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THE EFFECT OF TEMPERATURE VARIATION ON STUDIES OF COCONUT AND PALMOLINE OILS

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ABSTRACT

The effect of temperature on density of coconut and palmoline oils was observed at various temperatures using DMA48 (ADPAAR – made in Austria) density meter. The density linearly decreases with increase in temperature. The change in density per K, is in good agreement with Paquot observation, for these oils. The modified Rackett equation can be successfully employed to estimate the densities as a function of temperature of vegetable oils, if various fatty acid compositions of a particular oil and their critical constants are known.

Key words: Density, Temperature, Coconut oil, Palmoline oil.

INTRODUCTION

Theory

Molar volume (V_m) at a particular temperature, which is characteristic of a substance, can be obtained from its molecular weight and density at that temperature. From experimental results, it is found that V_m is a linear function of the carbon chain length for saturated fatty acids. Further, the introduction of an isolated double bond in a number of such a series of compounds has a uniform effect on molar volume. Garner and Ryder[1] observed a 16.8 cc/g mole increase in liquid molar volume for each -CH_2- added to a fatty acid chain for acids 8 : 0 to 12 : 0 at 50^0C.

Dorinson et al.[2] developed equations that included most saturated fatty acids at specified temperature. For the fatty acids, 2 : 0 to 9 : 0, the molar volume at 20^oC can be represented as -

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$$V_m = 16.89n + 23.62 \quad ...(1)$$

The molar volumes of fatty acids, 4:0 to 18:0 at 80ºC, can be written as -

$$V_m = 17.25n + 28.88 \quad ...(2)$$

where n is the number of carbon atoms.

Hammand and Lundberg[3] extended work of Dorinson et al.[2] by adding terms to account for unsaturation and temperature dependence. Their equations for saturated and mono-unsaturated fatty acids is -

$$V_m = 16.54C – 6.65D + 26.09 + (0.006C + 0.0085) (t - 20) \quad ...(3)$$

and for polyunsaturated fatty acids, it is -

$$V_m = 16.54C – 6.87D + 26.09 + (0.006C + 0.0085) (t - 20) \quad ...(4)$$

where C is the number of carbon atoms, d is the number of double bonds in the fatty acid chain and t is the temperature in ^{0}C. The method includes all commonly encountered fatty acids and incorporates their temperature dependency over a wide range. However, this method is not sufficiently accurate as it gives errors from 2% to 5%.

Costello and Bowden[4] used Verschaffelt equation (equation 5) for liquid density as -

$$d_1 - d_g = d_0 [1- (T/TC)]^m \quad ...(5)$$

where d_1 = Liquid density at temperature T and d_g = Gas density.

Using experimental data over a temperature range for individual fatty acids, two parameters d_0 and m are fed. The resulting equations gave a good representation of the data (to an extent of 0.3%). However, it was not suggested that this approach might be extended to estimate-to-estimate parameters without experimental data particularly for d_g.

Fisher[5] correlated fatty acid density with carbon chain length for the saturated fatty acids, 4 : 0 – 30 : 0. This correlation is of the simplest linear form -

$$d = b + mt. \quad ...(6)$$

Where d is the density in g/cc, b is the intercept and m is the slope of linear least square fit of the data.

This correlation was developed for temperature range of 20^0C – 80^0C and this is limited in applicability. Also the fatty acids, 10 : 0 – 30 : 0, have melting points either within the range or higher. So there is some question about the suitability of Fisher equation (equation 6) for those materials. More recently, Fisher[6] correlated saturated fatty acids critical temperature with other physical properties such as molar volume, normal boiling point and refractive indices. Rackett[7] developed equation for liquid density over a wide range of temperature and the same was modified by Spencer and Danner[8]. The modified Rackett equation has been successfully used for its suitability both; for hydrocarbons and non-hydrocarbons, whose critical properties are known.

The original Rackett equation -

$$V_S = V_C \times Z_c^{\frac{2(1-T)}{7}} \qquad ...(7)$$

and the modified Rackett equation -

$$V_s = \left(\frac{R_c T_c}{P_c}\right) Z_{RA}^{(1+\{1-T_{rr}\}^{2/7})} \qquad ...(8)$$

are generalized equations these are used to estimate the molar volumes of saturated liquids, V_s. The critical constants V_c, T_c and P_c are the critical volume, temperature and pressure, respectively.

T_r is the reduced temperature, R is the ideal gas constant and Z_{RA} is the Rackett parameter, a correlating parameter unique to each compound. The critical compressibility factor Z_c is always from Z_{RZ}.

The method of density estimation introduced here requires critical properties for the fatty acids. If the critical properties are not known, they must be estimated. The use of modified Rackett equation also requires a single reference density for the fatty acid.

