Natural and Marangoni convection in partially miscible liquid systems

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Abstract

This article deals with laboratory experiments and numerical simulations of convection and dissolution phenomena in partially miscible liquids. Transparent organic liquids (cyclohexane and methanol) are considered as a model system to study problems occurring during solidification of metal alloys with a miscibility gap. Non-invasive optical techniques are used to study stable and unstable convective solutal plumes, that are produced at the tip of a liquid droplet dissolving in a non-isothermal partially miscible liquid. Numerical simulations explain the observed behaviour and capture additional insights into the physics of the phenomenon, following from a delicate balance between counteracting buoyancy and surface tension-driven flows.

1. Introduction

On ground and microgravity-based research on partially miscible liquid systems is motivated by a large number of potential applications. A relevant example is the case of metal alloys. Dispersed drops may form in a matrix liquid with a miscibility gap during cooling of metal alloys. In this case, the proper understanding of the basic processes, related to natural (gravitational) and surface tension-driven (Marangoni) convection in the liquid phase, could in principle help to predict and control the behaviour of the cast material and indeed the properties of the final solidified alloy. The quality of the dispersion alloys, defined by the degree of homogeneity of the minority phase distribution, can be improved if a uniform dispersion of fine particles in the metal matrix is achieved \cite{1,2}. In terrestrial processes, sedimentation and buoyancy effects may result in a non-homogeneous and non-uniform composition of the alloy.

Optimization of the process therefore can be seen as a matter of searching, as systematically as possible, the conditions that lead to the aforementioned uniform dispersion of the drops.

In this paper, a basic research study on buoyancy and surface tension-driven flows is performed for a
A Wollaston prism interferometer is used to investigate the droplet dissolution and the related convective phenomena are correlated with ad hoc developed numerical models.

The laboratory experiments show that, in the earth’s gravity field and under temperature gradients, buoyancy and Marangoni effects simultaneously occur in the region close to the drop surface. Although, the latter effect is often masked by the dominant influence of the gravity, the interferometer allows one to make evident the interplay between both effects, which in turn depend on the intensity of applied thermal gradients.

The phenomena presented in the paper represent a new contribution to fundamental studies in fluid-dynamics.

We disclosed this new class of phenomena during preliminary tests carried out on ground in preparation of a sounding rocket experiment dealing with drops Marangoni migration and dissolution.

2. Experiments

2.1. Experimental set-up

Cyclohexane (C\textsubscript{6}H\textsubscript{12}) and methanol (CH\textsubscript{3}OH) exhibit a miscibility gap at ambient temperature and have been already investigated in literature due to the following interesting properties: (i) the two components have nearly same density; (ii) they are transparent, allowing direct visualization by optical and interferometric diagnostic devices; (iii) their mixture has a critical temperature slightly above the ambient temperature (45.7 °C [3]).

In this work, the experiments have been performed using a quartz cell 1 cm \times 1 cm \times 4 cm. The droplet is formed at the tip of a capillary (1 mm diameter) injecting methanol from the bottom side of the test cell filled by cyclohexane.

The drop is anchored to needle (or capillary tube) used to inject the liquid into the matrix (Fig. 1).

The temperatures at the top and bottom walls are controlled by Peltier elements. Hereafter, the drop liquid (methanol) is denoted as phase 1 and the liquid matrix (cyclohexane) as phase 2. The properties of the liquids under investigations are shown in Table 1. The interface tension has been measured at different temperatures in the laboratory of the University of Naples with a tensiometer based on the pendant drop method.

