Stern-layer parameters of alumina suspensions


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Abstract

The specific adsorption of Mg$^{2+}$ and S$_2$O$_8^{-2}$ ions onto the γ-alumina particle surface has been demonstrated. An estimation algorithm based upon the correlation between electrophoretic mobility and conductivity increment experimental data, employing a dynamic Stern-layer theory, has been developed and used to get the adsorption parameters into the Stern layer for different γ-alumina/Mg$^{2+}$ and S$_2$O$_8^{-2}$ aqueous solutions interface.

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1. Introduction

Metal oxides have a relevant position among the colloidal systems, due to their importance in industry and technology. The electrical properties of the oxide–water interface play an important role in the regulation of the chemical composition and physical properties of different aqueous systems. On the other hand, from the colloid science point of view, checking the validity of theoretical models of ion adsorption is needed to find appropriate colloidal suspensions. It is known that the existence of ions specifically adsorbed onto the particle surface, which form a Stern layer, has an important effect on electrokinetic measurements, and, therefore, it is necessary to test the novel electrokinetic models that assume that these ions can move tangentially inside that layer [1–4]. This mechanism is known as the dynamic Stern layer (DSL). Oxides are likely to present adsorption of some type of ions.

Measurements of electrokinetic phenomena and the utilization of a simple model to quantify them have traditionally estimated the ζ-potentials of colloidal particles. Classical theoretical models need the ζ-potential value as the unique free parameter. However, discrepancies found between ζ-potentials for the same system estimated using different theoretical approaches corresponding to different phenomena have shown that this procedure is not strictly valid for obtaining a good description of the interface [5].

Zukoski and Saville [6] showed that the inclusion of a dynamic Stern layer in classical models for electrophoresis and conductivity could reduce (or even eliminate) the discrepancies. The development of new theoretical approaches that supply, the same ζ-potential value, independent of the electrokinetic technique used, is a main subject of colloid science. The correlation of different electrokinetic phenomena, used in this work, is one way to obtain good results on the structure of the interface in colloidal systems.

The lack of detailed knowledge about the behavior of ions and solvent molecules in the close vicinity of the particle surface increases the number of free parameters in the theoretical models that include a dynamic Stern layer (for example, the drag coefficients for counter- and co-ions inside the Stern layer). Due to the fact that these extra parameters are not accessible through direct measurements, some authors [7] have questioned the possibility of using a dynamic Stern layer to justify their results, despite the use of this model by them to reconcile conductivity and electrophoretic mobility data on a polystyrene latex. However, we consider that the combined use of different electrokinetic techniques can be a valid method for obtaining an estimate of the Stern-layer parameters [8].

In this work the electrical double layer that is formed at the alumina–water interface has been studied. In order to establish the ability of alumina particles to specifically absorb ions, we have determined the isoelectric point of the suspensions by measuring the electrophoretic mobility of the particles. Once the specific adsorption is confirmed,
the Stern-layer parameters and the ζ-potential are estimated by the utilization of two distinct electrokinetic phenomena, namely electrophoresis and suspension electrical conductivity (in the low-frequency limit).

1.1. Materials and methods

The alumina used in this study was γ-Al2O3 manufactured by Goodfellow Cambridge Ltd. (England). This material is presented as a powder with a purity of 99.995%. In order to remove soluble salts and other impurities, the alumina was dialyzed in deionized water for 7 days. Deionized water was changed at the beginning and end of each day [9]. Thereafter, the alumina suspension was left to undergo sedimentation for 24 h. The suspension thus obtained was filtered through a filter with 0.1 µm of pore size dried, and stored. The initial conductivity of a cleaned Al2O3 suspension was 8.75 µS/cm, 4 µS/cm being the conductivity of the supernatant after the suspension was centrifuged.

The shape and size of γ-alumina particles were determined by transmission electron microscopy (TEM). The images showed that the particles are highly ordered crystalline grains with distinct planar faces. The radius of the particles was roughly 50 nm, with low polydispersity.

To obtain its surface charge density, the apparent specific surface area BET [10] of these particles was determined by N2 adsorption at 77 K using an Autosorb-1 (QuantaChrome) apparatus. The result was 142 m2/g.

