Spontaneous emulsification

Conxita Solans *, Daniel Morales, Maria Homs

Institute of Advanced Chemistry of Catalonia, Spanish National Research Council (IQAC-CSIC) and CIBER on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Jordi-Girona 18-26, Barcelona 08034, Spain

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ABSTRACT

Spontaneous emulsification may occur when immiscible liquids in non-equilibrium conditions are in contact. This phenomenon is triggered by gradients of chemical potential between the phases, which under certain conditions lead to negative values of free energy of emulsification. A summary of background information on spontaneous emulsification is first presented with emphasis on proposed mechanisms. It follows a description of recent developments, in both surfactant-free and surfactant systems. Applications based on the use of spontaneous emulsification to produce delivery systems and nanostructured materials with improved properties in a cost-effective way are also described.

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1. Background

The phenomenon of spontaneous emulsification, also known as self-emulsification, has been the focus of attention since long ago due to its intrinsic basic interest and also for its extensive use in numerous and diverse applications [1•]. In spontaneous emulsification, droplet formation can be achieved by contacting two immiscible liquids that are not in equilibrium without the need of external energy input. By contrast, if the immiscible liquids are in thermodynamic equilibrium, the energy to expand the interface, $\gamma\Delta A$ (γ being the interfacial tension and ΔA the increase in interfacial area), is large and positive and cannot be compensated by the small and positive entropy of dispersion, $T\Delta S$ (T being the absolute temperature and ΔS the increase in entropy). Consequently, the total free energy of formation, $\Delta G = \gamma\Delta A - T\Delta S$, is positive ($\Delta G > 0$), as exemplified in Fig. 1**a**, and external energy input (mechanical or thermal) is required to achieve emulsification. However, if the immiscible liquids are not in equilibrium, gradients in chemical potential between the phases may originate negative values of free energy of emulsification ($\Delta G < 0$), as schematically indicated in Fig. 1**b**, and emulsification is produced spontaneously. In practice, emulsification is often achieved by a combination of external energy input and internal chemical energy of the system (Fig. 1**c**). In particular, many temperature sensitive systems are initially heated around the phase inversion region because spontaneous emulsification is obtained afterwards when cooling the system. Note that the magnitude of the external energy input required in the combined process is considerably lower (Fig. 1c) than that required in the former one (Fig. 1a).

Considerable research effort has been devoted to the phenomenon of spontaneous emulsification since it was first discovered in 1879 by Johannes Gad [2]. Davies and Rideal reviewed the earlier findings on the subject about 60 years ago [3] and discussed three possible mechanisms for spontaneous emulsification based on interfacial turbulence, the development of transient (negative) values of interfacial tensions and "diffusion and stranding" (by which regions of local supersaturation develop giving rise to nucleation and growth of drops). These mechanisms have been prominent and other mechanisms, such as Marangoni flow, Rayleigh-Taylor instability, etc., have been proposed and described in comprehensive reviews [1•,3,4]. However, there is not yet a complete understanding on the mechanisms and dynamics of spontaneous emulsification. Observation of this phenomenon in systems with and without surfactant has allowed to clarify several aspects, namely, that (a) interfacial turbulence may not be the main factor causing spontaneous emulsification as addition of surfactant (in a surfactant-free system) or electrolyte can suppress completely turbulent flow and yet spontaneous emulsification is produced (nevertheless, it is recognized that turbulent flow increases the rate of emulsification); (b) low (negative) interfacial tensions are not required for spontaneous emulsification to take place, as in surfactant-free systems low values of interfacial tensions are achieved only close to a critical point but spontaneous emulsification has been also observed far from critical points; and (c) spontaneous emulsification can lead to big (micrometer size) or small (nanometer size) emulsion droplets, pointing to a diffusion driven process.

Study of simple systems, composed of water, oil, and an organic solvent, miscible with both water and oil (e.g., a short chain alcohol),

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* Corresponding author.
E-mail address: conxita.solans@iqac.csic.es (C. Solans).

