

Temperature Effect on the Sorption of Alkaline Earth Metal Cations on SiO₂ Surface

S.MUSTAFA, B.DILARA, A.NAEEM, N.REHANA AND S.MURTAZA
*National Centre of Excellence in Physical Chemistry
 University of Peshawar, Peshawar, Pakistan.*

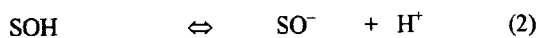
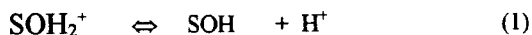
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Summary: The sorption of Ca²⁺ and Mg²⁺ ions on the silica was studied as a function of concentration and temperature. The extent of sorption of the metal cations was found to increase with the increase in both the concentration and temperature of the system. It was found that the Ca²⁺ ion with its smallest hydrated radii was able to reach the surface easily and was held more strongly as compared to Mg²⁺ ion. The sorption of metal cations was accompanied by the release of H⁺ to the bulk phase. The sorption data fitted the linear form of the Langmuir equation. The positive values of ΔH for the uptake of the metal ions on SiO₂ showed their sorption mechanism to be endothermic in nature. Both the positive ΔS and negative ΔG values confirmed the spontaneous nature of the sorption process.

Introduction

Oxides of iron, aluminum and silicon are important constituents of our soils. They are known to possess, pH dependent surface charges, when in contact with aqueous solutions. Oxides of silicon are generally negatively charged, while those of aluminum and iron have amphoteric character, carrying both the positive and negative charges depending upon the experimental conditions of the system [1- 4].

The interaction between water and oxide surface may result in the development of surface hydroxyl groups. These surface hydroxyl groups show an amphoteric character and the surface charges on the oxides/hydrous oxides are developed according to the mechanisms [5, 6].



where S shows the solid surface.

The pH at which the net charge on the surface is zero is called the point of zero charge (PZC). At pH above the PZC, the hydrous oxide is negatively charged and sorbs cations from the aqueous solutions and at pH below the PZC, the surface is positively charged and sorbs anions [7, 8].

Silica, being employed as adsorbent in the present investigation is commonly found in natural

aqueous systems as discrete mineral phases and is considered as an important sink for the trace metal ions [9].

As the availability of micronutrients and toxins in soil depends on the interaction of these materials with oxide/hydroxide particles, clay minerals and organic matter, the study of these interactions with common oxides/hydroxides like SiO₂, Al₂O₃, MnO₂, Fe(OH)₃ and Al(OH)₃ are also important from both the agricultural and environmental perspectives [6].

Surface and sorption properties of the SiO₂ have been investigated in great detail in the literature [6, 9]. However, the temperature effect studies on the ion exchange sorption of alkaline earth metal ions by the SiO₂ are very rare [10]. The present work, thus, describes the sorption of alkaline earth metal cations with the special reference to the effect of temperature. The results are of practical interest to the water industry, since the metal ions studied are known to be water pollutants and silica sand is generally used in water treatment.

Results and Discussion

Characterization of SiO₂

The surface area of SiO₂ is found to be 280 m²/g. The X-Ray diffraction pattern showed that the SiO₂ is amorphous in nature and the electron probe microanalysis of the sample gives 93% SiO₂ which

shows the sample to be hydrated in nature. Similar results are also reported elsewhere in the literature [11]. The PZC value 3.8 and the Fourier transform infrared (FTIR) spectrum of SiO₂ were the same as were reported in our earlier papers [2, 5].

Sorption of metal ions on SiO₂

The sorption of Ca²⁺ and Mg²⁺ ions on the SiO₂ surface is studied as a function of concentration and temperature at pH 5. The respective sorption isotherms at pH 5 are shown in Fig. 1 and 2, the uptake from the Figures, a continuous increase in the sorption of divalent metal ions on SiO₂ surface is observed with the increase in concentration of metal ions.

