# ANNALI

DELLA FACOLTA' DI AGRARIA DELL' UNIVERSITA'
SASSARI

## studi sassaresi

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# ELECTROCHEMICAL PROPERTIES OF Fe AND Al HYDROXIDES AS AFFECTED BY DIFFERENT SUPPORTING ELECROLYTES

## ABSTRACT

Potentiometric titration curves of Fe and Al hydroxides, carried out in presence of different electrolytes (KCl, Kbr, KI, $KNO_3$ , $KClO_4$) were elaborated by the Stern theory through a computered program.
The zero points of charge (zpc), calculated from the intersection point of the titration curves at different ionic strenght, varied from pH 7.10 to pH 7.65 for Fe hydroxides and from pH 9.10 pH 9.45 for Al hydroxides.
For Fe compounds, a good match was found between the experimental values and those calculated by the Stern model. High deviations were observed only with $KClO_4$, in whose presence a lowering of the zpc was registered.
Also in Al hydroxides the proposed model was not reliable below zpc, indicating that the surface interactions are somewhat involved in specific adsorption phenomena.

## RIASSUNTO

Le curve di titolazione di idrossidi di Fe e di Al, effettuate in presenza di elettroliti diversi (KCl, KBr,KI,$KNO_3$, $KClO_4$), sono state elaborate secondo la teoria di Stern attraverso un programma computerizzato. I punti di carica zero (zpc), determinati dall'intersezione delle curve di titolazione a diversa forza ionica, variavano da pH 7,10 a pH 7,65 per gli idrossidi di ferro e da pH 9,10 a pH 9,45 per gli idrossidi di alluminio.
Negli idrossidi di ferro si riscontrava un buon accordo tra i dati sperimentali e quelli calcolati secondo il modello Stern. Alte deviazioni venivano osservate solamente in presenza di $KClO_4$, per il quale si determinava un significativo abbassamento del zpc. Anche negli idrossidi di alluminio il modello proposto non risultava attendibile sotto lo zpc, indicando che le interazioni superficiali sono in qualche misura interessate da fenomeni di adsorbimento specifico.

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## INTRODUCTION

The ability of Fe and Al hydroxides to specifically adsorb ions (Jeune 1968; Vessey and Parks 1972; Quirk and Posner 1975) suggests that they play an important role in determining the availability of plant nutrients and their movement through the soil.

An exhaustive understanding of the interactions which are established between the ions and the charged sufaces has not been reached yet. Models which employ empirically modified Langmuir isotherms (Ryden et al. 1977; Syers et al., 1973; Gessa et al.1978) were found unsatisfactory as they do not give direct information about surface charge variations which occurr owing to ionic adsorption. The Stern model is considered to constitute a better approach in describing the ionic distribution in the vicinity of iron and aluminum hydroxide surfaces.

The objective of this paper is to study the effect of different anions on the variation of surface electric charges with pH in Fe and Al hydroxides.

## MATERIALS AND METHODS

Al $(OH)_3$ and $Fe(OH)_3$ were precipitated at pH 9.0 in presence of $NH_4OH$ from their chloride salts. The precipitates were then washed until free of $Cl^-$ and finally lyophilized.

Under X-ray analysis the Fe hydroxide was found to be amorphous, whereas the Al hydroxide partly crystallized as pseudobohemite and bayerite. BET specific surface of Al and Fe compounds was 182 and 234 $m^2g^{-1}$, respectively. The programmed measurements were elaborated by a Commodore CBM model 8032 computer controlling a C.Erba sorptomatic apparatus. The surface charge was determined by potentiometric titration curves, carried out using five different kalium salts — at 1.00N, O.10N and O.01N concentrations — with a Radiometer RTS 822 automatic system. A more detailed description of the procedure is reported in a previous paper (Melis et al.1983).

## THEORY

Fe and Al hydroxides are characterized by a variable charge which may result from proton association or dissociation of surface OH groups acording to the mechanism proposed by Parks and De Bruyn (1962):

$$M\text{-}O\Big|^{+}\;H_2\;\underset{-H^{+}}{\overset{+H^{+}}{\rightleftarrows}}\;M\text{-}O\Big|^{o}\;H\;\underset{-H^{+}}{\overset{+H^{+}}{\rightleftarrows}}\;M\text{-}O\Big|^{-}$$

where M refers to Fe or Al.

Other researchers prefer considering the surface charge as created by the adsorption or desorption of $H^+$ in the potential determining layer; for this reason, $H^+$ and $OH^-$ are called potential determining ions.

