Thethermodynamic interpretation ofsurface tension constantsof some vegetable oils locally produced in Nigeria

J B Yerima, and Simon Solomon,

Department of Physics, ModibboAdama University of Technology, P M B 2076 Yola, Nigeria

Abstract: - In this paper, the effect of temperature on the surface tension of five vegetable oils locally produced in Nigeria is carried out using capillary rise method. The results show that the surface tensions of these oils vary linearly with temperature. Based on this linear behavior, the thermodynamic constants such as critical temperature, surface tension at absolute zero Kelvin, molar volume, reference temperature and surface tension, exponent β, reference and critical pressures of the oils were calculated. The results show that the thermodynamic constants depend on the nature of the oils, that is, the oils have different thermodynamic constants.

Keywords: surface tension, vegetable oils, thermodynamic constants, temperature, capillary rise

I.   INTRODUCTION

Surface tension is one of the fundamental physical properties of a liquid that makes the free surface of a liquid behave like a stretched elastic membrane. This inherent property of a liquid alters its shape in such a way that the area of its free surface is minimum possible. In the light of the molecular theory, this arises, because the molecules in the bulk of the liquid experience zero resultant force due to their nearest neighboring molecules while the molecules in the surface of the liquid experience finite resultant force acting inwardly the bulk of the liquid due to excess neighboring molecules below them. Because of the inherent tendency of a liquid to contract, it behaves as if there exists in its surface a tension which acts equally in all directions. The surface tension of a liquid is defined as the force per unit length acting on either side of an imaginary line drawn in the surface in equilibrium. The direction of the force is tangential to the surface and perpendicular to the line (Emeka, 2003).

It has been observed that whenever a liquid is placed in contact with a solid, the liquid surface is in general curved. When a liquid gets in contact with a solid, there exists a boundary in which there is the surface tension in solid-liquid interface. The angle between the solid surface and the tangent to liquid surface drawn from the point where the liquid surface meets with the solid surface measured through the liquid is called the angle of contact. Those liquids whose angle of contact is acute or less than 90° rise in the capillary tube while those liquids having angle of contact obtuse or greater than 90° fall or depress in the capillary tube. Similarly, liquids with concave meniscus rise in the capillary tube and those having convex meniscus fall in the capillary tube. Examples of liquids with acute angle of contact and meniscus concave include water, alcohol, ether, glycerine and so on. In practice, angle of contact for such liquids that rise in capillary is small, nearly zero, when they are in contact with glass. Example of liquids with obtuse angle of contact and convex meniscus is mercury. It is crystal clear that the angle of contact also explains the shape of the liquid meniscus near a solid surface (Yerima and Ike, 2013).

In other words, surface tension can be explained in terms of cohesion and adhesion. Cohesion is the force of attraction existing between similar or like molecules while adhesion is the force of attraction between dissimilar or unlike molecules. Typical example of a situation where cohesion is greater than adhesion is cohesion existing between mercury molecules causing mercury to depress in glass tube. In another vein, adhesion between glass and water molecules is greater than cohesion between water molecules causing water to rise in glass capillary tube (Yerima*et al.,* 2015).

So far it has been established that liquids having acute angle of contact and concave meniscus have adhesion greater than cohesion and hence they rise in a capillary tube. Conversely, liquids with obtuse angle of contact and convex meniscus have cohesion greater than adhesion and they fall in capillary tube. Therefore the rise or fall of liquids in capillary tube due to surface tension depends on contact angle, liquid meniscus and intermolecular forces (Yerima*et al.,* 2015).
.   It is popularly known that the factors affecting surface tension of a liquid include temperature, nature of the liquid itself, impurities or contaminations (Yerima and Ahams, 2011) and so on. For example, detergents and temperature decrease surface tension of water. Consequently, the knowledge of surface tension has found useful applications in everyday life which include quality control in industries, upward movement of kerosene in wicks of lamp for lighting and stoves for cooking, enhances cleansing effect of soaps and detergents, movement of pond skater on water, and design of umbrella, raincoat and tents to mention but a few.

In this study, the surface tension and other related thermal parameters of shear butter oil, groundnut oil, cotton seed oil, soya bean oil, corn oil and palm oil are investigated at various temperatures. The results show that the surface tension linearly varies with temperature and as a result many other thermodynamic constant parameters of the oils in question were determined.

