Surface Chemistry

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Surface Wetting in Liquid–Liquid–Solid Triphase Systems: Solid-Phase-Independent Transition at the Liquid–Liquid Interface by Lewis Acid–Base Interactions**

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Many reactions such as phase-transfer catalysis, nanocrystal synthesis, electrochemical deposition, and self-assembly are usually carried out in liquid–liquid–solid triphase systems (LLSTSs), in which the two liquid phases are often an aqueous phase and a hydrophobic organic liquid phase.[1–4] To achieve desirable products, it is crucial to control the wetting process of the organic liquid on the surfaces of solid substrates in aqueous environment.[1,4] For those reactions involving structured and chemical stable solid substrates, typical routes to alter the surface wettability are restricted because of the untunable solid surface tension. Thus, structured surfaces require a new strategy for a tunable surface wettability that is independent of the solid phase.

To the best of our knowledge, inspiration from natural surfaces with special wettability properties, such as lotus leaves, water strider legs, spider silks, and fish scales, scientists have already made much progress on tuning the surface wettability.[5–10] These methods can be classified into two major categories: synthesis of functional materials and construction of hierarchical surface structures, which are all depending on control of the solid phase.[11–16] The liquid phase plays an equally important role for the surface wettability.[8,17–20] However, little attention has been paid to tuning the surface wettability through control of the interactions at the liquid–liquid interface.

Here we show that solid-phase-independent surface wetting transitions can be realized through control of the polar interactions at liquid–liquid interfaces. Investigations of the wetting process of polar oils on solid surfaces in acidic or basic aqueous phases show oleophilic to oleophobic and superoleophobic wetting transitions on nonresponsive smooth and microstructured surfaces. The switchable wettability is attributed to the decrease of the liquid–liquid interfacial tension (LLIT) which is caused by Lewis acid–base interactions at the oil–water interface. This study provides a strategy to control the wettability from a new point of view and may inspire scientists working on chemical reactions involving LLSTSs.

Lewis acid–base (AB) interactions, that is, electron-acceptor and electron-donor interactions, sometimes play a dominant role in wetting, adsorption, adhesion, dispersion, and other related interfacial phenomena, and thus attract widely the interest of chemists working in surface chemistry and colloidal science.[21–25] Based on the Lewis AB principle, liquids can be categorized into polar liquids with acid–base properties and apolar liquids.[22] Fowkes pointed out that an attractive force exists at the interface of a Lewis acidic liquid and Lewis basic liquid because of electron donor–accepter interactions, and this attractive force can greatly decrease the interfacial tension of these two phases.[26,27] Such Lewis AB interactions at the liquid–liquid interface might be used to tune the solid surface wettability in LLSTS (the solid surface is stable and nonresponsive).

In our studies, haloalkanes such as dichloromethane, 1,2-dichloroethane, and bromohexane were used as polar oils. In haloalkanes, the carbon atom, to which the halogen atom is attached, is slightly electropositive whereas the halogen atom is slightly electronegative. This difference in electronegativity results in an electrophilic carbon atom, that is, the Lewis acid, which can attract nucleophiles such as hydroxide ions, that is, Lewis bases. Therefore, haloalkanes can be considered as Lewis acidic oils in our studies. In contrast, apolar oils such as hexane, octane, and decane were used in control experiments. Aqueous solutions with pH values from 2 to 13 were used as tunable aqueous phases from acidic to basic. Smooth silicon substrates modified with a monolayer of fluoroalkylsilane (FAS) and trimethoxypropylsilane (TMS) molecules were used as stable and nonresponsive surfaces in the aqueous phase.

