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Gibb’s energy additivity approaches in estimation of densities of n-alkane-1-ol

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Abstract Density is important in numerous chemical engineering unit operations in mass and heat flow. In this study models for estimating the density of n-alkane-1-ol are correlated to the Martin’s rule of free energy additivity. Data available in literatures are used to validate and support the proposed equations. The density of n-alkane-1-ol can be easily estimated from its carbon number (z) and temperatures (T). The Bias and average absolute deviation in estimating of n-alkane-1-ol are 0.00% and 0.18%, respectively. The density outside temperature between 283.15 and 363.15 K may be possibly estimated by this model but accuracy may be low.

Index Terms - Alkane, Density, Gibb’s energy.

1. INTRODUCTION

Alcohol is any organic compound in which the hydroxyl functional group is bound to a carbon. Alcohols have been proposed as fuel, for lighting purposes, and for various uses in the chemical industry such as solvent and as raw material or intermediate in chemical synthesis of esters, organic and cyclic compound chains, detergents, paints, cosmetics, aerosols, perfumes, medicine and food, among others.[1] Density or specific gravity of liquid is important for equipment design, heat and mass transfer. The density data of n-alkane-1-ol as a function of temperature and its molecular weigh is needed to model the combustion processes and other applications, a similar procedure for correcting measured density and specific gravity data will be needed.

However, it is not always possible to find experimental data in the literature for the density various temperature of interest, consequently many researchers have developed models to predict the properties of different homologous series. There were many published mathematical models for prediction of density of the alcohols.Rackett equation [2] is a classical model for estimation of liquid density. The equation had been modified by Spenser and Danner [3].

$$\rho = \frac{M}{\frac{RT_c}{P_c} Z_{RA}^{(1+(1-T/T_C))^{2/T}}} \qquad (1)$$

where x, M, T_c and P_c, are mole fraction, molecular mass, critical temperature and pressure; T is the measured temperature in Kelvin; Z_{RA} is the Rackett compressibility factor; R is the universal gas constant.

However, the model is very complex. It requires the knowledge of critical temperature, critical pressure and compressibility factor, which in turn required the acentric factor of the molecule.

Recently, Phankosol et al. [4] proposed free energy of volumetric expansion model (eq. (2)) for predicting density of fatty acid methyl esters (FAMEs) and biodiesel.

$$\rho = \rho_0 e^{-G/RT} \tag{2}$$

when ρ_i and ρ_0 are densities of component i and reference; G is free energy of volumetric expansion; T is absolute temperature; R is the universal gas constant.

The free energy of volumetric expansion model is a good model for prediction of density of pure liquids or pure FAME. For biodiesel, which is a mixture of FAMEs, the Kay's rule for mass fraction was used for the calculation. Thus, in this study, two empirical equations based on free energy additivity are derived and proposed for predicting density of n-alkane-1-ol at different temperatures from its saturated carbon atom composition.

2. THEORY

For a n-alkane-1-ol compound having the molecular structure of $CH_3–(CH_2)_{z-1}–OH$, Martin [5] divided the molecule into different groups; OH, CH_2, CH_3. The free energy of transfer from solution to gas of the molecule was derived from the sum of the free energies of all the contribution groups.

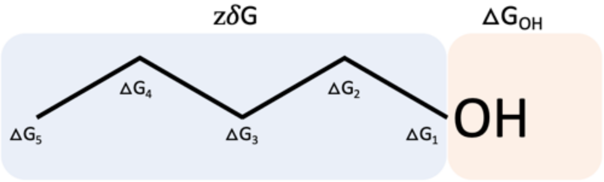


Figure 1
Correlation of free energy additivity and n-alkane-1-ol molecular structure.

$$\Delta G = \Delta G_{OH} + \Delta G_1 + \Delta G_2 + ... + \Delta G_Z \tag{3}$$

$\Delta G_1 ... \Delta G_z$ are the free energies of the methylene and methyl groups, which are not very different. Thus, they are average to δG and Eq. (3) is shortened to Eq. (4).

$$\Delta G = \Delta G_{OH} + z\delta G \tag{4}$$

where ΔG_{OH} is the free energy from the hydroxyl functional group; δG is the change in free energy/carbon atom; z is the number of carbon atoms.

