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MECHANISM OF CATION EXCHANGE ON SILICA GELS

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SUMMARY

The results of potentiometric studies of the polymerization of silicic acid and the mechanism of cation exchange on different ionic forms of silica gel are considered in terms of modern concepts of the properties of siloxane bonds.

INTRODUCTION

It is well known^{1,2} that orthosilicic acid is an extremely weak acid ($pK_1 \approx 9.8$). On the other hand, silica gel (polysilicic acid) and other highly dispersed silicas can exchange cations not only in neutral solutions, but even in acidic solutions (at pH 3–4 and higher)^{3–6}. This fact, as well as the location of the isoelectric point of sols and gels of silicic acid near pH 2 (refs. 6 and 7), shows that these more complex forms of silica contain strongly acidic centres or groups.

In order to ascertain the reason for this discrepancy and to study in more detail the mechanism of cation exchange on dispersed silicas, the changes in pK values of silicic acids in the initial stages of the polymerization of $\text{Si}(\text{OH})_4$ were followed potentiometrically; the same method was used to determine the pK of silica gel. The results obtained were then compared with our values and literature values for the adsorbabilities of various cations, ions of the elements of sub-groups I–IIIA of the periodic system, *d*- and *f*-cations, on different cation-substituted forms of silica gel. All the results thus obtained are considered in this paper in terms of modern concepts of the properties of Si–O bonds^{8,9}.

EXPERIMENTAL

A coarse porous silica gel with a specific surface area (B.E.T.) of *ca.* $600 \text{ m}^2 \cdot \text{g}^{-1}$ was prepared, as described earlier³. By means of ion exchange, we obtained from this sample a completely substituted calcium form and a mixed aluminium–hydrogen form of silica. Separate weighed portions of the hydrogen form of silica gel were titrated potentiometrically with solutions of LiOH, NaOH, KOH, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ in 0.1 *N* solutions of the corresponding perchlorates.

In the sorption experiments, we traced the cations of salt solutions by means of the corresponding radioisotopes and measured their adsorption radiometrically.

RESULTS AND DISCUSSION

In our previous work¹⁰⁻¹², the high protogeneity of the surface silanol groups of silicas, which enables cation exchange to occur on them in acidic media, was attributed to the well known^{8,9,13} effect of ($p \rightarrow d$) π conjugation in the chain of siloxane bonds. In particular, it was shown¹² that the influence of this factor becomes apparent in the first stages of polymerization, *i.e.*, in the formation of oligomers of silicic acids; on going from the dimer to the tetramer, the ionization constant increased, in our tests, by an order of magnitude. This may be explained by the relatively greater contribution of ($p \rightarrow d$) π conjugation to the decrease in the negative charge on the oxygen atoms of terminal Si-OH groups with lengthening of the chain of Si-O bonds¹³.

A further development of the polymerization process must obviously lead to an even greater strengthening of the silicic acids formed. In fact, although when titrating with various bases we obtained different pK values for silica gel (NaOH, 7.7; KOH, 7.3; Ca(OH)₂, see Fig. 1; Ba(OH)₂, 6.5), they all showed that hydrogen in the silanol groups of polysilicic acid is much more mobile than in monomeric orthosilicic acid. It should also be noted that our results agree satisfactorily with the pK value of 7.1 ± 0.5 obtained recently by an independent IR spectral method¹⁴.

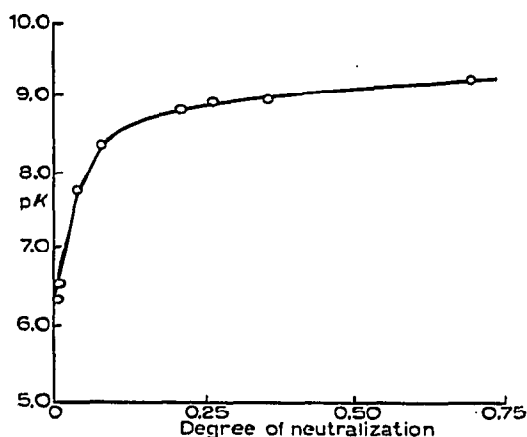


Fig. 1. Dependence of pK values of the silanol groups of silica gel on the degree of their neutralization (α) when titrating the gel with a solution of Ca(OH)₂ in 0.1 *N* Ca(ClO₄)₂.

