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DESCRIBING THE ADSORPTION OF POTENTIAL DETERMINING IONS ON VARIABLE CHARGE MINERAL SURFACES

RIASSUNTO

Caratterizzazione elettrochimica di superfici a carica variabile col pH.

È stato proposto un programma computerizzato per elaborare le curve di titolazione di superfici anfotere secondo la teoria del doppio strato elettrico. I punti di carica zero (zpc), determinati dall'intersezione delle curve di tiolazione effettuate a differente forza ionica, risultano a pH 3,15, 9,45 e 7,65 rispettivamente per gli idrossidi di Si, Al e Fe.
Il modello di Stern descrive in modo molto soddisfacente la relazione tra σ_0 e Ψ_0. L'elaborazione dei dati relativi alla silice è stata fatta con una procedura di calcolo diversa. I valori δ, che esprimono lo spessore dello strato di Stern, sono molto alti per le superfici di Si e risultano maggiori a forza ionica minore. Gli idrossidi di alluminio e ferro mostrano un diverso comportamento: i valori δ sono molto bassi ed aumentano con l'aumentare della forza ionica. I risultati ottenuti vengono discussi in termini di struttura delle superfici e di attività dell'elettrolita di supporto.

ABSTRACT

A computer program was developed to elaborate the titration curves of amphoteric surfaces according to the double layer theory. The zpc, identified from the intersection point of the titration curves carried out at different ionic strengths, fell at pH 3.15, 9.45 and 7.65 for Si, Al and Fe hydroxides, respectively. The Stern model described quite satisfactorily the relation between σ_0 and Ψ_0. Some problem was presented by Si surfaces which were then treated by a different calculation procedure.
The δ values, the Stern layer thickness, were very high for the Si surfaces and increased with decreasing ionic strength. A different behaviour was showed by Al and Fe hydroxides; in these cases δ values were very low and increased with increasing electrolyte concentration. These results were discussed in terms of surface structures and activity of the supporting electrolyte.

INTRODUCTION

The electric charge which characterizes the soil surface plays a fundamental role in the dynamic of plant nutrients. Such charge is pH dependent in Si, Fe and Al hydrous oxides and can be developed through amphoteric dissociation or protonation of the surface reactive groups. The resulting net charge, which can be determined by pH — titration curves, varies with electrolyte concentration, except at zpc. Therefore, zpc is identified by the intersection point of the titration curves carried out at different ionic strengths.

Recently several mathematical models have been applied for reversible soil colloid interfaces (Van Raij and Peech, 1972; Bowden et al, 1977; Wann and Uehara, 1978; Iniguez et Val, 1982).

In the present paper we report the results of a study concerning the variation of electric charges with pH in Si, Al and Fe hydroxides. A computer program was developed to elaborate the experimental data according to the double layer theory.

MATERIAL AND METHODS

Al $(OH)_3$ and Fe $(OH)_3$ were precipitated at pH ~ 9.0 in presence of NH_4OH from their chloride salts. Hydrous silica ($SiO_2 . H_2O$) was obtained by dissolving sodium silicate in distilled water and then adding concentrated HCl with gentle heating. The precipitates were then washed until free of Cl^- and finally lyophilized.

Under X-ray analysis the Si and Fe hydroxides were found to be amorphous, whereas the Al hydroxide partly crystallized as pseudoboehmite and bayerite. BET specific surface of Al, Fe and Si hydroxides was 182, 234 and 479 $m^2 g^{-1}$ 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 using a Radiometer RTS 822 automatic titration system (Dixit, 1980). A 0.25 g sample, placed in plastic vessel, was suspended in 20 ml KCl solution of different ionic strength and left to equilibrate for 24 hours, shaking occasionally. The titrations were carried out at pH - stat, by adding 0.05 N HCl or KOH with a gap of 0.5 pH unit under continuous magnetic stirring. The delivery of titrant was 0.5 ml min^{-1} with 50 seconds equilibrium time. The suspensions were maintained under constant N_2 pressure to avoid CO_2 contamination. The amount of titrant used in blank titrations was substracted from that consumed by the sample. The net electric charge was calculated from the amount of H^+ or OH^- adsorbed with respect to zpc.

