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The effect of changing interfacial tension on electrohydrodynamic processes in two-phase immiscible liquids

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Abstract

The interfacial tension is a crucial property of two-phase immiscible liquid. However, many researchers are not aware about the fact that its value is far from being constant for many pairs of liquids. The paper presents the measurements of interfacial tension time-dependencies for various oils against distilled water and assesses how it affects electrohydrodynamic processes in two-phase immiscible liquids. Primary results were obtained using an optical tensiometer (the pendant drop method). Further on, several computations of droplet electrodeformation were performed and compared to the relevant experimental data to independently check the reliability of the measurements. It was found that the decrease with time of the interfacial tension against water is specific for a lot of liquids, in particular, for many vegetable oils and even for transformer oils after it being used in power transformers. The change of the interfacial tension with time is shown to be a realistic cause for the emergence of the so-called cone-dimple mode of electrocoalescence, which was earlier reported in experimental studies. The paper includes experimentally measured properties (that need to be specified in numerical models) for many liquids.

Keywords: Interfacial tension change, vegetable oils, transformer oil, electrical deformation, electrocoalescence, numerical modeling.

1. Introduction

Electrohydrodynamic processes in two-phase immiscible liquids represent complicated multiphysics phenomena, which investigation is a complicated task for researchers [1, 2]. During the last fifteen years, many numerical models were developed for the description of typical cases of multiphase electrohydrodynamics [3–9]: conducting droplet motion in oil, droplet electrodeformation and electrocoalescence. However, the most part of them does not correspond perfectly to available experimental data due to unknown reasons. For example, it is a realistic challenge to describe numerically a cone-dimple mode of coalescence reported in experimental studies [10, 11] though some assumptions can be found in the literature [12].

The goal of the study is to shed a light on one possible drawback of experimental data that can prevent from getting good quantitative agreement between computations and observations. The drawback is changing with time interfacial tension (IT), which was reported few times in the literature [13, 14]. In these papers, IT values were measured for brine water with Grane crude oil and Marcol 52 with surfactant. One more paper [15] shows similar results for the distilled water and olive oil. In all cases, descending time-dependencies of IT were observed. Theoretical explanation of this effect is given in [16], where the temporal reduction of the IT is explained with "a net diffusion flux of surfactant to the interface." However, many experimental papers, e.g. [11, 17–19], present only constant values of the interfacial tension. So, the key question of the study is whether the described change of IT with time is specific for many pairs of liquids or not? Besides, how it affects the electrohydrodynamic processes in two-phase immiscible liquids?

The present investigation bases on the experimental measurements of the IT between water and various liquids and compliments them with some experimental and numerical data on droplet electrodeformation and coalescence. For the completeness of the information, all other liquid properties that need to be specified for numerical modeling were also measured for all investigated liquids and included in the paper.

2. Experiment and modeling

The interfacial tension was measured basing on a pendant drop method [20, 21] using optical tensiometer Theta Lite. The measurement was performed in the following way. The liquids were placed in advance in the experiment room to keep their temperature 22 ± 2 °C. The measuring cell was filled with one of the liquids (usually, oil), whereas another one was injected into the bulk using a syringe with steel needle. The needle tip was used straight (in the case of water in the syringe, since the water is denser and is pushed out down) or hooked (in the case of oil in the syringe, since the oil is less dense and is pushed out up).

The shape of the drop pending from the tip of the needle is determined by the balance of forces, which includes the surface tension between two liquids. The interfacial tension at the interface of liquids is related to the shape of the droplet through the following equation:

$$\gamma = \Delta \rho \cdot g \cdot R_0 / \beta, \tag{1}$$

where γ is the surface tension, β is the shape factor, $\Delta \rho$ is the difference in density between fluids at the interface, *g* is the gravitational constant, and *R*₀ is radius of drop curvature at the apex.

