Colloids and Surfaces A: Physicochem. Eng. Aspects 396 (2012) 233–237

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Anion-specific effects on the interaction forces between Al_2O_3 surfaces and dispersibility of Al_2O_3 colloids in electrolyte solutions

Toshihiro Isobe*, Yosuke Nakagawa, Mikiro Hayashi, Sachiko Matsushita, Akira Nakajima

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Japan

ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form
26 December 2011
Accepted 28 December 2011
Available online 5 January 2012

Keywords:
Atomic force microscopy
Force curve
DLVO theory

ABSTRACT

The interaction between an Al_2O_3 colloid and c-sapphire surface (0 0 0 1) was investigated in an aqueous solution containing citrate ion, Cl^-, $NO_3{}^-$ or Br^- using the colloidal probe method. The force curve measured in electrolyte solutions at pH = 4 showed a good agreement with the force curve predicted by the Derjaguin–Landau–Vervey–Overbeek theory at a long separation distance. The repulsive forces were observed at a shorter separation distance. The order of the strength of the repulsive force was citrate ion > Cl^- > $NO_3{}^-$ > Br^-, corresponding to the Hofmeister series. All the force curves measured in aqueous solutions at pH = 10 were the same. This is caused by the cation (K^+) selectively affecting surface interaction because the Al_2O_3 surface charged to negative at this pH. A particle size distribution measurement of the Al_2O_3 colloids in the 0.001–0.1 mol/L Cl^- and Br^- aqueous solution was carried out. The agglomerates of the Al_2O_3 colloids were observed in 0.1 mol/L Br^- solutions. However, Al_2O_3 colloids were well dispersed in the other aqueous solutions, which are reflected by the force curve results. Jump-in was observed only in the force curve measured in the 0.1 mol/L Br^- solutions and not in any other solutions.

1. Introduction

The Derjaguin–Landau–Vervey–Overbeek (DLVO) theory, which combines the effects of van der Waals force and electrostatic repulsion, describes the forces interacting between charged surfaces in a liquid [1]. The DLVO theory is useful for understanding the behaviour, i.e. dispersion and agglomeration, of colloids in a solvent. Recently, this theory has been improved to more accurately reflect the behaviour of colloids. Various researchers have attempted to experimentally verify the accuracy of the intermolecular and surface forces [2]. The surface force apparatus fabricated by Israelachvili et al. is a useful measurement tool [3]. Israelachvili et al. succeeded in observing the DLVO interaction between two mica surfaces in KNO_3, $CaNO_3$ and $BaCl_2$ solutions. Surface forces that are not considered in the classical DVLO theory have been reported (non-DLVO force). Horn et al. observed a periodic attractive and repulsive force [4] and reported that this oscillation originates in the liquid state near solid interfaces. Pashley described the short-range repulsive forces between mica surfaces in aqueous solutions of K^+ and Na^+ salts, which correspond to the surface ion hydration effects [5]. In contrast, long-range attractive forces attributable to hydrophobic interaction have been reported [6,7]. The hydrophobic surface was formed by a monolayer coating of hydrocarbon and fluorocarbon on the mica surfaces [6].

Recently, scanning probe microscopy (SPM) has been conducted to measure the DLVO/non-DLVO force [8–12]. Ducker et al. produced a colloidal probe from a SiO_2 particle. Furthermore, the DLVO force curve has been observed experimentally [8]. Polat et al. measured the interaction force between an α-alumina colloid and a sapphire substrate for various pH levels [9]. The interaction was repulsive at separations less than 5 nm under basic pH conditions, which is attributable to the hydration of the oxide surface. An extension of this study was done by Donose et al. [10,11]. Yilmaz et al. also researched the ion-specific effects on force curves; the non-DLVO force was explained using the Hofmeister series [12]. The Hofmeister series is a classification of ions in the order of their ability to change the water structure, as observed through the study of ion effects on the solubility of proteins [13]. The order of cations is usually given as $NH_4{}^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$, and the results obtained showed a good agreement with this permutation. The mechanism of the Hofmeister series is not entirely clear. However, the importance of specific interactions between ions and proteins or ions and water molecules contacting the proteins has been reported by Zhang and Cremer [14]. If the description in this work is accurate, the Hofmeister series does not sufficiently explain the results, because the solutions used did not contain proteins. Moreover, anions appear to have a greater effect than cations. Consequently, to analyse the non-DLVO force originating from the differences of various kinds of ions, the ion-specific effects of the anions should be estimated.

---

* Corresponding author. Present address: 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan. Tel.: +81 3 5734 3355; fax: +81 3 5734 2525.
E-mail address: isobe.t.ad@m.titech.ac.jp (T. Isobe).

0927-7757/$ – see front matter. Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2011.12.072

From the viewpoint of industrial applications, the relation between the above interactions and the properties of the colloidal suspensions is another interesting area of research. Traditionally, it has been generally accepted that the rheological properties of suspensions, slurries and pastes depend on the interaction between the particles in the solvents and affect the properties of the final products. Moreover, solid freeform fabrication, which also uses ceramic slurries, has been widely researched in the last few decades [15,16]. The dispersion and agglomeration of ceramic particles are key to the preparation of excellent products.

One of the simplest ways to evaluate a colloidal suspension is to measure particle size distribution (PSD), because the distribution can easily detect the agglomerates of particles. In this study, the ion-specific effects on the force curves were evaluated. The dispersibility of the Al_2O_3 particles was evaluated to confirm whether this measurement could describe colloidal behaviour.

