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The effect of monovalent electrolytes on the deprotonation of MAI₁₂-Keggin-ions

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Abstract

We study the deprotonation of MAl_{12} -Keggin ions in monovalent electrolyte solutions of varying composition and concentration by potentiometric titration. The Keggin exhibit very steep deprotonation, where the singly coordinated aquo groups lose protons within a narrow pH-range. Once the deprotonation is substantial the Keggin ions start to aggregate by dehydration and linkage of terminal functional groups into hydroxo bridges. In the present study we address three aspects with our experiments. We test the cation-specificity, the anion-specificity and the overall effect of electrolyte concentration with respect to the deprotonation behavior. Our results show that the cation series in chloride systems does not show any ion-specificity and all the curves coincide for the 100 mM solutions whereas the anion series in sodium systems does. The most structure-making anion (bromate) used in this study causes aggregation of the Keggin prior to the onset of aggregation in the presence of borderline and structure-breaking anions (chloride, nitrate, perchlorate). For the latter, no significant difference is observed. The fluoride ion causes a completely different behavior. No significant deprotonation pH effect is observed where deprotonation occurs in the absence of fluoride. At even higher pH, massive consumption of hydroxide occurs. Some possible scenarios for the behavior of the fluoride-containing systems are discussed.

Keywords: Keggin ions, cations, anions, potentiometry, fluoride

1. Introduction

Experimental investigation and modelling of interactions of trace components with metal-oxide substrates is of relevance in various areas (Buerge-Weirich et al. 2002; Muller and Sigg 1990; Pavlova and Sigg 1988). In this respect the study of anion adsorption to such minerals and concomitant modeling has been pioneered by Laura Sigg (Sigg 1980, Stumm et al. 1980, Sigg and Stumm, 1981). Since then the ligand exchange model has been continuously developed further and finds its application in modern surface complexation models (Hiemstra et al. 2007). For such advanced models, it is invaluable to study well-defined surfaces and involve multiple experimental and theoretical approaches to constrain the stoichiometries of the surface complexes formed by ligand exchange (Hiemstra and Van Riemsdijk 2006). One possibility is to study model colloids like goethite (see previous references) or single crystals (Waychunas et al. 2005; Waychunas et al. 2006) in attempts to gain full understanding and combine the molecular-level processes and the thermodynamic modelling. On colloids, the coordination chemistry at the surface is poorly known, while on single crystals charging phenomena were reported to occur that have not been previously discussed for particles (Lutzenkirchen et al. 2010b). In particular the charging on the oxide single crystals was interpreted to occur in the water film adjacent to the surface and not at the surface hydroxyls. More conclusive results that support this idea have been reported for silver halides (Selmani et al. 2014). Another suggestion has been to use large molecules as models for well-defined surfaces (Casey et al. 2005; Casey and Swaddle 2003) because in these molecules the coordination chemistry and speciation can be known with confidence.

The ϵ -Keggin ions $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ (referred to as Al_{13}) and $[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ (referred to as GaAl_{12}) have been used in that sense. An initial explicit link between Al_{13} and surface chemistry was published by Wehrli et al. (1990). Subsequently Keggin-ions have been used to study in detail dissolution processes (Furrer et al. 1999; Amirbahman et al. 2000; Forde and Hynes 2002; Yamaguchi et al. 2004). Furthermore, the acid base behavior of the MAl_{12} Keggin-ions has been studied in some detail experimentally (Furrer et al. 1992; Lee et al. 2002) and by advanced calculations (Rustad 2005). A broad review on the role of the Keggin ions in the aqueous aluminium chemistry has also been published (Casey 2006). Al_{13} is metastable with respect to gibbsite, remains metastable in solution for very long times at its natural pH (pH 4.5, at this pH the Keggin-ion is expected to be fully protonated, see (Furrer et al. 1992; Lee et al. 2002)), but slowly converts to the Al_{30} oligomer over years (Furrer et al. 2002). Fully protonated, it bears seven positive charges. It has been found to adsorb to mineral surfaces (Lutzenkirchen et al. 2010a). Interestingly it has been observed during the transformation of boehmite to gibbsite (Hernandez 1998). It is supposed to be toxic to plants (Parker et al. 1989) but has been infrequently found in the environment (Furrer et al. 2002). NMR has been used to characterize this small ion to an amazing extent (Phillips et al. 2000). Thus it is precisely known which kind of surface group is being deprotonated as the pH is increased. This reaction resembles the acid-base behavior of oxide minerals, but the deprotonation curve is extremely steep as shown in Figure 1. The data in that figure are taken from the literature, for Al_{13} and Al_{30} (Casey et al. 2005), gibbsite with high charge (Rosenqvist et al. 2002) and low charge (Adekola et al. 2011). Clearly the surface-charge densities of the various entities are in a similar range. Interestingly, the slope of the charge for Al_{30} shows similarities to those of gibbsite with high charge around pH 5.5 to 6.5 and of Al_{13} at pH > 6.5.

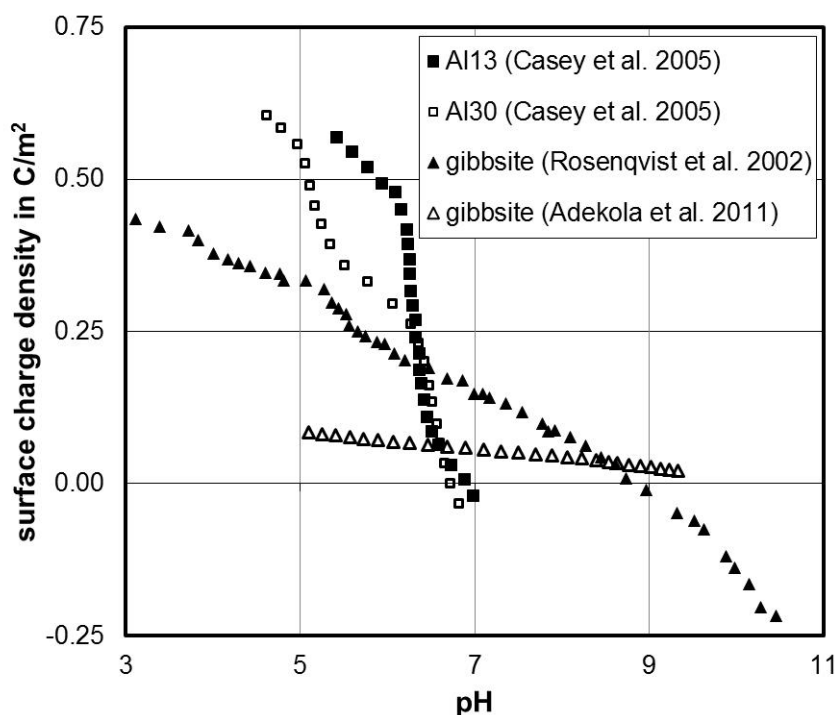


Fig. 1 Comparison of surface charge density as a function of pH between two gibbsite samples, Al₃₀ and Al₁₃. The squares are data for the Keggin ions (Casey et al. 2005), the triangles for gibbsite with high charge (Rosenqvist et al. 2002) and low charge (Adekola et al. 2011), see also Rustad (2005)

