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## Substrate-induced coagulation (SIC) of nano-disperse alumina in non-aqueous media: The dispersibility and stability of alumina in *N*-methyl-2-pyrrolidinone

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### ABSTRACT

This work investigated colloidal properties such as the zeta-potential, the electrophoretic mobilities and the wetting behaviour of alumina dispersed in non-aqueous media. Non-aqueous dispersions of alumina were prepared in the solvent *N*-methyl-2-pyrrolidinone (NMP). The wetting behaviour of alumina in NMP was characterized by the powder contact angle method and the Wilhemy plate method. The behaviour of the dispersion should provide information for the development of a substrate-induced coagulation (SIC) coating process of nano-sized alumina in non-aqueous media. SIC is a dip-coating process that coats pretreated but chemically different surfaces with nano-sized particles. It was found that the anionic surfactant dioctyl sulfosuccinate (AOT) had no stabilizing effect on alumina dispersed in NMP.

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### 1. Introduction

Substrate-induced coagulation (SIC) is a particularly attractive dip-coating method for depositing metal nanoparticles on different surfaces because of the high density of particles that can be achieved and the flexibility in the types of particles (such as metals, semiconductors or dielectric materials) that can be deposited. Using SIC offers the possibility to cover chemically different surfaces with finely dispersed nano-sized solids. Recently, aqueous as well as non-aqueous titania dispersions were investigated for the use in a SIC process [1]. SIC can also be performed in non-aqueous media to coat materials that are sensitive to hydrolysis [2–4]. In the past it has also been used to, e.g. prepare core-shell materials as cathode materials for Li-ion batteries [5–7]. As other examples SIC was used to coat printed wiring boards with a conducting carbon black layer [8,9] and to coat non-conductive surfaces such as teflon (PTFE) with conducting particles such as highly conductive carbon black [10]. Aqueous SIC was also used for the layer by layer preparation of electrodes or composite supercapacitors with defined thickness by multiple use of the coating process [11].

Aim of this work was to investigate alumina in non-aqueous media to find conditions for an SIC process. The experiments were planned with a special emphasis for the future use of the SIC process for Li-ion battery materials.

In the past the presence of trace polar impurities such as water were found to have a critical enhancement on the suspension stability dispersing alumina (stabilized by hydrophobic polymers) in non-polar media such as cyclohexane [12]. Higher concentrations of water lead to a rapid flocculation of the alumina dispersions. It has been found that the electrostatic contribution could be tailored by changing the organic-liquid media—if the acidity of the solvent increases the electrostatic charge on the alumina particles increased, which contributes to the stability of the alumina particles (size 0.65  $\mu\text{m}$ ) in the media [13]. In later work the same group investigated the stability of BaTiO<sub>3</sub> suspended in organic solvents (ethyl alcohol, acetone and toluene) using menhaden fish oil and phosphate esters as dispersants. Here – because of the low dielectric constants – steric stabilisation dominates this system [14]. A hydrophobically modified polymer stabilizes alumina in both water and toluene – while in the aqueous system the stabilization is caused by both electrostatic repulsion and steric hindrance, the steric hindrance by the absorbed polymer is responsible for the stabilization in toluene [15]. Alumina was dispersed in the azeotropic mixture of methyl ethyl ketone and ethanol where polyvinyl butyral was found to be the most effective dispersant—alumina powders were found to have positive surface charge [16]. In this

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**Table 1**  
Zeta-potential using the Hückel equation of Al<sub>2</sub>O<sub>3</sub> (diluted) and AOT in NMP.

