TEMPERATURE DEPENDENCE OF ORIENTATIONAL POLARIZABILITY AND ELECTRICAL POTENTIAL ENERGY IN SHEA (VITELLARIA PARADOXA) BUTTER OIL

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Abstract

The capacitance of parallel plates capacitor was measured at 50 Hz in order to study the static dielectric constant (k), orientational polarizability (α_o) and electrical potential energy (U_d) of shea butter oil (SBO) at various temperatures T. The results show that these quantities generally decrease with increasing temperature yielding the empirical equations $\alpha_o = \frac{6.362 \times 10^{-38}}{T}$ in Cm and $U_d = -700.5\left(444.\frac{3}{T} - 1\right)$ in Joules. The average values of the induced polarizability α = -1.432×10^{-40} Fm^2 (= polarizability volume $\alpha' = \alpha/4\pi\varepsilon_o$ = -1.287×10^{-30} m^3), electronic polarizability α_e = -1.302×10^{-41} Fm^2, ionic polarizability α_i = -1.302×10^{-42} Fm^2, permanent molar dipole moment μ_m = -1.623×10^{-30} Cm (= -0.487D), and transition temperature T_c = 444.3 K or 171.3 °C were calculated over the temperature range 303-363 K. The definite or non zero value of μ_m suggests SBO structure is non linear or its net bond moments show departure from coplanarity.

Keywords: dielectric constant, temperature, orientational polarizability, dipole moment, electrical potential energy, shea butter oil.

Introduction

Chemically, oils or liquid fats are carboxylic acids (esters) derived from the single alcohol, glycerol, and are known as glycerides. Oils are mostly extracted from living animals and plants as well as their dead remains in rocks underground. The physical and chemical properties of oil depend on its molecular weight (elements present) and the arrangement of atoms in the molecules or molecules themselves that constitutes the acid chains of the oil. A host of authors have studied both Physical and chemical properties of oils (Eromosele *et al.*, 1994; Eromosele and Pascal, 2002; Carey, 1998; Manji *et al.* 2006, 2007; Nkafamiya *et al.*, 2007; Miller *et al.*, 2005; Rakshit, 1997). Oils are used as fuel (kerosene, gasoline), lubricants (in moving parts of machines/engines to reduce friction and heat), cream (body and hair), medicinal purposes e.g. shea butter oil is used to cure diseases such as aromantism, rashes, bone fracture and so on, in cooking (vegetable oils), in making paints/soap and as dielectrics in capacitors to mention a few.

An insulator or dielectric material has no free electric charges (electrons) under ordinary circumstances. This does not mean that they cannot modify the electric field into which they are introduced. In other words, a dielectric is one that has poor conductivity, but an ability to hold a charge with an applied electric field. Examples of dielectrics include air, oil, paper, wax, ceramic, mica, and so on. In fact the most important and interesting electrical property of a dielectric is its ability to become polarized under the action of an external electric field. The atoms and molecules of dielectrics are influenced by an external field and hence the positive particles are pushed in the direction of the field while the negative particles in the opposite direction from their equilibrium position. Hence dipoles are developed and they produce a field of their own. The process of producing electric dipoles out of neutral atoms and molecules is referred to as polarization. A dipole is an entity in which equal positive and negative charges q are separated by a small distance x. In this case, the dipole moment has magnitude qx represented by a vector pointing from the negative charge in the direction of the positive charge. The unit of the dipole moment is the Debye (1 Debye = 3.33564×10^{-30} Coulomb-metre). The dielectrics are mostly useful engineering materials. The first fundamental experimental result discovered by Faraday showed that the capacitance of a capacitor is increased if the space between the conducting parallel plates is filled with a dielectric material. If C_o is the capacitance of the capacitor with the space between the conductors evacuated and C its capacitance when the space is filled with a dielectric, then the ratio $C/C_o = k$ is called relative permittivity or dielectric constant which is independent of the shape or dimensions of the conductors and is solely a characteristic of the dielectric medium (Serway, 1996). The dielectric constant of an insulator is a measure of its ability to transmit electrical potential energy. In electrical systems such as capacitors, the effectiveness of dielectrics is measured by their ability to store energy. The charge on a capacitor and its capacitance increases by a factor k while the electric field intensity and potential difference between the plates decrease by 1/k of their original values before the dielectric is introduced between the plates. The permittivity of the dielectric medium is defined as $\varepsilon = \varepsilon_o k$ where $\varepsilon_o = 8.854\times10^{-12}$ Fm^{-1} is an electric constant representing the permittivity of free space or vacuum. In another vein, the dielectric constant is a simple number, that is, the relative ratio of the square of the speed v of an electric field in a material to the square of the speed c of the electric field in a vacuum or air. The dielectric constant of a material is a directly measurable quantity which expresses on a macroscopic scale the overall result of the interaction which occurs on a microscopic scale between an externally applied electric field and the atoms or molecules of the material. In a nutshell, it is a macroscopic quantity that measures how effective an electric field is in polarizing the material. The dielectric constant is an important indicator of oil quality that is easy to measure (Hwang *et al*, 1994; Josep and Raman, 2003; Eromosele and Eromosele, 1993).