THEORY

It is now generally accepted that in potentiometric titrations H^+ and OH^- are the potential determining ions. Then the surface potential (Ψ_0) at a given pH with reference to zpc can be calculated by the Nernst relationship:

$$(1) \qquad \Psi_0 = \frac{RT}{F} \ln ((H)/(H)_{zpc})$$

which can be further simplified to give (at 25 °C):

$$(2) \qquad \Psi_0 = 1.97 \times 10^{-4} ((H)_{zpc} - (H))$$

The charge density (σ_0) is related to Ψ_0 by the Gouy - Chapman relation:

$$(3) \qquad \sigma_0 = (2\, n\, \epsilon KT/\pi)^{1/2} \, \mathrm{Sinh}\, (ze\, \Psi_0 \,/\, 2KT)$$

where n is the concentration of the equilibrium solution in number of ions/cm^3, ϵ is the dielectric constant, z is the valence of the counter ion, e is the electron charge, K is the Boltzman constant and T the absolute temperature in °K.

The Gouy — Chapman treatment of the double layer runs into difficulties when counter ion concentration and Ψ_0 are high (Adamson, 1982).

A more realistic approach was put forward by Stern who treated the double layer model considering the ions distributed into two shells. The overall electroneutrality is reached when:

$$(4) \qquad \sigma_0 = \sigma_1 + \sigma_2$$

The charge density (σ_1) in the first layer is given by:

$$(5) \qquad \sigma_1 = \frac{N\, z\, e}{1 + (N_A \varrho \,/\, Mn) \exp\, (-(ze\Psi_S + \phi \,/\, KT)}$$

where N is the number of available adsorbing sites/cm^2, N_A is Avogadro number, ϱ is density of solvent, M is molecular weight of solvent, Ψ_S is the electric potential in the Stern layer and ϕ accounts for specific adsorption of counter ions at the surface.

The charge density (σ_2) in the second layer is given by:

$$(6) \qquad \sigma_2 = (2n\epsilon KT/\pi)^{1/2} \, \mathrm{Sinh}\, (ze\Psi_S \,/\, 2KT)$$

The surface charge (σ_0) for a molecular condenser is also given by Gauss equation:

$$(7) \qquad \sigma_0 = (\epsilon' / \, 4\pi\delta) \, (\Psi_0 - \Psi_S)$$

where ϵ' is the average dielectric constant of the Stern layer and δ is the Stern layer thickness.

For Stern model an optimization program, involving a set of equations (1, 4, 5, 6, 7), was run to find out a suitable value of Ψ_S, using all the experimental values of σ_0 and Ψ_0 belonging to acid or alkaline side of zpc. The δ values were chosen arbitrarily in the range from 10^{-3} to 20 Å. The ϕ was assumed zero which means no specific electrolyte adsorption. The program was so conceived that when the sum of σ_1 and σ_2 did not vary any more the optimization cycle stopped with the best value of δ and Ψ_S. A similar calculation method could not be applied to Si due to a very large δ variation. Consequently these curves were elaborated involving each experimental point.

RESULTS AND DISCUSSION

In figures 1, 2 and 3 are depicted the potentiometric titration curves of Al, Fe and Si hydroxides. Their zpc, determined at pH 9.45, 7.65 and 3.15, respectively, are in agreement with earlier workers (Parks, 1965; 1967; Kinniburgh et al., 1975; Tschapek et al., 1974).

The Gouy-Chapman equation (3) does not describe satisfactorily experimental σ_0 whereas a good approximation of the relation σ_0 and Ψ_0 is given by the Stern model. The agreement between calculated and experimental σ_0 in Al and Fe is somewhat less satisfactory below zpc (Tables 1, 2). Our method, which allows the determination of numerical values like deviation (Tables 1, 2), should be preferable to simple graphic representations (Van Raij and Peech, 1972) because it permits to judge more closely the model application.

The Al and Fe data treated with Si procedure give high deviations between calculated and experimental σ_0 near zpc, probably due to the inaccuracy inherent in the method (Parks, 1965). Such deviations are relatively smaller in Fe than in Al indicating that the model is more suitable in the case of the former. Al titrations are notably influenced by the solubility, which increases rapidly with decreasing pH. In theory it would be possible to improve the accuracy by using a large quantity of material, but this leads to experimental difficulties (Block, 1968).