(a) External energy

Gibbs Free Energy

Formation Kinetic Barrier

Stabilization Kinetic Barrier

Emulsion

Non-Equilibrium Phases

B′
A′

B
A

Equilibrium Phases

$\Delta G \approx \gamma \cdot \Delta A > 0$

B
A

Equilibrium Phases

(b) Internal energy

Gibbs Free Energy

Non-Equilibrium Phases

A″
B″

Formation Kinetic Barrier

Emulsion

Stabilization Kinetic Barrier

$\Delta G < 0$

A
B

Equilibrium Phases

(c) Cooperation of external and internal energy

Gibbs Free Energy

Formation Kinetic Barrier

Stabilization Kinetic Barrier

Emulsion

Non-Equilibrium Phases

A′
B′

A
B

Equilibrium Phases
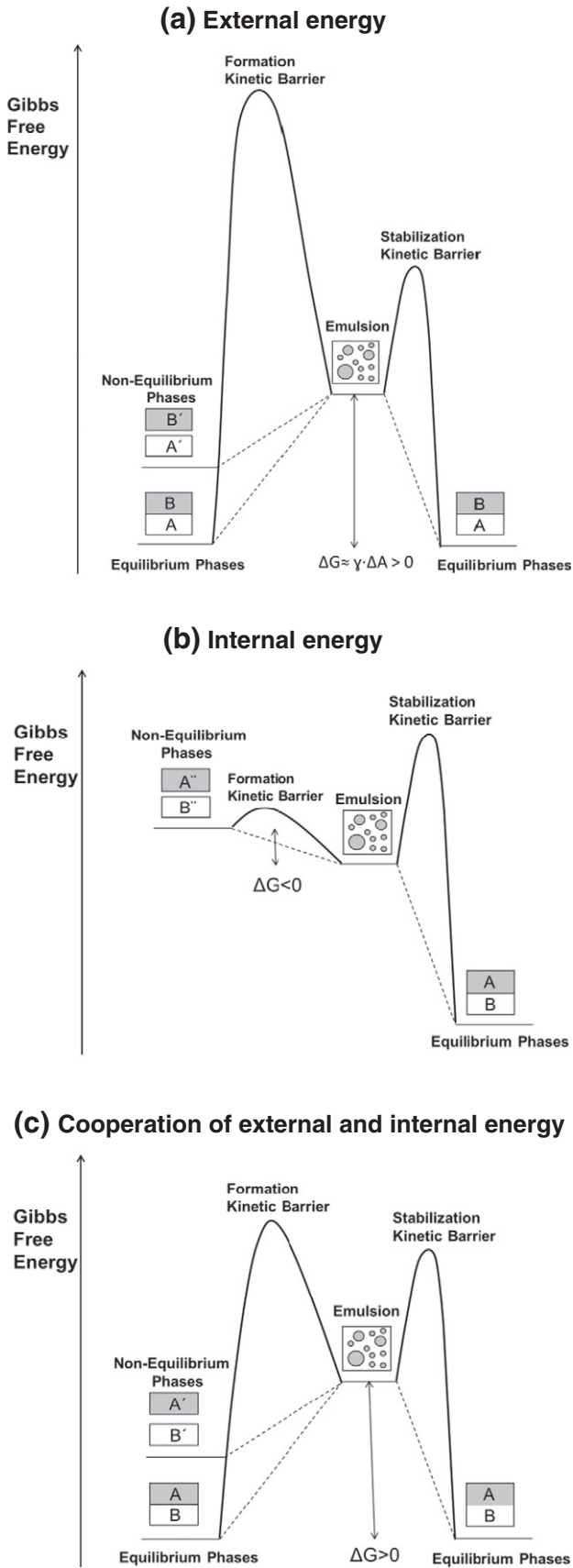
$\Delta G > 0$

A
B

Equilibrium Phases

Fig. 1. Schematic Gibbs free energy profiles of emulsification processes driven by (a) external energy, (b) internal energy, (c) cooperation of external and internal energy.

