Main Factors Controlling the Emulsification Process under Turbulent Conditions. 2. Experiment and data interpretation

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The emulsification was performed by a narrow-gap homogenizer [1]. Three different types of surfactant were studied: anionic SDS, nonionic Brij 58, and protein WPC. Soybean oil was used as oil phases. The electrolyte concentration was varied by addition of 10 or 150 mM NaCl to the surfactant solutions.

For all studied emulsifiers (protein, non-ionic and anionic surfactants; at high and low electrolyte concentrations) we observe two well-defined regions in the dependence of the mean drop size, d_{32}, on the initial surfactant concentration, C_S^{INI}. A considerable decrease of drop size is observed at low surfactant concentrations (Region 1, $C_S^{INI} < 0.1$ wt %), followed by a plateau region at high surfactant concentrations (Region 2, $C_S^{INI} >$ 0.1 wt %) - see Figure 1 for illustration of these trends.

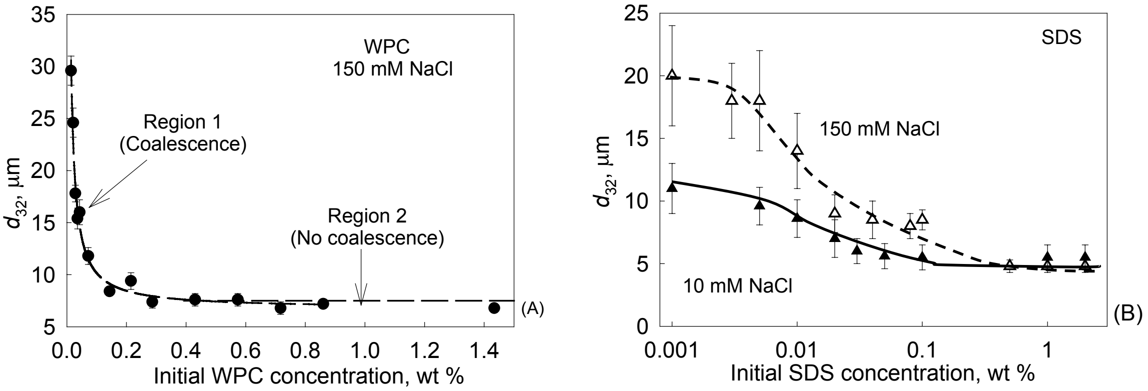

Figure 1. Mean volume-surface diameter, d_{32}, as a function of the initial emulsifier concentration, for emulsions stabilized by (A) WPC and (B) SDS.

At high emulsifier concentrations (in the plateau regions), the experimental data for d_{32} are described very well by the Kolmogorov-Hinze theory of emulsification, which states that the drop size is given by:

$$d_K \sim \varepsilon^{-2/5} \sigma^{3/5} \rho^{-1/5} \tag{1}$$

where σ is the interfacial tension, ρ is the mass density of the continuos phase, and ε is the average power density (rate of energy dissipation per unit volume) in the emulsification chamber. The agreement between eq 1 and the experimental data is illustrated in Figure 2 with two series of experiments: (1) at fixed σ_{OW} and different hydrodynamic conditions; (2) at fixed hydrodynamic conditions and different σ_{OW}.

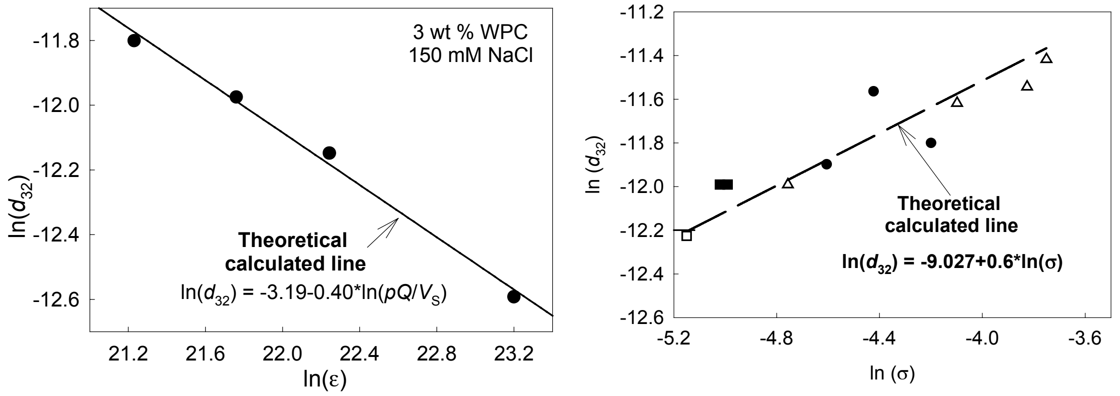

Figure 2. (A) Logarithm of the volume-surface diameter, d_{32}, vs ln(ε) for emulsions stabilized by 3 wt % WPC when σ = 10 mN/m. (B) ln(d_{32}) vs ln(σ), for emulsions prepared under equivalent hydrodynamic conditions, ε = 2.5×10^8 J/(m^3.s). In all experiments the oil volume fraction Φ = 0.28. The symbols represent experimental data, whereas the continuous line is calculated by eq 1.