For Si surfaces the Gouy-Chapman theory is not applicable at any pH value whereas Stern model is quite successful at low concentrations (Fig. 3). However, the model failed to describe 1 N curve from zpc till pH 6.0. The deviations between experimental and calculated σ_0 increase notably as zpc is approached (Table 3). The

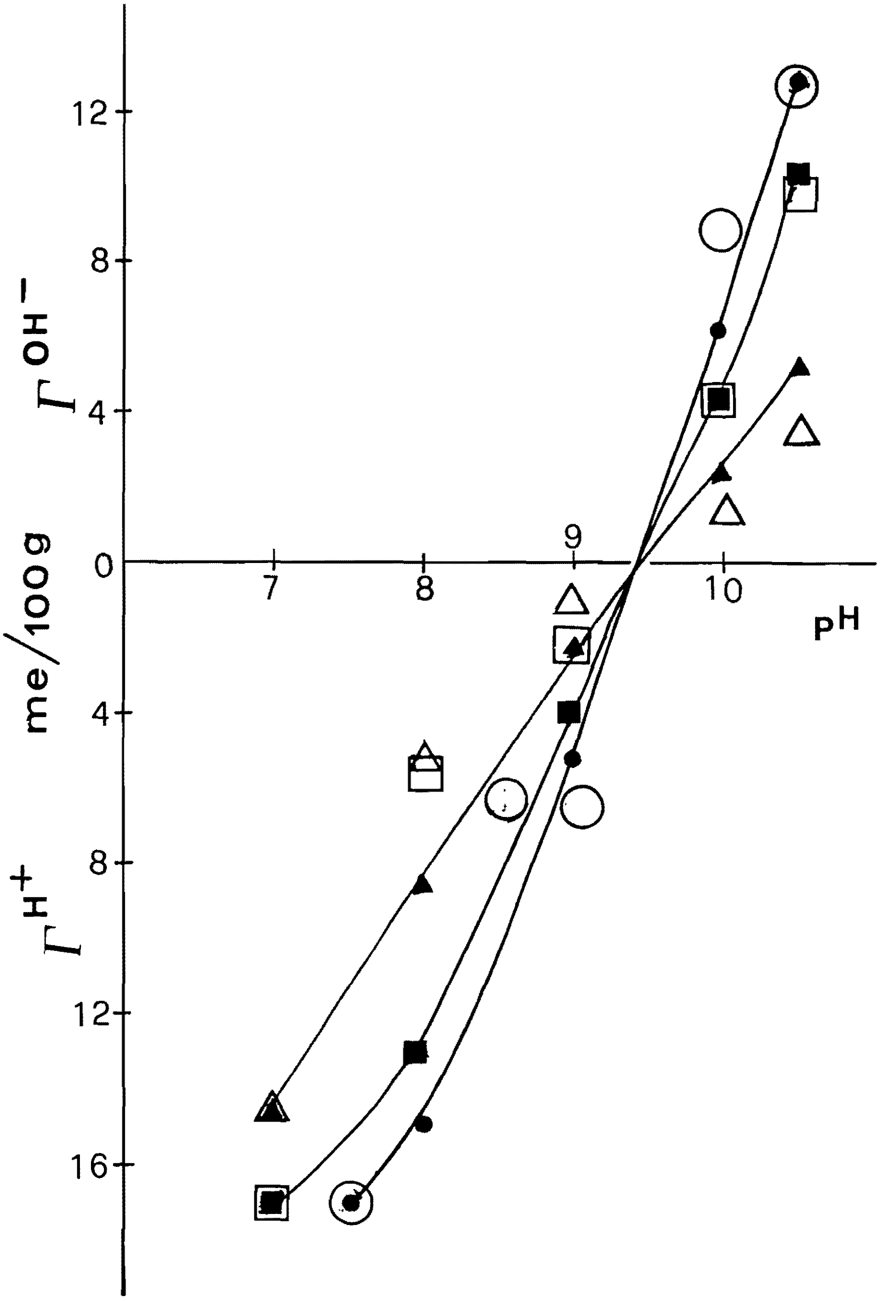


Fig. 1 - Experimental and calculated titration curves of Al at different KCl concentrations.
Experimental: ● 1 N; ■ 0.1N; ▲ 0.01N.
Calculated: O1N; □ 0.1N; △ 0.01N.

