Journal of Colloid and Interface Science 353 (2011) 512–518

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Contact angle and adsorption behavior of carboxylic acids on α-Al_2O_3 surfaces

David Megias-Alguacil *, Elena Tervoort, Cyrill Cattin, Ludwig J. Gauckler

ETH-Zürich, Non-Metallic Inorganic Materials, Department of Materials, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 6 July 2010
Accepted 29 September 2010
Available online 20 October 2010

Keywords:
Alumina
Adsorption
Carboxylic acids

ABSTRACT

The hydrophilic character of aluminum oxide surfaces may be altered through coating such surfaces with carboxylic acids. The initially hydrophilic nature of the solid substrate changes towards a less hydrophilic character as the bulk concentration and the chain length of the acids increases. The acids employed in this work (propionic, valeric and enanthic) show a certain affinity to the liquid–gas, solid–liquid and solid–gas interfaces, being the relative adsorption on them competitive. The adsorption behavior of these carboxylic acids is experimentally investigated combining pendant drop tensiometry, contact angle measurements on α-Al_2O_3 polycrystalline ceramics and adsorption on particles in aqueous suspensions, as a function of the hydrocarbon chain length of the acids and their bulk concentration, at pH equal to the acids' pKa. The hydrophilic character of the coated alumina decreases with the acids concentration upon a certain concentration beyond that, it increases. The minimum of hydrophilicity is reached right before bi-layer arrangements on the adsorption pattern of the acids on the solid substrates take place.

1. Introduction

Adsorption of amphiphiles become an important topic in a wide variety of processes ranging from detergency, water treatment [1], oil recovery [2,3] or ceramic processing [4] to adsorption on metals, of importance in technological areas like lubrication and corrosion [5].

Amphiphilic carboxylic acids can be also used to change the wettability of oxide particles in water by adsorbing on and hydrophobizing initially hydrophilic particles. These surface-modified particles have received great interest in recent years [6], because of their ability to strongly attach to fluid–gas interfaces, enabling e.g., highly stable foams [7,8] and capsules [9].

With water, the α-alumina surface reacts forming surface hydroxyl groups [1,10]. This surface hydroxyl groups can be protonated or de-protonated depending on pH and lead to a surface charge established by a mechanism involving a two-step process: surface hydration followed by a dissociation of the surface hydroxide [1]. The surface charge of alumina strongly depends on pH: below pH ≈ 9 [11] the protonated surface is charged positively, and at higher pH the surface is de-protonated and charged negatively.

The adsorption of carboxylic acids on alumina also greatly depends on pH [1,12–15] because it affects both the surface charge of the alumina and the de-protonation of the carboxylic group of the acids. The adsorption of a carboxylic acid is maximal at the pH equal to the acid's pKa value [13,15]. The carboxylic acids' adsorption on the alumina surface can be explained by the ligand-exchange model [15–17]. The oxygen atom of the surface hydroxyl group can act as a donor (Lewis base) and coordinate with protons or metal ions (Lewis acids), whereas the underlying structural Al(III) ion in the surface layer acts as a Lewis acid, which can exchange the (–OH) group for other coordinating anions. Thus, the specific adsorption of an organic molecule on the alumina surface can be described as a ligand exchange process involving a multistep reaction sequence [18] where the carboxylate ions of the acids substitute the surface hydroxyl groups of alumina.

When the solid surface is also in contact with a third medium, namely gas, there exist three different interfaces: solid–liquid, solid–gas and liquid–gas, which are available for the adsorption of the amphiphiles. The relative and competitive adsorption on these interfaces will determine the hydrophilic/hydrophobic character of the solid substrate. The purpose of the present work is therefore, to investigate the adsorption behavior of carboxylic acids containing between 2 and 6 carbons in the hydrophobic tail at different bulk concentrations when the gas is air, the liquid is water and the solid is highly pure α-alumina.

Understanding the adsorption behavior of carboxylic acids and their preferential attachment to the different interfaces involved is a key factor to explain the performance and control the properties of new soft materials of practical interest.

The adsorbed amount of an amphiphile on an interface, Γ, depends on the bulk amphiphile concentration, c, and this process may be described by means of an adsorption isotherm. One of the most commonly used non-linear isotherms, e.g., [19–21] is that of Langmuir [22]:

---

* Corresponding author. Fax: +41 44 632 11 32.
E-mail address: david.megias@mat.ethz.ch (D. Megias-Alguacil).

0021-9797/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2010.09.087

$$\Gamma = \Gamma_{\max}\frac{c}{c+a} \tag{1}$$

where a is the Langmuir–Szyszkowsky constant [23] and $\Gamma_{\max}$ the maximum concentration of adsorbed amphiphile. It is based on a lattice-type model with the assumptions that every adsorption site on the lattice is equivalent, that the probability for adsorption at an empty site is independent of the occupancy of neighboring sites, that there are no interactions between the monomers and that no intermolecular forces act between the latter [24].

Unfortunately, the adsorbed amount of amphiphile on the different interfaces cannot be directly measured, but instead has to be indirectly determined from other measurements. The adsorption of surface-active species on the liquid–gas interface, Γ_{LG}, may be obtained from the surface tension, γ, of amphiphile solutions using the Langmuir–Szyszkowsky's state equation [25], which relates the equilibrium interfacial tension, γ, to the bulk amphiphile concentration, c, as follows [26]:

$$\gamma = \gamma_0 - RT\,\Gamma_{\max}\ln\left(1+\frac{c}{a}\right) \tag{2}$$

where γ_0 is the interfacial tension corresponding to the amphiphile-free interface, e.g., when $c = 0$, and R and T have their usual meaning.

