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Nematic Emulsion: Optical Characterization

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Abstract The aim of this experience was to utilize the Inquiry Based Science Education, (IBSE) in order to offer the students a better understanding of the light-matter interaction. We have followed the phase separation process in mixtures of an organic monomer and nematic liquid crystals. The systems form liquid crystal droplets in a liquid crystal-saturated monomer matrix and in some cases the emulsions are stable over several months. Homogeneous droplet size distributions are obtained for faster cooling rates. We report the droplet size distribution and the behavior of optical rotation angle of solutions as liquid crystal percentage function. This work is an essential part of an apprenticeship developed during the "Professione Formatore in Didattica delle Scienze" Master, which takes place at the University of Calabria, with the authors taking part in it as trainees and that is gonna end in the month of October 2015.

Keywords: *IBSE (Inquiry-Based Science Education), Malus Law's, birefringence, optical rotation angle*

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1. Introduction

It was considered, on the basis of common experiences related to the cooperation and participation in the Master listed above, that the use of the IBSE methodology [1] and its five phases [2,3] , turns out to be the one most suitable to connote the best teaching approach:

1. Engagement

In this observation phase, students may be free to express their own opinions and observations, it will be the teacher's task to collect the most significant ones for the experience. The main aim is to attract the attention, stimulate curiosity, encourage the students' feeling of "wanting to know more.". This phase is by far the most important, because from its good organization, derives the success of the whole learning process.

2. Explore

After collecting comments and requests on what you want to investigate, the students are directed to the next stage, asking them to change the experience, in order to provide some answers. The teacher must be ready to receive suggestions from students who intend to experiment the phenomenon in a different way, flanking these ideas to those of the module. The principal purpose of this step is to record data and to analyze the results.

3. Explain

At this point it is necessary to introduce models, laws and theories to students. A correct vocabulary is required, and by providing it to them, they can explain, rigorous scientific way, their explorations' results, stimulating the autonomous research on the studied context.

4. Elaborate

The development of what has been studied and discovered in the earlier stages by applying it to other situations which may give rise to new questions and hypotheses to explore, enables students to achieve the transfer of learning.

5. Evaluate

The last phase involves the construction by the students of the final works that can be valued in different ways. The final product will be discussed in various ways: in front of the teachers or in a special occasion.

Before entering the practice of specific educational applications, it is important to remember that an introduction to basic concepts, which refers to the phenomenon of the light polarization, turns out to be necessary: in this area, some notes on the Law of Malus and the use of quality filters polarizers may allow a better approach. For what concerns the path used, some nodal parts may generally be represented as follows:

The first part of the didactic work is based on light polarization phenomena exploration.

This is followed by a "personalization" of the experience and, only later, to an introduction to the knowledge of the concepts related to the Law of Malus [4]: the intensity of a light radiation that passes through a polarizing filter, whose polarization axis forms an angle θ with the vibration plane of light radiation is given by:

$$I = I_0 \cos^2 \theta \tag{1}$$

The most innovative points of the didactic course are listed below:

- The typical "historic" approach of the MQ is exceeded;

- The approach to the concepts mentioned above, is carried out not in a systematic way (typical of Classical Mechanics), but in a more substantial one: it is based on the dual concepts of wave-particle;
- The fundamental Laboratorial approach is relative to what has been mentioned before.

Emulsions are dispersions of liquid droplets in a continuous liquid solvent, whose size ranges from hundreds of nanometers to some tenths of micrometers. Many kinds of emulsions have been investigated, both experimentally and theoretically [5,6]. Typical examples are dispersions of oil in the water or water in oil. Such systems are generally metastable, and considerable efforts have been devoted to get stable emulsions by choosing or adding specific molecules [5,6]. Vijay et.al. formed stable emulsions of 40wt% heptadecane in water using combination of Triton-X100 hollow polymeric particles. Adsorption and emulsification properties of amphiphilic poly(styrene-co-octadecyl maleamic acid salt) with comb-like architecture [7]. Nematic emulsions are droplets of nematic material floating in an isotropic liquid [8].