The results of the potentiometric measurements, which revealed a considerable mobility and hence the ability of the protons of the silanol groups of silica gel to undergo cation exchange, as well as their interpretation as cited above, are strongly supported by our sorption data. In accordance with other work³⁻⁶, these experiments showed that on both the hydrogen and the aluminium forms of silica gel (Fig. 2), which have compensating ions that are similar by nature (see below), the adsorbability of highly basic alkali metal and alkaline earth metal cations at $pH \leq 7$ increases regularly* with increase in their crystallographic radii, *i.e.*, from Li⁺ to Rb⁺ and from Ca²⁺ to Ba²⁺.

* As on strongly acidic cation-exchange resins¹⁵.

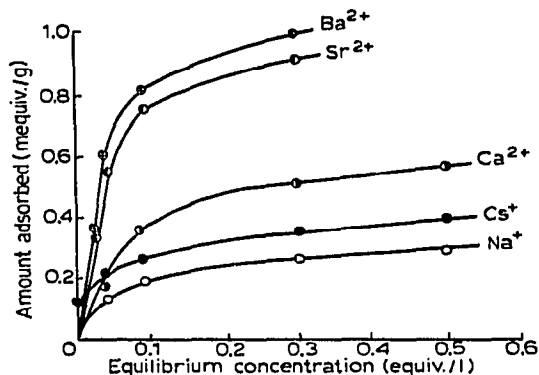


Fig. 2. Sorption isotherms of Na^+ , Cs^+ , Ca^{2+} , Sr^{2+} and Ba^{2+} cations on silica gel in the aluminium form; aqueous nitrate solutions at pH 4.5.

On the contrary, on the calcium^{16,17} and sodium forms of silica gel¹⁸, the order of sorption of these ions is reversed: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$ and $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Sr}^{2+} \approx \text{Ba}^{2+}$. A similar reversal of the usual sequence of adsorbabilities of these metal cations was also observed in potentiometric titrations of silica gel in the hydrogen form with various alkalis at pH > 10 (Fig. 3).

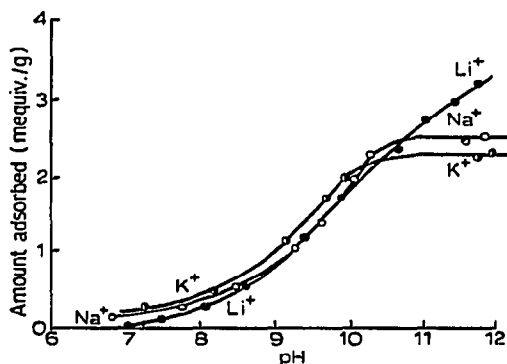


Fig. 3. Reversal of the adsorbability order of alkali metal cations in the high pH range when titrating silica gel with LiOH, NaOH and KOH solutions.

This reversal of the sorption series of cations of alkali metals and alkaline earth metals, *i.e.*, elements that have the lowest electronegativities⁸, X , with a change in the type of exchangeable cation (H^+ , $\text{Al}^{3+} \rightarrow \text{Na}^+$, Ca^{2+}) can, in our opinion, be given a convincing explanation in terms of the effects of $(p \rightarrow d)_\pi$ conjugation on the properties of surface Si-O bonds.