The electrophoretic mobility of the alumina particles was obtained with a Zetasizer 2000 (Malvern Instruments) by measuring zeta-potential (i.e., diffusion plane) at an electrokinetic unit, which moves as a whole when the particle is set into movement with respect to the liquid medium. It is assumed that the slipping plane is very close to the outer surface of the Stern layer (if not coincident with it). In the case of an indifferent electrolyte, the isoelectric point will be the same for all electrolyte concentrations, and it will also coincide with the point of zero charge. The nonexistence of a common isoelectric point for

2. Theory

When an oxide powder is in contact with water, a surface charge appears by proton transference with the liquid medium [11].

\[ \text{M–OH} + \text{H}_2\text{O} \leftrightarrow \text{M–O}^- + \text{H}_3\text{O}^+ , \]
\[ \text{M–OH} + \text{H}_2\text{O} \leftrightarrow \text{M–OH}_2^- + \text{OH}^- , \]

where M represents a metal cation. The first equation corresponds to a negatively charged surface and the second justifies the existence of a positive charge density. The electrical double layer is developed around the particle from the compensating counterions, which are into the liquid phase.

Due to this behavior, the H⁺ and OH⁻ ions are called potential-determining ions for metal oxide suspensions. The surface charge density of the particles will be

\[ \sigma_0 = F (I_{\text{H}^+} - I_{\text{OH}^-}) , \]

where \( I_1 \) is the adsorption density of the \( i \)-ion and \( F \) is the Faraday constant.

From Eqs. (2) and (3), we see that \( \sigma_0 \) must be pH-dependent. The pH-value where \( \sigma_0 = 0 \), if it exists, is called the point of zero charge (p.z.c.). Obviously, if the ions in the solution are not adsorbed onto the particle surface (indifferent electrolyte), the p.z.c. will not change when the concentration of the added electrolyte is varied. Oppositely, if the ions are adsorbed onto the particle surface (specifically adsorbed ions), the p.z.c. will become a function of the electrolyte concentration. In this case, the surface charge density has to be calculated from

\[ \sigma = F (I_{\text{H}^+} - I_{\text{OH}^-} \pm z I_{\text{i+}}) = \sigma_0 + \sigma_S , \]

where I is the specifically adsorbed ion, \( \pm z \) its valence, and \( \sigma_S \) is the charge density on the Stern layer, which is the region immediately close to the true particle surface where the adsorption of electrolyte ions takes place.

Another parameter, which allows us to detect the adsorption of ions on the particle surface, is the isoelectric point (i.e.p.). It is defined from an electrokinetic point of view. When the pH of the liquid medium is varied, the zeta potential, i.e., the potential at the slipping plane, could reach zero at a certain pH_{ieg}; this is the isoelectric point. The slipping plane defines the electrokinetic unit, which moves as a whole when the particle is set into movement with respect to the liquid medium. It is assumed that the slipping plane is very close to the outer surface of the Stern layer (if not coincident with it). In the case of an indifferent electrolyte, the isoelectric point will be the same for all electrolyte concentrations, and it will also coincide with the point of zero charge. The nonexistence of a common isoelectric point for
different electrolyte concentrations indicates that there are specifically adsorbed ions on the particle surface.

The adsorption phenomena can be described by different adsorption isotherms, depending on the details of the adsorption mechanism [3]. The adsorption \( X_i \) of an ionic species \( i \) \((i = 1, \ldots, N)\) onto an empty site \( S_i \) in the Stern layer can be represented by a dissociation reaction [2,3,11],

\[
S_i + X_i \leftrightarrow SX_i \quad (i = 1, \ldots, N)
\]  

with a mass-action equation

\[
[S_i]n_i^{\infty} = K_i \exp \left( \frac{z_i e}{kT} \Psi(\beta_i) \right) \quad (i = 1, \ldots, N),
\]  

where \( \beta_i \) represents the distance of closest approach of the ions to the particle surface, \( \Psi(\beta_i) \) is the electric potential at distance \( \beta_i \), \( T \) is the temperature, \( e \) is the proton charge, \( k \) is Boltzmann’s constant, \( z_i \) is the valence, \( n_i^{\infty} \) is the bulk number density and \( K_i \) is the dissociation constant for \( i \)-type ions.

