.3621	366.4	Gmehling et al., 1994

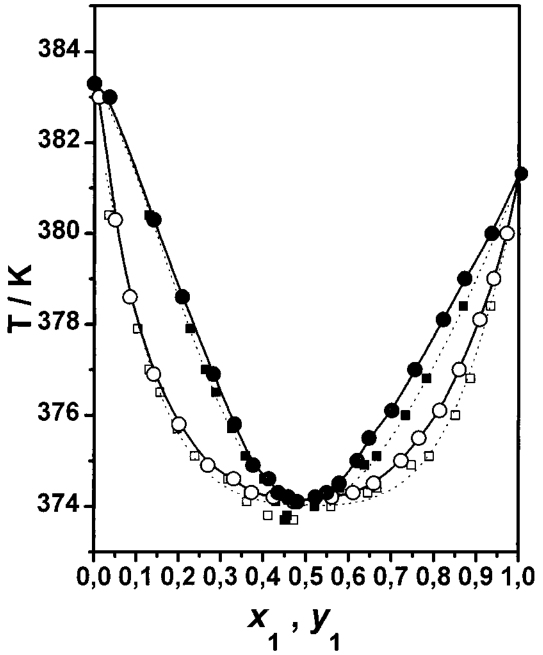

Figure 2. $T-x_1-y_1$ diagram at constant pressure, $P = 101.3$ kPa, of the system IBA (1) + toluene (2): (○, ●) our experimental data; (□, ■) Kireev et al. data, 1952; (—, ···) splined curves.

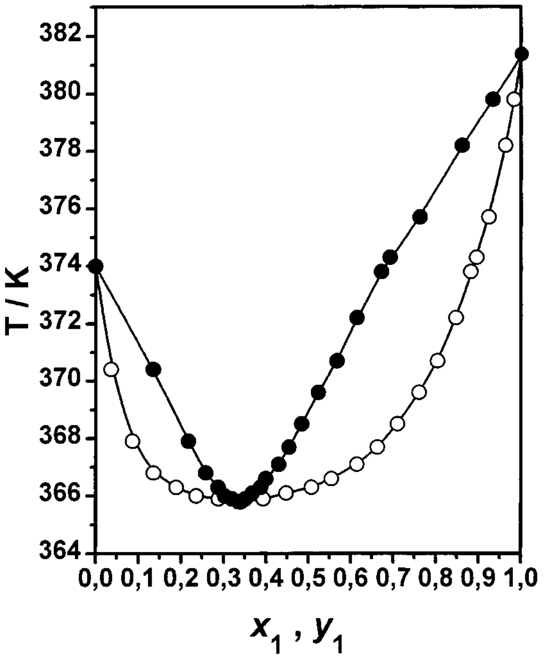

Figure 4. $T-x_1-y_1$ diagram at constant pressure, $P = 101.3$ kPa, of the system IBA (1) + methylcyclohexane (2): (○, ●) experimental data; (—) splined curve.

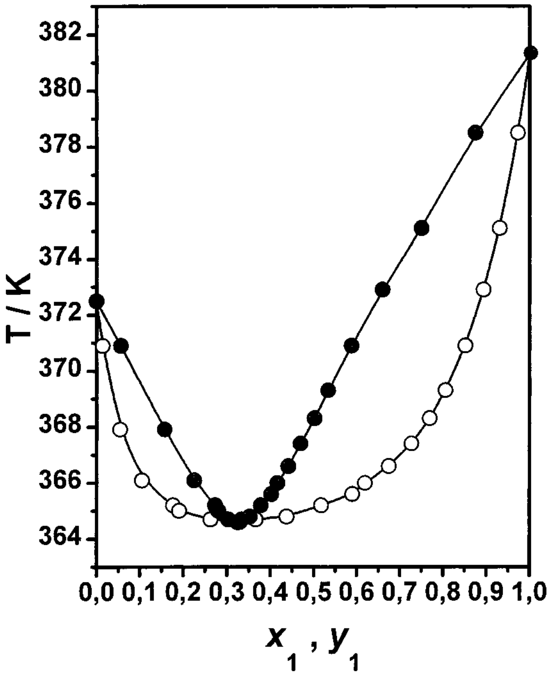

Figure 3. $T-x_1-y_1$ diagram at constant pressure, $P = 101.3$ kPa, of the system IBA (1) + isooctane (2): (○, ●) experimental data; (—) splined curve.