Sample	AOT (mmol l <sup>-1</sup> )	Electrophoretic mobility (10 <sup>-9</sup> m <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Zeta-potential (mV)
2	25	Failed	Failed
3	10	-0.84 ± 0.18	-7.5 ± 1.6
4	5	-1.34 ± 0.14	-11.8 ± 1.3
5	2	-1.44 ± 0.20	-12.7 ± 1.8
6	1	-2.08 ± 0.78	-18.3 ± 6.9
7	0.5	-2.49 ± 0.25	-21.9 ± 2.2
0	0	-2.84 ± 0.58	-24.9 ± 5.1

work none of the anionic dispersants (e.g. phosphate ester and Manhaden fish oil) used were efficient in dispersing the suspension. On the other hand alumina deposited by electrophoresis from an ethanolic suspension stabilized with polyacrylic acid showed a negative zeta potential strongly dependent on the polyacrylic acid concentration [17].

## 2. Experimental

### 2.1. Chemicals

Commercially available aluminium oxide (AEROXIDE Alu C, Evonik, Frankfurt, Germany) with a particle size of 13 nm and a BET surface area of 100 m<sup>2</sup> g<sup>-1</sup> was used. *N*-methyl-pyrrolidone (NMP) is an a-protic organic solvent. It has a high boiling point, 202 °C, and a freezing point of -24.4 °C. It has a density similar to that of water, 1.026 g/cm<sup>3</sup>, and a viscosity of 1.67 cP. The relative permittivity (or dielectric constant,  $\epsilon$ ) is 32.2 and the refractive index 1.4700. The solvent was chosen in respect to their later use of SIC in Li-ion batteries. Aerosol OT is the name commonly given to the compound dioctyl sulfosuccinate or bis-2-ethylhexyl sodium sulfosuccinate, which has the chemical formula C<sub>20</sub>H<sub>32</sub>O<sub>7</sub>SNa. It is an anionic surfactant with two doubly branched hydrophobic tails and is soluble both in water and in most common non-aqueous solvents [18,19]. The adsorption of AOT on alumina particles from hexane and cyclohexane was described in [20].

### 2.2. Dispersions

Alumina was dried in vacuum overnight and was added to NMP solutions with different AOT concentrations (see Tables 1–2). All dispersions contained 1 wt.% alumina and were stirred for 5 min, ultrasonicated for 15 min and stirred with a homogenizer for 10 min at >15,000 rpm.

### 2.3. Powder contact angle method

The powder contact angle method was used to investigate the wetting abilities of alumina. The alumina powder was put into the measuring cylinder of the tensiometer KRÜSS K12, GmbH, Hamburg. After the cylinder with the powder sample was put into contact with the liquid phase, the sample mass change as a func-

**Table 2**  
Zeta-potential using the Smoluchowski equation of Al<sub>2</sub>O<sub>3</sub> (diluted) and AOT in NMP.

Sample	AOT (mmol l <sup>-1</sup> )	Electrophoretic mobility ( $\mu$ /s)/(V/cm)	Zeta-potential (mV)
2	25	0.10	9.60
3	10	0.48	43.33
4	5	0.47	43.43
5	2	0.59	54.60
6	1	0.48	44.32
7	0.5	0.49	45.12
0	0	0.45	41.60

tion of time was measured. The evaluation of the measured data is based on modifications of the Washburn equation for a single capillary [21], which arises from the combination of the expression for the Laplace pressure and the Hagen–Poiseuille equation for steady flow conditions [22]. A more detailed description of the method is given in our earlier work [1].

### 2.4. The Wilhelmy plate method

The Wilhelmy plate method (KRÜSS K12 Users Manual (1996)) using the equilibrium technique, was applied, for determining the surface tension and their polar and dispersive components of the liquid sample NMP. A standard Pt plate (for surface tension determination of the liquid) and a standard PTFE plate (for the determination of dispersive components of surface tension of the liquid) were used.

The equilibrium technique was applied for determining the surface tension of the solvent. As a standard, a platinum plate was applied (contact angle  $\theta = 0^\circ$  for the majority of liquids). The examined liquid was brought into contact with the lower edge of the platinum plate. The contact angles between solid (PTFE) and liquid phase (NMP) were determined, using the dynamic technique. During measurement, the sample plate was immersed in a liquid, and pulled out afterwards, which enabled determination of the advancing and receding contact angles. The force onto the plate was measured depending on the immersion depth. A more detailed description of the method is given in our earlier work [1].