From this equation it is possible to find the Stern layer charge density due to the adsorption of \( i \)-type ions, which is given by [3]

\[
\sigma_i^0 = \frac{z_i e N}{kT} \exp \left[ \frac{z_i e}{kT} (\zeta - \frac{\sigma_d}{C_2}) \right] \quad (i = 1, \ldots, N),
\]  

with the parameter \( \gamma_i \) defined as

\[
\gamma_i = \begin{cases} 
\sum_{j \neq i} \frac{n_j^{\infty}}{K_j} \exp \left[ \frac{-z_j e}{kT} (\zeta - \frac{\sigma_d}{C_2}) \right], & \text{model 1} \\
0, & \text{model 2}
\end{cases} 
\]  

\((i = 1, \ldots, N),\)

where \( \zeta \) is the zeta potential, \( C_2 \) (= 130 µF/cm²) is the outer Stern-layer capacity, and \( \sigma_d \) is the surface charge density of the diffuse double layer immediately close to the Stern layer. Model 1 refers to adsorption of ions onto available free surface area, whereas model 2 represents adsorption of ions onto specific surface sites that are not available to other ionic species. \( N_i \) is the total number of Stern-layer sites for \( i \)-type ions in both adsorption models. In this work, the model 1 has been used.

The inclusion of the Stern-layer transport in the electrokinetic models is achieved by changing the boundary conditions at the particle surface [3]. In its final form, this modification consists in the appearance of a parameter \( \delta_i \), called the additional surface conductivity parameter, in the boundary condition. This parameter is given by the expression

\[
\delta_i = \frac{N_i}{K_i} \frac{\lambda_i}{\lambda_i^f(\beta_i)} \exp \left( \frac{z_i e \sigma_d}{kT C_2} \right) \quad (i = 1, \ldots, N),
\]  

where \( \gamma_i \) is given by Eq. (8), \( a \) is particle radius, \( \lambda_i \) is drag coefficient in the bulk, and \( \lambda_i^f(\beta_i) \) is drag coefficient in the Stern layer for \( i \)-type ions.

### 3. Results and discussion

Figure 1 shows the electrophoretic mobility of alumina versus pH of the liquid phase at various KCl concentrations. The sign of mobility values changes when pH varies, which indicates that H⁺ and OH⁻ are potential-determining ions for this system, as expected. All curves cross the pH axis at the same point, pH_{iep} = 9.2, which is, therefore, the common isoelectric point for all concentrations. This result shows that KCl is an indifferent electrolyte for alumina suspensions.

We have followed the method described by Hunter [11] to determine the p.z.c. of alumina particles in KCl electrolyte: 7 mg of Al₂O₃ are added to 40 ml of KCl electrolyte at various concentrations (10⁻² M, 5 × 10⁻³ M, and 10⁻³ M). The initial pH value is registered and the sample is then titrated with 10⁻³ M NaOH. The blank electrolyte (i.e., without alumina particles) is also titrated with the same base. Both curves are plotted together in the same diagram, and the subtraction of base volumes needed to get the same pH value for both samples is related with the relative surface charge of alumina particles. A similar procedure is used in the low pH interval, by using 10⁻³ M HCl solution. The relative surface charge density values obtained in this way are plotted against pH in Fig. 2. The point where the three curves cross each other can be identified as the point of zero charge, because only at that point the surface charge is independent of the concentration of the KCl electrolyte (there is not specific adsorption). Figure 2 shows that the point of zero charge is pH_{pzc} = 9.2, which is the same value as found for the isoelectric point. We can rescale the plot to show the absolute value of surface charge density (inset of Fig. 2). The coincidence of pH_{pzc} and pH_{iep} supports the conclusion that KCl electrolyte is an indifferent electrolyte for alumina suspensions.

When forces different from the electrical one drive adsorption of electrolyte ions at the particle surface, they can be regarded as being specifically adsorbed. When this adsorption mechanism takes place, the point of zero charge and the isoelectric point will change with the added electrolyte.

