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Static and dynamic wetting behaviour of ionic liquids

Iliana Delcheva, John Ralston, David A. Beattie, Marta Krasowska *

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Adelaide, Australia

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ABSTRACT

Ionic liquids (ILs) are a unique family of molecular liquids ('molten salts') that consist of a combination of bulky organic cations coupled to inorganic or organic anions. The net result of steric hindrance and strong hydrogen bonding between components results in a material that is liquid at room temperature. One can alter the properties of ionic liquids through chemical modification of anion and cation, thus tailoring the IL for a given application. One such property that can be controlled or selected is the wettability of an IL on a particular solid substrate. However, the study of wetting of ionic liquids is complicated by the care required for accurate and reproducible measurement, due to both the susceptibility of the IL properties to water content, as well as to the sensitivity of wettability measurements to the state of the solid surface. This review deals with wetting studies of ILs to date, including both static and dynamic wetting, as well as issues concerning line tension and the formation of precursor and wetting films.

Contents

1. Introduction

In contrast to aqueous solutions of common salts, ionic liquids (ILs) consist of ions in the absence of solvent molecules. These substances are usually composed of bulky organic cations coupled to organic or inorganic anions. Due to the delocalised charge in the organic components of these substances, as well as the steric mismatch between the IL ions, the formation of a stable crystal lattice is hindered. The presence of large asymmetric cations and strong hydrogen bonds can greatly decrease the temperature of the solid–liquid transition [1]. As a result, many of these organic salts are liquids at room temperature. The melting point of these materials is typically around or just below 100 °C.

ILs have gained considerable academic and industrial interest due to their unique properties, such as high thermal stability, non-flammability, and negligible vapour pressure. ILs are sometimes called 'designer' liquids because their properties (such as viscosity and refractive index) may be easily tailored by small variations of the chemical composition. Their intrinsic characteristics, together with the results obtained from tribological studies [2,3], suggest that these substances are among the potential candidates to replace conventional mineral oils as lubricants. In addition, ILs are being considered as electrolytes in energy applications (Li-ion batteries, electro-optical imaging, supercapacitors, etc.), and for this application, as well as many others, the wetting characteristics of the IL in contact with a solid substrate are critically important.

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* Corresponding author. Tel.: +61 8 8302 6861.
E-mail address: marta.krasowska@unisa.edu.au (M. Krasowska).

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As with any other liquid (molecular or solution), upon contact of an IL droplet with a solid substrate, the drop will evolve towards its thermodynamic equilibrium state: it either spreads completely on the solid, forming a thin (wetting) liquid film, or creates a three-phase (liquid, solid and the surrounding vapour) system, in which the three interfaces intersect at a three-phase contact line [4]. These two types of wetting regimes are referred to as complete and partial wetting, respectively. In the latter regime, the drop wets a certain area of the solid substrate, which is enclosed by the three-phase contact line. The contact angle that is formed at the contact line between the liquid–vapour and the solid–liquid interfaces when the system reaches its state of minimal free energy is called the equilibrium contact angle, θ_{eq}. This contact angle is a quantitative measure of the wetting properties.

2. Theory 1: static contact angles

The equilibrium contact angle is connected to the three interfacial tensions γ_{SV}, γ_{SL}, and γ_{LV} of the solid–vapour, solid–liquid, and liquid–vapour interfaces. This follows from the requirement of mechanical balance at every point of the contact line. Free energy minimisation leads to Young's equation[1]

$$\cos\theta_{eq} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}. \tag{1}$$

Young's equation can be rewritten in terms of the free energy of cohesion, W_C, and adhesion, W_A [6]. By definition, W_C is the work (free energy) per unit area required to isothermally split in two a column of condensed matter. During this process two new flat liquid–vapour interfaces are created; thus the cohesion free energy per unit area has the form:

$$W_C = 2\gamma_{LV}. \tag{2}$$

Analogously, W_A is defined as the work (free energy) per unit area required to isothermally split in two parts a column of two condensed phases in contact. In this case, a flat liquid–vapour and a flat solid–vapour interface, respectively, are created, while the initial solid–liquid interface is destroyed. W_A is thus given by:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}. \tag{3}$$

