Classification of Oil and Oil Mixes Emulsions via SPES Technology

INTRODUCTION

The wide applications of oil-in-water emulsions range from pharmaceuticals to beverages, from paints to specialty chemicals, and more. In its simplest form, an emulsion is a binary system of immiscible liquids forming droplets. One of the main features to be monitored is stability, which can be affected by external factors as storage methods, time, temperature, osmolarity, pH, surfactant, shear stress. Weak stability primarily affects the droplets size (eg. due to coalescence), with important consequences on eg. the organoleptic properties of a soft drink or the efficacy and safety of a pharmaceutical product. Particle analysis plays thus a fundamental role in the design, formulation, and QC of oil-in-water emulsions, enabling the observation of the growth process and the stability of the particles. In this application note the classification and characterization of oil-in-water emulsions via patented SPES technology and EOS Classizer™ ONE is presented.

PARTICLE ANALYSIS METHOD

Among the several methods currently adopted, optical ones have unique advantages, and therefore, have brought light scattering into the forefront of analytical methods in many scientific and industrial applications. Unfortunately, the number of parameters typically affecting the scattering properties of a given particle is such that the basic measure of the scattering power (or even the power removal from a light beam -extinction- from one particle) is far from being enough to recover something more than a rough estimate of its size. Things change appreciably when considering a collection of many scatterers, with the immediate drawback of introducing the need for mathematical inversion and ill-posed problems to interpret experimental real data.

EOS Classizer™ ONE particle analyser is based on patented Single Particle Extinction and Scattering (SPES) method. It introduces a step forward in the way light scattering is exploited for single particle characterization.

EOS Classizer™ ONE – front view

EOS Classizer™ ONE provides data that go beyond the traditionally optical approaches. EOS Classizer™ ONE discriminates, counts, and analyses single particles through their optical properties. It retrieves to the user several pieces of information such as: particle size distribution of the single observed populations, absolute and relative numerical concentrations, particle stability, information on optical particle structure and oversize. Classizer™ ONE works offline and online/real-time, enabling to verify consistency of intermediate and final formulations with target QbD, SbD, and Quality Control target expectations.

For a general introduction to SPES data please refer to the Application Note AN001/2021, available online along with other application notes and example of applications at EOS website: www.eosinstruments.com/publications/

APPLICATION EXAMPLES

The items discussed in this document are reported below, after a list the oil-in-water emulsions adopted for the discussion and the corresponding refractive index:

1. Silicone Oil n = 1.40
2. Castor Oil n = 1.47
3. Olive Oil n = 1.47
4. Mineral Oil n = 1.48
5. Liquid Paraffin n = 1.48
6. Calibrated Oils n = 1.50 - 1.53 - 1.55 - 1.59
7. Mixes of Oil emulsions
8. Non stability – droplet floating
9. Validation of sample stability due shear stress

1) Silicone Oil [n = 1.40]

The most common silicone oils are liquid polymerized siloxane with organic side chains. Silicone oils offer great thermal stability, and flowable forms at extreme temperatures. Silicone oils are largely used in many applications as lubricants, thermic fluid oils, hydraulic fluids, electrical insulators, and medical product. In Figure 1 a data set obtained with a typical oil-in-water emulsion of a small aliquot of silicone oil is presented. EOS Classizer™ software automatically estimates a RI of 1.40 in agreement with the expected value. This experimental parameter allows a better evaluation of the numerical particle size distribution of the emulsion as represented in Figure 2 and of the oversize analysis presented in Figure 3.

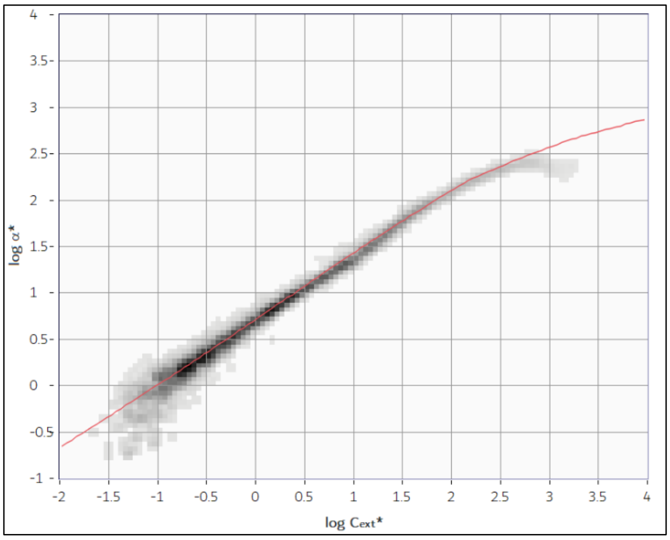

Figure 1 EOS CLOUDS of a silicone oil-in-water emulsion.