At lower emulsifier concentration, two qualitatively different cases were recognized. In the case of suppressed electrostatic repulsion (nonionic and protein type of emulsifier in presence of 150 mM NaCl) we found that d_{32} is a linear function of $1/C_S$, see Figure 3. This result can be explained [1] by making a mass balance of the protein initially dissolved in the aqueous phase (before starting the emulsification) and the protein adsorbed on the drop surface (after accomplishing the emulsification). This mass balance predicts that the slope of the dependence $d_{32}(1-\Phi)/\Phi$ vs. $1/C_S$ corresponds to a threshold value of the surfactant adsorption, Γ^*, which is needed to stabilize the drops against coalescence [1]. From the best linear fit through the experimental data, we determined $\Gamma^* = 1.9$ mg/m^2 for WPC solutions and $\Gamma^* = 1.4$ mg/m^2 for Brij 58 solutions, see Figure 3. As shown in Ref. [1], Γ^* does not depend on the oil volume fraction and on ε, which means that Γ^* can be considered as a characteristic of the used emulsifier. This is the typical case when no significant electrostatic repulsion occurs between the drops. In such systems, the drops coalesce during emulsification until Γ becomes equal to Γ^*. Once a sufficiently dense layer is formed, it ensures a strong steric repulsion, which stabilizes the drops against further coalescence.

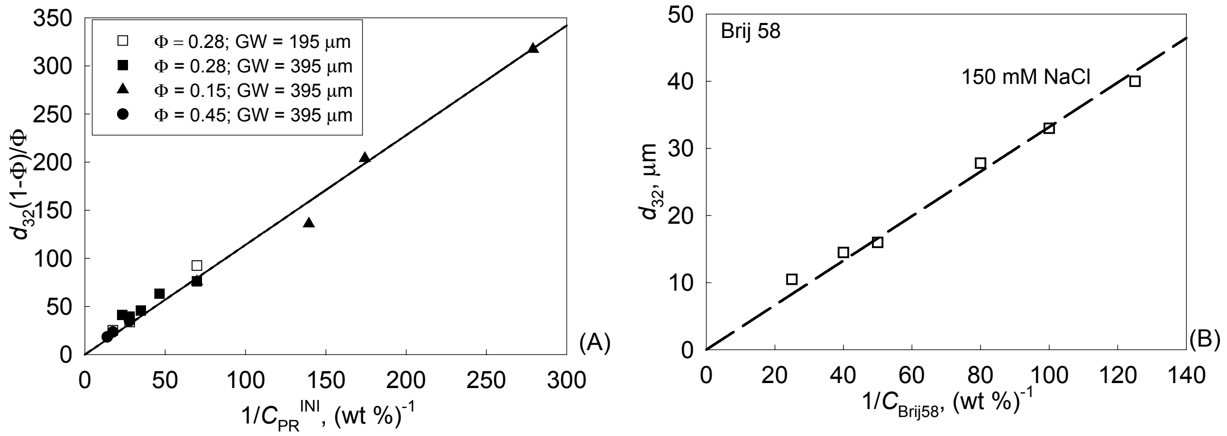

Figure 3. Mean diameter, d_{32}, as a function of the inverse initial surfactant concentration for emulsions stabilized by: (A) WPC, (B) Brij 58.

Our attempts to estimate the threshold emulsifier adsorption, Γ^*, in the systems with significant electrostatic repulsion between the drops (SDS + 10 or 150 mM NaCl), were unsuccessful. To reveal what is the interrelation between surfactant concentration and adsorption, on one side, and the mean drop size, on the other side, we analyzed the role of drop-drop interactions during emulsification [2]. The performed theoretical analysis showed that, for SDS + 150 mM NaCl, there is a threshold surface potential, $\Psi^* = -22$ mV, ensuring electrostatic stabilization of the emulsion drops during emulsification. This means that the emulsion drops would coalesce until the surface electric potential increases in magnitude, as a result of SDS adsorption, from 0 to ca. 22 mV. For emulsions stabilized by SDS + 10 mM NaCl, the theoretical estimates predict that no coalescence is expected to occur, even at very low surface coverage with surfactant, due to the strong electrostatic repulsion between the drops. These theoretical predictions were found to agree well with the experimental data for SDS stabilized emulsions [2].

References:

1. S. Tcholakova, N. D. Denkov, D. Sidzhakova, I. B. Ivanov, B. Campbell, "Interrelation of drop size and protein adsorption at various emulsification conditions", *Langmuir 19* (**2003**) 3084.
2. S. Tcholakova, N. D. Denkov, I. Ivanov, T. Danner, "Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow", *Langmuir, submitted.*