The influence of temperature on the ion exchange sorption of Ca²⁺ and Mg²⁺ was also undertaken in the range of 303 to 323K. The results obtained are given in the Fig. 1 and 2. the uptake of the metal ions is also observed to increase with increase in temperature. The increase in sorption with temperature may be attributed to the increase in the number of active sites on the surface. Bye *et al.* [12] also observed similar results while studying the sorption of metal ions on the oxides/hydroxides.

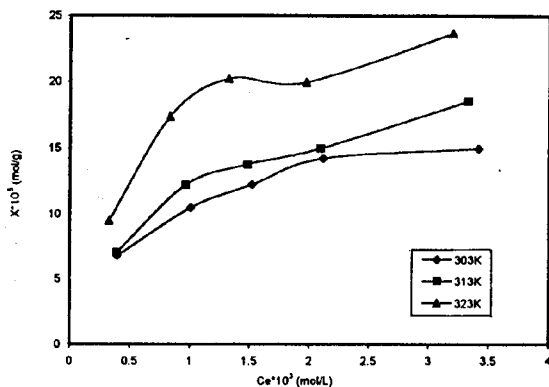


Fig. 1: Sorption of Ca²⁺ on SiO₂ at different temperatures.

The selectivity of the exchanger towards the metal ions mainly depends upon the ionic potential, pH of hydrolysis, ionic or hydrated radii of the metal cations [13]. In the present case the ionic radius of Ca²⁺ is larger than Mg²⁺ whereas the converse is true for their hydrated radii. Thus, Ca²⁺ ion with its smallest hydrated radii is able to reach the surface

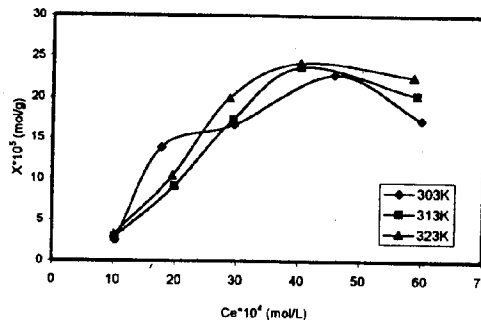


Fig. 2: Sorption of Mg²⁺ on SiO₂ at different temperatures.

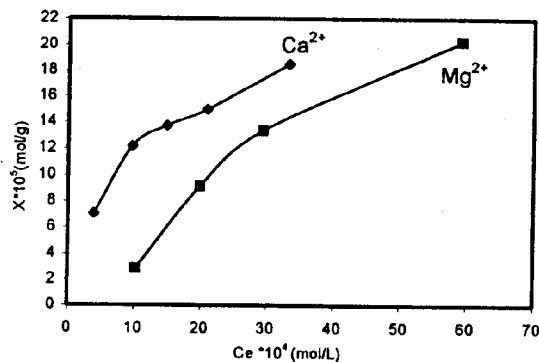


Fig. 3: Sorption isotherms of SiO₂ for various divalent metal ions at 313K.

easily and is held more strongly as compared to Mg²⁺ ion (Fig. 3). Similar trend was also observed elsewhere for the sorption of metal ions on the metal hydroxides [6].

The decrease in equilibrium pH of the solution shows that the sorption of metal ions is accompanied by the release of H⁺ ions from the solid into the aqueous phase according to the reaction:



where SOH, (SO)_nM²⁻ⁿ and n refers to the surface adsorption sites, surface complex of metal ions and number of H⁺ ions released respectively. The proposed mechanism agrees well with those reported by several researchers [5, 6].

The Langmuir equation, which gives a useful information about the sorption maxima (X_m) and

binding energy constant (K), was employed to the experimental data. The representative plots of Langmuir isotherms for Ca^{2+} are also presented in Fig. 4. Similar trend was also observed for Mg^{2+} ions. As is evident from these Figure, the present experimental data fit to the Langmuir equation [6] given in the form

$$\frac{C_e}{X} = \frac{1}{KX_m} + \frac{C_e}{X_m} \quad (4)$$

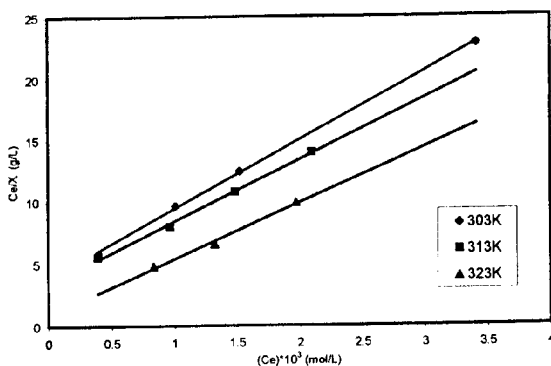


Fig. 4: Langmuir isotherms of Ca^{2+} sorption on SiO_2 at different temperatures.