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**Fig. 1.** Electrophoretic mobility of alumina suspensions versus pH at different KCl concentrations: (■) [KCl] = 10⁻² M, (○) [KCl] = 5 × 10⁻³ M, and (▲) [KCl] = 10⁻³ M.
Fig. 2. Relative and absolute surface charge density of alumina suspensions versus pH at different KCl concentrations: (■) [KCl] = 10^{-2} M, (●) [KCl] = 5 \times 10^{-3} M, and (▲) [KCl] = 10^{-3} M.

Fig. 3. Electrophoretic mobility of alumina suspensions versus pH at different MgCl\(_2\) concentrations: (■) [MgCl\(_2\)] = 10^{-4} M, (●) [MgCl\(_2\)] = 5 \times 10^{-5} M, and (▲) [MgCl\(_2\)] = 10^{-5} M.

concentration. Figure 3 shows the electrophoretic mobility of alumina suspensions versus pH at different MgCl\(_2\) concentrations. There is not a common cross point at zero ζ-potential. The curves cross the pH axis at a pH value that increases when the electrolyte concentration is heightened. This behavior can be explained if it is assumed that Mg\(^{2+}\) ions are adsorbed onto the particle surface. These ions displace H\(^+\) ions at the surface and, therefore, the electokinetic charge on the particle increases because Mg\(^{2+}\) ions have higher valence than H\(^+\) ions. Consequently, it is now necessary to have a pH higher than that in the case of no adsorption, because it more OH\(^-\) ions are needed to compensate for the electokinetic charge over the particles until the isoelectric point is reached. This effect can be observed in Fig. 3, where all isoelectric points are found at a pH higher than 9.2. As a conclusion, it is found that MgCl\(_2\) is not an indifferent electrolyte for alumina suspensions.

In order to determine if this adsorption mechanism is also present for negative bivalent ions we have measured the electrophoretic mobility of alumina suspensions with K\(_2\)S\(_2\)O\(_8\) as the added electrolyte. Due to the last result, S\(_2\)O\(_8^{2-}\) ions are the only ones that could be specifically adsorbed. Figure 4 shows the electrophoretic mobility of alumina suspensions versus pH at different K\(_2\)S\(_2\)O\(_8\) concentrations. As in the MgCl\(_2\) case, we do not find a common value for the isoelectric point for all concentrations, which means that K\(_2\)S\(_2\)O\(_8\) is not an indifferent electrolyte. We can see that the higher the electrolyte concentration, the lower the pH at which the electrophoretic mobility equals zero, and in all cases it is found that pH\(_{iep}\) < 9.2. This behavior is again explained by an adsorption mechanism of S\(_2\)O\(_8^{2-}\) ions onto the particle surface, where S\(_2\)O\(_8^{2-}\) ions substitute OH\(^-\) ions. Due to the higher valence of S\(_2\)O\(_8^{2-}\) ions, a larger number of H\(^+\) ions is required to compensate the S\(_2\)O\(_8^{2-}\) ions adsorbed onto the particle surface. Consequently, the isoelectric point is always present at a lower pH-value than in the case of no adsorption.

In Fig. 5 the electrophoretic mobility of alumina suspensions is shown as a function of KCl concentration (pH = 5).
Table 1
Experimental data and reduced zeta-potential values for alumina suspensions with KCl electrolyte

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>( \kappa a )</th>
<th>( \mu_e \times 10^8 ) (m²/V s)</th>
<th>( \zeta_{\text{mob}} / kT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻⁵ M</td>
<td>0.52</td>
<td>2.70±0.08</td>
<td>2.11</td>
</tr>
<tr>
<td>10⁻⁴ M</td>
<td>1.64</td>
<td>2.68±0.08</td>
<td>2.10</td>
</tr>
<tr>
<td>5 \times 10⁻⁴ M</td>
<td>3.67</td>
<td>2.74±0.2</td>
<td>2.04</td>
</tr>
<tr>
<td>10⁻³ M</td>
<td>5.20</td>
<td>2.76±0.06</td>
<td>1.96</td>
</tr>
<tr>
<td>5 \times 10⁻³ M</td>
<td>11.6</td>
<td>2.2±0.2</td>
<td>1.34</td>
</tr>
<tr>
<td>10⁻² M</td>
<td>16.4</td>
<td>1.32±0.11</td>
<td>0.76</td>
</tr>
<tr>
<td>5 \times 10⁻² M</td>
<td>36.7</td>
<td>0.8±0.4</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Fig. 6. Electrophoretic mobility of alumina suspensions as a function of MgCl₂ concentration: (●) pH = 11, (■) pH = 9.5.

