Determination of Hildebrand solubility parameter of pure 1-alkanols up to high pressures

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Abstract

An extended approach to determine Hildebrand solubility parameter (HISP) of pure 1-alkanols by precise calculation of the isothermal compressibility coefficient and heat capacities is proposed. The approach is introduced during its implementation for four pure polar 1-alkanols, namely 1-heptanol, 1-octanol, 1-nonanol and 1-decanol. The accuracy comparison of the presented approach with the experimental data shows that the mean absolute error of predictions of the isothermal compressibility coefficient, isobaric heat capacity and HISP with the proposed approach are 1.77, 1.32, 0.17% (for 1-heptanol), 1.54, 1.11, 0.18% (for 1-octanol), 2.90, 0.97, 0.28% (for 1-nonanol) and 1.39, 1.61, 0.39% (for 1-decanol), respectively. The proposed approach is also compared with the previous methods for calculation of the properties. The comparisons show that for all the three properties, the proposed approach provides significantly accurate results and better predictions. Additionally, to investigate the effects of variation of temperature and pressure as two key parameters on HISP in 1-alkanols, sensitivity analyses are conducted. The results of sensitivity analyses show that same as the non-polar substances, in the case of polar compounds, increase in pressure leads to an increase in HISP. Furthermore, when temperature does not change, HISP value approaches a constant value at high pressures. Moreover, the relationship between temperature and HISP is also linear.

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Nomenclature

a	coefficients of polynomial for density at atmospheric pressure
A	Coefficient of Tait equation
b	coefficients of polynomial for speed of sound
B	Temperature dependent term of density equation
c	coefficients of polynomial for speed of sound at atmospheric pressure
C	constant of density equation
C_p	isobaric heat capacity (J mol^{-1} K^{-1})
C_p^{ig}	isobaric ideal gas heat capacity (J mol^{-1} K^{-1})
C_p^{res}	isobaric residual heat capacity (J mol^{-1} K^{-1})
C_V	heat capacity at constant volume (J mol^{-1} K^{-1})
C_V^{res}	residual heat capacity at constant volume (J mol^{-1} K^{-1})
d	coefficients of polynomial for heat capacity at constant pressure
e	coefficients of polynomial for ideal gas heat capacity at constant pressure
ΔE	difference between molar energies of vapor (ideal) and liquid phases (J mol^{-1})
F	carbon atoms dependent term of Eq. (12)
i	counter
j	counter
k	counter
MAE	mean average error
MW	molecular weight (g mol^{-1})
num	number of data
P	pressure (Pa)
V_{mol}	molecular volume (m^3 mol^{-1})

T	Temperature (K)
T_r	reduced temperature
r	coefficients of polynomial for density at atmospheric pressure
R	universal gas constant
u	speed of sound (m s^{-1})
Y	real (observed) value
$\hat{Y}$	Predicted (calculated) value
Abbreviations	
HISP	Hildebrand solubility parameter
Subscripts	
0	reference
C	critical
T_0P	conditions in which temperature and pressure are T_0 and P, respectively
mol	molecular
Greek symbols	
α_P	thermal expansion coefficient (K^{-1})
δ	Hildebrand solubility parameter ($MPa^{0.5}$)
δ_d	dispersive term of solubility
δ_h	hydrogen bounding term of solubility
δ_P	polar term of solubility
ρ	density (kg m^{-3})
κ_T	isothermal compressibility coefficient (Pa^{-1})
κ_S	isentropic compressibility (Pa^{-1})
ω	acentric factor

1. Introduction

Owing to its significance in demonstrating the behavior of solutions and phase equilibrium predictions, solubility takes into account as one of the most important properties of a liquid [1-7]. The solubility parameters have been employed extensively in various applications such as solvent selection, polymer foaming and blending, coatings, surface characterizations, oil exploration, transportation and storage of natural gas [8-15].

Many researchers have suggested several definitions for the solubility. Among them, Hildebrand solubility parameter (HISP) introduced by Hildebrand and Scott [16, 17], is an index which has been widely used. HISP is as a measure of cohesive energy density and used in the context of regular solution theory where the difference in the solubility parameter of two substances provides a measure of how different are the intermolecular forces. [18-24]. HISP is defined as the square root of the cohesive energy density as an estimated numerical value indicating solvency. It forms the basis of understanding of miscibility (like dissolves like); close values of HISP for two materials means that they are miscible. In addition to the original one [16, 17], a modified version for HISP theory was also presented by Hansen [25, 26], in which HISP is divided into three terms of polar, dispersion and hydrogen-bond effects for solutions with stronger interactions among molecules.

The available experimental data for HISP is usually restricted to the ambient temperature and pressure [18]. Moreover, for only a few substances, the experimental data is reported [18]. Therefore, researchers have tried to develop methods to determine HISP at ambient and non-ambient conditions.

Studies of Sheldon et al. [27], Rai et al. [28] and Lewin et al. [29] are three examples of studies in which the authors introduced methods to calculate HISP at ambient conditions. In the study of

Sheldon et al. [27], acidity and Abraham's hydrogen-bond basicity were initially obtained by applying the group contribution approach. Then, HISP was estimated as the secondary property by correlation. In the study of Rai et al. [28], HISP was determined by employing configurational-bias Monte Carlo simulations and transferable potentials for phase equilibriums (TraPPE). The simulations were done for several organic liquids. The results presented the mean error of 3.3% for HISP predicted value, which was significantly lower than previous similar investigations such as Belmares et al. [30] and Stefanis et al. [31]. In the study done by Lewin et al. [29], estimation of HISP of acrylate, methacrylate and their binary mixtures was done using TraPPE-UA approach, which led to calculate this parameter precisely with a mean absolute error of 2%.

Investigations with the subject of prediction of HISP at non-ambient conditions are categorized into two groups themselves. In the first group, the impact of either pressure or temperature on HISP is neglected; for instance, Barton [32] suggested a linear function for HISP, which only depends on temperature. Likewise, a simple equation to calculate HISP as a function of temperature was proposed by Hildebrand [16]. Prausnitz and Shair [33] also presented correlations for HISP of eleven gases over a broad range of temperature. In another study, Verdier et al. [19, 34] used the internal pressure approach to consider the pressure dependence of HISP. They calculated HISP for some of the pure non-polar hydrocarbons, dead and live crude oils at the constant temperature of 303.15 K and the pressures up to 30 MPa. As the internal pressure approach is not an appropriate way to narrate the cohesive energy density reasonably, the prediction accuracy diminished drastically for the pressures higher than 30 MPa.

Moreover, Rai et al. [20] computed HISP as well as internal pressure for ethanol, n-hexane and benzene. They applied Monte Carlo simulations and TraPPE to obtain these two properties. In their study temperature was kept at a constant value of 303.15 K while pressure varied up to 300 MPa. Rai et al. [20] also compared the values of HISP and square root of internal pressure. It was found that the difference between HISP and square root of internal pressure was less than 10% for benzene in the whole range, but in the case of n-hexane, they diverged from the pressures more than 90 MPa. Nevertheless, the results showed that using the square root of internal pressure approximation to predict HISP at any pressure for fluids with strongly polar interactions such as ethanol leads to huge errors.

In the second group, the impacts of both temperature and pressure have been simultaneously investigated. As an example of these studies, Vargas and Chapman [35] employed one-third rule to correlate molecular weight, mass density and refractive index of non-polar hydrocarbons. Thereafter, they used these three properties to obtain some other ones such as HISP, viscosity, thermal conductivity, diffusivity and heat capacity. As mass density and refractive index are functions of temperature and the model constant was also fixed over a wide range of temperature and pressure, the temperature dependence of the other variables was estimated by using the one-third rule. Therefore, the solubility parameter was calculated by setting the mass density of a substance in the range of its condition. While temperature dependent equation of Vargas and Chapman's equation did work properly, Wang et al [18] introduced a new simple equation based on the fundamental thermodynamic relations to predict HISP with a better accuracy for four non-polar pure hydrocarbons at temperatures between 298 to 433 K and pressures up to 137 MPa.

Review of the literature shows that although a lot of studies have determined HISP of non-polar compounds at the non-ambient conditions with almost less errors, for polar substances, there has not been any successful effort yet. In other words, for many years the researchers have attempted to predict the HISP of polar compounds accurately, but they have not found any precise way. In general, there are two strategies to find an accurate calculation method for a property. One of them is developing a completely new approach and another one is modifying and generalizing a previously introduced approach or procedure. For example, as it was previously stated, while Vargas and Chapman [35] developed a new way to calculate HISP of non-polar compounds, Wang et al [18] modified their temperature dependent equation and provide higher precisions for HISP calculation of that type of materials. Although it seems that accurate prediction of HISP of polar compounds needs developing a new way, following in Wang et al [18] footsteps, we extend their method in way that it becomes applicable to calculate this property for 1-alkanols with precise estimation. 1-alkanols are one the most widely used polar solvents and providing a solution for the unsolved problem of calculation of the solubility parameter for them is taken into account as significance of the work for practical applications. The method is described thoroughly with the required background during its implementation for four members of 1-alkanols family namely, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol. As it is seen in Table (1), these alcohols are increasingly being used in many applications. The accuracy of the proposed approach in comparison to the previous one [18] is evaluated and after that uncertainty analysis is done. As it will be seen, the proposed approach is able to determine HISP up to high pressures accurately not only for 1-alkanols but also non-polar materials and other alcohols. Even the proposed procedure is accurate than Wang et al. [18] approach in prediction of HISP of non-polar compounds. Moreover, it is very simple. Finally, in order to provide an extensive insight, sensitivity analyses are conducted. It helps to understand the effects of variation of temperature and pressure as two key parameters on HISP better. The significant share of Dzida's work [36], from which a large of number of required property correlations have been employed, should be acknowledged. Using experimental data, Dzida [36] provided valuable accurate correlations for some important properties of these four 1-alkanols including density, speed of sound, internal pressures, isobaric thermal expansion and compressibility.

