

Preparation of (non-)aqueous dispersions of colloidal boehmite needles

Paul A. Buining, Chellappah Pathmamanoharan, Albert P. Philipse*,
and Hendrik N.W. Lekkerkerker

Van 't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht,
Padualaan 8, P.O.Box 80.051, 3508 TB Utrecht, The Netherlands

(* Author for correspondence)

Abstract

A novel hydrothermal alkoxide method is presented for the preparation of stable, aqueous dispersions of fairly monodisperse, charged colloidal boehmite needles. A polymer coating procedure for the needles is described which leads to sterically stabilized dispersions in organic solvents.

Keywords

Boehmite; aluminium alkoxides; colloidal needles; organic coating.

Introduction

This contribution summarizes our recent work on the preparation of stable dispersions of colloidal boehmite (AlOOH) needles in various solvents.

We investigate this preparation because of our interest in a fundamental study of anisotropic colloids (Lekkerkerker, 1989). For a quantitative study of, say, diffusion or sedimentation of colloidal rods, the particles have to meet a list of requirements. Ideally the rods are monodisperse, with a controllable size and shape, and able to form stable, non aggregated dispersions. Moreover, the interactions between the rods should be adjustable by appropriate surface modifications which allow, for example, a comparison between charged and sterically stabilized rods. An analogous comparison is possible for colloidal silica spheres (van Helden *et al*, 1981; Philipse and Vrij, 1989). Last, but certainly not least, we are seeking for a relatively simple synthesis which yields at least a few gram within a few days.

There are some well-known types of rod-like colloids, such as tobacco mosaic virus (Lauffer, 1944) and β -FeOOH particles (Zocher and Heller, 1930). All anisotropic colloids we are aware of, however, have some serious drawbacks with respect to the requirements mentioned above. Probably TMV is the best model system available at present. Yet it does not allow variation of particle length or application of surface modifications. Moreover, sample preparation is a laborious task.

We therefore develop an alkoxide route for the synthesis of boehmite needles to be used as model colloids. After an outline of this synthesis, we briefly describe in this communication the coating of the needles with polymer after which they form stable dispersions in organic solvents. Some observations are mentioned which confirm the needle shape, and the colloidal stability, of the boehmite.

Boehmite synthesis

First we attempted to improve a boehmite preparation described by Bugosh (Buining *et al.*, 1990; Bugosh, 1959). His method comprises the hydrothermal treatment of basic aluminium chloride solutions. We were able to prepare stable dispersions of fairly monodisperse boehmite fibrils. The fibril length (~ 300 nm, aspect ratio of ten), however, was difficult to vary systematically for reasons explained by Buining *et al.* (1990). Another drawback of the Bugosh method is the time consuming dissolution of aluminium powder in hot AlCl_3 solutions.

Afterwards we found a method which avoids these disadvantages (Buining *et al.*, 1991). This method employs the hydrothermal treatment of a 1:1 molar mixture of aluminium *sec*-butoxide and aluminium *iso*-propoxide, acidified with an excess aqueous HCl solution. The mixture composition which produces the most needle-like boehmite particles (Fig. 1) was determined more or less by trial and error. A scheme of the synthesis is given in Fig. 2. The average needle length, which lies in the range 100-500 nm, can be controlled with reagent concentrations in the initial synthesis mixture, as is illustrated in Fig. 3. Some representative characterization results for dispersions of the (polycrystalline) boehmite particles are given in Table I.

