



Advancing and receding angles – Dynamic contact angle measurements on mixed alkyl monolayers

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ABSTRACT

Mixtures of 1-decene and methyl-10-undecenoate with different mole fractions were used to prepared mixed monolayers on silicon (1 0 0) surfaces. The formed layers were characterized by dynamic contact angle measurements of two different liquids using the dynamic sessile drop method. The advancing and receding contact angles as well the calculated molar wetting free energies decreased with increasing mole fraction of methyl-10-undecenoate. Otherwise the molar dewetting free energies as well as the contact angle hysteresis stay nearly constant. A difference in the wetting and dewetting properties on mixed monolayers is observed, whereby mainly dispersive interactions are responsible for wetting. Furthermore we show that the contact angle hysteresis is independent of surface roughness, surface composition and surface free energy, which indicates that neither surface roughness nor heterogeneities are responsible for this hysteresis. We attribute the hysteresis to interactions between the liquid and the silicon substrate.

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1. Introduction

Contact angle measurements are of increasing interest in investigations of surface properties like self cleaning surfaces and superhydrophobicity [1–5]. Here two different variants are commonly used as they give a fast experimental overview of the macroscopic characteristics: static contact angle measurements [6] as well as advancing and retracting contact angle measurements (in the following dynamic contact angle) [7–24]. The preferred method for characterization, the dynamic contact angle measurements, is carried out on bare or monolayer-terminated surfaces. Most investigations were done on monolayers consisting of one type of molecule [7–16] while measurements on mixed monolayers are quite rare [17–24]. Extrand [7–9] performed investigations on the molar free wetting and dewetting energies on monolayer terminated surfaces consisting one type of molecule. Mixed monolayers on gold have been investigated by dynamic contact angle measurements [25] and the results were investigated with respect to the molar free energy [7].

Generally during dynamic contact angle measurements two specific contact angles occur: the advancing and receding contact

angle. The advancing contact angle θ_a can be measured by inflating a liquid drop on a substrate surface, while the receding contact angle θ_r arises by shrinking a liquid drop on the surface. The difference between the two angles is known as the contact angle hysteresis.

Different interactions between the liquid and the surface cause contact angle hysteresis. Generally the receding contact angle is smaller than the static contact angle. Compared to the static contact angle the advancing contact angle is either larger or in the cases of polar liquids about the same [20]. In the case of mixed monolayers the fraction of dispersive surface groups can play a role for the advancing contact angle of polar liquids, since these groups prevent an unhindered spreading of the polar liquid. On the other hand polar groups support a spreading of the polar liquids. Consequently, polar groups determine the receding contact angle, since the polar liquid sticks on these groups [26]. In contrast for dispersive liquids the polar groups are crucial for the advancing contact angle and the dispersive groups for the receding contact angle. Beside this also roughness and heterogeneity of a surface can influence the contact angle and as it has been shown that also perfectly flat and homogenous surfaces are characterized by contact angle hysteresis [9], further parameters has to be taken into account.

In the present work a series of mixed 1-decene (DEC)/methyl-10-undecenoate (MUD) monolayers on silicon were prepared and characterized by dynamic contact angle measurements. These films are prepared by covalent attachment of alkenes to a bare silicon surface, which is different from often described monolayers on gold or oxide surfaces [9,19,27,28]. The alkyl monolayer formation is

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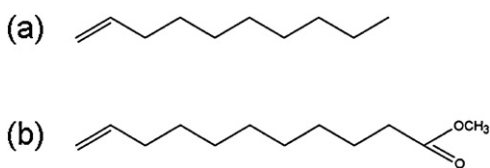


Fig. 1. Molecular structures of 1-decene (a) and methyl-10-undecenoate (b).

well-known and can be realized e.g. by thermal reaction [19,27–29]. By using terminal functionalized alkenes (e.g. carboxyl, hydroxyl, amino or ester groups) the properties of the monolayer can be easily modified which enables a wide variation of the surface properties [29–31]. Additionally the surface properties can be tuned gradually by mixing different alkenes [32]. Such mixed monolayers can act as nanostructures in hierarchical-structured surfaces which are known to influence the properties of liquids and the underlying microstructured substrate [33].

The aim of this study is to investigate the dependence of the dynamic contact angles and the associated molar wetting energies on the distribution of MUD within the DEC layer. Therefore we studied a series of monolayers with a different mixing ratio between DEC and MUD with the dynamic sessile drop method.

2. Experimental

All chemicals were of reagent grade or the highest available commercial grade quality (spectroscopic grade) and purchased from Merck KGaA (Darmstadt, Germany). Ultrapure water (>18.2 M Ω cm; 4 ppb TOC) was obtained from a Millipore Milli-Q Advantage water system (Millipore, Billerica, MA).

