Vapor−Liquid Equilibria for the Binary Systems *tert*-Butyl Alcohol + Toluene, + Isooctane, and + Methylcyclohexane at 101.3 kPa

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Vapor−liquid equilibria were measured for binary systems of *tert*-butyl alcohol with toluene, isooctane, and methylcyclohexane at 101.3 kPa using a recirculating still. Experimental values of the vapor pressure of non-oxygenated pure components have been obtained. The accuracy of experimental measurements was ±0.01 K in temperature, ±0.01 kPa in pressure, and ±0.001 in mole fractions. The results are thermodynamically consistent according to the point-to-point consistency test. The data were correlated with five liquid-phase activity coefficients models (Margules, Van Laar, Wilson, NRTL, UNIQUAC).

Introduction

Distillation is the most common operation in the chemical industry used for the separation of liquid mixtures. Efficient design of distillation towers, and other separation processes, requires accurate and complete vapor−liquid equilibria (VLE) data.

On the other hand, the composition of reformulated gasoline includes a large amount of oxygenated additives: methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and alcohols—methanol, ethanol, *tert*-butyl alcohol (TBA), isobutyl alcohol (IBA). These oxygenated compounds have elevated octane number and little pollutant effect (Chang, 1994).

The purpose of this work is to obtain VLE data of the binary mixtures of *tert*-butyl alcohol with three hydrocarbons—toluene, methylcyclohexane, and isooctane (2,2,4-trimethylpentane). These hydrocarbons are representative of aromatic, naftenic, and paraffinic hydrocarbons, which are the main fractions in the gasoline pool.

In the literature there are just a few publications where liquid−vapor equilibrium data of TBA−hydrocarbon are reported. Most of these works are old or do not include any verification of the thermodynamic consistency of data. Likewise, we have not found in the literature any reported liquid−vapor equilibrium data for the binary systems TBA + isooctane, TBA + methylcyclohexane, and TBA + toluene.

In this work, the results have been treated by considering the nonideality of both liquid and vapor phases, and the thermodynamic consistency of experimental data has been verified.

Experimental Section

Chemical. The reagents *tert*-butyl alcohol (2-methyl-2-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 analysis 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 $kg \cdot m^{-3}$ 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.

Apparatus and Procedure. The equilibrium vessel used in this work was an all glass, dynamic recirculating still described by Walas (1985), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer 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 between them and with the sensor element. 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 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).

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 (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 response peaks were integrated using a Hewlett-Packard

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

	ρ/kg·m^{-3}		η		T_b/K	
compound	exptl	lit.	exptl	lit.	exptl	lit.
TBA	780.51	781.60[b]	1.3849	1.3849[b]	355.7	355.6[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^o, Antoine Coefficients[a] *A*, *B*, and *C*, and Standard Deviations (σ) of Chemicals

toluene		methylcyclohexane		isooctane	
T/K	P_i^o/kPa	T/K	P_i^o/kPa	T/K	P_i^o/kPa
348.0	32.37	330.7	24.58	327.5	23.30
350.5	35.39	335.9	29.76	332.0	27.53
353.9	39.93	339.9	34.36	333.8	29.42
359.8	48.64	342.6	37.79	336.8	32.76
362.5	53.26	344.8	40.71	339.5	36.03
368.9	65.25	346.7	43.52	342.4	39.85
374.5	77.44	348.6	46.34	344.9	43.28
376.2	81.40	350.2	48.85	349.0	49.50
378.0	85.84	352.3	52.29	352.1	54.72
379.8	90.46	354.3	55.76	354.4	58.95
381.6	95.25	355.3	57.57	358.4	66.68
384.2	102.62	357.5	61.76	360.1	70.23
385.7	106.88	359.3	65.27	363.9	78.82
388.5	115.75	360.6	67.87	365.6	82.93
390.8	123.53	362.3	71.66	367.7	88.20
393.1	131.45	363.9	75.15	369.3	92.36
		365.5	78.79	371.6	98.67
		366.7	81.70	373.6	104.40
		368.0	84.95	374.6	107.19
		369.5	88.73	375.7	110.50
		370.3	90.80	377.3	115.53
		371.5	93.79	378.8	120.40
		373.0	97.88	380.2	124.95
		374.2	101.38		
		376.0	106.83		
		377.3	110.58		
		379.4	117.00		
		381.2	122.88		
		383.2	130.02		
		384.5	134.68		