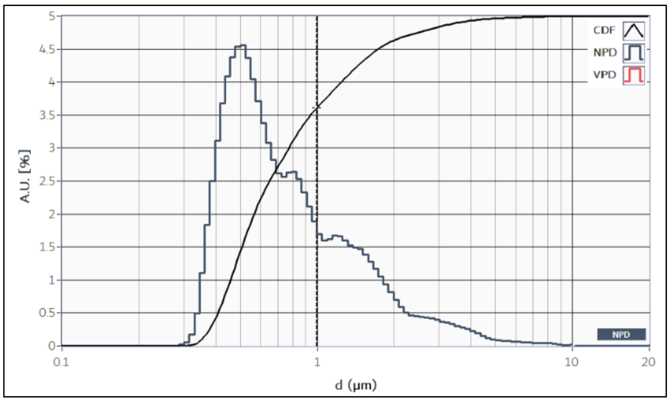

Figure 2 PSD of the emulsion of silicone oil in Figure 1.

The EOS Classizer™ software estimates an AVG diameter of 0.97 μm, a D50 of 0.66 μm, and a D[4,3] of 4.8 μm.

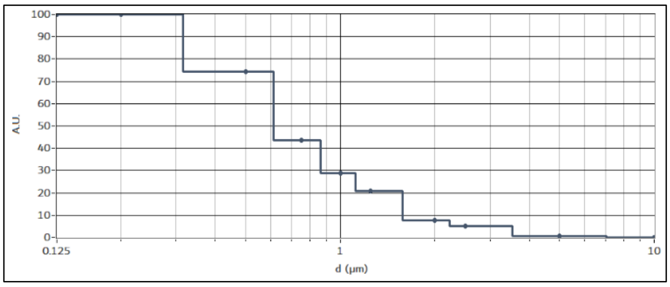

Figure 3 Oversize study of the oil-in-water emulsion in Figure 1.

2) Castor Oil [n = 1.47]

Castor oil is a vegetable oil pressed from castor beans with a colourless or pale-yellow aspect. The density is 0.961 g/cm3. It includes a mixture of triglycerides in which about 90% of fatty acids are ricinoleates. Oleic acid and linoleic acid are the other significant components. Castor oil and its derivatives are used in the manufacturing of soaps, lubricants, hydraulic and brake fluids, paints, dyes, coatings, inks, cold-resistant plastics, waxes and polishes, nylon, and perfumes. In Figure 4 the data set from an oil-in-water emulsion of a small aliquot of castor oil is presented. EOS Classizer™ software automatically estimates a RI of 1.47 in agreement with the expected value. As in the previous case, the unique ability of estimating the effective optical properties of the particles allows an accurate classification and sizing of the particles in suspension. In Figure 5 and in Figure 6 the numerical particle size distribution and the oversize of the castor oil emulsion are presented.

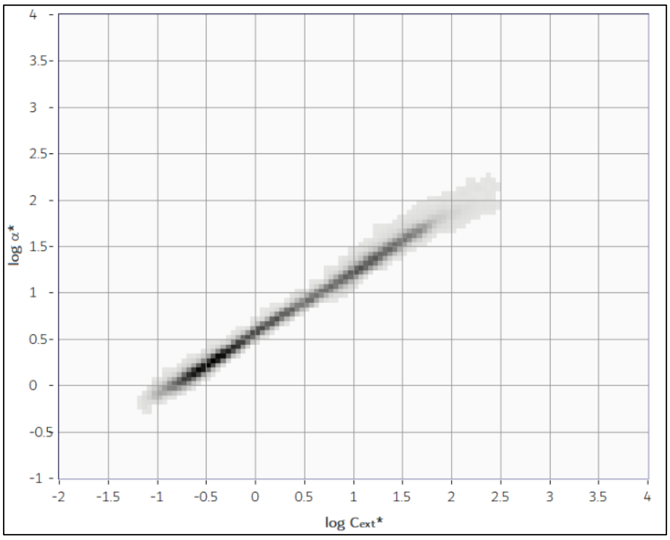

Figure 4 EOS CLOUDS of castor oil-in-water emulsion.