{Insert Table (1) here}

2. The background

In this section, first, HISP is introduced briefly. After that, the approach of Wang et al [18], which is going to be made applicable for 1-alkanols, is described.

2.1. Hildebrand solubility parameter (HISP)

Hildebrand solubility parameter (HISP) is defined as the square root of density of cohesive energy as follows [16, 17]:

$$\delta = \left(\frac{\Delta E}{V_{mol}}\right)^{\frac{1}{2}} \tag{1}$$

where ΔE and V_{mol} are the molar energy difference of vapor (ideal) and liquid, and molecular volume, respectively. Considering Hansen [25, 26] modification, HISP is written as the geometric mean of his three introduced terms. In other words:

$$\delta^2 = \delta_d^2 + \delta_P^2 + \delta_h^2 \tag{2}$$

where δ_d, δ_P and δ_h stand for dispersion, polarization/ electrostatic force and hydrogen bound interactions [25, 29, 37-39].

2.2. Wang et al. approach

In Wang et al. [18] approach, HISP at temperature and pressure of ‘T’ and ‘P’ is calculated at two stages using available HISP data for the reference conditions, whose temperature and pressure are ‘T_0’ and ‘P_0’. In the first stage, HISP at temperature and pressure of ‘T_0’ and ‘P’ is obtained by Eq. (3), which is the pressure effect describing equation and was originally introduced by Vargas and Chapman [35]. Then, by employing equation of Eq. (4), which was a more comprehensive form of HISP temperature dependency equation of Vargas and Chapman [35] and developed by the Authors [18], HISP is calculated at ‘T’ and ‘P’.

$$\delta^2_{T_0P} = \frac{\rho_{T_0P}}{\rho_0}(\delta_0^2 - P_0) + \frac{1-\alpha_{P.T_0P}}{\kappa_{T.T_0P}}\left(1 - \frac{\rho_{T_0P}}{\rho_0}\right) + P \tag{3}$$

$$\delta^2 = \frac{\rho}{\rho_{T_0P}}\left[\delta^2_{T_0P} + \frac{\alpha_P}{\kappa_T}T_0 - \frac{\rho_{T_0P}C_V^{res}(T-T_0)}{1000\,MW\,\alpha_P}\right] + \left(\frac{1+\kappa_T P}{\kappa_T}\right)\left(1 - \frac{\rho}{\rho_{T_0P}}\right) - \frac{\alpha_P}{\kappa_T}T \tag{4}$$

In these equations, T, MW, α_P, C_V^{res} and ρ stand for temperature (K), molecular weight (g mol^{-1}), thermal expansion coefficient (K^{-1}), residual heat capacity at constant volume (J mol^{-1} K^{-1}) and density (kg m^{-3}), respectively. The subscript ‘T_0P’ stands for the condition in which temperature and pressure are T_0 and P. The subscript zero also refers to the reference conditions in which the value of HISP is available. Thus, the solubility at reference condition (δ_0) must be determined. In this study, the reference condition is pressure of 0.1 MPa and temperature of 293.15 K. The values of δ_d, δ_P and δ_h of the investigated 1-alkanols at the reference condition are reported in Table (2). Using these values δ_0 is calculated from Eq. (2).

{Insert Table (2) here}

3. Determination of the solubility parameter

Investigation of the reference [18] shows that, theoretically, there is no substance limitation for using Eqs. (3) and (4). In other words, they have potential of employing for all the substances including alcohols. The accurate estimation of the right-hand sides of Eqs. (3) and (4) is regarded as the key point to calculate the solubility parameter precisely. In the study of Wang et al. [18], κ_T is obtained analytically from Eq. (5) by differentiating of the Tait equation (Eq. (6)). In addition, they used Eq. (7) to calculate the residual heat capacity at the constant pressure (C_P^{res}). As it will be discussed further (in the section 4), using these equations for polar compounds such as 1-alkanols leads to significant error in κ_T, C_P^{res} and HISP and for this reason, the approach of [18] is only applicable to calculate HISP of only non-polar substances. Having found this important point and while all of the attempts have focused on bringing a completely new method, it is concluded that accurate determination of HISP of 1-alkanols is simpler than we have been thinking about; Eqs. (3) and (4) becomes applicable for 1-alkanols if κ_T, C_P, C_V^{res}, C_P^{res} are calculated precisely, with the methods which are different from the introduced ones in the reference [18]. In fact, for many years, we have all of the things which need to calculate HISP of 1-alkanols, but we did not pay attention to them. As it will be discussed in the section 4, using the proposed extended method leads to significant decrease in the HISP prediction error and fixes the unsolved problem of calculation of HISP of 1-alkanols.

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{5}$$

$$\rho = \frac{\rho_0}{1 - Aln(\frac{B(T)+P}{B(T)+P_0})} \tag{6}$$

$$C_P^{res} = \left\{1\ \ 586 + \frac{0\ \ 49}{1 - T_r} + \omega\left[4\ \ 2775 + \frac{6\ \ 3(1 - T_r)^{\frac{1}{3}}}{T_r} + \frac{0\ \ 4355}{1 - T_r}\right]\right\}R \tag{7}$$

In Eq. (7), ω stands for acentric factor. Additionally, and T_r are the reduced temperature, determined by Eq. (8).

$$T_r = \frac{T}{T_C} \tag{8}$$

In Eq. (8), T_C is critical temperature. The values of MW and T_C for the four investigated alcohols are given in Table (3).

{Insert Table (3) here}

In the extended approach, the calculation of HISP is done at two stages. First, using the available correlations found in the literature, some of the required properties to calculate HISP from Eqs. (3) and (4) are obtained directly. After that, in the second stage, the remaining properties are determined by employing the first stage calculated ones. As it will be shown in the results and discussion part, following this strategy leads to compute all of the properties of 1-alkanols such as κ_T, C_P, C_V^{res}, C_P^{res} precisely. In this study, the approach is described during its implementation for four members of 1-alkanols family, namely, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol.

3.1. Stage I: Calculation of liquid properties from the correlations

In order to calculate HISP by the proposed approach, some properties of 1-alkanols such as density, speed of sound and residual isobaric heat capacity are needed. These properties are the ones which can be obtained through experiments. In the previous studies which will be introduced in this part, for each property, there have been enough experimental data as well as at least an accurate correlation. Therefore, there is no need to conduct any further experiments and the valuable previous found correlations are used. In this part, we provide details about the employed correlations of this study; in some cases, like density at atmospheric pressure. After that, we selected the most accurate one between two existing ones. It should be noted that it does only to prepare higher accuracy to calculate properties like HISP in the second stage and showing the priority of one correlation to another is not the main goal.

3.1.1. **Density**

Like other parameters in different fields of science [40-43], several works have tried to find various ways to predict density of a liquid. Two different relations are available to calculate the density of the studied alcohols at atmospheric pressure; the first equation was proposed by Assael et al. [44]:

$$\rho_0 = \rho_c \left\{ 1 + \sum_{i=0}^{6} a_i (1 + T_r) \right\} \tag{9}$$

This equation was obtained through correlation of data between a temperature range of 300 to 340 K. The second equation was suggested by Dzida [36] at a temperature range from 293 to 318 K and atmospheric pressure:

$$\rho_0 = r_0 + r_1 T + r_2 T^2 \tag{10}$$

The coefficient values in Eqs. (9) and (10) are listed in Table (4) and Table (5), respectively.

{Insert Table (4) and Table (5) here}

The two above equations are valid only at atmospheric pressure. However, in practical conditions, knowing the density of a wide range of temperatures and pressures is necessary. Therefore, Assael et al. [44] presented a relation, given below, to calculate the density of n-alcohols at any desired condition:

$$\frac{\rho - \rho_0}{\rho_0} = C log \left[\frac{B + P}{B + P_0} \right] \tag{11}$$

where ρ_0 is derived from either Eq. (9) or Eq. (10), C is a constant, 0.2000. B is also a temperature dependent function evaluated as the following [44]:

$$B = 520\quad 23 - 1240T_r + 827T_r^2 - F \tag{12}$$

For the investigated 1-alkanols, F is obtained by Eq. (13) [44]:

$$F = 0\quad 015C_n(1 + 11\quad 5C_n) \tag{13}$$

Where C_n is the number of carbon atoms in a 1-alkanol molecule.

3.1.2. **Sound speed**

As it was mentioned before, for a large number of important properties of the investigated 1-alkanols, Dzida [36] presented accurate correlations using experimental data up to high pressures. Speed of sound was one of them. Temperature dependency sound speed is determined by the equation given below at the atmospheric pressure and desired temperature, which was introduced by Dzida [36]:

$$u_0 = c_0 + c_1T + c_2T^2 \tag{14}$$

where the values of c_0, c_1, and c_2 coefficients for the investigated alcohols are given in Table (6).

{Insert Table (6) here}

Like the density, for the speed of sound, in practical conditions, it is required to compute the value at a broad range of temperatures and pressures. Eq. (15), which was found by Dzida [36], represents the relation among pressure, temperature and sound speed [36]:

$$P - P_0 = \sum_{i=1}^{m}\sum_{j=0}^{n} b_{ij}(u - u_0)^i T^j \tag{15}$$

where P_0 denotes the atmospheric pressure, 0.1 MPa.

After calculating all the other parameters, the speed of sound is computed by the solution of the polynomial function derived from Eq. (15). The values of coefficients of Eq. (15) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol are presented in Table (7).

