

Dielectric Properties of Oleic Acid in Liquid Phase

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Measurement of the static dielectric permittivity of liquid oleic acid at different temperatures from 289 K, above of the melting point, to 298 K are reported. These data, together with the dependence of the refractive index and density on temperature, are used in order to evaluate dielectric properties of oleic acid. The dipole moment and Kirkwood correlation factor are evaluated from experimental data using the Kirkwood-Fröhlich's statistical mechanical theory of dielectrics. The experimental results for the dipole moment are compared with conformational structure study of the oleic acid molecular followed by electronic structure calculations and the results are in good agreement. The correlation between the individual oleic acid dipole moment orientations are discussed taking into account the Kirkwood correlation factor.

Keywords: Polar Liquids, Dipole Moment, Fatty Acids, Kirkwood's Theory.

1. INTRODUCTION

From the technological point of view, unsaturated fatty acids, as well as their derivatives, have attracted great attention by their unique activities or functions as medical and industrial materials. The knowledge of dipole moment of molecules to nanotechnology is related within the functionality of these compounds producing designed products for specific applications.¹

The design of materials in nanoscale can be re-arranged through interactions such as: electrostatic dipole, hydrogen bonds, van der Waals interactions, hydrophobic and hydrophilic interactions. An example of this arrange is the induced self-aggregation where the arrangement of the molecules is driven under control through an external magnetic field or electrical field.²

Unsaturated fatty acids are widely distributed in biological tissues as a main constituent of biomembranes. In most cases, they are linked at 2 position of phospholipids and generate a large variety of the characteristics of membranes; i.e., they promote fluidity and control the phase transition behavior depending on the environmental condition.³ In technology for new materials, hydrophobic nanoparticles of copper capped with oleic acid were prepared to prevent oxidation.⁴ In spite of such importance, only a little is known about molecular-order structures and physicochemical properties even for the case of oleic acid, the more abundant monounsaturated fatty acid in nature

as component of vegetable oils (olive, sunflower, peanut, etc.). A high content of oleic acid in the composition of buriti oil, a vegetable oil extracted from fruits of the buriti palm (*Mauritia flexuosa* L.), a palm tree with large occurrence in the Amazon region, have been reported and some measurements of their electrical and optical properties were reported.⁵⁻⁷ Among the properties of the fatty acids, special attention is given to the dielectric properties, such as the dielectric permittivity and dipole moment. Mognaschi et al.⁸⁻¹¹ had reported dipole moment and Kirkwood correlation factor g for some saturated fatty acids in the liquid phase, and they pointed out that the study of the dielectric properties of fatty acids is a good source of information about their associative behavior.

In this work measurement of the static dielectric permittivity as a function of temperature is used in the framework of the Kirkwood-Fröhlich statistical mechanical theory of dielectrics¹²⁻¹³ to study polar oleic acid in the liquid phase. From our measurements and data on oleic acid, the dipole moment and the Kirkwood correlation factor, g , has been evaluated and is reported. This factor is important because gives information about the correlations between the orientations of dipole moments due to short-range ordering interactions. Since the dipole moment of the oleic acid in the gaseous phase has not been reported previously to our knowledge, we performed semi empirical and *ab initio* calculations based on quantum mechanics with optimized geometry of the molecule aiming to find a theoretical value for the dipole moment of the oleic acid, which is compared with that found experimentally.

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2. MATERIALS AND METHODS

Oleic acid (*cis*-9-octadecenoic acid) is a monounsaturated monocarboxylic fatty acid with molecular weight $M = 282.47 \text{ g}\cdot\text{mol}^{-1}$ and melting point of $13.4 \text{ }^\circ\text{C}$ (286.4 K). Oleic acid with purity above 99% was obtained from Sigma-Aldrich and used without further treatments.

The temperature dependence on the density of liquid oleic acid was obtained from literature data.¹⁴ The density was found to decrease linearly as the temperature increase:

$$d = d_0 + aT \quad (1)$$

with $d_0 = 0.902 \text{ g}\cdot\text{cm}^{-3}$ and $a = -6.20 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$.

