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# Density of α-Pinene, β-Pinene, Limonene, and Essence of Turpentine

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Densities of α-pinene, β-pinene, limonene, and essence of turpentine have been measured at 293.15, 298.15, 303.15, 308.15, and 313.15 K, at atmospheric pressure, with a mechanical oscillator densimeter. Benzene and cyclohexane were used as calibration fluids. The precision is of the order of 0.01 $kg \cdot m^{-3}$, while the accuracy is estimated to be 0.1%. A linear representation of the variation of the density with temperature reproduces the experimental data within 0.2%.

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**KEY WORDS:** density; essence of turpentine; limonene; α-pinene; β-pinene.

## 1. INTRODUCTION

In a recent paper [1], the importance of the thermophysical properties of the essence of turpentine obtained from the oleoresin of pine species (Pinus Pinaster, Ait.), and of its components, for the design and control of the industrial units used in the chemical processing of oleoresin was discussed. In that work, we presented measurements of the densities of α-pinene, β-pinene, and essence of turpentine at five temperatures, between 293.15 and 313.15 K, obtained with a mechanical oscillator densimeter, with an accuracy of 0.3%. Since that work several aspects were changed, namely, the calibration procedure and the temperature control. These modifications, described below, have resulted in an accuracy of 0.1%. The purification of α-pinene by distillation was perfected with a different distillation column, allowing us to obtain a purity of 99.85%.

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## 2. EXPERIMENTAL

Three different calibration fluids were used in the present work. Benzene and cyclohexane (Merck, p.a.), with a stated purity of 99.7 and 99%, respectively, were dried over calcium hydride and further distilled [2]. Water was triply distilled in a quartz still. The purity of the calibration samples after destillation was found to be 99.98% for benzene, 99.99% for cyclohexane, and better than 99.995% for water. The β-pinene and the limonene (Sarsynthese) were purified by distillation. To obtain very pure α-pinene, a commercial sample (Nares) was distilled in a packed column with 100 theoretical plates. From this distillation two samples, A and B, were obtained for the measurement of density. Two samples of essence of turpentine obtained from the distillation of the oleoresin extracted from Pinus Pinaster, A and B, were furnished by two industrial companies (A, Produtos Resinosos Naturais; B, Nares). The purity of these compounds was determined by gas chromatography, using a Carbowax column, 20 *M*. The results obtained are shown in Table I.

For the measurement of the densities we used a mechanical oscillator densimeter (Anton Paar, Type DMA 55). The density of a given sample

**Table I.** Compositions of Samples of Resinous Products in Weight Fraction

| | Sample | | | | | |
|---|---|---|---|---|---|---|
| % components | α-Pinene A | α-Pinene B | β-Pinene | Limonene | Turpentine A | Turpentine B |
| α-Pinene | 99.87 | 99.85 | 0.458 | 0.058 | 70.65 | 69.88 |
| Canfene | 0.129 | 0.129 | 0.148 | 0.143 | 1.113 | 0.998 |
| β-Pinene | — | 0.0167 | 94.01 | 0.062 | 12.25 | 14.61 |
| Myrcene | — | — | 3.01 | 0.053 | 0.420 | 0.659 |
| α-Terpinolene | — | — | 0.106 | — | 0.0665 | — |
| Limonene | — | — | 1.88 | 96.59 | 2.822 | 5.446 |
| β-Flandrene | — | — | 0.308 | — | 0.209 | 0.628 |
| *p*-Cimene | — | — | 0.041 | 1.416 | 0.172 | 0.035 |
| Terpinolene | — | — | — | — | — | 0.527 |
| Terpinene-1-ol-4 | — | — | — | 0.284 | 1.301 | 0.095 |
| Carifilene | — | — | — | 0.191 | 1.404 | 3.128 |
| α-Terpiniol | — | — | — | 0.344 | 0.653 | 1.909 |
| Unidentified | 0.001 | 0.0043 | 0.039 | 0.859 | 8.9395 | 2.085 |

depends on the period of vibration of the mechanical oscillator through the equation

$$\rho = \frac{(\rho_1 - \rho_2)(\tau^2 - \tau_2^2)}{\tau_1^2 - \tau_2^2} + \rho_2 \tag{1}$$

where $\tau_1$ and $\tau_2$ are the periods of vibration of the two calibration fluids with known densities $\rho_1$ and $\rho_2$. The calibration procedure and the working principle of these instruments have been described in previous papers [1, 2]. To obtain a precision of 0.01 $\text{kg} \cdot \text{m}^{-3}$ the difference between the densities of the calibration fluids cannot exceed 500 $\text{kg} \cdot \text{m}^{-3}$ and the densities must bracket the density of the sample; in addition, the temperature has to be controlled to 0.005 K.

The densimeter cell was located in a thermostat (Lauda D60 electronic) equipped with a cold source (cryostat Haake FK2) and a control unit (Lauda R52) with a platinum resistance sensor. The temperature of the fluid in the densimeter cell was controlled to within ±0.005 K and measured to within ±0.003 K with a thermistor, previously calibrated with a platinum resistance thermometer. Long-term temperature stability tests showed that the period of vibration was not affected by fluctuations in temperature commensurate with the accuracy of the temperature measurement. The measurement of the density is affected only by the error in the determination of the period of vibration and by the accuracy of the calibrating data. All the measurements were made at atmospheric pressure.