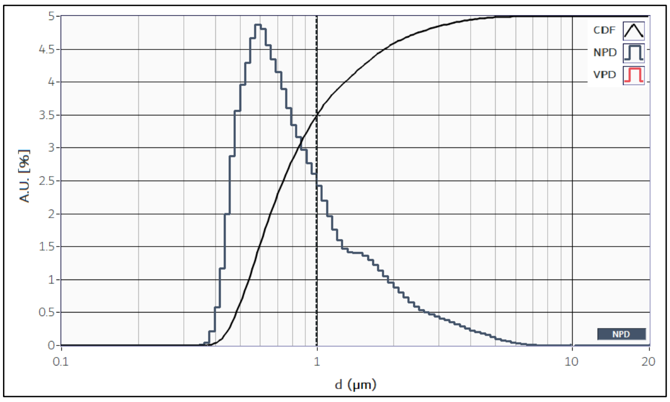

Figure 5 PSD of oil-in-water emulsion of castor oil.

The EOS Classizer™ software estimates an AVG diameter of 1.0 μm, a D50 of 0.74 μm, and a D[4,3] of 3.4 μm.

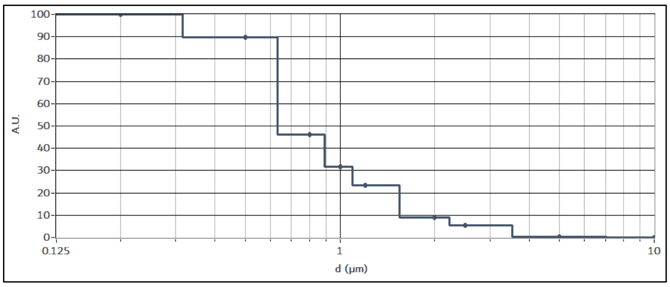

Figure 6 Oversize study of the oil-in-water emulsion in Figure 4.

3) Olive Oil [n = 1.47]

Olive oil is commonly used in cooking, dressing, fuel, and as ingredient in cosmetics, pharma, soaps. In Figure 7, Figure 8, Figure 9 the data from a typical oil-in-water emulsion of a small aliquot of castor oil are presented.

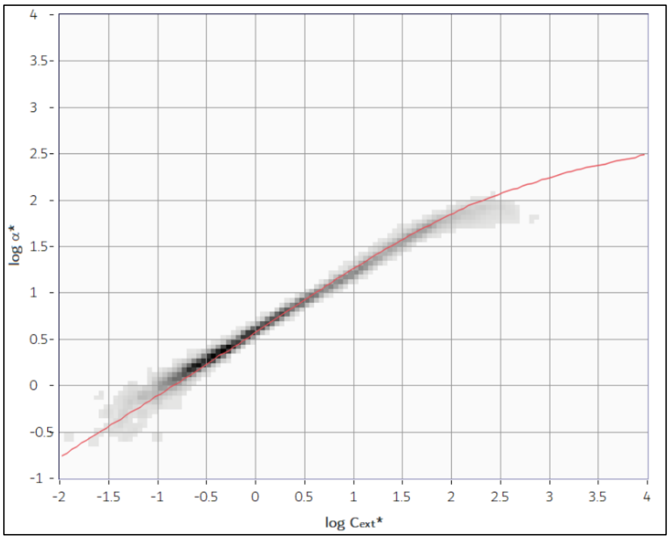

Figure 7 EOS CLOUDS of olive oil-in-water emulsion.

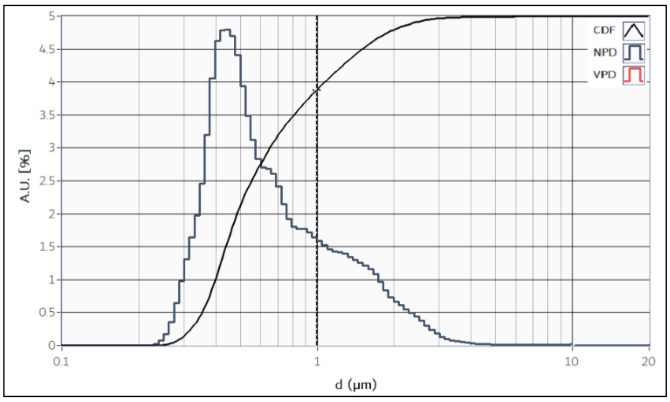

Figure 8 PSD of oil-in-water emulsion of olive oil.