Expanding the ΔG in Eq. (4) to the enthalpic and entropic forms (G=H-TS).

$$\Delta G = \Delta H_{OH} + T\Delta S_{OH} + zT\delta H - zT\delta S \tag{5}$$

Eq. (6) is obtained by combining Eqs. (2) and (5),

$$\ln \rho = \rho_0 - \frac{\Delta H_{OH}}{RT} + \frac{\Delta S_{OH}}{R} + \frac{z\delta H}{RT} - \frac{z\delta S}{R} \tag{6}$$

grouping.

$$\ln \rho = a + bz + \frac{c}{T} - \frac{dz}{T} \tag{7}$$

where

$$a = \rho_0 + \frac{\Delta S_{OH}}{R} \tag{8.1}$$

$$b = -\frac{\delta S}{R} \tag{8.2}$$

$$c = -\frac{\Delta H_{OH}}{R} \tag{8.3}$$

$$d = \frac{\delta H}{R} \tag{8.4}$$

Hence, Eq. (7) is proposed for calculation of density of n-alkane-1-ol at different temperatures.

3. METHODOLOGY

3.1. Experimental data

The experimental data for calculating density of five n-alkane-1-ol (propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol) in temperature range 283.15-363.15 K were obtained from Estrada-Baltazar et al.[6] and Mokhtaran et al.[7]

3.2. Numeric constants of equation (7)

The 4 numeric values of equation (7) (*a*, *b*, *c*, and *d*) for n-alkane-1-ol were solved according to Krisnangkura et al. [8] and they are briefly described below.
At constant T, equation (7) is reduced to equation (8):

$$\ln \rho = a_0 + b_0 z \tag{9}$$

where

$$a_0 = a + \frac{c}{T} \tag{9.1}$$

$$b_0 = b - \frac{d}{T} \tag{9.2}$$

Using density data of Estrada-Baltazar et al.[6] and Mokhtaran et al.[7], the lnρ-z and lnρ–1/T plots gave families of straight lines with average coefficient of determination (R^2) greater than 0.984 and 0.999 as shown in figsure 1 and 2, respec- tively. Shu et al. [24] showed that the c of FAMEs increased linearly with carbon numbers (C8–C18) with the R2 = 0.986. Also, Li et al. [13] and Roosta et al.[17] showed that the c of many organic com- pounds varied linearly with temperature.

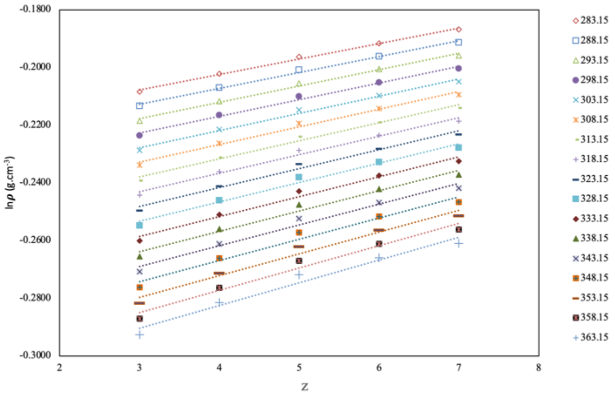


Figure 2
Plot of z and $\ln\rho$.