Figure 1 shows oil contact angles on the nonresponsive substrate as a function of the pH value in the aqueous phase. For FAS-modified surfaces, it is shown in Figure 1a that the contact angles of 1,2-dichloroethane are constant in acidic and neutral pH ranges. However, when the pH values are larger than 10, the contact angles dramatically increase with increasing pH. The contact angles increase from smaller than 50° to larger than 80°. For the TMS-modified surface, the contact angles of 1,2-dichloroethane increase from smaller

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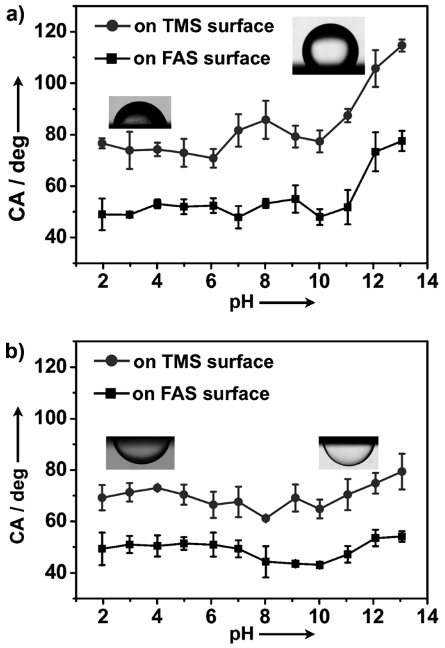

Figure 1. Contact angles (CA) of the oil droplets on nonresponsive substrates as a function of the pH value in the aqueous phase: a) 1,2-dichloroethane and b) hexane on FAS- (black line with ■) and TMS- (gray line with ●) modified smooth silicon surface, respectively. The insets are the photos of oil drops on the TMS surface in pH 3 (left) and pH 12 (right) aqueous phases, respectively. For 1,2-dichloroethane, the surface wettability transmits from oleophilic to oleophobic when the pH is increased to basic. For hexane, the surface wettability remains oleophilic throughout the whole pH range.

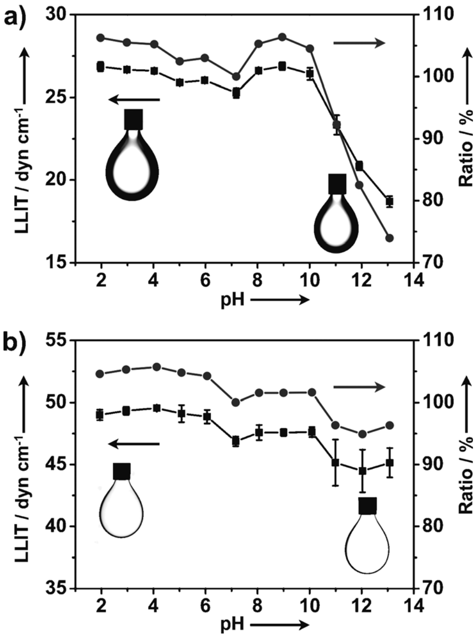

Figure 2. LLIT tunable by Lewis acid–base interactions. a) LLIT of 1,2-dichloroethane and b) hexane in the aqueous phase as a function of the pH value (black line with ■) and the ratio of the LLIT at a certain pH to the LLIT at pH 7 (gray line with ●). The insets show the pendant oil drops when the LLIT is measured in pH 3 (left) and pH 12 (right) aqueous phases, respectively. For the Lewis acid 1,2-dichloroethane, the LLIT dramatically decreases with increasing pH; a smaller pendant drop at pH 12 indicates the decrease of the LLIT. For apolar hexane, the LLIT shows almost no change from pH 2 to 13; the size of the two pendant drops are almost the same, indicating almost no change of the LLIT.

than 70° to larger than 110°, indicating that the solid surface wettability has transmitted from oleophilic to oleophobic (Figure 1 a, insets). In contrast, as shown in Figure 1 b, the contact angles of hexane are only slightly changed on FAS- and TMS-modified surface, no matter whether the aqueous phase is acidic or basic. The surface wetting transition is only observed when the Lewis acidic oil is placed in basic aqueous environment. Considering the solid surface is not pH-responsive, it is proposed that the surface wetting transition can be attributed to the tunable interfacial tension at the oil–water interface caused by Lewis AB interactions.

