Colloids and Surfaces A: Physicochem. Eng. Aspects 462 (2014) 244–251

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

NMR studies of emulsion microstructure approaching the phase inversion point

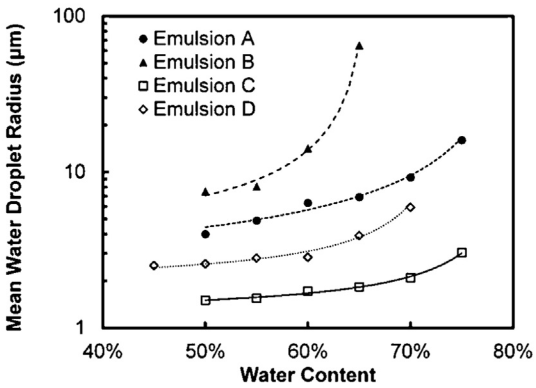
Nicholas N.A. Ling, Agnes Haber, Eric F. May, Einar O. Fridjonsson, Michael L. Johns*

School of Mechanical and Chemical Engineering, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

HIGHLIGHTS

- Emulsion droplet size distributions near the phase inversion point were monitored by NMR.
- Results are reproducible with two different NMR spectrometers.
- Crude oil emulsions showed an exponential droplet size increase as the inversion point was approached.
- The data can be quantitatively described by a model with a single free parameter.
- No evidence of o/w/o emulsions was observed near the phase inversion point.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 June 2014
Received in revised form 18 August 2014
Accepted 29 August 2014
Available online 19 September 2014

Keywords:
NMR
PFG
Emulsion droplet sizing
Water-in-oil emulsion
Emulsion inversion point

ABSTRACT

Bench-top Nuclear Magnetic Resonance (NMR) pulsed field gradient (PFG) methods were used to measure the droplet size distributions (DSD) of various water-in-oil (w/o) emulsions as their water content was increased towards the phase inversion point (PIP). Such concentrated, opaque emulsions are not readily interrogated with alternative droplet sizing techniques. However, monitoring of the DSD as the PIP is approached is needed to help establish how different potential mechanisms, such as divergence of mean droplet size and/or the formation of multiple emulsions, are involved in the inversion process. Two separate NMR spectrometers were used and found to give consistent results for the emulsion DSDs and their evolution as the PIP was approached. An exponential increase in mean emulsion droplet size was observed for various crude oil emulsion samples prepared by sequential droplet phase (water) addition under shear as the PIP was approached, which is consistent with the mechanism of droplet coalescence exceeding droplet break-up. However, for w/o emulsions consisting of a pure hydrocarbon liquid stabilized by artificial surfactants, no change in mean droplet size was observed as the PIP was similarly approached. The NMR data were also analyzed for the presence of multiple emulsions – these were distinctly evident in several samples but were of the local w/o/w type.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Macro emulsions (hereafter referred to as emulsions) are dispersed multiphase systems, where droplets of one liquid are dispersed in a secondary immiscible liquid, with typical radii of the order of micrometers. Such emulsions are thermodynamically

---

* Corresponding author. Tel.: +61 8 64885664.
E-mail addresses: agn.haber@gmail.com (A. Haber), michael.johns@uwa.edu.au (M.L. Johns).

http://dx.doi.org/10.1016/j.colsurfa.2014.08.031
0927-7757/© 2014 Elsevier B.V. All rights reserved.

unstable and will break (separate into distinct liquid phases) given sufficient time. As they have significant industrial importance (e.g. in food, agriculture, and oil and gas industries) the properties of an emulsion need to be well understood. The droplet size distribution is the main physical characteristic of such emulsion systems, and dictates a range of relevant functionalities (e.g. viscosity, stability, and turbidity). An ability to experimentally determine this droplet size distribution is thus essential [1–3].

Emulsion phase inversion is the phenomena whereby a change in a system property, typically phase concentration or temperature, causes an abrupt change in emulsion morphology (the droplet phase becomes the continuous phase and vice versa). In the work presented here, the emulsion phase inversion point (PIP) corresponds to the water content at which the transition from a water-in-oil (w/o) to an oil-in-water (o/w) emulsion occurs. The PIP is an important parameter for a number of reasons [4]. For example, in spite of it being essentially an instability, emulsion inversion has been used in the food, cosmetic and pharmaceutical industry to obtain emulsions with fine uniform droplets [5]. In the oil and gas industry, this inversion is often very desirable as it is much easier and economically viable to separate an oil-in-water (o/w) emulsion than a water-in-oil (w/o) emulsion [4,6,7] given the substantially lower continuous phase viscosity of the o/w emulsion. In some cases o/w emulsions are deliberately produced to reduce the viscosity of highly viscous crude oils so that they can be more easily transported through pipelines [8]. In the current work, we exclusively consider catastrophic phase inversion, which is initiated by a variation in phase composition [4] through the addition, under shear, of more of the droplet phase. The emulsion microstructure (droplet size distribution and morphology) approaching the phase inversion point is important, both in terms of predicting the emulsion microstructure post inversion as well as in terms of generating an improved physical understanding of the mechanisms that lead to the emulsion phase inversion. As discussed below, the general poor understanding and prediction of emulsion inversion is a consequence of the typically concentrated, opaque and unstable nature of such emulsions around the PIP, which makes interrogation using optical or even ultrasound techniques very difficult.

