Laws and mechanism of adsorption of cations by different ion-exchange forms of silica gel

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Abstract Using radioactive tracer method, the regularities of adsorption of over 30 mono-, di- and trivalent cations including transition metal and lanthanide ions on the H, Ca- and Al-forms of silica gel are established. It has been shown that the affinity of cations of the same charge to the silica gel surface depends both on the nature of the adsorbing ion and the nature of exchangeable cation on the surface. Adsorption of alkali earth metal ions on the Ca-form of silica gel increases with a decrease of their radius i.e. *an inversion* of the sequence of adsorption compared to H- or Al-form of this adsorbent or polymeric cation-exchange resins takes place. For lanthanide ions the sequence of adsorption is the same for all ion-exchange forms of the silica gel studied, namely, *an increase of adsorption with a decrease* of their crystallographic radius, i.e. from La^{3+} *to* Lu^{3+} takes place. The laws observed are explained by taking into account the fact that adsorption of cations by silica gel is determined by both electrostatic interactions and additional covalent/donor–acceptor interactions between the surface and cations. The latter is due to

formation of π-bonds between the electron pair in surface oxygen and vacant p-, d- or f-orbital of adsorbing cations.

1 Introduction

Silica gel is widely used as ion-exchange material for separation of radioactive isotopes, deactivation of waste-waters of isotopes production, treatment of recycled waters of nuclear plants, extraction and separation of transition and heavy metal ions, water purification, etc. This is due to selectivity of adsorption of ions on silica and modified silica surfaces, high thermo and radiation resistance of these materials. Despite the numerous studies in the field, it is interesting to establish the laws and mechanisms of adsorption of cations by different ion-exchange forms of silica gel and their relationship with the nature of the siloxane bond of the silica surface are not elucidated in full.

In a number of papers published from the 60 s of the last century, the regularities of adsorption of some cations by different ion-exchange forms of silica gel were established, and also the possibility of their chromatographic separation using this adsorbent has been shown (Ahrland et al. 1960; Ahrland 1963; Dushina and Aleskovsky 1963; Markova and Vydra 1966; Baran et al. 1969). By means of a titration technique, the amount of exchange of positive ions for silanol hydrogen on the surface of the silica sols has been measured as a function of pH at various electrolyte concentrations. At low pH cation exchange on silica surfaces would appear to obey the mass action law. At pH > 6 the observed amount of exchange is considerably less than

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predicted on the basis of a simple equilibrium (Allen and Matijeviéc 1970).

Authors (Tran et al. 2000) have studied the adsorption of several bivalent (Pb, Cu, Zn, Cd, Ni) and uranyl cations on silica gel in H-form in a wide range of pH of the system. It has been found a rapid metal uptake in the narrow range of pH, equal 2.5–4.5 for uranium (VI), 3.5–5.5 for lead, 3.75–5.75 for copper, 4–6 for nickel and 4.2–6.2 for zinc and 4.5–6.5 for cadmium. The adsorption was described by an ion-exchange mechanism where hydrogen ions of the surface silanol groups were replaced by monovalent hydrolyzed species of these cations.

Fumed oxides (silica and mixed oxides based on silica) have been shown to be efficient adsorbents for toxic metal ions such as Pb, Sr, Ni, Cd, and Cs (Gun'ko et al. 2004).

During the last decades, the majority of studies were devoted to fabrication of silica gel based adsorbents containing different surface functional groups for selective uptake of heavy metal/hazardous ions, concentration of precious metals, etc. Several typical examples are given below.