{Insert Table (7) here}

3.1.3. Residual isobaric heat capacity (C_P^{res})

In order to determine the isobaric heat capacity of pure organic liquids, Jovanovic et al. [45] recommended an empirical equation (Eq. (16)) providing a good prediction from atmospheric to high pressures. In that study [45], it was shown that this equation is more accurate than the previous ones, e.g., four-parameter equation proposed by Guseinov et al. [46] and five-parameter equation presented by Garg et al. [47].

$$\frac{1}{C_P} = d_0 + \frac{d_1}{T} + \frac{d_2}{T^2} + d_3TP \tag{16}$$

In Eq. (16), d_0, d_1, d_2 and d_3 are the coefficients whose values for the investigated alcohols are found in Table (8).

{Insert Table (8) here}

The heat capacity at constant pressure for the ideal gas is defined as [48]:

$$C_P^{ig} = R(e_0 + e_1T + e_2T^2 + e_3T^3 + e_4T^4) \tag{17}$$

where the values of e_1, e_2, e_3 and e_4 coefficients for different 1-alkanols are provided in Table (9).

{Insert Table (9) here}

Residual constant heat capacity is defined as the difference between real and ideal gas heat capacities:

$$C_P^{res} = C_P - C_P^{ig} \tag{18}$$

3.2. Stage II: Determination of the remaining properties from the stage I calculated ones

After calculation of the properties directly from the correlations in the first stage, other properties are obtained. Thermal expansion coefficient (α_P) is computed as follows:

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P \tag{19}$$

Moreover, C_V^{res} is calculated from Eq. (20) [48]:

$$C_V^{res} = C_P^{res} + R - (C_P - C_V) \tag{20}$$

In Eq. (20), R denotes the universal gas constant (8.314 J mol^{-1} K^{-1}). Furthermore, C_P-C_V is the difference between constant pressure and constant volume heat capacities (J mol^{-1} K^{-1}) which is obtained from Eq. (21):

$$C_P - C_V = \frac{\alpha_P^2 T}{\frac{\rho}{MW}\kappa_T} \tag{21}$$

At the end, having determined all of the required properties accurately, HISP is obtained from the Eqs. (3) and (4).

3.3. Summary

The method of calculation of HISP for the investigated 1-alkanols has been completely described so far. In this part to be employed more easily, it is explained one more time step by step:

1. Determine condition (temperature and pressure) in which HISP is going to be calculated.
2. Calculate the density at the reference condition. As it will be shown in section 4.1, Eq. (10) is better than Eq. (9) at predicting density at atmospheric condition.
3. Obtain the density at the investigated temperature and pressure.
4. Compute α_P at the investigated condition from Eq. (19).
5. Determine the speed sound at the reference and investigated conditions by Eqs. (14) and (15), respectively.
6. Obtain isobaric compressibility factor (κ_S) from the following equation:

$$\kappa_S = \frac{1}{\rho u^2} \tag{22}$$

7. Determine C_P from Eq. (16).
8. Find the isothermal compressibility coefficient by Eq. (23):

$$\kappa_T = \kappa_S + \frac{\alpha_P T^2}{\rho C_P} \tag{23}$$

9. Calculate C_P-C_V via Eq. (21).
10. Find C_P^{ig} by Eq. (17).
11. Use Eq. (18) to compute C_P^{res}.

12. Calculate C_V^{res} through Eq. (20).

13. Find δ^2 from Eqs. (3) and (4).

14. HISP is the square root of δ^2.

In order to understand better, the process flow chart of the proposed approach is illustrated in Fig. (1).

{Insert Fig. (1) here}

4. Results and discussion

4.1. The best equation for density at atmospheric pressure

Between Eqs. (9) and (10), the calculated density value closer to the experimental data pointed out in Table (10), is chosen. The results given in Table (10) show that the mean absolute error (MAE) of Eq. (3), computed by Eq. (24) given below, and employed in many studies in several studies like [49-53], is significantly less than that of computed for Eq. (4). Thus, to derive density, it is recommended that replace relation for ρ_0 used by Assael et al. [44] with Eq. (10). MAE is one of the parameters provides good description from the error and has wide application in error analysis as well as statistical modelling [54-57] and other types of studies [58-60]. It should be emphasized again, finding the most accurate equation to predict density is done to provide higher accuracy in calculation of HISP, and it is not one of the main goals of the study itself.

$$MAE = \frac{\sum_{k=1}^{num} \left| Y_k - \hat{Y}_k \right|}{num} \tag{24}$$

{Insert Table (10) here}

4.2. Verification of the proposed approach and comparison with the previous calculation methods

In this part, by using the previously published experimental data, the verification of the proposed approach is done. In addition, the abilities of the current and the analytical approaches, which was employed by Wang et al. [18], in the prediction of κ_T also compared together. It should be noted that to obtain the value of the analytical approach, first by rewriting Eq. (11), like Tait equation of state, the density as a function of pressure and temperature is formulized (Eq. (25)). After that, κ_T is obtained analytically from Eq. (5). In this case, as well as isobaric heat capacities, the prediction ability of Dzida's calculations [36] is also evaluated.

$$\rho = \rho_0(1 + Clog\left[\frac{B+P}{B+P_0}\right]) \tag{25}$$

Considering the critical role of density in calculating the other properties, the accuracy of the density is also checked at non-ambient conditions, using experimental data of Dávila et al. [61]. As the comparisons reported in Table (11) show, the vales of MAE of predictions for the four investigated 1-alkanols are only 0.13, 0.13, 0.08 and 0.07, respectively, so the provided way to calculate density offers high accuracy not only at atmospheric but also at other conditions.

{Insert Table (11) here}

4.2.1. Verification of the proposed approach

In order to verify the proposed approach, the experimental data reported in [32, 62, 63] is used. It should be mentioned that as it was stated in the introduction, there are a few number of experimental HISP data only at atmospheric pressure. The results are shown in Table (12). As it is seen, the mean absolute errors of prediction for the proposed approach for the four investigated 1-alkanols are 0.17, 0.18, 0.28 and 0.39%, respectively. Therefore, the proposed approach is verified. Moreover, it should be mentioned that as it is clearly stated in reference [48], Eq. (7) for calculation of the residual heat capacity is inaccurate for compounds with hydrogen bonds like alcohols, and for this reason, prediction of HISP by using this equation leads to unsatisfactory results. In addition, it should be also noted that as it was described in the introduction part, equation of state (internal pressure approach) can be used to calculate solubility as a function of pressure, but they do not work accurately for polar liquids that have hydrogen bonds such as alcohols and for this reason it has not been considered here for comparison purposes.

Furthermore, in this study like all of the previous studies done in the field of calculation of properties of 1-alkanols such as Dzida [36], Jovanovic [45] and Assael [44], the computed results were compared to the experimental data and there was no comparison to EoS, e.g. SAFT equations. First of all, it should be mentioned that comparison with those mentioned equations is not the goal of this study. Moreover, in reference [64] it was discussed that there are three main serious concerns about using and comparing the results of EoS, e.g. SAFT methods in the field of 1-alkanols. One of them is that although hydrogen bonding is electrostatic, in the SAFT the association term is non-electrostatic. Another one is that when association and dipolar terms are added, the number of adjustable parameters could reach six, which causes computational difficulties. Knowing this problem, several studies have suggested that the parameters of pure SAFT are calculated with the aid of mixture data. However, employing mixture data as inputs does not guarantee a realistic evaluation of SAFT. The last issue is that it is not easy to decide which of the complex dipolar models found in the literature is the most accurate because each group has developed dipolar model differently with a distinctive perspective and a systematic comparison of the performance of them is not available.

{Insert Table (12) here}

4.2.2. Comparison of the obtained isothermal compressibility coefficient

The obtained values of κ_T were compared by those reported by Dávila et al. [61]. As results in Table (13) shows, the values of MAE for κ_T of the current approach for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol were 1.77, 1.54, 2.90 and 1.39%, respectively. Therefore, the accuracy of the proposed strategy is confirmed. In this table, the calculations of Dzida [36] are also compared. As it is seen, for all the investigated 1-alkanols, especially 1-nonanol and 1-decanol, the current approach provides more accurate predictions than Dzida's [36] calculations. Moreover, these values for error are much less than the predictions of the mentioned analytical approach i.e. 6.63, 19.77, 23.45 and 27.04%.

{Insert Table (13) here}

4.2.3. Comparison of the obtained isobaric heat capacities

The values of error in prediction of isobaric heat capacities determined by the proposed approach and Dzida's calculation are compared together in Table (14). The experimental data of references [65, 66] are used for this purpose. The results reported in Table (14), which shows that like isothermal compressibility coefficient, in this case, the proposed approach provides more precise results. For the four investigated 1-alkanols, the errors of predictions of the proposed approach are 1.32, 1.11, 0.97 and 1.61% while these values for Dzida's calculation are 2.21, 1.87, 2.08 and 3.18%, respectively.

{Insert Table (14) here}

4.2.4. More details

In the aforementioned subsections, it has been showed that the proposed approach is an accurate one in the prediction of not only HISP but also κ_T and C_P^{res}. The only remaining point is the range of validation. The intersection of validation ranges of the applied equations is temperatures between 293.15 to 318.15 K and pressures up to 100 MPa, so the accurate prediction of the proposed approach is guaranteed in the mentioned range. It should be also mentioned that all the experimental data extracted for comparison purposed in this section are in the validation range of the proposed approach.

4.3. Uncertainty analysis

Uncertainty of the proposed approach is evaluated by the estimated standard uncertainty (ESU). It is calculated as follows [67]:

$$ESU = \frac{SD}{\sqrt{num_{data}}} \tag{26}$$

The values of ESU for the proposed approach in the predictions of HISP, κ_T and C_P^{res} are given in Table (15). As it is seen in this table, in all the cases, the proposed approach has an acceptable level of uncertainty.