It is known¹ that the surface of the common hydrogen form of silica gel can be represented schematically as shown in Fig. 4a. An exchange of the protons of a small (in acidic media) proportion of the surface Si-OH groups on strongly basic alkali metal or alkaline earth metal cations, Me_1^+ (Fig. 4b), leads to the appearance, on the oxygen atoms of the Si-O⁻Me₁⁺ groups, of a negative charge which increases with the basicity of the sorbed ion, Me_1^+ . This is due to the presence of OH groups

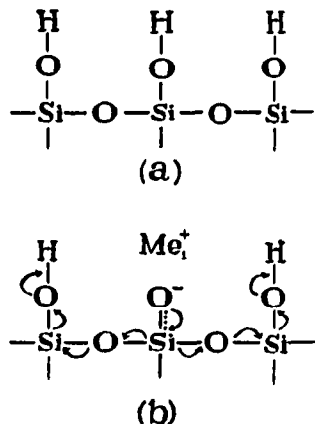


Fig. 4. Schematic representation of the surface of silica gel in acidic solutions (a) before and (b) after sorption of basic cations, Me_1^+ , on it. Me_1 : Li, Na, K, Rb, Cs, Ca, Sr, Ba with $X \leq 1$.

with a high electronegativity⁸ near every exchange centre, and the possibility of the electronic influence being transferred through the chain of Si–O bonds. Therefore, even from energy considerations*, on a silica surface with acceptor compensating ions (H^+ , Al^{3+} , etc.) from a group of alkali metal or alkaline earth metal cations, the ions with the lowest ionization potential must be sorbed preferably; this is, in fact, observed experimentally.

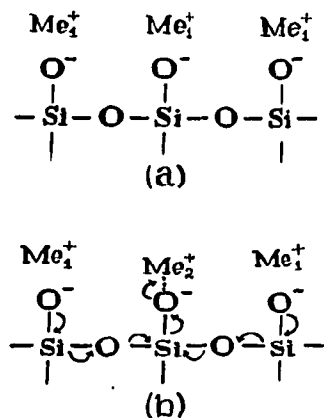


Fig. 5. Schematic representation of the surface of a silica gel salt form with basic counter ions, Me_1^+ , (a) before and (b) after the sorption of acceptor ions, Me_2^+ , on it. Me_1 : see Fig. 4; Me_2 : Be, Mg, Al, elements of *d*- and *f*-series with $X > 1$.

A different case occurs when cations are sorbed on the salt forms of silica gel with basic counter ions, Me_1^+ (e.g., Na^+ or Ca^{2+}), which are bound mainly electrostatically to the anionic oxygen in $\text{Si}-\text{O}^-\text{Me}_1^+$ groups (Fig. 5a). On such forms of silica, the ions sorbed most effectively will be those Me_2^+ ions which can compete

* Because of the increased ($p \rightarrow d$)_n interaction in $\text{Si}-\text{O}^-$ bonds^{8,9}.

most successfully with the silicon atom for the electronic density on the oxygen, thus providing a maximum degree of π interaction in the whole system of surface siloxane bonds near the exchange centre (Fig. 5b). These are, in fact, the most acceptor (least basic) ions, which explains, in particular, the reversal of the sorption series of alkali metal and alkaline earth metal cations on some silica gel salt forms¹⁶⁻¹⁸.

It is of interest to note that, unlike the cations of alkali metals and alkaline earth metals, the multivalent acceptor ions, e.g., of the rare-earth metals, gave the same sorption series on all investigated ionic forms of silica gel: $\text{La}^{3+} < \text{Ce}^{3+} < \text{Nd}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} \approx \text{Y}^{3+} < \text{Er}^{3+} < \text{Tm}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+} < \text{Sc}^{3+}$.

In the light of above considerations, the independence of the affinity order of trivalent acceptor cations (and of similar, in this sense, *d*-element ions¹⁷) of the nature of the silica surface, acceptor (Fig. 4) or anionic (Fig. 5), could be explained only by the fact that the π interaction in the $\text{O}^- - \text{Me}_2^+$ bonds of these ions far exceeds the energy changes in the surface siloxane bonds. Therefore, the sorbed acceptor ion is unable to "feel" the nature of the exchanged counter ion separated from it by a chain of Si-O bonds.

The results of our potentiometric and ion-exchange studies are also in good agreement with IR spectral data for cation-substituted silica gels¹⁶ and results for the adsorption of different substances (acetic acid, dioxan, pyridine) on them¹¹.

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