### 2.5. Turbidity measurements

In this study used concentration of 1 wt.% of alumina was too high to use common spectroscopic method for turbidity determination. Therefore the turbidity of dispersions was estimated by appearance.

### 2.6. Phase analysis light scattering (PALS) and dynamic and electrophoretic light scattering (DLS, ELS)

Phase analysis light scattering (PALS) detects the light scattered by particles moving relative to an interference fringe pattern, which is generated by the intersection of two laser beams. The beams are crossed and one is offset in frequency relative to the other by a couple of kilohertz. The time-domain phase information within the scattered signal is analysed to determine the electrophoretic mobilities of particles down to about 10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup>V<sup>-1</sup>. The PALS system and the analysis software were constructed in-house (Laser Light Scattering Science Group, Prof. John Thomas, University of South Australia, Adelaide, Australia). The measurements were done using a He–Ne Laser (632.8 nm) with a lock-in frequency of 2000 Hz. A voltage of 5 V, modulated at 30 Hz, was applied between palladium electrodes separated by 2.22 mm, giving an applied field of 22.5 V/cm.

The zeta-potentials were also determined by DLS and ELS using a Brookhaven Instruments ZetaPlus zeta-potential Analyzer at a wavelength of 674 nm. The samples were diluted with the non-solvent to a concentration of 0.01% w/v. The zeta-potential here was obtained (by the instrument) by the Smoluchowski model. The standard in NMP showed a zeta-potential of -51.97 mV at a temperature of 25 °C. The solvents viscosity 1.67 cP, the refractive index 1.4700 and the dielectric constant 32.2 were fed into the instrument.

### 2.7. Zeta potentials

The particle velocity  $v$  is proportional to the applied field strength  $E$ . For spherical particles this relationship takes the form:

$$v = \mu_E E \quad (1)$$

where  $\mu_E$  is called the electrophoretic mobility of the particle. Two different models can be used to calculate the zeta-potential from electrophoretic mobility. The solution given by Smoluchowski (1921) is for the thin double layer ( $\kappa_\alpha \gg 1$ ) case, and leads to:

$$\mu_E = [\varepsilon \zeta / \eta] \quad (2)$$

where  $\eta$  = liquid viscosity/Pa s,  $\varepsilon$  = permittivity and  $\zeta$  = zeta-potential/mV.

Hückel (1924) solved the electrophoresis problem for the opposite extreme of a very thick double layer (where the Debye length  $\kappa_\alpha \ll 1$ ).

$$\mu_E = [2\varepsilon \zeta / 3\eta](1 + \kappa_\alpha) \approx 2\varepsilon \zeta / 3\eta \quad (3)$$

With the small (21 nm) particles and low electrolyte concentrations (<0.04 mol/l) used here, it is appropriate to use Eq. (3) to calculate zeta-potentials from measured mobilities obtained from electrophoresis [1].

### 3. Results and discussion

#### 3.1. Wetting characteristics of alumina and NMP

The sorption characteristics of solid alumina and NMP were studied using the powder contact angle method. Using N-heptane with its excellent wetting abilities the contact angle is close to zero and  $\cos\varphi$  can be estimated to be 1. The constant  $c$  can be calculated directly to be  $7.8054 \times 10^{-6}$  (mean value of 7 measurements). NMPs surface tension  $\gamma_L$  was calculated to be  $41.34 \text{ mN m}^{-1}$  (3 measurements). The contact angle  $\varphi$  of alumina and NMP was calculated from the capillary velocity using the Washburn Equation and was found to be  $-89.88 \pm 0.09^\circ$  (4 measurements). The high contact angle of the powder lead to the decision to use dispersing agent for further experiments. A high contact angle between solid and liquid causes a low dispersibility. The surface between the two phases tends to minimize in such liquid which results in agglomeration of the dispersed solid phase. Aerosol OT (AOT) (bis-2-ethylhexyl sodium sulfosuccinate) was chosen as a solute as it has been used in aqueous SIC and is a very common surfactant in non-aqueous solvents [18,19]. NMPs disperse and polar components, the surface tension and the contact angle is published in [1].

