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Electrocapillarity in palm oil: evidence of induced non-linearity

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Abstract. Electrocapillarity has been studied both theoretically and experimentally in the class of liquids which include palm oil. Numerical results are presented for palm oil. The theory predicts the surface tension to be proportional to the square of the electric field intensity. However, the exponent of the electric field intensity obtained from experiment is 1.90. The results also show that the surface tension increases monotonically at low fields and that non-linearity is induced for a field intensity greater than $1.25 \times 10^6 \text{ V m}^{-1}$. The low-field dielectric constant is found to be 2.70.

1. Introduction

The variation in the surface tension of a liquid with applied electric field intensity has long been an observed phenomenon. In 1873, Lippman [1] investigated this effect in mercury and observed that the surface tension first increased and then later decreased with increasing field intensity. More recently, the surface tension of transformer oil has been observed to depend quadratically on the electric field intensity [2]; here, the surface tension was monitored by means of a modified Jaeger technique. The changes that were made to the standard Jaeger method allowed for the application of a uniform static electric field and controlled variation in the excess pressure. However, there is still no generally accepted explanation for this observation or how it depends on other properties of the liquid under test.

The macroscopic properties of a liquid are a result of the interaction between the molecules making up the bulk liquid. Thus whatever these properties might be, irrespective of whether they are mechanical, electrical, etc, they are all the result of the same interactions.

In this study we investigate electrocapillarity in palm oil in a static electric field. The capillary is that between a pair of parallel plates. Palm oil is an extract from the flesh of the oil palm fruit (*Elaeis guineensis*). It contains 50% saturated fats. Most of its unsaturated fatty acids are mono-unsaturates with many of the carbon chains being 16 or 18 atoms long. It also contains some small amounts of vitamin E and carotene. Thus, it is not a pure triglyceride.

Noting that the surface tension and dielectric constant are the two macroscopic properties which come directly into focus in this study, we try to present a theoretical

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basis for expecting the surface tension to change with the applied electric field intensity in such a class of liquids.

2. Theory

Since the observation of capillary ascent, various theories [3–5] have been put forward to try to explain this effect. These theories principally attempt to associate surface tension with the intermolecular forces acting in the liquid. Depending on the type of liquid any of the following types of force may be predominant: dipole–dipole, dipole-induced dipole, London dispersion and hydrogen bonding [6, 7]. In the class of liquids which includes palm oil, there is reason to believe that the London dispersion and hydrogen types of force will predominate despite the fact that palm oil molecules are polar.

Now, when a liquid rises to a height h in a capillary, the potential energy gained by the liquid column is equivalent to raising a mass whose value is that of the liquid column through a height $\frac{1}{2}h$ [8]. This energy comes from the change in the areas of the exposed interfaces involved in the problem (i.e. solid–vapour, solid–liquid and liquid–vapour) following Young's relation [9]. It has been shown by Tabor [10] that the potential energy is exactly half the energy released in this change. For zero contact angle, the potential energy can be shown to be given, following Tabor, by

$$U = \gamma 2wh \quad (1)$$

for a pair of parallel plates of width w separated by a distance d ($\ll w$), where γ is the surface tension.

Let the equilibrium height of the liquid column after the application of an electric field of strength E_{ex} be $h = h_0 + \Delta h$, where h_0 is the height in zero field and Δh is the resulting change in height. Then the total potential energy of the liquid column is divided between the mechanical and electrical components. The electrostatic energy stored in the medium is equal to the work done in raising the liquid through the extra height Δh and is given by

$$U_E = F_E \cdot \Delta h = \frac{1}{2}k_0(k_r - 1)wd \Delta h E_{\text{ex}}^2 \quad (2)$$

where k_0 is the permittivity of free space and k_r is the dielectric constant.

It follows that the induced surface energy is given by (2). Consequently, the induced surface tension resulting from the application of the field is

$$\Delta\gamma = \frac{1}{4}k_0(k_r - 1)dE_{\text{ex}}^2. \quad (3)$$

Hence,

$$\gamma = \gamma_0 + \frac{1}{4}k_0(k_r - 1)dE_{\text{ex}}^2 \quad (4)$$

where γ_0 is the zero-field surface tension. This leads to the total capillary rise

$$h = h_0 + \frac{1}{2}[k_0(k_r - 1)/\rho g]E_{\text{ex}}^2 \quad (5)$$

by balancing $\Delta\gamma$ with the excess height. ρ is the density of the liquid and g the gravitational acceleration.