The dielectric constant of oil can change due to the presence of contaminants (water, particles, etc.) or changes in the chemistry of the oil (additive depletion or oxidation). In general, the value of the dielectric varies with the frequency of the applied field. This paper discusses static dielectric that is below electric field frequencies of 106 Hz.(Carey, 1998; Carey and Hayzen, 2001). Dielectric constants of materials at these frequencies are called static because they show virtually no frequency dependence in this frequency region. Temperature affects the value of the dielectric constant although the effect is relatively small (0.05 %) of hydrocarbons lubrication oils. The density of the oil also influences the dependence of the dielectric constant on temperature - the less dense an oil, the fewer number of oil molecules per unit volume. A smaller number of molecules per unit volume implies that there is less interaction with the electric fields and therefore a decrease in the dielectric constant. As the temperature increases, the density decreases and hence the dielectric constant of the oil also decreases. Other things that will change the dielectric constant of oil include an increase in viscosity, changes in acid number or base number and additive depletion or decrease in viscosity caused by addition of less dense oil will result to decrease in dielectric constant.

We can easily distinguish different types of oils by measuring their dielectric constants using capacitors. The only other common technology capable of this is infrared spectroscopy. However, this method typically requires an expensive instrument and expert interpretation. By contrast, measuring the dielectric constants using capacitors offers a quick, simple, low cost alternative to permit the differentiation between different classes of oil. In this study, the parallel plates capacitor technique is employed and the dielectric of interest is one of the Nigerian vegetable oils known as shea butter oil (SBO). This oil is extracted from the seed of shea plant (Vitellaria paradoxa) popularly known in northern part of Nigeria in "Hausa language" as "kadanya". Previous studies have shown that it has some medicinal, nutritional and cultural values (Fatima, 2010). In this paper, we have studied the temperature dependence of orientational polarizability, induced polarizability and electrical potential energy with the intention of exploring the potentials of SBO in energy storing devices like capacitors and so on.

Theory

When a dielectric is placed in an external field, it is likely to experience three major types of polarizations namely orientation polarization, electronic polarization and ionic polarization. Orientation polarization occurs only in polar substances because such substances contain permanent molecular dipoles. The existence of such permanent dipole moment is purely a matter of molecular geometry. These permanent molecular dipoles can rotate about their axis of symmetry to align with the applied field which exerts a torque on them. This additional polarization effect is accounted by an orientational polarizability term α_o (Pillai, 2005; Kakani and Hemrajani, 2002; Blakemore, 1985).

With electronic and ionic polarization processes, the force due to the applied field E is balanced by elastic binding forces, but for orientation polarization no such forces exist.

In thermal equilibrium with no field applied the permanent dipoles contribute no net polarization since they are randomly oriented. When E is applied, dipole alignment is largely offset by thermal agitation. However, since it is observed that the orientation polarization is of the same order as the other forms of polarization, it is only necessary for one dipole in 10^5 to be completely aligned with the field to account for the effect. Whereas the orientational polarizability α_o is temperature dependent, since the higher the temperature the greater is the thermal agitation and the lower is α_o (Atkins and Paula, 2002; Blakemore, 1985; Pillai, 2005; Sharma and Sharma, 1999).

On the other hand, the induced (or distorting/deforming) polarizability factor, α is a function of molecular structure and is largely independent of temperature (Pillai, 2005; Clyde, 2004). The polarizabilities α_e and α_i are known as electronic polarizability and ionic poalarizability respectively and are collectively referred to as induced polarizability. The three major kinds of polarizabilities are linearly related in the form of $\alpha = \alpha_e + \alpha_i = 11\alpha_i$ where $\alpha_i = 0.1\alpha_e$ (Pillai, 2005; Atkins and Paula, 2002).