The EOS Classizer™ software estimates an AVG diameter of 0.73 µm, a D50 of 0.54 µm, and a D[4,3] of 3.2 µm.

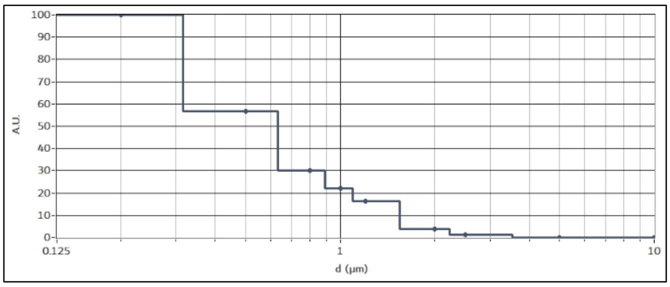

Figure 9 Oversize analysis of olive oil emulsion.

4) Mineral Oil [n = 1.48]

Mineral oil is used as a lubricant, a cutting fluid, and as a conditioning oil for jute fibres selected for textile production. In Figure 10, Figure 11, Figure 12 the data from a typical oil-in-water emulsion of a small aliquot of castor oil are presented.

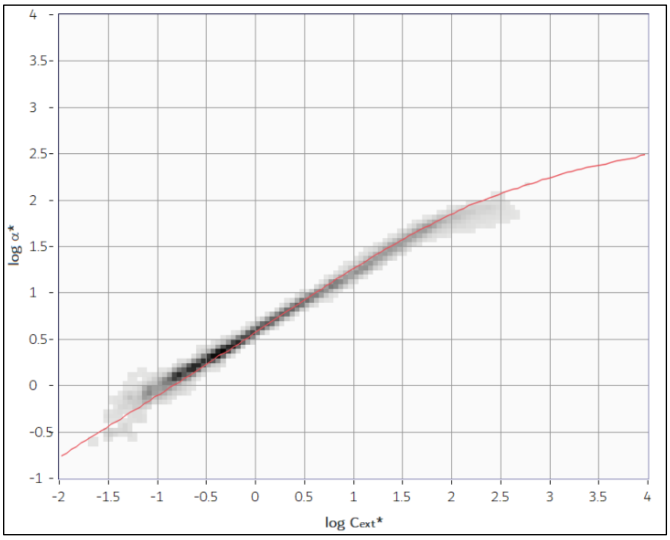

Figure 10 EOS CLOUDS of mineral oil-in-water emulsion.

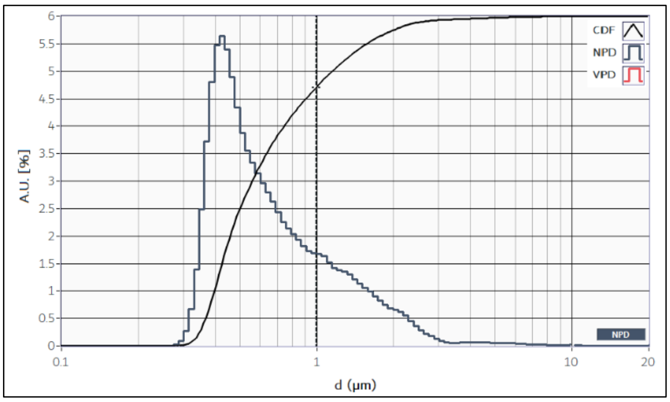

Figure 11 PSD of oil-in-water emulsion of mineral oil.

The EOS Classizer™ software estimates a RI of 1.48 as expected for this sample, an AVG diameter of 0.81 µm, a D50 of 0.56 µm, and a D[4,3] of 5.4 µm.