The adsorption of amphiphiles on the solid–liquid interface, Γ_{LG}, can be determined by differential concentration determination of such molecules in the supernatant of particulate suspensions, before and after some equilibrating time.

Finally, the adsorption on the solid–gas interface, Γ_{SG}, is likely the less accessible quantity of all. Its determination demands the previous determination of the adsorption on the other two interfaces plus an additional experimental acquisition, e.g., the equilibrium contact angle, θ, measured between the tangent on a liquid amphiphile solution drop and the solid substrate at the triple contact point solid–liquid–gas.

The contact angle is determined by the force balance between the interfacial tensions involved, according to the Young's equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta \tag{3}$$

where γ_{SG} is the surface tension of the solid in contact with the gas phase, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_{LG} is the surface tension of the liquid in contact with the gas phase. Taking the derivative of the Young's equation in respect to the concentration, it follows, in logarithmic form [26,27]:

$$\frac{\partial\gamma_{SG}}{\partial\ln c} = \frac{\partial\gamma_{SL}}{\partial\ln c} + \cos\theta\frac{\partial\gamma_{LG}}{\partial\ln c} + \gamma_{LG}\frac{\partial\cos\theta}{\partial\ln c} \tag{4}$$

On the other hand, the Gibbs' equation relates the interfacial tension with the amount of adsorbed amphiphile:

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial\ln c} \tag{5}$$

This equation is valid as long as the adsorption is monomolecular and the adsorption process is reversible. Applying Eq. (5) to the different interfaces involved, Eq. (6) gives the relationship between the adsorption of amphiphile on them and the contact angle, as follows:

$$\Gamma_{SG} = \Gamma_{SL} + \Gamma_{LG}\cos\theta - \gamma_{LG}\frac{c}{RT}\left(\frac{d\cos\theta}{dc}\right) \tag{6}$$

Knowing the concentrations of adsorbed amphiphile on the solid–liquid and liquid–gas interfaces and the variation of the contact angle with respect to the concentration, the Eq. (6) gives then the unknown concentration of the adsorbed amphiphile on the solid–gas interface [27].

2. Materials and methods

Solutions of different carboxylic acids, namely, propionic (propanoic, CH_3CH_2COOH), valeric (pentanoic, $CH_3(CH_2)_3COOH$) and enanthic (heptanoic, $CH_3(CH_2)_5COOH$) acid (Fluka, Switzerland) were prepared by dilution of the latter in double distilled water. All measurements were performed at a pH corresponding to the pKa value of the acids, e.g., pH $\approx$ 4.7–4.8, at which the maximum adsorption occurs, as has been determined in a previous study [15]. All pKa values are taken from [28] at 25 °C and zero ionic strength, unless otherwise stated.

The aluminum oxide employed in this work was prepared in two forms: flat disks and particles powder. The alumina disks were made from a high purity α-alumina powder (RCHP-DBM, Reynolds Chemicals, Reynolds Alumina & Ceramics, 3199 S Reynolds Rd, Bauxite, Arkansas, AR 72011 United States 99.99% Al_2O_3), with a reported average particle size of d_{50} = 480 nm. Powder compacts were prepared by isostatic pressing at 2000 bar resulting in green densities of 50–52% v/v. Sintering of these bodies was carried out in air, for 1–2 h at a maximum temperature of 1650 °C. In a second sintering run, hot isostatic pressing (HIP) was performed for 1 h at 1500 °C and 2000 bar under argon atmosphere. The final density of the sintered specimens was 3.98 g/cm^3 as determined by Archimedes' method, which corresponds to 100% of the theoretical density of alumina, thus indicating an absence of pores. The alumina disks were then ground and polished in order to obtain the best surface finishing possible. First, a total abrasion of 0.4 mm in 0.02 mm steps was obtained in several grinding steps using plastic bonded diamond abrasive wheels. Second, several lapping steps were performed on a Stahli FLM 300 machine for lapping and polishing by gradually reducing the size of the diamond particles in the lapping suspension and by changing the corresponding lapping disk. In the last step, a plastic lapping disk and 1 μm diamond lapping suspension were used. After each polishing and lapping step the sample surface was inspected using an optical microscope in order to ensure a homogeneous surface finishing before going to the next step. Surface roughness was better than $Ra < 10^{-2}$ μm as measured with a Hommel-T-1000-Surface-Roughness-Tester-Profilometer (Hommel-Etamic, Switzerland). The alumina surfaces prepared after these parameters did not show any pores.

The α-Al_2O_3 powder (Ceralox HPA-0.5, 99.99% Al_2O_3, Sasol North America Inc., Tucson, USA) had an average particle diameter, d_{50} = 200 nm, specific surface area of 10 m^2/g, determined by BET adsorption, and density of 3.98 g/cm^3.

2.1. Contact angle measurements (static sessile drop method)

For the measurements of the contact angle, the alumina disks above described were used. Prior to any contact angle measurements, the alumina disks were carefully cleaned in order to remove surface contamination like grease, dust or organic traces that could influence contact angle measurements through surface pinning of the liquid drop and or contamination of the liquid when the latter is put into contact with the sample surface. Piranha-cleaning, a chemical cleaning process, was performed by immersing samples for at least 10 min in a mixture of seven equivalents of concentrated sulfuric acid (96% H_2SO_4) and three equivalents of hydrogen peroxide (30% H_2O_2). This mixture is extremely corrosive and a very strong oxidant which decomposes almost any organic material in an exothermic reaction. The samples were then rinsed 10 times with a lot of distilled water to remove any sulfuric acid. Subsequent to the cleaning procedure, the samples were stored in double distilled water in order to minimize contamination of the freshly cleaned samples prior to contact angle measuring. In order to avoid the contamination of