The refractive index depending on temperature was measured using an Abbè's refractometer provided with the temperature controlled by circulating thermostated through it. The refractive index depends linearly of the temperature:

$$n = n_0 + (dn/dT)T \quad (2)$$

where $n_0 = 1.467$ and $dn/dT = -3.8 \times 10^{-4} \text{ K}^{-1}$, in good agreement with values reported in the literature.¹⁴

The dielectric permittivity dependent on temperature was measured with a General Radio capacitance bridge in the liquid phase from 289 K, above the melting point, to 298 K. A three-electrode cell for measurements on liquids was used with electrical field of $100 \text{ V}\cdot\text{m}^{-1}$ and the results were found to be independent of field intensity and frequency. All the measurements were obtained in a frequency of 20 kHz. At this frequency, the permittivity values can be considered as static, because the relaxation times of most of the fatty acids are of the order of 10^{-10} s .¹⁵ All the DC measurements were repeated several times, exhibiting good repeatability and, consequently, the results can be considered a confirmation of the results reported here. More details about experimental setup can be found elsewhere.⁵

Since experimental data are not available for both the dipole moment and geometries of the molecule of oleic acid, were performed *DFT* calculations based on quantum mechanics with systematic geometry optimizations.

In this work we used the following methodology (the molecular structure is shown in Fig. 1): the electronic structure of the systems is examined using Hartree-Fock based approaches within the framework of the Gaussian¹⁶

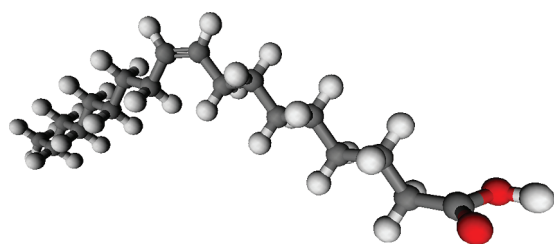


Fig. 1. Oleic acid (1-unsaturated bond) in the natural conformation.

packages. The standard basis sets, 6-31G, 6-31G*, 6-311G, 6-311G*, were used for all calculations, yielding similar qualitative results. The geometries of the analyzed structures were fully optimized using Hartree-Fock, a procedure used successfully in previous studies.¹⁷⁻²¹

To obtain a more realistic description of the electronic transitions, it is necessary to use methods specially developed to handle these aspects, and we have adopted the Intermediate Neglect of Differential Overlap/Spectroscopic - Configuration Interaction (INDO/S-CI) method²² in this investigation, by using on the average 220 configurations (singlet/triplet) with the geometries obtained from *ab initio* RHF (Restricted Hartree-Fock) calculations and 3-21G* basis set. Also state-of-art Density Functional Theory was employed to simulate the dipole moment using B3LYP functional and several basis set as 6-31G, 6-31G, 6-31G*, 6-311G, and 6-311G*.

3. RESULTS AND DISCUSSION

In Table I are summarized the experimental results obtained for the refractive index, mass density, and dielectric permittivity in temperatures from 289 K to 298 K. The table

Table I. Refractive index, mass density, and dielectric properties of the oleic acid depending on the temperature.

T (K)	n	d ($\text{g}\cdot\text{cm}^{-3}$)	ϵ	P_M ($\text{cm}^3\cdot\text{mol}^{-1}$)
289	1.4615	0.892	2.50	51.85
290	1.4608	0.891	2.40	50.68
292	1.4600	0.890	2.33	50.03
294	1.4592	0.888	2.24	48.87
296	1.4585	0.887	2.11	47.38
298	1.4577	0.886	2.03	46.38

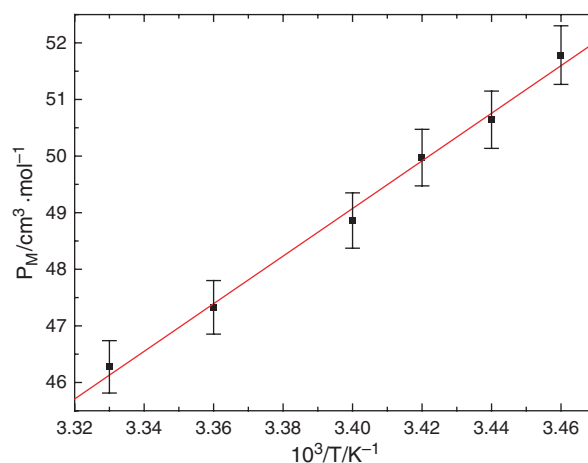


Fig. 2. P_M (Molar polarization) as a function of $1/T$ (temperature) where is the experimental values obtained up to 10 independent measurements and—is the fit by Eq. (3) showing a good concordance experimental/theoretical results.