	A	B	C	σ^b
TBA	14.84264	2645.04	−96.7956	
isooctane	13.80220	2999.098	−45.9600	0.0623
methylcyclohexane	13.64381	2891.014	−53.8124	0.0557
toluene	13.84529	2998.040	−58.7957	0.0476

[a] $\ln(P_i^o/\text{kPa}) = A - B/((T/\text{K}) + C)$. [b] $\sigma = [\sum(P_i^o - P_{i\,\text{calc}}^o)^2/(N - p)]^{1/2}$, where N is the number of points and p is the number of parameters.

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 TBA (1) + Toluene (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
383.8	0	0		
379.3	0.0236	0.1504	2.814	0.983
375.7	0.0464	0.2440	2.602	0.992
371.4	0.0821	0.3621	2.512	0.986
370.4	0.0878	0.3769	2.528	0.998
368.6	0.1090	0.4156	2.386	1.011
366.2	0.1529	0.4842	2.151	1.010
363.5	0.2083	0.5518	1.978	1.021
361.7	0.2503	0.5807	1.847	1.067
360.4	0.3140	0.6189	1.645	1.105
359.5	0.3846	0.6547	1.468	1.149
358.3	0.4802	0.6928	1.300	1.258
357.8	0.5213	0.7072	1.245	1.323
357.2	0.5787	0.7281	1.181	1.423
357.0	0.6108	0.7464	1.155	1.447
356.8	0.6398	0.7620	1.134	1.477
356.5	0.6891	0.7828	1.094	1.577
356.1	0.7397	0.8124	1.074	1.649
355.7	0.8083	0.8509	1.045	1.803
355.6	0.8414	0.8703	1.030	1.902
355.5	0.9005	0.9082	1.008	2.154
355.5	0.9178	0.9200	1.002	2.272
355.4	0.9343	0.9362	1.006	2.275
355.5	0.9578	0.9565	0.998	2.407
355.6	0.9719	0.9712	0.995	2.386
355.7	1.000	1.000		

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

T/K	x_1	y_1	γ_1	γ_2
372.5	0	0		
369.5	0.0133	0.0976	4.453	0.992
367.5	0.0249	0.1565	4.083	0.991
361.5	0.0737	0.3273	3.562	0.984
358.4	0.1199	0.4159	3.115	0.983
356.9	0.1790	0.4710	2.545	1.013
356.2	0.1815	0.4786	2.580	1.010
355.1	0.2080	0.4969	2.427	1.038
353.9	0.2780	0.5414	2.071	1.076
353.6	0.3411	0.5592	1.763	1.144
353.1	0.4096	0.5743	1.537	1.252
352.6	0.4911	0.6050	1.377	1.368
352.4	0.6604	0.6692	1.141	1.728
352.5	0.7437	0.7054	1.064	2.033
352.6	0.7887	0.7368	1.044	2.197
352.8	0.8304	0.7695	1.027	2.383
352.9	0.8466	0.7783	1.015	2.527
353.1	0.8700	0.8053	1.014	2.603
353.3	0.8894	0.8259	1.010	2.720
353.5	0.9091	0.8435	1.001	2.957
354.0	0.9338	0.8780	0.996	3.121
353.9	0.9305	0.8722	0.995	3.118
354.4	0.9524	0.9050	0.991	3.337
355.0	0.9752	0.9438	0.986	3.722
355.1	0.9837	0.9611	0.982	3.711
355.3	0.9910	0.9767	0.992	4.215
355.7	1.000	1.000		

3396 integrator. The experimental error in these measurements was less than ±0.001 mole fraction.