Previous work on the deprotonation of these Keggin ions has shown that, depending on their concentration, the ions start to aggregate at different charge conditions in a titration. At this point of aggregation, the deprotonation curves typically flatten as colloid formation inhibits further buffering of the pH. The lower the concentration of the Keggin ion, the higher the degree of deprotonation that can be achieved prior to the onset of aggregation. In the present work we have collected titration data in different ionic media of monovalent salts. This included study of cation effects, and we carried out a series of experiments in 100 mM chloride solutions. Recently, it has been shown that simple anions show specific effects on negatively charged sapphire single crystals (Lützenkirchen, 2013). Therefore, the occurrence of a cation effect on a positively charged substrate cannot be excluded. In a second series of experiments a number of anions were tested in sodium systems while the background electrolyte concentration was kept constant at 100 mM. Ion-specific effects are of broad interest and have also been observed for the behavior of polyoxometallates. Thus Pigga et al. (2010) observed very strong effects in the self-assembly of Keggin ions. The negatively charged {Mo₇₂Fe₃₀} ions formed larger self-assemblies in the presence of the larger (structure breaking) monovalent ions in chloride systems. No study on the effects of co-ions was reported. Furthermore, we extended the previous work on variation of ionic strength (Furrer et al. 1992) to lower salt concentrations.

A priori, it is not clear if and how electrolytes and electrolyte concentrations will affect the behavior of the Keggin ions. One intent of the present paper is to report macroscopic data on this issue.

Another set of experiments was performed with fluoride. In this case the interest is in the stability of the Keggin ions after substitution of terminal surface groups (aquo- or hydroxo) with fluoride. The interaction of fluoride with mineral surfaces had already been studied in the course of Laura Sigg's Ph.D. thesis (Sigg, 1980, Stumm et al. 1980, Sigg and Stumm 1981). Fluoride has often been considered as a ligand that allows the determination of the active surface sites. Unfortunately, complications will typically arise due to complex formation between fluoride and mineral constituents enhancing dissolution and potentially changing the surface. In this respect fluoride interaction with Al-bearing minerals has been extensively studied (Nordin et al. 1999). The interaction of fluoride with monomeric Al (Phillips et al. 1997), Al₁₃ (Allouche and Taulelle 2003) and GaAl₁₂ (Yu et al. 2003) has been studied in much detail and the latter can be fluorinated. There is agreement that the aquo groups

are first exchanged with aqueous fluoride. With time hydroxo bridges (μ -OH groups) become fluorinated, but no agreement exists as to whether the inter- vs. intra groups are concerned. Very recent theoretical work (Jin et al. 2014) was performed on this topic and Bino et al. (2002) reported the structure of a fluoride-bridged Fe(III) Keggin structure. In the present work we try to relate the knowledge about the aqueous Al-F chemistry to interpret titration data in the presence of fluoride.

2. Material and Methods

2.1 Experimental

Solutions were prepared from 18.2 MOhm resistance water. Care was taken to remove carbon dioxide, which may have entered the solution after preparation, before starting titrations by flushing Argon over the solutions for extended times. The Argon was sent through washing bottles of sulfuric acid, sodium hydroxide and a solution containing the background electrolyte solution used in the experiment to avoid evaporation. The argon was flushed over the solution during the titration as well.

The Keggin ions were prepared as previously described (Lutzenkirchen et al. 2010a). The stock-solution has a total gallium concentration of 2.8 mM, which is basically identical to the resulting concentration of the Keggin ion. This stock solution contains chloride ions from the Al and Ga salts used in the synthesis as well as sodium ions from the NaOH solution used in the synthesis. The quantities of these ions are small compared to the major ionic medium ionic strength investigated for 25 μM MAI_{12} (i.e. 100 mM) and amount to less than 1 mM. However, they do affect the ionic strength of the lower salt media studied here (1 mM and 10 mM added NaCl). The overall ionic strengths in those media arising from sodium and chloride ions are 2.6 and 11.6 mM, respectively. The MAI_{12} concentration in these systems is 44 μM and the resulting contributions from the synthesis are therefore higher than in the previous case.

All systems were first acidified with HCl and subsequently titrated with NaOH solution. While this procedure introduces foreign sodium and chloride ions into the system, the quantities are rather low compared to the 100 mM background electrolyte concentrations and because the concentration of the Keggin ion were kept at 25 μM to have an extended range of Z_B (as defined below). The ionic-strength dependence was studied in NaCl to avoid the presence of foreign ions in particular for the lowest ionic strength studied.

The pH electrode was calibrated daily against eight commercial buffer solutions. The voltage was recorded and transferred to pH and then to proton concentrations $[\text{H}^+]$ using the Davies equation (linear coefficient 0.2) was used to calculate activity coefficients for the proton. Additionally the initial titration of the acidic solution with standardized NaOH was used to calibrate the apparatus before each titration. Both procedures produced the same results. The calibration parameters of the measurement system did not change significantly over the experimental period (in terms of slope and EMF_0). The good reproducibility observed when comparing the data makes us confident in our results.

The amount of protons reacted per Keggin ion was calculated according to the following equation

$$Z_B = [(\text{TOTH}^+ - \text{TOTOH}^-) - ([\text{H}^+] - [\text{OH}^-])]/\text{TOTMAI}_{12}$$

Here, $\text{TOTH}^+ - \text{TOTOH}^-$ is the concentration calculated from the amount of standardized acid and base solution added to the system. $[\text{OH}^-]$ is calculated from the $[\text{H}^+]$ values using the pK_w for water at the respective ionic strength. Furthermore, in the above equation M is either Al or Ga. A value of $Z_B = 0$ is taken as the reference point and corresponds to the initial charge of the Keggin ion (7+), while at $Z_B = -7$ the charge of the Keggin-ion would vanish. The Keggin ion contains 12 aquo groups that can in principle be deprotonated. Thus $Z_B = -12$ would mean deprotonation of all aquo groups. The μ_2 -OH groups can in principle also be deprotonated but this reaction is expected to take place at higher pH (as further discussed later). Before this deprotonation may occur the Keggin ions will aggregate. By this process the Keggin ions lose their model compound character.