The shape factor was calculated from the Young-Laplace equation, which is represented by three dimensionless equations of the first order (Fig. 1):

$$dx/ds = \cos\phi, \tag{2}$$

$$dz/ds = \sin\phi, \tag{3}$$

$$d\phi/ds = 2 + \beta z - \sin\phi/x. \tag{4}$$



Fig. 1. Schematic of variables used for the shape factor calculation.

Other mechanical properties of working fluids were measured using a rolling-ball viscometer Lovis 2000 M for dynamic viscosity and digital density meter DMA 5000 M for mass density. The relative permittivity and electrical conductivity were measured using a standard cell with stainless steel plane parallel electrodes; the cell represents two round electrodes with the diameter of 50 mm and the interelectrode distance 2 mm.

Electrical deformation of droplets was captured using a high-speed camera (500 frames per second) and then processed with in-house image processing program. The dependence of droplet deformation on time and the steady-state values were obtained for every experimental test. Numerical simulation of the corresponding processes was performed in COMSOL Multiphysics. Computations employ the arbitrary Lagrangian-Eulerian method for two-phase description [22]. Since the main results of the paper concerns experimental measurements of the interfacial tension dependence on time, a thorough description of the numerical model is omitted here; all necessary details can be found in [23, 24].

3. Results and discussion

The interfacial tension was measured for distilled water with one silicone (PDMS-50), two transformer, and nine vegetable oils. The latter are olive, corn, rape, peanut, linseed, grape-seed, cotton-seed, hemp-seed, and mustard-seed oils. The corresponding data are presented in Figs. 2, 4, and 5. All measurements were made with time resolution 10 points per second during the first 10 seconds and then 1 point per second; the uncertainty is less than 0.2 mN m^{-1} .

The IT has descending time-dependencies for nearly all tested oils; moreover, the falling off continues even after 300 s. An average decrease in the tension is about 20–40% during 5 minutes. The linseed oil shows the strongest lessening in the IT—more than 50%. Quite a stable tension was observed only for grape-seed oil among all vegetable ones.





To check independently whether the measurement data are correct, we employed an idea of estimating the IT basing on the comparison of experimental and numerical results on the electrodeformation dependence on droplet radius [25]. Two sets of measurements were done for olive oil and distilled water couple. In the first one, contact time between two phases before voltage turn-on was about 8 ± 3 s, which corresponds to the interfacial tension value approximately equals 19.1 mN m⁻¹. For the second set of measurements, a water droplet was exposed in oil during 300 s, which corresponds to 15.8 mN m⁻¹. Then the numerical simulation of electrodeformation was performed with the previously measured interfacial tension values.



Fig. 3. Experimental dependencies of droplets' deformation on their radii at the average field strength of 2.95 kV cm⁻¹ for different interfacial tension 15.8 and 19.1 mN m⁻¹ (circles), and the interpolation of numerical simulation results (dashed lines); the two-phase liquid is olive oil and distilled water couple.

All corresponding data (computational and experimental) are presented in Fig. 3. As one can see, the dependencies for two sets of data are clearly different. Moreover, the numerical results agree nearly perfectly with the observed data. We found that the longer the contact time the higher the deformation degree.

All the above confirms that temporal dependencies of the IT measured with the pendant drop method are realistic and need to be used to get correct computational results. These results are in line with investigation of Xu at al. [26], where it is stated that the presence of amphiphilic, interfacially active compounds in vegetable oils cause a time-dependent decrease in interfacial tension unlike the surface tension one, for which such amphiphilic impurities lack significant surface activity.

The situation is different for two tested transformer oils. The first one is new whereas the second one—after operation in a power transformer. The new oil (Fig. 4, curve 1) exhibits nearly constant IT (the decrease is about 3% and finishes after 100 s). In turn, the aged sample behavior (Fig. 4, curve 2) was like that of many vegetable oils—significant decay with time, which continues even after 300 s. The decreasing behavior of the interfacial tension for the aged mineral (not vegetable) oil is an unexpected result. However, it can be explained by complicated electrochemical processes in power transformers, which can introduce many impurities into transformer oil.