Curve di titolazione sperimentali e calcolate di Al a diversa concentrazione di KCl.
Sperimentali: ● 1 N; ■ 0.1N; ▲ 0.01N.
Calcolati: O1N; □ 0.1N; △ 0.01N.

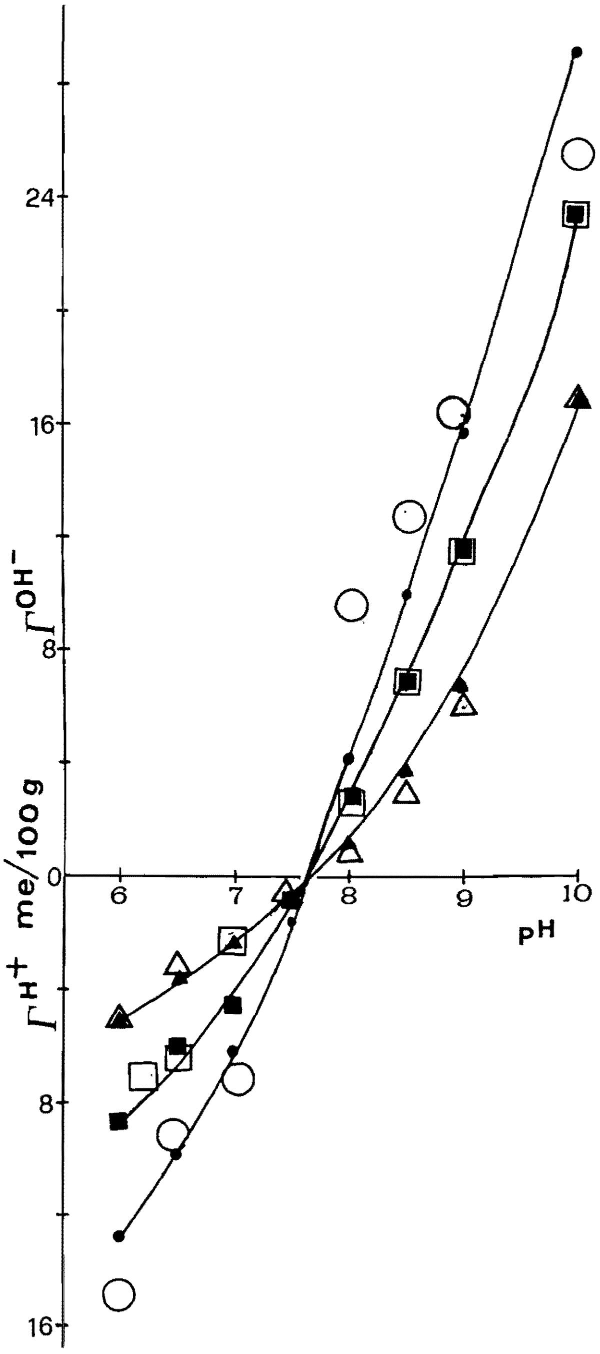


Fig. 2 - Experimental and calculated titration curves of Fe at different KCl concentrations; for legend see fig. 1.

Curve di titolazione sperimentali e calcolate di Fe a diversa concentrazione di KCl; per la legenda vedi fig. 1.

