

ZETA POTENTIAL MEASUREMENTS USING THE ELECTROACOUSTIC METHOD FOR QUARTZ AND HEMATITE

E.E. Ferreira¹ , P.R.G. Brandao² , A.E.C. Peres³

¹ Graduate Course on Mining and Metallurgy Engineering

² Department of Mining Engineering

³ Department of Metallurgy and Materials Engineering

^{1,2,3} UFMG - Federal University of Minas Gerais

Rua Espírito Santo, 35, sala 702 - Belo Horizonte, MG - CEP: 30160-030 - Brazil

pbrandao@demin.ufmg.br

ABSTRACT

The electroacoustic method is a new, fast and versatile way to measure zeta potential of inorganic particles. This method is based on the transference of momentum from a particle to the liquid phase due to the oscillatory motion of the particle, which is caused by the application of an alternating electric field. This transference of momentum will result in the development of an acoustic wave, which amplitude is related to the net surface charge of the particle. In order to verify the applicability of this method to mineral and ore samples, measurements of zeta potential versus pH have been carried out on two minerals – quartz and hematite – with and without a support electrolyte (KNO₃), at the concentration 10⁻² moles per liter. Some results for the quartz sample were contradictory to the expected ones, since the presence of the inert electrolyte (KNO₃) did not cause a decrease in the zeta potential values, as predicted by the electric double layer theory, but instead they increased relatively to the curve without electrolyte. For hematite, the results in the presence of electrolyte, in the alkaline pH range, were consistent with the electric double layer theory, yielding lower zeta potential values. In the acidic pH range, the values of zeta potential with electrolyte were approximately the same as the values without electrolyte. Hematite also yielded the isoelectric point at pH = 8.0, which was higher than the value obtained by the Mular & Roberts method, which was pH=6,1. The deviation from the electric double layer theory, for both quartz and hematite samples, maybe be due to the following reasons: 1) the effect of ions in solution, that also contribute to the electroacoustic signal, through the ion vibration potential (IVP) for the quartz sample; 2) for hematite, the inertial effect, due the coarser particle size and particle coagulation, caused the increase of all zeta potential values, thus resulting in the displacement of the IEP to pH=8,0; in the case of the acidic pH range, particles aggregation had the same effect, which in turn

raised the inertial factor and therefore the zeta potential values.

This study demonstrated that the ESA-8000 instrument works well with finer particles, below 8µm. However, in the presence of a support electrolyte, the ESA signal generated by the electrolyte should be subtracted from the signal of the particles. However, the equipment used was unable to do this.

INTRODUCTION

The electroacoustic method is a new, fast and versatile way to measure zeta potential and particle size distribution. There are two kinds of effects: 1) when a sound wave passes through the particle suspension, it creates a potential difference, called the ultrasonic vibration potential (UVP); it was firstly described by Debye in 1933 (Hunter, 1998); 2) the contrary effect occurs when an alternating potential difference is applied in two electrodes, the particles in suspension also will move and their oscillatory motion provokes the transference of momentum from the particles to the liquid phase. This transference of momentum will result in the development of an acoustic wave, and its amplitude is related to the net surface charge of the particles; it is called Electrokinetic Sonic Amplitude (ESA), and was discovered by T.Oja; G.L.Peterson and D.W.Cannon in 1985 (Hunter, 1998).

According to O'Brien's equations, the associated dynamic mobility is related to the ESA signal through the following equation (Kissa, 1999):

$$ESA(\omega) = A(\omega) \mu_d \phi \Delta \rho \quad (1)$$

Equation (1) shows that the magnitude of the ESA signal is a function of the following variables: the density difference between the particle and the liquid (solvent) ($\Delta\rho$); the volume fraction of the particles (ϕ).

In this equation, $ESA(\omega)$ is the electrokinetic sonic amplitude at the angular frequency (ω) and $A(\omega)$ is a characteristic coefficient for each apparatus.

Considering a spherical particle in a dilute suspension (< 10 vol. %) and a thin electric double layer ($Ka > 50$), O'Brien has related the dynamic mobility to zeta potential values by equation (2) (Kissa, 1999).

$$\mu_d = \frac{2\varepsilon\xi}{2\eta} G(\alpha) [1 + f(\lambda, \omega)] \quad (2)$$

where: ξ - zeta potential;

ε - permittivity of the liquid;

η - viscosity of the liquid;

μ_d - dynamic mobility of the suspension;

$G(\alpha)$ - particle inertial factor;

$[1+f(\lambda, \omega)]$ - factor proportional to the tangential component of the electric field, where λ is a surface conductance parameter and ω is the angular frequency.