The experimental cell is positioned along the axis of a Wollaston interferometer to visualize the concentration field and therefore the mass transfer at the liquid–liquid interface. In particular, a lateral shearing interferometer based on 10’ Wollaston prism has been used. A detailed description of the experimental technique is reported in [4,5].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (m\textsuperscript{2}s\textsuperscript{-1})</td>
<td>5 \times 10\textsuperscript{-9}</td>
</tr>
<tr>
<td>(\rho_1) (kg m\textsuperscript{-3})</td>
<td>0.782 \times 10\textsuperscript{3}</td>
</tr>
<tr>
<td>(\rho_2) (kg m\textsuperscript{-3})</td>
<td>0.769 \times 10\textsuperscript{3}</td>
</tr>
<tr>
<td>(\nu_1) (m\textsuperscript{2}s\textsuperscript{-1})</td>
<td>1.03 \times 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>(\nu_2) (m\textsuperscript{2}s\textsuperscript{-1})</td>
<td>1.275 \times 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>(\beta_1) (dimensionless)</td>
<td>4.62 \times 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>(\beta_2) (dimensionless)</td>
<td>-4.95 \times 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>(\beta T_1) (K\textsuperscript{-1})</td>
<td>1.14 \times 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>(\beta T_2) (K\textsuperscript{-1})</td>
<td>1.14 \times 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>(C_p1) (J kg\textsuperscript{-1} K\textsuperscript{-1})</td>
<td>2.51 \times 10\textsuperscript{3}</td>
</tr>
<tr>
<td>(C_p2) (J kg\textsuperscript{-1} K\textsuperscript{-1})</td>
<td>1.86 \times 10\textsuperscript{3}</td>
</tr>
<tr>
<td>(\chi_1) (J m\textsuperscript{-1}s\textsuperscript{-1} K\textsuperscript{-1})</td>
<td>2.02 \times 10\textsuperscript{-1}</td>
</tr>
<tr>
<td>(\chi_2) (J m\textsuperscript{-1}s\textsuperscript{-1} K\textsuperscript{-1})</td>
<td>1.25 \times 10\textsuperscript{-1}</td>
</tr>
<tr>
<td>(\sigma_T) (dyne m\textsuperscript{-1} K\textsuperscript{-1})</td>
<td>17.42</td>
</tr>
</tbody>
</table>
2.2. Behaviour of a droplet dissolving under isothermal conditions

When the drop dissolution occurs at isothermal conditions, after an initial transient time, a stable buoyant plume is formed above the droplet, continuously carrying methanol towards the top of the test cell (see Fig. 1).

This behaviour can be explained by the fact that, for sufficiently small values of the methanol concentration, the density of the methanol–cyclohexane system is a decreasing function of the methanol concentration (even though the pure methanol is heavier than the pure cyclohexane, see Fig. 2). Therefore, the liquid surrounding the drop (initially pure cyclohexane) becomes lighter when the methanol drop dissolves and an upward flow is driven by buoyancy.

The dissolution rates of droplets with different initial volumes have been measured at different temperatures. Fig. 3 shows the results obtained when the temperature is 35°C (similar behaviour was also found for T = 25°C). The dissolution time is obviously an increasing function of the initial droplet volume.

The experimental results have been compared with theoretical predictions based on the following equation for the interface dissolution velocity:

\[
V_t \approx \frac{D(\partial c/\partial n)_{2}}{c_1 - c_2},
\]

where \( D \) is the diffusion coefficient and the concentration gradient at the droplet–matrix interface has been estimated by the concentration distribution measured by the interferometer.

Order of magnitude estimations based on the previous equation have been also performed.

The measured and estimated speeds are in sufficient agreement and show the same general trends when the drop volume increases. The results are not reported due to space limitation.

Fig. 4 shows the comparison between experimental and numerical results, for a droplet with initial volume of 3 µl in normal gravity (1 g) conditions and in an ideal zero gravity environment (corresponding to purely diffusive conditions).

The results summarized in Fig. 4 show a good agreement between the experimental results and the
numerical results corresponding to 1g conditions. Moreover, as expected, the presence of solutal buoyant convection in the Earth gravity environment results in larger mass transfer and therefore in higher dissolution rates, compared to purely diffusive conditions.

### 2.3. Convective instabilities in presence of temperature gradients

If a temperature gradient $\nabla T$ is applied to the liquid matrix, heating the top wall of the test cell and cooling the bottom one, different phenomena may occur according to the magnitude of the temperature gradient.