Authors (Baba et al. 1984) have studied the ion-exchange adsorption of copper and cadmium ions on silica gel from aqueous ammonium nitrate solution of various concentrations. It was found that the surface of silica gel acts as an ion exchanger of weakly acid type, and that metal ions adsorbed can be desorbed with dilute acid solutions. It was determined that copper and cadmium are adsorbed according to the cation-exchange reaction $GH_2 + MeNH_3^{2+} = GMeNH_3 + 2H^+$ (here G- gel, Me-metal). The apparent equilibrium constants for this reaction were evaluated as $K_{Cu} = 4.3 \times 10^{-13}$ and $K_{Cd} = 5.1 \times 10^{-20}$ mol/dm^3 for 1 mol/dm^3 ammonium nitrate solution. Based on these results, the selective separation of copper from cadmium on silica gel is considered to be possible.

Materials that contain functional groups to complex dissolved metal ions, i.e. modified silica, are effective to remove hazardous ions from aqueous media (Jal et al. 2004). The use of inorganic materials, especially silica, has significant advantages over conventional organic/polymeric support, namely, high surface area to enhance adsorption capacity, greater physical and chemical robustness to withstand a variety of harsh environments. Highly structured mesoporous silica with incorporated bridging/complex-forming functional groups (mercapto or amino) are excellent adsorbents for adsorption of Hg (Jaroniec and Olkhovyk 2006) or Cu and Pb ions (Blitz et al. 2006).

Aguado et al. (2009) have prepared amino functional mesoporous silica materials to develop efficient adsorbents of heavy metals in wastewater. It has been shown that materials functionalized by grafting with monoamine, diamine and triamine organic chains exhibit remarkable uptake capacities in respect to Cu, Ni, Pb, Cd, and Zn ions.

The nitrogen anchoring points to metal species number ratio decreases in the sequence Pb > Cd > Zn ≥ Cu ≥ Ni, the same diminution order found for adsorption percentage. The copper adsorption has been studied in detail from both kinetic and equilibrium points of view, the adsorption of Cu ions can be described by Langmuir isotherms on the all three amino-forms of the adsorbent. No discussion on the mechanisms of adsorption is given.

Authors (Yin et al. 2010) synthesized and characterized a novel inorganic–organic composite material, i.e. silica gel microspheres encapsulated by imidazole functionalized polystyrene. Adsorption of Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), Pd(II), Pt(II), Ag(I), and Au(III) from aqueous solutions by this material has been measured. The highest adsorption capacity was detected for Au(III). The adsorption data were described by Langmuir isotherms. This material was used to pre-concentrate Au(III) before its determination by flame atomic adsorption spectrometry.

Walcarius and Mercier (2010) presented a review with ca. 400 references on the use of functionalized mesoporous silica and organically-modified silica-based materials for removal of inorganic and organic pollutants from aqueous solutions. Also various synthetic methods to prepare such nanoengineered adsorbents and their application to remove heavy metal species, toxic anions, radio nuclides, and a wide range of organic pollutants are described.

Tzvetkova and Nickolov (2012) have used modified and unmodified silica gel for removal of heavy metal ions from aqueous solutions. It has been shown that adsorption depends on the pH, and the highest adsorption capacity was found for the uptake of Hg(II) ions on silica gel modified by 2-aminothiazole.

The objective of our study was to establish the laws and mechanisms of adsorption of cations by different ion-exchange forms of silica gel and their relationship with the nature of the siloxane bond on the silica surface. Starting from Pauling (1960), it has been supposed that there might be a pπ–dπ interaction between Si atom and elements having free electron pair. It has been shown in a number of studies that there is an additional π-interaction in siloxane bonds ≡SiO which is the cause of considerable covalence of this bond (Voronkov 1961; Syrkin 1962; Lazarev 1966). The degree of this covalence is determined by the nature of cation bound to the O atom. It means that the bond O–Me^{n+} in functional group Si–O–Me^{n+} should possess some covalence, the degree of which increases with an increase of the acceptor ability of the Me^{n+} ion (Lazarev 1966). This is due to competition between the silicon and metal ion for the free electron pair (electron density) on the O atom.

