



Dissolution dynamics of miscible liquid/liquid interfaces



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ABSTRACT

The recent achievements gained in understanding of the dissolution dynamics of miscible interfaces are reviewed. Our consideration is restricted to isothermal systems with the mass transfer purely driven by inhomogeneities in the field of concentration. Both experimental and theoretical works are examined. The attention is given to the effects of dynamic surface tension, interfacial diffusion, dynamics of the contact line, and to solutal convective flows. We conclude that, despite ubiquitousness and importance of physical processes involving miscible interfaces, the physics that defines the thermo- and hydrodynamic evolution of such interfaces is still not properly understood, especially in respect to dissolution rate at a miscible liquid/liquid phase boundary and to wetting properties at liquid/solid boundary. A consistent theoretical description for the slowly miscible binary systems is given within the phase-field (Cahn–Hilliard) approach. Nevertheless, there are just a few modelling works that take into account all the effects pertinent to miscible liquid/liquid interfaces.

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1. Introduction

A contact of two miscible liquids (two components of a binary mixture) initiates a mixing process that in general includes the diffusive mass transfer and the generation of hydrodynamic flows. As a result of the mixing an initial non-equilibrium state of a binary mixture is transformed into a state of thermodynamic equilibrium. Such an equilibration takes usually rather long time periods, so the visible phase separation could be observed for hours after the initial contact of two miscible liquids. We call this mixing the dissolution process. An everyday example would be the honey dissolution in tea. One can regularly observe, that for such a system, a clear honey/tea interface is visible at the time of honey droplet immersion and may remain visible for hours if the mixture temperature is low. In addition, one may notice that the phase boundary tries to retain its shape even being agitated. Nevertheless, as time goes by, the molecules of honey and water interdiffuse; this smears the interface, so the interface becomes completely invisible at some point. In the state of thermodynamic equilibrium, the honey/water mixture becomes wholly homogeneous.

The experiments with the honey/water mixture aimed at understanding of the physics of miscible interfaces were even staged on board of the International Space Station [1]. Some other classical experiments in which the behaviour exhibited by miscible interfaces is very similar to immiscible ones in the sense of exhibiting non-zero interfacial tension are reviewed by Petitjeans and Kurowski [2].

Some other binary mixtures, e.g. isobutyric acid (IBA)/water or 1-butanol/water, are characterised by limited solubilities. If, for instance, a droplet of IBA is immersed into a finite volume of water, then the

molecules of IBA and water interdiffuse until the saturation (equilibrium) concentrations are attained in every phase. That is, the final state of thermodynamic equilibrium may be heterogeneous in such systems.

Based on the above observations one should conclude that the concept of a phase boundary, endowed with the surface tension, is needed for an accurate description of the dissolution process of liquid/liquid mixtures (both for completely and partially miscible systems). The interface thickness and the surface tension associated with the boundary separating two miscible liquids are time-variable. This idea that the miscible interface should be endowed with the dynamic surface tension was first raised by Korteweg and others (see e.g. [3]).

Another peculiarity of the dissolution process in liquid/liquid mixtures, which is generally well accepted, but is still rarely used in modelling of the real-life processes, is inaptitude of the Fick's law (i.e. proportionality of the diffusion flux to the concentration gradient) to define the rate of the interfacial diffusion. This is an obvious observation for partially miscible systems, for which the interfacial diffusion is absent in an equilibrium state despite the fact that such a state may be heterogeneous, i.e. with strong concentration gradient across the phase boundary.

The appearance of the liquid/liquid interface ultimately stems from the difference in intermolecular interactions within phases. At macro-scale this difference is defined by the surface tension coefficient. It is also obvious that diffusion of a molecule in the bulk and near the interface occurs differently, as the difference in the intermolecular forces gives rise to a potential barrier that molecules need to overcome in order to diffuse from one phase to another. We may say, that immiscible liquids that are usually characterised with high surface tension coefficients, have so

high potential barrier that the interfacial mass exchange is excluded. Miscible liquids are characterised by lower but non-zero surface tension coefficients and non-zero rates of interfacial diffusion. Hence, the surface tension has a two-fold action on the interface shape and the interfacial diffusion [4,5].

In perfect gaseous mixtures, molecules are dispersed and, as a result, the intermolecular interactions are weak. The diffusion coefficients of gases are larger by four orders (compared to diffusion coefficients in liquids), so the thermodynamic equilibration occurs much faster. In gases, the concept of interface is not needed: there are two inter-penetrating continua with diffusion driven by random walks of molecules.

2. Engineering applications

There are numerous instances of slowly miscible multiphase systems. A trivial one is cleaning (or waste treatment), when grease (an oily viscous substance) that fills the pores of a rough surface, is effectively removed by applying a solvent. Next, we would like to examine some similar processes that represent the variations of the solvent-based (or miscible) displacement of a solute from a porous medium. These are the vegetable oil extraction [6], enhanced oil recovery [7,8], aquifer and soil remediation [9,10], etc. [11]. Even an intravenous drug delivery could be considered as the dissolution of a liquid miscible droplet through porous body tissues [12]. In such processes, the hydrodynamic flows within porous media are rather slow and the diffusion and capillary effects play essential roles in the overall mass transport.

