No migration of ionic liquid under temperature gradient

Wei Huang*, Xiaolei Wang

College of Mechanical & Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, China

HIGHLIGHTS

• No migration of ionic liquid was observed under temperature gradient.
• The strong Coulombic force increases bonding strength at liquid/solid interface.
• Surface tension of ionic liquid is promoted by ions alternation.
• The Coulombic interactions in interior part increase the droplet’s cohesive work.
• The no migration property reinforces the possibility of ionic liquid as lubricant.

GRAPHICAL ABSTRACT

Droplet migration under temperature gradient is ubiquitous throughout science and engineering. For the molecular type lubricants, the migration performance can be well described by a dynamic model based on Marangoni effects. However, no migration of ionic liquid droplet was observed under temperature gradient. The abnormal behavior may originate from a combination of ordering structure of ions in the interfaces as well as the Coulombic interactions in interior part. The finding reinforces the possibility of ionic liquid as lubricant.

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1. Introduction

Thermo-capillary migration is an important phenomenon that surface thermal gradients will drive liquid to flow from warm to cold regions. The physical explanation of the movement is that the thermal gradient produces a gradient of interfacial tension along the droplet surface, which propels the droplet toward regions where its interfacial tension would be reduced [1]. This thermally induced migration plays a key role in the fluidic controls and mechanical lubrication aboard spacecraft due to the changeable temperatures (−60 to −200 °C) and microgravity [2]. Oil migration not only reduces the amount of fluid available for lubrication, it also increases the exposed surface area of the fluid [3]. As a direct result, the lifetime of spacecraft is reduced.

Usually, an anti-migration coating [4] or mechanism geometry [5] is proposed to obstruct liquid migration. Besides, seeking novel lubricants with low migration tendency is also an effective way

* Corresponding author at: Yudao street 29#, Nanjing, China.
E-mail address: huangwei@nuaa.edu.cn (W. Huang).

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for the spacecraft moving assemblies to sustain acceptable performance throughout the operational lifetime [6].

Ionic liquids (ILs) are organic salts with melting points below 100 °C and its potential as lubricant was recognized for the first time in 2001 [7]. After that, lots of group carried out research works in this area [8–11]. Thanks to their properties of thermal stability, non-volatile and reasonable viscosity–temperature behavior, ILs appear to be suitable candidates as new aerospace lubricants [12–14]. In this paper, distinct migrating manner of ILs was observed and the authors believe that this phenomenon, up to now unexplored, is of particular interest in the field of space lubrication.

2. Experimental details

Here we will focus on the thermally driven droplet on horizontal surface. The apparatus used in this study includes two temperature-controlled aluminium blocks placed on a horizontal platform. A metal (304 stainless steel) substrate with surface roughness Ra in the range of 10–20 nm was attached between the cooling and heating blocks, so that a temperature gradient could be generated along the surface. Each time, the lubricant was dripped at the same location of the warm side and the motion of the droplet was monitored with a camera. Detailed description of the instrument and test process can be found in relevant literatures [15,16].

In this study, 1-ethyl-3-methylimidazolium tetrafluoroborate (99.9% purity) IL ([Emim][BF4]) was chosen for its potential application prospects. The [Emim]+ cations form a pillar with the β-carbon of the ethyl group sticking out of the imidazolium-ring plane [17]. For comparison, several popular molecular type lubricants used in space were also tested, including polyalphaolefin (PAO), silicone and perfluoropolyether (PFPE). Their chemical structures are shown in Fig. 1. Before the migration test, a rotation viscometer was used to analyze the viscosity of the liquids. The contact angle was measured by a contact angle goniometer using an optical subsystem to capture the profile of a pure liquid on a solid substrate. Surface tension of the lubricants was measured by the Wilhelmy plate method. By measuring the surface tensions at a variation temperature of the lubricants, the thermal coefficient of surface tension can be obtained. A summary of the main properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PAO</th>
<th>Silicone</th>
<th>PFPE</th>
<th>IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>η (mPa·s)</td>
<td>45</td>
<td>100</td>
<td>833</td>
<td>45</td>
</tr>
<tr>
<td>θ (°)</td>
<td>7±1</td>
<td>/</td>
<td>/</td>
<td>90±1</td>
</tr>
<tr>
<td>γ (°)</td>
<td>29.02</td>
<td>20.53</td>
<td>18.74</td>
<td>45.56</td>
</tr>
<tr>
<td>dy/dT</td>
<td>-0.0814</td>
<td>-0.0456</td>
<td>-0.0337</td>
<td>-0.0795</td>
</tr>
</tbody>
</table>

Table 1: Physical properties (20 °C) of the liquids.

The droplets of the molecular type lubricants, as expected, migrate at different levels along the temperature gradient. However, the IL remains stationary during the time test. Fig. 3 presents the velocity of induced migration as a function of the time. It shows that the highest initial velocity of the molecular type liquid reaches 2.5 mm/s and it decreases gradually and flattens later. For IL, the visible rate is zero. During the experimental process, the no migration behavior was also found when using several kinds of other ILs even under a higher temperature gradient of 5.0 °C/mm and a droplet volume of 10 μL.