Coating with polymer

The aqueous dispersions are stabilized by electrostatic repulsions between the (positively) charged needles. When transferred to weakly polar solvents such as toluene, the particles flocculate. To attain stability in such solvents, a protective polymer layer on the needles is required. However, attaching polymer on the surface of the needles without losing colloidal stability is not a straight

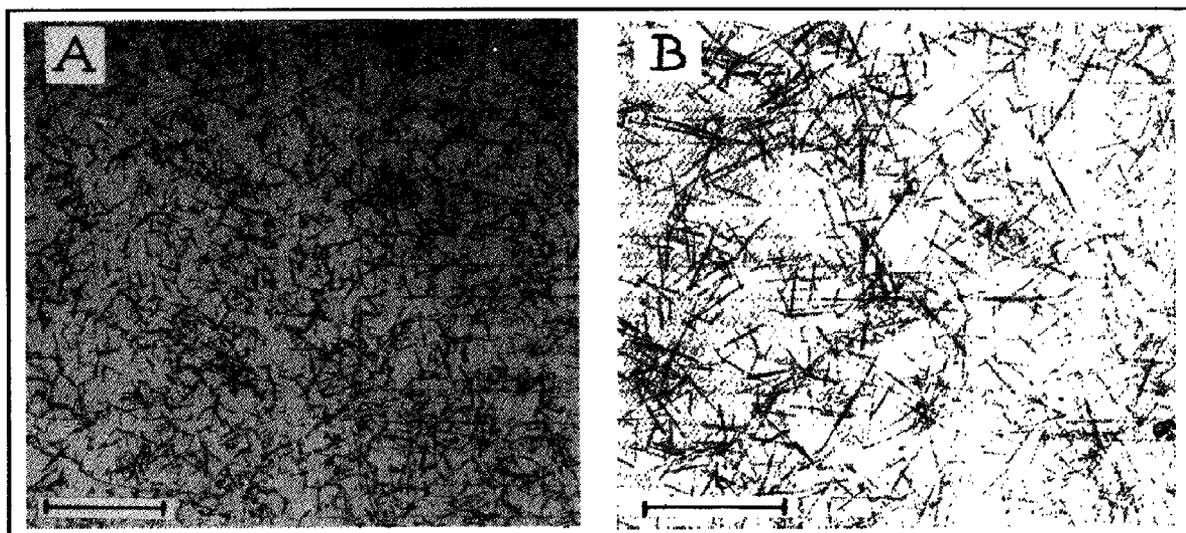


Fig. 1 Transmission micrographs of boehmite needles with (A) average length 137 nm (code ASB5) and (B) 306 nm (code ASBIP1). Bar is 1 μm .

forward procedure. One has to change the solvent composition gradually from water, which is a good solvent for uncoated boehmite, to an appropriate polymer solvent for the needles coated with polymer. The polymer grafting procedure has to take place during this gradual solvent change.

This coating process was developed recently for the surface coating of silica spheres with polyisobutene ($M \sim 1500 \text{ g mol}^{-1}$) modified with a polar anchoring group (Pathmamanoharan, 1988). We used a similar process for attaching the polyisobutene to boehmite, which comprises the following steps (Buining *et al.*, to be published).

First the boehmite needles are transferred from water to propanol by a distillation procedure. Then a solution of the modified polyisobutene in tetrahydrofuran is added to the dispersion in propanol. During distillation of tetrahydrofuran toluene is slowly added to further lower the solvent polarity. Distillation is continued until the needles are dispersed in pure toluene.

The resulting needles are indeed stable in toluene and other solvents of comparable or lower dielectrical constant, such as cyclohexane. This clearly points to the presence of the polymer on the boehmite surface. This polymer cannot be removed from the surface by repeated sedimentation-redispersion procedures. The polymer attachment was also corroborated by other techniques, such as infrared and element analysis (Buining *et al.*, to be published).