#### 3.2. Stability of alumina dispersions in NMP

In previous work carbon black [2] and titania suspensions [1] in NMP were investigated using the same conditions as in this work. The alumina dispersions were less stable than carbon black and titania dispersed in the same media, but stable enough to be handled in the lab and in a SIC process.

##### 3.2.1. Stability of alumina dispersions in water

Alumina (1 wt.%) was added to a  $2.7 \text{ mmol l}^{-1}$  AOT and  $40 \text{ mmol l}^{-1}$  LiCl in an elongated beaker, possible conditions used for aqueous SIC of titania [23]. The dispersion was stirred for 5 min, ultrasonicated for 15 min and stirred with a homogenizer for 10 min at >15,000 rpm. The alumina particles floated, so the experiment was stopped at this point.

##### 3.3. Zeta-potential of alumina dispersed in NMP

Alumina in NMP had a zeta-potential of  $-25.0 \text{ mV}$ . Adding AOT decreases the magnitude of the zeta-potential (see Fig. 1 and Table 1). Solution 0, because it had the highest zeta-potential and stability was chosen for further non-aqueous SIC experiments. A dispersion of 1 wt.% showed a stability of over 2 h, while all the

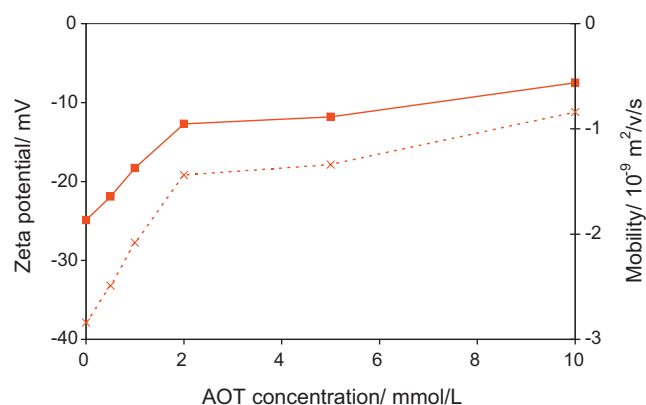


Fig. 1. Mobility continuous line, ( $\times$ , dotted line, right-hand scale) and zeta potential ( $\blacksquare$ , left-hand scale) measured using PALS for 1% alumina samples that have been diluted (for transparency) in solutions of AOT in NMP, plotted against the final solution concentrations of AOT.

other dispersions were stable for just a few minutes. LiCl was added to investigate its destabilisation on the dispersion, but the experiments failed because the electrolyte concentration was too high.

The experiments were redone using ELS and diluting the dispersions to a concentration of  $0.001 \text{ mol/l}$  alumina. The results are presented in Fig. 2 and Table 2. Alumina in NMP showed a zeta-potential of  $41.60 \text{ mV}$ , increasing the AOT concentration to  $2 \text{ mmol l}^{-1}$  lead to an increase of the magnitude of the zeta-potential. However, an AOT concentration of  $25 \text{ mmol l}^{-1}$  lead to a strong decrease in the magnitude of zeta-potential, which could also be observed in a shorter stability of the dispersions in the lab. LiCl ( $0.005 \text{ mol/l}$  and  $0.001 \text{ mol/l}$ ) were added to NMP. Again these experiments failed, because the electrolyte concentration was too high.

#### 3.4. Discussion of charging mechanisms of alumina/AOT in NMP

Most literature of alumina dispersed in organic media with low dielectric constant describes steric hindrance as a the predominant stabilisation mechanism [14,12]. However, NMPs dielectric constant is 32.2 so steric hindrance and electrostatic repulsion are comparable to water and the predominant stabilization mechanism would be explained by electrostatic forces [15]. Paik et al. found that the electrostatic contribution could be tailored by changing the organic-liquid media, they suggest that a suitable dispersant for alumina particles should be acidic like linolenic acid [13].