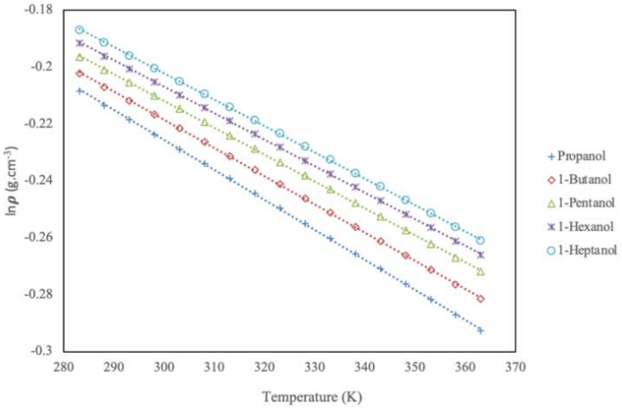


Figure 3 Plot of T and $\ln\rho$.

Thus, a_0 and b_0 are the intercept and the slope of the $\ln\rho - z$ plot. Similarly, b and d are the intercept and the slope of the $b_0 - 1/T$ plot. The a_0 and b_0 are summarized in table 1.

Table 1
Value of a_0, b_0 from $\ln\rho$ and z plot (eq. (5)).

1/T (K^{-1})	a_0	b_0	R^2
0.003531697	-0.223816	0.005349	0.996
0.003470415	-0.229223	0.005496	0.994
0.003411223	-0.23466	0.005644	0.993
0.003354016	-0.240125	0.005794	0.992
0.003298697	-0.24562	0.005945	0.990
0.003245173	-0.251145	0.006098	0.989
0.003193358	-0.2567	0.006252	0.987
0.003143171	-0.262286	0.006408	0.986
0.003094538	-	0.006565	0.984

1/T (K^{-1})	a_0	b_0	R^2
	0.267903		
0.003047387	-0.273551	0.006724	0.983
0.003001651	-0.279231	0.006884	0.981
0.002957267	-0.284943	0.007046	0.979
0.002914177	-0.290687	0.00721	0.978
0.002872325	-0.296463	0.007375	0.976
0.002831658	-0.302273	0.007542	0.975
0.002792126	-0.308116	0.007711	0.973
0.002753683	-0.313993	0.007881	0.972

Thus, a and c are the intercept and the slope of the a_0−1/T plot. Similarly, b and d are the intercept and the slope of the b_0−1/T plot.

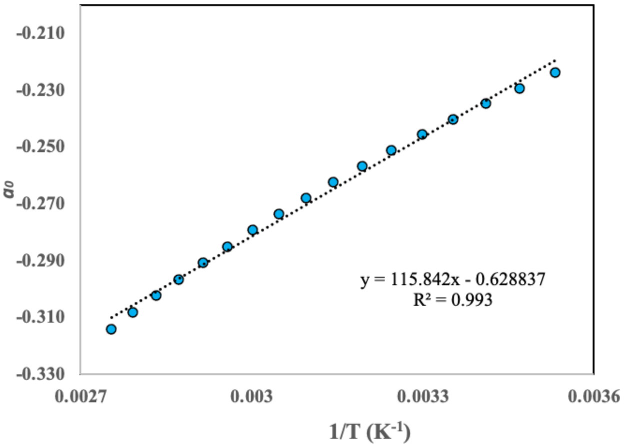


Figure 4
Plot of a_0 and 1/T.

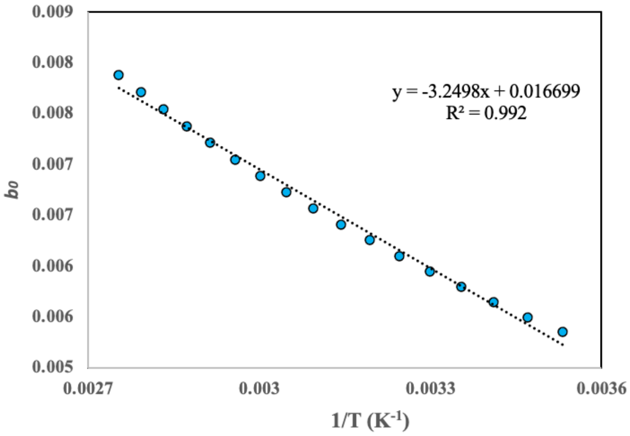


Figure 5
Plot of b_0 and 1/T.