For the molecular type lubricants, they appear a similar migration performance. The migration results can be well described by a dynamic model based on Marangoni effects [18]. Considering a droplet moving on a solid surface in response to a positive thermo capillary stress τ(x) are as follow [19]:

\[ \tau(x) = \frac{dy}{dT} \times \frac{dT}{dx} \]

where \( \gamma \) is the liquid–vapor surface tension, \( T \) is the liquid surface temperature. The stress produces a velocity gradient in the liquid could be written as[20]:

\[ \frac{dV(x,z)}{dz} = \frac{\tau(x)}{(T)} \]

where \( z \) is in the direction perpendicular to the solid surface, \( V(x,z) \) is the liquid velocity in the x direction, and \( \eta(T) \) is the temperature.
dependent viscosity. Assuming liquid at the metal surface without slip, the velocity of the liquid flow is approximately a linear function of \( z \), then:

\[
V(x, z) = \frac{\tau(x)}{(1)} z
\]  

(3)

Thus, the equation governing the drop average velocity at \( x \) is as follows:

\[
V(x) = \frac{\tau(x)}{(1)} z
\]  

(4)

where \( z(x) \) is the film thickness at \( x \). Based on the simplified theoretical model, the migration can be specified by the balance between the viscous force and the driving force of surface tension gradient. The lubricant PAO possesses the highest \( dy/dT \) and the lowest \( \eta \) among the liquids (see Table 1). Thus, PAO experiences the highest migration velocity. Correspondingly, PFPE shows the lowest velocity because of its high \( \eta \) and low \( dy/dT \) values. The one exception is IL. Since the values of \( \eta \) and \( dy/dT \) is similar to PAO, the migration velocity of IL is expected to be close to that of PAO according to the Eq. (4).

A question then arises: why does IL exhibit no migration behavior? Different from molecular type lubricants, ILs are complex because they combine properties from molten salts and organic liquids. The abnormal performance may be connected with the complex interface and internal properties of ILs. To explain the unusual phenomenon, the droplet was discussed from the viewpoints of: (1) IL/solid interface, (2) IL/gas interface and (3) the interior of the droplet, shown in Fig. 4.

In the IL/solid interface, strong Coulombic force increases bonding strength between the liquid and substrate. The IL/solid interface consists of the layer of ions in direct contact with the substrate. Theoretical investigations show that the ions orientation and position at liquid/solid interfaces are well-ordered [21,22]. Such structures have also been confirmed by atomic force microscopy [23,24] and X-ray reflectivity [25] experimentally. As is known, metals are highly polarizable with free electrons [26]. Since the innermost layer of ILs in the interface is cation rich [27], strong Coulombic forces could be formed between the cations and induced charges (free electrons). While for the interface of molecular type liquid/solid, the associated force is mainly of geometric origin [28]. So, the ILs near the IL/solid interface experience more attraction than those of molecular type liquid, which can generate greater adsorption energies in the interface. Thus, the boundary layer migration could be effectively inhibited.

In the IL/gas interface, surface tension of IL was promoted by ions alternation. In the outermost layer, ions of one charge are surrounded by ions of the opposite [29]. Similar arrangement of ions at the IL/gas interface is also concluded according to the calculation of cation–anion interaction energies [30] and surface entropy [31]. This ordered orientation of the cations and the anions, as a chain structure, forms a strong electrostatic interaction in the outer shell, which will, no doubt, elevate the IL surface tension (see Table 1). This speculation can also be confirmed from the highest contact angle (\( \theta = 57 \pm 1^\circ \)) of [Emim][BF_4] among the four liquids. In addition, for the same liquid volume used, the highest contact angle naturally results in the smallest initial contact area between the IL and the substrate, which might further weaken the driving force on the droplet. Apparently, the high surface tension helps to prevent liquid migration.

The interior part is inferred to improve the droplet’s cohesive work. The physical properties of ILs are governed by a complex combination of unscreened Coulomb, van der Waals, dipole, and hydrogen bonding interactions, which seldom occur together in other materials [32]. The calculated interaction energy of ion pairs ([Emim][BF_4]) is about –85.2 kcal/mol [33], which is an order of magnitude higher than the intermolecular interaction energy in molecular type liquid [34]. The Coulombic interactions are considered to be the major source of attraction in ILs and this strong attraction should contribute to the cohesion of the droplet, which could resist droplet deformation and migration. Meanwhile, the contact angle can also be related to the droplet’s cohesive work. As shown in Table 1, the IL presents the highest contact angle, which means the attractive force of the ions in IL is stronger for each other than the intermolecular interaction in the molecular type liquids. As a result, the adhesion work between metal surface and IL could be lower than that of molecular type lubricant. In other words, the higher adhesion work between metal surface and molecular type lubricant help the lubricant migrate.

4. Summary and outlook

In this study, experiments were carried out to investigate small liquid lubricant droplets propelled across a chemically homogeneous metal surface by a constant thermal gradient. The migration model of the traditional molecular type lubricants could generally be predicted by the Marangoni effects. However, no migration of IL droplet under temperature gradient was observed. Possible mechanisms could be the ordering structures of ions in the interfaces as well as the Coulomb force in interior part. Besides that, attention should be paid on the high energy molecular structure of IL at the gas/liquid interface and the high liquid/solid interaction. Since the high energy structure would lead to no-slip flow boundary while the high liquid/solid interaction might result in the local solid deformation. These are important directions for future research.

From a tribological perspective, ILs are increasingly attracting interest due to their high thermal stability and enhanced viscosity. The finding of no migration property will reinforce the possibility of ILs as space lubricants to minimize migration loss since oil supply is always restricted. Moreover, the no migration property also makes ILs attractive to minimal quantity lubrication system due to an inevitable temperature gradient originated from friction heat.

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References


