EVALUATION OF STABILITY OF AQUEOUS DISPERSIONS USING ZETA POTENTIAL DATA[1]

AVALIAÇÃO DA ESTABILIDADE DE DISPERSÕES AQUOSAS UTILIZANDO DADOS DO POTENCIAL ZETA

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ABSTRACT

Surface properties of nanomaterials through the determination of the zeta potential (ZP) are important characteristics influencing the dispersion stability. Water was used as a dispersant and cetyltrimethylammonium bromide (CTAB) was adsorbed on nanoparticles. The ZP was obtained using the electrophoretic light scattering method. Magnitude and the sign of zeta potential of various metal oxide nanoparticles (NPs), active carbon and hydroxyapatite dispersed in water depend highly of the compound and environment. For example, in the case of naked TiO_2 at pH 7, the zeta potential increased from -12.7 to 8.2 mV for $AgTiO_2$. Most oxides and hydroxyapatite aqueous dispersions exhibit high stability. Stability in all investigated systems is mostly influenced by pH. In addition, measurements of the zeta potential at different pHs allow prediction of the macroscopic behavior of the dispersions.

Keywords: active carbon, colloidal solution, hydroxyapatite, oxides.

RESUMO

Propriedades de superfície de nanomateriais obtidas da determinação do potencial zeta (PZ) são características importantes que influenciam a estabilidade de dispersões. A água foi utilizada como dispersante e o brometo de cetiltrimetilamônio (CTAB) foi adsorvido nas nanopartículas. O PZ foi determinado utilizando o espalhamento eletroforético de luz. A magnitude e o sinal do potencial zeta de várias nanopartículas de óxidos metálicos (NPs), carbono ativo e hidroxiapatita dispersos em água, dependem muito do composto e do ambiente. Por exemplo, no caso de TiO2 nu a pH 7, o potencial zeta aumentou de -12,7 para 8,2 mV para AgTiO2. A maioria dos óxidos e dispersões aquosas de hidroxiapatita apresenta alta estabilidade. A estabilidade em todos os sistemas investigados é influenciada principalmente pelo pH. Além disso, medidas do potencial zeta em diferentes pHs permitem predizer o comportamento macroscópico das dispersões.

Palavras-chave: *carvão ativo, solução coloidal, hidroxiapatita, óxidos.*

INTRODUCTION

Nanoparticles (NPs) exhibit unique chemical and physical properties with enhanced performance over their bulk counterparts. These characteristics depend upon their shape, size, and local environment that are related to the formation of aggregates or a stable dispersion. Surface charge of NPs play an important role in their aggregation behavior, reactivity, and toxicology (JIANG et al., 2009; MURDOCK et al., 2008).

Electrostatic repulsion forces that are due to surface charges on the particles provide the sources of stabilization of the colloidal dispersions. Two other effects namely steric hindrance and a combination of electrosteric repulsions can also be responsible for stabilization. The electrostatic interaction between NPs can be predicted from surface potential, ionic strength (a proxy for Debye length) and particle size. The experimental determination of the surface potential is generally a difficult task but it is well approximated by the more accessible zeta potential. Zeta potential (ξ) is the well-known parameter used to describe the surface-force interaction and the stabilization behavior of the particles in the dispersions. Zeta potential values depends by many factors, such as the powder source, the electrolyte concentration (ionic strength), the particle concentration and size, the solution pH and the state of hydration (YU et al., 2003; HEISER et al., 2010). Available techniques are unable to measure accurately this property, and it is estimated by the corresponding zeta potential, the electric potential of a particle on the inner boundary of its diffuse layer.

Zeta potential can be obtained from measurement of the electrophoretic mobility of nanomaterials dispersed in aqueous media by well-established methods that are described in the standards (VARENNE et al., 2015). They are classified as methods based on acoustic electrophoresis (VARENNE et al., 2015) or on optical electrophoresis (VARENNE et al., 2015). The electroacoustic spectroscopy (EAS) as an acoustic electrophoresis method and the electrophoretic light scattering (ELS) uses phase analysis light scattering (PALS) as optical electrophoretic methods are routinely used in many laboratories. The Zeta potential value obtained from measurements of the electrophoretic mobility of a nanomaterial is considered apparent if no correction for the surface conductivity is used in calculation. The measurements of the electrophoretic mobility of a nanomaterial are performed while an electric field is applied on a dispersion of the nanomaterial in an appropriate dispersion medium. Particles with a high zeta potential with positive or negative charge repel each other. For the nanoparticle dispersions to be considered stable, the zeta potentials of particles must be more positive than +30 mV or more negative than -30 mV.