To study the Lewis AB interactions at the oil–water interface, we measure the LLIT of polar and apolar oils as a function of the pH value in the aqueous phase. The experiments are performed from pH 2 to 13. Through analyzing the shape of the pendant drop hanging on the needle, the LLIT can be calculated (Figure 2, insets).

It is shown in Figure 2 a (black line with ■) that for 1,2-dichloroethane, the LLIT was constant in acidic and neutral pH ranges. However, when the pH values are larger than 10, the LLIT dramatically decreases with increasing pH value. The size and shape of the pendant drop can directly reflect the LLIT value. The pendant drop at pH 12 is smaller than that at pH 3, indicating the decrease of the LLIT (Figure 2 a insets). The ratio of the LLIT measured at a certain pH value to the LLIT at pH 7 is used to quantitatively show the effect of the pH value on the LLIT (see the Supporting Information and the gray line with ● in Figure 2 a). The LLIT at pH 13 decreases to about 73 % relative to that at pH 7. To exclude the effect of ionic strength on the change of the LLIT, we measured the LLIT in a sodium chloride solution at concentrations of 0.01 and 0.1 M, the ionic strength of which is the same as in basic solutions at pH 12 and 13 (see Figure S1 in the Supporting Information). The LLIT in the sodium chloride solution only slightly increases. This indicates that the decrease of the LLIT is induced by the pH change. A similar tendency can be observed in other haloalkanes such as dichloromethane and bromohexane (see Figure S2 in the Supporting Information). In contrast, as shown in Figure 2 b for apolar oil-like hexane, the LLIT is constant from pH 2 to 13. The size and shape of the pendant drop also shows no large difference, indicating almost no change of the LLIT (Figure 2 b, insets). For other apolar oils such as octane and decane, the LLIT shows a similar tendency and is not affected by the pH value (see Figure S3 in the Supporting Information). This result can be explained by Fowkes theory.[24,25] For the haloalkane oils with Lewis acidic properties in an basic aqueous environment (pH > 7), attractive force may exist at the oil–water interface because of electron donor–accepter interactions. Such attractive force can further decrease the LLIT. This effect is similar to the effect of surfactants added to the LLSTS. The decrease of the LLIT makes the oil drop tend to form a spherical shape and increase its contact angle on the solid surface. When the aqueous environment becomes neutral or acidic, the attractive force at the oil–water interface disappears. The LLIT and the contact angle recover to their original values (see Figure S4 in the Supporting Information). In contrast, for apolar oils, no attractive force exists at the oil–water interface, no matter whether the aqueous environment is acidic or basic. Therefore, their contact angles and LLIT are constant from pH 2 to 13.