Based on the above considerations, we have performed a complex study on adsorption of over 30 cations by H-, Ca

and Al-forms of silica gel as a function of the added amount, valence and chemical nature of adsorbing cations as well as nature of exchangeable ions on the surface, solution pH, by using direct measurements of the adsorbed amount of radioactive tracer ions. The laws observed were interpreted applying the described ideas about the nature of chemical bonds of surface functional groups of different ion-exchange forms of the silica gel.

2 Materials and methods

A synthesized silica gel (SiG) with specific surface area of 710 g m^{-2} and high porosity (0.90 cm^3 g^{-1}) has been applied in our study. Ca-form of silica gel was obtained by treatment of silica by 0.3 M Ca(OH)$_2$. This sample was treated by radioactive Ca^{45} nitrate solution to obtain radioactive (labeled) Ca*–SiG with activity of 3–15 × 10^7 Bq g^{-1}. Other ion-exchange forms of silica gel were produced by treatment of Ca-gel with salt nitrates at pH 3.

Adsorption on Ca*–SiG was determined from the radioactivity of solution after 2-h contact of the adsorbent with solution of the salt studied. It has been shown in kinetic experiments that this time was more than enough to reach adsorption equilibrium. Typically, the equilibrium adsorption time in our systems was several minutes. The adsorbed amount of ions on the other ion-exchange forms of the SiG was determined based on the radioactivity of the sorbent after its contact with labeled cations (Na-22, Cs-134, Sr-90, Co-60, Zn-65, Cd-115, Ba-133, Sc-46, Y-91, La-140, Ce-144, Nd-148, Tb-160, Lu-177) in solution. The isotopes were tested for radiochemical cleanness, i.e. absence or possible presence of other isotopes in the material for study which, in the event of their high adsorption affinity to the surface, could distort the true value of adsorption of the investigated ion, even in the case of trace amounts of the contaminant in the sample. For several isotopes having radiochemical impurities, we have performed additional purification using a special method developed in our laboratory. For this purpose we have conducted several cycles of adsorption of "radiochemically contaminated" isotopes on the silica gel during which the preferentially adsorbing contaminant isotopes had chance to be accumulated on the surface, i.e. be removed from the solution of the labeled ion under study. Measurements of the radioactivity of solutions and silica gel were performed using classic MST 17 type Geiger-Müller counter and counting device PS-100 (produced in the former USSR) as described in book (Spycin et al. 1955) and paper (Baran et al. 1969). The sample of radioactive adsorbent was thoroughly rinsed by demineralised water to remove the excess of electrolyte, dried at 110–120 °C and ground. Then its radioactivity was measured taking into account the

necessary corrections for the background radiation, for decay and self-weakening of radiation in the sample for measurement.

3 Laws of adsorption on Ca-silica gel

The adsorbed amount of ions on Ca*-form of silica gel was determined as the displaced amount of Ca*$^{2+}$ from Ca*–SiG versus concentration of different cations in solution at initial pH 5.8–5.9 for mono-and bivalent ions and at pH 1.8 for trivalent ions. So, the displaced amount of Ca*-ions was equalized to the amount of adsorbing cations.

Equivalence (i.e. the equality of the adsorbed amount of cations and displaced amount of Ca*-ions from Ca*–SiG expressed in milli-equivalents per g) of adsorption of cations was proved by independent experiment. For this purpose we have determined (1) the adsorbed amount of different ions from the displacement of labeled Ca*-ions from the surface, and (2) by direct measurements of adsorption of radioactive (labeled) cations by the non-labeled Ca-form of the silica gel, i.e. from the radioactivity of the adsorbent itself. Concentration of several displaced from the surface (adsorbed on Ca–SiG) ions such as Ag$^+$, Tl$^+$, Mg^{2+}, Fe^{2+}, etc. was determined by usual chemical-analytical methods after their desorption as a result of treatment of the sorbent with 0.1 M HNO$_3$ solution.