II. THEORY OF THE EFFECT OF TEMPERATURE ON SURFACE TENSION

In general, surface tension γ is dependent on temperature T. The general trend is that surface tension decreases with the increase in temperature vanishing at a temperature called the critical temperature T_c. Guggenheim and Katayama stated that the general formula forsurface tension as a function of temperature is given by (Adam 1941;Gennes*et al.*, 2002)

$$\gamma = \gamma^* \left(1 - \frac{T}{T_c}\right)^n \qquad\qquad 1$$

where $\gamma^* = \gamma_o(1 - \beta T_o) = \frac{kT_c}{V^{\frac{2}{3}}}$is a constant being the surface tension of a liquid at absolute zero,V is the molar volume of a liquid, T_c is the critical temperature,n is an empirical factor (n=11/9) yields good result for organic liquids andk is the Eotvosconstantvalid for almost all substances, a typical value of k=2.1×10^{-7} JK^{-1}mol$^{-2/3}$ (Eotvos, 1886). For water V=18 ml/mol and T_c=374 ^{o}C.If the temperature variation is small, then we use the fact that n≈1 for the linear estimate, we have (Adam, 1941)

$$\gamma = \gamma^*(1 + \alpha T) \qquad\qquad 2$$

where $\alpha = -\frac{1}{T_c} = \beta\gamma^*$. It is generally easier to find the reference surface tension γ_o, reference temperature T_o and the critical temperature T_c and rewrite equation (2) as

$$\gamma = \gamma_o[1 + \beta(T - T_o)] \qquad\qquad 3a$$
$$or\gamma = \gamma_o(1 - \beta T_o) + \gamma_0\beta T \qquad\qquad 3b$$

Using the condition γ goes to zero at $T_c$in equation (3b), we get

$$\beta = \frac{1}{T_c - T_o} \qquad\qquad 4a$$
$$orT_o = T_c + \frac{1}{\beta} \qquad\qquad 4b$$

Also, the rate of decrease of γ with temperature which is equivalent to the slope of the graph of γ versus T given by

$$\frac{d\gamma}{dT} = \gamma_o\beta \qquad\qquad 5a$$
$$or\gamma_o = \frac{1}{\beta}\frac{d\gamma}{dT} \qquad\qquad 5b$$
$$or\gamma_o = \frac{slope}{\beta} \qquad\qquad 5c$$

Thus T_o and γ_o can be calculated from equations (4b) and (5b) respectively. In the reference with website en.wikipedia retrieved 2007, it is stated that the constant γ_o is defined by vanderwaals as

$$\gamma_o = kT_c^{\frac{1}{3}}P_o^{\frac{2}{3}} \qquad\qquad 6a$$
$$orP_c = \left(\frac{\gamma^*}{kT_c^{\frac{1}{3}}}\right)^{\frac{3}{2}} \qquad\qquad 6b$$

where k is a universal constant (2.1×10^{-7} JK^{-1}mol$^{-2/3}$) for all liquids and P_c is the critical pressure of the liquid although later experiments found k to vary to some degree from one liquid to another.

III. METHOD

The experimental set up and procedures of measuring surface tension of the five locally produced vegetable oils in Yola, Nigeria using capillary rise method were presented in Dikko et al (2015). The values of surface tension of the five vegetables oils measured at different temperatures are recorded in Table 1. In this paper, we introduced new concepts to determine the thermodynamic constantsof the vegetable oils such as molar volume V, critical temperatureT_c, surface tension at absolute zero Kelvin γ^*, exponent β, reference surface tension$\gamma_o$and reference temperature T_o of the vegetable oils and the results are recorded in Table 2.

IV.   RESULTS AND DISCUSSION

Table 1 Surface tension (mN/m) of vegetables oils at different temperature (Dikko et al., 2015)

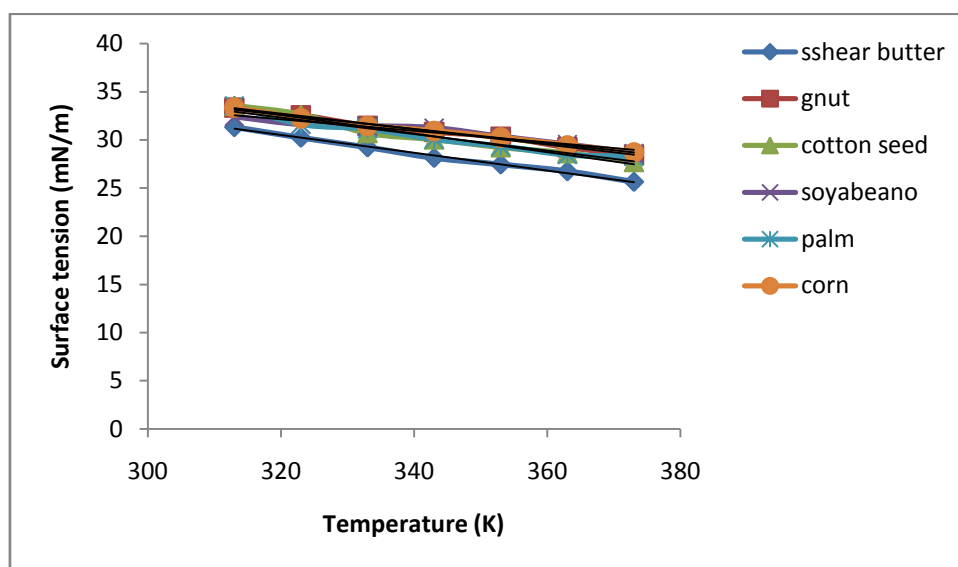| T (K)	Shear butter	Groundnut	Cotton seed	Soya bean	Palm	Corn
313	31.32	33.33	33.54	32.42	33.55	33.34
323	30.22	32.54	32.62	31.61	31.62	32.23
333	29.22	31.43	30.71	31.44	31.14	31.44
343	28.12	30.81	30.05	31.24	30.05	30.91
353	27.44	30.32	29.24	30.33	29.33	30.24
363	26.73	29.12	28.62	29.52	28.44	29.43
373	25.63	28.42	27.71	28.61	28.25	28.71