The Stern theory of the electrical double layer assumes that the surface charge is balanced by the ions present at the solid - liquid interfacies, distributed between the Stern and diffuse layers. The parameters which caracterize the Stern model can be calculated by the simultaneous analysis of the following equations:

$$\sigma_o = \sigma_1 + \sigma_2$$

$$\sigma_1 = \frac{Nze}{1 + (A\rho / M\eta) \exp\left[-\frac{(ze\,\Psi_d + \phi)}{kT}\right]}$$

$$\sigma_2 = \left(\frac{2\,\eta\,e\,kT}{\pi}\right)^{1/2} \sin h \frac{ze}{2kT}\,\Psi_d$$

$$\sigma_o = \frac{\epsilon'}{4\pi\delta}\,(\Psi_o - \Psi_d)$$

$$\Psi_o = \frac{RT}{F} \ln \frac{H^+}{H_o^+} = 2 \times 10^{-4}\,(pH_o - pH) \text{ at } 25^\circ C$$

where:

$\sigma_o$ = surface charge density ($esu/cm^2$)
$\sigma_1$ = charge in the Stern or compact layer ($esu/cm^2$)
$\sigma_2$ = charge in the diffuse layer ($esu/cm^2$)
N = number of adsorption sites on $cm^2$ of surface ($10^{15}/cm^2$)
z = counter ion valence
e = electron charge
A = Avogadro's number
$\rho$ = density of water

M = molecular weight of water
$\Psi_d$ = potential on the plane between the Stern and diffuse layer (statvolts)
$\phi$ = specific adsorption energy
k = Boltzmann constant
T = absolute temperature
$\eta$ = electrolyte concentration (ions/cm$^3$)
$\epsilon$ = dielectric constant of water
$\epsilon'$ = dielectric constant in Stern layer
$\delta$ = thickness of the Stern layer
$\Psi_o$ = surface potential (statvolts)
R = gas constant (ergs/deg. mole)
F = Faraday constant ($2.895 \times 10^{14}$ statcoulombs)
$H^+$ = hydrogen ion activity in soil solution
$H_o^+$ = hydrogen ion activity at zero point of charge
$pH_o$ = zero point of charge

## RESULTS AND DISCUSSION

The zpc values of Fe and Al hydroxides, determined in presence of different supporting elecrolytes, were calculated from potentiometric ritration curves: those obtained with $KClO_4$ and KCl are reported in Fig. 1.

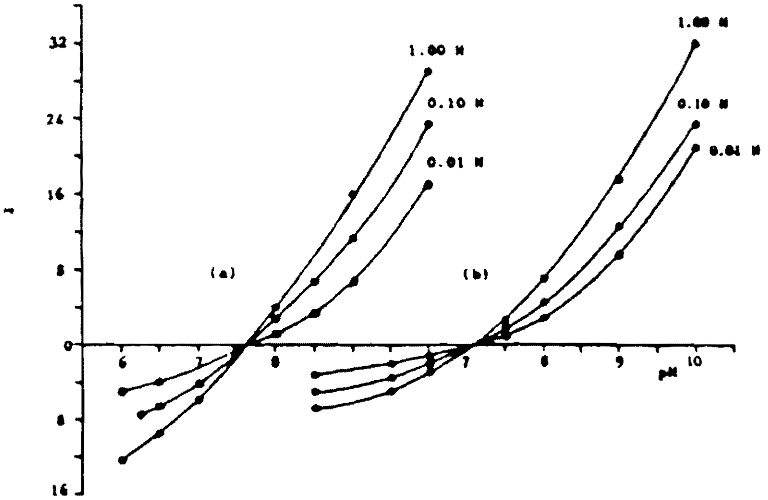

Fig. 1 - Potentiometric titration curves of Fe hydroxides in presence of KCl (a) and $KClO_4$ (b).
Curve di titolazione potenziometrica di idrossidi di ferro effettuate in presenza di KCl (a) e $KClO_4$ (b).

In Fe hydroxides they vary from pH 7.10 to pH 7.65 (tab.I) showing that the $ClO_4^-$ anion induces a marked lowering in the zpc. Some influence of the supporting electrolyte is also observed in Al hydroxides: the zpc values determined with $ClO_4^-$ and $NO_3^-$ are lower than those with the other anions.

By elaborating the experimental data, according to the equation system reported above, the values of surface charge density ($\sigma_o$) and surface potential ($\Psi_o$) which best agree with the proposed model were calculated (Melis et al.1983). The thickness of the Stern layer ($\delta$), the Stern potential ($\Psi_S$), the Stern and the diffuse layer charge density ($\sigma_1$ and $\sigma_2$) where determined by the same procedure. Excepted the data related to $ClO_4^-$ ions, in Fe hydroxides at 0.1N contentration, there was no great gap between the experimental and calculated $\sigma_o$, as per the low percentual deviations between them. (Fig. 2).