Titrations were carried out at room temperature. Between the experiments the temperature did not vary by more than 2 degrees. High-precision titration data require better temperature control. However, in many cases such control is not possible and most oxide titrations have been carried out under conditions similar to ours. It is beneficial to the experimental work that the system is buffering so strongly during the deprotonation of the Keggin ions.

The titrations were carried out using a Metrohm Dosimat for supplying known volumes of standardized NaOH solution (0.1 M) to the reaction vessel. The set-up was calibrated in-situ by titrating an acidic solution (HCl) of

the respective ionic medium of known volume with a standardized NaOH solution. At pH close to pH 4.5, which is the buffered pH achieved by dissolving millimolar concentrations of Keggin ions into these unbuffered solutions, a known amount of Keggin ion solution was added to the known volume of the respective electrolyte solution. The pH = 4.5 solution is reached when the Keggin ion is dissolved in water because of some terminal waters deprotonating. These were not accounted for in the calculations. Since the conditions were identical in all the titration runs, this procedure does not affect the comparison of the different. The solution was magnetically stirred at all the times and the stirring speed (about 600 rpm) was never changed during the series of experiments reported here. The pH of the resulting solution was about 4.5. After flushing purified argon over this solution for at least 2 hours, known volumes of standardized NaOH solution were added to the system. After two minutes the pH was recorded and another addition was made. In the flat initial region of the titration curve, the pH stabilized rapidly. On the steep part of the curve strong buffering was observed. The pH always decreased due to the release of protons from the Keggin ions. The decrease in pH slowed down with time. We did not attempt to achieve equilibrium but were interested in comparing different solutions. To assure comparability care was taken to carry out all the experiments following exactly the same protocol in terms of volume additions and waiting times. Once the buffering on the steep part of the titration curve in a given system stopped (i.e. the pH increased again significantly) some further additions were made and then the titration was stopped.

In the case where a sodium-fluoride-containing system was studied a fluoride-sensitive electrode was introduced. A separate blank titration for the same conditions (in terms of ionic strength, total Al and total F) has been carried. The electrode was calibrated against four solutions of known fluoride concentrations in the same medium as later used for the experiment. The ratio of fluoride to Keggin ion was much higher compared to the value used by Allouche and Taulelle (2003), i.e. $F/Al_{13} = 2/1$. We used a ratio of $F/Al_{13} = 25$, which means that there is enough fluoride to replace all aquo groups and either all inter- or intra hydroxide bridges. To replace all aquo and all hydroxyl groups would require a ratio of 36. However, it is known that the replacing the hydroxide bridges is a slow process (Yu et al., 2003) and we will discuss later that we expect the added fluoride replaces the aquo groups. The study of the fluoride-bearing system is delicate since it is not clear to what extent a fluorinated Keggin ion will persist under our conditions. Presumably, the ions will aggregate when enough fluoride anation has reduced the molecular charge and allowed colloid formation. However, during the addition of fluoride no visible aggregation occurred, which was always observable at the end of the titrations in the absence fluoride. Since for the fluoride-containing system no further studies were carried out involving e.g. NMR or other direct spectroscopies, our interpretation will accordingly be rather tentative but we hope that our results stimulate more research.

2.2 Calculations

Thermodynamic calculations were carried out using Phreeqc, version 2 (Parkhurst and Appelo 1999), ECOSAT (Keizer and van Riemsdijk 1994) and a modified version of FITEQL2 (Westall 1982).

The aim of the calculations was to evaluate the aqueous-phase behavior of the Al and Al/F systems and to test some hypotheses with respect to the reaction of the Keggin ions in the presence of fluoride with respect to their deprotonation. For the thermodynamic calculations stability constants were taken from the Minteq.v4 database provided with Phreeqc. The formation constant for Al_{13} was taken from Öhman et al. (2006) and is self-consistent with the hydrolysis constants for Al included in the Minteq.v4 data base. Relevant reactions are given in supplementary information. For the calculations on the deprotonation of Al_{13} we adopted the reaction scheme previously proposed (Furrer et al. 1992). Calculations were carried out to gain an idea in which direction the fluorination would drive the deprotonation of the Keggin ions. Recent theoretical work (Jin et al. 2014) on the substitution of various groups present on Al_{13} by fluoride reported Al-O distances for various cases. We used those results for the Al-OH₂ groups for the bare Al_{13} , for the substituted Al_{13} cases F_{inter} and F_{intra} , in which 6 distinct hydroxide bridges were replaced by fluoride. The distances within the MUSIC framework (Venema et al. 1998) yield pK values for the protonation of one Al-OH (i.e. the first one). The respective values were then used to calculate all pK values within the 6x2 model by applying the same differences in the pK values as given previously for the bare Al_{13} (Furrer et al. 1992).

3. Results and discussion

3.1 Effect of NaCl concentration

Figure 2A shows the results of potentiometric titrations obtained in the GaAl_{12} solutions for three different NaCl concentrations. The data show the expected steep deprotonation of Keggin around pH 6. The deprotonation reaches $Z_B = -6$ (i.e. loss of 6 protons from the Keggin ion) before the curve starts to level off. This departure from the steep curve is indicative of agglomeration of the Keggin ions. The agglomeration is irreversible and its onset depends on the total concentration of Keggin ion (Furrer et al. 1992).

Several points are worth noting. First the shift of the deprotonation reactions to higher pH with increasing NaCl concentration agrees with the trend reported previously for Al_{13} for a variation from 0.1 M to 1 M KNO_3 media (Furrer et al. 1992).

