

# Zero Point Charge and Surface Stability Constants for $\text{Co}^{2+}$ Adsorption from Aqueous Solutions on Kaolin

SHAKILA BEGUM AND FARID ULLAH KHAN

*Pakistan Council of Scientific and Industrial Research Laboratories,  
Peshawar, Pakistan*

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**Summary:** Surface charge of kaolin was estimated from the potentiometric titrations of kaolin in various background electrolyte solutions at 298 K. No point of intersection for the zero charge was observed at pH 3.5 as the starting point indicating that, at low pH, the amorphous components of kaolin were adsorbed in the aqueous phase whereas the three various electrolyte solutions initially adjusted to about pH 8.48 gave the point of intersection. The  $\text{pH}_{\text{PZC}}$  was 5.96. The surface stability constants were measured in the temperature range (298 - 328 K) at pH 6.5. As the reaction was exothermic, like  $X_{\text{m}}$  the maximum adsorption, the values of the stability constants also decreased with increasing temperature showing high strength of bond between the adsorbent and adsorbate at low temperatures.

## Introduction

Kaolin is an adsorbent used for the recycling of radioactive elements as well as for the treatment of nuclear waste water [1]. Ceramic filters were installed in houses in Kuwait for the purification of tap water. They reduced the natural radioactivity of the water, the gross  $\alpha$ -activity, by a factor of  $2.18 \pm 18\%$  and the gross  $\beta$ -activity by  $1.53 \pm 1.6\%$  [2]. The tap water was a mixture of natural Brackish water and water produced by the desalination of sea-water. More work is required to gain insight into the characteristics and behaviour of this adsorbent.

Kaolin, has been employed by several investigators [3-5] as an adsorbent for the removal of toxic contaminants from water and waste water. Much has been reported about the adsorption mechanism and the factors affecting the adsorption processes [6,7]. However, little attention has been given to surface stability constants for  $\text{Co}^{2+}$  adsorption from aqueous solutions at various temperatures, and the determination of the point of zero charge for kaolin. Therefore, in continuation of our previous work [4] we studied the surface stability

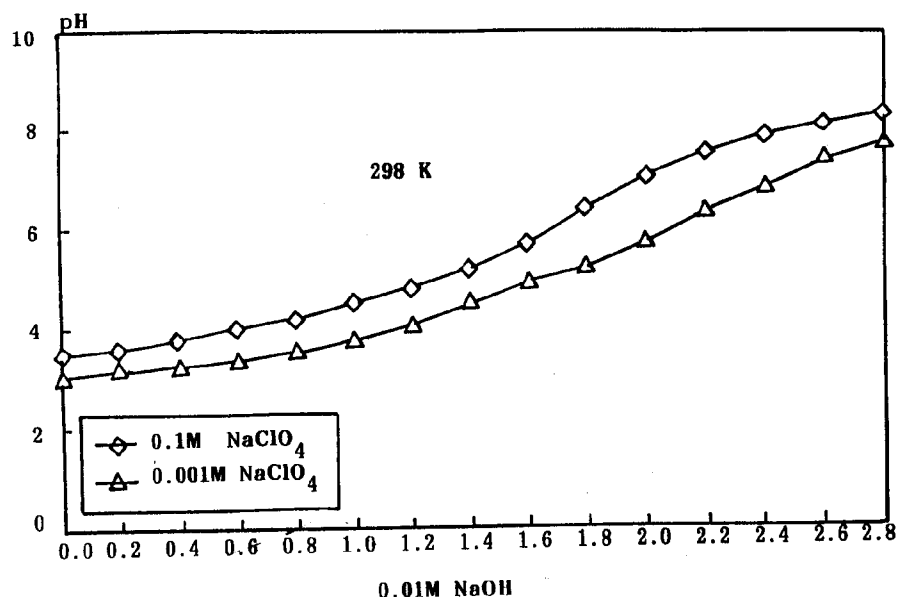


Fig. 1: Determination of zero point charge for kaolin

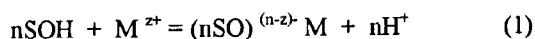
constants for the adsorption of  $\text{Co}^{2+}$  from aqueous solutions and measured the zero point charge for kaolin, which has not previously been reported in the literature.

### Results and Discussion

No point of intersection for the zero charge was observed at pH 3.5 as the starting point (Fig. 1) which showed that, at low pH, the amorphous components of kaolin were adsorbed in the aqueous phase. Fig. 2 depicts plots of three various electrolyte solutions initially adjusted to about pH 8.48. The point of intersection of the three electrolyte solutions fell at pH 5.96 which indicated the zero point charge.

#### Stability constants

The adsorption of the metal ions on kaolin may be treated as surface complex formation between the surface sites and the adsorbate metal cations denoted as,



where SOH is the surface adsorption sites;  $[(\text{SO})^{(n-z)-} \text{M}]$  is surface complex of the metal ion, and  $n$  is the number of  $\text{H}^+$  released. The number of

$\text{mg L}^{-1}$  of  $\text{H}^+$  released to the aqueous phase as a result of the metal ions adsorption (Table-1) were estimated from the volume of NaOH solution used for maintaining constant pH during the adsorption experiments [4].

The stability constant,  $K_{(\text{int})}$ , of surface complex,

$[(\text{SO})^{(n-z)-} \text{M}]$  may be written [8] as,

$$K_{(\text{int})} = \frac{[(n\text{SO})^{(n-z)-} \text{M}] [\text{H}^+]^n \exp(-nF\psi_0/RT)}{[\text{SOH}]^n [\text{M}^{z+}] \exp(-zF\psi_0/RT)} \quad (2)$$

Where  $\psi_0$  is the surface potential at the plane of adsorption,  $R$  and  $T$  are the gas constant and absolute temperature, respectively.