Thus, the typical oil extraction begins with crashing of the natural feedstock. Then, the oil is collected from the surface of grains by dissolution using an appropriate solvent; the solvent is pumped through a porous medium formed by the feedstock grains [13,14]. Further, the solvent is separated from the solute using, e.g., solvent evaporation. The most common solvent nowadays is the petroleum-derived hexane, and supercritical carbon dioxide is considered to be a promising substitute [6,14]. In practice, the solvent is provided in excessive quantities, which introduces additional problems with its further separation and utilization. Additionally, the rate of extraction is variable, and the initial, e.g. 50%-extraction requires much less time compared to the latter parts making preferable to derive only, e.g. 50% of oil, and discard the rest of the feedstock [6].

Miscible injection used for the enhanced oil recovery (instead, of the classical immiscible water injection) can bring such advantages as (i) reduced capillary pressure, (ii) reduced viscosity of the solvent/oil mixture, (iii) dissolution of oil from the dead-end pores, and others [9]. The method has been tested by injection of hydrocarbon gases (CH_4 or liquefied petroleum gases) [8], and of carbon dioxide (CO_2), as supercritical CO_2 dissolves oil [15].

The industry-used oil extractors generate complex intensive flows of a solvent to secure the full coverage of the feedstock [16]. In petroleum engineering, the full coverage of the oil reservoir is difficult to achieve mostly because of instability of the liquid/liquid displacement to viscous fingering or gravity override or underdrive [17]; and the bypassed oil blobs are hardly accessible for the recovery.

The soil remediation [9,10] also has its own distinct features. Firstly, oil extraction and enhanced oil recovery deal with the confined reservoirs, while aquifer remediation usually involves contaminants that are spilled at the ground surface of unconfined aquifers. Secondly, in aquifer remediation processes, it is important that both the contaminants present and the chemical flushing agent introduced into aquifers be removed.

Hence, the physical effects involved by all these processes are similar, but the differences in tasks and configurations make them different, so semi-empirical approaches developed by, e.g., petroleum engineers to describe the enhanced oil recovery do not necessarily translate to aquifer remediation processes. Despite numerous research works focused on understanding of these engineering processes, their current understanding remains mostly semi-empirical owing to poor

comprehension of the underlying physics. A detailed theoretical and numerical description of dissolution required for modelling is not currently available, as it is highly complicated by the necessity to track the evolution of the interface between inter-diffusing liquids, which can be quite complex and include topological modifications, by generation of surface flows, and by a lack in knowledge of the diffusion dynamics under strong concentration gradients.

In this review, we first present the theoretical model which captures all the physical effects pertinent to the evolution of a binary mixture. After, we review the recent experimental and theoretical advances at the understanding of particular features of the model.

3. Theory: Cahn–Hilliard–Navier–Stokes equations

A consistent physics-based macroscopic description of the evolution of miscible multiphase systems is given within the framework of the phase-field (or diffuse-interface) approach. The main idea of this approach is to smear the interfacial boundary. One system of the Navier–Stokes equations is solved for the entire multiphase mixture. Typically, the thickness of a phase boundary is just several molecular layers, i.e. zero for the macroscopic theory, and this makes the limit of zero thickness critically important for the approach. It should however be noted that, in the vicinity of the thermodynamic critical point, the phase boundary is thick, which justifies the interface smearing.

To take the surface tension effects into account, the specific free energy function f is defined as a function of density, concentration, and concentration gradient [18],

$$f(\rho, C, \nabla C) = f_0(\rho, C) + \frac{\epsilon}{2} |\nabla C|^2. \quad (1)$$

Here, f_0 is the classical part of the free energy, C is the solute concentration defined as the mass fraction of the solute in the mixture, and ϵ is the capillary coefficient that is assumed to be very small so the second term is not-negligible only at the places of strong gradients of concentration, i.e. at interfaces.

Function f_0 can either be written on the empirical basis or derived from a molecular level theory. This function should be written so to reproduce the behaviour defined by the phase diagram, which can be of different forms [19]. For instance, the mixture with the upper critical solution temperature (such a mixture in equilibrium is either homogeneous or heterogeneous at the temperature below the critical point, and always homogeneous at supercritical temperatures) can be defined by the free energy function originally proposed by Landau [19],

$$f_0 = a(C - C_{cr})^2 + b(C - C_{cr})^4. \quad (2)$$

In this expression, C_{cr} is the solute concentration in the critical point, and coefficients a and b are the phenomenological parameters which define the choice of a particular binary mixture. Function (Eq. (2)) has two minima for negative values of a and one minimum for positive a . Two minima characterising a system below the critical point are associated with two different phases, while in supercritical conditions the binary mixture is homogeneous and is characterised by the only minimum of the free energy function.

Another expression that might be preferred for the states more distant from the critical point is the “regular solutions” function [20,18] (also known as the Flory–Huggins theory for polymer mixtures),

$$f_0 = C \ln(C) + (1 - C) \ln(1 - C) + \psi C(1 - C). \quad (3)$$

Here ψ is a phenomenological parameter.

The evolution of binary mixture to its thermodynamic equilibrium is defined by the hydrodynamic model. In general, the mixture density is a function of pressure, temperature, and concentration, but the dependencies on the first two quantities are removed by assumption that

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