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Liquid-State Volumetric Properties of a Set of Alcohols with Up to Five Carbon Atoms

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Abstract: This work provides density data (~1300 values) of 14 alcohols with up to five carbon atoms at $p \in [0.1\text{--}40]$ MPa and $T \in [278\text{--}358]$ K. The information obtained is modeled with a convenient reformulation of the Tait equation from which the volumetric coefficients, α and β , are derived both analytically and numerically. The general EoS containing α and β is also used for checking the consistency of the hypothesis on the invariability of the cited thermophysical parameters. The results obtained can be considered reliable because of the low estimated errors between the experimental data and those of the literature, which are below 0.4% for volume, while for the volumetric coefficients there is always a reference diverging 10%, or less, from the proposed model estimations. By including the averages of α and β into the general state of equation the errors increase, being <15%, compared to those based on the Tait equation. Hence, the assumption on the stability of the volumetric coefficients in this working interval is sufficient to make rough estimations of the molar volume of the selected alcohols.

Keywords: alcohols; p - ρ - T ; equations of state; volumetric coefficients

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1. Introduction

One option to reduce the dependence that today's society has on fossil fuels (oil, coal, natural gas, etc.) is its replacement by biofuels obtained from renewable raw materials, such as certain natural resources and biomass. Biofuels can be solid, liquid, or gaseous. The group of liquids includes, as most prominent, biodiesel and bioalcohols. Of the latter, obtained mainly by the fermentation of starch or sugar, biomass, and residues, the bioethanol and biomethanol appear as the more highlighted; moreover, the use of higher alcohols has been demonstrated for the near future, generating a wide range of bioalcohols, such as biopropanol and even biopentanol [1]. Likewise, in recent years, the interest in using bioalcohols as fuels has been addressed towards isomers made of 4 or 5 carbon atoms. This is due to their high energy density and cetane-index, high combustion quality, and their lower moisture absorption, compared to primary alcohols. Moreover, by themselves they are compatible with currently available compression ignition engines (diesel engines) and by forming blends with diesel or biodiesel [2]. This is a significant advantage since it implies that their use does not require drastic modifications, or replacement of the existing engines.

Currently, diesel engines can reach common-rail pressures up to 2000 bar [3]. Thence, the intended use of these alcohols as fuels requires an extensive knowledge of their properties under those extreme conditions.

This work addresses the analysis of the volumetric behavior of 14 alcohols, $C_nH_{2n+1}(OH)$, five normal and nine isomers, formed by up to five carbon atoms, from methanol ($n = 1$) to pentanol ($n = 5$), in the interval of pressures, $p \in [0.1\text{--}40]$ MPa, and temperatures, $T \in [278\text{--}358]$ K. The literature contains dense information on densities for some of the selected alcohols [4–20], while, for others, the existing information is scarce [21–23]. The

main characteristics of the information gathered from literature are summarized in Table 1, detailing the number of references concerning each alcohol, the temperature range and maximum pressure of the measurements, and their specific references. For those alcohols highly referenced in the literature, only the three most recent have been selected. Although the initial idea was to obtain measurements for alcohols with $n \geq 3$, the values for methanol and ethanol were also determined to validate the experimental technique deployed in this work, comparing them with those from literature. The main goal of this work is to expand the existing high-pressure density database, including original data for the 3-methylbutan-2-ol, measured here for the first time. The (p, ρ, T) information acquired in this work is used to check the validity of an equation of state (EoS), similar to that of Tait [24] for the compounds of this nature. In addition, other volumetric parameters are calculated.

Table 1. References having high-pressure density data of the selected alcohols for this work. For the alcohols showing a large number of references, only the three most recent are indicated.

