



## Faradaic reactions' mechanisms and parameters in charging of oils

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### ABSTRACT

Leaky dielectric liquids, e.g. oils, constitute a class of conductors capable of being electrified to possess a net charge. Faradaic reactions have been recently demonstrated to be responsible for the electrification of such liquids as canola oil in electrostatic atomizers. Here we explain the fundamental chemical kinetics of the mechanisms responsible for charging of these oils at metallic electrodes and measure their parameters. Three main mechanisms of the electrode faradaic reactions of oil are recognized. (i) Cathodic reduction of protons resulting from fatty acid dissociation accompanied by anodic reactions with formation of metallo-organic deposits (metal salts of fatty acids). (ii) Redox reactions with participation of dissociated water molecules (the impurities) absorbed from the surrounding humidity. (iii) Redox reactions on a sharp pin electrode (either being a cathode or an anode) at higher voltages (with the magnitude above about 4 kV) leading to the Coulombic repulsion of charged oil from this electrode and the emergence of a toroidal vortex-like circulation in the oil bath. The electrochemical findings are corroborated by the results obtained by means of the Infrared spectroscopy and Raman spectroscopy of the electrode deposits, and the introduction of a novel method of measurement of the electric conductivity of oils used to establish the kinetic constants of the Frumkin-Butler-Volmer kinetics in the form of the Tafel plot.

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### 1. Introduction

The concept of the leaky dielectric model was introduced in the mid-1960s to explain the electrically-driven behavior of such seemingly insulating liquids as, for example, transformer oils [1–3]. The leaky dielectrics, which are essentially poor ionic conductors, possess an electric conductivity and are capable of polarization and/or electrification, revealing a net bulk charge in the polarized near-wall layers due to the intrinsic electro-kinetics mechanisms [4,5]. Conductivity of such liquids has been measured, albeit being very small [6]. The existence of ions in leaky dielectric liquids is attributed to dissociated impurities [7], to self-dissociation under strong electric fields, or to direct charge injection [8], and essentially its origin is still debated.

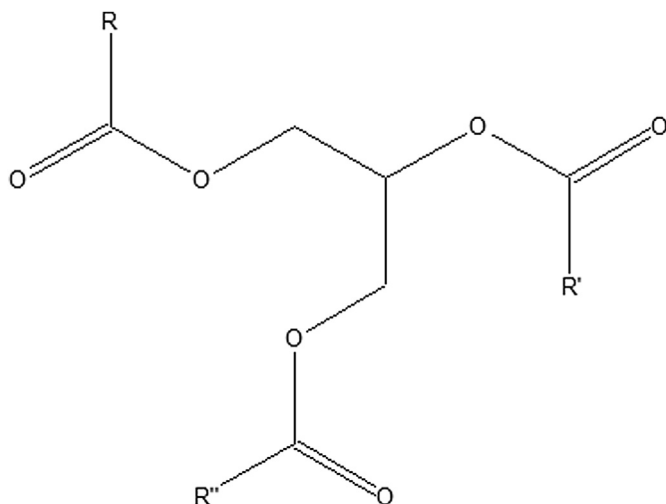
Electrochemical reactions were shown to be a contributing factor responsible for electrification of oil in electrostatic atomizers [9]. This implies that such 'dielectric fluids' as oils are essentially weak electrolytes, i.e. leaky dielectrics [3,4] with a possibility of faradaic reactions responsible for charge transfer at the electrode

surfaces. Since oils were not in focus of electrochemistry for a long time, the nature and origin of charge carriers in oils are still a mystery. In hydrocarbon oils, they are either attributed to impurities present or to spontaneous dissociation of oil molecules [10,11]. Water is considered one of the major impurities and is shown to have significant effect on conductivity of hydrocarbon liquids [12,13]. Unsaturated organic liquids with polarizable structures (like the carbonyl group) can absorb significant quantities of water [13]. Such liquids, including vegetable oils, are typically thought to contain several hundreds of ppm of water and can dissolve more than 1000 ppm of water at saturated conditions [13,14]. Vegetable oils are in focus in the framework of the electrostatic atomization, in particular, in relation to the food-processing industry and formation of carcinogenic compounds. Triglycerides are the main components of vegetable oils. Triglycerides possess three fatty acids on a glycerol backbone. The general structure of a triglyceride is shown in Fig. 1. Overall, the R groups can be saturated or unsaturated long hydrocarbon chains. For example, the fatty acid constituents of canola oil [15] used in the present experiments are listed in Table 1.