For sufficiently small values of the temperature gradient $\nabla T$, the methanol plume is very similar to the one observed in isothermal conditions. If $\nabla T$ exceeds a critical value, the aforementioned mechanism undergoes a transition to a complex oscillatory flow pattern with a new spatial-temporal behaviour.

The oscillatory convection mode is due to the combined action of thermocapillary and buoyancy effects. The vertical temperature gradient along the drop–matrix interface causes an interface tension gradient, leading to thermocapillary (or Marangoni) convection; consequently, the matrix liquid layers surrounding the drop exhibit a downward motion. At the same time, being the liquid layer close to the drop lighter than the liquid matrix, far away from the drop, the buoyancy forces tend to bring the fluid upward. As a result of these counteracting forces, an oscillatory convective motion is generated.

For a droplet with initial volume of the order of 3–5 μl, the critical $\nabla T$ is of the order of 1 K/cm.

The interferometer patterns (see e.g. Fig. 5) clearly show that the solute plume is periodically released from the drop with a characteristic oscillation frequency depending on the experimental conditions.

A clear evidence of the counteracting effects responsible for the onset of the instability is the boundary layer separation seen along the drop surface (see Fig. 6).

The separation points correspond to the detachment of the aforementioned liquid layer driven by surface tension forces close to the interface. This phenomenon exhibits an outstanding theoretical kinship with the corresponding phenomenon, well-known by aerospace engineers, characterizing the separation of air boundary layers from thin wing airfoils. Owing to solutal buoyancy forces, that oppose to downward motion, this surface boundary layer has not enough momentum to reach the bottom region of the drop.
Table 2
Summary of experimental results for different drop volumes

<table>
<thead>
<tr>
<th>Volume (µl)</th>
<th>gradT (°C/cm)</th>
<th>Flow regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.82</td>
<td>x</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
<td>x</td>
</tr>
<tr>
<td>1</td>
<td>1.13</td>
<td>x</td>
</tr>
<tr>
<td>1.9</td>
<td>0.93</td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>0.67</td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>1.69</td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td>0.82</td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td>1.16</td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td>1.76</td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>1.08</td>
<td>x</td>
</tr>
<tr>
<td>4.3</td>
<td>0.72</td>
<td>x</td>
</tr>
<tr>
<td>4.9</td>
<td>0.27</td>
<td>x</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>x</td>
</tr>
<tr>
<td>5</td>
<td>0.95</td>
<td>x</td>
</tr>
<tr>
<td>5</td>
<td>1.17</td>
<td>x</td>
</tr>
</tbody>
</table>

For this reason, return flow is initiated prior to reach the drop base. The restoring upward force, due to stabilizing density gradients, restricts the flow (downward motion and return rising flow) to a relatively small portion of the upper part of the drop (see Fig. 6).

The surface motion transfers warm liquid from the top to the bottom region of the drop until separation occurs. Buoyancy and continuity bring the fluid upward again, resulting in a closed toroidal vortex.

This behaviour appears in the fringes pattern in the form of a couple of curls that are initially formed close to the drop surface and then are transported upward by the buoyancy effects. The phenomenon behaves as a disturbance travelling towards the top (i.e. a perturbation of the solutal and flow field periodically rising along the symmetry axis).

Instead of a steady regular plume, release of solute occurs in the form of discrete events separated by certain time (and thus space) intervals. The instability in fact leads somehow to a periodic release of lighter fluid in the surrounding liquid (Fig. 5).

A systematic analysis has been carried out to determine the critical temperature gradient $\nabla T$ for different initial volumes of the droplets. The results show that the critical temperature gradient is an increasing function of the initial volume of the droplet (see Table 2). If the stability diagram is represented in the Marangoni–Rayleigh non-dimensional plane, the experimental results can be summarized as in Fig. 7. Here, the Marangoni and Rayleigh numbers are defined as

$$Ma = \frac{\Delta \sigma d}{\mu \alpha} \quad Ra \approx \frac{g \Delta \rho d^3}{\mu \alpha}.$$  

Fig. 7 shows that the oscillatory instability arises when the two driving forces (buoyancy and surface tension) are of comparable orders of magnitude (i.e. for $Ra = Ma$). It must be pointed out, however, that the experimental conditions refer to a limited range of drops volumes, because the gravity effect makes not possible to investigate drops larger than 5 µl.