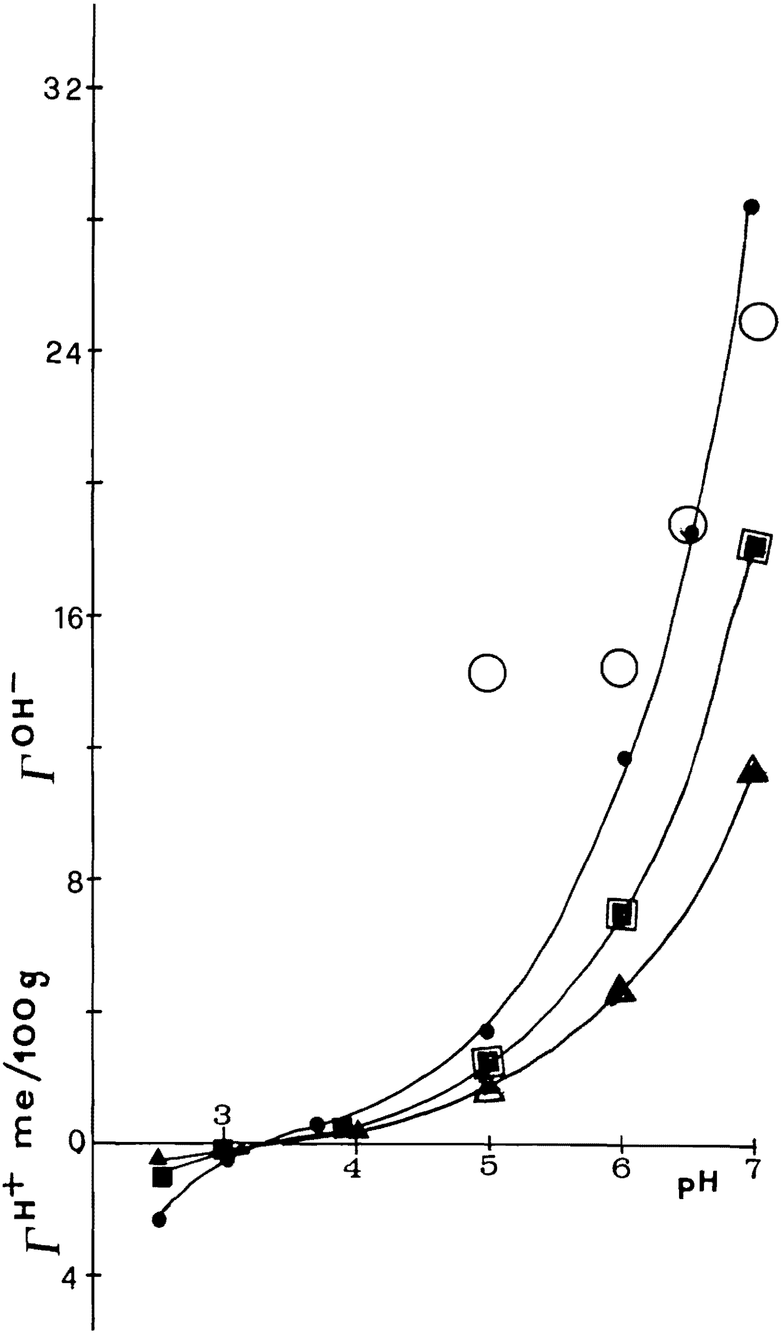


Fig. 3 - Experimental and calculated titration curves of Si at different KCl concentrations; for legend see fig. 1.

Curve di titolazione sperimentali e calcolate di Si a diversa concentrazione di KCl; per la legenda vedi fig. 1.

Table 1 - **Experimental and calculated values related te titration curves of Al hydroxide. Valori sperimentali e calcolati delle curve di titolazione di idrossido di alluminio.**

	Experimental		Calculated					
pH	Ψ_0 stat volt $x10^{-4}$	σ esu/cm^2 $x10^4$	*δ Å	Ψ_s $x10^{-4}$	σ_1 esu/cm^2 $x10^4$	σ_2 esu/cm^2 $x10^4$	σ_0 esu/cm^2 $x10^4$	* Deviation %
				1.0 N KC1				
10.5	—2.066	—2.0291	0.30	—0.783	—0.3435	—1.6832	—2.0262	17.20
10.0	—1.082	—1.0463		—0.421	—0.5228	—0.8822	—1.4050	
9.0	0.885	0.7292		0.132	0.7289	0.2761	1.0053	
8.5	1.869	1.7123	0.49	0.102	0.7548	0.2128	0.9677	27.20
7.5	3.838	2.6630		1.089	0.2411	2.4132	2.6542	
				0.1 N KC1				
10.5	—2.066	—1.6483	0.04	—1.919	—0.0091	—1.5394	—0.7313	4.99
10.0	—1.082	—0.7609		—1.014	—0.0264	—0.7049	—1.5481	
9.0	0.885	0.6024		0.393	0.0545	0.2603	0.3149	
8.0	2.853	2.0921	0.39	1.144	0.0273	0.8076	0.8303	36.03
7.0	4.822	2.5994		2.698	0.0037	2.5982	2.6014	
				0.01 N KC1				
10.5	—2.066	—0.8243	0.16	—2.038	—0.0008	—0.5298	—0.5306	33.52
10.0	—1.082	—0.3487		—1.070	—0.0025	—0.2367	—0.2392	
9.0	0.885	0.3487		0.822	0.0033	0.1772	0.1805	
8.0	2.853	1.3634	0.08	2.607	0.0004	0.7754	0.7759	30.48
7.0	4.822	2.3147		4.404	0.0005	2.3112	2.3112	