The relative permittivity of a substance is large if its molecules are polar or highly polarizable. In molecules in which the dipole is temperature dependent, the Clausius-Mosotti equation for molar polarizability is given by (Pillai, 2005: Clyde, 2004; Yavorsky and Detlaf, 1980)

$$\left(\frac{k-1}{k+2}\right)V_m = \frac{N_A}{3\varepsilon_o}\left(\alpha + \frac{\mu_m^2}{3k_BT}\right)$$
1a

and
$$r = \left(\frac{V_m}{N_A}\right)^{\frac{1}{3}}$$
1b

where k = dielectric constant, N_A = Avogadro's number (6.02×10^{23}), ε_o = permittivity of free space (8.854×10^{-12} Fm^{-1}), μ_m = permanent dipole moment, k_B = Boltzmann constant (1.38×10^{-23} J/K), V_m = molar volume, r = intermolecular distance, α = induced polarizability and T = absolute temperature. The second term in bracket on the right hand side of equation (1a) stems from the thermal averaging of the electric dipole moment in the presence of an applied field which is simply referred to as the orientational polarizability given by (Pillai, 2005; Kakani and Hemrajani, 2002).

$$\alpha_o = \frac{\mu_m^2}{3k_B T} \qquad 2$$

The weak, attractive London forces between the atoms, molecules or ions of any substance are described by the molar potential energy function (Clyde, 2004)

$$U_L = \frac{\left(-1.8\times 10^{-18}\right)\alpha^2 N_A}{(4\pi\varepsilon_o)^2 r^6} \qquad 3$$

where r is the shortest particle-particle distance in the substance. These forces alone causes the condensation of a gas to a liquid or solid for substances such as the noble gases, which do not have additional potential energies resulting from dipole-dipole interactions, ionic bonding, metallic bonding, or covalent bonding. Such substances have relative low melting and boiling points as well as small heats of sublimation and vaporization.

The electrical potential energy of a polar substance is the sum of the potential due to the dipole-dipole interaction and one due to the induced dipole effect, yielding (Clyde, 2004)

$$U_d = -\frac{2\mu_m^2\left[\left(\mu_m^2/3k_B T\right)[+\alpha]N\right]_A}{(4\pi\varepsilon_o)^2 r^6} \qquad 4$$

We can eliminate r by taking the ratio of U_d in equation (4) to U_L in equation (3) to get the equation of the reduced electrical potential energy given by

$$\frac{U_d}{U_L} = \frac{2\left(\frac{\mu^2}{\alpha}\right)\left[\frac{1}{3Tk_B}\left(\frac{\mu^2}{\alpha}\right)+1\right]}{\left(1.8\times 10^{-18}\right)} \qquad 5$$

Inserting the value of μ_m^2/α obtained from the ratio of the slope to the intercept of a graph represented by equation (1) into equation (5) gives

$$\frac{U_d}{U_L} = A\left(\frac{B}{T}+1\right) \qquad 6$$

where $A = 2\mu_m^2/\alpha$ and $B = \mu_m^2/3k_B\alpha$ are constants whose signs depend on that of α.

The negative derivative of equation (4) with respective to r gives the expression of the force responsible for the energy given by

$$F = -\frac{dU_d}{dr}$$

$$= \frac{12\mu_m^2\left[\left(\mu_m^2/3k_B T\right)[+\alpha]N\right]_A}{(4\pi\varepsilon_o)^2 r^7} \qquad 7$$

When the molecules are at minimum separation r_o, the net force becomes zero. This condition demands that the term in square bracket in the numerator equals zero giving the transition temperature as

$$T_c = -\frac{\mu_m^2}{3\alpha k_B} \qquad 8$$

This is the temperature at which the arrangement of the molecules or their bonds are changed in a way that the net polarization disappears in the new phase. The change in the arrangement of the molecules on heating may be due to changes in (i) molecular structure e.g. from nonlinear to linear (ii) angle between bonds and (iii) number of charges or dipoles in the dielectric. These changes in the molecular arrangement in the dielectric may be microscopic where no physical changes are observed or macroscopic where physical changes are observed, for example, when liquid changes to vapour. In this case, the transition temperature on microscopic scale is likely to be the thermodynamic equilibrium temperature T_o or on macroscopic scale it is likely to be the boiling point of the liquid. This fact can be reconciled by measuring the boiling point of the liquid experimentally.

Experiment

A parallel plate capacitor of dimensions 15 cm×15 cm and plates separation of 1 mm was constructed. The three sides of the capacitor were firmly closed with thin layers of insulator and the fourth side left open through which SBO was introduced between the plates of the capacitor. The capacitor with air as dielectric between its plates was connected to power supply and its capacitance C_{air} was measured using capacitance meter. The oil was slightly heated above room temperature so that it was easily poured into the space between the plates. The capacitance with its contents was immersed in water inside water bath containing an automatic electric temperature regulator (electric heater and automatic stirrer). The capacitor and its contents in the water bath were allowed to cool back to room temperature, 303 K. At this juncture, the capacitor with oil as dielectric was connected to power supply and its capacitance measured using the capacitance meter. The capacitance of the capacitor and its contents immersed in water was heated to a constant temperature (308 K) by means of the temperature regulator was measured. This procedure was repeated ten more times at intervals of 5 K up to a maximum value of 363 K. The static dielectric constant of SBO at the mains frequency (50 Hz) was calculated from the ratio of C_{oil}/C_{air} at various temperatures in the range 303-363 K and recorded in Table 1.