Table 1 show that there is an excellent agreement between these two values. This means that during adsorption of di-and trivalent cations the whole amount of Ca-ions is displaced from the adsorbent surface.
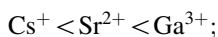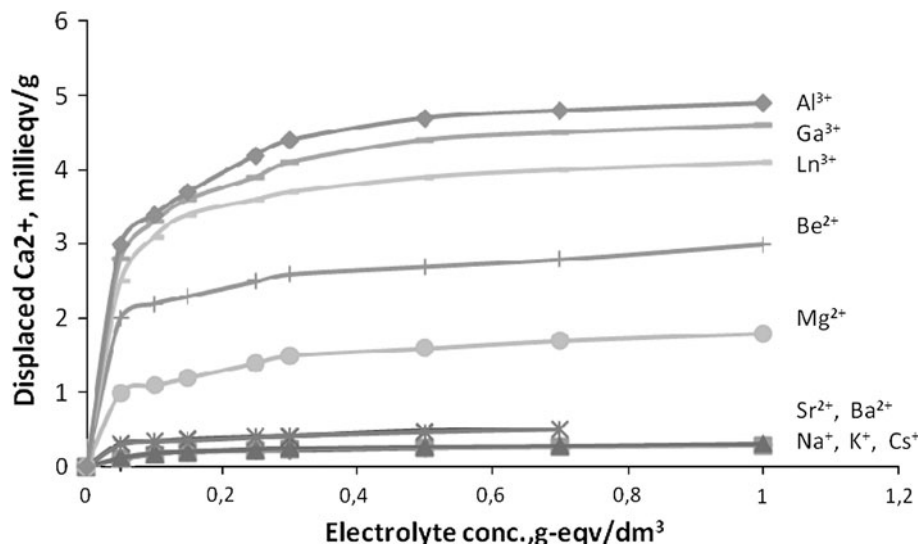
Curves of replacement of Ca*$^{2+}$ ions from the Ca*–SiG, characterizing the adsorption of different ions, by mono-, di- and trivalent cations are shown on Fig. 1. It is seen that:

1. adsorption versus ion concentration curves remind Langmuir type isotherms;
2. adsorption of cations substantially increases with their valence; for example:

Table 1 Comparison of adsorbed amounts of cations by Ca–SiG measured by direct adsorption of corresponding labeled ions and from the displaced amount of labeled Ca*$^{2+}$ from the surface

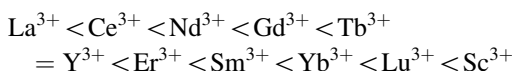| Cation	Adsorption by Ca–SiG, meqv/g	Amount of displaced Ca*$^{2+}$, from Ca*–SiG, meqv/g
Sc*$^{3+}$	3.40	3.30
Y*$^{3+}$	3.13	3.04
La*$^{3+}$	2.40	2.44
Er*$^{3+}$	3.38	3.28
Co*$^{2+}$	1.59	1.50
Ni*$^{2+}$	2.25	2.27

$Cs^+ < Sr^{2+} < Ga^{3+}$;

Typically, the plateau value of adsorption of monovalent alkali metal ions reaches 0.2–0.3 meqv/g, divalent ions −1.8 to 2.5 meqv/g and trivalent cations—up to 3–4 meqv/g.

3. for ions of the same charge the adsorbed amount *increases* with a *decrease* of their crystallographic radius:

$Ba^{2+} < Sr^{2+} < Mg^{2+} < Be^{2+}$ or $In^{3+} < Ga^{3+} < Al^{3+}$
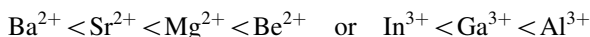
This is contrary to the laws observed for ion-exchanger resins (Helfferich 1962) or silica gel in H-or Al-form (see below).