Fig. 4. The experimental time-dependencies of the interfacial tension between transformer oils and distilled water, curve 1—new oil, curve 2—oil after operation in a power transformer.

Measuring interfacial tension for silicone oil and distilled water couple is a challenging task. The IT (Fig. 5, curves 1–3) shows descending time-dependencies when it is measured for "oil in water" realization of the

pendant drop method (i.e., when oil drop was injected into the bulk of water using a syringe with hooked steel needle). It is an unexpected result due to PDMS-50 is a clean synthetic liquid that is free of surfactants and fatty acids like those that present in vegetable oils. There is one more strange fact—different decrease behaviors of the IT were observed, which highly inhibited the reproducibility of measurements.



Fig. 5. The experimental time-dependencies of the interfacial tension between silicone oil PDMS-50 and distilled water for two cases when the oil drop was introduced into the bulk of water (curves 1–3) and vice versa (curves 4–5).

One of possible explanations of this fact is as follows. Oil droplet can interact with the metal needle, which can lead to ion injection from the latter and, accordingly, distort the measurements. The ion injection is a well-known phenomenon that emerges at the interface between metal and a low-conducting liquid and provides electrohydrodynamic flows [27, 28]. Usually, high electric field strength is needed for the process; however, the so-called electrochemical ion injection can take place even in the absence of the electric field. In particular, the effect was earlier observed for PDMS-5 [29].

The chosen way to lessen this problem was to replace the hooked needle with the straight one and introduce a water droplet into the bulk of oil. In such a configuration, it was difficult for oil to become sufficiently charged owing to big volume of the latter, unlike the previous case. The new results (Fig. 5, curves 4–5) show better reproducibility and stability over time, though some decay in the interfacial tension is still observable. The decrease was approximately 3% for three minutes of the interaction and can be caused again by the ion injection since such a configuration only reduces but do not cancel completely the phenomenon. Another important change was the establishment of the same interfacial tension starting value, which equals 40.5 mN/m. In the case of olive oil, the same substituting the measurement approach left the results unchanged, which confirms the change in the interfacial tension to be realistic for vegetable oils.

As above, experimental data on a single droplet electrodeformation (like those presented in [15]) were used to check the correctness of the IT measurements. A single water droplet was introduced into oil (PDMS-50) and stressed with high voltage created by pair of plane electrodes. A high-speed video camera was used to record the droplet shape after the voltage turn-on, and the data were numerically processed. The deformation degree was calculated according with the following parameter:

$$D = (a-b) / (a+b),$$
 (5)

where a, b are the axes of the deformed droplet along the external electric field direction and normally to it, respectively.

Fig. 6 shows the experimental dependence of a droplet deformation on time (dashed line). Several local maximums in the deformation are caused by fluctuations of the applied voltage. Two computations were performed (according to the numerical technique described in [23]) with different values of the tension—37.5 and 39.5 mN m⁻¹ (Fig. 6, solid lines). These values were estimated from two sets of measurements (Fig. 5), taking into account the contact time between phases, which consists of the time for the increase in the volume of the droplet, the droplet separation time from the tip of the needle, and the droplet falling time before applying

an external electric field, and it was no more than 20–30 seconds. As one can see, there is quite a good agreement (the same steady-state deformation value) between the experiment and numerical simulation when the higher value of interfacial tension was used.



Fig. 6. Time-dependence of a droplet deformation (the solid curves correspond to the numerical simulations with two values of the interfacial tension, the dashed one—to the experiment); the two-phase liquid is silicon oil (PDMS-50) and distilled water couple, droplet radius R = 1.76 mm, the steady-state voltage $V_0 = 10.0$ kV.