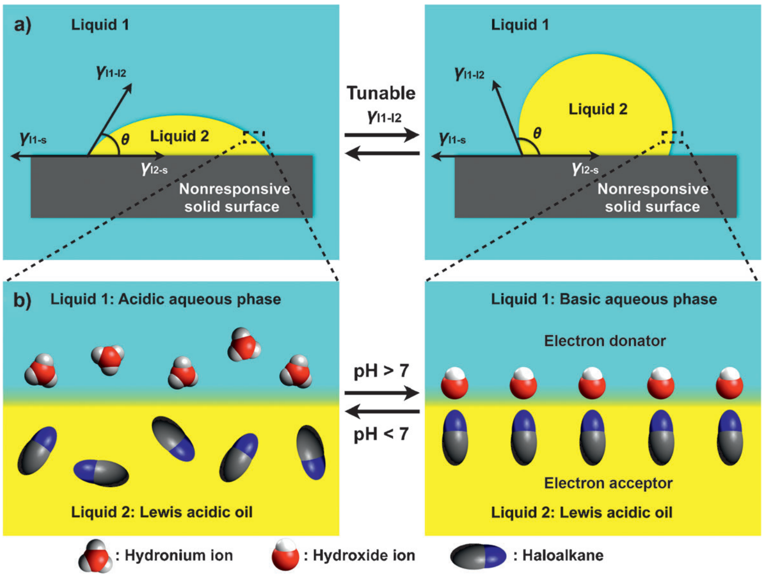

Figure 3. Tuning the surface wettability through control of the polar interactions at the liquid–liquid interface which is independend of the solid phase. a) Oil contact angles on nonresponsive solid surfaces in aqueous phase. b) For a Lewis acidic oil in acidic or basic aqueous phase, Lewis acid–base interactions, that is, electron-acceptor and electron-donor interactions may appear or disappear at the liquid–liquid interface and thus influence the contact angles and the LLIT.

By measuring the LLIT, we confirm that surface wetting transitions are caused by Lewis AB interactions at the liquid-liquid interface. In fact, this study provides a strategy to control the surface wettability from a new point of view. As shown in Figure 3a, according to the Young equation, the contact angle of a liquid dropped on a smooth solid surface is governed by γ_{l1-l2} (liquid 1–liquid 2 interfacial tension), γ_{l1-s} (solid–liquid 1 interfacial tension), and γ_{l2-s} (solid–liquid 2 interfacial tension). If the solid surface is modified with stable nonresponsive materials, γ_{l1-s} and γ_{l2-s} are pH-independent. Then, γ_{l1-l2} is the sole parameter that can influence the contact angle. Once γ_{l1-l2} is tunable, control of the solid wettability by liquid–liquid interactions can be realized. In our studies, we use Lewis AB interactions to effectively tune γ_{l1-l2}. For example, as shown in Figure 3b, for a Lewis acidic oil drop in aqueous solution at a pH change from acidic to basic the Lewis AB interactions will alter the LLIT and furthermore influence the contact angle of the oil drop on the solid surface.

The microstructures of a solid substrate can greatly enhance the surface wettability. By introducing microstructures on smooth hydrophobic or oleophobic surfaces, these surfaces will become superhydrophobic or superoleophobic.[31–34] In our system, we have already shown that smooth oleophilic surfaces can switch to oleophobic by control of the Lewis AB interactions at the oil–water interface. We expect that the wetting transition can be enlarged by introducing microstructures. Figure S5 in the Supporting Information shows a silicon substrate with micropillar array structures. After modification with FAS, the substrate is oleophilic for 1,2-dichloroethane in acidic aqueous phase (pH 3). When the aqueous phase changes to basic (pH 12), the 1,2-dichloroethane drop displays a spherical shape with contact angle larger than 150°, indicating that the surface becomes superoleophobic (Figure 4a). In this case, a basic aqueous solution is trapped in the microstructures of the surface. After contact with a Lewis acidic oil, there are Lewis AB interactions at the oil–water interface within the microstructures of the surface, which will largely enhance the oleophobicity of the surface (Figure 4a). In contrast, owing to the absence of Lewis AB interactions at the oil–water interface, no matter whether the aqueous phase is acidic or basic, the apolar hexane drop always spreads on the microstructured surface (Figure 4b). The wettability is switched by tuning the LLIT while the solid surface tension is nontraditionally controlled. Our studies indicate that strategies of tuning the surface wettability in LLSTSs are more versatile than strategies used in air–liquid–solid triphase systems (ALSTSs). In ALSTS systems, once a liquid phase such as water or some oil is chosen, the liquid–air interfacial tension is constant. Therefore, the chemical composition of the surface and the structure of the solid substrate are the two important factors that influence the surface wettability.[31–34] In contrast, in our studies, we showed that except for the above-mentioned two factors, polar