It has been shown also that adsorption of transition metal (d-elements) and lanthanide ions (f-elements) *increases* with their charge (for Me^{3+} ions from 3.2 to 4.5 meq/g and for Me^{2+} ions from 1.8 to 2.5 meq/g) and with *decreasing their radius*:

$La^{3+} < Ce^{3+} < Nd^{3+} < Gd^{3+} < Tb^{3+}$
$= Y^{3+} < Er^{3+} < Sm^{3+} < Yb^{3+} < Lu^{3+} < Sc^{3+}$

This means that adsorption of d- and f-elements on Ca–SiG is determined not only by their charge but also by their "basicity", i.e. affinity to electrons. The inverse dependence between affinity of cations to silica gel and their crystallographic radius is demonstrated also by adsorption series of mono-and bivalent ions. For example, adsorption of Ag^+ (r = 0.113 nm) or Zn^{2+} (r = 0.083 nm) is higher than that for Tl^+ (r = 0.149 nm) or Cd^{2+} (r = 0.103 nm), respectively.

It is interesting to note that adsorption of cations Fe^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} or Cd^{2+} (r = 0.082–0.083 nm) is higher compared to Mg^{2+} having even smaller radius (r = 0.078 nm). This is an evidence of increased affinity of complex-forming cations to the surface, i.e. cations with significant ability to donor–acceptor interactions/bond formation. This is in line with above

stated considerations about the contribution of covalent, donor–acceptor interactions—on the top of electrostatic forces-into the energy of adsorption bonds in Si–O–Me^{n+} surface groups.
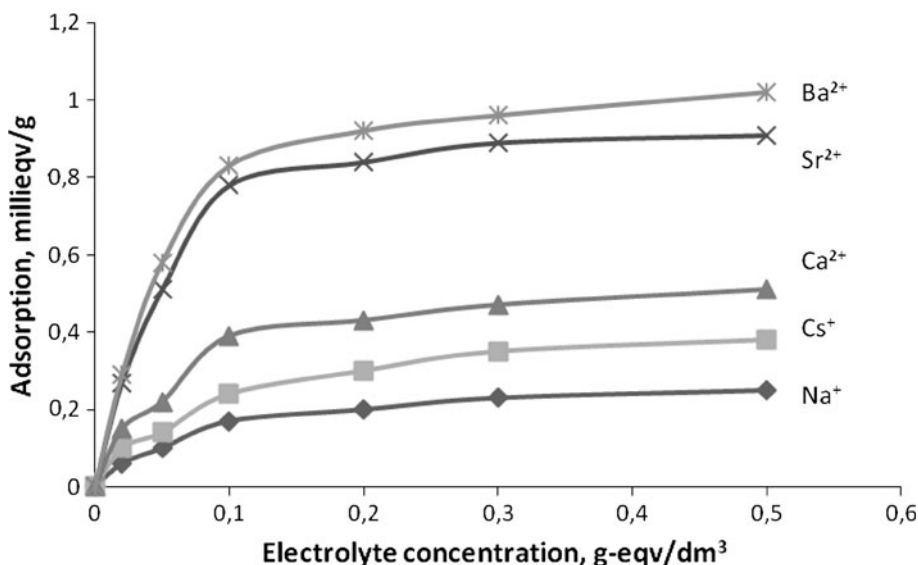
4 Adsorption by H-and Al-forms of silica gel

It has been shown that adsorption of alkali and alkali earth metal ions by H–SiG, in full agreement with literature data (Ahrland et al. 1960; Markova and Vydra 1966; Baran et al. 1969), increases with rising their crystallographic radius: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $Ca^{2+} < Sr^{2+} < Ba^{2+}$ (Figs. 2, 3). This regularity is also in line with the sequence of adsorption of these ions by strongly acidic cation -exchange resins (Helfferich 1962). At the same time, this sequence is opposite to that observed for the Ca-form of the silica gel (see above).