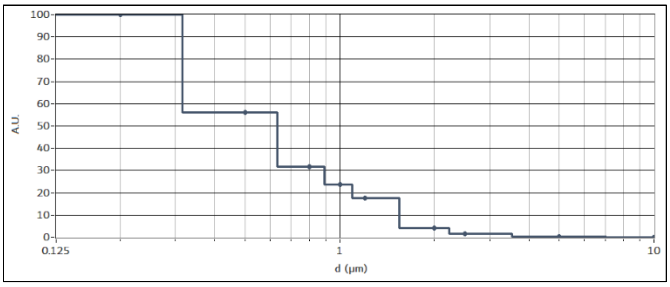

Figure 12 Oversize analysis of mineral oil emulsion.

5) Liquid Paraffin [n = 1.48]

Liquid paraffin is a very highly refined mineral oil used in cosmetics and medicine. It is a transparent, colorless, nearly odourless, and oily liquid that is composed of saturated hydrocarbons derived from petroleum. In Figure 13, Figure 14, Figure 15 the data set obtained with a water emulsion of liquid paraffin are presented.

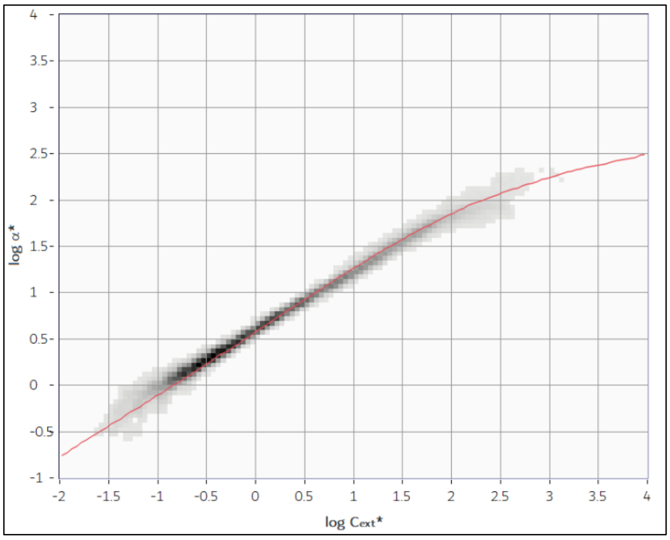

Figure 13 EOS CLOUDS of liquid paraffin emulsion in water.

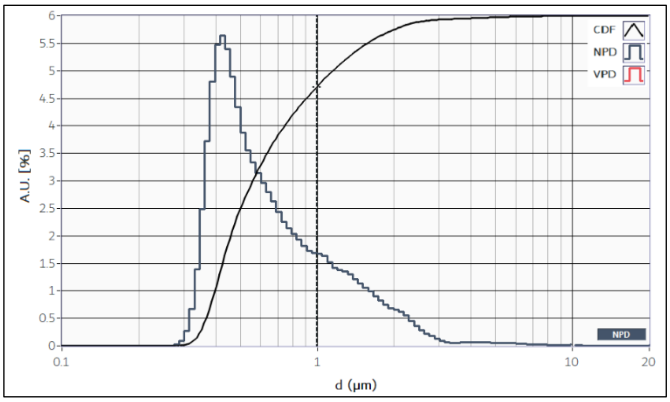

Figure 14 PSD of oil liquid paraffin emulsion.

The EOS Classizer™ software estimates a RI of 1.48 as expected, an AVG diameter of 0.81 μm, a D50 of 0.56 μm, and a D[4,3] of 5.4 μm.

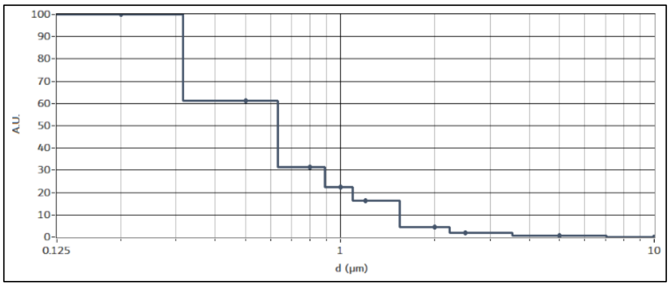

Figure 15 Oversize analysis of sunflower oil emulsion

6) Calibrated Oils [n = 1.50 - 1.53 - 1.55 - 1.59]

Commercial synthetic oils are available on the market for different application as specialty lubricant or microscope immersion. In Figure 16 the oil-in-water emulsions of four calibrated oils are presented. In Figure 17 and Figure 18, the cumulative particle size distributions and the oversize of four calibrated oils are presented.