The silicon (1 0 0) substrates (>3000 Ω cm, n-type) were cleaned in acetone (at 40 °C), ethanol (40 °C), ‘piranha’ (volume ratio H₂SO₄:H₂O₂ 3:2, 80 °C, CAUTION: Piranha solution is highly corrosive and should be handled with care), and finally rinsed with Millipore water. The native oxide layer on the cleaned silicon substrates was etched for about 2 min in hydrofluoric acid (aqueous solution, 3–4%) leading to a hydrogen terminated silicon surface. To prevent oxidation the substrates were transferred directly into the reaction flask containing ~20 ml of 1-decene/methyl-10-undecenoate mixture (the mixtures were prepared in molar fractions, the chemical structures of the two molecules are shown in Fig. 1) dissolved in mesitylene (volume ratio 1:2). The reaction solution was deoxygenated prior to use for at least 30 min with argon. For the monolayer formation the solution with the silicon was heated up to 160–170 °C under a constant argon flow for at least 5 h. Such a reaction time of a few hours is found to be suitable for the formation of monolayers with all-trans conformation of the alkyl chains [34]. The modified substrates were cleaned in acetone and ethanol and finally rinsed with ultrapure water.

Dynamic contact angle measurements were carried out under ambient conditions with an OCA20 contact angle meter (Data Physics Instruments, Filderstadt, Germany) by using the dynamic sessile drop technique. Here, a liquid drop with a volume of around 1 μ l is growing on a syringe tip and picked up by the surface. In contrast to the static contact angle measurement, the syringe tip never leaves the liquid drop. The liquid was inflated and sucked up from the surface and the advancing and receding angles were obtained.

To investigate the roughness of the prepared mixed monolayers a Level-Atomic Force Microscope (Anfatec Instruments, Oelsnitz, Germany) was used. The measurements were carried out under ambient conditions in the dynamic noncontact mode. All measurements in one set of samples were performed with the same probe ($k = 5$ N/m; $\nu = 160$ kHz) to avoid differences in the spring constant and slight geometric deviations of the cantilevers.

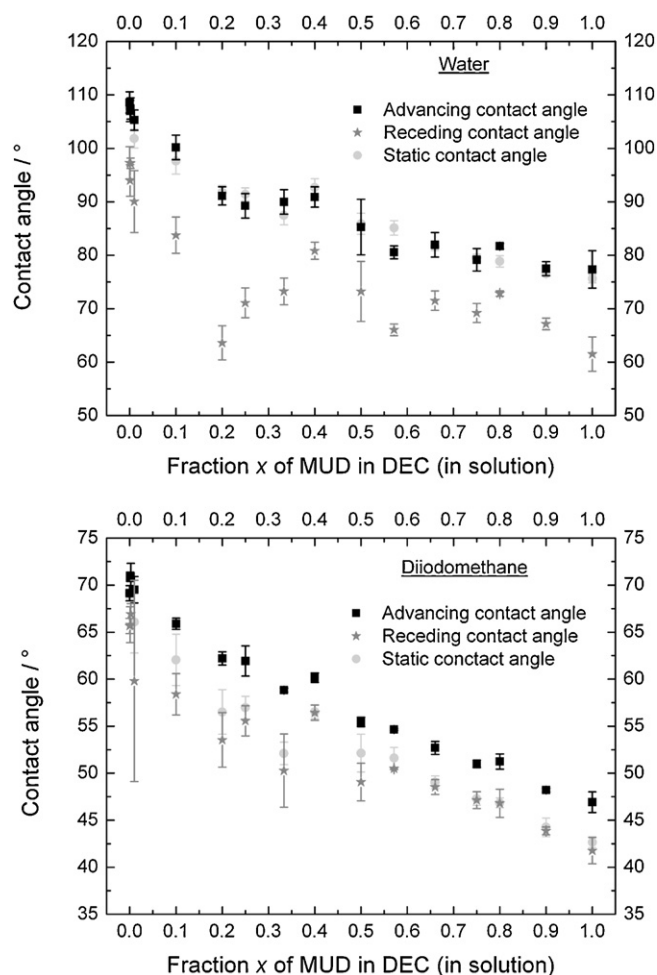


Fig. 2. Advancing contact angles (squares) and receding contact angles (stars) of water (upper diagram) and diiodomethane (lower diagram) of mixed monolayers (DEC/MUD) as a function of mole fraction of MUD in solution. Static contact angles (circles) are shown as comparison and obtained from Ref. [32].

3. Results

After the preparation of pure and mixed alkyl monolayers with varying composition of MUD and DEC as described earlier [35,36], the samples were investigated with dynamic contact angle measurements. Typical results are shown in Fig. 2, where the advancing and receding contact angles of water (Fig. 2 upper part) and diiodomethane (Fig. 2 lower part) are displayed as a function of MUD concentration. Each data point represents the averaged measurement results of five different areas on each of at least two different samples, which also creates the errors of the data points.

Both liquids show generally the same behavior: with increasing MUD content the dynamic contact angles decrease, which can be explained by the higher surface tension and the higher polarity of MUD compared with DEC. Looking in more detail similar characteristics as for the static contact angles can be found: a comparably strong decrease of the angles for very small MUD concentrations (<0.01) followed by a weaker decrease ending in a plateau between MUD contents of 0.2 and 0.4. For higher concentrations again a drop in the contact angles is seen [32]. Interestingly the static contact angle for water is similar to the advancing angle while for diiodomethane the static and receding angles are nearly the same.

From the measured dynamic contact angles we calculated the molar free wetting and dewetting energies, which are shown in Fig. 3, where the molar free energies of water (Fig. 3 upper part)

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