{Insert Table (15) here}

4.4. Calculation of Hildebrand solubility parameter and sensitivity analysis

The accuracy of the proposed approach and its superiority to the previous ones have been shown so far. Now, in this part, HISP is calculated by using the proposed approach. HISP is calculated for the four investigated 1-alkanols at temperatures of 293.15, 298.15, 303.15 and 318.15 K and the pressure close to 1atm (0.1MPa) as well as pressures between 10 to 100 MPa at the intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 MPa. The values are indicated in Table (16). In addition to HISP, the values of the isothermal compressibility coefficient and the residual isobaric heat capacity are given in Table (16).

{Insert Table (16) here}

Table (16) provides information about the trend of variation of HISP with temperature and pressure. However, it is hard to understand the details of behaviors from that (for example, variation is linear or not). Therefore, in order to bring more extensive insight and understand easier, the effects of pressure and temperature variations on HISP are also shown in Figs (2) and (3), respectively. Same as non-polar substances studied previously in the reference [1], for the alcohols studied here, as presented in Fig. (2), HISP has an upward trend with increase in pressure. The reason is that the intermolecular forces increase at higher pressures [68-70]. At a constant temperature, the higher pressure for a liquid means that there is further distance from the gas state [68-70]. Therefore, cohesive energy and intermolecular forces increase by increase in pressure. The studies in which the impacts of pressure on other intermolecular forces related parameters like viscosity have been investigated have also confirmed that a liquid at higher pressures has more intermolecular forces [71]. Moreover, when temperature does not change, at higher pressures HISP approaches a constant value. The reason is significant increasing in intermolecular forces at higher pressures, which was also observed in the studies with topic of investigation of the effects of pressure on the other intermolecular related parameters like viscosity [71]. Furthermore, as presented in Fig. (3), HISP decreases as the temperature increases, which is in agreement with the reported values for some alcohols including methanol, ethanol and 1-butanol [14]. It is because of lowering the cohesive energy-intermolecular forces with raise in temperature [68-70]. In addition, HISP of studied alcohols is less sensitive to pressure and temperature changes in comparison to non-polar substances. It is because of the point that the influence of pressure and temperature on the cohesive energy and intermolecular forces are more for non-polar compounds. Comparing the changes in viscosity as an intermolecular force related parameter for hydrocarbons and 1-alcanols series with the same carbon atom numbers, which are available in [71-74], also proved the higher sensitivity of the non-polar compounds.

{Insert Fig. (2) and Fig. (3) here}

4.5. Investigation of the generality of the proposed approach

In this part, in order to investigate the generality of the proposed approach, its validity for non-polar compounds is checked. In addition, HISP of some other alcohols is calculated with the suggested procedure and the errors are evaluated.

4.5.1. Non-polar compounds

Four non-polar compounds investigated by Wang et al. [18], namely benzene, toluene, n-heptane and n-dodecane are selected to check the validity of the proposed approach for this type of materials. The employed references to obtain the required properties as well as the mean absolute error of prediction for each item are indicated in Table (17). As it is seen in this table, the proposed approach not only is accurate for non-polar compounds but also provides more accurate predictions than Wang et al. [18] approach.

{Insert Table (17) here}

4.5.2. Other alcohols

In order to check the generality of the proposed approach for other alcohols, HISP values of the ones listed in Table (18) are calculated, and the errors are evaluated. The details of calculations, including the used references and obtained mean absolute errors, are presented in Table (18). According to this table, for the alcohols investigated here, the proposed approach also provides high accuracy; the maximum mean absolute error of prediction is only 0.88%. In addition, this table shows that in addition to the primary alcohols, the proposed approach is able to determine HISP of some secondary alcohols precisely.

{Insert Table (18) here}

4.6. The ability of the proposed approach to calculate surface plasmon

As discussed in the references like [75], surface plasmon is one of the properties a material which describes the coherent delocalized electron. It can be determined by using the Maxwell equations. Therefore, if the approach is conducted to obtain the value of HISP, and then, HISP is employed in the developed method of Vargas and Chapman [35], refractive index and in consequence, surface plasmon is calculated.

5. Conclusion

An extended approach to calculate the Hildebrand solubility parameter (HISP) of pure 1-alkanols was introduced. In this approach, all the parameters in HISP relation were computed accurately. Especially, isothermal compressibility coefficient (κ_T) was obtained much more accurate than the previous methods. Moreover, the prediction error of heat capacities was decreased drastically by considering the simultaneous effects of both temperature and pressure, rather than just considering temperature dependency as conducted by the past approach. The application of the approach was shown for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol as four member of 1-alcohols family. The comparison of the proposed and the past approaches with the previously published experimental data showed that for the four mentioned alcohols the errors of prediction of the current approach were 1.77, 1.54, 2.90, 1.39% (for the isothermal compressibility coefficient), 1.32, 1.11, 0.97, 1.61 (for the residual isobaric heat capacity) and 0.17, 0.18, 0.28, 0.39% (for HISP). The comparison of the prediction ability of the proposed approach with previous ones also showed that the proposed approach provided significantly more accurate results for deriving solubility parameter as well as isothermal compressibility coefficient and heat capacities. Furthermore, in order to provide an extensive insight from the impacts of variation of temperature and pressure as two key performance parameters on HISP, sensitivity analyses were conducted and the results were interpreted. As shown by sensitivity analyses, HISP has a direct relationship with pressure and at high pressures, the values of HISP at a constant temperature approach a limiting value. Moreover, a converse linear decrement in HISP by increase in temperature is observed at constant temperature. In addition, it was found that in comparison to the non-polar, for polar compounds, HISP is less sensitive to these two parameters. The further done investigations also showed that the proposed approach is able to determine HISP of non-polar compounds more accurately than Wang et al. [18] approach while for some other alcohols it provides precise estimation. Separate calculation of the three terms Hansen's solubility parameter for polar compounds like alcohols is suggested as one of the further possible developments of the presented work.

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Figure captions:

Fig. (1): The flow chart of the proposed procedure of calculation of properties by which HISP is calculated. In this flowchart, the process of calculation is described stage by stage.

Fig. (2): Effect of pressure on HISP of the investigated alcohols at different temperatures: (a) 1-heptanol and 1-octanol; (b) 1-nonanol and 1-decanol

Fig. (3): Effect of temperature on HISP of the investigated alcohols at different pressures: (a) 1-heptanol and 1-octanol; (b) 1-nonanol and 1-decanol

Table captions:

Table (1): Some important applications of the studied alcohols

Table (2): The values of δ_d, δ_P and δ_h for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol at 0.1 MPa and 293.15 K

Table (3): MW and TC of the studied alcohols [48]

Table (4): The coefficients values of Eq. (9) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [44]

Table (5): The coefficients values of Eq. (10) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [36]

Table (6): The coefficients values of Eq. (14) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [36]

Table (7): The coefficients values of Eq. (15) for 1-heptanol, 1-octanol, 1-nonanol and 1-

decanol [36]

Table (8): The coefficients values of Eq. (16) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [45]

Table (9): The coefficients values of Eq. (17) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [48]

Table (10): Comparison of calculated and experimental densities at atmospheric pressure for the investigated 1-alkanols in kg m-3

Table (11): Comparison of calculated and experimental densities of the investigated 1-alkanols at non-ambient conditions

Table (12): Comparison of calculated and experimental HISP at atmospheric pressure for the investigated 1-alkanols in MPa0.5

Table (13): Comparison of calculated and experimental isothermal compressibilities for the investigated 1-alkanols in TPa-1

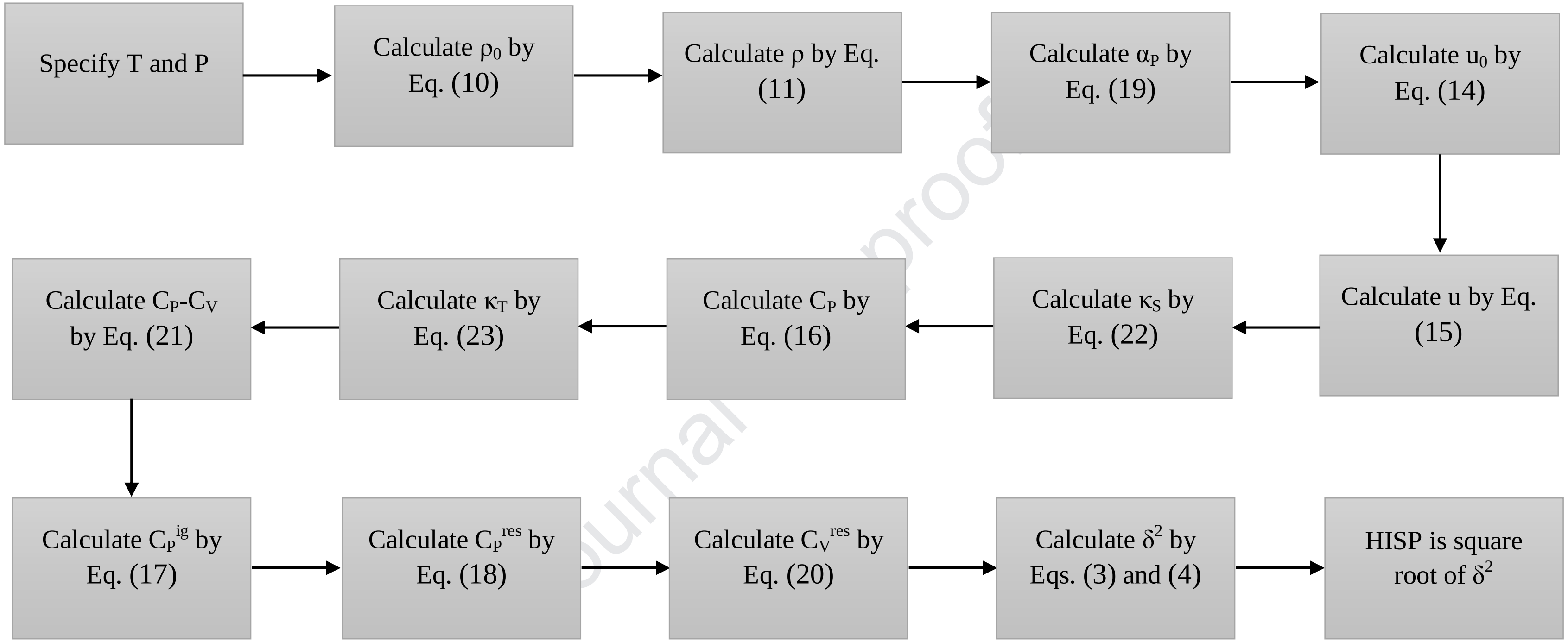
Table (14): Comparison of calculated and experimental isobaric heat capacities

Table (15): Comparison of ESU of the proposed and the previous approaches in prediction of HISP, isothermal compressibility coefficient and residual isobaric heat capacity

Table (16): HISP, isothermal compressibility coefficient and residual constant pressure heat capacities calculated by the proposed approach of the current study. The values are reported in MPa0.5, TPa-1 and J mol-1 K-1, respectively.