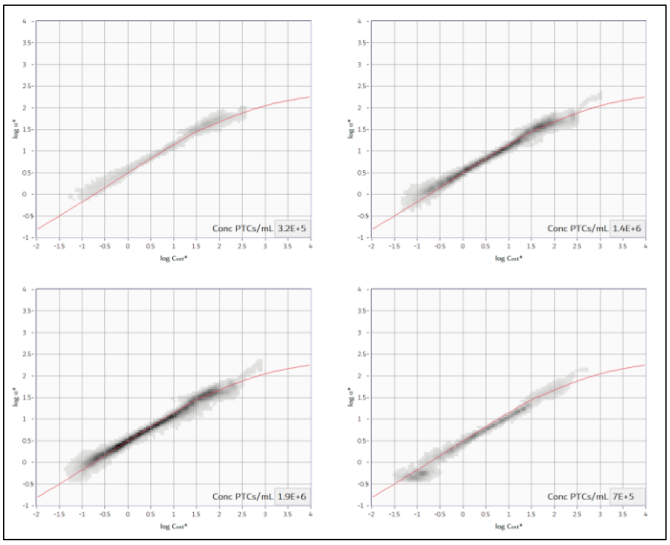

Figure 16 EOS CLOUDS of calibrated oils n = 1.50, 1.53, 1.55, 1.59. The effective refractive indexes determined automatically by the software are respectively 1.51, 1.53, 1.55, and 1.60. The red lines in all the EOS CLOUDS are the expected position for n= 1.50, here just as a guide for the eye.

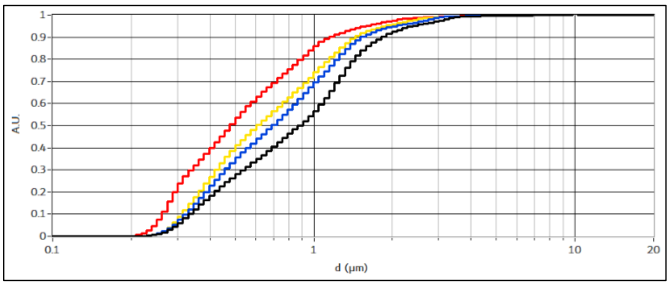

Figure 17 Cumulative particle size distributions of the calibrated oils in Figure 16. Respectively, the black line is n=1.50, the blue one is n=1.53, the yellow one is n=1.55, and the red one is 1.59.

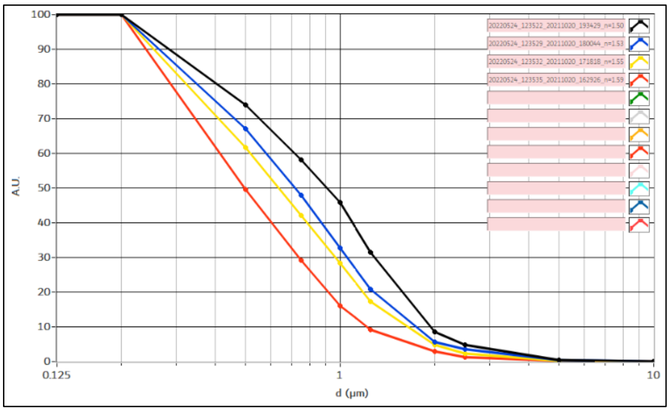

Figure 18 Oversize analyses of the calibrated oils in Figure 16.

7) Emulsions of Oil Mixes

A more complex case is the presence of multiple oils with different refractive indexes in the same liquid. Two cases are considered here. The former deals with a mixture of two pre-emulsified oils (Figure 19). In the latter, small aliquots of two oils are first mixed, then emulsified in water (Figure 20).