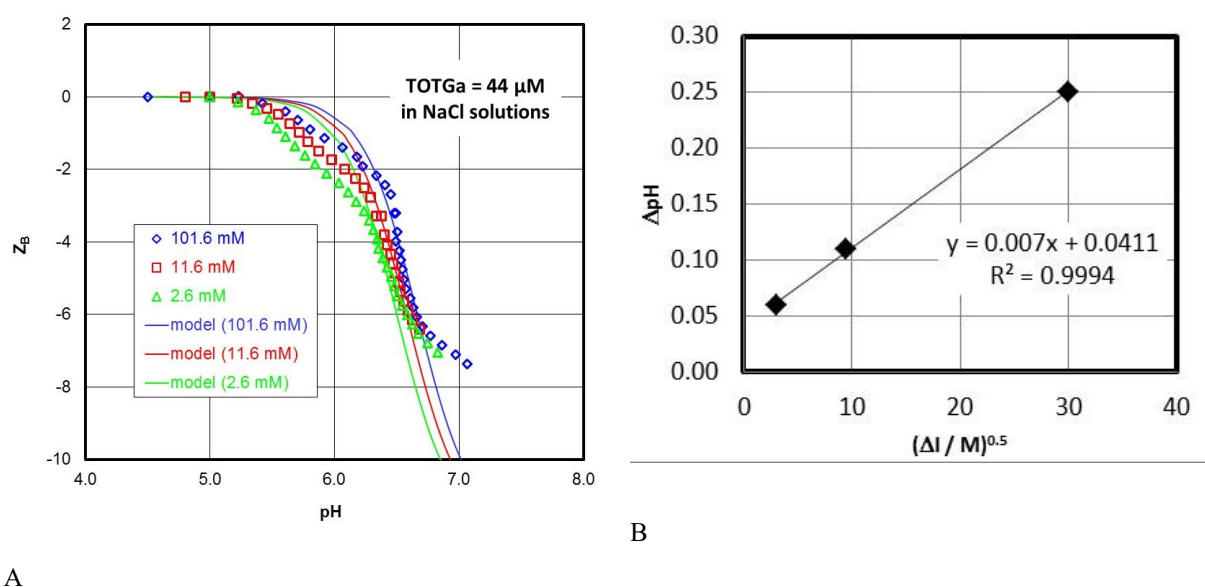


Fig. 2 (A) Effect of variation of the sodium chloride concentration on the titration curve of GaAl_{12} . The lines are model calculations that describe the Z_B values between approximately -3 and -6. (B) pH - shift of the Z_B curves as a function of the square root of the change in ionic strength.

Second, we did not find any significant effect of the salt medium concentration on the aggregation process that can be tentatively associated to a departure from the steep deprotonation, which frequently occurs at $Z_B = -6$ (Furrer et al. 1992). If this was comparable to the related process in colloidal systems, higher salt concentrations should lead to aggregation at higher Z_B values, corresponding to lower degrees of de-protonation or higher absolute charge. Our data do not concur with this expectation.

Figure 2A also includes model calculations based on the 2×6 model of Furrer et al. (1992). The model lines describe the Z_B values between -3 and -6 very well. The data for Z_B between 0 and -3 will be discussed in more detail elsewhere (Lützenkirchen et al., in preparation). From the model lines in Figure A we estimated the shift of the curves with decreasing ionic strength and plot them as a function of the square root of the difference in ionic strength on Figure 2B. The point to the right is from the paper of Furrer et al. (1992) and fits exactly on a linear extrapolation of our two points. Since there are only three points, the trend is to be taken with caution. We did not attempt to include any model including ionic-strength correction to the de-protonation equations. Application of the Davies equation to an ion with a charge of +7 would induce huge changes that do not appear to be real based on the available results.

3.2 Effect of the nature of monovalent cations in chloride systems

In Figure 3 we present the results of the titrations in chloride systems with different monovalent cations at constant Keggin ion concentration and overall salt concentration of 100 mM. Our results do not display any significant difference between the various cations. In particular no difference in the onset of the agglomeration can be found. The data are highly reproducible and indicate as one would expect that changing the identity of the co-ion would not affect the deprotonation. For related Al-bearing systems, including sapphire-c single crystals (Lützenkirchen 2013) in chloride series and particulate aluminum oxide at low salt concentrations (Johnson et al. 1999) in nitrate salts no cation-effects on zeta-potentials have been observed. At high salt concentrations (1 M) on particulate aluminium oxide in nitrate salts (Johnson et al. 1999), and on sapphire-r single crystals (Lützenkirchen 2013) cation effects in the chloride salts did occur and were of the same sequence, i.e. the structure-making ions showed weaker interaction. The hexagonal rings of ideal oxygen terminated sapphire-c are retrieved on the Keggin ions, which might explain the observed similarities in the behavior of the two latter. In general anion effects are rather expected on positively charged surfaces (e.g. Sprycha, 1984) such as the Keggin ions (c.f. next section). In general, cationic counterions have a considerable effect on the stability and reactivity of polyoxometalate ions, but these are usually anionic. Here, for polyoxocations, one expects a large effect from counteranions, not cations, which is consistent with our observations.

Unlike for the sapphire-c systems (Lützenkirchen, 2013) we do not observe any effect of the co-ions. The difference between sapphire-c and the Keggin-ions might be in the differences of the intrinsic charges of both. While for sapphire-c the measurable negative electrokinetic charge mainly arises from physical hydroxide adsorption to the water film of a flat surface with low or zero charge at the plane of the surface hydroxyls (Lützenkirchen et al. 2014), the Keggin-ions have high intrinsic surface charge densities (see Figure 1). Thus on sapphire-c the unexpected co-ion effect would arise from competition between anions while the absence of the co-ion effect on the Keggin-ions is due to the intrinsic charge.

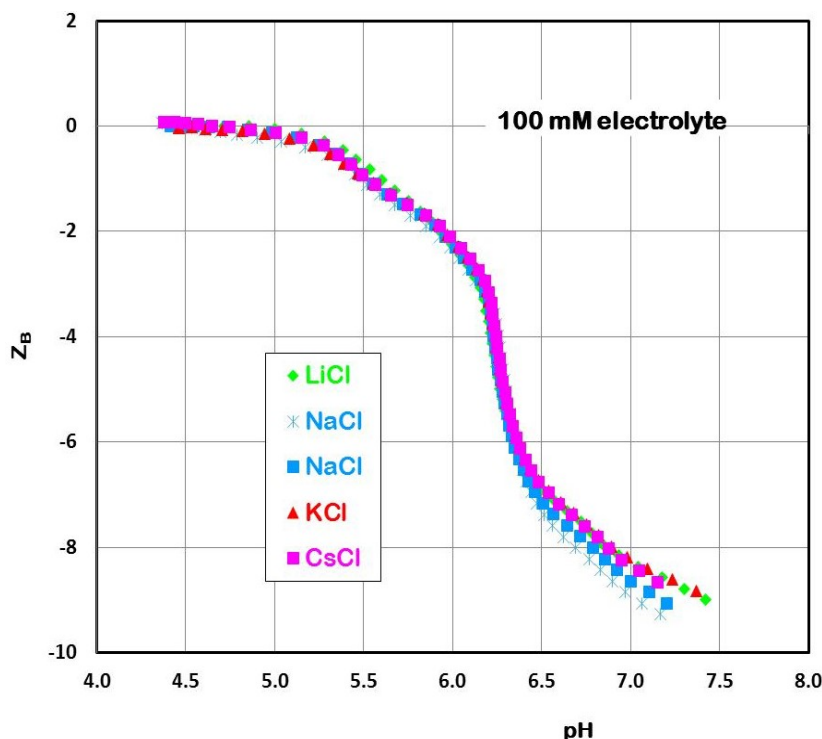


Fig. 3 Titration results for 25 μM GaAl_{12} solution in different chloride systems at 100 mM

3.3 Effects of the nature of monovalent anions in sodium systems

In Figure 4 we present the results obtained with various monovalent sodium salts. Chloride, nitrate and perchlorate are typical anions used in “innocent” or “inert” background electrolytes. Bromate is a more unusual ion, known though to behave as a structure maker in colloidal-stability investigations (Dumont and Watillon 1971).