Alcohol	No. of References	$\Delta T/K/p/MPa$	Selected References
methanol	45	283–423/40	[4,5,13]
ethanol	43	233–473/40	[5,12,13]
propan-1-ol	27	288–313/40	[5,13,14]
propan-2-ol	21	293–403/140	[15–17]
butan-1-ol	28	293–363/100	[5,18,19]
butan-2-ol	8	283–393/140	[6,7,20]
2-methylpropan-1-ol	7	283–363/66	[8–10]
2-methylpropan-2-ol	3	303–363/66	[6,9,10]
pentan-1-ol	14	293–323/35	[5,11,18]
pentan-2-ol	3	233–433/100	[21–23]
pentan-3-ol	2	233–433/100	[21,23]
2-methylbutan-1-ol	1	293–323/400	[23]
2-methylbutan-2-ol	1	293–323/400	[23]
3-methylbutan-2-ol	0	-	-

2. Materials and Methods

2.1. Materials

The alcohols used in this work were from Sigma-Aldrich with the highest commercial quality. The purity indicated by the manufacturer was checked using gas chromatography GC, and the moisture using the Karl–Fischer method. Those products that showed moisture higher than 300 ppm, were subsequently treated with molecular sieve, from Fluka, 3 Å for several days until the water content was kept under this threshold. Before use, the compounds were also degasified with ultrasound for several hours. The final purity, measured by GC, was slightly higher than that given by the manufacturer. However, as an additional quality control, the density ρ and refractive index n_D of all alcohols was determined at atmospheric pressure and at 298.15 K, such as indicated below, being our measurements in agreement with those provided in literature [25–29], Table S1 (Supplementary Material). The water used for calibration was obtained in our laboratory by multiple distillation, degassing it before use, being the final conductance smaller than 1 μS .

2.2. Apparatus and Experimental Technique

2.2.1. Characterization of Pure Compounds

The characteristics of the equipment used to assess the quality of the compounds are indicated. A chromatograph Varian, model 450, equipped with a HP-5 column and FID was employed for determining the purity of the compounds. The moisture was determined using a Karl–Fischer coulometric titrator, model C-20, from Mettler. Densities ρ , were measured with an Anton-Paar-60/602 digital densimeter, ($\rho \pm 0.02$) $kg \cdot m^{-3}$, calibrated with water and nonane as usual in our laboratory [30]. For the n_D 's a refractometer type Abbe, from Suzi, was used, with a reading precision of $n_D \pm 0.0005$. Both devices were

connected to a circulating water bath Polyscience 1166D, keeping a temperature control at $T \pm 0.01$ K.

2.2.2. Measurements of p - ρ - T

Densities of alcohols selected for this work were measured into the following temperature and pressure intervals: $p \in [0.1\text{--}40]$ MPa and $T \in [278.15\text{--}353.15]$ K. An installation like that shown in Figure 1 was designed and built in our laboratory.

Figure 1. Installation for measuring p - ρ - T . 1: densimeter; 2: frequency-meter; 3: thermometer; 4: thermostatic bath; 5: computers; 6: pressure gauge; 7: high-pressure generator; 8: vacuum pump; 9: syringe; 10–12: valves; 13: T-junction; 14: reservoir.

The mechanical oscillation densimeter, from Anton Paar, model DMA-512, with an estimated uncertainty of $\pm 0.1 \text{ kg} \cdot \text{m}^{-3}$, was connected to a circulating bath Haake C25P to stabilize the temperature into the measuring cell at $T \pm 0.01$ K. The oscillation period was achieved with a frequency-counter from the same manufacturer, model DMA-60, with an 8-digit reading display. A manual pressure generator HiP, model 50-6-15, was used, indicating the raised pressure in the digital manometer AE (6), model DMM-Evolution, whose reading uncertainty is $(0.15\%)p$. The cell temperature was monitored with a digital thermometer ASL F25, $T \pm 0.01$ K.

The calibration of the densimeter was done by conveniently modifying the procedure of Lagourette et al. [31], which relates the density of a substance with the period, Λ , of a response wave of a vibrating tube holding the sample by Equation (1).

$$\rho(p, T) = a(T)\Lambda^2(p, T) + b(p, T) \quad (1)$$

To obtain the parameters a and b , the response period is measured when the cell is full of water at different calibration pressures and temperatures, and also when it is submitted to vacuum at different temperatures. From this information and considering the reference values for the density of water [32], the parameters a and b are calculated using Equation (2).

$$a(T) = \frac{\rho_w(T, 0.1 \text{ MPa})}{\Lambda_w^2(T, 0.1 \text{ MPa}) - \Lambda_0^2(T)} \quad b(T, p) = \rho_w(T, p) - a(T)\Lambda_w^2(T, p) \quad (2)$$

It should be noted that Equation (2) just provides values for a and b at calibration conditions, but it does not allow interpolation; however, the former expressions provide a discrete mesh of values for a and b . As densities are to be evaluated at different tempera-

tures and pressures, in this work the polynomials described by the following equations are used to relate the mentioned constants with T and p . That is,

$$a(T) = a_0 + a_1T \quad b(T, p) = b_0 + b_1T + b_2p \quad (3)$$

Hence, the calibration is constituted by a set of parameters for Equation (3) that enable the interpolation of a and b constants within the calibration T, p -interval to be used in Equation (1). These parameters of the calibration curve were obtained by a *least-squares* fitting of the calculated values with Equation (2) at different temperatures and pressures, which are summarized in Table 2.