It was important to clarify whether the law observed, namely, the reverse of the sequence of adsorption on H–SiG to that for the Ca–SiG, has general character, i.e. is it valid also for lanthanide and complex-forming d-elements. To elucidate this problem, we have studied in detail the adsorption of these metal ions by H–SiG in a wide range of the equilibrium pH values of solution. Figure 4 shows that the affinity of lanthanide and transition metal ions to H-silica gel in a wide pH interval changes similarly to that revealed for the Ca–SiG (see above), for example:

$La^{3+} < Ce^{3+} < Nd^{3+} < Y^{3+} < Tb^{3+} < Sc^{3+}$
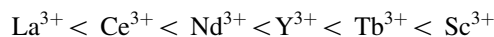
The adsorption behaviour of different cations by Al-form of the silica gel is similar to that on the H-form. Determination of adsorption of labeled cations Na^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Y^{3+} and La^{3+} by direct measurements of the radioactivity of the adsorbent shows (Figs. 2, 3, 4) that:

Fig. 2 Adsorption isotherms of alkali and alkali earth metalions from their nitrates by Al-form of silica gel at equilibrium pH 4.5

Fig. 3 Adsorption isotherms of several cations from their nitrates by Al-form of silica gel at equilibrium pH 2.7
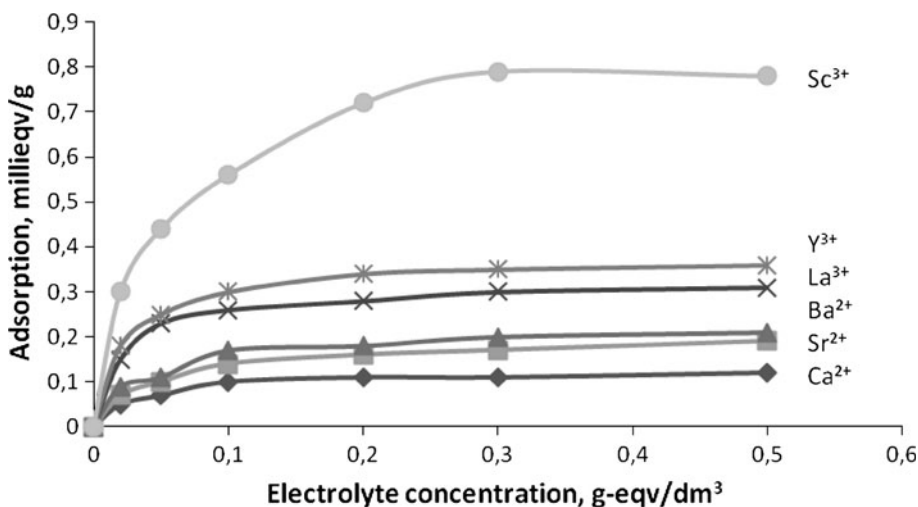
1. the adsorbed amounts of cations by Al–SiG at the same equilibrium pH are typically higher compared to that established for H–SiG;

2. adsorption of cations strongly increases with pH both for H- and Al- forms of the adsorbent, especially in pH region 3–6 for H-form (Fig. 4);

3. the adsorbed amounts substantially increase with rising the charge of the cation; and

4. the adsorption of alkali and alkali earth metal ions *increases with increasing their radius* (i. e. $Na^+ < Cs^+$ and $Ca^{2+} < Sr^{2+} < Ba^{2+}$) while adsorption of complex-forming and trivalent acceptor ions of Sc-subgroup, vice verse, *increases with decreasing their radius*, i.e. $La^{3+} < Y^{3+} < Sc^{3+}$.

5 Discussion

According to literature data, the major mechanism of adsorption of cations on silica gel is ion- exchange with replacement of hydrogen ions of the surface silanol groups, especially at low pH values. In the case of bivalent cations adsorption of monovalent hydrolyzed species of these cations is supposed. Adsorption of heavy and transition metal ions on functionalized surfaces of the silica gel is governed by interactions of different nature (electrostatic, complex-forming, hydrogen bonds, etc.) which are beyond the topic of our study.