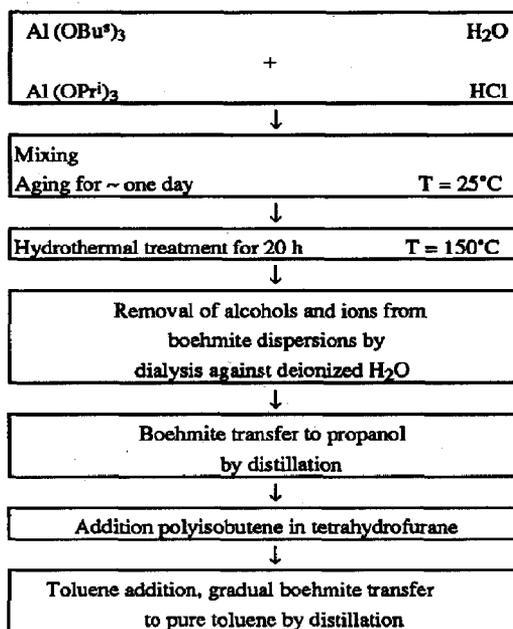


Fig.2 Scheme of the hydrothermal synthesis of boehmite needles and the subsequent polymer coating procedure.

Dispersion properties

The following qualitative observations illustrate the marked difference between ungrafted and grafted needles.

Dialyzed dispersions of the boehmite in water exhibit permanent birefringence at boehmite volume fractions as low as 0.3%. The permanent (partial) alignment of needles at these low concentrations requires long range electrostatic forces, which indeed must be present in deionized water because of the large Debye length (see Table I). Grafted needles in cyclohexane only exhibit flow-induced streaming birefringence at volume fractions roughly above 10%. This must be due to the fact that these uncharged needles have a much smaller effective interaction volume.

A similar difference between grafted and ungrafted needles was (visually) observed for the relaxation time of streaming birefringence in dispersions with no permanent alignment of particles. At a given concentration this time is clearly much longer for the needles in water, than for the coated boehmite needles in cyclohexane. This points to a relatively slow rotational diffusion of the needles in water, which probably also manifests the presence of significant electrical double layer interactions. We note here that these observations on birefringence properties of the various dispersions indicate non-aggregated needles.

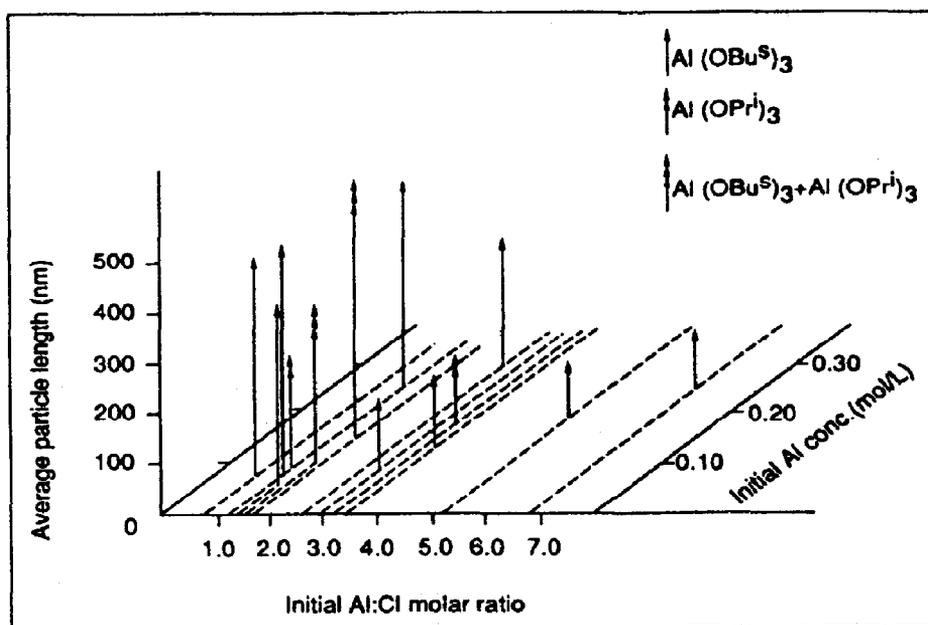


Fig.3 Average boehmite needle length as a function of the alkoxide type and the initial aluminium concentration and aluminium/chloride ratio in the synthesis sketched in fig.2.