Table 2. Calibration constants of the Anton Paar DMA-512.

a_0	a_1	b_0	b_1	b_2
5.7258×10^4	-2.2876×10^1	-6.7907×10^3	2.8953×10^{-1}	-2.1857×10^{-4}

2.3. Modeling

Density data were correlated using a form of the Tait equation [24] for the molar volume ($v = M/\rho$). That relationship is obtained from the definition of the isothermal compressibility coefficient, making the slope, $(\partial v/\partial p)_T$, guided by a hyperbolic relationship of the type:

$$\frac{\partial v}{\partial p} = \frac{A}{B + p} \quad (4)$$

$$\int_{v_0}^v dv = \int_{p_0}^p \frac{A}{B + p} dp \quad \text{whose solving produces}$$

$$v = v_0 + A \ln \left(\frac{B + p}{B + p_0} \right) \quad (5)$$

A common variation of this equation to define the relationship $v = v(T)$ is to establish the coefficients A and B as a functions of temperature, i.e., $A(T)$, $B(T)$, and to choose a reference volume at a reference pressure, p_0 , but at different temperatures, $v_0(p_0, T)$. The indicated relationships are adequately represented by quadratic functions in such a way that Equation (5) can be used over a wide range of temperatures and pressures. This is,

$$v(p, T) = v_0(p_0, T) + A(T) \ln \left[\frac{B(T) + p}{B(T) + p_0} \right] \quad (6)$$

where:

$$v_0(T) = v_{00} + v_{01}T + v_{02}T^2; \quad A(T) = A_0 + A_1T + A_2T^2; \quad B(T) = B_0 + B_1T + B_2T^2 \quad (7)$$

The parametrization procedure to correlate Equation (6) with the experimental data consists of the following stages:

- define the first relationship of Equation (7) in the isobaric corresponding to the reference pressure (0.1 MPa);
- establish the parameters of the coefficients $A(T)$ and $B(T)$.

For both stages, the Simplex method from Nelder-Mead, Lagarias [33] is used to minimize the variance, s_v , of the model, expressed as:

$$s_v = \left[\sum_{i=1}^N (v_{i,\text{exp}} - v_{i,\text{cal}})^2 / N \right]^{1/2} \quad (8)$$

where N is the size of the dataset and the subindices “exp” and “cal” refer to experimental observations and calculated values, respectively.

The two volumetric coefficients, the expansion coefficient, α , and that of isothermal compressibility, β , were both derived from the Tait equation to provide more solid evi-

dence of the reliability of the obtained parametrizations. Given their definitions, these two coefficients inform about the stability of the slope of the volume. The expressions for both are:

$$\alpha(p, T) = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left[v_{0,T}(T) + A_T(T) \ln \left(\frac{B(T)+p}{B(T)+p_0} \right) - A(T) \frac{p_{0,T}(B(T)+p_0) + (p-p_0)(B_T(T)-p_{0,T})}{(B(T)+p)(B(T)+p_0)} \right] \quad (9)$$

$$\beta(p, T) = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left[\frac{A(T)}{B(T)+p} \right] \quad (10)$$

where $v_{0,T}(T) = (\partial v_0 / \partial T)_p$, $A_T(T) = (\partial A / \partial T)_p$, $B_T(T) = (\partial B / \partial T)_p$, $p_{0,T}(T) = (\partial p_0 / \partial T)_p$.

Although in this work the reference pressure, p_0 , was chosen to be independent from temperature, Equation (9) is generally applicable to any other hypothesis of this quantity. For example, Ihmels and Gmehling [34] modified the Tait equation by proposing a reference pressure for each isothermal matching with the vapor pressure of the pure compound. For this modification, our derived expression for the volumetric expansion coefficient also applies.