Statistical analysis

The average absolute deviations (AAD), Bias, standard error ($\sigma_{\bar{x}}$) and coefficient of determination (R^2) were calculated by equations (10), (11), (12) and (13), respectively:

$$AAD(\%) = \frac{100}{N} l \sum_{i=1}^{N} \left[\left| \frac{P_{exp} - P_{cal}}{P_{cal}} \right| \right] \tag{10}$$

$$Bias(\%) = \frac{100}{N} l \sum_{i=1}^{N} \left[\frac{P_{exp} - P_{cal}}{P_{cal}} \right] \tag{11}$$

$$\sigma_{\bar{x}} = \frac{\sigma}{N} \tag{12}$$

$$R^2 = \left[\frac{N \sum_{i=1}^{N} P_{exp} P_{cal} - \left(\sum_{i=1}^{N} P_{exp} \right) \left(\sum_{i=1}^{N} P_{cal} \right)}{\sqrt{\left[\sum_{i=1}^{N} P_{exp}^2 - \left(\sum_{i=1}^{N} P_{exp} \right)^2 \right] \left[\sum_{i=1}^{N} P_{cal}^2 - \left(\sum_{i=1}^{N} P_{cal} \right)^2 \right]}} \right]^2 \tag{13}$$

where P_{exp} stands for experimental value reported elsewhere, P_{cal} is the calculated value and N is the number of data points.

4. RESULTS AND DISCUSSION

The numeric values of *a*, *b*, *c* and *d* obtained from the a_0–1/T (figure 2) and the b_0–1/T (figure 3) plots were -0.628837, 0.016699, 115.842 and -3.2498, respectively. After substituting these numeric values into equation (7), the numeric form of equation (10) is obtained for estimating the density of n-alkane-1-ol:

$$\ln \rho = -0.628837 + 0.016699z + \frac{115.842}{T} - \frac{3.2498z}{T} \tag{10}$$

where ρ is density (g/cm^3)

z is the number of carbon atoms on the fatty acid chain

T is absolute temperature (K)

Table 2 summarizes the density of different n-alkane-1-ol at temperature between 283.15 and 363.15K, together with AD(%). It can be seen that the calculated density are good agreement with the literature values at all temperatures.

Table 2
density of n-alkane-1-ol at different temperatures calculated by Eq. (10) and AD (%).

Temp. (K)	Density (g/cm^3)				
	Propanol	n-Butanol	n-Pentanol	n-Hexanol	n-Heptanol
283.15	0.8154	0.8197	0.8240	0.8283	0.8326
	0.431*	0.336	0.271	0.323	0.374
288.15	0.8101	0.8145	0.8190	0.8234	0.8279
	0.286	0.183	0.116	0.181	0.250
293.15	0.8051	0.8096	0.8142	0.8187	0.8233
	0.167	0.055	0.015	0.062	0.148
298.15	0.8002	0.8048	0.8095	0.8142	0.8190
	0.071	0.051	0.125	0.036	0.066
303.15	0.7955	0.8003	0.8051	0.8099	0.8148
	0.002	0.136	0.213	0.114	0.004
308.15	0.7910	0.7959	0.8008	0.8057	0.8107
	0.053	0.199	0.282	0.172	0.039
313.15	0.7867	0.7917	0.7967	0.8017	0.8068
	0.083	0.242	0.331	0.212	0.064
318.15	0.7825	0.7876	0.7927	0.7979	0.8031
	0.094	0.266	0.362	0.233	0.072
323.15	0.7785	0.7837	0.7889	0.7941	0.7994

* *AD(%)*

Percent differences between the calculated by equation (10) and literature density values are listed in the parentheses, at 283.15-363.15 K are summarized in table 3 and shown relative deviation (D (%)) in figure 4. The estimated density values for n-propanol, n-butanol, n-pentanol, n-hexanol and n-heptanol agrees well with the literature values. The highest absolute difference is 0.60% (propanol). The Bias and AAD (%) were 0.00% and 0.18%, respectively.