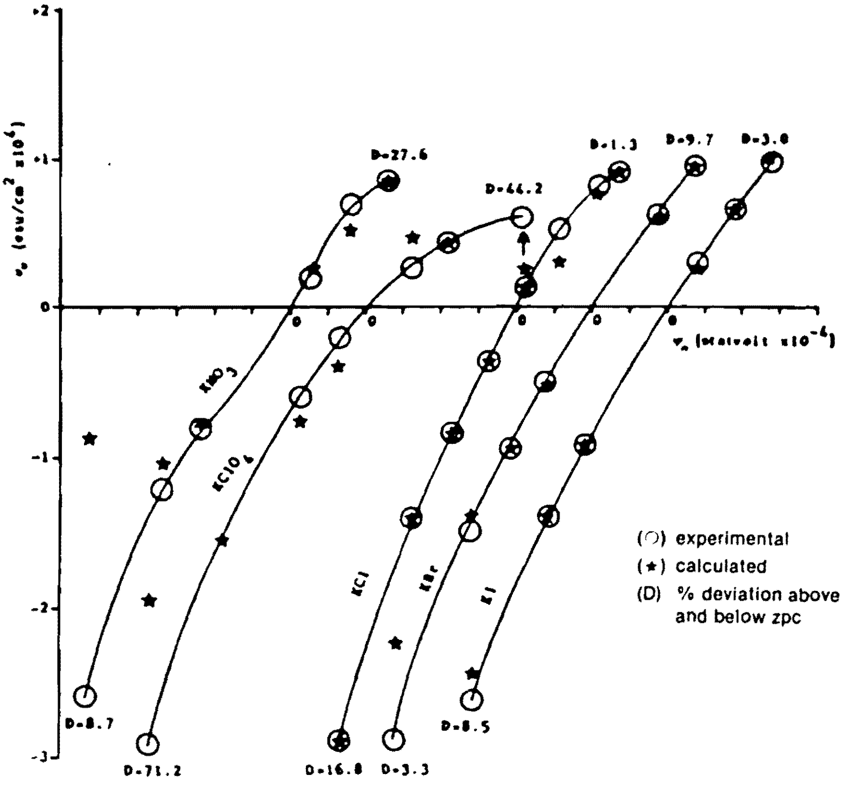

Fig. 2 - Variation of surface charge density ($\sigma_o$) in function of surface potential ($\Psi_o$) at 0.10 N concentration in Fe hydroxides.
Variazione della densità di carica superficiale ($\sigma_o$) in funzione del potenziale superficiale ($\Psi_o$) alla concentrazione 0.10 N in idrossidi di ferro.

The highest deviations were found above zpc at 1.ON electrolyte concentration. In Al hydroxides (Fig. 3) a good match occurs for all the supporting electrolytes above zpc, being the deviation less than 5%, whereas it is very high below zpc, excepted for KBr.

Above zpc the Stern layer thickeness values ($\delta$) (table I) grow as electrolyte concentration increases — both for Fe and Al hydroxides — irrespective of the anionic species employed. Excepted for $KClO_4$ the same trend is observed below zpc, being much more regular in Fe compounds.

Since cation adsorption mainly occurs above zpc, for the same concentration the $\delta$ values should be expected equal for all the electrolytes as only K salts were used. Actually, they are always lower than the ionic diameter of the non hydrated