Thus, we expect the surface tension to depend on the square of the externally applied electric field intensity, if the other parameters in equation (4) remain constant. It is

obvious that this change in the surface tension will cause an increase in the stored potential energy as evident from equation (1). One other useful feature of (4) is that it permits investigation of the dependence of the dielectric constant of the liquid on electric field intensity. This will show up as a deviation in the plot of the liquid height versus squared field intensity from a straight line. It thus provides us with a method of studying non-linear dielectric effects by means of electrocapillarity. However, we do not wish to discuss this phenomenon here, despite its relevance.

It should be noted that, in the above treatment, we have not restricted the liquid to being polar or non-polar.

3. Experimental method and observations

The experimental arrangement consists of a pair of parallel metal plates, each of width 50 mm, made in such a manner as to allow for adjustable plate separation, which formed the capillary. One of its ends is lowered below the free surface of the liquid under test in a reservoir while electrical contacts provided at the opposite end enabled connection to a high-voltage DC source. The potential difference across the plates is measured using an avometer while the liquid ascent is measured using a travelling microscope.

The maximum applied field in this set-up is limited more by electrophoresis than by dielectric breakdown. This causes sparks, resulting in an abrupt change in the liquid level within the capillary. To increase this limit, the liquid is well filtered.

For each reading of the liquid meniscus level, a mean time of 15 min is allowed for it to reach equilibrium. Increasing the field caused the shape of the liquid meniscus to tend towards a planar structure. This limit was, however, not attained. The cross sectional view of the meniscus changed from semi-circular to semi-elliptical. This implies a reduction in excess pressure and changes the contact angle towards higher values. It should be noted that the meniscus level while increasing the field strength is slightly less than that observed while decreasing it. This may be due to either of the following reasons.

- (i) While decreasing the voltage, the oil clings to the metal surface.
- (ii) There may exist a hysteresis loop for the polarisation curve. As a result, if the applied field is removed, the remnant polarisation causes a rise in the liquid level.

The experiments were carried out at room temperature (about 300 K).

4. Results and discussion

The results expressed in terms of the change Δh in liquid column height as a function of the electric field intensity E_{ex} are shown in figures 1 and 2 for two different plate separations ($d = 0.3$ mm and 0.6 mm). Figure 1 is a log-log plot of Δh versus E_{ex} while figure 2 is a linear plot of Δh against E_{ex}^2 . In the absence of any induced non-linearity, both plots are expected to be straight lines. The figures clearly show induced non-linearity. From figure 1, non-linearity sets in at a field strength of about 1.25×10^6 V m⁻¹. Using figure 1 we obtain, from its slope, the power of the field intensity dependence as 1.90. This is slightly different from the value of 2.00 predicted by the theory.

Using the slope of the plots in figure 2, we can calculate the dielectric constant of the liquid in the low-field region. However, we have determined the dielectric constant by performing a linear regression on the values of Δh and E_{ex}^2 using an IBM PC. From this

