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Emulsion Droplet Size Distribution by PFG NMR: High Concentrations, Small Radii, and Suspo-Emulsions

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1. Introduction

Emulsions are heterogeneous systems of a liquid dispersed in another one in the form of droplets having radii in the order of micrometers. Emulsions are widely applied in many fields of high commercial importance, for example adhesives, cosmetics, paints, food, pharmaceuticals, and in plant protection. Many properties such as viscosity, turbidity, stability to coalescence and sedimentation, and rheological behaviour depend on the droplet size distribution of a dispersion [1]. Generally light scattering, electron microscopy, confocal scanning laser microscopy (CSLM), acoustic spectroscopy, dielectric spectroscopy techniques and centrifugal sedimentation are used to assess oil droplet size distributions in emulsions [2]. However, all those techniques can either be employed for highly diluted emulsions only or else require an elaborate and destructive preparation of the sample. Pulsed field gradient (PFG) spin echo NMR has already been successfully used to determine the emulsion droplet size distribution many years ago [3] and has received new attention recently [4]. It can be applied to concentrated opaque emulsions without dilution or destructive pretreatment, and it has the advantage of being chemically specific and thus applicable to multi-component mixtures. In this work, O/W emulsions of up to 90% (w/w) are investigated by the pulsed field gradient spin echo technique and droplet size distribution before and after dilution is determined and compared with the results from laser scattering (Malvern).

2. Experimental and discussion

Paraffin oil is emulsified into water with CH_3-$(CH_2)_{12}(0CH_2CH_2)_8 0H$ as surfactant. Diffusion measurements have been carried out on a BRUKER Avance300 spectrometer equipped with a DIFF25 gradient probe (max. gradient strength 1000 G/cm). Incrementing the time of diffusion Δ in a stimulated echo experiment at three different gradient strengths results in a dataset of three decay curves (Fig.1). Data are evaluated with a global set of fitting parameters assuming a log normal distribution to represent droplet sizes with the two parameters a_0 (radius median) and σ (standard deviation of the distribution). D of the oil is fixed ($9*10^{-12}$ m^2/s at 25°C).

The theory for spherical confinement has already been outlined by Packer et al. [3] and was expanded to include other geometries plus a constant field gradient [5]. In Fig.1, attenuation of the normalized signal of the oil vs. diffusion time is shown for a sample containing 40% of oil. According to theory [3] attenuation is expected to be independent of diffusion time Δ at large values of time Δ, if diffusion of the whole particle is negligible. We instead observe a continuous decrease at long times Δ and at all three gradient strengths used. Only a model which takes account of diffusion of the whole

droplet additionally permits good fitting. The result obtained (a_0 = 0.35μm, σ = 0.33, volume averaged radius a_V = 0.43μm) is then within error to the one of the light scattering measurement (LS: a_V = 0.40μm; cf. Fig.2).
PFG-NMR can be applied to any concentration of oil, even at 90 % (w/w) of oil. We can tell from our PFG-NMR experiments that it is the oil that forms the dispersed phase even at that extreme concentration although we have no information on the size and shape of the micelles. Fitting a log normal distribution of droplet sizes results in a very good fit, if we include the diffusion of the whole droplet into our model (a_0=0.12μm, σ=0.61, a_V=0.24μm, fig.2). It is obvious that this result from NMR is quite different from the one from light scattering, the latter obtained at high dilution (fig.2). There is a considerable change in the distribution of radii according to PFG-NMR when diluting from 90% to 40%, as would be expected. The PFG-NMR method thus clearly has advantages when we deal with highly concentrated emulsions from industrial sources. We can even investigate creamed emulsions by this technique and compare the distribution of the size of radii within the creamed layer to that of the pristine emulsion and to a redispersed sample.

3. Conclusions

The ability of PFG-NMR to deal with highly concentrated samples without dilution and in a non-destructive way is most valuable for industrial samples which can be investigated without being changed during sample preparation. It is however important to include diffusion of the whole droplet into the model if radii are small and to use a dataset acquired at three different gradient strengths in order to obtain reliable results.

References

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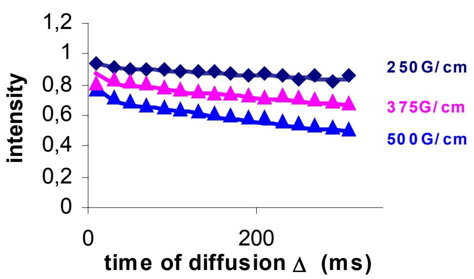

Fig. 1 Normalized amplitude of the stimulated echo vs. time of diffusion (global fit including restricted diffusion as well as diffusion of the whole particle).

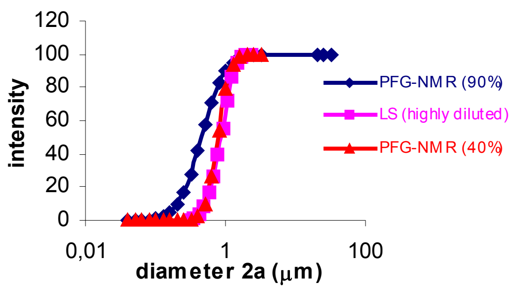

Fig. 2 Droplet size distribution of an emulsion of paraffin oil obtained by PFG-NMR and light scattering (LS).