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Wetting study of imidazolium ionic liquids

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ABSTRACT

In this work, we present a systematic contact angles study of a series of 1-alkyl, 3-methyl-imidazolium ionic liquids (ILs) on well-defined polar and nonpolar monolayer surfaces supported on Si wafers. The advancing and receding contact angles of ILs were used to determine the surface energy of the monolayer surfaces using Neumann's equation-of-state and Zisman's critical surface tension approaches. In parallel, the contact angles of conventional probe fluids (molecular liquids) including water, formamide, methylene iodide, ethylene glycol, and hexadecane were determined on the same surfaces. The results obtained showed a great deal of similarity in wetting behavior of ionic vs molecular probe fluids: the contact angles of both sets of liquids followed the same patterns in accord with the surface tension of the fluid. A good agreement was found between the surface energy determined by different sets of liquids.

1. Introduction

Ionic liquids (ILs), broadly defined as salts of organic cations with low melting point (<100 °C), have drawn significant attention of the researchers. The potential applications of ILs are numerous including catalysis, organic and organometallic synthesis [1–4], electrodeposition and synthesis of nanoparticles [5], extraction and separation technologies [6], etc. For the applications involving heterogeneous systems and transport of ILs in capillary, fibrous, or porous environments, interfacial properties such as wettability and adhesion of ILs are critical. This subject, however, has received so far only limited attention. Electrowetting properties of imidazolium-based ILs have been investigated for smooth Teflon [7] and for films of protected Au particles [8]. In communication [9], the authors reported contact angles for several ILs on "ultralyophobic" surfaces and concluded that ILs were useful probe fluids. It is noted that the authors of these studies used only nonpolar, low-energy surfaces, so the effect of surface composition and polar surface functionalities on wetting of ILs has not been investigated. Next, with the exception of work [7], the contact angles of ILs were reported for complex, heterogeneous (rough) surfaces, so a direct comparison of wetting behavior of ILs and conventional probe fluids (molecular liquids) commonly used for the surface analysis was impossible.

In this work, we present a first systematic investigation of the contact angles of ILs for well-defined polar and nonpolar surfaces of organosilicon monolayers supported on smooth substrates (Si wafers). The main focus of this work is a comparison of wetting of ionic vs molecular probe fluids and the applicability of ILs for the surface energy characterization of solids.

2. Experimental

2.1. General information

All solvents (HPLC grade), sulfuric acid, and potassium dichromate were obtained from Sigma-Aldrich and used as received. All organosilanes were obtained from Gelest and used as received unless specified otherwise. Water was purified using a Millipore Milli-Q system.

2.2. Si substrates

Pretreatment of Si wafers, their reaction with silanes and handling of the monolayers was done in accord with the general procedure optimized in our previous works [10,11]. Silicon wafers (International Wafer Service, 100 mm disks, 100 orientation, P/B doped, resistivity from 20 to 40 ohm cm, thickness ~450–575 μm) were cut into ~1 × 1 cm pieces. The wafers were cleaned by soaking in saturated solution of potassium dichromate in concentrated sulfuric acid for 1 h at room temperature. The wafers were rinsed with copious amounts of MilliQ water, dried in a clean oven for at least 1 h at 100 °C, and used in the reactions with organosilanes (within 30 min or sooner). Ellipsometric thickness of the native oxide layer for cleaned Si wafers was in the range 1.5–2.2 nm (for details of the ellipsometry analysis, see below).

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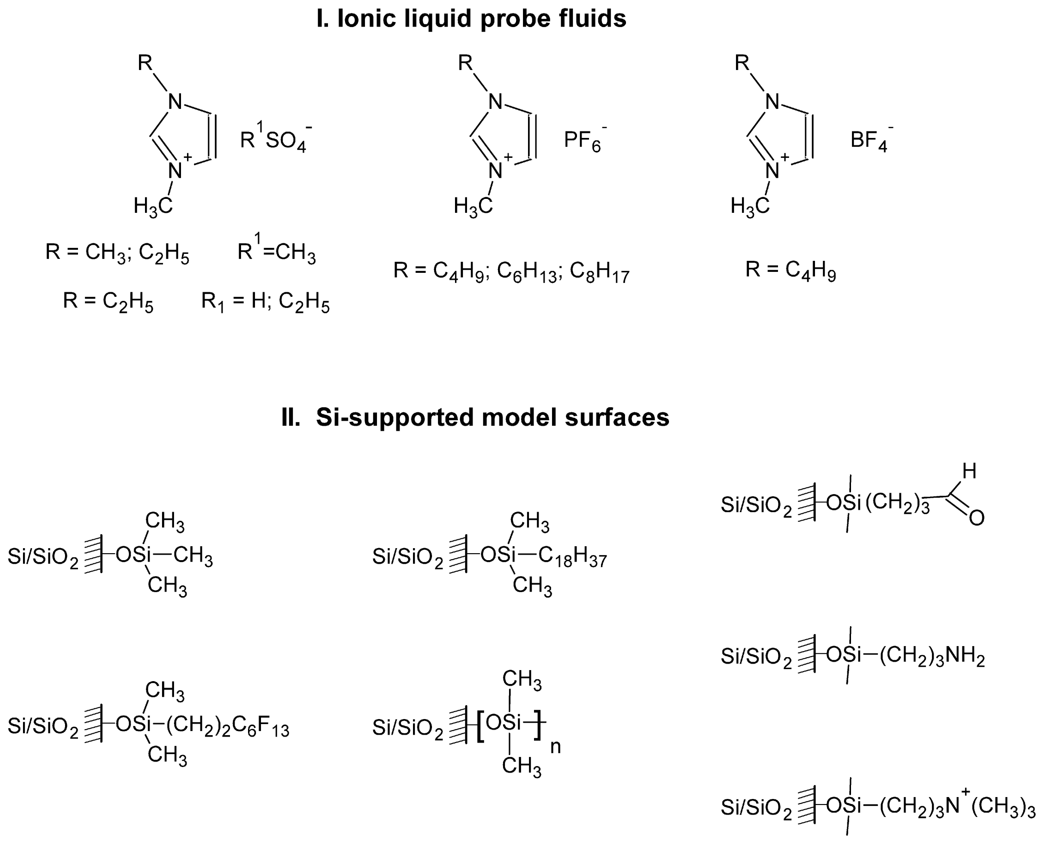