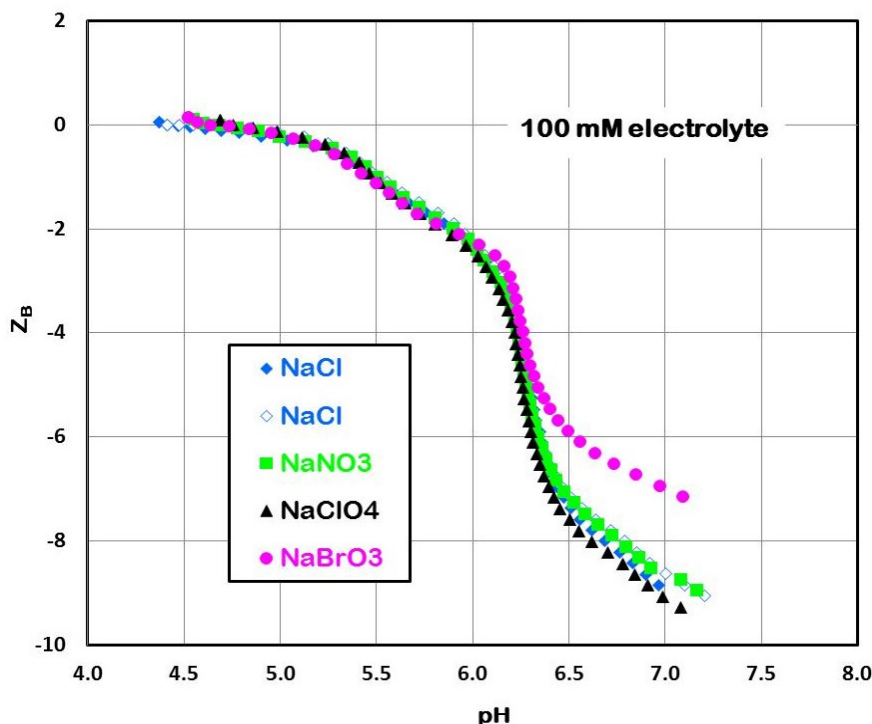


Fig. 4 Titration results for 25 μM GaAl_{12} solution in different sodium systems at 100 mM

As for the variation of the cations, no significant effect is observed in the solutions of common background electrolytes (Figure 4). Sodium solutions of chloride, nitrate and perchlorate yield nearly identical results. The data for the strongly structure-breaking perchlorate might be shifted a bit below the nitrate and chloride data, which do not differ from each other. This trend would be in line with the observation that the structure-making bromate ion causes different de-protonation behavior. Clearly the onset of agglomeration is slightly below $Z_B = -5$. Independent evidence for strong interaction of iodate and bromate with aluminium oxides (Franks et al. 1999), corroborates our results and supports the idea that these ions are interacting with aluminium minerals beyond pure physical shielding of charge. Such interaction of fluoride with aluminium bearing systems is known (Yu et al., 2003). From the extensive research conducted on polyoxometalate systems (Hill, 1998), counter-ions are important if they coordinate to the oxygen-ring system in the molecule (for GaAl_{12} the diameter of such a ring is about 5.25 Å) and thereby neutralize molecular charge. In some cases, the counter-ions form cationic bridges between anionic polyoxometalate ions, making for macromolecular structures in solution or dropping the molecules out of solution as insoluble solids, either crystalline or amorphous. Nominally inert counter-ions have a similar profound effect on the kinetics of isomerization (Johnson et al. 2013), electron exchanges (Czap et al. 2006) and ligand exchanges.

Related to the study of Pigga et al. (2010) we find that the structure making anions have a more profound effect on the aggregation of the GaAl_{12} ions. In their study the structure breaking cations had caused stronger self-assembly of their negatively charged Keplarate ions.

3.4 The influence of fluoride

Fluoride is known to act as a strong complexing agent that can enhance aluminium mineral dissolution as mentioned in the introduction. Aqueous solution speciation involves various Al-F complexes with up to six

fluoride ions per aluminium ion. In this case all first-shell water molecules are then replaced by fluoride and the sign of charge of the ion is reversed because of the stepwise anation. The interaction of fluoride ions with the Al-bearing Keggin ions is complex and involves kinetics as discussed in the literature cited above. To obtain a first hint on the effect of fluoride on the deprotonation of the fluorinated Keggin ions we have carried out a tentative experiment. We believe that the results discussed below will merit further investigations. On Figure 5 we compare the titrations curves for 25 μM Keggin ion solutions in a bare NaCl system and in a system containing about 0.6 mM F^- . The titration curve distinctly differs in the presence of fluoride.

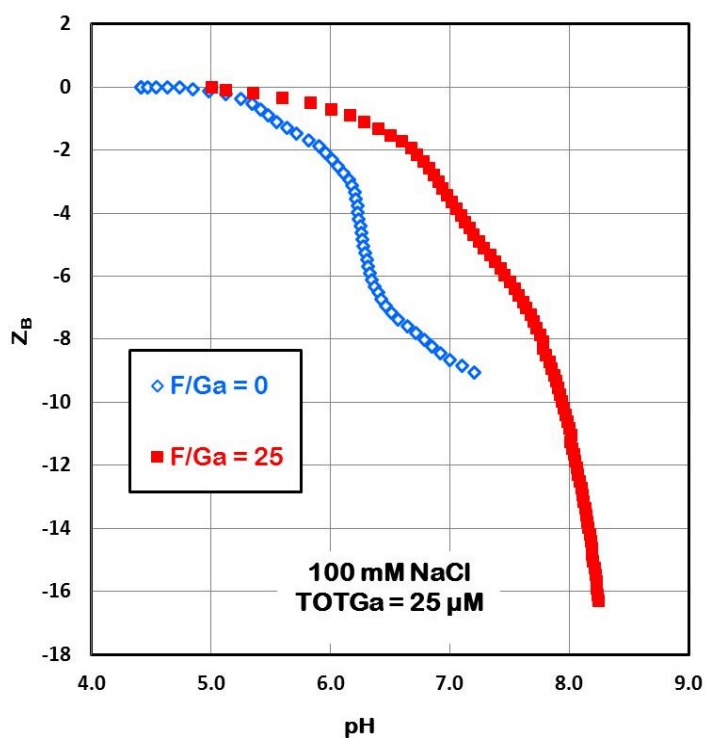


Fig. 5 Titration of 25 μM GaAl_{12} solution in 100 mM NaCl in the absence of NaF (open triangles) and in the presence of 0.63 mM NaF