Table II. Dipole moment of fatty acids using different methods based on DFT approach and ZINDO/S-CI.

Fatty acid	Dipole moment (D)						
	Molecular modeling				Experiments		
	ZINDO/S-CI	B3LYP 6-31G	B3LYP 6-31G*	B3LYP 6-311G	B3LYP 6-311G*	Debye	Kirkwood
Oleic acid	2.64	2.53	2.42	2.59	2.48	2.47 ± 0.05	2.63 ± 0.05

$$1D = 3.328 \times 10^{-30} \text{ C}\cdot\text{m}.$$

shows too the molar polarization (P_M) depending on temperature calculated from the Kirkwood-Fröhlich's equation

$$P_M = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \left(\frac{M}{d} \right) = \frac{N_A}{3} \left[\alpha + \frac{(\mu^*)^2}{3\varepsilon_0 k_B T} \right] \quad (3)$$

where ε is the dielectric constant, M is the molecular mass, N_A is the Avogadro's number, α is the molecular polarizability (polarizability volume) of the molecule, μ^* is the apparent dipole moment, ε_0 is the electrical permittivity in vacuum, T is the absolute temperature, and k_B is the Boltzmann's constant. The Eq. (3) shows a linear function behavior as $y = a + bx$ for molar polarization and dependence with reciprocal of the absolute temperature (the angular coefficient is $b = N_A (\mu^*)^2 / (9\varepsilon_0 k_B T)$ and $x = T^{-1}$). The plot of the molar polarization (3) as function of the inverse absolute temperature, $1/T$ for oleic acid is shown in Figure 2. By fitting the experimental data using linear regression the value of the angular coefficient b was found equal to $42.06 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ and the apparent dipole moment was estimated as $\mu^* = 2.63 \pm 0.05D$. It was utilized the molar polarization from the Debye's theory to find the dipole moment of the oleic acid and the value obtained was $\mu = 2.47 \pm 0.05D$, but we stress that this theory is valid for gases, not for liquids.

By the Kirkwood-Fröhlich's theory the apparent dipole moment is related to the correlation factor by the equation $\mu^* = g^{1/2} \mu$, where μ is the dipole moment in the ideal gas phase. Since the dipole moment of oleic acid in the gaseous phase is not known, were adopted the values calculated using quantum mechanics. These theoretical values are shown in Table II, where one report the experimental values too. As it is well known that *ab initio* calculations are more adequate to represent a molecular structure is possible to find out very good experimental/theoretical rate. Indeed, these results presented in Table II shows both possibilities, *trans* and *cis* conformer equally probably for the liquid structure.

Table II shown the values of the Kirkwood correlation factor obtained using the experimental value for the apparent dipole moment of the oleic acid, $\mu^* = 2.63 \pm 0.05 D$, and the different values for μ calculated by the modeling methods listed in the Table II. At first sight, the values of g are very nearby for both, *trans* and *cis* conformer of the molecule of oleic acid. Second, when related to the results calculated by empirical methods the correlation among dipole moments of each molecule

occurs mainly with antiparallel orientation. When calculated using values obtained taking account configuration interactions (INDO/S-CI) and *ab initio* methodologies, we observe that $g \approx 1.0$, meaning that there is a weak correlation between dipole moments.

4. CONCLUSION

We have demonstrated an experimental/theoretical approach for realizing dielectric permittivity of liquid oleic acid as molecular liquids including different temperatures from 289 K to 298 K. The dipole moments of the oleic acid presented are reported at first time at our knowledge. Kirkwood correlation factor g estimated using the ratio between experimental measurement and theoretical calculations by *ab initio* modeling methods indicates that orientational correlation among dipole moments of each molecule is antiparallel. This feature could direct be followed by the quantum nature of organic structure as a single compound as predicted by the *ab initio* calculations.

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