The particle inertial factor is a function of the particle radius (a), the angular frequency (ω) and the kinematic viscosity (ν); it is given by equation (3) and associated equation (4).

$$G(\alpha) = \left[1 - \frac{i\alpha \left(3 + 2 \left(\frac{\rho - \rho_0}{\rho_0} \right) \right)}{9(1+i) \sqrt{\left(\frac{\alpha}{2} \right)}} \right]^{-1} \quad (3)$$

$$\alpha = \frac{\omega a^2}{\nu} \quad (4)$$

It was pointed out (Hunter, 1998) that if the particle had a small dielectric permittivity, i.e. similar to water's, the dynamic mobility can be related to zeta potential simply by equation (5). This equation is an analogue to the Smoluchowski equation, which applies to the classical electrophoretic mobility.

$$\mu_d = \frac{\varepsilon\xi}{\eta} G(\alpha) \quad (5)$$

In order to check the applicability of this method to mineral and ore samples, measurements of zeta potential versus pH have been carried out for pure samples of two minerals: quartz and hematite, with and without a support electrolyte (KNO_3), at the concentration of 10^{-2} moles per liter.

EXPERIMENTAL

Equipment

The ESA-8000 device, made by Matec Applied Sciences, with a fixed frequency of 1.0 MHz, was used throughout this study; it had the following attachments and components: a microcomputer; the SP-80 ESA probe and a computer-controlled burette.

A microelectrophoresis apparatus, Rank Brothers brand, model II, and the Mular & Roberts method (Mular and Roberts, 1966) were used in order to comparing those results.

Samples

The experiments were carried out on pure samples of two minerals: quartz and hematite. These mineral samples were ground in a ceramic ball mill until grain sizes below $38\mu m$. The hematite sample was further separated in two size ranges, using a Warman Cyclosizer, and the experiments were carried out with the wide size sample, below $38\mu m$ and with the overflow from the Cyclosizer, below $7.2\mu m$.

Reagents

Potassium nitrate (KNO_3) was used as the inert support electrolyte in the concentration of 10^{-2} moles per liter; potassium hydroxide and nitric acid were used as pH modifiers. All reagents were analytical grade ones.

Procedure

The experiments were carried out with and without the support electrolyte, using the potentiometric-titration function of the ESA-8000 unit. Before each test, this instrument was calibrated against a standard quartz colloidal suspension: Ludox TM, made by Du Pont. An ultrasonic device and a mechanical stirrer were used to keep the samples well dispersed.

RESULTS AND DISCUSSION

Quartz sample

The curve of zeta potential versus pH for the quartz sample by the ESA method, Figure 1, does not show an isoelectric point (IEP). A similar result was obtained by microelectrophoresis, Figure 2, which confirmed that it is a characteristic of the sample. Comparing the curves

of zeta potential versus pH (Figure 1), with and without electrolyte, one sees that the addition of the 10^{-2} moles per liter KNO_3 solution had the effect of increasing all the zeta potential values. According to the electric double layer (EDL) theory, when an indifferent electrolyte is added to a mineral suspension it promotes the compression of the diffuse part of the double layer, which should cause necessarily the decrease of the zeta potential values. The above results show an effect contrary to that predicted by the theory.

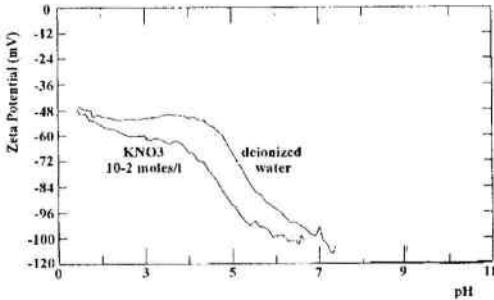


Figure 1 - Curve of zeta potential versus pH for quartz with and without KNO_3 by the electroacoustic method.

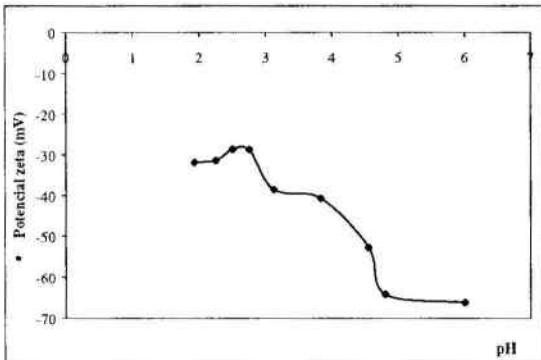


Figure 2 - Curve of zeta potential versus pH for quartz with KNO_3 10^{-2} moles per liter by microelectrophoresis.