Table (17): Checking the validity of the proposed approach for calculation of HISP of the selected non-polar compounds.

Table (18): Checking the validity of the proposed approach for calculation of HISP of the other alcohols



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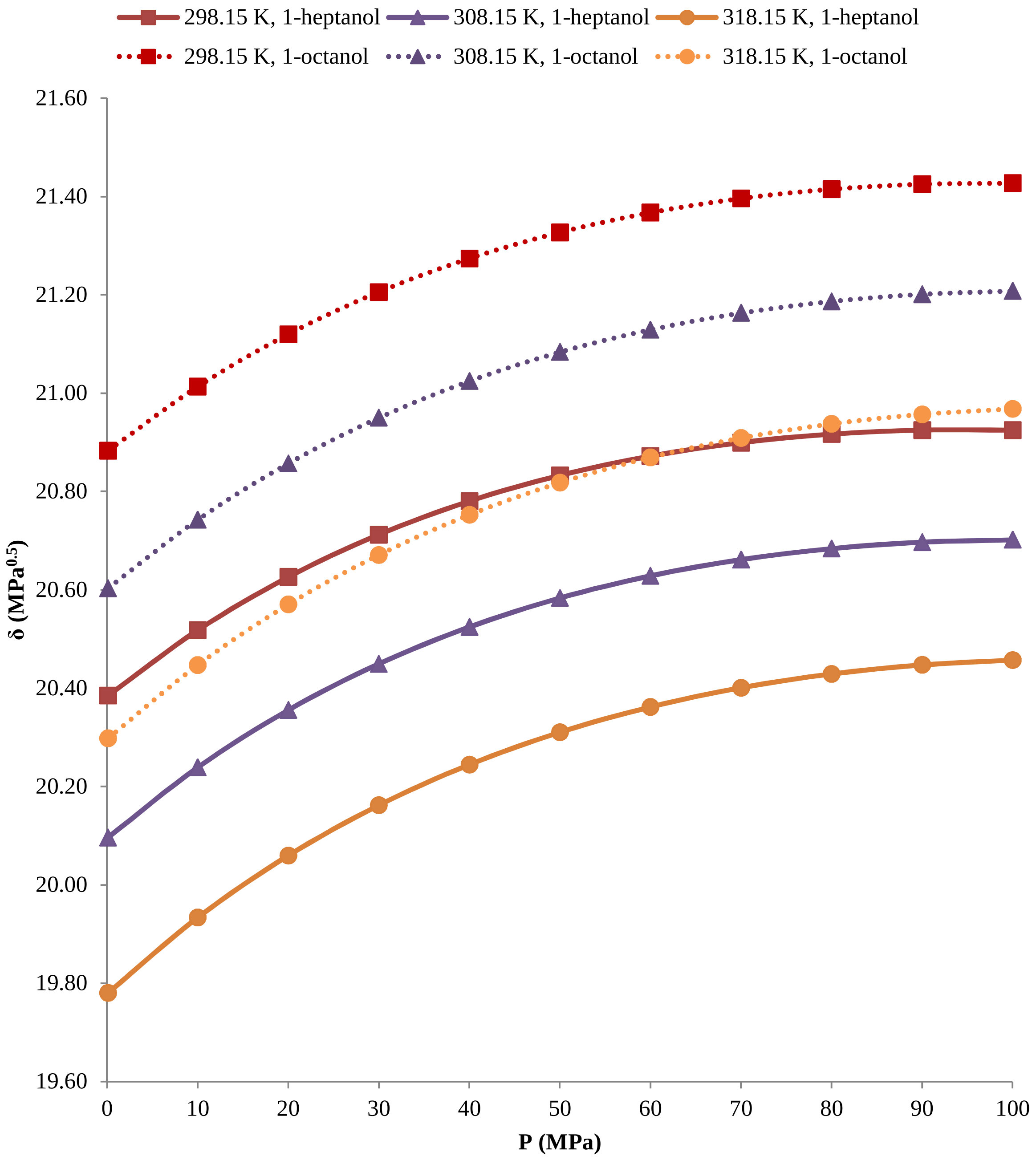
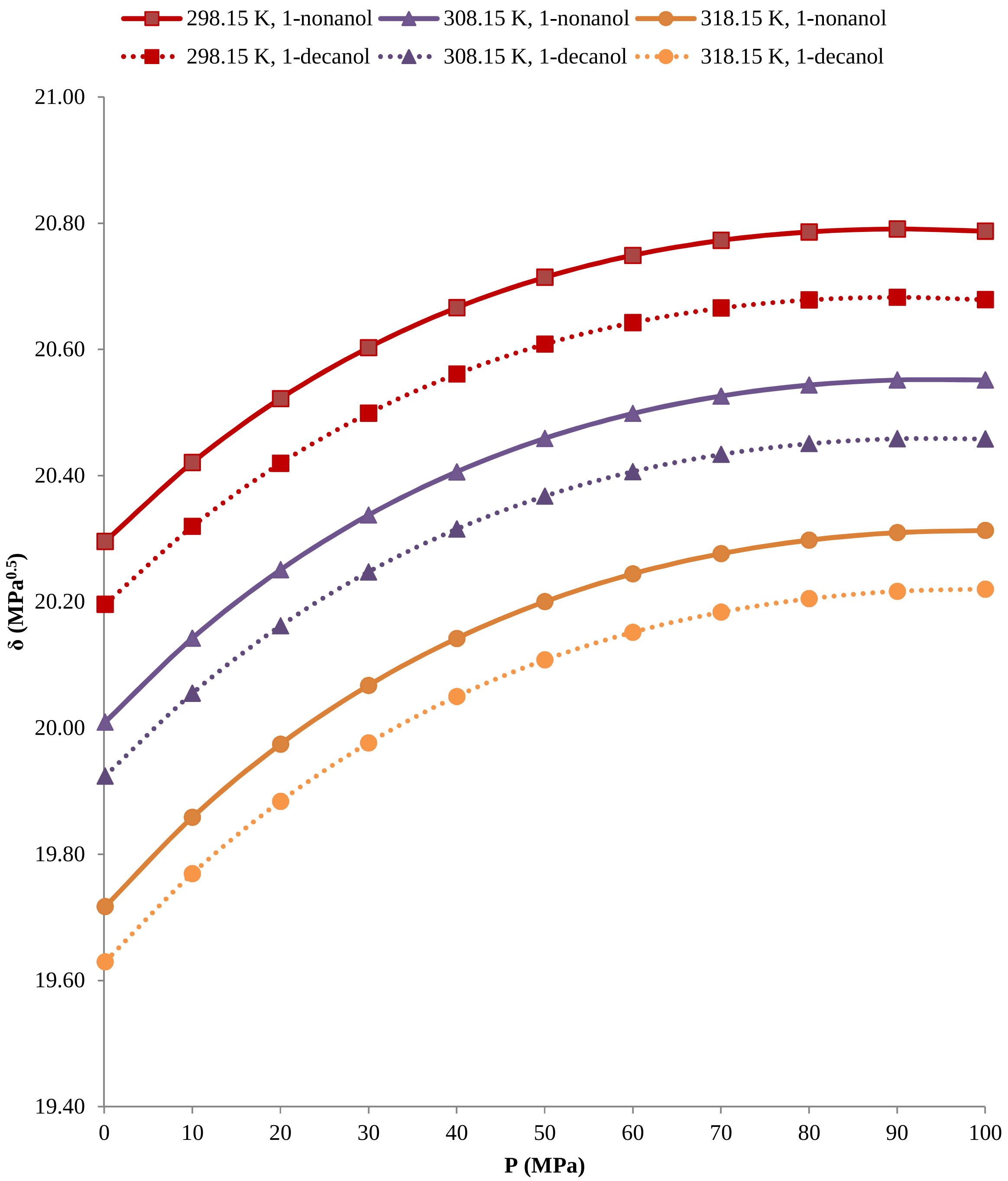
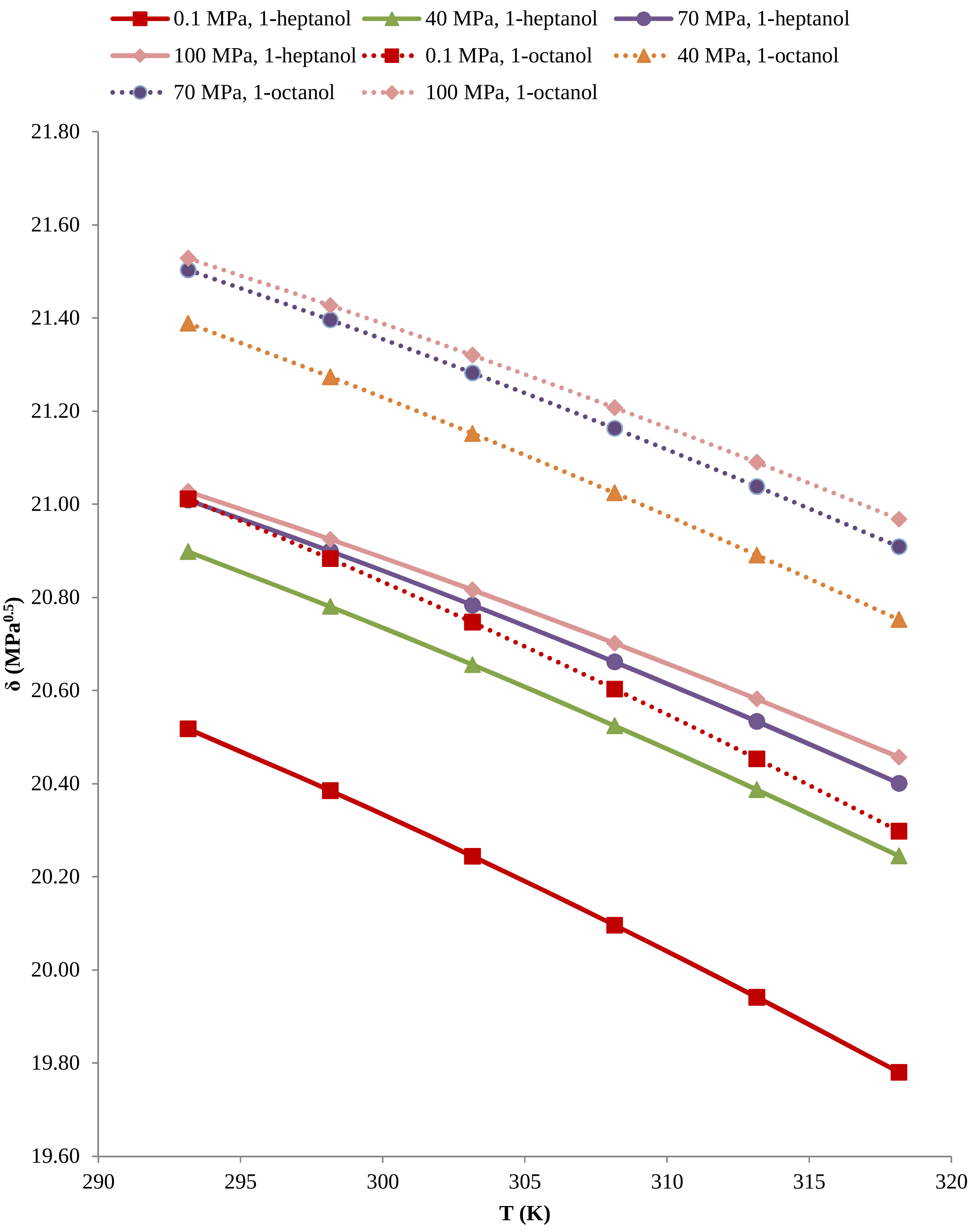