Fig. 7. Electrophoretic mobility of alumina suspensions as a function of K₂S₂O₈ concentration: (●) pH = 5, (■) pH = 8.75.

Fig. 8. Conductivity increment of alumina suspensions as a function of MgCl₂ concentration (pH = 11).

Fig. 9. Conductivity increment of alumina suspensions as a function of K₂S₂O₈ concentration (pH = 8.75).

a unique parameter to characterize the e.d.l., the \( \zeta \)-potential, and it will be estimated from electrophoretic mobility data. Table 1 shows the electrophoretic mobility data and the \( \zeta \)-potential values of alumina suspensions with KCl electrolyte estimated using O’Brien and White electrophoresis theory [12]. The presence of indifferent ions reduces the electrophoretic mobility value and, consequently, the \( \zeta \)-potential value, when the concentration is increased, but it does not affect the sign of that quantity. The reason for this behavior is that the diffuse layer thickness depends on the added electrolyte concentration and, also, that the existence of indifferent ions in the medium influences the adsorption ability, by screening, of the potential-determining ions (H⁺ or OH⁻). Therefore, the charge density on the surface of the alumina particles is a function of KCl concentration, but without any sign inversion, which is only determined by the pH value.

However, the situation is very different when the added electrolyte contains ions that can be specifically adsorbed. This is the case of bivalent ions Mg²⁺ and S₂O₈²⁻. In Fig. 6 it is shown the electrophoretic mobility of alumina particles as a function of MgCl₂ concentration for two different pH values and it is observed that the electrophoretic mobility varies and, eventually, shows an inversion of sign when the concentration is increased. The sign inversion takes place when the pH of the liquid medium is close to 9.2, which is the isoelectric point for indifferent electrolyte KCl. Analogously, it can be seen from Fig. 7 that S₂O₈²⁻ ions is specifically adsorbed at alumina surface because an increase in the concentration of those ions can, at the appropriate pH value, invert the sign of the electrophoretic mobility.

When the specific adsorption of ions onto the particle surface is present, more parameters than the \( \zeta \)-potential alone are necessary to fully characterize the electrical double layer. Therefore, it is needed more information than that obtained from a unique electrokinetic phenomenon. In addition to the electrophoretic mobility data, we have determined the conductivity increments of alumina suspensions with MgCl₂ and K₂S₂O₈ electrolytes. In this way, we get two information sources for the electrical double layer parameters.

In Figs. 8 and 9 the conductivity increments of alumina suspensions as a function of MgCl₂ and K₂S₂O₈ concentration are plotted, respectively. It was not possible to perform measurements in the region of electrolyte concentrations above 5 \times 10⁻⁴ M, since some coagulation in the alumina samples was observed.

From electrophoretic mobility and conductivity increment data obtained for each suspension we can estimate the \( \zeta \)-potential values \( \zeta_{\text{mob}} \) and \( \zeta_{\text{cond}} \), respectively, using the theory of O’Brien [13] for the electric conductivity of colloidal
Zukoski and Saville [5] found that lower values than those here obtained are found. To calculate this magnitude from the electrophoretic mobility and conductivity measurements is generally higher than those obtained from electrophoretic mobility data, lower values than those here obtained are found. Zukoski and Saville [5] found that \( \zeta \)-potential values estimated from conductivity increment measurements are generally higher than those obtained from electrophoretic mobility data, and this fact led them to question the validity of the standard electrokinetic theory.

In Tables 2 and 3, the experimental results of electrophoretic mobility and conductivity increments are shown for alumina suspensions with MgCl\(_2\) and K\(_2\)S\(_2\)O\(_8\) added electrolyte, respectively. We have put in columns 5 and 6 the dimensionless \( \zeta \)-potential values calculated from electrophoretic mobility and conductivity increments using the standard electrokinetic theories with our algorithm. It can be observed that there is disagreement between the two values and that the \( \zeta \)-potential values obtained from conductivity measurements are higher than those ones estimated from electrophoresis data.