Consider the effect of changing interfacial tension on the electrical coalescence of two equal water droplets. If the latter are introduced one by one and therefore have different contact time with oil, the interfacial tension can be not the same. Computations were performed for two 1 mm water droplets in olive oil with equal (15.8 mN m⁻¹) and different IT values (15.8 and 19.1 mN m⁻¹). The average electric field strength is 2.45 kV cm⁻¹, which is a little below the threshold value for the transition from coalescence to non-coalescence. Fig. 7 presents droplets' shape immediately before their touching. In the first case, the shape is symmetrical (a cone-cone mode), whereas in the second—a cone-dimple mode is emerged. So, changing IT can be one more reason for observing a cone-dimple mode in experiments like in [10, 11].



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At last, Table I summarizes properties of investigated liquids. This set of properties is necessary and sufficient for macroscopic numerical modeling of electrohydrodynamic processes in two-phase liquids, e.g. using the arbitrary Lagrangian-Eulerian method (as in models above) or the phase-field one.

Liquid	Density, kg m ⁻³	Dynamic viscosity, mPa s	Relative permittivity	Electrical conductivity, S m ⁻¹	Interfacial tension against distilled		
					After 10 s	After 60 s	After 300 s
Corn oil	917 ± 1	56 ± 4	3.06 ± 0.02	$(6.96 \pm 0.05) \times 10^{-11}$	23.9 ± 0.7	22.5 ± 0.4	20.1 ± 0.1
Rape oil	917 ± 1	57 ± 4	3.06 ± 0.02	$(2.17\pm0.02) \times 10^{-11}$	26.7 ± 0.2	25.4 ± 0.2	23.6 ± 0.5
Peanut oil	912 ± 1	66 ± 4	3.00 ± 0.02	$(4.99 \pm 0.02) \times 10^{-10}$	23.5 ± 1.0	19.8 ± 0.5	15.9 ± 0.2
Linseed oil	922 ± 1	47 ± 4	3.08 ± 0.02	$(1.72\pm0.02) \times 10^{-9}$	10.0 ± 0.2	8.0 ± 0.1	5.60 ± 0.05
Grape-seed oil	920 ± 1	54 ± 4	3.09 ± 0.02	$(0.81\pm0.01) \times 10^{-11}$	25.5 ± 0.1	25.2 ± 0.1	24.8 ± 0.1
Cotton-seed oil	918 ± 1	55 ± 4	3.07 ± 0.02	$(2.83\pm0.03) imes 10^{-10}$	26 ± 1.0	24.5 ± 0.6	22.2 ± 0.4
Hemp seed oil	919 ± 1	53 ± 4	3.06 ± 0.02	$(6.55\pm0.05) \times 10^{-11}$	10.9 ± 0.3	8.2 ± 0.2	6.5 ± 0.1
Mustard-seed oil	918 ± 1	57 ± 4	3.04 ± 0.02	$(1.77\pm0.02) \times 10^{-10}$	21 ± 1.0	16.4 ± 0.3	13.2 ± 0.1
Olive oil	911 ± 1	70 ± 5	2.85 ± 0.02	$(1.0\pm0.5) \times 10^{-11}$	18.7 ± 0.3	17.0 ± 0.2	15.8 ± 0.1
Sunflower oil	918 ± 1	56 ± 4	-	$(2.50\pm0.05) \times 10^{-11}$	18.5 ± 0.6	15.4 ± 0.4	-
Transformer oil #1 (new)	855 ± 1	16.0 ± 1.5	2.15 ± 0.02	_	42.6 ± 0.3	41.8 ± 0.4	41.0 ± 0.5
Transformer oil #2 (after operation)	861 ± 1	15.5 ± 1.5	1.90 ± 0.02	_	29.5 ± 0.7	27.6 ± 0.4	24.9 ± 0.4
Silicone oil (PDMS-50)	958 ± 1	52 ± 2	2.59 ± 0.02	$(2\pm 1) \times 10^{-12}$	40.2 ± 0.3	39.7 ± 0.3	_

Table 1. Properties of all investigated liquids at 22 ± 1 °C.