Knowing the values of the densities of similar samples obtained with the same instrument previously [1, 2], benzene and cyclohexane were chosen as calibration fluids. At 298.15 K, the densities of benzene and cyclo-

**Table II.** Densities of Calibrating Fluids, in $\text{kg} \cdot \text{m}^{-3}$

| $T$ (K) | $\rho_{\text{(water)}}$ | $\sigma_\rho$[a] | $\rho_{\text{(c-hex.)}}$ | $\sigma_\rho$ | $\rho_{\text{(benz.)}}$ | $\sigma_\rho$ | $\rho_{\text{(benz)}}$ literature | $\sigma_\rho$ |
|---|---|---|---|---|---|---|---|---|
| 293.15 | 998.206 | 0.005 | 778.58[b] | 0.01 | $879.02_4$ | 0.007 | 879.02[b] | 0.01 |
| 298.15 | 997.047 | 0.008 | 773.844[c] | 0.015 | 873.592[c] | 0.015 | 873.65[b] | 0.01 |
| 303.15 | 995.648 | 0.005 | 769.14[b] | 0.01 | $868.36_0$ | 0.007 | 868.32[b] | 0.01 |
| 308.15 | 994.031 | 0.005 | 764.49[b] | 0.01 | $862.99_9$ | 0.007 | 862.96[d] | — |
| 313.15 | 992.214 | 0.005 | 759.97[e] | 0.01 | $857.60_3$ | 0.007 | 857.60[d] | — |

[a] The absolute accuracy of the data.

[b] From Ref. 3.

[c] Unpublished value [8].

[d] From Ref. 7.

[e] From Ref. 4.

hexane were determined by Câmara e Sousa et al. [8] with a pycnometer. At all other temperatures the density of benzene was obtained with the present equipment with cyclohexane and water as calibration fluids. The densities of cyclohexane at other temperatures were obtained from the work of Tanaka [3] and Goates and Grigg [4], and those of water were obtained from the equation of state published by Sato et al. [5], which reproduces the values of the IAPS equation [9] for the density of water, within 0.01 $kg \cdot m^{-3}$. Table II shows the densities of the calibration fluids along with their standard deviation, as well as selected literature values for benzene. It can be shown that the measured values obtained for the density of benzene agree with the literature values selected as the most reliable [7, 3] at 293.15, 303.15, and 313.15 K, but they are not within their mutual uncertainty at the other two temperatures, 298.15 and 308.15 K. At 298.15 K the density of benzene measured with the densimeter is $(873.581 \pm 0.0096)\ kg \cdot m^{-3}$, consistent with the value obtained by Câmara e Sousa et al. with a pycnometer $(873.592 \pm 0.015\ kg \cdot m^{-3})$ [8]. The values of Tanaka [3] are somewhat higher, but no explanation was found for this difference. At 308.15 K only three other values of the density of benzene were found in the literature, but they were not suitable for comparison with the present data as they are less accurate.

## 3. RESULTS AND DISCUSSION

The densities of $\alpha$-pinene, $\beta$-pinene, limonene, and essence of turpentine were measured at five temperatures, at 0.1 MPa. The standard deviation obtained using Eq. (1) was 0.01 $kg \cdot m^{-3}$, the deviations being larger at 298.15 K for all substances. This is due to the fact that the error in the densities of the calibration fluids is slightly higher at this temperature, as already explained. Table III gives the experimental results.

The experimental values of the density were fitted as a function of temperature with a linear equation of the form

$$\rho = A - BT \qquad (2)$$

where $\rho$ is in $kg \cdot m^{-3}$ and $T$ is in K.

The values of the parameters A and B for all the liquids are presented in Table IV. This table also includes the standard deviation of the fit. Figure 1 shows the deviations between the experimental data and the calculated values using Eq. (2) for all the samples studied. The standard deviation of the fits never exceeds 0.07%, which is commensurate with the claimed accuracy of the data. These equations can be used to calculate the density of $\alpha$-pinene with an error smaller than 0.15%, at a $2\sigma$ level,