Table I. Some properties of representative boehmite dispersions

solvent	<i>ungrafted</i> ¹⁾	<i>grafted</i> ²⁾
	water	toluene, cyclohexane
(average) needle length	281 nm	191 nm
spread in length	46%	28%
needle thickness	12 nm	12 nm
Debye length	~ 100 nm ³⁾	—
particle mass density	3.01 g/cm ³ ⁴⁾	2.10 g/cm ³

1) laboratory code ASBIP8

2) laboratory code ASBIP8g

3) deionized dispersion

4) literature value

The viscosity of aqueous boehmite dispersions is high. Dispersion ASBIP 8 at a volume fraction of only 0.3%, for example, has a (zero-shear) viscosity relative to water of about 600. The grafted (ASBIP8g) needles in cyclohexane produce a much lower viscosity at comparable concentrations. We attribute this viscosity difference, again, to a difference in interaction between the needles.

Conclusions

Stable dispersions of fairly monodisperse, charged boehmite needles with a controllable length can be prepared by a simple and rapid hydrothermal treatment of an aqueous acid aluminium alkoxide mixture. The needles can be modified with polyisobutene to form stable dispersions in organic solvents such as toluene and cyclohexane.

Preliminary observations on the viscosity and optical properties of the various dispersions confirm their stability and the needle shape. It is clear that the boehmite synthesis and modification can be further improved. For example, a further decrease in polydispersity of needle length would be profitable. It is also clear that a quantitative study is needed for a more accurate evaluation of particle and dispersion properties.

The results so far, nevertheless, clearly indicate that the boehmite dispersions are promising candidates for a future study of sterically stabilized and charged rod-like colloids, as referred to in the introduction.

Acknowledgements

Monique Bosboom and Yvonne Veldhuizen are thanked for their contribution to this work. We also acknowledge the support of Dr. Ben Jansen and his group of the Geochemistry department of the Utrecht University.

References

- Buining, P.A., Pathmamanoharan, C., Bosboom, M., Jansen, J.B.H. and Lekkerkerker, H.N.W. (1990). Effect of hydrothermal conditions on the morphology of colloidal boehmite particles: implications for fibril formation and monodispersity. *J. Am. Ceram. Soc.*, **73**, 2385-90.
- Buining, P.A., Pathmamanoharan, C., Jansen, J.B.H. and Lekkerkerker, H.N.W. (1991). Preparation of colloidal boehmite needles by hydrothermal treatment of aluminium alkoxide precursors. To appear in *J. Am. Ceram. Soc.*, **74**.

- Buining, P.A., Veldhuizen, Y., Pathmamanoharan, C. and Lekkerkerker, H.N.W. Preparation of a non-aqueous dispersion of sterically stabilized boehmite rods. (To be published).
- Bugosh, J. (1959). Fibrous alumina monohydrate and its production. *U.S. Patent* no. 2915475.
- Helden, A.K., Jansen, J.W. and Vrij, A. (1981). Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents. *J. Colloid Interface Sci.*, **81**, 354-368.
- Lauffer, M.A. (1944). The size and shape of tobacco mosaic virus particles. *Am. Chem. Soc.*, **66** 1188-1194.
- Lekkerkerker, H.N.W. (1989). Crystalline and liquid crystalline order in concentrated colloidal dispersions: an overview. In: *Phase transitions in soft matter* (T. Riste and D. Sherrington, eds.), pp. 165-177. Plenum Press, New York.
- Pathmamanoharan, C. (1988). Preparation of monodisperse polyisobutenen grafted silica dispersions. *Colloids and Surfaces*, **34**, 81-88.
- Philipse, A.P. and Vrij, A. (1989). Preparation and properties of nonaqueous model dispersions of chemically modified, charged silica spheres. *J. Colloid Interface Sci.*, **128**, 121-136.
- Zocher, H. and Heller, W.Z. (1930) *Z. Anorg. Chem.*, **186**, 75.