Characterisation of colloidal suspensions using Nuclear Magnetic Resonance (NMR) techniques is a significant scientific undertaking [9–11]. NMR offers various insights into both molecular orientation and transport kinetics within the various phases present. Molecular self diffusion is quantified using NMR pulsed field gradient (PFG) techniques, ultimately enabling a non-invasive measurement of the droplet size distribution (DSD) of the emulsion under investigation [12,13,9]. In comparison to other methods used to determine emulsion droplet sizes (e.g. microscopic observations, light scattering methods, ultrasound spectrometry, electrical conductivity) the non-invasive NMR techniques can readily be employed on concentrated and opaque emulsions. In addition it can be interpreted so as to provide quantitative sizing and characterisation of multiple emulsions (emulsions within emulsions) [14,15]. In our case w/o/w multiple emulsions are relevant, in which there is an inner droplet water phase along with a continuous water phase. A further observation with respect to the use of NMR techniques to size emulsions, is that the technique is commercially available on bench-top NMR apparatus [16]. Lingwood et al. [17] and Fridjonsson et al. [18] both demonstrated how NMR chemical shift differences on such instruments can be used to unambiguously differentiate the oil and water NMR signals.

In this paper the emulsion droplet size distributions were measured using NMR PFG techniques for various water-in-oil (w/o) emulsions as a function of water content approaching the emulsion phase inversion point (PIP). This was performed for various continuous phase oil viscosities, using both industrial crude oils and ‘model oils’ consisting of a single component (pure hydrocarbon). These measurements were performed on two different bench-top NMR spectrometers (one commercial and one bespoke) and two different methods of preparing the various emulsions were considered (individual composition formation versus gradual concentration with water whilst shearing). In this manner, the change in droplet size as the PIP is approached by water addition was quantified; the NMR data were also assessed for the presence of any multiple emulsions or other complex emulsion morphologies.

2. Background

2.1. Relevant NMR theory

The measurement of free, unrestricted self-diffusion of molecules in a liquid by NMR pulsed field gradient (PFG) methods was first demonstrated by Stejskal and Tanner [19]. The method essentially relies on signal attenuation due to random motion (diffusion) of the molecules between two imposed magnetic field gradients. The resultant NMR signal loss (S/S_0) is described by:

$$\ln\left(\frac{S}{S_0}\right) = -D\left(\gamma g \delta\right)^2\left(\Delta - \frac{\delta}{3}\right), \tag{1}$$

where D is the self-diffusion coefficient of the relevant molecules and Δ, δ and g are the temporal duration between application of the two magnetic field gradients, the duration of a single magnetic field gradient and the strength of the magnetic field gradient, respectively. The gyro-magnetic ratio, γ, was that of the ^{1}H nucleus ($\gamma = 2.68 \times 10^8\ \mathrm{T}^{-1}\ \mathrm{s}^{-1}$) for all of the NMR measurements presented here. The NMR signal S is thus measured as a function of g, δ or Δ enabling the extraction of D via application of Eq. (1). The NMR pulse sequence most commonly employed to achieve this with respect to emulsion characterisation is based on a stimulated echo signal, as presented in Fig. 1.

In the case of restricted diffusion inside a spherical geometry (e.g. an emulsion droplet), the NMR signal attenuation ($I = S(g)/S(g=0)$) can be approximated as [20]:

$$\ln I(D, a, g, \delta) = -2\gamma^2 g^2 \sum_{m=1}^{\infty} \frac{1}{\alpha_m^2(\alpha_m^2 a^2 - 2)}\left[\frac{2\delta}{\alpha_m^2 D} - \frac{\psi}{(\alpha_m^2 D)^2}\right] \tag{2a}$$

$$\psi = 2 + \exp^{-\alpha_m^2 D(\Delta-\delta)} - 2\exp^{-\alpha_m^2 D\Delta} - 2\exp^{-\alpha_m^2 D\delta} + \exp^{-\alpha_m^2 D(\Delta+\delta)} \tag{2b}$$

where α_m is the mth positive root of the equation:

$$J_{\frac{5}{2}}(\alpha a) - \frac{1}{\alpha a} J_{\frac{3}{2}}(\alpha a) = 0 \tag{2c}$$

and J_k is a Bessel function of the first kind of order k with a being the droplet radius. Eq. (2) assumes that the NMR signal phase (ϕ) distribution is a Gaussian shape. An alternative to Eq. (2) exists in which it is assumed that the duration of the applied magnetic field gradient, δ, is equal to zero [21]. More recently, Lingwood et al. [17] demonstrated that the use of the block gradient pulse (bgp) approximation method to describe restricted diffusion inside spherical droplets (emulsion droplet sizing) offered improved accuracy compared to the assumption of a Gaussian phase distribution or an infinitely short δ over all practical experimental parameter space considered. The bgp method is based on the generalised gradient waveform set of methods [22–24], in which an eigenfunction expansion is used to solve the Bloch–Torrey equation in the presence of a piecewise-constant gradient waveform [25]. Details regarding the derivation can be sourced from [26] and our implementation for emulsion droplet sizing, as is employed in the work presented here, is detailed in [17].

Download English Version:

https://daneshyari.com/en/article/592572

Download Persian Version:

https://daneshyari.com/article/592572

Daneshyari.com