Results and discussion

Table 1 Dielectric constant, orientational polarizability and electrical potential energy at various temperatures and other calculated parameters

T(K)	k	$\alpha_o \times 10^{-40}$ ($C^2m^2J^{-1}$)	U_d (J)	Other calculated parameters
303	2.5	2.10	-326.67	α_o = -1.432×10^{-40} Fm^2 α' = $\alpha/4\pi\varepsilon_o$ = -1.287×10^{-30} m^3 α_e = -1.302×10^{-41} Fm^2 α_I = -1.302×10^{-42} Fm^2 μ_m = -1.623×10^{-30} Cm (= -0.487D) T_c = 444.3 K (=171.3 °C) V_m = 4.3×10^{-6} m^3 atT = 303 K r (303 K) = 1.93×10^{-10} m = 0.193 nm U_L = -34730.6 J (T = 303 K; r = 0.193×10^{-10} m)
308	2.49	2.07	-309.99	
313	2.4	2.03	-293.85	
318	2.32	2.00	-288.22	
323	2.23	1.97	-278.07	
328	2.15	1.94	-248.38	
333	2.06	1.91	-234.13	
338	1.98	1.88	-220.31	
343	1.89	1.85	-206.88	
348	1.8	1.83	-193.85	
353	1.72	1.80	-181.18	
358	1.64	1.78	-168.86	
363	1.55	1.75	-156.89	

The results in Table 1 reveal that k and α_o decrease with temperature while U_d increases.

Figure 1 represents the variation of molar polarization P_m with temperature T.

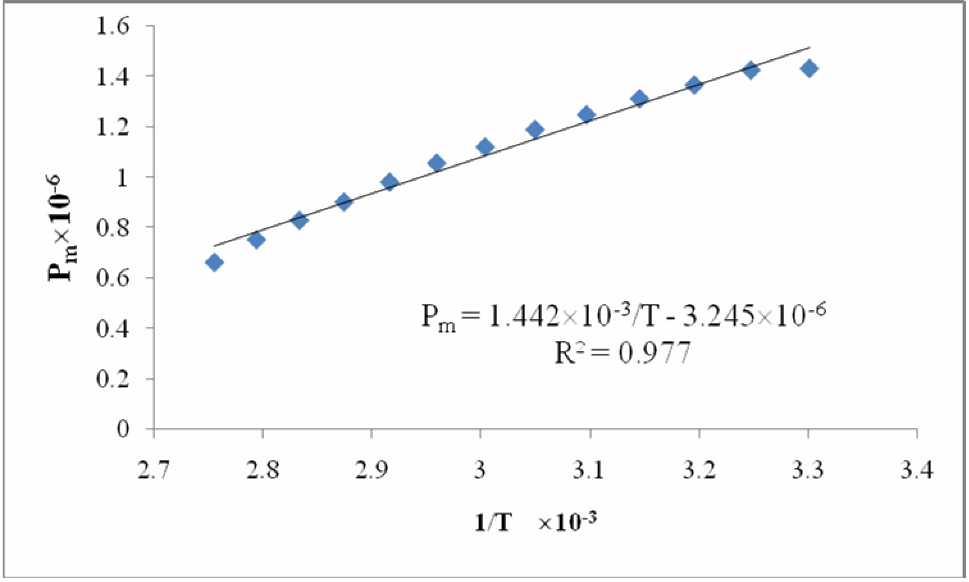

Fig. 1 Variation of molar polarization with temperature

Using the molar volume $V_m = 4.3\times10^{-6}$ m^3 (Fatima, 2010) the graph of molar polarization, $P_m = (k-1)V_m/(k+2)$ against 1/T represented by equation (1) has slope

$$(\downarrow m\uparrow 2\ N\downarrow A/\ [\![9\varepsilon]\!]\downarrow(ok\downarrow B) = 1.442\times [\![10]\!]\uparrow(-3)$$

from which $\mu_m^2 = 2.634\times10^{-60}$ or $\mu_m = \pm1.623\times10^{-30}$ Cm (= ± 0.487D). The possible explanations for the plus or minus sign of μ_m include: (i) μ_m is a vector quantity with two possible magnitudes each having same sign with corresponding value of α. (ii) when the magnitude of μ_m is negative it means μ_m points away from the positive charge or the bond angle is obtuse (iii) when the magnitude of μ_m is positive it means μ_m points towards the positive charge or the bond angle is acute. (iii) the definite or non zero value of μ_m suggests SBO is polar substance with non linear structure whose net bond moment shows departure from coplanarity.

