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# Behavior and kinetic of hydrolysis of amine boranes in acid media employed in chemical vapor generation.

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**Abstract**

The behavior of $NaBH_4$ (THB) and the amine boranes, $NH_3BH_3$ (AB), *tert*butyl$NH_2BH_3$ (TBAB), $Me_2NHBH_3$ (DMAB) was investigated in continuous flow chemical vapor generation of $H_2Se$ from aqueous $Se^{IV}$ coupled with atomic absorption spectrometry. Unexpected higher efficiency of $H_2Se$ generation was obtained with amine boranes compared to THB (TBAB > AB >THB) using millimolar concentration of reductant (0.001-0.1 mol $L^{-1}$) under strongly acidic conditions (HCl, $HClO_4$, $H_2SO_4$, $HNO_3$, 0.5-5 mol $L^{-1}$ $H^+$). Analytical applicability of the CVG system was tested by the determination of $Se^{IV}$ in natural water samples certified reference materials, using 0.01 mol $L^{-1}$ TBAB in 0.5 M $H_2SO_4$. In order to explain this unexpected higher efficiency of amine boranes with respect of THB, the kinetic of hydrolysis of AB, TBAB and DMAB was investigated in acid media typically employed in chemical vapor generation for trace element determination. The kinetic was investigated by monitoring the rate the hydrogen gas evolved during hydrolysis, using a laboratory made thermostated reaction cell. Kinetics were measured for AB, TBAB and DMAB in 0.1, 0.5, 5 mol $L^{-1}$ HCl or $HClO_4$ reaction media and in 0.1 mol $L^{-1}$ cysteine + 0.1 mol $L^{-1}$ HCl or $HClO_4$ buffer, for reaction times from 0 to 30 min. Under strongly acidic conditions, the rates of hydrogen evolution produced by amine boranes hydrolysis appear to be much slower than those predicted by a pseudo-first order reaction and using the rate constants reported in the literature. This suggests that, at elevated acidities (5 mol $L^{-1}$ HCl or $HClO_4$) the hydrolysis of amine boranes takes place in two steps, generating a first amount of $H_2$ (0.67-1.15 moles) much faster than the remaining about two moles. This evidence indicates a different mechanism of hydrolysis to the one accepted in the literature for amine boranes. The relatively high efficiencies of $H_2Se$ observed with amine borane reduction of inorganic $Se^{IV}$ at elevated acidities can be addressed to the action of borane intermediates, most probably amine borane cations, formed during amine borane hydrolysis in the same reaction conditions.

## 1.Introduction

Chemical vapor generation (CVG) of volatile derivatives, hydrides and /or free atoms, of the heavier elements of the Group 14 (Ge, Sn, Pb), Group 15 (As, Sb, Bi), Group 16 (Se, Te) and of the elements of Group 12 (Zn, Cd, Hg), is one of the most powerful sample introduction techniques for ultra-trace element determination in atomic and mass spectrometry [1,2]. Aqueous phase derivatization with tetrahydridoborate (-1) (THB) salts, $MBH_4$ (M=Na, K), have been employed as the reagents in almost all cases and their use have been expanded to the CVG of some transition and noble metals [2]. In spite of the relatively fast hydrolysis of THB in aqueous solution, which requires alkaline stabilization and cold storage, only few papers are devoted to the use alternative borane reagents in CVG that are more stable to hydrolysis as amine borane complexes, [3,4,5,6,7,8].

Due to their different rate of hydrolysis, which are about from 5 to 8 orders of magnitude lower than that of THB [9], amine-boranes found some useful applications in mechanistic study on CVG [3,5,6], whereas there are few reports on analytical applications of amine boranes to trace element determination by CVG atomic spectrometry [4,7,8]. From investigation on the most reactive substrates, $Hg^{II}$ and $Sb^{III}$ in 1 mol $L^{-1}$ HCl reaction media [4], it resulted evident a linear correlation between the reaction efficiency of volatile products and the logarithm of second order rate constant of hydrolysis of boranes.

However, the use of kinetic data for the hydrolysis of boranes in aqueous media must be considered with some cautions because they are obtained under a limited range of acidities and solution composition, which are often very different from the condition employed in analytical CVG. In the case of THB strong deviations from kinetics and mechanism of hydrolysis are reported both in strongly alkaline and acidic media [9, 10] and this can be addressed to the stepwise mechanism of hydrolysis of THB. In the hydrolysis of THB, the four moles of hydrogen are generated stepwise and with different rates while, simultaneously, $[BH_4]^-$ is converted to $H_3BO_3$ through hydridoboron

intermediates of the type $[L_xBH_{4-x}]^z$ (L=$H_2O$, $OH^-$ etc, x=1-3 and z = 0, +1, −1 is the charge) according to the sequence of reactions:

$$[BH_4]^- \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} [BH_3(H_2)] \xrightarrow[-H_2]{k_1} [LBH_3]^z \xrightarrow[-H_2]{k_2} [L_2BH_2]^z \xrightarrow[-H_2]{k_3} [L_3BH]^z \xrightarrow[-H_2]{k_4} H_3BO_3 \qquad (1)$$