Results and Discussion

Antoine constants for methylcyclohexane, toluene, and isooctane were obtained from our own vapor pressure measurements using the same still as for binary systems; the results are shown in Table 2. The constants were calculated by a nonlinear optimization method to minimize the mean relative deviation, MRD(P). The results obtained are in good agreement with the data found in the literature: Willingham et al. (1945), Forziati et al. (1949), Myers et al. (1979), Ambrose and Townsend (1963), Suska et al. (1970), Nicolini and Laffitte (1949). The Antoine constants for *tert*-butyl alcohol (Table 2) were taken from Aucejo et al. (1998).

VLE data (T, x_1, and y_1) along with calculated activity coefficients at 101.3 kPa are presented in Tables 3−5. Furthermore, $T-x_1-y_1$ diagrams are shown in Figures 1−3. In these figures, the line represents the model that fits better the experimental data obtained. All the systems show a minimum boiling temperature azeotrope. The composition and boiling temperature of the azeotropes are

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 TBA (1) + Methylcyclohexane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
374.0	0	0		
368.2	0.0288	0.1885	4.146	0.983
364.2	0.0555	0.2873	3.768	0.994
360.9	0.0942	0.3737	3.249	1.003
358.1	0.1565	0.4535	2.630	1.021
356.1	0.2427	0.5084	2.048	1.087
354.9	0.3368	0.5470	1.662	1.186
354.4	0.3879	0.5749	1.545	1.225
354.0	0.4533	0.5929	1.385	1.330
353.7	0.5067	0.6110	1.291	1.421
353.4	0.5576	0.6325	1.229	1.511
353.3	0.6166	0.6593	1.163	1.622
353.2	0.6216	0.6590	1.157	1.650
353.2	0.6608	0.6801	1.124	1.727
353.1	0.6934	0.6959	1.100	1.822
353.2	0.7317	0.7176	1.071	1.927
353.2	0.7487	0.7282	1.062	1.980
353.3	0.7972	0.7583	1.034	2.176
353.4	0.8248	0.7789	1.023	2.297
353.5	0.8284	0.7847	1.022	2.276
353.9	0.8864	0.8400	1.007	2.524
354.6	0.9297	0.8906	0.991	2.730
355.0	0.9594	0.9322	0.990	2.894
355.3	0.9786	0.9630	0.991	2.969
355.5	0.9870	0.9769	0.990	3.032
355.7	1.000	1.000		

Table 6. Composition (y_{az}) and Boiling Temperature (T_{az}) of the Azeotropic Mixtures (P = 101.3 kPa)

	exptl		lit.		
system	y_{az}	T_{az}	y_{az}	T_{az}	ref
TBA + toluene	0.949	355.4	0.953	354.7	Gmehling et al. 1994
TBA + isooctane	0.675	352.4			
TBA + methylcyclohexane	0.705	353.1	0.720	352.0	Gmehling et al. 1994

Table 7. Thermodynamic Consistency Test of Van Ness−Byer Gibbs. Mean Absolute Deviations MAD(y) and MAD(P)

system	MAD(y)	MAD(P)/kPa
TBA + toluene	0.0032	0.41
TBA + isooctane	0.0054	0.41
TBA + methylcyclohexane	0.0022	0.45

summarized in Table 6 together with the corresponding literature values. In all cases, the azeotropic composition has been obtained by 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.

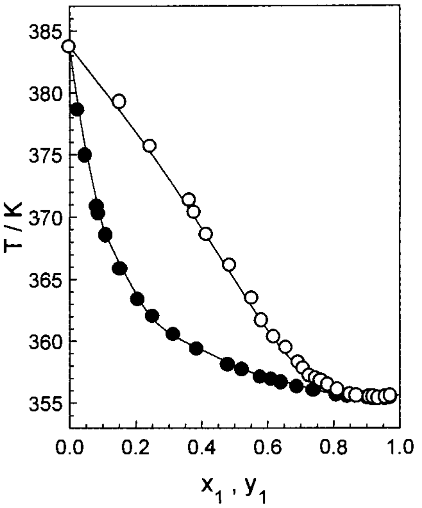

Figure 1. T−x_1−y_1 diagram at constant pressure, P = 101.3 kPa, of the system TBA (1) + toluene (2): (○, ●) experimental data; (—) Margules model.