Table 3
Statistical analysis between the density of n-alkane-1-ol data available in literature [3, 4] over the temperature range 283.15-363.15 K and those estimated by equation (10)

Alcohols	**Bias(%)**	**AD$_{min}$(%)**	**AD$_{max}$(%)**	**AAD(%)**
Propanol	-0.14	0.00	0.60	0.18
n-Butanol	0.06	0.04	0.27	0.18
n-Pentanol	0.17	0.02	0.38	0.23
n-Hexanol	0.04	0.03	0.24	0.16
n-Heptanol	-0.13	0.00	0.07	0.16
Average	**0.00**	**-**	**-**	**0.18**

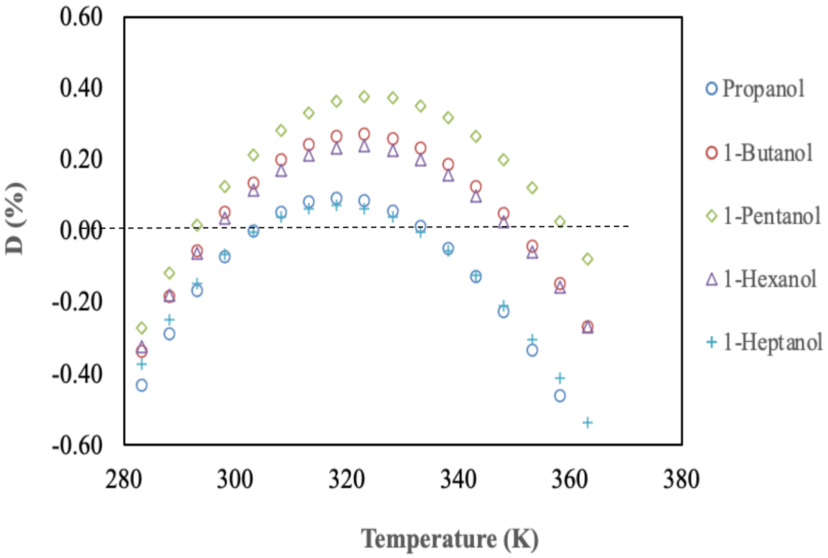


Figure 6.
Relative deviations (D(%)) between density of n-alkane-1-ol by equation (10) and the experimental values reported by Estrada-Baltazar et al.[6] and Mokhtaran et al.[7]

The estimated density values for five n-alkane-1-ol at 298.15 K showed the lowest AAD of 0.07%, while temperature from 363.15 K gives the highest AAD of 0.35%. The overall AAD of 5 types of n-alkane-1-ol were 0.183%. The overall AAD of five n-alkane-1-ol was better than those of the Rackett's equation modified by Spenser and Danner with (5.7%)

The correlation between the estimated and literature density values of n-alkane-1-ol at 283.15 to 363.15 K is shown in figure 6. The slope and intercept of the plot is 0.9947 and 0.0042 with the R^2 of 0.992 and the standard error was 0.002.