The calculated volumetric coefficients are compared with those found in the literature. The data are sparsely distributed among several references [26,35–42], showing different experimental techniques. In the first six references the volumetric coefficients are compared directly from Equations (9) and (10). However, the values provided by Egorov [41,42] are average values (see Equation (11)) of the isothermal compressibility over pressure, while those of Riddick et al. [26] are averaged over temperature, $t \in [0, 40]$ °C, at atmospheric pressure. The main characteristics of the literature data on volumetric coefficients are summarized in Table 3. Thus, an additional expression based on Equations (9) and (10) is used to enable the comparison between the proposed model and these last references.

$$\hat{y} = \frac{1}{\varphi_1 - \varphi_0} \int_{\varphi_0}^{\varphi_1} y(\varphi | \bar{\varphi}) d\varphi \quad (11)$$

Table 3. Description of the literature dataset on the volumetric coefficients (α and β).

Ref.	Type of Ref	Alcohols *	p or T Averaged	T -Range K	p -Range MPa
[26]	α	●, ■, ◆, +, ×, ▽, ▲, ▼, *	T	273–313	0.1
[35]	α	●	None	278–300	0.6–45
[36]	α	●, ■, ◆, ▽, ▲, ▼	None	278–328	5–45
[37]	α	◆	None	278–328	5–45
[38]	β	●, ■, ◆, ▽	None	298–333	0.1
[39]	α	◆, +, △, *	None	298–328	0.1
[40]	β	●, ■, ○, □, +, ×, ▽, ▲, ▼, *, *, *	None	293, 298	0.1
[41]	β	□	p	278–323	0.1–[10–100]
[42]	β	△	p	323	0.1–[10–100]

* (●) methanol; (■) ethanol; (○) propan-1-ol; (□) propan-2-ol; (◆) butan-1-ol; (+) butan-2-ol (×) 2-methylpropan-1-ol; (△) 2-methylpropan-2-ol; (▽) pentan-1-ol; (▲) pentan-2-ol; (▼) pentan-3-ol; (*) 2-methylbutan-1-ol; (*) 2-methylbutan-2-ol; (*) 3-methylbutan-2-ol.

In the Equation (11) we denote by y either the volumetric coefficients α or β , and $\hat{y}$ their corresponding averaged values. Moreover, φ is the variable to which y is (T or p) averaged over the interval $\varphi \in [\varphi_0, \varphi_1]$, while $\bar{\varphi}$ is its complementary variable, which is held constant at an arbitrary condition. Therefore, the function, $y(\varphi | \bar{\varphi})$ reads as y -function of φ at constant $\bar{\varphi}$. It is frequent to find in the literature [26], average values of the volumetric thermal coefficients; so, the simplest way to estimate approximate values of the molar volumes,

v , and densities, $\rho = M_m/v$, is to assume that the volumetric coefficients are constant over a more or less wide range of conditions and solve the following differential equation of state:

$$\frac{dv}{v} = \alpha dT - \beta dp \Rightarrow v(p, T) = v_0(p_0, T_0) \cdot \exp[\hat{\alpha}(T - T_0) - \hat{\beta}(p - p_0)] \quad (12)$$

Equation (12) holds when the volumetric coefficients are constant over the integration interval. In this work, the derivatives of the molar volume, Equations (9) and (10) are used to test the above relationship for all datasets. For this, the average values of the volumetric coefficients are determined over the entire p - T domain according to the following expression:

$$\hat{y}_{pT} = \frac{1}{(T_1 - T_0)(p_1 - p_0)} \int_{p_0}^{p_1} \int_{T_0}^{T_1} y(p, T) dT dp \quad (13)$$

where $\hat{y}_{pT}$ is the average of a generic volumetric coefficient, and the subscript indicates that this is done throughout the domain. The selected integration interval for T was [278–313] K, except for 2-methylpropan-2-ol, for which it took 303 and 338 K, to avoid the solid–liquid saturation curve. However, on average the entire pressure range is used.