298.15 K, 1-heptanol
308.15 K, 1-heptanol
318.15 K, 1-heptanol
298.15 K, 1-octanol
308.15 K, 1-octanol
318.15 K, 1-octanol
δ (MPa^0.5)
21.60
21.40
21.20
21.00
20.80
20.60
20.40
20.20
20.00
19.80
19.60
0
10
20
30
40
50
60
70
80
90
100
P (MPa)

(a)

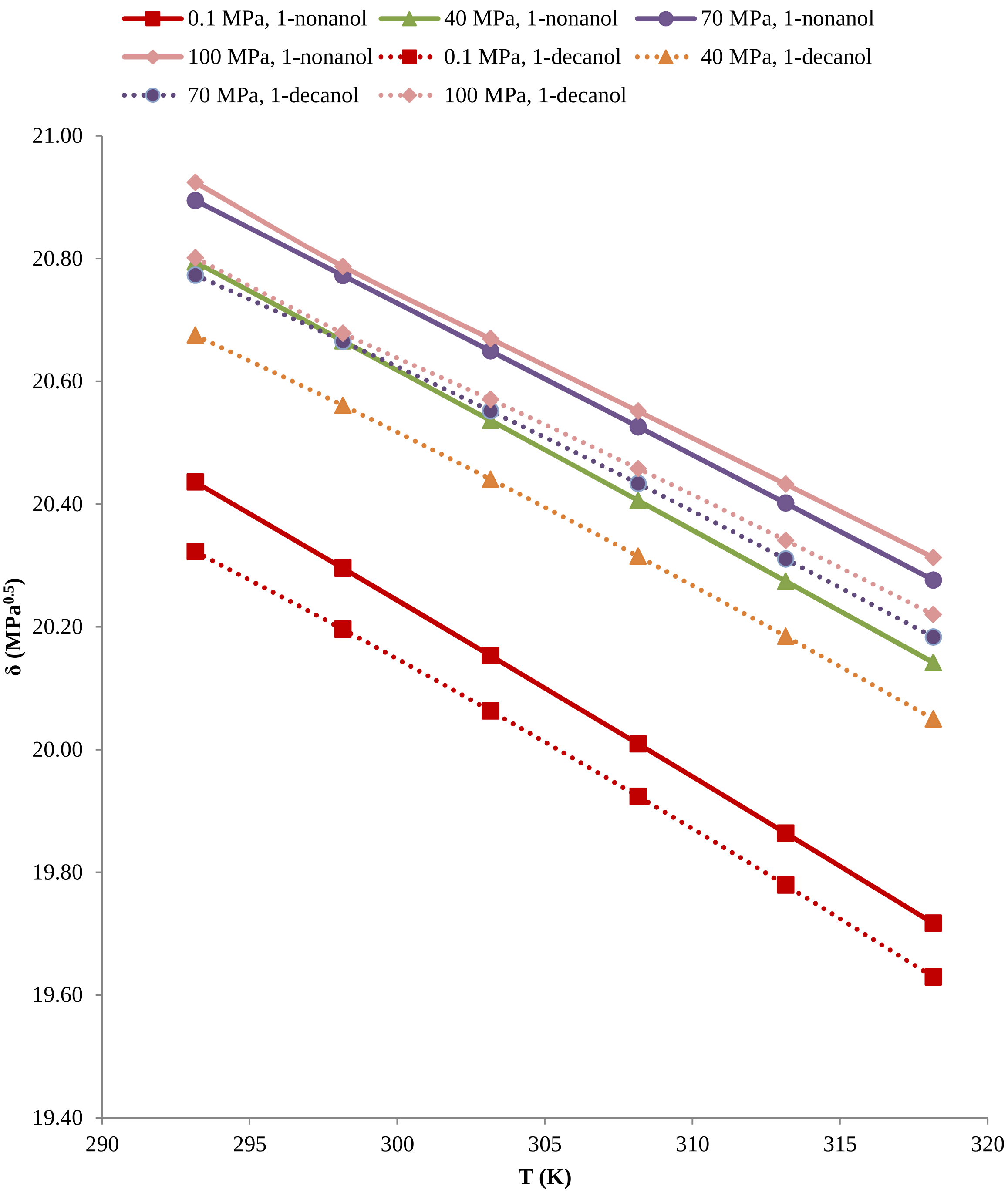


(b)

Fig. (2): Effect of pressure on HISP of the investigated alcohols at different temperatures: **(a)** 1-heptanol and 1-octanol; **(b)** 1-nonanol and 1-decanol


0.1 MPa, 1-heptanol
40 MPa, 1-heptanol
70 MPa, 1-heptanol
100 MPa, 1-heptanol
0.1 MPa, 1-octanol
40 MPa, 1-octanol
70 MPa, 1-octanol
100 MPa, 1-octanol
21.80
21.60
21.40
21.20
21.00
20.80
20.60
20.40
20.20
20.00
19.80
19.60
δ (MPa^0.5)
290
295
300
305
310
315
320
T (K)

(a)



(b)

Fig. (3): Effect of temperature on HISP of the investigated alcohols at different pressures: **(a)** 1-heptanol and 1-octanol; **(b)** 1-nonanol and 1-decanol

Table (1): Some important applications of the studied alcohols [76-79]

Compound	**Applications**
1-heptanol	Fruit taste perfumes (because it smells pleasant) , plasticizer of polymers, detergents which are used in toilets
1-octanol	Additive for fuels, plasticizer, non-pesticidal agricultural chemicals
1-nonanol	Production of artificial lemon oil, Intermediate in lemon taste perfume manufacture
1-decanol	Additive for fuels, lubricant, additive in paint industry

Table (2): The values of δ_d, δ_P and δ_h for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol at 0.1 MPa and 293.15 K

Compound	**δ_d (MPa)$^{0.5}$**	**δ_P (MPa)$^{0.5}$**	**δ_h (MPa)$^{0.5}$**
1-heptanol [26]	16.0	5.3	11.7
1-octanol [26]	17.0	3.3	11.9
1-nonanol [80]	16.8	4.8	10.6
1-decanol [26]	17.5	2.6	10.0

Table (3): MW and T_C of the studied alcohols [48]

Compound	MW (g mol^{-1})	T_C (K)
1-heptanol	116.203	631.90
1-octanol	130.230	652.50
1-nonanol	144.257	668.90
1-decanol	158.284	684.40

Table (4): The coefficients values of Eq. (9) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [44]