Our study shows that sequences of adsorption of cations depend both on the nature of ion compensating the surface $Si–O^-$ charge (H^+, Ca^{2+}, Al^{3+}) and on the nature of adsorbing ions. Namely: an inversion of series of adsorption of di-, and trivalent cations on Ca- silica gel compared to ion-exchange resins and/or H- or Al-forms of the silica gel takes place, whereas no inversion of series of adsorption for lanthanide and complex-forming ions has been observed. To understand and explain these laws let us first inspect the structure of the H-silica gel surface being in
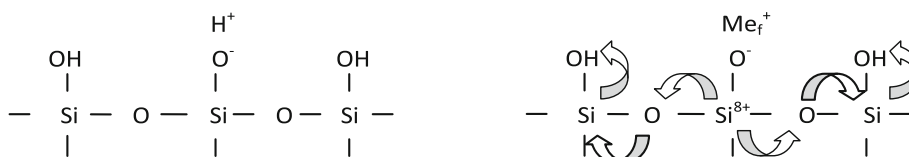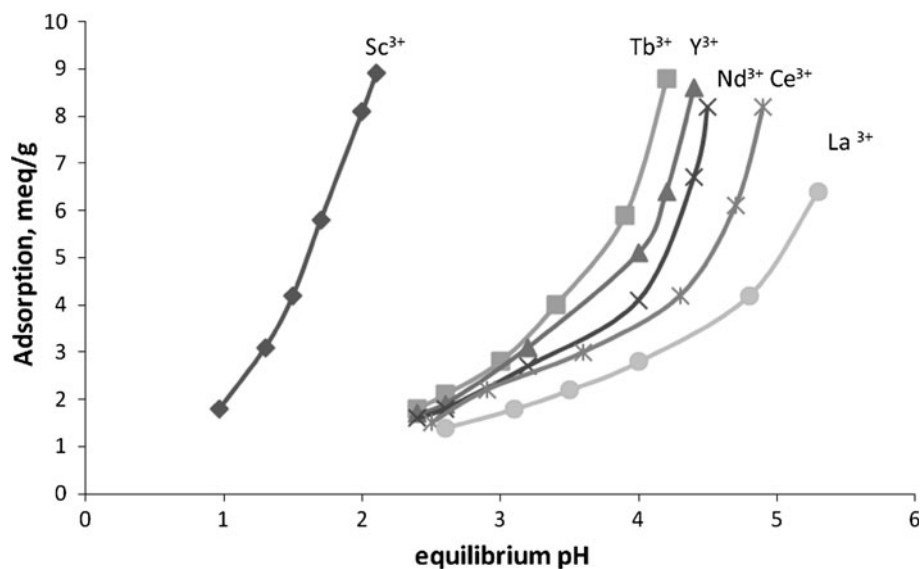
Fig. 5 Schematic description of the silica gel surface in H-form in acidic media before and after adsorption of "basic" cations with low electron-negativity (Li, Na, K, Rb, Cs, Ca, Sr, Ba). The *arrows* show the direction of the shift of electron density
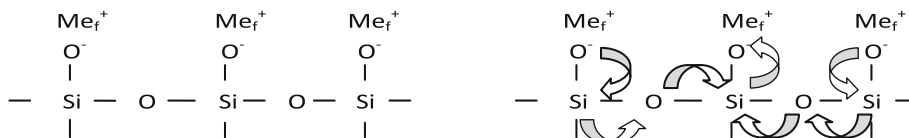
Fig. 6 Schematic description of the silica gel surface with basic exchangeable cations before and after adsorption of electron-acceptor cations like Be, Al, -d and f- elements. The *arrows* show the direction of the shift of electron density
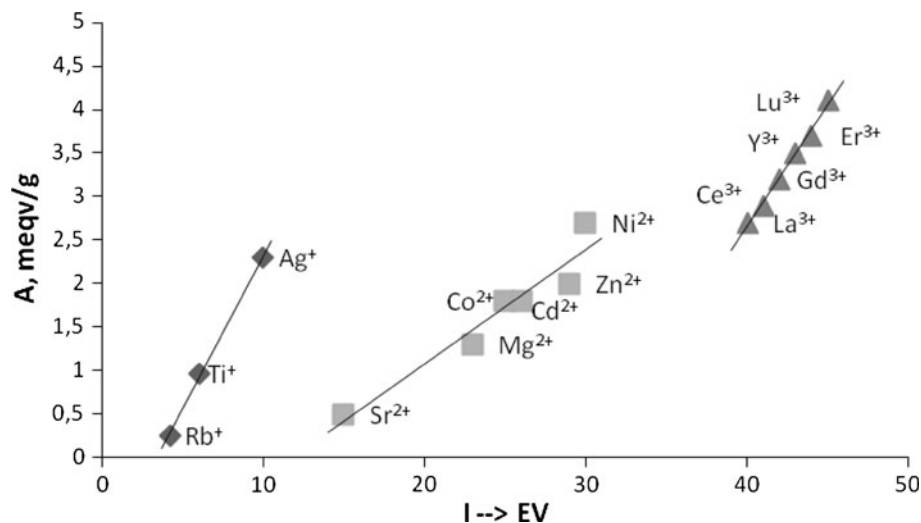
contact with acidic solution (pH 2–5) of salts studied. The surface has a small number of strongly acidic exchange groups in the neighborhood of non-dissociable silanole groups (Fig. 5). The presence of OH-groups with high electron-acceptor ability on the surface leads to the shift of an electron pair from the silicon toward oxygen which results in an appearance of effective positive charge on the Si atom in Si–O H (or Si–O Me^{n+}) groups (Fig. 5). This intensifies the $d\pi$–$p\pi$ interaction between Si and anionic O in these groups. Obviously, the degree of polarity of the O–Me^{n+} bond increases with a decrease of the electron-acceptor ability of the compensating cation characterized by the potential of ionization of the ion.