* Average values on alkaline or acid side of zpc.

same behaviour was noticed elaborating with our program the data of Tschapek et al. (1974) who pointed out that titrations are difficult near pH 3.0. Our experience indicates that near zpc in addition to titration difficulties there is some surface reactivity which makes the system unstable.

As expected by the theory, Ψ_0 and Ψ_s are zero at zpc (Fig. 4); this confirms the reliability of our Stern model calculations.

The Stern layer thichness of Si surface evidences a trend different from that of Al and Fe compounds. In fact, in Si δ increases with decreasing electrolyte concentration at each pH value (Table 3). The values obtained are very high: for example in 1 N concentration δ is 1.98 Å at pH 7.0; the value increases to 8.46 Å at pH 5.0. This is probably due to very small δ_0 which give rise to a distribution of hydrated K^+ ions in a very large shell. This is so much true that with dilution δ increases as expected.

In the case of Al and Fe we can make following observations: i) at any concentration, the δ value is very low with reference to a monolayer of K^+ or Cl^- ions whose radius is 1.33 and 1.81 Å respectively; ii) the thickness tends to increase with con-

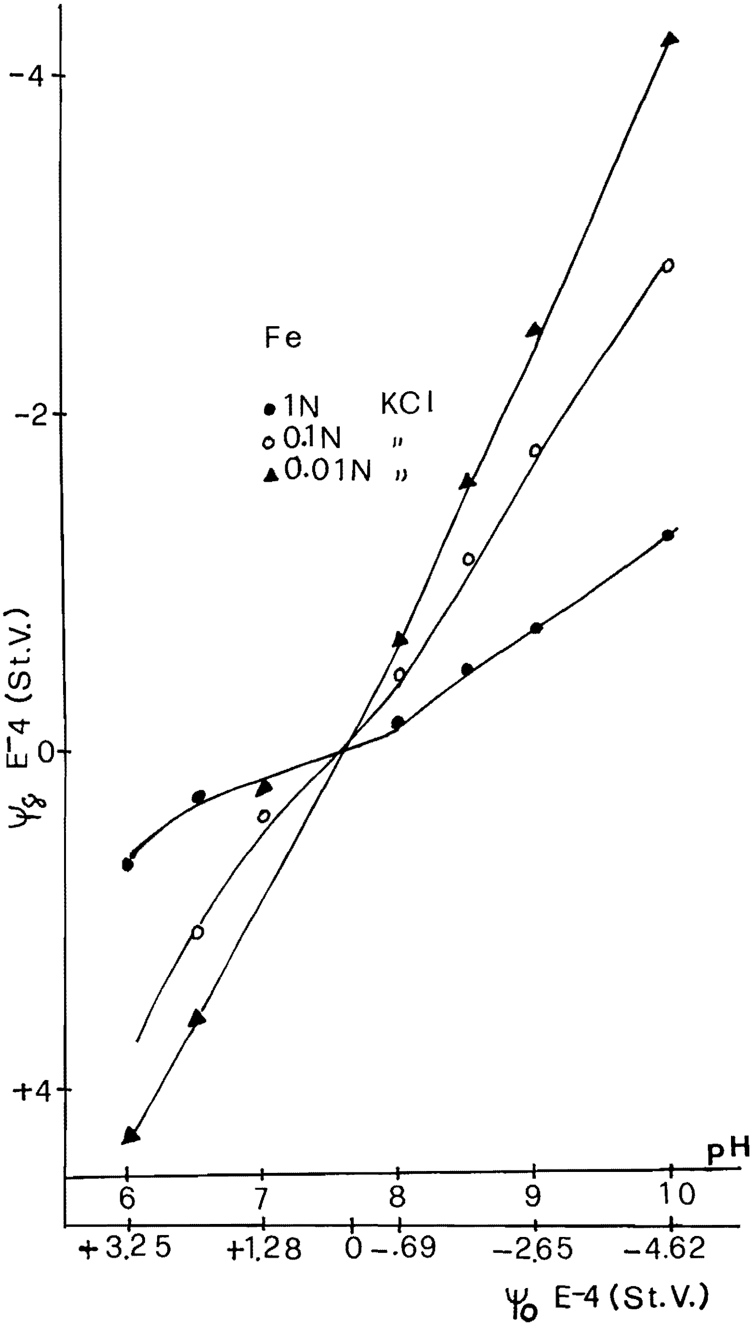


Fig. 4 - Relationship between Ψ_o and Ψ_δ of Fe.
Relazione tra Ψ_o e Ψ_δ di Fe.

Table 2 - **Experimental and calculated values related to titration curves of Fe hydroxide.**