enabled to gain insights on the phenomenon of spontaneous emulsification. In experiments in which water was contacted, without stirring, by oil containing sufficient amount of alkanol, it was shown that alcohol diffuses into the aqueous phase and that the local supersaturation produced near the interface gives rise to emulsification [1•]. Ruschak and Miller [5••] introduced the "diffusion path theory" presenting an analysis on how the regions of local supersaturation could develop. The solution of diffusion equations in ternary systems for semi-infinite immiscible phases showed that, under certain assumptions, the set of compositions in the system is independent of time and can be plotted directly on the ternary phase diagram, the so-called "diffusion path". Fig. 2 illustrates the diffusion path, abcdW, when an oil/polar co-solvent (e.g., alcohol) mixture, with composition a, is contacted with water. The spontaneous emulsification takes place, between c and d, in the aqueous phase. If the equilibrium phase behavior of a system is known, this theory predicts the occurrence of emulsification and also in which phase it takes place. It also predicts proportionality between the interfacial displacement from the initial surface of contact of the phases and the square root of time (enabling to estimate the overall diffusivity, assuming that the diffusion coefficients of all species in both phases are equal). The diffusion path theory was experimentally confirmed not only in simple water/alkanol/oil systems but also in systems containing surfactants [1•,6]. However, it predicts only the behavior in the initial stages of the process.

It has been evident since long ago that equilibrium phase diagrams constitute an important tool in the study of spontaneous emulsification. Considering the phase diagram of a ternary water/co-solvent/oil system, spontaneous emulsification occurs below the binodal (or coexistence) curve (Fig. 3). The binodal curve defines the region of compositions in a phase diagram across which transition from miscibility of the components (single phase) to conditions where the mixtures are unstable or metastable (multiphase) occur. The spinodal curve, also indicated in Fig. 3, separates metastable from unstable regions (in real systems is not a sharp boundary as a result of fluctuations). Vitale and Katz [7••] called "ouzo effect" the spontaneous emulsification produced when solutions of oil dissolved in a solvent are brought in the metastable region, between the binodal and the spinodal curves, by the addition of water. They chose the term ouzo after the common Greek anise-flavored beverage, which results from the spontaneous emulsification of anethole when a large amount of water is added to a homogeneous solution concentrate containing water (about 55%), ethanol (about
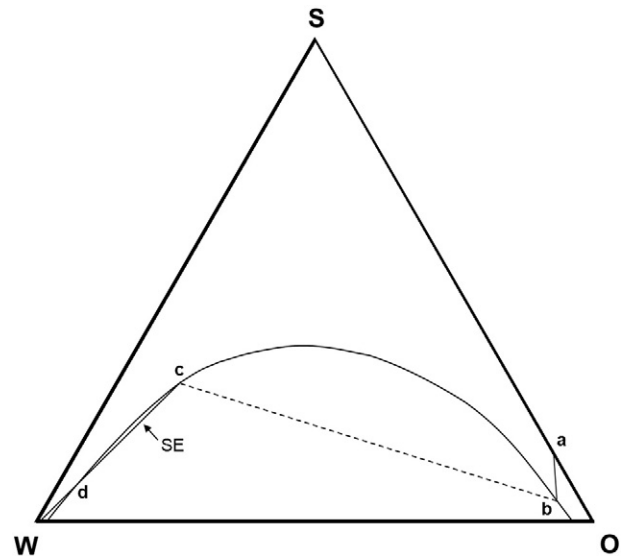

Fig. 2. Diffusion path (abcdW) in a typical water (W)/co-solvent (S)/oil(O) system when composition a is contacted with water. Spontaneous emulsification (SE) is produced in the aqueous phase. Adapted with permission from Miller [6]. Copyright 1988.