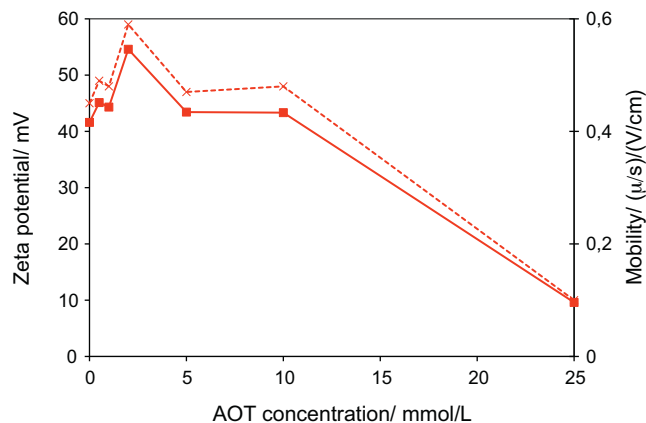


Fig. 2. Mobility continuous line, ( $\times$ , dotted line, right-hand scale) and zeta potential ( $\blacksquare$ , left-hand scale) measured using ELS for 1% alumina samples that have been diluted (for transparency) in solutions of AOT in NMP, plotted against the final solution concentrations of AOT.

In earlier work on carbon black dispersed in NMP, AOT had the effect of a simple electrolyte. Higher concentration lead to a higher destabilisation of the dispersions [2]. When titania is dispersed in a medium that does not accept protons easily, such as NMP, the material is unable to donate them and may be even forced to accept them which results in positively charged titania particles [1]. In this work alumina showed first a negative zeta-potential (see Table 1 and Fig. 1). Alumina in NMP without any additive showed the highest stability. The anionic surfactant AOT in NMP had a destabilizing effect on the alumina dispersion.

Mukherjee et al. reported no stabilizing influence of anionic surfactants in their solution on alumina—an azeotropic mixture of methyl-ethyl-ketone and ethanol (0.1% moisture). In the believe of the authors alumina contains soda and form an ion pair with the anionic functional head of the dispersants [16].

Fowkes et al. suggested that the charging of alumina particles goes back to acid–base interactions [24,25]. The zeta-potential of alumina in water is positive—for metal oxides in water the zeta-potential is dependent on the pH of the solution, the crystal structure and is positive below the isoelectric point [26]. This strongly supports the presence of traces of water in the experiments listed in Table 2 and plotted in Fig. 2. Traces of water are believed to stabilize alumina in non-polar media. For example found Somasundaran et al. that alumina dispersed in non-polar media solvents are stabilized significantly by the presence of water [12]. So traces of water would also explain the increase in stability with increasing AOT concentration (from 0.5 to 2 mmol<sup>-1</sup>). It was proven in earlier work that AOT at these concentrations does not form micelles in dry NMP [27]. On the other hand, physical adsorbed water forms a polar environment and benefits to the adsorption of AOT [20]. The critical micelle concentration (cmc) of AOT is 2.23 mmol<sup>-1</sup> in water (at 303 K) [18]. As the surfactant is soluble in both NMP and water it is possible that at higher AOT-concentrations (from 2 to 25 mmol<sup>-1</sup>) the surfactant forms micelles in water. At these concentrations a further decrease in the stability of the alumina dispersion was observed.

### 3.5. Conclusions

The anionic surfactant AOT does not, but trace water does improve the magnitude of zeta-potential of alumina dispersed in the a-protic, polar, organic solvent NMP. Alumina dispersed in dry (or slightly moist) NMP shows the best colloidal behaviour to be further used in non-aqueous SIC experiments. A dispersion of 1 wt.% showed a stability of over 2 h.

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