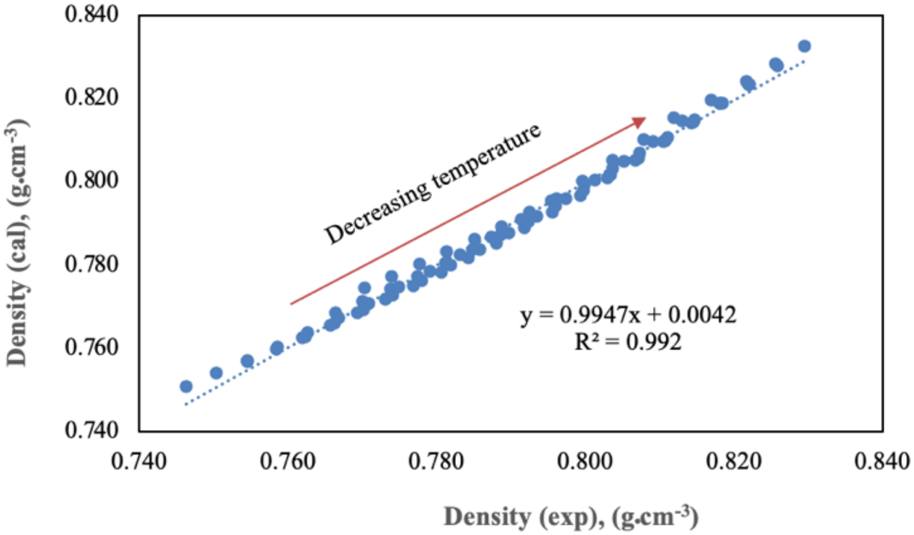


Figure 7.
Correlation of the estimated density to the experiment values n-alkane-1-ol [6, 7] at 283.15 to 363.15 K.

Estimation of Density of n-alkane-1-ol from Molar mass (M).

The molar mass is an intensive property of the substance, that does not depend on the size of the sample. can also be calculated from fatty acid composition. Thus, it would be if the density of n-alkane-1-ol can be estimated from molar mass values. The z can be converted to M is following;

$$M = OH + (z-1)CH_2 + CH_3 \qquad (11)$$

Substitution these molar mass of oxygen (O), hydrogen (H) and carbon (C) are 16, 1 and 12, respectively into equation (11).

$$z = \frac{M-18}{14} \tag{12}$$

Equation (13) is obtained by combining Equations (10) and (12).

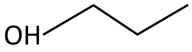
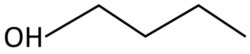
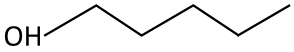
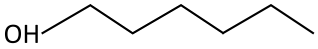
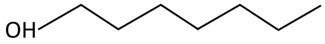
$$\ln\rho = -0.650307 + 0.011928M + \frac{120.0203}{T} - \frac{0.2321257M}{T} \tag{13}$$

where ρ is density (g/cm^3)

M is the molar mass of n-alkane-1-ol

T is absolute temperature (K)

Table 4 The formular of n-alkane-1-ol, *z* and molar mass

n-alkane-1-ol formular	*z*	Molar mass (M)
Propanol (C_3H_8O)  	3	60
n-Butanol ($C_4H_{10}O$)  	4	74
n-Pentanol ($C_5H_{12}O$)  	5	88
n-Hexanol ($C_6H_{14}O$)  	6	102
n-Heptanol ($C_7H_{16}O$)  	7	116

The estimated density values of n-alkane-1-ol estimated by equation (13) with molar mass in table 4 and shown relative deviation (D (%)) in figure 4. The overall AAD of 5 types of n-alkane-1-ol at 283.15 to 363.15 K were 0.183%.