Fig. 1 Variation of surface tension of vegetable oils with temperature

In Table 1, the surface tension of vegetable oils decrease linearly with temperature and the least square method yields the following regression lines (Fig. 1) and equations (7):

$$\gamma_{sb} = -0.0922T + 60.0, R^2 = 0.9940$$
$$\gamma_{gn} = -0.0803T + 58.4, R^2 = 0.9925$$
$$\gamma_{cs} = -0.0963T + 63.4, R^2 = 0.9707 \qquad\qquad 7$$
$$\gamma_{so} = -0.0597T + 51.2, R^2 = 0.9497$$
$$\gamma_{pa} = -0.0860T + 59.8, R^2 = 0.9551$$
$$\gamma_{co} = -0.0739T + 56.2, R^2 = 0.9923$$

where the subscripts sb, gn, cs, so, pa, and co represent shear butter, groundnut, cotton seed, soya bean, palm and corn oils respectively.

Table 2 Constant thermodynamic parameters of vegetable oils

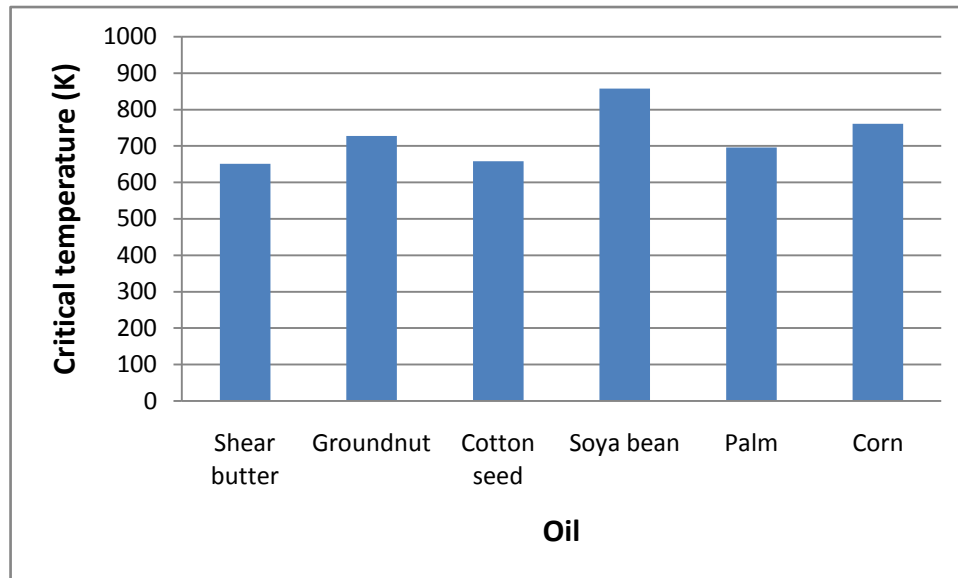| Oil	T_c(K)	γ^* (mN/m)	P_c(N/m^2)	V (ml/mol)	β(mK^{-1}N^{-1})	γ_o(mN/m)	T_o (K)	P_o(N/m^2)
Shear butter	650.8	60.0	47797.9	108.7	-0.0256	3.60	611.8	770.9
Groundnut	727.3	58.4	45898.8	133.7	-0.0235	3.41	684.8	600.1
Cotton seed	658.4	63.4	51917.7	101.8	-0.0240	4.02	616.7	898.7
Soya bean	857.6	51.2	37677.9	208.6	-0.0228	2.62	813.7	312.2
Palm	695.3	59.8	47559.1	120.7	-0.0241	3.58	653.7	690.8
Corn	760.4	56.2	43329.7	151.5	-0.0234	3.16	717.7	498.4