On the other hand, from the intercept, we have $N_A\alpha/3\varepsilon_o = -3.245\times10^{-6}$ in m^3 giving $\alpha = -1.432\times10^{-40}$ Fm^2 (or equivalent polarizability volume $\alpha' = \alpha/4\pi\varepsilon_o = -1.287\times10^{-30}$ m^3). The negative sign of α corresponds to negative μ_m confirming SBO has nonlinear structure. Now since $\alpha = \alpha_e + \alpha_i$ and $\alpha_i = 0.1\alpha_e$ (Pillai, 2005) then $\alpha_e = -1.302\times10^{-40}$ Fm^2 and $\alpha_i = -1.302\times10^{-41}$ Fm^2.

Now substituting the value of $\mu_m^2/3k_B$ in equation (2) gives the orientational polarizability

$$\alpha_o = \frac{6.362\times10^{-38}}{T}.$$

Also substituting the values of r(303 K) = 1.93×10^{-10} m and α calculated from equation (1b) and intercept respectively and that of the constants N_A, π and ε_o into equation (3) gives $U_L = -34730.6$ J.

Also the ratio $\frac{\mu_m^2}{\alpha}$ appears in the expression of the reduced potential energy function in a polar substance. Therefore, substituting the calculated value of $\frac{\mu_m^2}{\alpha} = -1.840\times10^{-20}$ J (= -1.150 eV) into equation (5) and rearranging, gives

$$\frac{\mathbf{U_d}}{\mathbf{U_L}} = 0.0204\left(444.\frac{3}{T} - 1\right).$$

This is the equation of reduced potential energy of SBO as a function of temperature. Now since U_L is independent of T it means this ratio represents the variation of U_d with T for all values of r. Thus, substituting the value of U_L = -34730.6 J into the equation of reduced potential energy it finally yields $\mathbf{U_d} = -700.5\left(444.\frac{3}{T} - 1\right)$ in Joules from which the values of U_d at different temperatures were calculated and recorded in Table 1.

Similarly, inserting the values of k_B, α and μ_m into equation (5) yields T_c = 444.3 K or 171.3 °C. Substituting this value of T_c in the expression of reduced energy in the preceeding paragraph reduces the electrical potential energy U_d = 0 at T_c. This means at $T \geq T_c$ both induced and orientational polarization processes cease which may be due to rearrangement of the atoms/molecules from nonlinear to linear structure in the system. This change in the molecular structure of the system suggest phase transition in this system whereby the molecules rearrange themselves in such a way that the liquid SBO and its vapor coexists in the same phase. In this light, T_c = 444.3 K is the boiling point or thermodynamic equilibrium temperature near its boiling point.

Conclusion

The capacitance of parallel plates capacitor was measured at various temperatures in order to determine the static dielectric constant, orientational polarizability and electrical potential energy of SBO at the mains frequency (50 Hz). The results show that these parameters decrease with increasing temperature. The average values of the induced polarizability α =-1.432×10^{-40} Fm^2 (= polarizability volume $\alpha' = \alpha/4\pi\varepsilon_o$ = -1.287×10^{-30} m^3), electronic polarizability α_e = -1.302×10^{-40} Fm^2 Fm^2, ionic polarizability α_i = -1.302×10^{-41} Fm^2

and permanent dipole moment

μ_m = -1.623×10^{-30} Cm (= -0.487D) were computed. The corresponding empirical equations for orientational polarizability $\alpha_o = \frac{6.362 \times 10^{-38}}{T}$ and reduced electrical potential energy $\frac{\mathbf{U_d}}{\mathbf{U_L}} = 0.0204\left(444.\frac{3}{T} - 1\right)$ as functions of temperature were deduced. Also using the calculated value of r(303 K) = 1.93×10^{-10} m gives U_L = -34730.6 J and hence the reduced energy equation reduces to $\mathbf{U_d} = -700.5\left(444.\frac{3}{T} - 1\right)$ which does not exist at temperatures greater than T_c. Finally, the transition temperature T_c = 444.3 K at which all polarization processes completely vanish in SBO is likely to be its boiling point on macroscopic scale point of view or thermodynamic equilibrium temperature near its boiling point on a microscopic scale concept.

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