where C_e is the equilibrium concentration and X is the amount of metal ions sorbed, K is the binding constant and X_m is the maximum sorption capacity of the exchanger.

The values of the (X_m) and (K) obtained from the slopes and intercepts of the straight lines are given in Table 1. As is obvious the values of both the X_m and K for Ca^{2+} and Mg^{2+} ions increase with the rise in temperature indicating the greater stability of the metal surface complexes $(\text{SO})_2 \text{M}^{z-n}$ at higher temperatures. The present values of the X_m and binding constant (K) are comparable with the values reported in the literature [6,12].

Table-1: Sorption maxima (X_m) and binding energy constant (K) for the exchange of Ca^{2+} and Mg^{2+} on SiO_2 at pH 5.

Temp. (K)	$(X_m) \times 10^3$ (mol/g)		K (L/g)	
	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
303	17.90	17.10	1462	1697
313	20.0	19.20	2754	1862
323	22.27	24.98	5019	2035

Thermodynamic parameters

The enthalpy and entropy of the metal ions sorption on SiO_2 can be computed by using the following equation (5).

$$\text{Log } K = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (5)$$

where K is the binding constant, R is the gas constant [$\text{J}/(\text{mol}\cdot\text{K})$], T is the absolute temperature (K), and ΔS [$\text{J}/(\text{mol}\cdot\text{K})$] and ΔH [kJ/mol] are the changes in entropy and enthalpy of the system respectively.

The changes in enthalpy ΔH and entropy ΔS of adsorption of different metal ions evaluated from the linear plots of $\log K$ with the reciprocal of temperature (Fig. 5, 6), are collected in Table 2. The positive ΔH values indicate that the sorption process for Ca^{2+} and Mg^{2+} ions on the SiO_2 surface is endothermic in nature. The relatively higher value of ΔH indicates a greater dependence of Ca^{2+} ions sorption on the temperature while the lower value of ΔH for Mg^{2+} reveals that temperature has little effect upon its sorption on SiO_2 surface. The

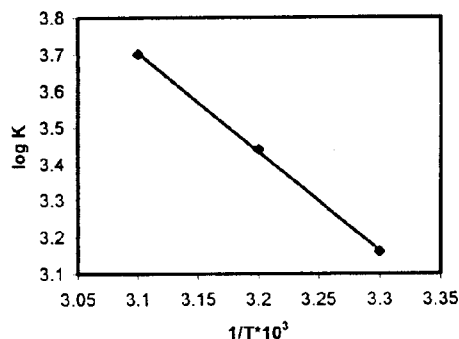
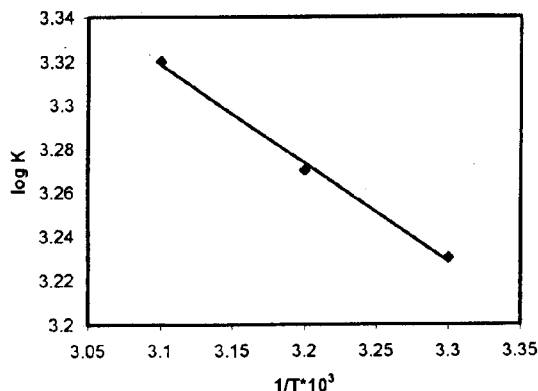


Fig. 5: Plot of $\log K$ vs. $1/T$ for Ca^{2+} .

endothermicity of the sorption process is probably due to the partial dehydration of the metal cations before their adsorption, as in the process of dehydration large amount of energy is needed to strip the metal ions from their hydration sheath. The enthalpy of adsorption during this study was observed to be 8.66 and 51.70 kJ/mol respectively for the sorption of Mg^{2+} and Ca^{2+} on SiO_2 . In addition, the values of ΔH obtained here are also

Fig. 6: Plot of $\log K$ vs. $1/T$ for Mg^{2+} .Table-2: Enthalpy, entropy and free energy changes of Ca^{2+} and Mg^{2+} exchange on SiO_2 .