Zukoski and Saville argued that electrokinetic transport properties cannot be completely established from the knowledge of a unique parameter as the \( \zeta \)-potential. It is necessary to evaluate the different parameters that result from a more detailed model of the interface, such as the \( \zeta \)-potential and several other quantities related to the adsorption of ions. In this way, we will use a model electrokinetic theory with dynamic Stern layer [3] and we will construct a method for obtaining the \( \zeta \)-potential and Stern-layer parameters by applying the combination of two electrokinetic techniques: electrophoresis and suspension conductivity.

The \( \zeta \)-potential is a characteristic parameter of the system at equilibrium and, consequently, it should be independent of the experimental method used to obtain it. This will be the first condition we will introduce, although it is not enough to determine completely the set of Stern-layer parameters. We first have built our estimate of the mentioned parameters by following the next points:

- The now established equality condition for \( \zeta \)-potentials estimated by electrophoretic mobility and conductivity increment measurements: \( \zeta_{\text{mob}} = \zeta_{\text{cond}} \).
- Some parameters appear in the equations of the model forming products and, therefore, they can be treated as encapsulated in a unique parameter, allowing us to reduce the number of free parameters that have to be found out.
- We will impose, based on estimations found in the literature and on physical grounds, hypotheses about the order of magnitude and numerical value of some of the parameters. We will establish, in this way, variation ranges for the different parameters of the model.

If we look at the additional surface conductivity parameter (Eq. (9)) that appears in Stern-layer models, we see that the drag coefficient ratios in the bulk and in the Stern layer for each ion, \( \lambda_i/\lambda_i' \), are multiplied by the site densities \( N_i \). Consequently, these four parameters, i.e., two for co-ions and two for counterions \( i = 1, 2 \), are summarized by only two free parameters: \( eN_i(\lambda_i/\lambda_i')(\beta_i) \) \( (i = 1, 2) \). The determination of the value of these free parameters and the \( \zeta \)-potential is based on the potential equality condition mentioned before, calculated from the experimental data of electrophoretic mobility and conductivity increment. In principle, we will assume that the parameter values will be unique for an experimental system, independent of the added electrolyte concentration [6], because they depend only on the type of ion present in the suspension and on the surface properties of the particle.

However, this consideration makes it impossible to find a set of adsorption parameter values that satisfy the \( \zeta \)-potential equality condition for all electrolyte concentrations used in the electrophoretic mobility and conductivity increment measurements. There are three reasons for this: (i) we have more experimental data for each electrolyte than free parameters, (ii) measurements are not completely free of experimental error, and (iii) the adjustment algorithm is based on the discrete variation of the different Stern-layer parameters. Consequently, we will replace the equality condition of \( \zeta_{\text{mob}} \)
and \( \zeta \text{cond} \) by the minimization condition of the quantity \( S \), defined by

\[
S = \sum (\zeta_{\text{mob}} - \zeta_{\text{cond}})^2, \tag{10}
\]

where the sum is over all the different electrolyte concentrations used in the measurements. With this procedure, instead of obtaining a unique \( \zeta \)-potential value from electrophoretic mobility and conductivity increment data for each electrolyte concentration, we find two different values, but they are closer each other than in the case in which a dynamic Stern layer is not taken into account. The correct value for the \( \zeta \)-potential for each concentration is assumed to be the mean value.

The mobility versus pH curves (Figs. 1, 3, and 4) show the existence of a “plateau,” for all values of electrolyte concentration, when \( pH < 7 \). In this region, therefore, it can be asserted that the charge density is approximately constant when the \( pH \) value is slightly varied and that it attains its largest positive value. For this reason, this region is the most adequate to effect \( \zeta \)-potential adjustment from an experimental point of view. The \( S_2O_8^{2-} \) ion is a counterion in this \( pH \) range, and we have chosen the \( pH \) value 5 for performing the adjustment in the \( K_2S_2O_8 \) electrolyte case. Figures 8 and 9 show the experimental data corresponding to this election.