The aim of the present study was to explore the applicability of the validated protocols for zeta potential measurements to the characterization of a series of dispersions including particles made of titanium oxide, active carbon, hydroxyapatite and magnetic particles that find their way to applications in sunscreen, sensors and prosthesis.
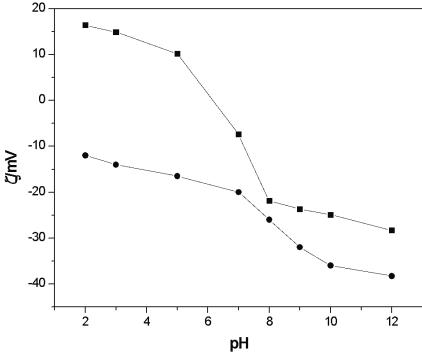
MATERIAL AND METHODS

Millipore water system was used to provide ultrapure water (MilliQ®). The evaluation of zeta potential was carried out with disposable cells (DTS 1070, Malvern). They were rinsed with filtered ultrapure water with a 0.22 µm filter followed by filtered absolute ethanol (LabSynth) with a 0.2 µm membrane (Millipore) and filtered ultrapure water again. They were stored in a dust-free environment before use. Before and after washing, these cells were inspected for any scratch and cleanness. Electrodes presented inside and outside of cells were cleaned. The zeta potential data is an average of three successive measurements of the same dispersion.

All investigated NPs such as titanium oxide and $AgTiO_2$ (PINTON, 2017; POMPEU, 2018), PbO and CuO (CADÓ, 2016), magnetic active carbon (FINGER, 2016) and hydroxiapatite were prepared in our laboratory.

Aqueous sodium chloride solution, used to achieve dilutions of samples to evaluate zeta potential of dispersed materials, were prepared using sodium chloride (purity 99 %, Vetec) and MilliQ water. The solution was filtered with 0.22 µm filter before use. A Zetasizer Nano ZS (Malvern) equipped with a Laser source of wavelength of 633 nm was used for zeta potential measurements. For the measurements, the protocols defined in the literature were followed (VARENNE et al., 2015). Dispersions of each NPs (1% m/m) were prepared in water. All samples were sonicated during 5 minutes to make them homogeneous. Cetyltrimethylammonium bromide (5 mmol/L, CTAB, Sigma-Aldrich) of an analytical reagent grade was used for the stabilization of the suspensions. Hydrochloric acid (HCl, Synth) and sodium hydroxide (NaOH, Synth) were used for adjusting the pH during zeta potential measurements.

RESULTS AND DISCUSSION

Figure 1 shows he measured zeta potential values as a function of pH for the aqueous suspension of active carbon (AC) and magnetic AC. It can be observed that the AC dispersion has high negative values for zeta potential (-10 mV to -40 mV) within the pH range from 2.0 to 12.0, which indicates stable dispersions in acidic and basic pH values. More importantly, the zeta potential values for the AC are far from the isoelectric point (i.e. point of zero charge), which indicates that this pH range (3.0-10) results in strong electric repulsion forces between the AC nanoparticles. This repulsion prevents the aggregation of the AC by non-covalent interactions such as π - π interactions or H-bonding. We attribute this phenomenon to the oxygen functionalities at the surface of the AC. The presence of magnetic $NiFe_2O_4$ nanoparticles on AC surface promotes a shift in potential to more positive values due to surface charge on $NiFe_2O_4$ leading to an isoelectric point close to pH 7.0.

Figure 1 - Zeta potential of active carbon (·) and NiFe$_2$O$_4$/active carbon (■) dispersions as a function of pH.

Source: author.

Figure 2 shows the changes of the zeta potential during an increase of pH for TiO$_2$ and AgTiO$_2$ aqueous dispersions. The increase of NaOH caused a decrease of the zeta potential and an increase of particle size as pointed out in the literature for ZnO (MARSALEK, 2014). In acidic pH the TiO$_2$ nanoparticles have a positive and a negative charge at alkaline pH. The addition of silver shifts the zeta potential to positive values and displaces the isoelectric point of the dispersions. This effect occurs by the increase of positive charge in the TiO$_2$ molecule.