Consequently, Eq. (1) can be re-written as

$$\cos\theta_{eq} = \frac{2W_A}{W_C} - 1. \tag{4}$$

Young's equation applies to ideally rigid, chemically inert and homogeneous solid surfaces that are smooth at the atomic level; however, real solid substrates rarely possess all these characteristics. In real systems, in which surfaces usually are rough and/or chemically heterogeneous, the contact line is immobile not only when the local contact angle has reached its equilibrium value, but also when it falls in a more or less wide range of contact angle values. These local contact angles correspond to metastable states, i.e. to local minima of the free energy of the system. Among all of these states, only the ones corresponding to the lowest and highest value of the contact angle can be meaningfully characterised. These are known as the receding, θ_{rec}, and the advancing, θ_{adv}, contact angles. The equilibrium contact angle falls in-between, $\theta_{rec} \le \theta_{eq} \le \theta_{adv}$ [7], and the difference, $H = \theta_{adv} - \theta_{rec}$, is called contact angle hysteresis.

3. Theory 2: dynamic contact angles

Wetting phenomena find many applications in industrial and engineering processes such as flotation, production of high quality coatings, paints and lubricants, and printing. Most of these processes rely on dynamic wetting, i.e. the motion of a liquid, advancing or receding over a surface due to either the unbalanced interfacial tensions at the contact line or the application of an external force on the system [4,8]. The contact angle θ, measured when the contact line is in motion, is the dynamic value. In general, for a Newtonian liquid, two types of mechanisms influence the dynamic wetting process: viscous hydrodynamic flow in the bulk of the liquid and friction at the moving contact line. Two models, each emphasising one of the mechanisms, are usually employed to describe dynamic wetting.

The first model, the so-called hydrodynamic approach, is based on the assumption that the excess free energy, which is due to deviations of the shape and the contact angle of the droplet from those at equilibrium, is dissipated by the viscous flow in the moving liquid. For low capillary numbers, $Ca = V\eta / \gamma_{LV}$, for the fluid phase in motion, the relation between the dynamic contact angle and the velocity of the contact line, V, was determined by Cox [9] and Voinov [10]. In a simplified form (for small contact angles and low viscosity surrounding fluid) it reads:

$$V = \pm \frac{\gamma_{LV}}{9\eta} \frac{\left(\theta^3 - \theta_{eq}^3\right)}{\ln\left(\frac{L}{L_S}\right)}, \tag{5}$$

where η is the viscosity of the liquid, L stands for a characteristic length, such as the droplet size, and L_S is a slip length (accounting for a slip boundary condition at the contact line). The positive sign of the velocity denotes an advancing contact line, while the negative: a receding one. More complex expressions for solid-liquid-liquid systems, accounting for the viscosities of both of the fluids, also exist [9]. Although derived for small contact angles, θ, and a 'liquid wedge' geometry, this equation was shown to describe well the process of dynamic wetting also for spreading drops and for contact angles up to $\theta_C \approx 13 / 18\pi$ (130°) [11].

The other model usually used to describe the dynamics of wetting attributes the dissipation of the excess free energy to the interactions between the molecules of the liquid and the solid phase at the contact line. Blake [12] suggested that the spreading of the liquid is determined by the processes of adsorption and desorption of molecules at the contact line; the movement of the wetting line in a given direction is attributed to a disturbance of the adsorption/desorption equilibrium, characterised by frequency k_0, due to the out of balance free energy per unit area $\gamma_{LV}(\cos\theta_{eq} - \cos\theta)$. According to the molecular-kinetic (MK) model, the macroscopic result of this disturbance is the motion of the contact line with a velocity, V, dependent on the dynamic contact angle, θ:

$$V = \pm 2k_0\lambda \sinh \frac{\gamma_{LV}\left(\cos\theta_{eq} - \cos\theta\right)\lambda^2}{2k_B T}. \tag{6}$$

Here λ denotes a microscopic characteristic length scale related to an average distance between 'adsorption sites', k_B is the Boltzmann constant, and T is the absolute temperature. When the argument of the hyperbolic sine function is very small, Eq. (6) can be reduced to the linear form:

$$V = \frac{\gamma_{LV}}{\zeta}\left(\cos\theta_{eq} - \cos\theta\right), \tag{7}$$

where $\zeta = k_B T / k_0\lambda^3$ denotes the 'contact line friction' coefficient and has the physical dimensions of a shear viscosity.

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[1] Named after the famous English scientist Thomas Young, who was the first to suggest in his paper from 1805 that "*for each combination of a solid and a fluid, there is an appropriate angle of contact, between the surface of the fluid, exposed to the air, and to the solid*" [5].

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