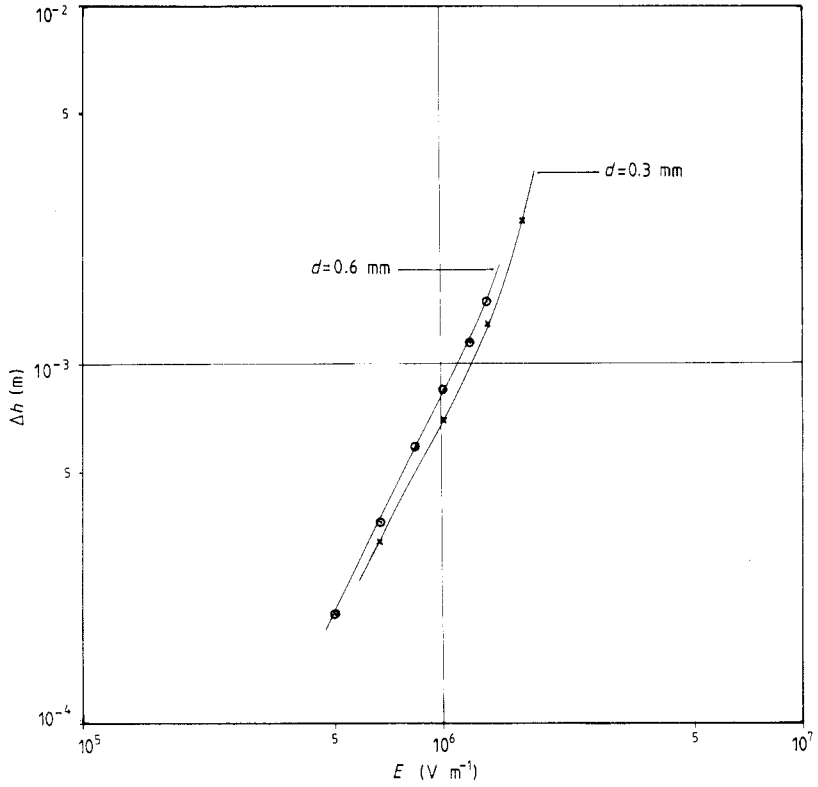


Figure 1. Change in height (Δh) versus electric field intensity (E_{ex}).

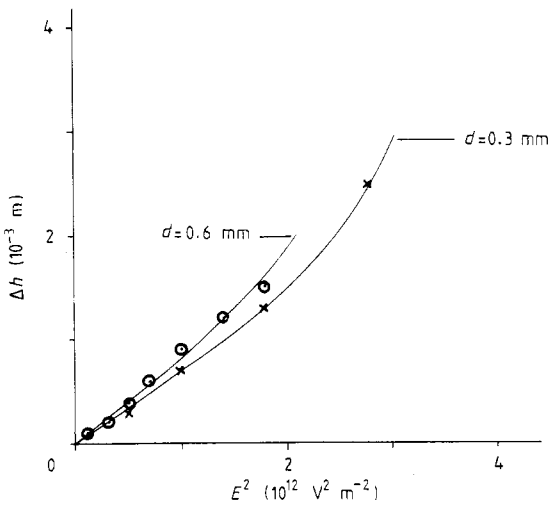


Figure 2. Change in height (Δh) versus electric field intensity squared (E_{ex}^2).

we have obtained the dielectric constant as 2.738 for $d = 0.3$ mm and 2.683 for $d = 0.6$ mm. These results are quite close.

The figures show that, after non-linearity has set in, the liquid column height increases more rapidly with a change in field intensity. We can attribute this non-linearity to an increase in the dielectric constant with applied field. It follows that $\Delta k_r < 0$, where Δk_r is the zero-field dielectric constant minus the high-field dielectric constant. In the literature this is called the 'positive saturation effect without inversion' [11]. One fact is, however, not clear from this result, i.e. whether all the change in dielectric constant is purely a non-linear dielectric effect or whether other effects, e.g. electrocalorific effect [12], predominate. It is justifiable to expect an electrocalorific effect in this investigation as a result of the Joule heat caused by the current that must flow through the dielectric. However, it is difficult to estimate the degree of significance of this effect.

Also, as mentioned previously, we see that the field causes the contact angle to change. Incorporating a changing contact angle, which is increasing, in the above derivations would imply a more rapid increase in the liquid column height than is expected from a simple quadratic dependence. However, the results show that this more rapid variation sets in at some value of the field strength corresponding to the onset of non-linearity. Thus the beginning of the deviation from linearity might be linked with the changing contact angle. Since no attempt was made to measure the contact angle in this experiment it is difficult to justify the above statement.

5. Conclusion

Electrocapillarity in palm oil has been found to be a quadratic function of an applied electric field intensity in the region of low field strength. Within the field region studied, there does not seem to be any saturation of this effect and thus the surface tension increases monotonically with increasing electric field intensity. The dielectric constant of the liquid may be estimated by this method and in palm oil it is in the range $2.683 \leq k_r \leq 2.738$ in the linear region. Induced non-linearity sets in at a fairly moderate field intensity of 1.25×10^6 V m⁻¹. This has been attributed to a changing dielectric constant and contact angle. It follows that the non-linear dielectric effect can be investigated by this simple method.

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