Table 7. Thermodynamic Consistency Test of Van Ness−Byer Gibbs

system	MAD(y)	MAD(P)/kPa
IBA + toluene	0.0047	0.18
IBA + isooctane	0.0028	0.16
IBA + methylcyclohexane	0.0062	0.16

Results and Discussion

The vapor pressures $P°$ of pure isobutyl alcohol are presented in Table 2 and Figure 1. This figure shows that these values are in close agreement with those reported in the literature (Ambrose and Sprake, 1969; Biddiscombe et al., 1963; Brown et al., 1970; Suska et al., 1970). Antoine constants for this component were obtained from the experimental values of vapor pressure obtained, and they are presented in Table 2. The constants were calculated by a nonlinear optimization method to minimize the mean relative deviation, MRD(P). Antoine constants for methylcyclohexane, toluene, and isooctane were obtained from our own vapor pressure measurements in a previous work (Martínez-Soria et al., 1999); the values are shown in Table 2.

VLE data (T, x_1, and y_1) along with calculated activity coefficients at 101.3 kPa are presented in Tables 3−5, and $T-x_1-y_1$ diagrams are shown in Figures 2−4. In Figure 2 we plotted our experimental data along with Kireev et al. (1952) data. All the systems show a minimum boiling temperature azeotrope. The compositions and boiling temperatures of the azeotropes are summarized in Table 6 together with the corresponding literature values. In all cases, the azeotropic composition was obtained from the best polynomial fit of the function $(x_1 - y_1) = f(x_1)$. Azeotropic temperatures were 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

Table 8. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞, and 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 + Toluene				
Margules	1.216[a]	0.986[a]		3.375	2.681	0.0031	0.28
Van Laar	1.220[a]	1.002[a]		3.388	2.724	0.0028	0.28
Wilson	3145[b]	1059[b]		3.516	2.899	0.0027	0.34
NRTL	1519[b]	2710[b]	0.508[a]	3.501	2.883	0.0027	0.34
UNIQUAC	85.16[b]	942.7[b]		3.233	2.844	0.0033	0.27
			IBA + Isooctane				
Margules	1.792[a]	1.272[a]		6.004	3.569	0.0088	0.29
Van Laar	1.806[a]	1.271[a]		6.090	3.565	0.0079	0.15
Wilson	5875[b]	401.4[b]		6.172	4.231	0.0077	0.19
NRTL	1829[b]	4383[b]	0.508[a]	6.418	3.817	0.0075	0.16
UNIQUAC	−1135[b]	3269[b]		5.740	3.602	0.0091	0.19
			IBA + Methylcyclohexane				
Margules	1.857[a]	1.242[a]		6.405	3.373	0.0115	0.19
Van Laar	1.946[a]	1.253[a]		6.994	3.514	0.0110	0.20
Wilson	6902[b]	490.7[b]		9.776	3.796	0.0058	0.18
NRTL	2326[b]	5966[b]	0.508[a]	10.997	3.939	0.0092	0.17
UNIQUAC	−987.4[b]	3112[b]		7.562	3.541	0.0087	0.12

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

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

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$, x_i is the mole fraction of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, P is the system pressure, P_i° is the vapor pressure of the pure component i calculated with the Antoine equation, B_{ii} is the second virial coefficient of the pure gas, B_{ij} is the cross second virial coefficient, and V_i° is the molar volume of the saturated liquid. The molar virial coefficients B_{ii} and B_{ij} were estimated by means of the Pitzer and Curl equations (1957) with the correction 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, 1995).

The thermodynamic consistency of the results was tested by the point-to-point method of Van Ness et al. (1973), modified by Fredenslund et al. (1977). A four-parameter Legendre polynomial was used for the excess Gibbs energy. According to Fredenslund et al. (1977), the P, T, x, and y data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase $\delta(y)$ is less than 0.01. According to this method, the results obtained were consistent, as can be seen in Table 7.

In Figure 2, it can be seen that there are appreciable deviations between our experimental data and the Kireev et al. data for mole fractions of TBA greater than 0.45. These deviations may be due to experimental errors in the Kireev et al. data, since these data are not thermodynamically consistent according to the test of Van Ness. The value of $\delta(y)$ obtained for these data is greater than 0.01, and the errors calculated for most points corresponding to values of $x_1 > 0.45$ are especially high.

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

$$F = \sum_{i=1}^{i=N}\left[(y_{\text{exp}} - y_{\text{calc}})^2 + \left(\frac{T_{\text{exp}} - T_{\text{calc}}}{T_{\text{exp}}}\right)^2\right]_i \tag{2}$$

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 8.

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