3. Results and Discussion

3.1. Comparison to Literature Data

The values of density measurements for each of the alcohols at the working pressures, $p \in [0.1\text{--}40]$ MPa, and temperatures, $T \in [278.15\text{--}353.15]$ K, are summarized in Table S2. The limits of these two variables were conveniently delimited for methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol, considering the values established by the corresponding solid–liquid and vapor–liquid saturation curves, and also by the restriction of the experimental apparatus. Experimental results obtained were compared with those of literature indicated in Table 1, expressing the corresponding relative deviations graphically, see Figure 2. It is remarkable for all compounds the increase in the discrepancy observed as the temperature increases. However, the greatest difference observed ($\approx 1\%$) corresponds to pentan-3-ol, in relation to the values by Wappmann et al. [21]. For the rest of the alcohols, the relative deviations are in an interval oscillating in $\pm 0.4\%$. A complementary discussion on some concrete cases is detailed below:

- methanol and ethanol: up to $T \approx 320$ K, the literature values and those provided in this work deviate up to $\pm 0.2\%$ for the whole pressure range considered here. At higher temperatures, the deviations increase up to 0.4% . These values are acceptable, confirming the suitability of the experimental method used in our work.
- propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, pentan-1-ol: a strong increase in the relative deviations between the experiments and literature is observed for these compounds as temperature increases. Nevertheless, the differences are below 0.4% .
- 2-methylpropan-2-ol: experimental data provided for this compound is limited by its solid–liquid saturation curve. It is also observed that the deviations are insensitive to an increase in the temperature, and the deviations are within the interval established by other alcohols.
- pentan-2-ol, pentan-3-ol, 2-methylbutan-1-ol, 2-methylbutan-2-ol, 3-methylbutan-2-ol: literature data for these systems are scarce, therefore no objective comparison of our measurements can be made. At $T = 280$ K, pentan-3-ol shows the highest deviation observed in this work, $\approx 1\%$. No p - v - T data have been found for 3-methylbutan-2-ol, so the information presented here is novel.

Figure 2. Percentage deviation between our measurements and those from the available literature. (○) [4], (○) [5], (○) [12], (○) [13], (○) [14], (◆) [15], (◆) [16], (◆) [17], (◆) [18], (◆) [19], (○) [20], (×) [6], (◆) [7], (○) [8], (×) [9], (◆) [10], (×) [11], (×) [21], (×) [22], (×) [23].

3.2. Modeling Results

The parameters resulting from the indicated procedure, for Equations (6) and (7), are presented in Table 4. It is noteworthy that the order of magnitude of the deviations between the model estimations and the experimental data, $10^{-8} \text{ m}^3 \text{ mol}^{-1}$, coincides with the uncertainty of the apparatus. A progressive increase in the deviations with the molecular weight of the alcohol is observed, with a maximum difference corresponding to 3-methylbutan-2-ol (Figure 3), typical of the difficulty in measuring the heavier alcohols.

Table 4. Fitted values of parameters of Equations (6) and (7) using Equation (8). Outcomes from Equation (6) are in $\text{m}^3 \cdot \text{mol}^{-1}$. Inputs to that equation are expected in T/K and p/kPa.

	$10^5 \times v_0$	$10^{10} \times v_1$	$10^{11} \times v_2$	$10^6 \times A_0$	$10^8 \times A_1$	$10^{11} \times A_2$	$10^{-4} \times B_0$	$10^{-2} \times B_1$	$10^0 \times B_2$	$10^9 \times s_v$
methanol	32.866	37.288	76.018	−16.611	10.286	−19.777	43.734	−22.164	32.938	8.75
ethanol	48.783	13.636	10.671	−40.286	25.316	−44.825	71.715	−39.966	61.146	14.8
propan-1-ol	62.470	5.4.825	12.419	−23.618	11.888	−21.057	90.632	−46.439	64.448	27.4
propan-2-ol	63.633	91.502	14.736	−18.870	13.270	−29.532	46.334	−25.666	40.837	41.4
butan-1-ol	78.391	−78.209	15.459	−23.165	10.210	−17.778	87.189	−43.003	57.707	25.1
butan-2-ol	76.892	−10.920	17.811	−52.048	31.730	−54.940	104.11	−58.654	87.161	41.0
2-methylpropan-1-ol	79.101	−17.516	16.101	−48.429	27.575	−45.900	94.187	−50.772	72.759	25.7
2-methylpropan-2-ol	75.148	−27.973	23.040	34.296	−16.367	−49.358	44.287	−22.237	30.621	37.2
pentan-1-ol	94.496	−39.692	17.359	−53.125	28.621	−45.914	86.932	−43.902	59.740	13.7
pentan-2-ol	92.731	−47.508	20.494	−64.773	23.970	−9.411	52.288	−25.572	35.112	42.3
pentan-3-ol	90.103	−25.972	21.102	53.000	−33.857	45.474	−48.323	97.447	−18.894	49.1
2-methylbutan-1-ol	91.903	29.320	17.217	−122.59	65.366	−94.969	240.78	−130.16	18.111	43.8
2-methylbutan-2-ol	91.025	−55.381	22.791	−193.32	128.08	−223.73	156.09	−95.595	15.575	54.5
3-methylbutan-2-ol	91.082	−47.755	20.931	−171.27	117.06	−215.51	148.87	−90.316	15.234	59.0