Compound	**ρ_c (kg m^{-3})**	**a_0**	**a_1**	**a_2**	**a_3**	**a_4**	**a_5**	**a_6**
1-heptanol	267	1.841512	0.656310	0.561043	-0.343507	0.0	0.0	0.0
1-octanol	266	-3.533725	54.85805	-199.6525	345.7972	-285.0304	90.54450	0.0
1-nonanol	265	3.500512	-6.128173	9.354806	-3.990277	0.0	0.0	0.0
1-decanol	264	2.250129	3.402373	-14.54532	20.62086	-8.993219	0.0	0.0

Table (5): The coefficients values of Eq. (10) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [36]

Compound	**r_0 (kg m^{-3})**	**r_1 (kg m^{-3} K^{-1})**	**$r_2 \times 10^4$ (kg m^{-3} K^{-2})**
1-heptanol	983.002	-0.3993296	-5.07848
1-octanol	983.294	-0.3955131	-4.92143
1-nonanol	995.338	-0.4618601	-3.75632
1-decanol	989.849	-0.4188373	-4.34218

Table (6): The coefficients values of Eq. (14) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [36]

Compound	**c_0 (m s^{-1})**	**c_1 (m s^{-1}K^{-1})**	**$c_2 \times 10^3$ (m s^{-1}K^{-2})**
1-heptanol	2497.354	-4.416949	1.65176
1-octanol	2560.249	-4.714394	2.16735
1-nonanol	2555.809	-4.560609	1.89642
1-decanol	2696.695	-5.376703	3.21792

Table (7): The coefficients values of Eq. (15) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [36]

Compound	**j**	**b_{1j} (K^{-j} MPa s m^{-1})**	**b_{1j} (K^{-j} MPa s^2 m^{-2})**	**b_{1j} (K^{-j} MPa s^3 m^{-3})**
1-heptanol	0	0.4261233304	$2.06383455 \times 10^{-4}$	0.0
	1	$-8.23147105 \times 10^{-4}$	0.0	0.0
	2	0.0	0.0	$-2.76888747 \times 10^{-4}$
1-octanol	0	0.2803665851	$3.16738349 \times 10^{-4}$	0.0
	1	0.0	$-4.20983029 \times 10^{-7}$	0.0
	2	$-1.04835117 \times 10^{-6}$	0.0	0.0
1-nonanol	0	0.2823007509	$3.19513200 \times 10^{-4}$	0.0
	1	0.0	$-4.18349839 \times 10^{-7}$	0.0
	2	$-1.05123867 \times 10^{-6}$	0.0	0.0
1-decanol	0	0.2594264772	$3.33303397 \times 10^{-4}$	0.0
	1	0.0	0.0	0.0
	2	$-7.41555104 \times 10^{-7}$	$-1.58502851 \times 10^{-9}$	0.0

Table (8): The coefficients values of Eq. (16) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [45]

Compound	**d_0 (J^{-1} mol K)**	**d_1 (J^{-1} mol K^2)**	**d_2 (J^{-1} mol K^3)**	**d_3 (J^{-1} mol MPa^{-1})**
1-heptanol	4.66609×10^{-3}	-2.16604×10^{0}	5.58774×10^{2}	7.34137×10^{-9}
1-octanol	4.33262×10^{-3}	-2.01110×10^{0}	5.07371×10^{2}	5.55320×10^{-9}
1-nonanol	2.02861×10^{-4}	1.03810×10^{0}	-7.60159×10^{1}	2.95724×10^{-9}
1-decanol	3.60921×10^{-3}	-1.58784×10^{0}	3.94315×10^{2}	3.04769×10^{-9}

Table (9): The coefficients values of Eq. (17) for 1-heptanol, 1-octanol, 1-nonanol and 1-decanol [48]

Compound	**e_0**	**$e_1 \times 10^3$**	**$e_2 \times 10^5$**	**$e_3 \times 10^8$**	**$e_4 \times 10^{11}$**
1-heptanol	7.935	18.023	14.223	-20.320	8.262
1-octanol	9.193	18.228	16.682	-23.641	9.580
1-nonanol	10.350	19.105	19.007	-26.878	10.891
1-decanol	11.637	19.130	21.517	-30.271	12.247

Table (10): Comparison of calculated and experimental densities at atmospheric pressure for the investigated 1-alkanols in kg m^{-3}

Calculation method	**Temperature (K)**			**MAE (%)**
	298.15	**308.15**	**318.15**	
		1- heptanol		
Exp. [61]	818.50	811.40	804.30	-
Eq. (10)	818.80	811.73	804.55	0.04
Eq. (9)	949.82	947.88	945.89	16.82
		1- octanol		
Exp. [61]	821.40	814.50	807.50	-
Eq. (10)	821.62	814.68	807.65	0.02
Eq. (9)	946.37	944.26	942.09	15.94
		1- nonanol		
Exp. [61]	823.20	816.50	809.80	-
Eq. (10)	824.24	817.35	810.38	0.10
Eq. (9)	945.55	943.27	940.92	15.53
		1- decanol		
Exp. [61]	825.50	818.70	811.90	-
Eq. (10)	826.37	819.55	812.64	0.10
Eq. (9)	943.45	940.99	938.48	14.94

Table (11): Comparison of calculated and experimental densities of the investigated 1-alkanols at non-ambient conditions

Compound	**Experimental data source**	**Number of experimental data points**	**MAE (%)**
1-Heptanol	Dávila et al. [61]	21	0.13
1-Octanol	Dávila et al. [61]	21	0.13
1-Nonanol	Dávila et al. [61]	21	0.08
1-Decanol	Dávila et al. [61]	21	0.07

Table (12): Comparison of calculated and experimental HISP at atmospheric pressure for the investigated 1-alkanols in $MPa^{0.5}$

Method	Temperature (K)			MAE (%)
	298.15	308.15	318.15	
1-heptanol				
Experimental [32, 62, 63]	20.37	20.07	19.73	-
The present approach	20.39	20.10	19.78	0.17
1-octanol				
Experimental [32, 62, 63]	20.85	20.55	20.27	-
The present approach	20.88	20.60	20.30	0.18
1-nonanol				
Experimental [32, 62, 63]	20.24	19.96	19.66	-
The present approach	20.30	20.01	19.72	0.28
1-decanol				
Experimental [32, 62, 63]	20.25	19.92	19.45	-
The present approach	20.20	19.92	19.63	0.39

Table (13): Comparison of calculated and experimental isothermal compressibilities for the investigated 1-alkanols in TPa^{-1}

Compound	Experimental data source	Number of experimental data points	Method	MAE (%)
1-heptanol	Dávila et al. [61]	21	The present approach	1.77
			Dzida's calculation [36]	2.68
			The analytical approach employed in [18]	6.63
1-octanol	Dávila et al. [61]	21	The present approach	1.54
			Dzida's calculation [36]	2.62
			The analytical approach employed in [18]	19.77
1-nonanol	Dávila et al. [61]	21	The present approach	2.90
			Dzida's calculation [36]	4.67
			The analytical approach employed in [18]	23.45
1-decanol	Dávila et al. [61]	21	The present approach	1.39
			Dzida's calculation [36]	2.76
			The analytical approach employed in [18]	27.04

Table (14): Comparison of calculated and experimental isobaric heat capacities

Compound	Experimental data source	Number of experimental data points	Method	MAE (%)
1-heptanol	Fulemet al. [65]	94	The present approach	1.32
			Dzida’s calculation [36]	2.21
1-octanol	Fulemet al. [65]	92	The present approach	1.11
			Dzida’s calculation [36]	1.87
1-nonanol	Nazievet al. [66]	78	The present approach	0.97
			Dzida’s calculation [36]	2.08
1-decanol	Fulemet al. [65]	94	The present approach	1.61
			Dzida’s calculation [36]	3.18

Table (15): Comparison of ESU of the proposed and the previous approaches in prediction of HISP, isothermal compressibility coefficient and residual isobaric heat capacity

Compound	property	ESU	Unit
1-heptanol	HISP	0.08	$MPa^{0.5}$
	κ_T	6.03	TPa^{-1}
	C_P^{res}	0.97	$J\ mol^{-1}\ K^{-1}$
1-octanol	HISP	0.07	$MPa^{0.5}$
	κ_T	14.21	TPa^{-1}
	C_P^{res}	1.00	$J\ mol^{-1}\ K^{-1}$
1-nonanol	HISP	0.08	$MPa^{0.5}$
	κ_T	13.64	TPa^{-1}
	C_P^{res}	0.45	$J\ mol^{-1}\ K^{-1}$
1-decanol	HISP	0.08	$MPa^{0.5}$
	κ_T	13.22	TPa^{-1}
	C_P^{res}	0.98	$J\ mol^{-1}\ K^{-1}$

Table (16): HISP, isothermal compressibility coefficient and residual constant pressure heat capacities calculated by the proposed approach of the current study. The values are reported in MPa$^{0.5}$, TPa^{-1} and J mol^{-1} K^{-1}, respectively.