Valori sperimentali e calcolati delle curve di titolazione di idrossido di ferro.

	Experimental		Calculated					
pH	Ψ_0 stat volt x10^{-4}	σ esu/cm^2 x10^4	*δ A	Ψ_S stat volt x10^{-4}	σ_1 esu/cm^2 x10^4	σ_2 esu/cm^2 x10^4	σ_0 esu/cm^2 x10^4	* Deviation %
				1.0 N KC1				
10.0	—4.625	—3.6000		1.273	—0.1946	—2.8901	—3.0852	
9.5	—3.641	—2.7370		1.092	—0.2400	—2.4235	—2.6633	
9.0	—2.657	—2.0220	0.44	0.774	—0.3473	—1.6611	—2.0083	26.83
8.5	—1.673	—1.2331		0.525	—0.4637	—1.1062	—1.5694	
8.0	—0.688	—0.5178		0.206	—0.6695	—0.4298	—1.0992	
7.0	1.279	0.7595		0.012	0.8375	0.0250	0.8626	
6.5	2.263	1.2233	0.80	0.022	0.6574	0.4631	1.1200	11.99
6.0	3.247	1.5582		0.647	0.4025	1.3740	1.7770	
				0.1 N KC1				
10.0	—4.625	—2.9101		—2.856	—0.0030	—2.9072	—2.9102	
9.0	—2.657	—1.4401		—1.791	—0.0106	—1.4012	—1.4111	
8.5	—1.673	—0.8482	0.29	—1.163	—0.0222	—0.8223	—0.8452	1.31
8.0	—0.689	—0.3554		—0.475	—0.0496	—0.3158	—0.3653	
7.5	0.295	0.1381		0.064	0.0800	0.0423	0.1223	
7.0	1.279	0.5524	0.80	0.356	0.0569	0.2355	0.2924	16.77
6.5	2.263	0.7992		1.044	0.0205	0.7279	0.7534	
6.25	2.755	0.9247		1.210	0.0210	0.8617	0.8827	
				0.01 N KC1				
10.0	—4.625	—2.0914		—4.235	—0.0001	—2.0902	—2.0912	
9.0	—2.657	—0.8286		—2.502	—0.0005	—0.7244	—0.7249	
8.5	—1.673	—0.4734	0.09	—1.584	—0.0013	—0.3775	—0.3789	10.28
8.0	—0.688	—0.1578		—0.659	—0.0040	—0.1401	—0.1441	
7.5	0.2952	0.0986		0.145	0.0073	0.0302	0.0375	
6.5	2.263	0.4463	0.73	1.585	0.0014	0.3778	0.3792	25.77
6.0	3.247	0.6313		2.288	0.0006	0.6291	0.6297	