According to Hunter (Hunter, 1998), the electroacoustic signal from the particles is influenced by another signal from the ions, which are capable also to produce an ESA effect, which should be subtracted from the total signal.

O'Brein et alii, 1994, pointed out that the electrolyte presence, in addition to the signal effect, causes a reduction in the impedance of the system, what implies in the decrease of the applied voltage in the electrode. They proposed a procedure in order to calibrate this apparatus for ionic solution: a polyacrylic acid solution and a colloidal suspension of quartz (Ludox). This procedure is carried out using an electronic circuit, which is linked to the electrode, in the ESA-8000 unit. However, the commercial equipment did not incorporate

that electronic circuit.

Hematite sample

The sample of hematite with a wide size distribution ($<38\mu\text{m}$) showed typical curve of zeta potential versus pH, as shown in Figure 3. The presence of the electrolyte (KNO_3), at the concentration of 10^{-2} moles per liter, reduced the values of zeta potential in the basic pH range, which agrees with the electric double layer theory, due to the compression of the diffuse part of the EDL. However, in the acidic pH range, the values of zeta potential, with the electrolyte, were approximately the same as compared to the values without the electrolyte. This behavior is probably due to the particles coagulation, what promotes an increase in the apparent particle size (actually the aggregate size); consequently, the inertial factor rises, therefore, the zeta potential value increases, too.

Comparing the IEP values obtained by the electroacoustic method (pH 8.0 to 8.5, Figure 3) with the data from the Mular & Roberts method (Figure 4), the value of the PZC was pH=6.1. For hematite, the expected value should be the latter.

This difference is due to the particles wide size distribution (all under $38\mu\text{m}$, with the mean diameter at about $9.1\mu\text{m}$). For this sample, it was necessary to calculate the effective radius, in order to estimate the inertial factor for the particles distribution. This was done by using a spreadsheet developed by Hunter (Hunter, 1998). The effective radius thus calculated was $3.0\mu\text{m}$. However, during the experiment, those particles with a coarser size had a much higher inertial factor and probably they did not contribute to the ESA signal. However, the software took their inertial effect account, so, the calculated zeta potential was greater. This is seen in equation (2), where the inertial factor multiplies the value of the dynamic mobility in order to correct it.

Experimentally, this was tested by the use of virtual values of the effective radius during the experiments, i.e. by using the software that runs the ESA-8000 equipment for modeling the zeta potential values. In this case, when the values of the effective radius increased, all the zeta potential values also increased; therefore, all the curves were shifted to higher pH values.

Figure 5 shows the zeta potential values versus pH for the overflow of the hematite sample; its effective radius was $1.4\mu\text{m}$, calculated by the spreadsheet. The experiments carried out in deionized water (without a support electrolyte) exhibited the IEP at pH = 6.1, which agrees with the PZC determined by the Mular and Roberts method, Figure 4.

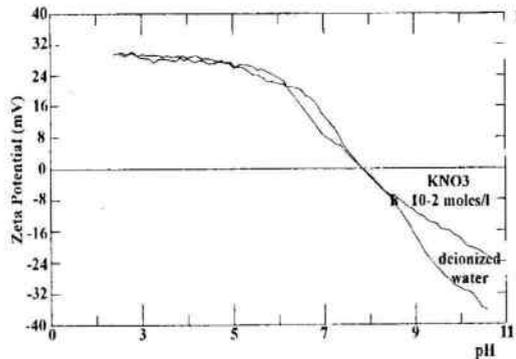


Figure 3 - Curve of zeta potential versus pH for hematite with and without KNO_3 by the electroacoustic method.

These experiments demonstrated how the coarser particles caused the increase in the inertial factor and consequently an increase in all zeta potential values. Hunter pointed out that the particle size range for which this equipment works well is below $10\mu\text{m}$ (Hunter, 2000). It agrees with the fact that the presence of particles coarser than this limit brought about an increase in the zeta potential values and caused a displacement of the corresponding curve, which resulted in the switch of the IEP to a higher pH value.