The use of liquid crystal in emulsions changes the nature of interactions between dispersed particles and host matrix, which is due to anisotropic properties of liquid crystal as it is confirmed by the drastic reduction of stability when liquid crystal loses its anisotropy (for example by heating).

The light consists of more electromagnetic waves that vibrate on different planes. Each electromagnetic radiation, that is a wave of cross-cutting nature, is associated with an electric field **E** and a magnetic field **B**. All electromagnetic waves vibrate on an infinite number of planes perpendicular to the direction of propagation. If this light passes through a polarizing optical filter, the light emerging, will be a ray whose electric vector vibrates on a single plane. If the plane is vertical, the wave is vertically polarized; if the plane is horizontal, the wave is horizontally polarized; these two types of polarization are called linear. In other words, the radiation outbound, has the component of the electric field that oscillates in a direction perpendicular to the filter and that's why we can speak of polarized light, [11].

When the electric field E is perpendicular to the magnetic field B we cannot see anything; when E is parallel to B, the light passes, if E is inclined by an angle ***α***, we can see an intermediate light.

When a beam of polarized light goes through a optically active substance, the polarization plane of the light rotates by a certain angle, whose value depends not only on the nature of the substance, the thickness of the layer, the temperature and the wavelength light; in the case of a solution, the rotatory power is also a function of the concentration of the solution and the nature of the solvent, [12]. It is possible, by measuring the angle of rotation, to determine the concentration of certain substances present in solution.

2. Experimental Part

2.1. Emulsions

Nematic emulsions are generally found by stirring and/or quenching a homogeneous solution of nematic liquid crystal and an isotropic solvent.

TL202 (Merck) was used as a nematic liquid crystal. Bisphenol A glycerolate diacrylate (Aldrich) was the monomer [9,10], inhibited with 4.500 ppm monomethyl ether hydroquinone whose chemical formula is reported in Figure 1.

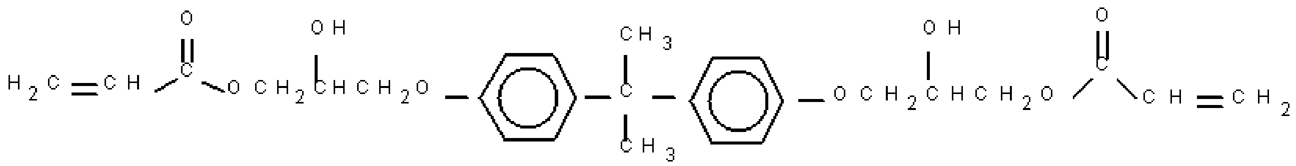

Figure 1. Chemical formula of Bisphenol A glycerolate diacrylate

Table 1 shows some physical parameters of these components.

Table 1. Some physical parameters of monomer and liquid crystal

Component	Refractive indices	η/cSt @20 °C	T_{N-I}/°C
Monomer	n=1.5570	≈$15x10^5$	/
TL202	n_o=1.5230 n_e=1.7081	37	83.4

Mixtures were prepared by weighting the appropriate amount of components in vials and subsequently by stirring them at 100°C for ten minutes. The droplets average diameter has been measured every day for several months by a light scattering the apparatus, paying attention to the same marked area. Such values were confirmed from measurements on magnified photographs. The samples were not stored in a temperature controlled place just to test their stability even in the presence of slight thermal fluctuations. The critical solution temperature of emulsions, i.e. the temperature at which the droplets completely dissolve in the matrix, was determined with a polarizing microscope (Polarizing Microscope Leica DM750 P) by increasing the sample temperature with a programmable hot stage (Linkam PR 600) at a rate of 0.1°C/min. A cold nitrogen cooling system was used in order to lower the temperature.

In order to obtain uniform and micron-sized droplets, the emulsions were heated at temperatures well above their critical solution temperature at a rate of 0.1°C/min and then, they were cooled at different rates. The cooling rate was measured with an automatic chronometer.