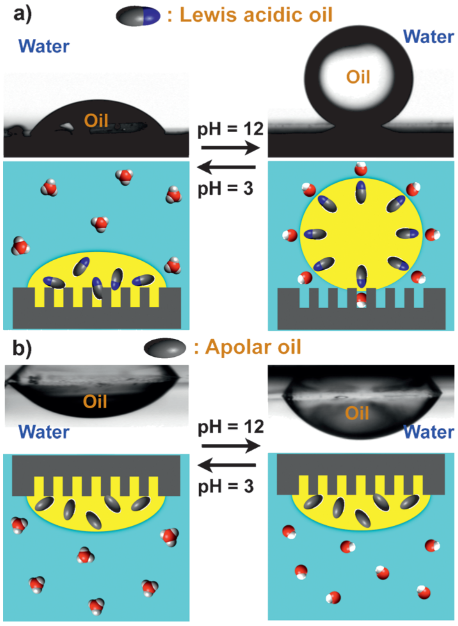

Figure 4. Wetting transition of oils on a nonresponsive microstructured surface by tuning the pH of the aqueous phase. a) For the Lewis acidic oil (1,2-dichloroethane), an oleophilic-to-superoleophobic transition is observed, which is caused by the Lewis AB interactions at the oil–water interface within the microstructures of the surface. b) For the apolar oil (hexane), the surface remains oleophilic because of the absence of Lewis AB interactions.

interactions at liquid–liquid interface are the third parameter for tuning the surface wettability.

In conclusion, a strategy for tunable surface wettability which is independent of the solid phase is presented. Through control of the Lewis AB interactions at the liquid–liquid interface, a tunable liquid–liquid interfacial tension can be achieved. Consequently, oleophilic-to-oleophobic and superoleophobic wetting transitions can occur on nonresponsive smooth and microstructured surfaces, respectively. The Lewis acidic oils used in our studies are haloalkane molecules, which belong to a group of widely and commonly used hydrophobic solvents. These polar oils play an important role in organic synthesis, catalytic reactions, and industrial processes. Our study not only provides a new strategy to control wetting processes of polar oils on solid surfaces but may also result in applications of oil–water–solid triphase systems for chemical reactions.

Experimental Section

Instruments and characterization: Scanning electron microscopy images of the substrate were measured with a field-emission scanning electron microscope (JSM-6700F, Japan).

Control of the pH value in the aqueous phase: The basic aqueous phases at pH 8–14 were prepared by dissolving NaOH in deionized water at preassigned concentrations. The acidic aqueous phase at pH 1–6 was prepared by dissolving H_2SO_4 at a preassigned concentration. A pH meter was used to measure the pH of the aqueous phase. Then the solid surface was exposed to aqueous phases of different pH values to study the wetting transition. The solid surface was washed with deionized water several times before it was exposed to a new aqueous phase.

Liquid–liquid interfacial tension (LLIT) measurement: The LLIT between two immiscible liquids was measured on an OCA20 machine (Data-Physics, Germany) at ambient temperature. The oil drop was gradually squeezed out from a needle with a diameter of 2 mm surrounded by the aqueous phase. When the volume of the oil drop reached its maximum value, the shape of the droplet was captured. The LLIT can be calculated by the shape of the pendant drop.

Contact angle measurements in the aqueous phase: Contact angles were measured on an OCA20 machine at ambient temperature. The oil drops (about 2 μL) were dropped carefully onto the substrates immersed in aqueous phase. A scheme shows the method of contact angle measurements in the aqueous phase (see Figure S6 in the Supporting Information). The average value of five measurements at different positions of the same sample was adopted as the contact angle.

Materials: Silicon wafers with microstructures were obtained by a lithographic etching porcess. The dimensions of the silicon pillars in our experiment were 100 × 100 μm, the distance between two adjacent pillars was 50 μm, and the height of the silicon pillars was 30 μm.

Modification with FAS and TMS: Cleaned silicon substrates were put into a sealed container together with a piece of glass coated with about 0.5 mL FAS or TMS. Then the container was evacuated, and the vacuum was maintained overnight.

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