3. Numerical simulations

3.1. Numerical model

A numerical code has been developed to simulate the real experimental conditions, solving the field equations with a finite volume formulation.

The model is based on the assumption that a spherical drop is bounded by a liquid/liquid interface, whose radius changes in time due to the dissolution. The hypothesis of spherical surface is acceptable since, at the experimental conditions, the drop volumes and the density differences between the two phases are very small.

The moving boundary problem is based on the introduction of a phase-field variable $\phi$ changing smoothly but rapidly through the interface region from one phase to the other (drop phase $1 \rightarrow \phi = 1$, matrix phase $2 \rightarrow \phi = 0$).
The mass species diffusion is governed by the equations

\[
\frac{\partial C_i}{\partial t} = \phi [\nabla \cdot (\nabla C_i) + D \nabla^2 C_i],
\]

(1)

\[
\frac{\partial C_2}{\partial t} = (1 - \phi) [\nabla \cdot (\nabla C_2) + D \nabla^2 C_2],
\]

(2)

where \(D\) is the diffusion coefficient.

The behaviour of the two phases is coupled through the equilibrium concentration values imposed on interface sides

\[
C_1|_i = C_{1(e)}(T),
\]

(3)

\[
C_2|_i = C_{2(e)}(T).
\]

(4)

The flow field is governed by the continuity, and Navier–Stokes equations

\[
\nabla \cdot \mathbf{V} = 0,
\]

(5)

\[
\frac{\partial (\rho \mathbf{V})}{\partial t} = -\nabla p - \nabla [\rho \nabla \phi] + \nabla \cdot [\mu \nabla \mathbf{V}] + \mathbf{F}_g,
\]

(6)

where

\[
\rho = \rho_{1(o)} \phi + \rho_{2(o)} (1 - \phi),
\]

(7a)

\[
\mu = \mu_1 \phi + \mu_2 (1 - \phi).
\]

(7b)

The Boussinesq approximation is used to model the buoyancy forces

\[
\mathbf{F}_g = g [\beta_1 (C_1 - C_{1(o)})] \phi + g [\beta_2 (C_2 - C_{2(o)})] (1 - \phi) + \rho g [\beta_{T1} (T - T_{1(o)})] \phi + \rho g [\beta_{T2} (T - T_{2(o)})] (1 - \phi),
\]

(7c)

where \(\beta_1\) and \(\beta_2\) are the solutal expansion coefficients, \(\beta_{T1}\) and \(\beta_{T2}\), the thermal expansion coefficients.

The temperature distribution is governed by the energy equation

\[
\frac{\partial \rho C_T}{\partial t} = [\nabla \cdot (\rho C_T \nabla T) + \nabla \cdot (\lambda \nabla T)],
\]

(8)

where the thermal conductivity \(\lambda\) and the specific heat \(C_T\) are computed as

\[
\lambda = \lambda_1 \phi + \lambda_2 (1 - \phi),
\]

(9a)

\[
C_T = C_{P1} \phi + C_{P2} (1 - \phi).
\]

(9b)

The tracking of the interface between the phases is accomplished by the solution of a special continuity integral equation for the volume of the liquid drop taking into account the release or absorption of solute through the interface. The liquid drop is assumed to be a sphere of radius \(R\) increasing due to growth or decreasing due to dissolution. Using mass balance, one obtains for the time evolution of the radius

\[
\frac{dR}{dt} = D \frac{1}{S} \oint C_1|_i - C_2|_i \left( \frac{\partial C_2}{\partial n} \bigg|_i - \frac{\partial C_1}{\partial n} \bigg|_i \right) \, dl,
\]

(10)

where \(S\) is the surface of the drop, and

\[
\frac{\partial C}{\partial n} = \nabla C \cdot \hat{n} = \lambda \frac{\partial C}{\partial x} + \beta \frac{\partial C}{\partial y},
\]

(11)

\[
\hat{n} = -\frac{\nabla \phi}{|\nabla \phi|} = (\alpha, \beta).
\]

(12)

After the computation of the radius at the new time step \((n + 1)\), then the distribution of the phase variable \(\phi\) is re-initialized to take into account the volume change i.e. \(\phi = 1\) for \(r < R\) and \(\phi = 0\) for \(r > R\).