2.2. Optical activity

The optical rotation measurement of optically active substances (SOA) is carried out via the polarimeter. In our case we have used an optical polarimeter Optech (see Figure 2) with the following characteristics:

- Nicol prisms;
- adjustable light source LED monochrome (589.3nm);
- reading scale: 0-180 ° with 0.05 ° accuracy;

Figure 2. Optical Polarimeter

To carry out the measurements, we broke the emulsions by adding acetone, used as a solvent, and we measured the angle of rotation of the solutions obtained and transferred in a polarimetric tube of 100 mm.

3. Results and Discussion

Figure 3 shows some polarising optical microscope photographs of 30 wt % TL202 nematic emulsions in Bisphenol A glycerolate diacrylate.

Radii can be varied from less than 1 to 10 μm by choosing the appropriate cooling rate. If the cooling rate is higher than 50°C/min, homogeneously micron-sized droplets can be obtained all over the cell. A typical population of emulsion droplet sizes, as obtained from magnified photographs, is reported in Figure 4.

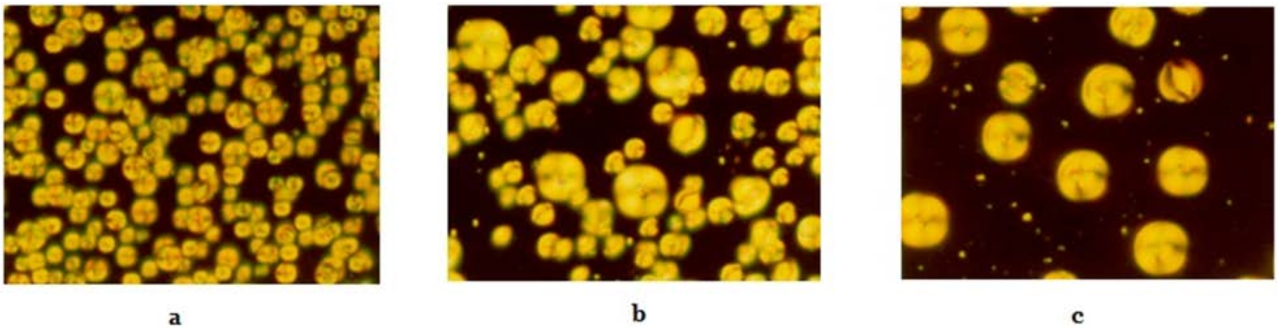

Figure 3. Polarising optical microscope photographs of nematic emulsions of a) 30 wt % TL202, b) 20 wt % TL202, c) 10 wt % TL202 in Bisphenol A glycerolate diacrylate

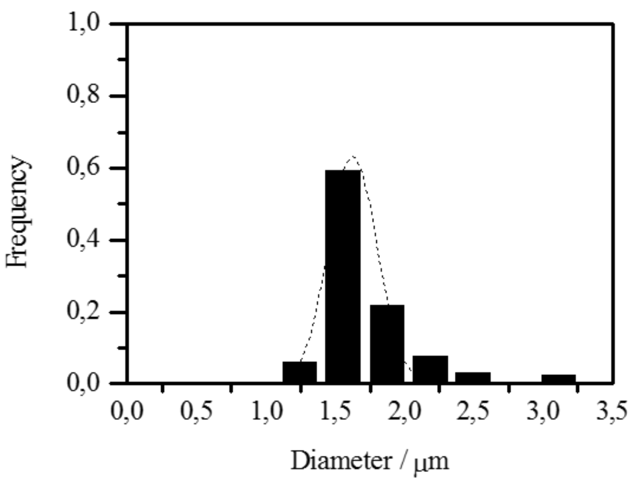

Figure 4. Histogram of distribution of droplet diameter for a typical emulsion (30 wt % TL202)