**Table III.** Densities and Standard Deviations of Turpentine and Three of Their Components, in $kg \cdot m^{-3}$

| $T$ (K) | Turpentin A |  | Turpentine B |  | α-pinene A |  | α-Pinene B |  | β-Pinene |  | Limonene |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $\rho$ | $\sigma_\rho$ | $\rho$ | $\sigma_\rho$ | $\rho$ | $\sigma_\rho$ | $\rho$ | $\sigma_\rho$ | $\rho$ | $\sigma_\rho$ | $\rho$ | $\sigma_\rho$ |
| 293.15 | $884.05_6$ | 0.008 | $863.75_1$ | 0.007 | $858.47_6$ | 0.007 | $857.72_5$ | 0.007 | $867.15_1$ | 0.007 | $845.70_8$ | 0.007 |
| 298.15 | $878.38_7$ | 0.016 | $859.59_4$ | 0.014 | $853.83_5$ | 0.013 | $853.39_2$ | 0.013 | $862.80_2$ | 0.014 | $842.16_1$ | 0.012 |
| 303.15 | $874.55_8$ | 0.009 | $854.71_2$ | 0.007 | $849.09_6$ | 0.007 | $848.91_3$ | 0.007 | $858.87_8$ | 0.007 | $837.68_9$ | 0.007 |
| 308.15 | $871.41_2$ | 0.009 | $851.79_3$ | 0.007 | $845.97_4$ | 0.007 | $845.11_2$ | 0.007 | $855.39_8$ | 0.008 | $834.33_7$ | 0.007 |
| 313.15 | $867.50_1$ | 0.009 | $847.60_7$ | 0.007 | $842.05_2$ | 0.007 | $841.61_7$ | 0.007 | $851.26_2$ | 0.008 | $830.30_2$ | 0.007 |

**Table IV.** The Coefficients A and B of Eq. (2)

| | Turpentine A | Turpentine B | $\alpha$-Pinene A | $\alpha$-Pinene B | $\beta$-Pinene | Limonene |
|---|---|---|---|---|---|---|
| A $(kg \cdot m^{-3})$ | 1118.22 | 1098.55 | 1096.70 | 1094.88 | 1096.66 | 1072.73 |
| B $(kg \cdot m^{-3} K^{-1})$ | 0.802 | 0.802 | 0.814 | 0.810 | 0.784 | 0.774 |
| $\sigma$ $(kg \cdot m^{-3})$ | 0.80 | 0.51 | 0.57 | 0.38 | 0.25 | 0.30 |

between 293.15 and 313.15 K, which is slightly higher than the estimated accuracy of 0.1% of the data. This is probably due to the small number of experimental points used in the fit. In the case of $\beta$-pinene and limonene these equations must be used with care, because the samples used had purities of 94.01 and 96.59%. Strictly speaking they should be used only for these compositions, with an error smaller than 0.1% at a $2\sigma$ level, but they can be used as an estimate of the densities of "pure" $\beta$-pinene and limonene with an uncertainty of 0.5%. In the case of the essence of turpentine samples, the error in using Eq. (2) is smaller than 0.2% at a $2\sigma$ level.

It is noteworthy that, although the major impurity in the $\beta$-pinene samples is normally $\alpha$-pinene [1], sometimes either limonene or myrcene is the main impurity, as in the present samples. This is caused by the normal seasonal variation of the composition of the extracted oleoresin. Therefore,

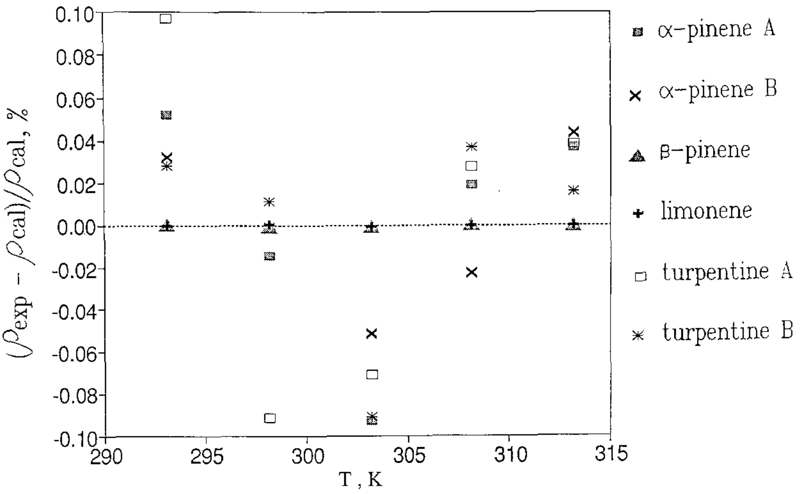

**Fig. 1.** Deviations between the experimental data and the values calculated from Eq. (2).

it would be of major importance in this field to know the densities of the pure components of these mixtures very accurately, which has not yet been achieved due to the inherent difficulties in their purification. Work is under progress to overcome this difficulty.

A more detailed comparison between these results and the results previously reported [1, 2] shows that the main impurity in the $\beta$-pinene sample affects the value of $d\rho/dT$. In fact the values are 0.784 $\mathrm{kg \cdot m^{-3} \cdot K^{-1}}$ for $\beta$-pinene and 0.774 $\mathrm{kg \cdot m^{-3} \cdot K^{-1}}$ for limonene, the main impurity in the $\beta$-pinene sample. In the work previously reported, the samples of $\beta$-pinene used had a larger fraction of $\alpha$-pinene, and the values of $d\rho/dT$ were closer to the values obtained for pure $\alpha$-pinene.

It would be interesting to develop further studies of these effects to substantiate more general correlations between the densities of the samples and their composition, as already tried in a previous work [1]. Once the purification problem is solved we look forward to continuing this work.

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