The Marangoni condition at the drop interface reads (hereafter the subscripts \(s\) and \(n\) denote directions parallel and orthogonal to the interface, respectively)

\[
\mu_1 \frac{\partial V_s}{\partial n} \bigg|_1 - \mu_2 \frac{\partial V_s}{\partial n} \bigg|_2 = \sigma T \frac{\partial T}{\partial s}.
\]

(13)

Depending on the interface’s orientation and on the side (phase (1) or phase (2)) on which computations are performed, gradients are discretized by forward or backward schemes. Further details on the method are reported in [5].

4. Results and discussions

The results of the numerical simulations are in sufficient agreement with the experimental findings (Figs. 8, 9, 10).

The mathematical model and the associated numerical algorithm have proven to be able to “capture” the complex time-dependent phenomena and to provide information and data about the intrinsic nature of the instability. For instance, the numerical simulations show that the curls in the interference fringes pattern correspond to the presence of a toroidal convection
Fig. 8. Experimental (a) and numerical (b) results. The composition distribution is shown at different times (the oscillation period is 19 s; the time interval between two numerical images is 3 s).

Fig. 9. Measured dissolution rates at isothermal conditions ($T = 25\,^\circ C$ and $35\,^\circ C$) and in presence of a prescribed temperature difference ($\Delta T = 10\,^\circ C$).

Fig. 10. Drop dissolution rate in presence of a temperature difference of $10\,^\circ C$. Comparison between 1 g and 0 g results.

<table>
<thead>
<tr>
<th>Droplet volume (μl)</th>
<th>Oscillation period (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
</tr>
</tbody>
</table>

The comparison between the computed and measured oscillation frequencies is summarized in Table 3. Roll periodically released at the peak of the dissolving drop.

Moreover computations obtained “switching off” surface tension effects, have proven that the presence of the Marangoni effect is crucial in determining this kind of flow instability. In absence of Marangoni effect the solutal jet is not broken into discrete events and the aforementioned characteristic curls do not appear.
The results refer to experiments performed at different droplets volumes, in correspondence of the critical temperature gradients. The numerical results are in sufficient agreement with the experimental values and show that the oscillation period increases with the drop size.

The numerical simulations also show that, for a prescribed drop volume, the oscillation frequency is an increasing function of the temperature gradient.

An interesting experimental result is shown in Fig. 9: the dissolution process for a droplet with prescribed volume is slower when the matrix is subject to an imposed temperature gradient, compared to the isothermal case.

To explain this behaviour, numerical simulations have been carried out at the same experimental conditions (corresponding to an imposed temperature difference of $\Delta T = 10^{\circ}C$) in presence or in absence of the Earth gravity field.

The results (see Fig. 10) show that the dissolution speed is larger in zero gravity conditions, where only Marangoni flow are present, and this is in agreement with the experimental finding, because in the gravity field and in presence of temperature gradients buoyancy and Marangoni effects are counteracting, resulting in smaller dissolution speeds.

5. Conclusions

The laboratory experiments have shown that in the Earth gravity field buoyancy and surface tension-driven convection arise close to a drop dissolving in a liquid matrix. At isothermal conditions or in presence of sufficiently small temperature gradients, buoyancy effects prevail with an upward flow (plume) starting from the tip of the drop.

In presence of relatively high-temperature gradients, when Marangoni effects are of the same order of buoyancy effects, an oscillatory convective instability appears.

The oscillation frequency has been evaluated for different drop volumes or, correspondingly, for different values of the Rayleigh and Marangoni characteristic numbers.

A numerical model, based on a volume control method, has been developed to correlate the experimental results and to explain the instability mechanism, following from the delicate balance between counteracting buoyancy and thermally driven surface tension forces.

References