As depicted in figure 3, the zeta potentials of hydroxyapatite dispersions are always negative indicating a high stability of hydroxyapatite dispersions. The zeta potential measurements indicated that the most stable condition for hydroxyapatite dispersions are at pH higher than 5.

As shown in figure 4, PbO presents an isoelectric point in neutral pH. The surface charge of PbO has a positive character in acid medium, and it changes to a negative character in basic medium. The CuO has an isoelectric point at pH close to 4, which shows that the CuO surface charge has a negative character when dispersed in pH solutions above 4.

It is known that the presence of CTAB shifts the zeta potential to more positive values due to their cationic charge that improves the dispersion stability (MARSALEK, 2014).
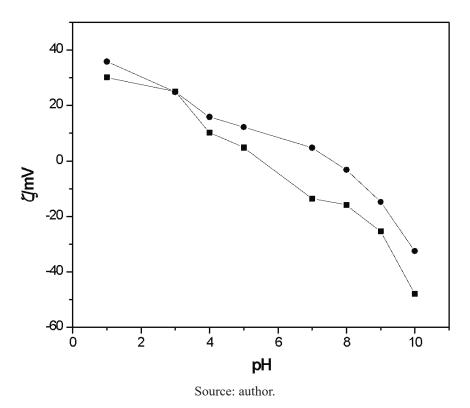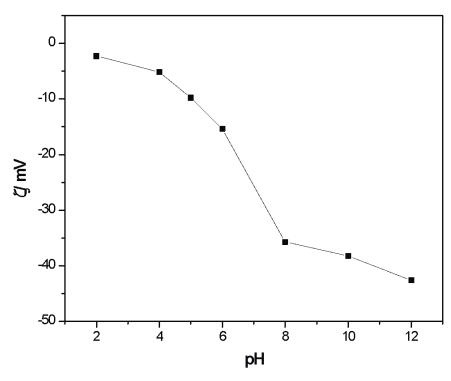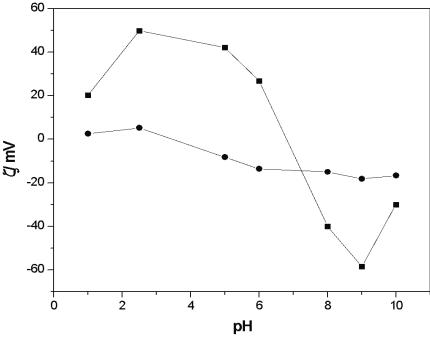
Figure 2 - Zeta potential of TiO_2 (■) and $AgTiO_2$ (·) dispersions as a function of pH.

Source: author.

Figure 3 - Zeta potential of hydroxyapatite aqueous dispersions as a function of pH.

Source: author.

Figure 4 - Zeta potential of dispersions of PbO (■) and CuO (·) as a function of pH.

Source: author.

Zeta potential is affected by factors such as solution pH, ionic strength, and types of ionic species. Due to the protonation/deprotonation of the surface groups of NPs, the addition of NPs would change the initial solution pH (SUTTIPONPARNIT et al., 2011). They concluded that this decrease in the solution pH causes the increase in the zeta potential of TiO_2 particles at high particle concentration, since it commonly shifts to a more positive value as pH decreases. The change in the sign of zeta potential at low particle concentration suggests the adsorption of appreciable counterions on the particle surface. In our case, the dominate counterions Cl^- come from the introduced NaCl. The influence of solution pH on the zeta potential of different oxide NPs are depicted in Figures 2 and 4. This strong dependence of zeta potential on pH can be explained by the protonation/deprotonation of the surface groups of NPs. Metal oxide NPs are usually hydrated in an aqueous atmosphere, and their surface is completely covered by the corresponding hydroxyl groups, as confirmed by the infrared measurements (DHAKSHINAMOORTHY et al., 2012). If we denote >M-OH as the surface groups of metal oxide NPs, then it becomes >M—OH_2· in an acidic and >M-O in a basic environment.

CONCLUSIONS

Stability of dispersions of oxides can be influenced by the environmental conditions such as pH and the presence of surfactants. The stability of dispersions can be monitored by measuring the zeta potential. Suspensions of hydroxyapatite are stable in all pH range (5 to 12). Most oxides exhibit

an isoelectric point close to neutral pH. The presence of surfactant such as CTAB improves the dispersion stability. The proposed protocol was found to be precise under repeatability conditions and defined precision conditions. In conclusion, this methodology is acceptable for the analyses of hydroxyapatite and oxides dispersions stability under different environmental conditions.

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