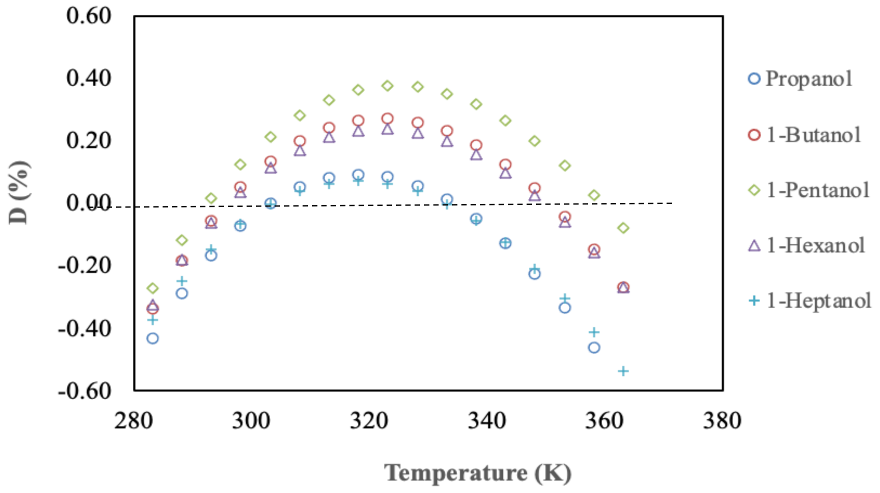


Figure 8.
Relative deviations (D(%)) between density of n-alkane-1-ol by equation (13) and the experimental values reported by Estrada-Baltazar et al.[6] and Mokhtaran et al.[7]

The densities of n-alkane-1-ol estimated by equation (13) (at different temperatures) were very close to those calculated using the z (equation (10)). The correlation between the reported density and estimated values using equation (13) (85 data points) is linear with the slope, intercept, R^2 and standard error of 1.000, 0.000, 1.000, and 0.000, respectively.

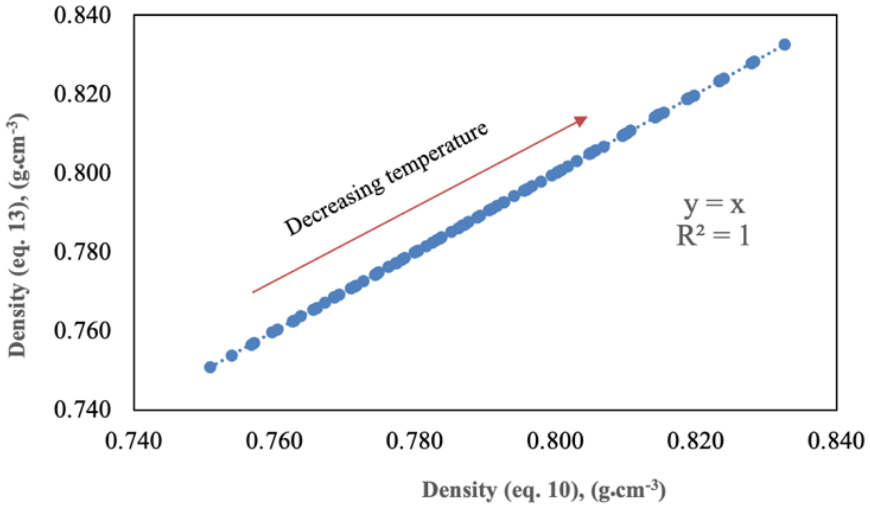


Figure 9.
Correlation of the estimated n-alkane-1-ol density of equation (10) and equation (13) at 283.15 to 363.15 K.

Results in this study showed that the free energy additivity rule can be extended to estimate the density of pure n-alkane-1-ol as well. It is better than the Rackett equation modified by Spenser and Danner. Also, all the coefficients have their physical meaning, which may be easy for future improvement. On the other hand, the method described in this study is simple for estimation the density of n-alkane-1-ol.

The sensitivity of density (Eq. (14) and Eq.(15)) can be obtained by differentiating equation (10) and equation (13) with respect to z and M, respectively. Equation (14) and equation (15) shows that the change in density per carbon atom and density per molar mass, respectively depends on the temperature.

$$\frac{d\ln\rho}{dz} = 0.016699z - \frac{3.2498z}{T} \qquad (14)$$

$$\frac{d\ln\rho}{dM} = 0.011928 - \frac{0.2321257}{T} \tag{15}$$

Generally, the increment in temperature tends to decrease the density of the n-alkane-1-ol with out effected of carbon chain length and molecule size shows in equation (14) and equation (15).

CONCLUSION

This work provides a simple empirical correlation of the density of n-alkane-1-ol. Thus, the derived equation can then be used to estimate density of the n-alkan-1-ol at different temperatures with good accuracy. The density values outside of this temperature range may be possibly predicted by the correlation but the accuracy may be lower.

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