This reference density can be easily located in most of the handbooks. The reference density must be for the liquid state. However, if a reference density is not available, a linear interpolation or extrapolation of fatty acid, molar volumes at the same temperature and with the same degree of unsaturation can be used with some reduced accuracy.

Finally, the density of the vegetable oil ρ_{oil} is given by -

$$\rho_{oil} = \frac{\left(\sum x_i MW_1\right)}{R\left(\sum \frac{X_1 T_{C_1}}{P_{C_1}}\right)} \frac{1}{\left(\sum_{x_i} Z_{RA_1}\right)^{\left(1+(1-T_r)^{2/7}\right)}} + F_C \quad ...(9)$$

RESULTS AND DISCUSSION

Density is one of the most important and basic physical properties of any matter that exists in any physical state. Reports on measurements and theoretical estimates on density of vegetable oils at different temperatures are meager in literature. The densities of coconut and palmoline oils at various temperatures adopting the modified Rackett equation are calculated and compared with the experimental values. Density values (Experimental), and the values obtained using least squares analysis and finally, the values obtained adopting modified Rackett equation are represented in Tables 3 and 4 and represented graphically in Fig. 1 to 6. It is observed that there is a good agreement between the experimental and least squares analysis values, and the theoretical density (experimental) values do not coincide with values obtained using modified Rackett equation. The reason can be attributed, to the different origins of the oil. Even though the oil is same, the fatty acid composition may not be the same. Further, the fatty acid composition changes with the geographical conditions, fertility, seed etc. From these studies, the modified Rackett equation can be successfully employed to estimate the densities as a function of temperature of different vegetable oils, if the various fatty acid composition of a particular oil and their critical constants are known.

Table 1: Experimental densities of coconut oil

Temperature (K)	313	318	323	328
Density (g/c.c.)	0.9053	0 .9026	0.9	0.8974

Table 2: Experimental densities of palmoline oil

Temperature (K)	313	318	323	328	333	338
Density (g/c.c.)	0.8985	0.8953	0.894	0.892	0.8953	0.8945

Table 3: Experimental and calculated densities of coconut oil

Temperature (K)	Density (g/c.c.) (Experimental)	Density (g/c.c) (d = K + IT)	Density (g/c.c.) (Rackett equation)
313	0.9053	0.906724	0.910782
318	0.9026	0.903664	0.908011
323	0.9	0.900604	0.905237
328	0.8974	0.897544	0.90246

Table 4: Experimental and calculated densities of palmoline oil

Temperature (K)	Density (g/c.c.) (Experimental)	Density (g/c.c.) (d = K + IT)	Density (g/c.c.) (Rackett equation)
313	0.8985	0.899	0.909604
318	0.8953	0.8964	0.907523
323	0.894	0.8926	0.906118
328	0.892	0.8902	0.904824