The uniformity of the droplets dimension can be explained by the fact that a faster cooling rate in the separation phase procedure, allows to get smaller droplets in a highly viscous matrix, which prevents droplets from moving, merging and growing in different ways. At low concentrations (less than 5 wt %) TL202 dissolves in the monomer matrix and no emulsion is formed. At higher TL202 concentrations, phase separation is obtained with an increasing droplet density for higher liquid crystal contents. In order to investigate the stability of such emulsions, the samples were scanned at a constant heating rate and the critical solution temperature, T_{cs}, was determined as a function of the liquid crystal content. At the highest concentrations, the temperature at which disappearance of TL202 emulsions is observed is equal within experimental errors to the clearing point of liquid crystal and it is independent from liquid crystal content. The stability of TL202 droplets is a consequence of the liquid crystalline state. When it disappears droplets become unstable and form a single phase system with the monomer. With intermediate liquid crystal content ($5 <$ wt % TL202 < 15) droplets disappear at a temperature lower than TL202 clearing temperature. We attribute the emulsion disappearance to the increase of liquid crystal solubility in monomer matrix with temperature, i.e. the already low liquid crystal droplet density becomes zero. In order to quantify the percentage of monomer inside liquid crystal droplets, we have studied the variation of liquid crystal clearing temperatures for increasing concentrations of monomer. Droplets of TL202 has higher purity, it can be due to the fact that the TL202 liquid crystal has fluorine and chlorine components, which allow a better phase separation. A lower matrix contamination by liquid crystal implies in our opinion, a higher value of matrix viscosity and consequently, a longer droplet stability.

Table 2. Data relative to rotation angle vs % of liquid crystals

% Liquid Crystal	Rotation angle
5	101,5
10	105,05
15	110,5
30	116,7
40	122,55
60	129,5

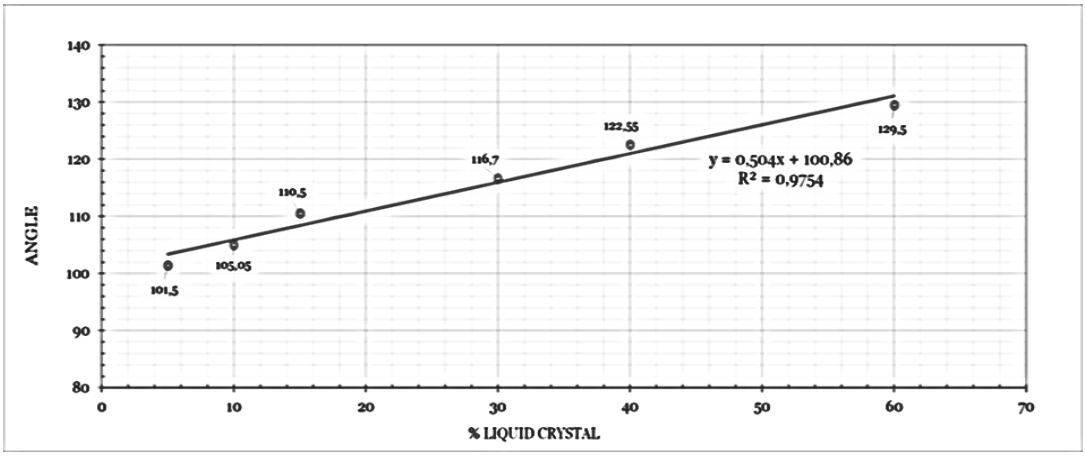

Figure 5. The behavior of the angle of rotation as a function of the percentage of liquid crystal

Table 2 shows the percentages of the liquid crystal contained in the different solutions. We've determined the trend of the rotation angle as a function of the percentage of the liquid crystal present in each emulsion. As anyone can see from Figure 5, the trend that is obtained is linear. The trend line has a good value of R^2.

4. Conclusions

The use of polarizers, and implicitly, law of Malus applications, provides a clearer vision of the physical properties and, specifically, of quantum of matter ones. The wave-particle duality is therefore evident, not as an alternative aspect, but as an intrinsic property of matter. We have investigated the stability and the electro-optical properties of a composite formed by a monomer and nematic liquid crystals. Such systems show uniform micron-size droplet distributions if they are prepared by fast quenching. They remain also stable for several months if the liquid crystal solubility in the monomer matrix is low.

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