P (MPa)	**T (K)**																	
	293.15			**298.15**			**303.15**			**308.15**			**313.15**			**318.15**		
	HISP	κ_T	C_P^{res}	HISP	κ_T	C_P^{res}	HISP	κ_T	C_P^{res}	HISP	κ_T	C_P^{res}	HISP	κ_T	C_P^{res}	HISP	κ_T	C_P^{res}
1-heptanol																		
0.1	20.52	785.29	90.55	20.39	804.91	94.79	20.24	831.69	98.87	20.10	856.37	102.77	19.94	882.12	106.49	19.78	908.97	110.03
10	20.65	721.06	89.07	20.52	739.98	93.21	20.38	759.58	97.18	20.24	779.90	100.98	20.09	800.97	104.59	19.93	822.80	108.01
20	20.75	668.42	87.59	20.63	684.58	91.63	20.49	701.28	95.50	20.36	718.53	99.19	20.21	736.33	102.69	20.06	754.71	106.01
30	20.83	624.58	86.12	20.71	638.70	90.06	20.58	653.23	93.83	20.45	668.21	97.42	20.31	683.62	100.82	20.16	699.50	104.03
40	20.90	587.34	84.68	20.78	599.86	88.52	20.66	612.73	92.19	20.52	625.95	95.68	20.39	639.55	98.97	20.24	653.53	102.08
50	20.95	555.20	83.24	20.83	566.44	86.99	20.71	577.98	90.56	20.58	589.82	93.95	20.45	601.99	97.15	20.31	614.47	100.16
60	20.98	527.09	81.83	20.87	537.28	85.48	20.75	547.74	88.96	20.63	558.47	92.25	20.50	569.47	95.35	20.36	580.76	98.26
70	21.01	502.24	80.43	20.90	511.57	83.99	20.78	521.14	87.37	20.66	530.94	90.57	20.53	540.98	93.57	20.40	551.29	96.38
80	21.02	480.09	79.04	20.92	488.69	82.51	20.80	497.49	85.80	20.68	506.52	88.91	20.56	515.76	91.82	20.43	525.24	94.53
90	21.03	460.17	77.67	20.92	468.15	81.05	20.81	476.31	84.26	20.70	484.67	87.27	20.57	493.23	90.09	20.45	502.01	92.71
100	21.03	442.16	76.31	20.92	449.59	79.61	20.82	457.19	82.72	20.70	464.98	85.65	20.58	472.96	88.38	20.46	481.14	90.91
1-octanol																		
0.1	21.01	758.40	99.76	20.88	779.98	104.37	20.75	802.44	108.79	20.60	825.82	113.00	20.45	850.14	117.00	20.30	875.46	120.78
10	21.14	698.50	98.35	21.01	716.77	102.87	20.88	735.69	107.19	20.74	755.28	111.30	20.60	775.55	115.20	20.45	796.53	118.87
20	21.24	648.87	96.94	21.12	664.65	101.37	20.99	680.93	105.59	20.86	697.72	109.60	20.72	715.02	113.40	20.57	732.84	116.98
30	21.32	607.27	95.55	21.21	621.13	99.88	21.08	635.38	104.01	20.95	650.03	107.92	20.81	665.08	111.62	20.67	680.54	115.10
40	21.39	571.77	94.17	21.27	584.10	98.41	21.15	596.75	102.44	21.02	609.73	106.26	20.89	623.02	109.87	20.75	636.63	113.24
50	21.44	541.02	92.80	21.33	552.12	96.95	21.21	563.48	100.89	21.08	575.10	104.62	20.95	586.99	108.13	20.82	599.13	111.41
60	21.48	514.08	91.44	21.37	524.15	95.50	21.25	534.45	99.36	21.13	544.97	102.99	21.00	555.70	106.41	20.87	566.66	109.60
70	21.50	490.23	90.10	21.40	499.45	94.07	21.28	508.85	97.84	21.16	518.45	101.38	21.04	528.23	104.71	20.91	538.19	107.80
80	21.52	468.94	88.77	21.41	477.43	92.66	21.30	486.08	96.33	21.19	494.90	99.79	21.06	503.87	103.02	20.94	513.01	106.03
90	21.53	449.80	87.45	21.42	457.66	91.25	21.32	465.67	94.84	21.20	473.81	98.21	21.08	482.10	101.36	20.96	490.53	104.28
100	21.53	432.47	86.15	21.43	439.79	89.87	21.32	447.24	93.37	21.21	454.81	96.65	21.09	462.50	99.71	20.97	470.32	102.54
1-nonanol																		
0.1	20.44	731.98	130.90	20.30	753.72	131.59	20.15	776.24	132.30	20.01	799.56	133.02	19.86	823.73	133.75	19.72	848.79	134.49
10	20.56	675.33	129.85	20.42	693.81	130.51	20.28	712.86	131.18	20.14	732.48	131.85	20.00	752.69	132.54	19.86	773.51	133.23
20	20.66	628.26	128.80	20.52	644.28	129.42	20.39	660.72	130.04	20.25	677.57	130.68	20.11	694.86	131.32	19.97	712.59	131.97
30	20.73	588.70	127.75	20.60	602.81	128.33	20.47	617.23	128.92	20.34	631.97	129.51	20.20	647.04	130.11	20.07	662.43	130.71
40	20.79	554.86	126.72	20.67	567.44	127.25	20.54	580.27	127.80	20.41	593.34	128.35	20.27	606.66	128.91	20.14	620.23	129.47
50	20.84	525.49	125.68	20.71	536.83	126.18	20.59	548.37	126.69	20.46	560.09	127.20	20.33	572.01	127.71	20.20	584.13	128.23
60	20.87	499.71	124.66	20.75	510.02	125.12	20.62	520.48	125.58	20.50	531.10	126.05	20.37	541.87	126.52	20.24	552.80	127.00
70	20.89	476.85	123.64	20.77	486.29	124.06	20.65	495.86	124.49	20.53	505.55	124.92	20.40	515.37	125.35	20.28	525.30	125.78
80	20.91	456.41	122.63	20.79	465.12	123.01	20.67	473.92	123.40	20.54	482.83	123.78	20.42	491.83	124.17	20.30	500.93	124.57
90	20.91	438.01	121.62	20.79	446.07	121.96	20.67	454.22	122.31	20.55	462.46	122.66	20.43	470.77	123.01	20.31	479.16	123.36

100	20.92	421.33	120.62	20.79	428.84	120.93	20.67	436.42	121.24	20.55	444.07	121.55	20.43	451.78	121.86	20.31	459.56	122.16
1-decanol																		
0.1	20.32	719.93	118.32	20.20	734.09	123.18	20.06	761.20	127.78	19.92	778.00	132.11	19.78	805.62	136.17	19.63	823.08	139.95
10	20.44	665.33	117.18	20.32	682.72	121.97	20.19	700.70	126.49	20.06	719.26	130.75	19.91	738.44	134.73	19.77	758.23	138.43
20	20.54	619.76	116.04	20.42	634.92	120.75	20.29	650.53	125.20	20.16	666.59	129.44	20.03	683.11	133.29	19.88	700.10	136.92
30	20.62	581.33	114.90	20.50	594.72	119.54	20.38	608.45	123.92	20.25	622.54	128.01	20.11	636.98	131.86	19.98	651.76	135.41
40	20.68	548.37	113.77	20.56	560.32	118.34	20.44	572.54	122.65	20.32	585.03	126.74	20.18	597.79	130.44	20.05	610.82	133.92
50	20.72	519.72	112.65	20.61	530.47	117.15	20.49	541.44	121.38	20.37	552.62	125.32	20.24	564.00	129.03	20.11	575.59	132.44
60	20.75	494.52	111.53	20.64	504.27	115.97	20.53	514.19	120.13	20.41	524.27	124.07	20.28	534.51	127.63	20.15	544.91	130.96
70	20.77	472.15	110.43	20.67	481.04	114.79	20.55	490.07	118.88	20.43	499.23	122.71	20.31	508.50	126.24	20.18	517.89	129.50
80	20.78	452.13	109.33	20.68	460.28	113.62	20.57	468.55	117.64	20.45	476.91	121.41	20.33	485.36	124.86	20.20	493.89	128.06
90	20.79	434.07	108.23	20.68	441.59	112.46	20.57	449.20	116.41	20.46	456.87	120.10	20.34	464.61	123.50	20.22	472.40	126.62
100	20.80	417.70	107.15	20.68	424.66	111.30	20.57	431.69	115.19	20.46	438.76	118.83	20.34	445.88	122.14	20.22	453.02	125.19

Table (17): Checking the validity of the proposed approach for calculation of HISP of the selected non-polar compounds.

Compound	The used literature to obtain properties	MAE of prediction of HISP		The range of validation[*]	
		Wang et al. [18] approach	The proposed approach	Pressure (MPa)	Temperature (K)
benzene	[18, 32, 45, 62, 81]	1.91	1.01	0.1-70.0	293-468
toluene	[18, 32, 45, 62, 81]	1.27	0.46	0.1-137.5	293-468
n-heptane	[18, 32, 45, 62, 81]	1.64	0.61	0.1-137.4	293-468
n-dodecane	[18, 32, 45, 62, 81]	2.05	1.08	0.1-137.4	293-468

[*] The range of validation for both approaches is the same.

Table (18): Checking the validity of the proposed approach for calculation of HISP of the other alcohols

Compound	The used literature to obtain properties	MAE of prediction of HISP	The range of validation	
			Pressure (MPa)	Temperature (K)
1,2-propanediol	[45, 82]	0.69	0.1-101	293-318
1,3-propanediol	[45, 82]	0.74	0.1-101	293-318
1,2-butanediol	[45, 83]	0.55	0.1-101	293-318
1,3-butanediol	[45, 83]	0.71	0.1-101	293-318
2-ethyl-1-hexanol	[45, 84]	0.88	0.1-101	293-318

Research Highlights:

- An extended approach for accurate estimation of HISP of 1-alkanols is presented.
- The approach is applicable for the investigated alcohols up to high pressures.
- The approach is much more accurate than the previous methods.
- For 4 investigated alcohols, prediction errors are only 0.17, 0.18, 0.28 and 0.39%.
- Sensitivity analyses to find impacts of temperature and pressure on HISP are done.

Conflict of Interest Statement

*We declare that we have no financial or personal relationships with other people or organizations that could inappropriately influence (bias) our work entitle "**Determination of Hildebrand solubility parameter of pure 1-alkanols up to high pressures**".*

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