Temp. (K)	ΔG (kJ/mol)		ΔH (kJ/mol)		ΔS (kJ/mol)	
	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
303	-18.34	-18.68				
313	-20.65	-19.58	51.70	8.66	231	90
323	-22.96	-21.76				

comparable in magnitude with the values reported elsewhere [14].

The conclusions drawn from ΔH values are also supported by the positive values of ΔS . The values of ΔS are found to be 231 and 90 J/mol.K for Ca^{2+} and Mg^{2+} ions respectively. The positive values of entropy show the metal ions to be less hydrated in the interface than in the bulk solution. Thus, the present values of ΔS confirm that the sorption of Ca^{2+} and Mg^{2+} by SiO_2 is a spontaneous process.

The values of ΔG were calculated from the following relationship:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

The observed values of ΔG were found to be negative and further decreased with increase in temperature which besides the spontaneous nature of the process also show that the overall process of exchange is favoured at higher temperatures (Table 2). The present findings are in fair agreement with those reported previously [5,12].

Finally, it is observed that all the thermodynamic parameters found in this study fall within the range of parameters calculated by other

workers [5, 6, 10, 15, 16] for the adsorption of transition metal ions on various substrates.

Experimental

Reagents

Analytical grade reagents were used without further purification. The pH of the suspension was carefully adjusted with the NaOH and HNO_3 solutions. All the experiments were performed in the presence of N_2 to bubble out the CO_2 gas.

Preparation and characterization of the silica

White pellets of silica were ground to fine powder by means of grinding machine model Siebt Technik Type TS, 250. Powdered silica was suspended in conductivity water and was stirred at 50 °C for one hour at pH 3.92 and was left overnight. Silica was dialyzed for three days at 27 °C with daily changes of water. The sample was filtered, washed with conductivity water and was dried at room temperature in open air. Finally, it was dried at 105 °C for three days in vacuum.

The sample thus prepared was characterized by X-ray diffractometry, FTIR, EPM, surface area and point of zero charge (PZC). The method of characterization was the same as that reported in our earlier papers [2, 5].

Sorption studies of SiO_2

The sorption experiments were performed by taking 0.1g sample in 40ml of divalent metal ion along with 0.1M $NaNO_3$ in conical flasks. The pHs of the suspensions were adjusted as 5 with standard NaOH or HNO_3 solution and were stoppered. Then suspensions were equilibrated at different temperatures for 24 hours in thermostated end-to-end shaker bath, Labortechnik type LE-209. Preliminary experiments showed that 24 hours are sufficient for the equilibration of the system. After equilibration, pHs of the suspensions were noted and were readjusted to the initial pH value and volume of the acid or base used was noted. Afterwards, suspensions were centrifuged and supernatants were separated for analysis. The concentrations of the metal ions in supernatant were determined with the help of Perkin Elmer model 3100 atomic absorption spectrophotometer. The amount of the metal ion adsorbed was calculated from the difference between initial and equilibrium concentrations of the metal ions.

Conclusions

From the discussion above it is inferred that SiO₂ behaves as weak acid cation exchanger. The sorption of both the Ca²⁺ and Mg²⁺ was observed to increase with the increase in concentration and temperature. The mechanism of the metal ions uptake was found to be the cation exchange with the protons from the solid. The affinity of the SiO₂ towards the metal ions was found in the order: Ca²⁺ > Mg²⁺. The positive values of both the enthalpy (ΔH) and entropy (ΔS) and negative values of (ΔG) showed that the process of adsorption is endothermic and spontaneous.

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