Transient interfacial phenomena in miscible liquids

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Abstract:

Composition gradients in miscible liquids can create volume forces resulting in various interfacial phenomena. They are more difficult to study than in the case of immiscible liquids: they are weak and transient in time. In this work we present some experimental evidences of interfacial phenomena in miscible liquids and numerical simulations of miscible drops and diffuse interfaces.

Key words:

miscible liquids, interfacial phenomena

1. Effective interfacial tension

Investigations of capillary phenomena in miscible liquids begin from the work by Korteweg \cite{7}. He introduced additional volume forces in the equations of motion called now Korteweg stresses. Direct experimental confirmation of this theory is difficult because possible effects are weak and time dependent, and they can be distorted by other phenomena. Some properties of miscible liquids are studied experimentally and theoretically (see e.g. \cite{1}, \cite{2}, \cite{8}, \cite{6}, \cite{10}; more complete literature review cannot be given here because of space limitations).
If the diffusion coefficient is sufficiently small, existence of capillary forces in miscible liquids can be confirmed experimentally. One of the experimental techniques developed for this purpose is based on spinning drop tensiometry. It is conventionally used to determine interfacial tension for immiscible liquids [13], [5]. It was first used for miscible liquids in [8]. This study was continued in [11], [9]. Since the interface between miscible fluids is transient, the results of spinning drop tensiometry are difficult to interpret. However, it is now established that the capillary force exists. Systems with critical solution temperatures are especially amenable to study by spinning drop tensiometer because an immiscible system can be converted to a miscible one by only changing the temperature without disturbing the concentration gradients. One such system is isobutyric acid and water. Below 27 °C, a mixture of IBA and water will form two phase, the lighter of the two is rich in IBA and the more dense phase is rich in water. Figure 1 shows a isobutyric acid rich drop in the aqueous phase after the temperature was raised to 30 °C [9].

![Figure 1: Capillary instability in miscible liquids.](image)

2. Interfacial waves

In the isothermal case under the assumption that the liquids have the same and constant density we have the system of equations

\[
\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} = d\Delta c, \tag{2.1}
\]

\[
\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \Delta v_x - K \frac{\partial c}{\partial x} \Delta c, \tag{2.2}
\]

\[
\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \Delta v_y - K \frac{\partial c}{\partial y} \Delta c. \tag{2.3}
\]
\[ \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0. \] (2.4)

Here \( c \) is the composition, \( c = 0 \) corresponds to one pure liquid and \( c = 1 \) to another one, \( v = (v_x, v_y) \) is the velocity vector, \( \rho \) is the density, \( \nu \) the kinematic viscosity, \( K \) is a positive parameter, \( d \) the diffusion coefficient.

This model describes various capillary phenomena and in particular capillary waves which appear when the curvature of the interface between two liquids varies in space creating a pressure difference. This is related to the capillary instability that can result in splitting of a jet into drops in immiscible liquids (see Section 3).

We discuss here propagation of waves which we call interfacial to distinguish them from the capillary waves. They are also related to capillary phenomena but their manifestation and mechanism of propagation are different. Consider a plane interface between two liquids and suppose that its width differs in space. Then the effective interfacial tension, which is in the inverse proportion to the interface width, also varies in space creating a force directed along the interface. This force can lead to the motion of the interface and of the neighboring liquid. Experimentally this effect can be observed if we change locally the interfacial tension by adding chemicals or by heating the interface.

The variable interface width creates a force directed along the interface. This results in appearance of two vortices near the perturbation. They begin to propagate from the center of the domain to the side walls (Fig. 2b). The concentration perturbations propagate together with the vortices. After hitting the wall the vortices change their structure and the direction of rotation (Fig. 2c), then they propagate to the center of the domain (Fig. 2d), meet there, cross each other, propagate further to the walls (Fig. 2e,f). This effect is studied analytically with the help of a simplified model problem [3].

Figure 2: Level lines of the composition and of the stream function after: (a) 0.05 s, (b) 0.95 s, (c) 1.45 s, (d) 2.0 s, (e) 2.95 s, (f) 3.6 s
3. Behavior of drops

In the immiscible case, a drop of a liquid surrounded by another liquid will minimize its surface and become spherical. What happens with miscible liquids? Numerical simulations show that the drop becomes circular in the 2D case if the value of $K$ is sufficiently large (Fig. 4). These simulations are carried out for the case of variable density and viscosity and correspond to a drop of water in honey. It is interesting to note that in the simulations shown in Figure 4 the drop oscillates being longer periodically in the $x$ or in the $y$ direction. Such behavior is well known for usual immiscible drops.

The next simulation concerns miscible jets, long cylindrical drops. In the immiscible case there exists the capillary instability that can split the jet into small drops. In the miscible case it depends on the diffusion coefficient. If it is small, the instability can be observed (Fig. 5).

It is well known that immiscible drops and bubbles move in a temperature gradient because the interfacial tension depends on temperature. This creates a fluid flow that pushes the drop to the place with a higher temperature. The simulations show that miscible drops also migrate in temperature gradients (Fig. 6). Here we assume that $K$ decreases with temperature, and the temperature increases from the left to the right. The pressure inside
the drop is practically constant and higher than the pressure outside the drop.

References


Figure 6: Migration of a miscible drop in a temperature gradient: level lines of the composition (dashed lines) and of the stream function (solid lines).