By assuming the Nerstain relationship [8] i.e.

$$\psi_0 = \frac{2.303RT}{F} (\text{PZC}-\text{pH}) \quad (3)$$

Equation (2) may be written as,

$$K_{(\text{int})} = K' \exp 2.303 [(z-n) (\text{PZC})-\text{pH}] \quad (4)$$

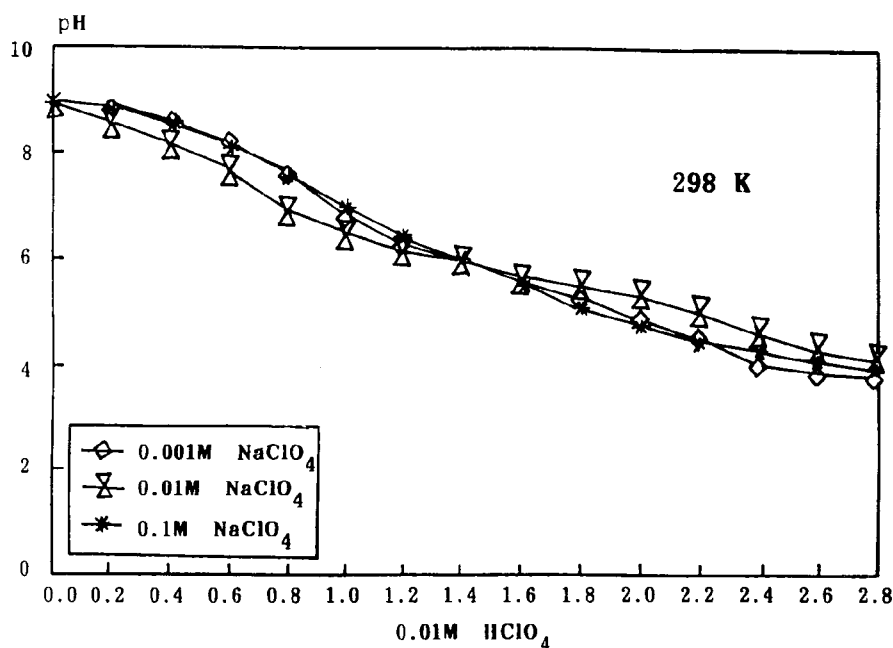


Fig. 2: Zero point charge for kaolin

 Table-1: Adsorption data for the  $\text{Co}^{2+}$  on kaolin

<sup>a</sup> pH	<sup>b</sup> Temperature K	$C_{X_m}$ $\text{mg g}^{-1}$	$^d\text{H}^+_{\text{rel}}$ $\text{mg L}^{-1}$	$\text{pK}_{(\text{int})}$
6.5	298	1.79	0.31	5.93
	308	1.71	0.19	6.35
	318	1.65	0.18	6.42
	328	1.52	0.19	6.52

a,b,c,d, as described earlier [4].

where  $K'$  is the apparent stability constant of the surface complex, and may be determined from the experimentally measured parameters. By substituting the values of PZC ( $\text{pH}_{\text{PZC}} = 5.96$ ), pH (6.5),  $n$ , and  $K'$  in eq. (4), known from the experimental data, the values of  $\text{pK}_{(\text{int})}$  were calculated for  $\text{Co}^{2+}$  at different temperature (Table-1). As the reaction was exothermic, like  $X_m$ , the maximum adsorption, the values of the surface stability constants also decreased with increasing temperature showing high strength of bond between the adsorbent and adsorbate at low temperatures.

### Experimental

The kaolin was supplied by Forte Ceramics Industries, Peshawar, Pakistan. The clay sample was ground, sieved through 105- $\mu\text{m}$  sieve and then

heated at 120°C for dryness. The clay was characterized by XRD, IR, chemical analysis and differential thermal analysis before subjecting it to adsorption studies as described elsewhere [4].

### Potentiometric titrations

A mass of 0.6 g of China clay in 29 mL background electrolyte concentration was kept overnight in a double-walled cell. The reaction vessel was then connected to a water circulating bath with temperature variations of  $\pm 0.5$  via a water circulating pump. Initially the pH of the suspension was adjusted to about 3.5 at 298 K before starting each titration experiment, using 0.01M  $\text{HClO}_4$ . The suspension was then allowed to equilibrate for 2 hours with constant stirring, using a magnetic stirrer at constant temperature. The titration experiments were performed in 0.1, 0.001 M  $\text{NaClO}_4$  solutions at 298 K. Titrations were made by the addition of standardized solution of NaOH (0.01 M  $\text{L}^{-1}$ ). After each addition (0.2 mL) of NaOH, the suspension was equilibrated for 5 minutes with constant stirring, and the corresponding pH was observed, at the end of which the pH remained constant. The volume of 0.01M NaOH used were plotted against pH (Fig. 1).

The same experiment was repeated by first adjusting the initial pH to about 8.84 using 0.01M NaOH with constant stirring at 298 K. After each addition (0.2 mL) of 0.01 M HClO<sub>4</sub>, in various electrolyte solutions, the corresponding pH was observed, at the end of the which the pH remained stable. The volume of 0.01 M HClO<sub>4</sub> was plotted against pH (Fig. 2).

#### Conclusions

1. By adjusting high pH as the starting point, the determination of the p<sub>H</sub>PZC of kaolin was favourable because at low pH, the amorphous components of kaolin were adsorbed in the aqueous phase.

2. As the reaction was exothermic, the stability constants decreased with increasing temperature indicating that at low temperatures, high strength of bond existed between the adsorbent and adsorbate.

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