The complexity of the aqueous Al-F chemistry requires the discussion of various possible scenarios that might be relevant to the observations in the absence of further spectroscopic investigations:

1. The Keggin ion is destroyed by the excess of fluoride due to the formation of dissolved Al-F complexes. This scenario was experimentally elucidated by a blank titration.
2. The hydroxo bridges of the Keggin ion are replaced by fluoride. This scenario was evaluated by MUSIC type calculations. They were in turn based on recent theoretical work on Al_{13} (Jin et al. 2014). We focus on the two extreme cases, i.e. the substitution of $\mu_2\text{OH}$ inter- and intra-trimers of Al constituting the Keggin ion by F^- (F_{inter} and F_{intra}), shown in Table 1 in the respective publication (Jin et al. 2014). Fluoride replacement of $\mu_2\text{-OH}$ has been spectroscopically confirmed by ^{19}F -NMR, but the concentrations were much lower than we employ here (Yu et al. 2003).
3. The aquo groups of the Keggin ion are replaced. In this case the stability of the fluorinated Keggin ion is the relevant issue. Replacement of these terminal groups would be very fast on our experimental times scale. The rates of exchange of bound waters from the fully protonated forms of these structures fall into the millisecond time scale and these will accelerate as cationic charge is removed from the molecule by fluoride uptake. In contrast, the rates of isotopic exchange into $\mu_2\text{-OH}$ are hours to weeks (Casey 2006).

The three scenarios are discussed in some detail in the subsequent sections.

3.4.1 Addition of fluoride leads to destruction of the Keggin ions

In Figure 6, a blank titration involving the same amounts of Al and F as in the respective titration curves where the Keggin ions are initially present is shown. In the absence of the synthesized Keggin ion, the titration results in a very different curve. Strong buffering occurs at much lower pH in the blank experiment. Therefore, this scenario is unlikely to explain the observed titration curve of the Keggin ions in the presence of fluoride, even though the blank titration was carried out in the absence of gallium. These results also show that the Keggin ion remains stable in the presence of F^- for $pH < 7$ during the time of the experiments.

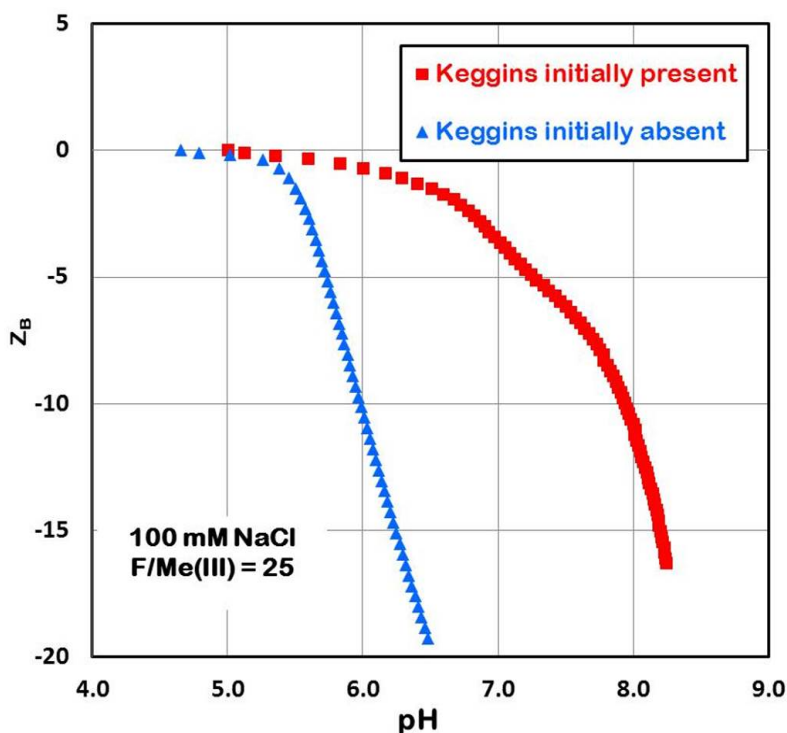


Fig. 6 Titration of 0.32 mM Me^{3+} (TOTGa + TOTAL) in 100 mM NaCl for solutions in which Keggin ions are initially present (squares) or absent (triangles)

3.4.2 Addition of fluoride leads to replacement of hydroxo-bridges in the Keggin ion

The replacement of hydroxo-bridges by fluoride is detectable at lower fluoride-to-ion concentrations via ^{19}F -NMR, so it is likely to occur at our much higher concentrations of ligand. Also likely is that the acceleration of substitution rates at the charge on the molecule is reduced by progressive replacement of the bound waters with fluoride ion, which should proceed at millisecond timescales or faster. Certainly, substitution of the hydroxo-bridges could proceed on the time scale of our experiments (i.e. three hours). No data are available for our conditions that would allow a definitive statement. However application of a MUSIC-type model (based on recent theoretical work (Jin et al. 2014) using the procedure given in detail elsewhere (Venema et al. 1998) as explained in section 2.2) results in predictions of the deprotonation curves shown in Figure 7. The relevant Al-O distance for the unsubstituted Keggin ion is 1.979 \AA based on the calculations by Jin et al., which results in a log K value for the first deprotonation couple of -14.96 (at infinite dilution). The distance based on structure data (1.9145 \AA) would give a value for the first deprotonation couple of -12.25 (at infinite dilution), which is much larger than the estimate from the theory-paper, but remarkably close to the value reported by Furrer et al. (i.e. -12.48 in 0.1 M KNO_3). The estimates in this paper at the lowest ionic strength (2.6 mM) is -12.18 .

The replacement of the hydroxo-bridges by fluoride shortens the Al-O distances for the aquo groups according to the theoretical calculations (Jin et al. 2014). This causes stronger deprotonation of the aquo groups compared to the unsubstituted Keggin ion. However, the contrary is observed experimentally (i.e. the titration curve with

Keggin-ions in the presence of fluoride is shifted to higher pH compared to that of Keggin-ions in the absence of fluoride, Figure 5), suggesting that the substitution of the hydroxo-bridges plays a minor role in the present conditions, very likely because the aquo groups are substituted, as discussed below. Following the theoretical estimates for the distances on the unsubstituted Keggin-ion, its deprotonation occurs at much higher pH than experimentally observed. We therefore take the theoretical results as self-consistent input parameters to the calculations in Figure 7 that allow no more than comparison between the cases.

It appears that the intra-6-bridges have a more profound effect on the Al-O-distances of the aquo-groups than the inter-6-bridges (according to Table 1 in Jin et al.). This finds its repercussion in the MUSIC calculations in Figure 7.