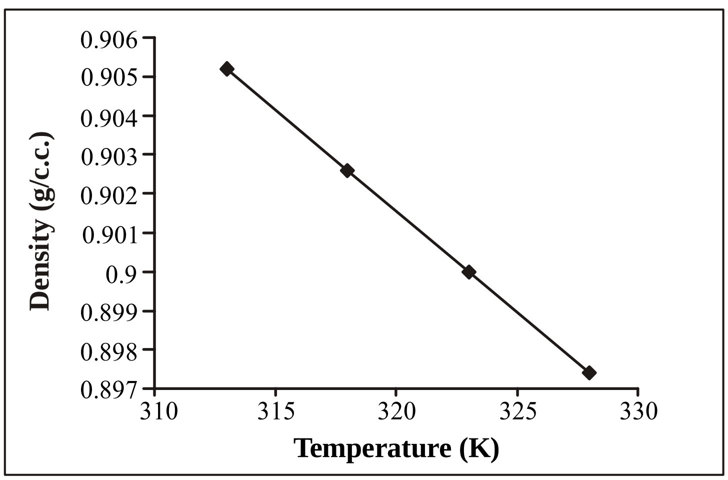

Fig. 1: Density vs. temperature (Experimental) of coconut oil

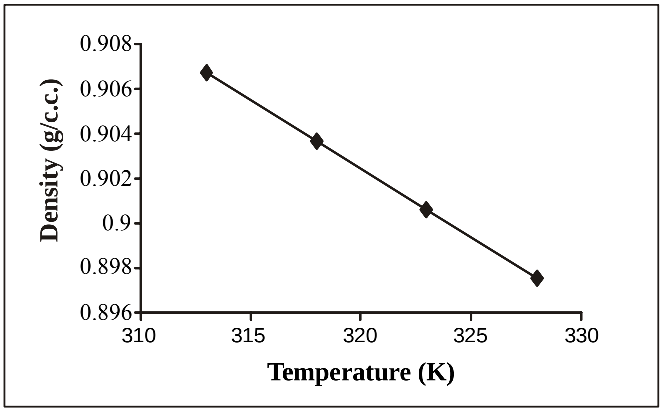

Fig. 2: Density vs. temperature (d = K + IT) of coconut oil

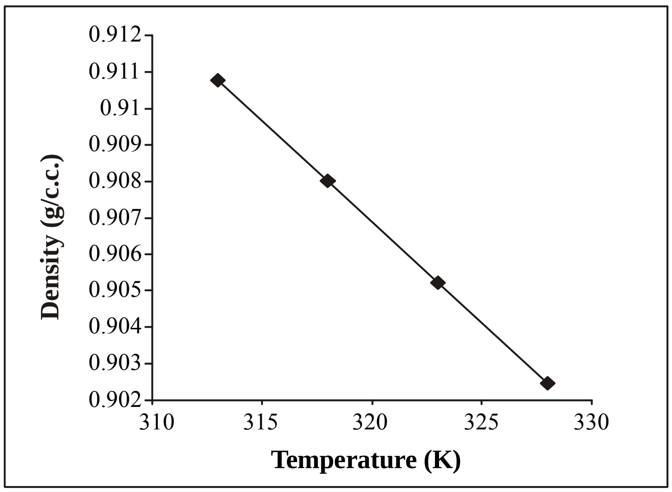

Fig. 3: Density vs. temperature (Rackett equation) of coconut oil

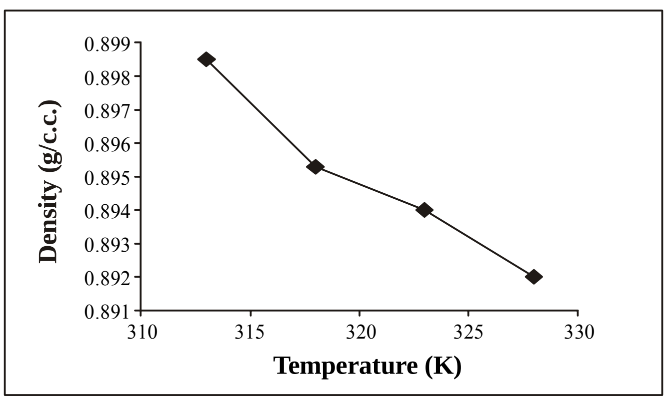

Fig. 4: Density vs. temperature (Experimental) of palmoline oil

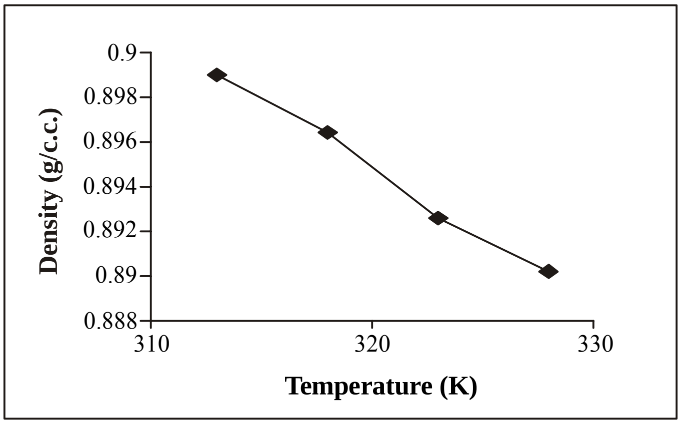

Fig. 5: Density vs. temperature (d = K + IT) of palmoline oil

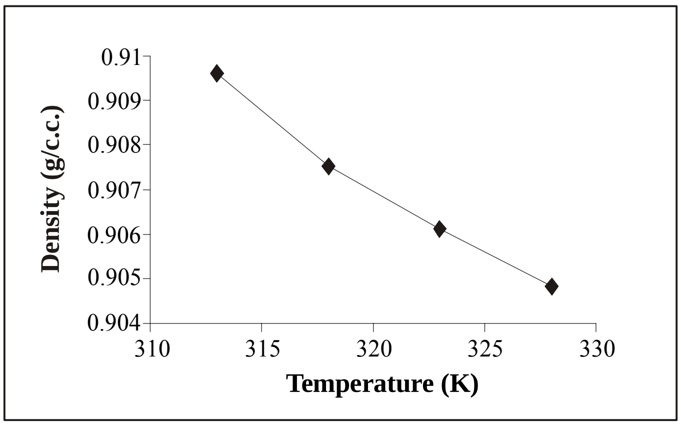

Fig. 6: Density vs. temperature (Rackett equation) of palmoline oil

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