In addition to triglycerides, oils include micro-constituents. Some of them, such as tocopherols (i.e. vitamin E, sometimes added on purpose), exist naturally. Some others, such as peroxides

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**Fig. 1.** General structure of triglycerides with different possible combinations of long-chain fatty acids.

(compounds with an oxygen-oxygen single bond), free fatty acids (FFA), etc., could result from degradation during processing or storage. It should be emphasized that tocopherols are antioxidants which scavenge free radicals, while autoxidation or hydrolysis of vegetable oil result in free fatty acids (FFA) among other products. Additionally, one may refer to the CODEX standard for the whole range of additives, micro-constituents and their accepted levels in refined vegetable oil [16].

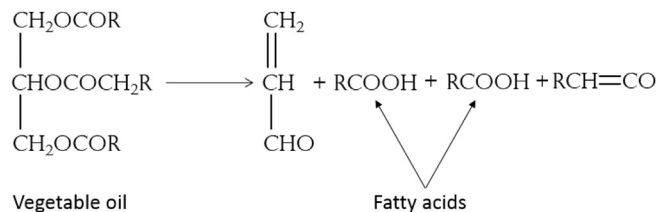
Production of vegetable oils involves different degrees of heating used to increase the yield. In heated or fried (e.g. for cooking) oils, the above-mentioned content of micro-constituents can change [15,17–19]. The content of tocopherol (vitamin E) in palm oil decreases at elevated temperatures [17]. For example, heating palm oil at 255 °C for 15 min led to a decrease in tocopherol concentration from 79.9 mg/L to 64.1 mg/L [18]. In the case of soybean oil, the peroxide content was reported to marginally increase in time (on the scale of hours) during frying [18].

The literature dealing with oil pyrolysis listed numerous products resulting from oil cracking. One of the most typical first reactions during oil pyrolysis is given in Fig. 2. The radicals RCHCO formed in such reactions further decompose into smaller compounds [15]. However, one of the common consequences of heating/frying of oil is an increase in the free fatty acid content in the oil. A study on pure tricaprin (representing saturated essential oil), which was heated at 190 °C for 3 h in a slow stream of dry air revealed formation of 2.5% FFA [19]. Free fatty acids listed in Table 1 are weak carboxylic acids. FFA may be also considered as a weak electrolyte, albeit too weak when compared to the traditional carboxylic acid electrolytes, such as acetic and formic acids.

In the electrostatic atomizers [8], electrodes are perfect conductors (metals attached to a battery). Such electrodes sustain electric current, have zero tangential electric field (being isopotential as conductors) and also sustain Faradaic reactions

**Table 1**  
Fatty acids in canola oil [15].

Acid	Formula	wt.%	Number of C atoms
Oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	60	18
Linoleic	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	20	18
Linolenic	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	10	18
Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	2	18
Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	4	16



**Fig. 2.** Decomposition of vegetable oil at pyrolysis temperatures producing fatty acids [15].

[9,20]. Essentially the faradaic reactions at the electrodes operating in the kinetics-limited regime (rather than in the diffusion-limited regime) are responsible for liquid electrification. Using certain similarity with gas ionization, the slow faradaic reactions are called 'glowing' reactions, as it is done, for example, in relation to the corrosion reactions [21], or in general in electrochemistry [22]. The kinetics of faradaic reactions follow the Butler-Volmer law [22,23], or the Frumkin-Butler-Volmer law [22,23] (with the presence of the polarized layer being accounted for).

The following sections describe the kinetics mechanisms of faradaic reactions in oils in detail: first, the reactions associated with fatty acids and resulting in formation of metallo-organic deposits (metal salts of fatty acids) on the anode; second, the reactions associated with the impurities (the water molecules); and third, the reactions associated with charging of neutral oil molecules at high voltages. The electrochemical findings are interpreted in the framework of the Frumkin-Butler-Volmer law and conclusions are drawn at the end.

## 2. Faradaic reactions in oils involving fatty acids

The electrode reactions can be attributed in the first approximation solely to the free fatty acids present in oil. The free fatty acids may dissociate according to the following reaction



where RCOOH stands for a general fatty acid.

Then, the following two overall faradaic reactions can occur at the electrodes. Namely, the overall cathodic reduction of hydrogen



and the anodic oxidation reaction



where M stands for an anode metal involved in the reaction. Note that the anodic reaction (3) is quite similar to the formation of soap molecules which are sodium or potassium salts of fatty acids.

The question is whether the anodic reaction (3) is possible with such typical atomizer electrode materials as the transition metals like iron, nickel, etc. (involved in stainless steel) or zinc and copper (like in brass), which possess valences higher than one, and the R

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