Stability of Emulsions from Multiwavelength Transmission Measurements

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Droplet populations are generated from the dynamic equilibrium between the breakup and coalescence phenomena occurring during the emulsification process. Adequate estimation of the droplet size and droplet size distribution is important, not only because they are related to the manufacturing process but also because the droplet size distribution provides information of the properties of the dispersed phase and the stability of the emulsions. This paper reports on a novel spectroscopy method that provides quantitative information for the assessment of the stability of liquid−liquid emulsions. The quantitative criterion is based on measurements of droplet populations as a function of the dispersed phase concentration. This technique is applied to fresh and aged emulsions of saturated hydrocarbons and monomers. The method reported for evaluation of the stability of emulsions is easy, inexpensive, and highly reproducible.

Introduction

Emulsions are dispersions of droplets of one liquid in another immiscible liquid that exhibit varying levels of stability. The dispersions are achieved by mechanical and/or chemical means and typically involve the use of surfactants. The extent of the stability is tailored to the application. In most cases, the emulsions are manufactured with a specification in mind (for example, the generation of a given surface area to enhance mass transport) or a particular rheological behavior. The droplet size distribution has an important effect on the stability and other important properties of liquid−liquid emulsions; therefore, measurement of the droplet size distribution has received considerable attention.[1−5] Droplet sizes can be estimated from light transmission, reflectance, and light scattering data. In the diluted regime, Mie theory can be used for the interpretation of transmission and angular scattering data. Mie theory describes the absorption and scattering behavior of spherical particles of any size and refractive index, and it has shown to be very successful in a large variety of applications.[6−8] Techniques for the estimation of particle size distribution from multiwavelength spectral data have been reported in the literature.[8−10] However, most of these techniques require that the shape of the particle size distribution (PSD) be known or rely on the advantages inherent in the mathematical properties of particle size distributions such as log-normal, Gaussian, etc. In addition, most measurement techniques rely on a limited number of wavelengths and do not address issues related to differences in chemical composition.[10,11] The spectroscopy technique proposed herein utilizes a broad wavelength range (190−820 nm), and it is based on the regularized solution to the inverse scattering problem posed by the multiwavelength turbidity equation. As such, it does not require prior assumptions regarding the shape of the PSD.[12−15] In addition, the proposed method can take into consideration changes in the chemical composition of the components involved in the emulsion (dispersed phase and emulsifier). This technique has been successfully applied to the continuous estimation of the droplet size distribution (DSD) in liquid−liquid emulsions.[16−18] The aim of this paper is to assess emulsion stability on the development and implementation of the multiwavelength spectroscopy technique. The quantitative analysis is based on the determination of droplet size and DSD to emulsions of saturated hydrocarbons and monomers as a function of the dispersed phase concentration. The stability criterion is developed from the observation that, if an emulsion is diluted, the dilution ratio necessary to reduce the emulsion droplet size is directly related to the emulsion stability. In the context of this paper. the terms PSD and DSD will be used interchangeably.

Proposed Method

Liquid−liquid emulsions have limited stability and are known to undergo dramatic changes in the DSD as their stability decreases.[19,20] When an emulsion is diluted the chemical potential changes, leading to a change in surface area which implies a change in the DSD. Therefore, if the DSD can be monitored as a function of the dilution ratio, changes in the DSD can be used as leading indicators of the stability of the emulsion. Changes in the DSD can be quantified continuously using multiwavelength transmission spectroscopy.

The UV−vis spectra of particle suspensions are known to contain information on the absorption and scattering properties of the particles.[9] The interpretation of the spectra can be done in terms of the PSD, the particle shape, and the chemical composition of the oil phase and emulsifier. For spherical particles, Mie theory relates the transmission, $\tau(\lambda_0)$, measured at a given wavelength, λ_0, and the normalized particle size distribution, $f(D)$, through the following equation:[7,9,21]

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