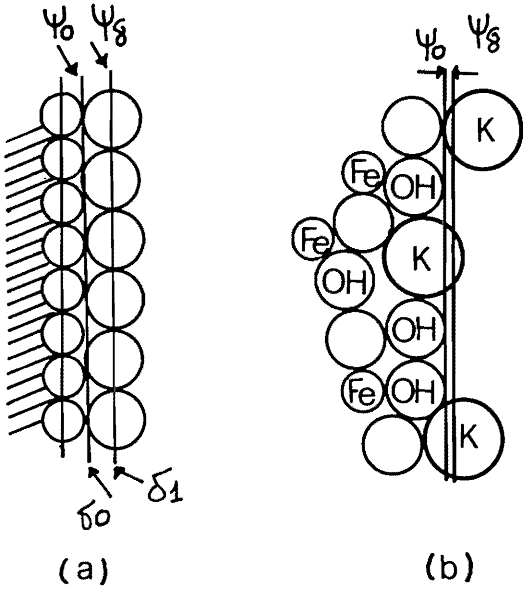
* Average values on alkaline or acid side of zpc.

centration. Concerning the first observation, it is possible to hypothesize the presence of cavities on the surface which, being partly occupied by K^+ or Cl^-, reduce the δ value in accordance with the model presented by Bowden et al. (1977) (Fig. 5).

The concentration effect is very difficult to explain; if we consider a rigid surface structure, i.e. not alterable by electrolyte concentration, the behaviour observed suggests an influence of the anion on the cation distribution above zpc and vice versa. Such influence may be discussed in terms of surface affinity for the ion carrying a charge of the same sign; above zpc an higher affinity of surface towards the anion should favour its attraction and consequently disfavour the cation adsorption.

Table 3 - **Experimental and calculated values related to titration curves of Silica.**
Valori sperimentali e calcolati delle curve di titolazione di silice idrata.

	Experimental		Calculated					
pH	Ψ_0 stat volt x10^{-4}	σ esu/cm^2 x10^4	$^*\delta$ A	Ψ_S x10^{-4}	σ_1 esu/cm^2 x10^4	σ_2 esu/cm^2 x10^4	σ_0 esu/cm^2 x10^4	Deviation %
				1.0 N KC1				
7.0	—7.577	—1.7101	1.98	—0.477	—0.4898	—1.0030	—1.4930	12.78
6.5	—6.593	—1.1262	2.71	—0.211	—0.6662	—0.4387	—1.1050	1.89
6.0	—5.609	—0.7172	3.76	—0.010	—0.8395	—0.0206	—0.8602	21.02
5.5	—4.625	—0.4163	5.26	—0.049	—0.8021	—0.1029	—0.9051	117.00
5.0	—3.641	—0.2054	8.46	—0.001	—0.8475	—0.0035	—0.8510	315.00
				0.1 N KC1				
7.0	—7.577	—1.0962	2.66	—1.474	—0.0154	—1.0900	—1.1060	0.88
6.5	—6.593	—0.6383	4.26	—8.903	—0.0305	—0.6206	—0.6411	0.41
6.0	—5.609	—0.3972	6.07	—5.579	—0.0450	—0.3724	—0.4174	5.00
5.5	—4.625	—0.2414	8.62	—0.273	—0.0627	—0.1800	—0.2427	0.76
5.0	—3.641	—0.1264	13.44	—0.071	—0.0794	—0.0467	—0.1261	0.26
				0.01 N KC1				
7.0	—7.577	—0.6871	3.59	—2.415	—0.0005	—0.6844	—0.6849	0.25
6.5	—6.593	—0.4392	5.23	—1.780	—0.0011	—0.4393	—0.4404	0.16
6.0	—5.609	—0.2772	7.56	—1.221	—0.0021	—0.2754	—0.2774	0.14
5.5	—4.625	—0.1683	10.91	—0.771	—0.0035	—0.1655	—0.1690	0.22
5.0	—3.641	—0.1081	13.80	—0.504	—0.0048	—0.1060	—0.1108	2.21



(a) (b)

Fig. 5 - Distribution of ions and potential at the solid-liquid interface: a) ideal surface; b) hydroxide surface allowing counter ion penetration (from Bowden et al., 1977.
Distribuzione ionica e potenziale all'interfacies solido-liquido: a) superficie ideale; b) superficie dell'idrossido che consente la penetrazione del controione (da Bowden et al., 1977).

In conclusion, it can be said that the computer program developed is very useful to describe the adsorption of potential determining ions on variable charge surface in accordance with the double layer theory.

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