4. Conclusion

The case when the interfacial tension against water decreases with time is specific for a lot of liquids, in particular, for many vegetable oils and even for used transformer oils. Typical lessening is about 20–40% during 300 s and can be as high as 50%. In turn, there are liquids, for which it seems that IT changes though it is not so (like in the case of silicone oil PDMS-50). The feasible reason for such artificial change is electrochemical ion injection from a metallic needle into dielectric liquid, which provides emergence of the Coulomb force even without an external electric field. At last, just some liquids show quite a stable IT against water, e.g., new transformer oil and grape-seed oil.

The observed time-dependencies of the interfacial tension for various liquids show realistic reason for some disagreements between the experimental data and computations when the latter unreasonably disregard the phenomenon. In particular, the difference in interfacial tension values for two equal water droplets suspended in oil can be the primary cause for the emergence of the so-called cone-dimple mode of electrocoalescence. However, some modifications are required to be developed and introduced to numerical models when one needs to describe transient multiphase electrohydrodynamic process in the case of changing IT.

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References

- Atten P., Electrohydrodynamics of dispersed drops of conducting liquid: From drops deformation and interaction to emulsion evolution, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 7 (1), pp. 2–12, 2013.
- [2] Mhatre S., Vivacqua V., Ghadiri M., Abdullah A.M., Al-Marri M.J., Hassanpour A., Hewakandamby B., Azzopardi B., and Kermani B., Electrostatic phase separation: A review, *Chem. Eng. Res. Des.*, Vol. 96, pp. 177–195, 2015.
- [3] Raisin J., Reboud J.-L., and Atten P., Electrically induced deformations of water-air and water-oil interfaces in relation with electrocoalescence, *J. Electrostat.*, Vol. 69, pp. 275–283, 2011.
- [4] López-Herrera J.M., Popinet S., and Herrada M.A., A charge-conservative approach for simulating electrohydrodynamic two-phase flows using volume-of-fluid, J. Comput. Phys., Vol. 230, pp. 1939–1955, 2011.
- [5] Lin Y., Skjetne P., and Carlson A., A phase field model for multiphase electro-hydrodynamic flow, *Int. J. Multiph. Flow.* Vol. 45, pp. 1–11, 2012.
- [6] Huang X., He L., Luo X., Yin H., and Yang D., Deformation and coalescence of water droplets in viscous fluid under a direct current electric field, *Int. J. Multiph. Flow.* Vol. 118, pp. 1–9, 2019.
- [7] Casas P.S., Garzon M., Gray L.J., and Sethian J.A., Numerical study on electrohydrodynamic multiple droplet interactions, *Phys. Rev. E.*, Vol. 100, 063111, 2019.
- [8] Y. Zhou, H. Dong, Y.H. Liu, Z.J. Yang, T. Liu, M. Li, molecular dynamics simulations of the electrocoalescence behaviors of two unequally sized conducting droplets, *Langmuir.*, Vol. 35, pp. 6578–6584, 2019.
- [9] Roy S., and Thaokar R.M., Numerical study of coalescence and non-coalescence of two conducting drops in a nonconducting medium under electric field, J. Electrostat., Vol. 108, 103515, 2020.
- [10] Anand V., Roy S., Naik V.M., Juvekar V.A., and Thaokar R.M., Electrocoalescence of a pair of conducting drops in an insulating oil, J. Fluid Mech., Vol. 859, pp. 839–850, 2019.
- [11] Anand V., VJuvekar.A., and Thaokar R.M., Modes of coalescence of aqueous anchored drops in insulating oils under an electric field, *Colloids Surfaces A Physicochem. Eng. Asp.* Vol. 568, pp. 294–300, 2019.