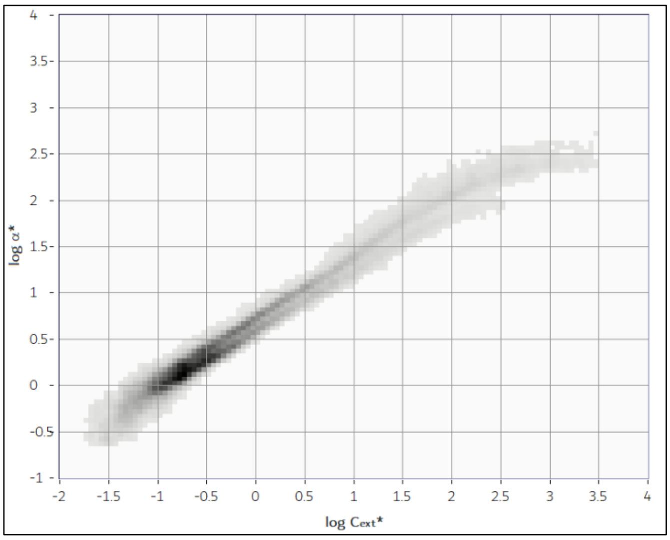

Figure 19 EOS CLOUDS of a mix of two oil emulsions with different refractive indexes (1.40, 1.47). Two narrow data clouds are observed and are related to the two separated population of oil emulsions dispersed in the water.

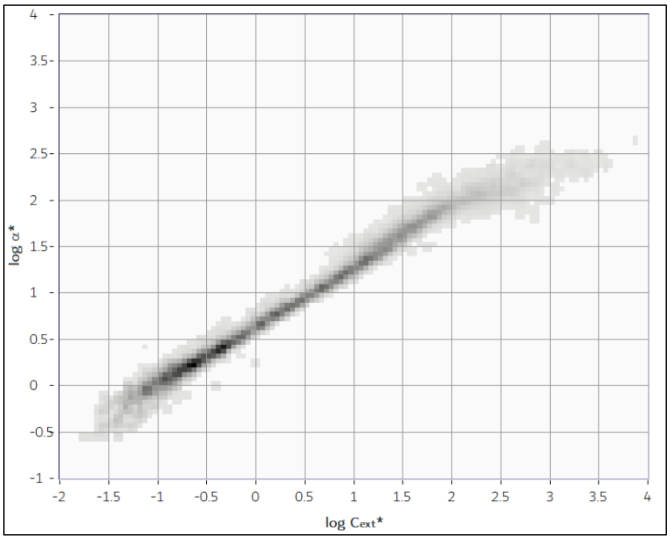

Figure 20 EOS CLOUDS of a blend of two oils with different refractive indexes (1.40, 1.47) and emulsified in water. A single data cloud is observed since the two oils are present in the droplets. The software retrieves an effective average RI of 1.44.

If the oils are mixed before emulsifying, both are present in the droplets suspended in the liquid. The resulting optical property, namely the RI, of the emulsion is expected to be the weight average of the RIs of the two oils. Accordingly, the EOS Classizer ONE provides the user with a single population which RI is the average between the original bulk values of the oils. By changing the volume fraction of the two oils in the blend before the emulsification, it is possible to create emulsions with intermediate RI values, as shown in Figure 21. It is not possible to distinguish the blends based on the sole PSD, but nevertheless the slightly different positions on the 2D EOS CLOUDS for the different blends provides an estimate of the original concentrations.

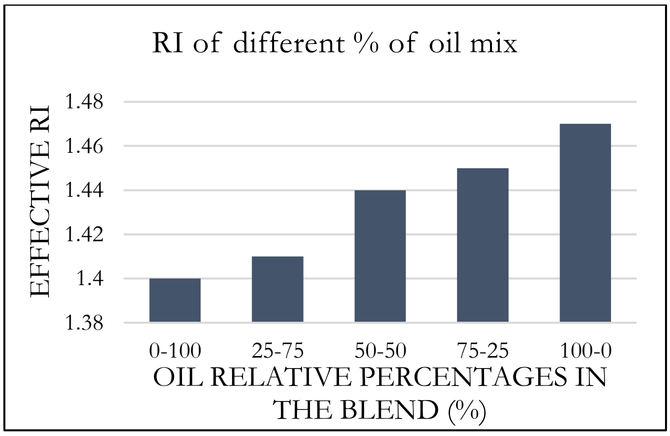

Figure 21 Measured refractive index of the emulsions based on the percentage of mix between the two starting oils (RI of 1.40 and 1.47, respectively).

8) Emulsion non stability due to floating

Emulsion stability is important in industrial applications, as coatings, food products, agrochemicals, personal care, and petroleum. Mechanisms such as creaming, flocculation, and coalescence cause emulsion breakdown. In Figure 22 we study the stability of an emulsion of silicon oil measuring the oversize at different times. The decreasing percentage of large diameter tails over time due to instabilities is evident.