Figure 3. Deviations, Equation (8), between the measured data and those by the model, Equations (6) and (7).

Equation (6) acceptably represents the experimental information $v = v(p,T)$, from a qualitative and quantitative point of view. The accuracy of the proposed modeling can be observed in Figure 4. In the latter, the alcohols are grouped with respect to the position of the -OH functional group as well as their structure, distinguishing linear from branched chains. It can be seen that the molar volumes of the isomers are almost identical to each other, which is evidenced in Figure 4c. In addition, Figure 4f,g clearly depicts the variation of the mole volume of alcohols with temperature at constant $p = 4$ bar and with pressure at constant temperature of $T = 298$ K, being the first more acute than the second in the range of the experimental conditions.

Figure 4. Experimental p - v - T data for (λ) methanol, ($\bullet$) ethanol, ($\bullet$) propan-1-ol, ($\bullet$) propan-2-ol, ($\bullet$) butan-1-ol, ($\bullet$) butan-2-ol, ($\bullet$) 2-methylpropan-1-ol, ($\bullet$) 2-methylpropan-2-ol, ($\bullet$) pentan-1-ol, ($\bullet$) pentan-2-ol, ($\bullet$) pentan-3-ol, ($\bullet$) 2-methylbutan-1-ol, ($\bullet$) 2-methylbutan-2-ol, ($\bullet$) 3-methylbutan-2-ol. Lines and surfaces correspond to values calculated with model of Equation (6). (a) Linear primary alcohols; (b) branched primary alcohols; (c) secondary alcohols; (d) secondary pentanol-isomers detail; (e) tertiary alcohols; (f) primary alcohols v - T at constant p ; (g) primary alcohols p - v at constant T .

As mentioned in Section 2.3, the values of the α and β coefficients are calculated using Equations (9) and (10), and also with Equation (11) when it is necessary to average the last two quantities. The calculations made with the proposed model here, similar to that of Tait, are compared with the values collected from literature according to Table 3. The estimated overall Mean Absolute Relative Deviations (MARD), Equation (14), for each component corresponding to each reference are summarized in Table 5.

$$MARD = \frac{100}{N_{lit}} \cdot \sum_{k=1}^{N_{lit}} \left| \frac{y_{k,lit} - y_{k,calc}}{y_{k,lit}} \right| \quad (14)$$

where $y_{k,lit}$ and $y_{k,calc}$ are the generic volumetric coefficients of the “k-th” observation both extracted from the literature and calculated, respectively; N_{lit} is the number of observations contained in each reference database.

Table 5. Comparison between literature values of the volumetric expansion coefficient and isothermal compressibility to those computed with Equations (9)–(11).

Compound/Ref.	α					β			
	[35]	[36]	[37]	[39]	[26]	[38]	[40]	[41] *	[42] *
methanol	0.81				0.66	0.92	0.82		
ethanol		2.43			0.46	0.82	0.45		
propan-1-ol		13.71			9.05	2.34	5.65		
propan-2-ol			1.73	3.98			2.06	64.04	
butan-1-ol				4.72	4.47	2.74	4.69		
butan-2-ol					23.52		1.74		
2-methylpropan-1-ol				4.08	5.46				
2-methylpropan-2-ol									10.62
pentan-1-ol		10.89			1.84	1.17	1.88		
pentan-2-ol		17.12			9.14		1.19		
pentan-3-ol		18.02		4.75	27.99		0.53		
2-methylbutan-1-ol							10.25		
2-methylbutan-2-ol					11.69		7.17		
3-methylbutan-2-ol							11.68		

* Errors provided for a comparison made, in the same interval as the one used in this work. If the comparison is made using the whole reference interval, the MARD for both references would be 77.20 and 24.48, respectively.