- [12] Dobrovolskii I.A., Vasilkov S.A., and Chirkov V.A., Electrohydrodynamics of conducting droplets suspended in a low-conducting liquid: The effect of the difference in mobilities of positive and negative ions, J. Electrostat., Vol. 124,103828, 2023.
- [13] Hellesø S.M., Atten P., Berg G., and Lundgaard L.E., Experimental study of electrocoalescence of water drops in crude oil using near-infrared camera, *Exp. Fluids.*, Vol. 56, 122, 2015.
- [14] Xia Y., and Reboud J.L., Hydrodynamic and electrostatic interactions of water droplet pairs in oil and electrocoalescence, *Chem. Eng. Res. Des.*, Vol. 144, pp. 472–482, 2019.
- [15] Chirkov V.A., Gazaryan A.V., Kobranov K.I., Utiugov G.O., and Dobrovolskii I.A., A modification of the phasefield method to simulate electrohydrodynamic processes in two-phase immiscible liquids and its experimental verification, *J. Electrostat.*, Vol. 107, 103483, 2020.
- [16] Sjöblom J., Mhatre S., Simon S., Skartlien R., and Sørland G., Emulsions in external electric fields, Adv. Colloid Interface Sci., Vol. 294, 102455, 2021.
- [17] Chen X., Liu P., Qi C., Wang T., Liu Z., and Kong T., Non-coalescence of oppositely charged droplets in viscous oils, *Appl. Phys. Lett.*, Vol. 115, 023701, 2019.
- [18] Sun Y., Yang D., He L., Luo X., and Lü Y., Influence of alkali concentration, electric waveform, and frequency on the critical electric field strength of droplet–interface partial coalescence, *Chem. Eng. Sci.* Vol. 208, 115136, 2019.
- [19] Deka D.K., and Pati S., Electrocoalescence dynamics of two unequal-sized droplets, *Colloids Surfaces A Physicochem. Eng. Asp.*, Vol. 664, 131152, 2023.
- [20] Song B., and Springer J., Determination of interfacial tension from the profile of a pendant drop using computeraided image processing, J. Colloid Interface Sci., Vol.184, pp. 64–76, 10996.
- [21] Berry J.D., Neeson M.J., Dagastine R.R., Chan D.Y.C., and Tabor R.F., Measurement of surface and interfacial tension using pendant drop tensiometry, J. Colloid Interface Sci., Vol. 454, pp. 226–237, 2015.
- [22] Supeene G., Koch C.R., and Bhattacharjee S., Deformation of a droplet in an electric field: Nonlinear transient response in perfect and leaky dielectric media, J. Colloid Interface Sci., Vol. 318. pp. 463–476, 2008.
- [23] Utiugov G., Chirkov V., Reznikova M., Application of the arbitrary Lagrangian-Eulerian method to simulate electrical coalescence and its experimental verification, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 15 (2), e02009, 2021.
- [24] Utiugov G.O., Chirkov V.A., and Dobrovolskii I.A., The experimental verification of electrodeformation and electrocoalescence numerical simulation based on the arbitrary Lagrangian–Eulerian method, *in: 2020 IEEE 3rd Int. Conf. Dielectr.*, IEEE, pp. 529–532, 2020.
- [25] Chirkov V.A., Reznikova M.P., Lashko A. V., and Dobrovolskii I.A., a method to determine the interfacial tension for the conductive medium/liquid dielectric couple, in: 2018 IEEE 2nd Int. Conf. Dielectr., IEEE, pp. 1–4, 2018.
- [26] Xu T., Rodriguez-Martinez V., Sahasrabudhe S.N., Farkas B.E., and Dungan S.R., effects of temperature, time and composition on food oil surface tension, *Food Biophys.*, Vol. 12, pp. 88–96, 2017.
- [27] Stuetzer O.M., Ion drag pressure generation, J. Appl. Phys., Vol. 30, pp. 984–994, 1959.

- [28] Shrimpton J., Charge Injection Systems, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009.
- [29] Gazaryan A., Sitnikov A., Chirkov V., Stishkov Y., a method for estimation of functional dependence of injection charge formation on electric field strength, *IEEE Trans. Ind. Appl.*, Vol. 53, pp. 3977–3981, 2017.