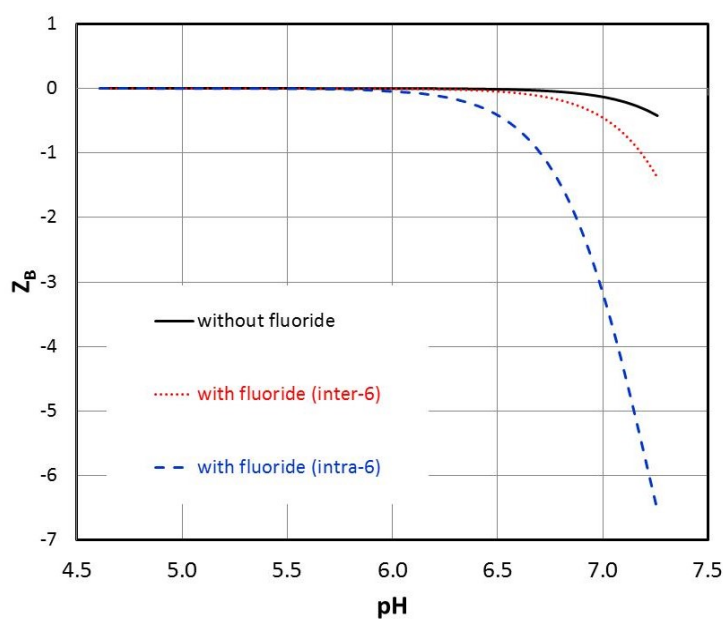


Fig. 7 Calculated deprotonation of fluorinated Al_{13} for two distinct cases (dotted and dashed lines) as compared to the pure Al_{13} (full line) based on a MUSIC type approach (Venema et al. 1998). The inter-6 and intra-6 models correspond to the cases where 6 hydroxo-bridges (fast or slow) are replaced by fluoride. Input data to the MUSIC approach (bond distances) for these two cases have been recently published (Jin et al. 2014)

3.4.3 Addition of fluoride leads to substitution of aquo groups

Several points would appear to support this scenario. First it is known that the substitution of the aquo groups is fast (Allouche and Taulelle 2003; Yu et al. 2003) resulting in a compound that is stable for some time (Yu et al. 2003). The aquo groups are those that cause the deprotonation of the unsubstituted Keggin ion. Consequently once they are substituted they cannot deprotonate. The substitution (if complete) would cause the loss of positive charge and the Keggin ions would bear a negative charge of up to -5. Since the anation of the molecule causes a reduction of charge, the progressive replacement of bound waters might accelerate the aggregation since the electrostatic repulsion between molecules is reduced.

Based on the above it would be possible to understand, why the Keggin ions are not deprotonated in the usual pH-range (i.e. below pH 6.5). However, we also need to understand what causes the strong decrease in Z_B at the higher pH. One possibility could be that the species is not stable at the high pH. Another possibility is that the fluoride is replaced by hydroxide ions.

Aqueous speciation calculations (Figure 8) suggest that, at equilibrium, Al_{13} is dissolved by F^- at low pH. However, the substitution of aquo- and hydroxo-groups by F^- cannot be considered yet in the calculations and might contribute to the (meta-)stability of the Keggin ion (see section 3.4.1). Above about pH 7 the most stable species is the aluminate ion. Therefore, according to the calculation, the Keggin ultimately become unstable. Fluoride complexes in that pH-range are of no importance according to the speciation calculations. Thus the additional hydrolysis of aluminium ($\text{OH}/\text{Al} = 2.46$ in Al_{13} and $\text{OH}/\text{Al} = 4$ in the $\text{Al}(\text{OH})_4^-$) could explain the additional consumption of protons (it would amount to 1.54 times 13 in terms of Z_B , sufficient to explain the data). In turn, the enhanced Al hydrolysis would lead to a release of F^- . Since nothing is known on the stability of fluorinated Keggin in this pH-range, some uncertainty remains.

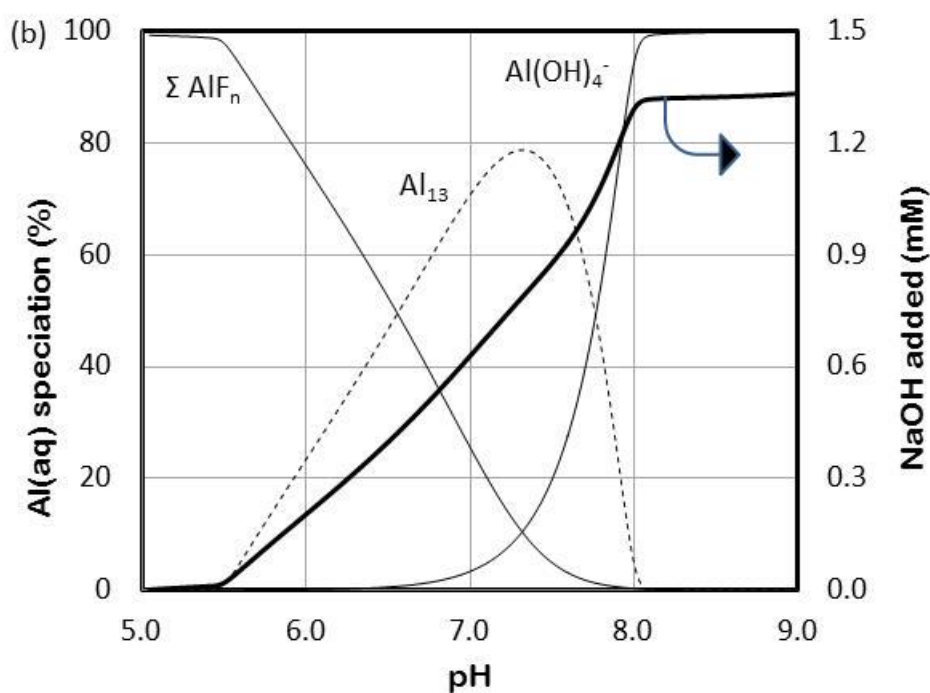
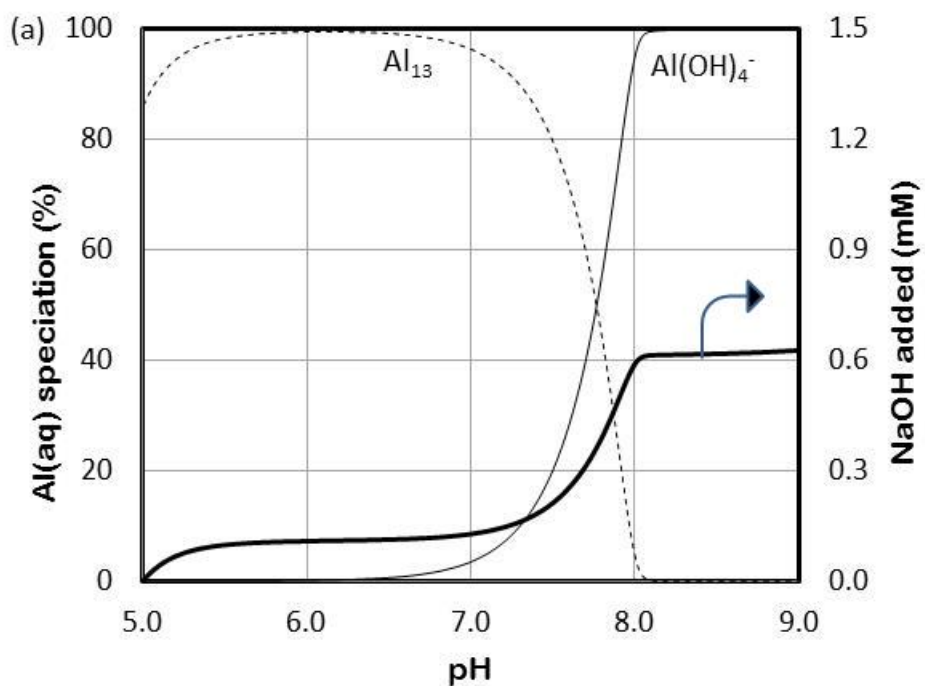