Fig. 2Critical temperatures of vegetable oils

The critical temperature T_c is the temperature at which the surface tension vanishes. Now putting surface tension equals zero in the regression equations (7), the critical temperatures for each of the vegetables oils were calculated and recorded in Table 2. At the critical temperature, the liquid-solid surface tension vanishes and liquid-liquid vapor surface tension becomes significant. At this junction the adhesive forces of liquid/vapor, kinetic energyof the molecules and contact angle are maximum and cohesive forces minimum (Yerima*et al.,* 2015). Thus, this implies that the critical temperature is attributed to phase transition temperature (boiling point or thermodynamic equilibrium temperature) at which the configuration of the structure of the liquid is expected to change at microscopic level. The change in the configuration of the structure could be change in dimensions of the molecules, angle between bonds, bond lengths, molecular entanglement to mention but a few. Fig. 2 shows the critical temperatures of the vegetable oils with soya bean oil having the highest value and the shear butter oil the least. This means soya bean oil has the highest boiling point (orstrongest molecular bond)and shear butteroil has the lowest boiling point (or weakest molecular bond).

The coefficients of temperature T in the empirical equations (7) represent the rate of decrease of surface tension with temperature with soya bean oil having the highest and cotton seed oil the least. This means that soya bean oil is the most likely preferred oil for cooking edible food since decrease in surface tension favors digestion of food (Yerima*et al,.* 2015). This is to say that since the temperature of the stomach is higher than that of edible food, in the light of surface tension only, food cooked with soya bean oil is expected to digest faster than food cooked with the other oils.On the other hand, the constants or intercepts in the linear regression equations (7) assuming n≈1 represent the surface tension of the oils when T becomes zero i.e. the surface tension of oil cooled to absolute zero Kelvin. At this temperature, the oilhas solidified and the surface tension is that of solid-solid interface and no longer that of liquid-solid interface. Thus the intercept predicts the surface tension of solid. At this juncture, the molecules are at rest and the cohesive force is maximum (Yerima*et al.,* 2015).

In another vein, the molar volume $V = \left(\frac{kT_c}{\gamma^*}\right)^{1.5}$ was calculated for each vegetable oil and the results recorded in Table 2. The results show that corn oil has the highest value and cotton seed oil has the lowest value i.e. one mole of corn oil has the lowest number of molecules per unit volume and cotton seed oil has the highest since one mole of all substances contain 6.02×10^{23} molecules. Also, the exponent $\beta = -\frac{1}{\gamma^* T_c}$ was computed for each oil and the values are recorded in Table 2 with soya bean oil having the largest value and shear butter oil having the least. The reference surface tension $\gamma_o = \frac{1}{\beta}\frac{d\gamma}{dT}$ was calculated with cotton seed oil having the largest value while soya bean oil having the smallest value. On the other hand, the reference temperature $T_o = T_c + \frac{1}{\beta}$ for each oil was computed with soya bean oil having the highest value while the shear butter oil the least. The reference temperature T_o is a function of T_c and has value less than T_c by an amount $\frac{1}{\beta}$ since the exponent β is known to be negative. It is the temperature at which both the liquid-solid interface and liquid-vapor interface coexist before the critical temperature is reached at which the liquid-vapor only exists. At T_o both the surface

tension of the liquid-solid interface and the surface tension of the liquid-vapor interface coexist. At T_c only the surface tension of liquid-vapor interface is significant i.e. the molecular structure and configuration of the heating liquid has taken new arrangement or position entirely. Finally, the critical pressure $P_c = \left(\frac{\gamma^*}{kT_C^{1/3}}\right)^{1.5}$ corresponding to T_c was calculated for each of the oils and the results show that cotton seed oil has the largest value while the soya bean has the smallest value (Table 2). Also the reference pressure $P_o = \left(\frac{\gamma_o}{kT_0^{1/3}}\right)^{1.5}$ corresponding to T_o was computed and recorded in Table 2. It has the same trend as T_c but has lower values. On the overall, soya bean oil has the highest values of T_c, β and T_o and the lowest values of γ^*, γ_o and P_c. Also, shear butter oil has the lowest values of T_c and T_0. Cotton seed oil has the highest values of γ^*, γ_o and P_c and least value of V.

V. CONCLUSION

In this paper, a review of the effect of temperature on the surface tension of five vegetable oils using the capillary rise method was made. The thermal constant parameters of the oils such as the surface tension at absolute zero, critical temperature and pressure, molar volume, exponent, reference surface tension and temperature were computed. The results show that these thermal constants depend on the nature of the individual liquids. The critical temperature is referred to as phase transition temperature at which the surface tension of solid-liquid interface vanishes and that of liquid-vapor interface becomes significant. At this temperature, the liquid molecular structure and configuration are changed at the subatomic level even though the physical appearance of the liquid still remains the same. On the other hand the molar volume of the oil reveals the concentration or number of molecules per unit volume of the oil. The significance of the other thermal constants of the oils is hinged on that of critical temperature and molar volume.

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