As mentioned, the agreement between the estimations made with the version presented of Tait equation and those from literature is reasonably good. However, an outlier was found when comparing with reference [41] in β , since for almost all compounds there is a reference showing a discrepancy around 10% or less. Despite this, the concordance of the proposed model with the available information, both from literature and our experimental data, shows the reliability of the obtained parametrizations for each pure compound.

Assuming that the volumetric coefficients are constant over the working range of p and T provided interesting results. Thus, Equation (13), particularized for both alpha and beta coefficients, is introduced into Equation (12) to determine the $v(p, T)$ of pure compounds. The corresponding calculations are summarized in Table 6; in addition, the increase in relative error is also calculated when the last equation is considered instead of the first. For each compound, the hypothesis of constant volumetric coefficients throughout the range lead to an increase in estimation errors, which are below 15%, and even below 10% for most of them, except for the tert-butanol. This result was expected, but even so, the increments are small and the reliability of the rough estimates made with the simplified equation of state, Equation (12), could be accepted, which would be quite useful to calculate $v(p, T)$ values.

Table 6. Averaged values, Equation (11), of α/K^{-1} and β/kPa^{-1} within the range $T \in [278\text{--}353]$ K and $p \in [0.1\text{--}40]$ MPa along with MARDs related to molar volume estimations made with Equation (6) (rigorous) and Equation (12) (simplified) equations of state.

	$10^4 \hat{\alpha}_{pT} \text{ K}^{-1}$	$10^7 \hat{\beta}_{pT} \text{ kPa}^{-1}$	MARD Tait Equation (6)	MARD Equation (10)	ΔMARD^*
methanol	10.68	9.926	0.01	0.19	12.38
ethanol	9.828	9.122	0.02	0.20	10.93
propan-1-ol	9.266	8.088	0.03	0.19	5.71
propan-2-ol	9.794	9.059	0.04	0.23	5.04
butan-1-ol	8.771	7.631	0.02	0.18	7.31
butan-2-ol	9.812	7.942	0.03	0.23	6.16
2-methylpropan-1-ol	8.858	8.108	0.02	0.20	9.05
2-methylpropan-2-ol	12.22	11.48	0.03	0.18	5.75
pentan-1-ol	8.249	7.216	0.01	0.16	15.03
pentan-2-ol	9.228	7.675	0.03	0.21	6.51
pentan-3-ol	9.725	7.393	0.03	0.23	5.96
2-methylbutan-1-ol	8.740	7.216	0.03	0.25	8.10
2-methylbutan-2-ol	10.78	8.343	0.03	0.21	6.00
3-methylbutan-2-ol	10.00	7.573	0.03	0.24	6.09

* $\Delta\text{MARD} = (\text{MARD}[\text{Equation (12)}] - \text{MARD}[\text{Equation (6)}]) / \text{MARD}[\text{Equation (6)}] \cdot 100$.

4. Conclusions

This work reports the experimental data of the variables p - ρ - T of 14 alcohols (primary, secondary and tertiary) with up to five carbon atoms. A database with more than 1300 values was generated, see SM, within the intervals of $p \in [0.1\text{--}40]$ MPa, and $T \in [278\text{--}358]$ K. The measured values are acceptable and agree well with those existing in literature, presenting relative errors of the order of 0.4%. For several alcohols, the range of p and T measurements was extended compared to the literature; measurements for 3-methylbutan-2-ol, are published for the first time in this work, and the values obtained being consistent with those found for the other alcohols. The modeling with a different version of the original Tait equation provided good results. From it, other derived properties were estimated, such as the volumetric coefficients, whose comparison with those from literature certified the stability of the parametrization carried out. The use of the averages of the last two quantities in the general EoS containing the alpha and beta coefficients, provided acceptable rough estimates of the molar volumes in the working interval, but showing higher errors ($5 \leq \Delta\text{MARD} \leq 15$) than those obtained with the modified Tait equation.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/liquids2010001/s1>, Table S1: Densities and refractive indices of pure alcohols at $T = 298.15$ K and atmospheric pressure (≈ 98.9 kPa), Table S2: Experimental p, ρ, T values.

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