Fig. 8 Predicted distribution of Al and F (left y-axis) and sodium hydroxide consumption (right y-axis) as a function of pH for the conditions of the experimental data shown in Figure 6 Top (a): Without F. Al_{13} prevails and is a highly hydrolyzed Al-state ($\sim Al(OH)_{2.46}$). No consumption of OH^- is needed below $pH < 7$ so the pH increases rapidly with NaOH addition. Above $pH = 7$, $Al(OH)_4^-$ is formed, which consumes OH^- . Bottom (b): With $[F^-] = 0.63$ mM. The non-hydrolyzed Al-fluoro complexes prevail at low pH. Al_{13} is formed when the pH increases, followed by $Al(OH)_4^-$, which consumes more OH^- . This explains the different titration curves with or without F. No precipitation is considered. Calculations are based on the speciation scheme by Öhman et al. (2006).

Measurements involving a fluoride-sensitive electrode support the release of fluoride in solutions of adequately high pH values (>7). Besides the co-incidence of the steep decrease in Z_B with aqueous speciation, there is also coincidence with other processes as shown in Figure 9. The uptake of fluoride by gibbsite was calculated by a recent comprehensive model for gibbsite systems (Karamalidis and Dzombak 2011).

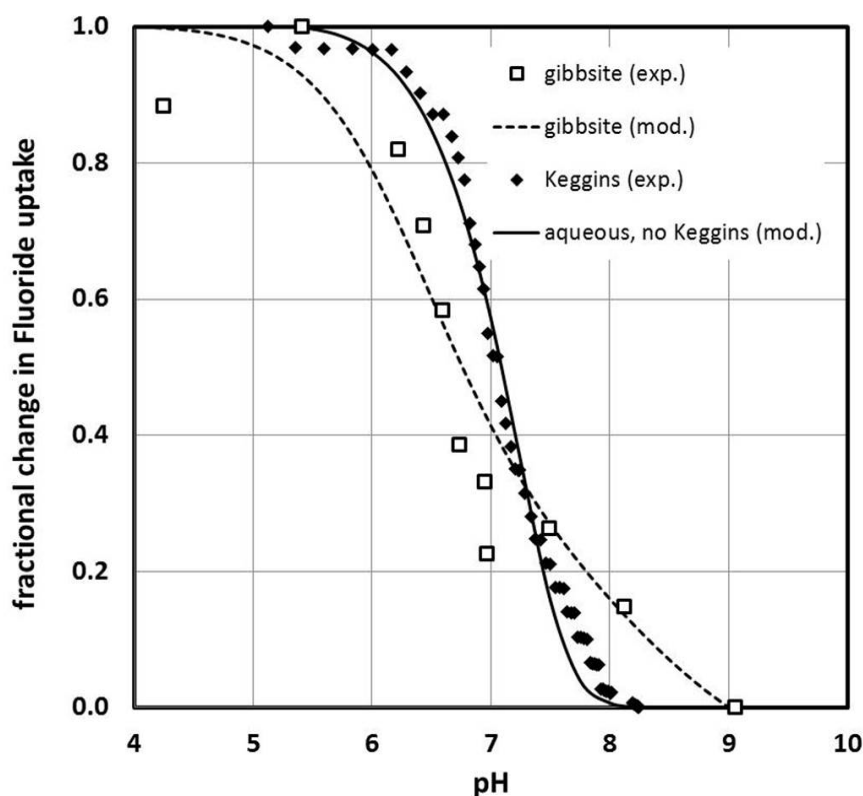


Fig. 9 Fractional change in F-uptake in aqueous complexes (full line) on gibbsite (modelled and experimental) and in the Keggin ion system (measured by an ISE electrode)

Overall, this is all supporting the idea that the fluoride is released from the Keggin ions. Replacing the fluoride by hydroxide would allow a maximum change of Z_B by 12, while the experimental value is higher in absolute values. Destruction and subsequent formation of aluminate ions in turn can explain the data.

4. Conclusions

We have studied the deprotonation of MAI_{12} -Keggin under previously unexplored conditions. The observations can be summarized as follows:

- (i) Variation of the ionic strength from 2.6 to approximately 100 mM NaCl background electrolyte caused a shift of the deprotonation curve to higher pH with increasing NaCl concentration. This agrees with previous measurements (Furrer et al. 1992)
- (ii) Cation-specific effects do not occur in the simple monovalent electrolyte systems, as is expected. Because the MAI₁₂-Keggins are polyoxocations, such results are to be expected based on simple shielding and lack of interactions beyond charge screening. .
- (iii) Anion specific effects appear to indicate that structure breaking anions primarily serve as charge screeners, while the structure making anion bromate promotes early aggregation in agreement with previous reports for particulate alumina systems.
- (iv) The fluoride-containing system shows distinctly different behavior. We find fluoridation changes the acid-base chemistry of the molecule such that no deprotonation of the Keggin ion occurs. We investigate possible interpretations concerning fluoridation of aquo and/or bridging hydroxo groups, that can be expected from previous spectroscopic studies by Yu et al. (2003). The absence of deprotonation and the observed release of fluoride is best explained by fluoridation of the aquo-groups which is known to be fast. The release of fluoride at higher pH coincides with release of fluoride from gibbsite.

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