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# Isobaric vapor–liquid equilibria for the binary systems isobutyl alcohol + isobutyl acetate and *tert*-butyl alcohol + *tert*-butyl acetate at 20 and 101.3 kPa

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## Abstract

New consistent vapor–liquid equilibrium data for the binary systems isobutyl alcohol (IBA) + isobutyl acetate (IBAc) and *tert*-butyl alcohol (TBA) + *tert*-butyl acetate (TBAc) are reported at 20 and 101.3 kPa. The IBA + IBAc system, which deviates positively from ideal behavior, can be described as symmetric solution and presents azeotrope at both pressures. The TBA + TBAc system shows positive deviations from ideal behavior and presents azeotrope only at 20 kPa. The activity coefficients and boiling points of the solutions were correlated with their composition by the Wilson, UNIQUAC, NRTL and Wisniak–Tamir equations.

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## 1. Introduction

Isobutyl acetate (IBAc) and *tert*-butyl acetate (TBAc) are solvents widely used in chemical industry. They are used alone or in solvent blends in applications including coatings, inks, adhesives, industrial cleaners and degreasers. Both acetates are produced by esterification of acetic acid with the corresponding alcohol. Final purification of acetates in traditional technologies is a relative complex procedure due to the existence of a minimum boiling point azeotrope in the isobutyl alcohol (IBA) + IBAc mixture and a low relative volatility region in the *tert*-butyl alcohol (TBA) + TBAc system at atmospheric pressure.

The separation can be improved by adding an agent that alters the relative volatility of the components (extractive distillation) or making a simple change in pressure, provided that the azeotropic composition is sensitive to pressure (pressure swing distillation).

Unfortunately, azeotropic data frequently are not available at different pressures. The present work was undertaken to measure the phase equilibrium properties (VLE data) of the two systems mentioned at 20 and 101.3 kPa. Further, we can use these properties to simulate the pure components recovery without adding a separating agent and to find a feasible sequence in which the columns operate at different pressures. Some VLE data are available in literature for these related mixtures [1,2], but only at atmospheric pressure.

The VLE data were found to be thermodynamically consistent at all pressures and were correlated with their composition by Wilson, UNIQUAC and NRTL equations.

## 2. Experimental

### 2.1. Chemicals

IBA (99.5 mass%, *HPLC grade*), IBAc (>99 mass%, *analytical grade*), TBA (>99.5 mass%, *HPLC grade*) and TBAc (>99 mass%, *analytical grade*) were purchased from Aldrich

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Table 1
Densities $d$, refractive index $n_D$ and normal boiling points $T_b$ of pure components

| Component | $d$ (kg m$^{-3}$) | | $n_D$ (298.15 K) | | $T_b$ (K) | |
|---|---|---|---|---|---|---|
| | Experimental | Literature | Experimental | Literature | Experimental | Literature |
| IBA(1) | 797.83[a] | 797.8[a,b] | 1.3937 | 1.3939[b] | 381.15 | 380.81[b] |
| IBAc(2) | 866.12[c] | 867.70[b,c] | 1.3876 | 1.3880[b] | 389.85 | 389.80[b] |
| TBA(3) | 775.40[d] | 775.43[d,e] | 1.3851 | 1.3852[e] | 355.60 | 355.57[e] |
| TBAc(4) | 860.53[a] | 861.6[a,b] | 1.3840 | 1.3842[f] | 370.86 | 371.15[f] |

[a] Measured to 298.15 K.
[b] Taken from TRC tables [3].
[c] Measured to 293.15 K.
[d] Measured to 303.15 K.
[e] Taken from Daubert and Danner [4].
[f] Taken from Mato and Cepeda [2].

Ltd. The reagents were used without further purification after chromatography failed to show any significant impurities. The water content was small in all chemicals (<0.05 mass%). Before measurements, the liquids were dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The densities and refractive indexes of pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter and an Abbe refractometer Atago 3T, respectively. Temperature was controlled to ±0.01 K with a thermostated batch. The accuracy in density and refractive index measurements is ±0.01 kg m$^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature. Appropriate precautions were taken when handling the reagents in order to avoid hydration.

### 2.2. Apparatus and procedure

The equilibrium vessel was an all-glass, dynamic-recirculating still equipped with a Cottrell circulation pump described by Walas [5]. The apparatus Labodest VLE 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific model 5622 calibrated at the Spanish *Instituto Nacional de Técnica Aeroespacial*. The accuracy is estimated to be ±0.02 K. The temperature probe was calibrated against the ice and steam points of distilled water. The apparatus is equipped with two digital pressure sensors: one for the low pressure region with an accuracy of ±0.01 kPa, and another for the high pressure region with an accuracy of ±0.1 kPa. The manometers were calibrated using the vapor pressure of ultrapure water.

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was turned on. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed withdrawal of small volume samples (1.0 μL).

### 2.3. Analysis

Composition of the sampled liquid and condensed vapor phase was determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionisation detector was used together with a 30 m, 0.454 mm i.d., capillary column, DB-MTBE (J & Scientific). The GC response peaks were treated with Chrom-Card for Windows, version 1.21. Column, injector and detector temperatures were 393, 498 and 523 K, respectively, for all systems. Very good peak separation was achieved under these conditions and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. At least two analyses were made of each liquid and vapor composition. The standard deviation in the mole fraction was usually less than 0.001.

## 3. Results and discussion

The pure component vapor pressure $P_i^0$ for isobutyl alcohol was taken from Ref. [6]. For isobutyl acetate, *tert*-butyl alcohol and *tert*-butyl acetate, pure component vapor pressures were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 2. The measured vapor pressures were correlated using the Antoine equation:

$$\ln(P_i^0)\,(\mathrm{kPa}) = A_i - \frac{B_i}{T(\mathrm{K}) + C_i} \qquad (1)$$

whose parameters $A_i$, $B_i$ and $C_i$ are reported in Table 3 together with those of the isobutyl alcohol. The vapor pressures were correlated with a mean absolute deviation (MAD P) of 0.05% for IBAc, 0.09% for TBA and 0.11% for TBAc. In Fig. 1, it can be observed that the parameters presented in

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