



Historical perspective

Physical chemistry of highly concentrated emulsions

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ABSTRACT

This review explores the physics underlying the rheology of highly concentrated emulsions (HCEs) to determine the relationship between elasticity and HCE stability, and to consider whether it is possible to describe all physicochemical properties of HCEs on the basis of a unique physical approach. We define HCEs as emulsions with a volume fraction above the maximum closest packing fraction of monodisperse spheres, $\varphi_m = 0.74$, even if droplets are not of polyhedron shape. The solid-like rheological behavior of HCEs is characterized by yield stress and elasticity, properties which depend on droplet polydispersity and which are affected by caging at volume fractions about the jamming concentration, φ_j . A bimodal size distribution in HCEs diminishes caging and facilitates droplet movement, resulting in HCEs with negligible yield stress and no plateau in storage modulus. Thermodynamic forces automatically move HCEs toward the lowest free energy state, but since interdroplet forces create local minimums – points beyond which free energy temporarily increases before it reaches the global minimum of the system – the free energy of HCEs will settle at a local minimum unless additional energy is added. Several attempts have been undertaken to predict the elasticity of HCEs. In many cases, the elastic modulus of HCEs is higher than the one predicted from classical models, which only take into account spatial repulsion (or simply interfacial energy). Improved models based on free energy calculation should be developed to consider the disjoining pressure and interfacial rheology in addition to spatial repulsion. The disjoining pressure and interfacial viscoelasticity, which result in the deviation of elasticity from the classical model, can be regarded as parameters for quantifying the stability of HCEs.

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1. Introduction

Among the most important and interesting categories of complex fluids are emulsions, which have numerous applications in food, cosmetic, and mining industries, and are also encountered in petroleum industries. Over the years, a great deal of effort has been expended on understanding and controlling the structure and rheological properties of emulsions to ensure acceptable quality, processability, and performance of final products. Generally, emulsions are classified according to the distribution of the oil and aqueous phases. A system that consists of oil droplets dispersed in a water phase is known as an oil-in-water (o/w) emulsion, while a system of water droplets dispersed in an oil phase is known as a water-in-oil (w/o) or inverse emulsion.

For monodisperse spheres arranged in a face-centered cube crystalline structure, it is well known that the volume fraction of the closest packing of monodisperse particles, φ_m , which is the geometrical limit for loading a dispersed phase in suspensions, is about 0.74. For random close packing, φ_m is about 0.64 [1]. However, polydisperse spheres can shift φ_m to higher concentrations. This threshold can be overcome in emulsions where the concentration for a dispersed phase can reach even 0.99 [2,3]. A transition through the critical concentration φ_m in emulsions becomes possible if the liquid droplets are compressed and transformed into polyhedrons to fill the space much more tightly, with very narrow continuous phase layers between neighboring dispersed liquid droplets (Fig. 1). The obtained system is called a highly concentrated emulsion (HCE), also known as a high internal phase emulsion (HIPE) or gel emulsion. Practically, HCEs can be made by imposing gravitational forces on a dilute emulsion, through sedimentation or creaming. Alternatively, they can be made by adding the dispersed phase slowly over time to a continuous phase containing a proper surfactant. The peculiar rheological behavior of emulsions gives rise to their application in many fields. Presently, there is considerable interest in HCEs due to their numerous potential industrial applications—e.g., cosmetics and personal care, food, oil recovery, and mining industries [4].

The compressed structure of droplets in HCEs induces close contact among interfacial layers, and consequently creates an interdroplet repulsion, called interdroplet interaction in this work, which is crucial for stabilizing droplets against coalescence. Additionally, compressed droplets have a significant spatial repulsion, which can be modeled by different approaches such as increase in interfacial area [5–8] and contact mechanics [9,10]. Because compressed droplets have a higher interfacial area, they also have a higher interfacial energy (interfacial tension between two immiscible phases multiplied by interfacial area). Therefore, the spatial repulsion originating from interfacial tension scales with Laplace pressure, which is the ratio of interfacial tension to droplet size, $\Pi_L = \sigma/R$. While the interfacial tension acts

parallel (tangential) to the interface [11], the repulsion force between two droplets pushed against each other is perpendicular to the touching interfaces.

The viscoelastic properties of HCEs have been studied widely, both experimentally and theoretically [5–8,12–23]. It has been shown that viscoelastic properties depend on the mean diameter of dispersed particles, polydispersity, interfacial tension, and particularly on the dispersed phase volume fraction, although it is accepted that by considering the area–volume mean droplet size, polydispersity does not have a pronounced effect [24]. In this review paper, we discuss the physics underlying the relationship between rheology and stability in HCEs in order to determine:

- Whether it is possible to describe all physicochemical properties of HCEs based on a unique physical approach;
- Whether there is a correlation between rheological properties and the stability of HCEs; and
- What role surfactants play in HCEs.

This review article provides the necessary background and key concepts about HCEs. In Section 2, we discuss the structure of HCEs. Microscopic and macroscopic properties of HCEs will be covered in Sections 3 and 4, respectively. In Section 5, we review the stability of HCEs. We conclude the relationship between stability and the elasticity of HCEs in Section 6.

2. Structure of HCEs

Two levels of structure can be considered for an emulsion: the interfacial geometry of individual droplets, and the positional configurations of droplets. The deformable nature of droplets provides the possibility of different interfacial configurations, which range from spherical to nearly polyhedral. The positional configurations of droplets can be classified as ordered or disordered. For both classes of emulsion, the structure is strongly dependent on the volume fraction.

There are some ambiguities in the definition and characterization of some specific states of HCEs that need to be clarified. Many liquids undergo a glass transition when rapidly cooled, and their viscosity increases by orders of magnitude for only modest decreases in temperature. This drastic increase in viscosity is not accompanied by significant structural changes; instead, the dynamic slows dramatically [25]. In colloidal systems, as the concentration of the dispersed phase is increased, the system exhibits an increase in viscosity. At some volume fraction, while the system structurally still resembles a liquid, random motions within the system are slow enough that it can be considered

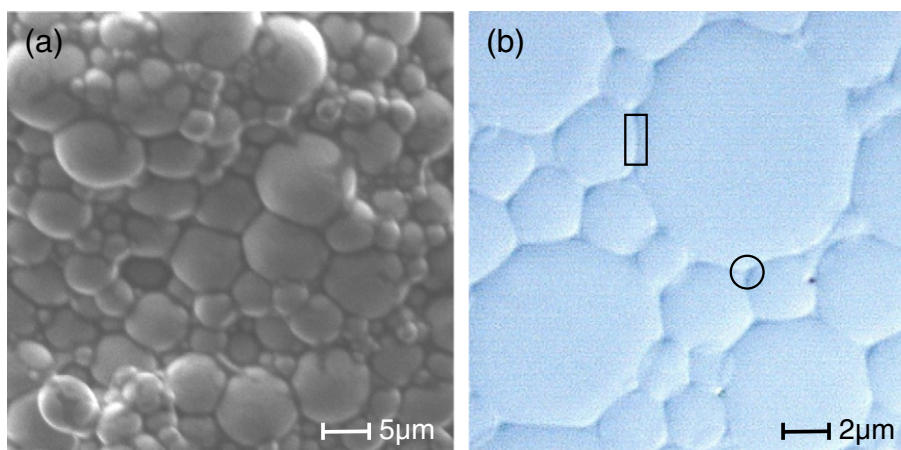


Fig. 1. (a) Typical compressed nature of HCE droplets in a scanning electron micrograph, and (b) indication of Plateau border (circle) and an interdroplet film (rectangle) in a typical optical microscopic picture of an HCE [by authors].

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