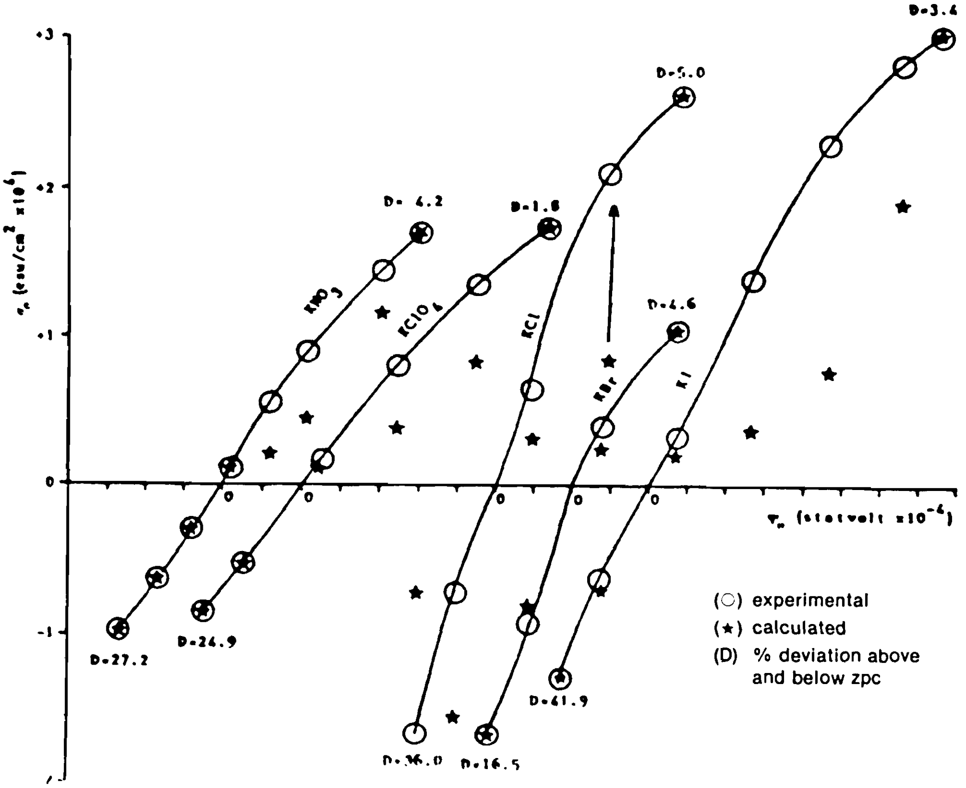

Fig. 3 - Variation of surface charge density ($\sigma_o$) in function of surface potential ($\Psi_o$) at 0.10 N concentration in Al hydroxides.
Variazione della densità di carica superficiale ($\sigma_o$) in funzione del potenziale superficiale ($\Psi_o$) alla concentrazione 0.10 N in idrossidi di alluminio.

$K^+$ ion (2.66 Å). This can be explained in accordance with the model proposed by Bowden et al. (1977) which hypothesizes the presence of cavities on the surface where ions, like $K^+$, can be placed.
Analagous considerations can be made about the $\delta$ values below zpc, as they are always lower than the dimensions of the anions. However, the increase of the Stern la layer thickness with increasing anion radius is clearly evident.

The influence of the electrolyte concentration on the $\delta$ values can be interpreted taking into account that ion-surface interaction is more or less affected by the associated counterions, depending on the ionic strenght of the solution. Therefore, we can hypothesize that the lower the counterion activity the stronger the ion-surfce interaction: as a result, the Stern layer thickness decreases as decreasing electrolyte concentration.

*Table 1* **zpc and Stern layer thickness values ($\delta$)** in Fe and Al hydroxides.
Valori relativi allo zpc ed allo spessore dello strato di Stern negli idrossidi di Al e di Fe.

| Supporting electrolyte | zpc | | Stern layer thickness (Å) | | | |
|---|---|---|---|---|---|---|
| | | | IRON | | ALUMINUM | |
| | Fe | Al | above zpc | below zpc | above zpc | below zpc |
| KCl | 7.65 | 9.45 | 0.44 | 0.80 | 0.30 | 0.49 |
| | | | 0.29 | 0.80 | 0.04 | 0.39 |
| | | | 0.09 | 0.73 | 0.16 | 0.08 |
| KBr | 7.40 | 9.40 | 0.94 | 1.93 | 0.29 | 0.85 |
| | | | 0.44 | 0.75 | 0.04 | 0.61 |
| | | | 0.19 | 0.45 | 0.03 | 1.04 |
| KI | 7.40 | 9.35 | 0.67 | 2.23 | 0.56 | 1.28 |
| | | | 0.46 | 0.68 | 0.23 | 0.74 |
| | | | 0.25 | 0.12 | 0.07 | 0.82 |
| $KNO_3$ | 7.40 | 9.10 | 0.97 | 1.74 | 0.84 | 0.92 |
| | | | 0.75 | 0.79 | 0.71 | 0.85 |
| | | | 0.17 | 0.43 | 0.29 | 0.74 |
| $KClO_4$ | 7.10 | 9.20 | 0.96 | 2.38 | 0.90 | 1.51 |
| | | | 0.56 | 2.87 | 0.71 | 1.80 |
| | | | 0.26 | 3.13 | 0.19 | 1.19 |

The three $\delta$ values reported were determined at 1.00N, 0.10N and 0.01N supporting electrolyte concentration, respectively.

The different behaviour of the $ClO_4^-$ anion on iron hydroxides and of all the other anion (excepted Br) in Al hydroxides suggests that some specific adsoption occurs. In fact, the decrease in the zpc and the high percentual deviation indicate that the surface groups are involved into chemioadsorption reactions which cause a modification of the surface characteristics of the solid phase. Therefore, in these cases the proposed model seems to be unreliable.

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