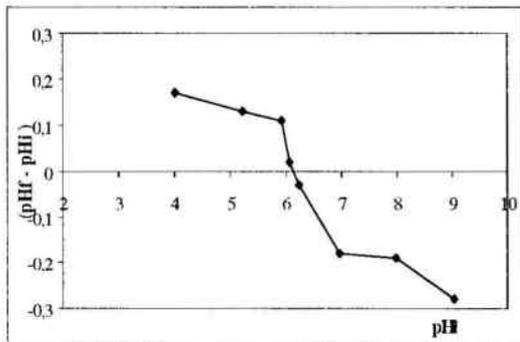


Figure 4 - Curve of $(\text{pH}_f - \text{pH}_i)$ versus pH_i by the Mular & Roberts method to determine the PZC of hematite.

When the electrolyte was added, the isoelectric point of the finer hematite sample (Cyclosizer overflow, below $7.2\mu\text{m}$), dropped as the electrolyte concentration increased, Figure 5. These results are totally in disagreement with the electric double layer theory, since the IEP is an invariant point, provided that the support electrolyte is truly indifferent. In this case, KNO_3 is well known to be non-specific, regarding adsorption onto hematite. Therefore, the effect is probably caused by the action of the electrolyte on the dielectric permittivity (ϵ) and on the variable $[1+f(\lambda, \omega)]$ in equation (2). This variable $[1+f(\lambda, \omega)]$ is proportional to the tangential electric field and is responsible for the electrophoretic motion (O'Brein et alii, 1995). In the case of a fixed frequency device, such as the ESA-8000 apparatus,

$f(\lambda, \omega)$ the value of 0,5 is assumed and the dielectric permittivity is taken as equal to that of water. However, the electrolyte will modify these two variables and the equipment does not take these changes into account. As the factor $[1+f(\lambda, \omega)]$ increases, all zeta potential value (ξ) will decrease. This can be inferred from equation (2).

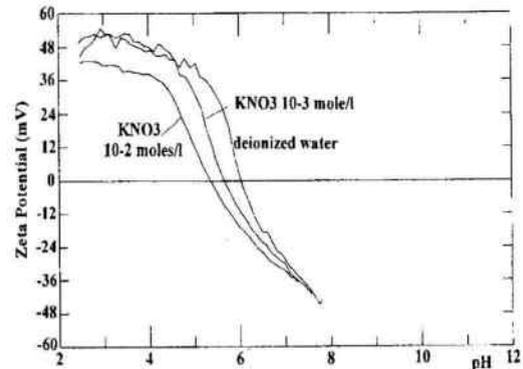


Figure 5 - Curve of zeta potential versus pH for fine hematite (below $7.2\mu\text{m}$) with and without KNO_3 by the electroacoustic method.

CONCLUSIONS

The ESA instrument used in this study can yield fast, reproducible and accurate zeta potential and electrophoretic mobility values. Curves of zeta potential versus pH can be obtained easily; therefore, the IEP values are readily determined. Also, zeta potential individual readings can be achieved promptly.

However, there are certain limitations for which there is no warning, hence, misleading results can be obtained, if precautions are not taken. The most important are the following:

- 1) in addition to the particles, the ions in solution also contribute to the ESA signal; this collateral effect is not easily compensated for. Thus, even relatively dilute solutions of electrolytes (such as 10^{-3} moles/liter) should be avoided. The electrolyte effect is to diminish every zeta potential absolute value; therefore the IEP's will be displaced to lower (more acidic) pH values;
- 2) the ESA equipment employed uses a single frequency (1.0MHz); as a consequence, it can handle only suspensions having particles smaller than $10\mu\text{m}$; under this limit, the correction inertial factor must still be calculated, for the average particle radius. If larger particles are allowed, the zeta potential values will drift to higher absolute values and the corresponding IEP's to higher pH (less acidic) figures, too.

REFERENCES

- Hunter, R.J. Recent Developments in the Electroacoustic Characterisation of Colloidal Suspensions and Emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 141, p.37, 1998.
- Hunter, R.J. Personal communication, by e-mail, 2000.
- Hunter, R.J. Estimation of Effective Radius of a Distribution. Application Note no. 101, Matec Applied Sciences, 11p., 1998.
- Kissa, E. *Dispersions - Characterization, Testing and Measurement*. New York: Marcel Dekker, 708p, 1999.
- Mular, A.L. and Roberts, R.B. A Simplified Method to Determine Isoelectric Points of Oxides. *CIM Bulletin*, Nov., p.1329, 1966.
- O'Brien, R.W., Garside, P., Hunter, R.J. The Electroacoustic Reciprocal Relation. *Langmuir*, 10, p.931, 1994.
- O'Brien, R.W, Cannon, D.W., Rowlands, W.N. Electroacoustic Determination of Particle Size and Zeta Potential. *Journal of Colloid and Interface Science*, 173, p. 406-418, 1995.