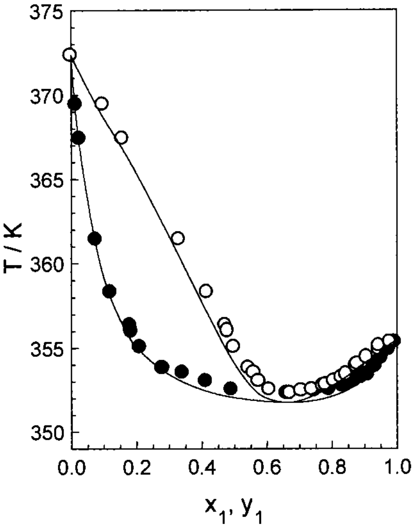

Figure 2. T−x_1−y_1 diagram at constant pressure, P = 101.3 kPa, of the system TBA (1) + isooctane (2): (○, ●) experimental data; (—) Wilson model.

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
			TBA + Toluene				
Margules	1.1324[a]	0.9384[a]		3.103	2.556	0.0066	0.18
Van Laar	1.1394[a]	0.9560[a]		3.125	2.601	0.0065	0.21
Wilson	2707.3[b]	1128.8[b]		3.113	2.765	0.0069	0.34
NRTL	1505.2[b]	2346.6[b]	0.507[a]	3.107	2.743	0.0069	0.33
UNIQUAC	96.715[b]	875.21[b]		3.051	2.732	0.0071	0.33
			TBA + Isooctane				
Margules	1.5317[a]	1.2496[a]		4.626	3.489	0.0077	0.46
Van Laar	1.5456[a]	1.2611[a]		4.691	3.529	0.0077	0.46
Wilson	5101.8[b]	147.72[b]		4.590	3.643	0.0081	0.43
NRTL	1828.9[b]	3324.7[b]	0.417[a]	4.618	3.618	0.0079	0.60
UNIQUAC	−774.46[b]	2424.5[b]		4.073	3.724	0.0081	0.59
			TBA + Methylcyclohexane				
Margules	1.5243[a]	1.1003[a]		4.592	3.005	0.0065	0.41
Van Laar	1.5523[a]	1.1139[a]		4.722	3.046	0.0053	0.37
Wilson	4629.9[b]	503.35[b]		4.755	3.203	0.0052	0.48
NRTL	1812.6[b]	3552.4[b]	0.590[a]	4.740	3.244	0.0047	0.45
UNIQUAC	−610.81[b]	1975.6[b]		4.004	3.072	0.0030	0.29

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

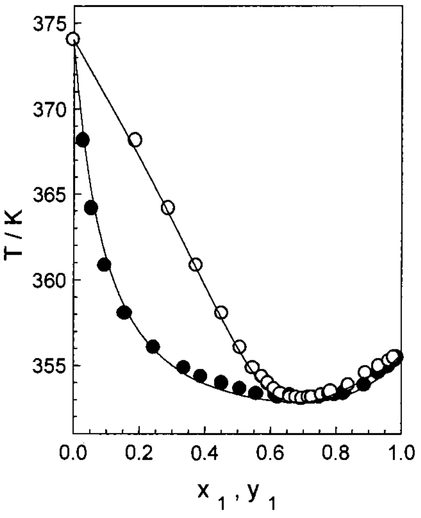

Figure 3. $T-x_1-y_1$ diagram at constant pressure, $P = 101.3$ kPa, of the system TBA (1) + methylcyclohexane (2): (○, ●) experimental data; (—) UNIQUAC model.

The activity coefficients γ_i were calculated by taking into account the nonideality of the vapor phase, from the following equation:

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

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and where 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^{o} is the vapor pressure of the pure component i calculated by Antoine equation, B_{ii} is the second virial coefficient of the pure gas, B_{ij} is the cross second virial coefficient, and V_i^{o} is the molar volumes of saturated liquid. The correction for nonideality of the vapor represented by the exponential term in the eq 1 contributed less than 3% to the activity coefficients; in general, its influence was only important at very diluted concentration. 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). Critical properties of both components and molar volumes of 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 excess Gibbs free 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.

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 following objective function:

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

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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