In the \( MgCl_2 \) electrolyte case, we also want to require the bivalent ion \( Mg^{2+} \) to be a specifically adsorbed counterion, in order to detect the maximum influence of the dynamic Stern layer. We have to choose a \( pH \) value that provides a negative charge density at particle surface. For \( pH \) values much higher than 9.2 this condition is fulfilled, and we have chosen the \( pH \) value 11 for the adjustment with this electrolyte.

The charging mechanism of the alumina surface consists in the adsorption of \( H^+ \) and \( OH^- \) potential-determining ions and we assume that this adsorption is homogeneous. Therefore, we will assume that the adsorption of \( Mg^{2+} \) and \( S_2O_8^{2-} \) ions takes place over the entire free surface area of the particles. This assumption is consistent with the adsorption model 1 in Eq. (8). At \( pH 5 \) the surface charge density is positive, the added counterions during the charging process are \( OH^- \) ions (which have a limiting equivalent conductance of 198.0 cm\(^2\)/(Ω g eq)), and \( S_2O_8^{2-} \) ions are specific adsorbed counterions. Similarly, at \( pH = 11 \) the surface charge density is negative, the added counterions during the charging process are \( H^+ \) ions (which have a limiting equivalent conductance of 349.65 cm\(^2\)/(Ω g eq)), and \( Mg^{2+} \) ions are specific adsorbed counterions. \( K^+ \) and \( Cl^- \) ions are not specifically adsorbed, and, therefore, we only have adsorption of counterions, and not of co-ions. This fact permits us to disregard co-ion adsorption. The number of adjustable free parameters is now reduced to two: \( eN_{Mg^{2+}}(\lambda_{Mg^{2+}}/\lambda_{Mg^{2+}}(\beta_1)) \) and \( K_{Mg^{2+}} \) in the case of \( MgCl_2 \) electrolyte and \( eN_{S_2O_8^{2-}}(\lambda_{S_2O_8^{2-}}/\lambda_{S_2O_8^{2-}}(\beta_1)) \) and \( K_{S_2O_8^{2-}} \) in the case of \( K_2S_2O_8 \) electrolyte. The limiting equivalent conductances of \( Mg^{2+} \) and \( S_2O_8^{2-} \) ions is 53 cm\(^2\)/(Ω g eq) and 86 cm\(^2\)/(Ω g eq), respectively.

As can be seen in columns 7 and 8 of Tables 2 and 3, when the effect of a dynamic Stern layer is included in the theories, the \( \zeta \)-potential values obtained from electrophoretic mobility experiments become higher, and those estimated from conductivity increments remain unchanged. This is the result from numerical calculation. We think that the absence of variation in zeta potential calculated from the conductivity increment is a consequence of the extremely large double layer of our systems (in all cases \( \kappa a < 3 \) and only for the case \( \kappa a = 6.36 \), the new zeta potential is \(-2.27 \), while the old was \(-2.31 \)). We think that for very large double layers, the effect of the diffuse layer is dominant on the surface conductance mechanism that results from a dynamic Stern layer. At intermediate \( \kappa a \)-values, the relative importance of

**Table 2**

Experimental data and reduced zeta-potential values for alumina suspensions with \( MgCl_2 \) electrolyte

<table>
<thead>
<tr>
<th>[MgCl(_2)]</th>
<th>( \kappa a )</th>
<th>( \mu e \times 10^6 )</th>
<th>( \Delta K )</th>
<th>Without Stern layer</th>
<th>With dynamic Stern layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m(^2)/N s)</td>
<td></td>
<td></td>
<td>( \zeta_{\text{mob}}/kT )</td>
<td>( \zeta_{\text{cond}}/kT )</td>
</tr>
<tr>
<td>10(^{-5}) M</td>
<td>0.9</td>
<td>-1.63 ± 0.07</td>
<td>300 ± 80</td>
<td>-1.95</td>
<td>-2.86</td>
</tr>
<tr>
<td>5 × 10(^{-5}) M</td>
<td>2.01</td>
<td>-1.26 ± 0.05</td>
<td>180 ± 90</td>
<td>-1.32</td>
<td>-3.32</td>
</tr>
<tr>
<td>10(^{-4}) M</td>
<td>2.85</td>
<td>-1.08 ± 0.14</td>
<td>100 ± 30</td>
<td>-1.37</td>
<td>-3.09</td>
</tr>
<tr>
<td>5 × 10(^{-4}) M</td>
<td>6.36</td>
<td>-0.55 ± 0.06</td>
<td>20 ± 30</td>
<td>-0.55</td>
<td>-2.31</td>
</tr>
</tbody>
</table>