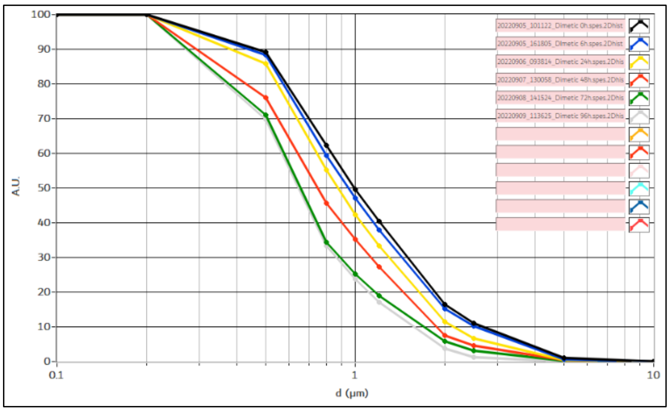

Figure 22 Oversize distributions of an emulsion of silicon oil studied over time at room temperature.

CONCLUSIONS

The capability of EOS Classizer™ ONE and SPES patented method fits the need of a value-added application in the characterization of oil emulsions. SPES data provide physical and statistical information, as PSD, oversize, effective refractive index, an estimate of the behavior and stability. Each characteristic can be crucial to improve the knowledge and the quality of an oil-in-water formulate.

RELEVANT PUBLICATIONS AND REFERENCES

Presentation of Single Particle Extinction and Scattering (SPES) method for particle analysis
AN001-2021 Analysis of Polymeric Particle Mixes via SPES Technology – an introduction to SPES method

AN006-2021 Multiparametric Classification of Particles as a Pathway to Oversize Analysis in Complex Fluids via SPES Technology

Potenza MAC *et al.*, «Measuring the complex field scattered by single submicron particles », AIP Advances 5 (2015)

Example of CFA application of SPES technology
AN002-2021 Continuous SPES Flow Analysis CFA-SPES

Example of PCA application of SPES technology
AN005-2022 Multiparametric Principal Component Analysis of Heterogeneous Samples via SPES Technology

Classizer™ ONE with Sample Manager Autosampler
AN008-2022 Automatic Liquid Sample Management, Dilution, and System Cleaning with EOS Sample Manager

AN009-2022 Standardize SPES Operative Procedure of Liquid Samples Analysis via EOS Autosampler

Example of SPES application to aggregates
AN003-2021 Addressing the Issue of Particle Wetting and Clustering by means of SPES Technology

Potenza MAC *et al.*, «Single-Particle Extinction and Scattering Method …», ACS Earth Space Chem 15 (2017)

SPES application to non-spherical particles
AN004-2021 Addressing the Classification of Non-Spherical Particle by means of SPES Technology

Simonsen MF *et al.*, «Particle shape accounts for instrumental discrepancy in ice …», Clim. Past 14 (2018)

Example of SPES application to emulsions w/o payload in environmental waters
AN012-2021 Monitoring the Fate of a Lipid/ZnO Emulsion in Environmental Waters

AN015-2022 Classification of Oil and Oil Mixes Emulsions via SPES Technology

Examples of SPES application to particle analysis and behavior characterization in biotech applications
AN011-2021 Quantitative Classification of Particles in Biological Liquids via SPES Technology

Sanvito T *et al.*, «Single particle extinction and scattering optical method unveils in real…", Nanomedicine 13 (2017)

Potenza MAC *et al.*, «Single particle optical extinction and scattering allows real time quantitative…», Sci Rep (2015)

Example of SPES application to oxide particles, abrasives, and industrial slurries w/o impurities
Potenza MAC *et al.*, «Optical characterization of particles for industries», KONA Powder and Particle 33 (2016)

AN013-2022 Analysis of Abrasives via SPES Technology

Example of SPES application to ecotoxicity analysis
Maiorana S *et al.*, «Phytotoxicity of wear debris from traditional and innovative brake pads», Env Int., 123 (2019)

Example of SPES application to aerosol analysis
Mariani F *et al.*, «Single Particle Extinction and Scattering allows novel optical …», J Nanopart Res 19 (2017)

Cremonesi L *et al.*, «Multiparametric optical characterization of airborne dust …. », Env Int 123 (2019)

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EOS S.r.l. – viale Ortles 22/4, 20139 Milano (Mi) – Italy
email: info@eosinstruments.com   Phone: +39 02 56660179

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