Fig. 1. Structures of the ionic liquids probe fluids and Si-supported monolayer surfaces.

2.3. *Reactions of Si wafers with organosilanes*

Alkyl-terminated surfaces were obtained by the reactions of $(CH_3)_3SiN(CH_3)_2$ and $C_{18}H_{37}Si(CH_3)_2N(CH_3)_2$. Dried plates in glass vials (one plate per vial) were covered with 10 mL of 5% (w) toluene solutions of silane and stored at room temperature overnight. After completion of the reactions, the plates were isolated and rinsed with 2 × 20 mL of toluene, 3 × 10 mL of acetone, and 3 × 10 mL of water, and dried in an oven at 60 °C. Fluorinated surfaces were obtained via the reaction of $C_6F_{13}(CH_2)_2Si(CH_3)_2N(CH_3)_2$. The silane was synthesized from the corresponding chlorosilane (Gelest) as described in [12]. The reactions with plates were carried out at 4 °C using 0.1% (w) solution of silane in toluene for 1 h. Postreaction washing of the surfaces prepared was similar to that for the alkylsilanes. Oligo(dimethylsiloxane) surfaces were obtained by the reaction of $(CH_3)_2SiCl_2$ in vapor phase. The Si plates were suspended using a sample holder (hollow glass cylinder with slots) in a flask containing 0.5 mL of silane and sealed. There was no direct contact between the liquid and the wafers during reaction. The flasks were left at room temperature overnight. After the completion, the plates were rinsed and handled as described above.

Polar surfaces were prepared from silanes containing aldehyde ($CHO(CH_2)_4Si(OC_2H_5)_3$) and amino ($NH_2(CH_2)_3Si(OC_2H_5)_3$) groups. The reaction conditions were identical to those used for alkylsilanes. The amine-terminated surfaces were further used to prepare surfaces with trimethylammonium ($N(CH_3)_3^+$) groups. The reactions were carried out using 5% (w) solution of methyl iodide in dimethylformamide for 12 h at room temperature. After the completion, the plates were rinsed with dimethylformamide (2 × 10 mL), ethanol (5 × 10 mL), and water (5 × 10 mL), and dried at room temperature.

For each silane, 6–8 batches of surfaces were prepared. Structures of the surfaces prepared are shown in Fig. 1.

2.4. *Ellipsometry and XPS characterization*

Ellipsometry was done with an Inomtech Automatic Ellipsometer ($\lambda = 651.3$ nm) at 70° angle of incidence (measured from the normal to the surface). For each individual sample, the ellipsometric angles (Δ and Ψ) were obtained as average of three measurements taken in different spots of the sample. Calculations of the monolayers thickness (d_2) were performed with the Inomtech software using the two-slabs model with the following parameters: Si substrate (refractive index, $n_S = 3.858$ and $k_S = 0.018$), layer 1, native silicon oxide ($n_1 = 1.457$, d_1); and layer 2, organosilicon film (n_2, d_2); medium, air ($n_m = 1$). Thickness of the native silicon oxide layer (d_1) was determined for each individual plate prior to the reaction with silanes. The refractive indices of the monolayers (n_2) were assumed to be equal to those of neat silanes [13]. Values of the monolayer thickness reported in Table 1 were obtained

Table 1
Characteristics of the surfaces prepared.[a]

Surface group	Thickness (nm)	XPS composition[b] (at%)			
		C	O	Si	F (or N)
$-Si(CH_3)_2(CH_2)_2C_6F_{13}$	1.03	9.0 (10.4)	29.2 (30.6)	21.9 (42.0)	39.9 (17.0)
$-Si(CH_3)_3$	0.27	27.3 (10.5)	28.3 (46.7)	44.4 (42.8)	–
$-Si(CH_3)_2C_{18}H_{37}$	1.31	60.2 (26.1)	20.2 (24.1)	19.6 (45.4)	–
$-[OSi(CH_3)_2]_n$	1.12	26.5 (22.1)	25.1 (34.8)	48.5 (43.1)	–
$-Si(CH_2)_3CHO$	5.15	48.7 (42.3)	38.7 (42.7)	12.6 (15.0)	–
$-Si(CH_2)_3NH_2$	1.18	44.5 (24.0)	30.8 (38.8)	18.5 (31.7)	6.1 (5.5)
$-Si(CH_2)_3N(CH_3)_3^+I^-$	1.43	37.3 (18.5)	42.4 (42.0)	16.8 (36.5)	3.6 (2.9)

[a] Water and hexadecane contact angles for these surfaces are listed in Table 3.

[b] Data for 15° take-off angle (~1.5 nm sampling depth). In parentheses—data for 75° take-off angle (~7 nm sampling depth).