**Table 3**

Experimental data and reduced zeta-potential values for alumina suspensions with \( K_2S_2O_8 \) electrolyte

<table>
<thead>
<tr>
<th>[K(_2)S(_2)O(_8)]</th>
<th>( \kappa a )</th>
<th>( \mu e \times 10^6 )</th>
<th>( \Delta K )</th>
<th>Without Stern layer</th>
<th>With dynamic Stern layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m(^2)/N s)</td>
<td></td>
<td></td>
<td>( \zeta_{\text{mob}}/kT )</td>
<td>( \zeta_{\text{cond}}/kT )</td>
</tr>
<tr>
<td>10(^{-6}) M</td>
<td>0.28</td>
<td>1.71 ± 0.13</td>
<td>430 ± 130</td>
<td>2.31</td>
<td>2.26</td>
</tr>
<tr>
<td>5 × 10(^{-6}) M</td>
<td>0.64</td>
<td>1.64 ± 0.08</td>
<td>390 ± 110</td>
<td>2.70</td>
<td>3.98</td>
</tr>
<tr>
<td>10(^{-5}) M</td>
<td>0.9</td>
<td>1.52 ± 0.06</td>
<td>340 ± 140</td>
<td>2.57</td>
<td>4.29</td>
</tr>
<tr>
<td>5 × 10(^{-5}) M</td>
<td>2.01</td>
<td>1.26 ± 0.11</td>
<td>260 ± 100</td>
<td>1.83</td>
<td>4.92</td>
</tr>
<tr>
<td>10(^{-4}) M</td>
<td>2.85</td>
<td>1.12 ± 0.09</td>
<td>240 ± 90</td>
<td>1.08</td>
<td>5.20</td>
</tr>
</tbody>
</table>
the dynamic Stern layer increases, and finally, at extremely low electrical double layer, the general effect is again negligible. Finally, in column 9, the “more correct” ζ-potential values are calculated as the mean values of columns 7 and 8.

The Stern-layer parameters, which satisfy the minimization condition for S, have been used for the estimation of the ζ potential with the inclusion of a dynamic Stern layer. The values of these adjusted parameters have been $eN_{\text{Mg}^2+}(\lambda_{\text{Mg}^2+}/\lambda_{\text{Mg}^2+}^\prime(\beta_1)) = 5.5 \ \mu\text{C/cm}^2$ and $pK_{\text{Mg}^2+} = 5.5$ in the case of the MgCl$_2$ electrolyte and $eN_{\text{S}_2\text{O}_8^{2-}}(\lambda_{\text{S}_2\text{O}_8^{2-}}/\lambda_{\text{S}_2\text{O}_8^{2-}}^\prime(\beta_1)) = 6.5 \ \mu\text{C/cm}^2$ and $pK_{\text{S}_2\text{O}_8^{2-}} = 5.0$ in the case of K$_2$S$_2$O$_8$ electrolyte.

The conclusions of this work are:

- The specific adsorption of Mg$^{2+}$ and S$_2$O$_8^{2-}$ onto the γ-alumina particles has been demonstrated. This result open the possibility of having a colloidal system which permits us to accomplish an experimental test of the different electrokinetic theories that claim the presence of a dynamic Stern layer as a basic mechanism for the interpretation of the experimental results.
- An algorithm based upon the minimization of the square difference between ζ-potential values obtained from two different electrokinetic techniques has been constructed and used to obtain “more correct” ζ-potential values of γ-alumina suspensions in aqueous MgCl$_2$ and K$_2$S$_2$O$_8$ electrolytes. In principle, this procedure can be applied to other systems that present ions adsorption.

- The Stern-layer parameters can be obtained following the presented method, with the utilization of electrokinetic theories that include a dynamic Stern layer.

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References