Distribution of the electron density on Si–O–Me^{n+} surface with basic exchangeable cations like Na^+ or Ca^{2+} is shown by Fig. 6. Practically all Si atoms are connected with anionic O having much higher electron density than oxygen in Si–OH groups. The chemical bond in Si–O–Me^{n+} groups has obviously mainly ionic character. At the same time the contribution of a covalent component to the energy of bond between Si–O^- and Me^{n+} ion should be also taken into account due to π interaction of the electron pair on O and vacant d-or f- orbital of the adsorbing Me^{n+} cation.

The "basicity" of adsorbing ions/their electron acceptor ability is known to be characterized by their potential of ionization. In line with the above considerations, there is a linear dependence between the adsorbed amount of cations of given oxidation state on Ca-silica gel surface and their total ionization potential, as it is clearly demonstrated by Fig. 7.

These considerations are valid also for Al-form of the silica gel which surface has electron-acceptor character.

6 Conclusions

For silica-gel with "basic" exchangeable cations (Na-, Ca-forms) and with ionic Si–O–Me^{n+} bond, adsorption of electron-acceptor ions, with high electro-negativity, i.e. high ionization potential like Be, Mg, d-and f-elements, the additional $p\pi$–$p\pi$ and $d\pi$–$p\pi$ or $f\pi$–$p\pi$ covalent interactions should be correspondingly taken into account. This explains the inversion of the adsorption sequence of ions of transition and lanthanide elements by these adsorbents, i.e. an increase of their adsorption with decreasing their crystallographic radius.

The polarity of O–Me^{n+} bond on the surface of H-or Al-forms of silica gel increases with decreasing the electron acceptor ability of the ion, i.e. with its ionization potential. This is reflected in higher adsorption of ions with low ionization potential, i.e. "basic" adsorbing ions, with low electro-negativity (Na, K, Rb, Cs, Ca, Sr, Ba).

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