2. Materials and methods

2.1. Zeta potential

A sapphire wafer with a (0 0 0 1) orientation (SA100510; AS One Corporation, Japan) and commercial Al_2O_3 beads (CB-A10; Showa Denko K.K., Tokyo, Japan) were used for this research. The zeta potentials of both a sapphire wafer and Al_2O_3 beads were measured using a commercial apparatus (ELS-6000; Otsuka Electronics Co. Ltd., Osaka, Japan). The Al_2O_3 beads were dispersed into 0.01 mol/L NaCl solutions at a solid–liquid ratio of 0.1 g/L by ultrasonication for 15 min. Then, the pH was adjusted by adding either an HCl or NaOH solution. The average zeta potential was obtained from five measurements.

2.2. Force curve measurement

To prepare the Al_2O_3 colloidal probe, commercial Al_2O_3 beads (particle size 10 μm), tipless triangle cantilevers (PNP-TR-TL-50; Nanoworld AG, Switzerland) and epoxy glue (Araldite #1600; Showa Highpolymer Co. Ltd., Tokyo, Japan) were used. The Al_2O_3 bead was picked up by a micromanipulator (Model M331; Suruga Seiki Co. Ltd., Shizuoka, Japan). It was then glued to the cantilever. A sapphire wafer was cut into approximately 1 cm × 3 cm plates and cleaned using acetone and ethanol for 15 min. After drying, the substrates were immersed in an O_3 atmosphere at room temperature for 15 min to remove organics. Force curve measurements were conducted by a scanning probe microscope (SPM; JSPM-5200; JEOL, Tokyo, Japan). The SPM was set up as described in a previous study for measurements in a liquid [17]. The electrolyte solutions used in this study were prepared from the salts presented in Table 1 and ion-exchanged purified water (Auto Still, Model WG-250; Yamato Scientific Co. Ltd., Tokyo, Japan). The obtained deflection signal vs. z-piezo position was converted into force vs. probe-to-surface separation using the reported method [17]. The obtained force was normalised by the curvature of the sphere, because the area over which the interaction occurs affects the force [18].

Table 1
Electrolyte solutions used for this study.

Salts	Concentration [mol/L]	pH	pH control additive
KBr	0.001–0.1	4.0	HBr
KNO_3	0.001–0.1	4.0	HNO_3
KCl	0.001–0.1	4.0	HCl
Potassium citrate	0.001–0.1	4.0	Citric acid
KBr, KNO_3, KCl, potassium citrate	0.01	10	KOH

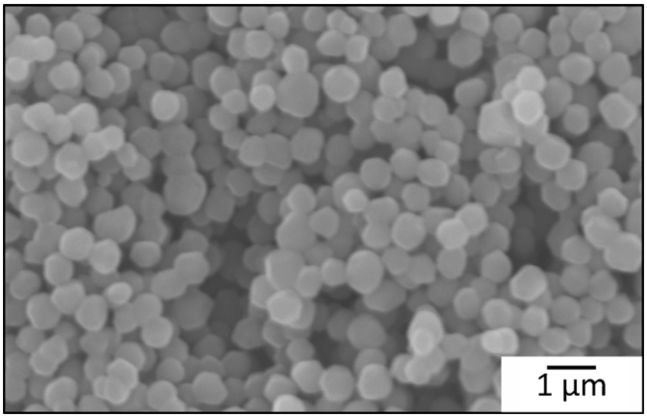

Fig. 1. Scanning electron micrograph of the Al_2O_3 powder used for particle dispersion test.

2.3. Dispersion and agglomeration test

KCl and KBr were dissolved in ion-exchanged purified water. HCl and HBr were used to adjust the pH and anion concentration of the obtained solutions to 4.0 and 0.001–0.1 mol/L, respectively. Al_2O_3 powder with average particles size of 1.1 μm (AA-07, Sumitomo Chemical Co. Ltd., Tokyo, Japan) was mixed with the solutions, which were then treated by ultrasonication for 10 min. The SEM micrograph of the Al_2O_3 powder is shown in Fig. 1. The PSD of the Al_2O_3 powder in the suspension was immediately estimated by laser diffraction (9320HRA (X-100); Nikkiso Co. Ltd., Tokyo, Japan).

3. Calculations

The interaction force between two solid surfaces is the sum of their van der Waals interaction (F_{vdw}) and electrostatic interaction (F_{ele}) [19].

$$F_{\text{total}} = F_{\text{vdw}} + F_{\text{ele}} \tag{1}$$

The attractive van der Waals interaction between a sphere and a flat surface is given by Eq. (2).

$$F_{\text{vdw}} = \frac{A_H R}{6x^2} \tag{2}$$

where A_H, R and x denote the Hamaker constant, the radius of the sphere and the distance between the surfaces of the sphere and flat surface, respectively. In the case of low surface potentials, the electrostatic force F_{ele} between a sphere and a flat surface is given as

$$F_{\text{ele}} = 2\pi\varepsilon_0\varepsilon_r\kappa R \cdot \exp(-\kappa x)\frac{2\Psi_s\Psi_p \mp \exp(-\kappa x)(\Psi_S^2 + \Psi_P^2)}{1 - \exp(-2\kappa x)}, \tag{3}$$

where ε_0 denotes the permittivity of free space, ε_r denotes the relative permittivity, ψ_s is the potential on the sphere surface and ψ_p represents the potential on the flat plate. In addition, κ denotes the inverse of the Debye length, which is given as

$$k = \sqrt{\frac{\sum_i n_i e^2 z_i^2}{\varepsilon_0\varepsilon_r kT}}, \tag{4}$$

where e denotes the electron charge, k is the Boltzmann constant, T denotes the absolute temperature, n_i denotes the concentration of ions of type i in the bulk and z_i denotes the valence of such ions. Finally, the equation that is normalised by the radius of the sphere