where $k_1$, $k_2$, $k_3$ and $k_4$ are the rate constants for each of the steps of hydrolysis. The stability of the hydridoboron intermediates toward hydrolysis increases with decreasing number of hydrogen atoms bound to boron, $k_1 > k_2 > k_3 > k_4$ [5]. In agreement with the kinetic laws reported for the different hydridoboron species involved in the hydrolysis of THB [10,11], only two species, $[BH_4]^-$ and, to a much lesser extent $BH_3(H_2O)$, have a rate of hydrolysis dependent on acidity. The lower rate of hydrolysis of THB strongly acidic conditions can be addressed to formation of borane cations, e.g. $[(H_2O)_2BH_2]^+$, which are resistant to acid hydrolysis [5,9,11].

For the Brønsted acid catalysed hydrolysis of amine boranes:

$$R_3NBH_3 + HA + 3H_2O \rightarrow H_3BO_3 + R_3NH^+ + A^- + 3H_2 \qquad (2)$$

the accepted mechanism for hydrolysis is the displacement of the ligand following the protic attack [12,13,14] as shown in Scheme 1.

$$R_3NBH_3 + HA \xrightarrow{slow} \left[ R_3N \begin{matrix} \diagup HA \\ \diagdown BH_3 \end{matrix} \right]^{\ddagger} \longrightarrow R_3NH^+ + A^- + BH_3(H_2O) \xrightarrow[H_2O]{fast} H_3BO_3 + H_2$$

Scheme 1 – Brønsted acid-catalysed hydrolysis of amine-boranes. [14].

Some recent evidences suggested that in strongly acidic aqueous solutions (5-10 mol $L^{-1}$ $HClO_4$ or HCl) borane ammonia may undergo hydrolysis according a different reaction pathway from that

reported in Scheme 1. In particular, the most interesting evidence is that in strongly acidic conditions a first mole of hydrogen is generated with a higher rate with respect to the other two [5]. This suggested the hypothesis that one mole of hydrogen was released before the displacement of the ligand forming a borane cation [5]:

$$H_3NBH_3 + H_3O^+ \rightarrow [H_3NBH_2(H_2O)]^+ + H_2 \qquad (3)$$

It does not appear that further studies on the kinetic of acid catalyzed hydrolysis of amine-borane have been reported in the literature after those of Kelly and coworkers [12,14] and Ryschkewitsch [13], published more than 38 year ago. These studies brought to the definition of the mechanism of Brønsted acid-catalysed hydrolysis of amines boranes (Scheme 1) which is still accepted and considered valid in the current literature [15].

This work starts with the observation that in the CVG of $H_2Se$ from $Se^{IV}$ by aqueous THB and amine boranes the generation efficiencies of $H_2Se$ obtained with amine boranes under analytical reaction conditions ( $0.5 < [H^+] < 5$ mol L-1, $10^{-3} <$ [Borane] $< 0.1$ mol $L^{-1}$) were greater than that obtained by THB (TBAB > AB > THB). In order to clarify these anomalous behavior of $Se^{IV}$ with respect to those observed for $Hg^{II}$ and $Sb^{III}$ (THB > AB > TBAB) [4], the kinetic of acid-catalyzed hydrolysis of amine boranes was investigated for a better insight into the mechanism of hydrolysis these borane complexes.

The results reported in the present paper, while pointing the potentialities of amine boranes in analytical CVG of selenium, represent useful support for the comprehension of the mechanisms operating in CVG and highlights the limitations of the kinetics and mechanisms of the acid-catalyzed hydrolysis of amine boranes reported in the literature.

# 2. Experimental

## 2.1. Reagents

Borane ammonia (AB), borane *tert*-butylamine (TBAB) and borane dimethylamine (DMAB) complexes (assay 97%,) and $NaBH_4$ (THB) (assay 98%,) were from Sigma-Aldrich. NaOH (Pellets, 98%,) was from Fluka Chemika, Sigma-Aldrich. Stock solution of 1000 mg $L^{-1}$ of selenite ($H_2SeO_3$ in $HNO_3$, AS standard solution) was from Fluka. Analytical grade inorganic acid, 37% HCl, 65% $HClO_4$ and 96% $H_2SO_4$ (RPE-for analysis) was from Carlo Erba. Stock solutions of 10 % $NaBH_4$ were prepared in 1 mol $L^{-1}$ NaOH and stored at 4 °C. $NaBH_4$ solutions were prepared daily by appropriate dilution of the stock solution. In all the working solutions of amine-boranes and $NaBH_4$ the final concentration of NaOH concentration was 0.05 M.

Certified reference materials of natural waters were obtained by NRC Canada (SLRS-6, River water) and NIST (USA) (1640a, Trace elements in natural water).

## 2.2. Apparatus and measurements

### 2.2.1. CVG of hydrogen selenide

The efficiency of generation of hydrogen selenide was tested using a continuous flow reaction system coupled with miniature hydrogen diffusion flame atomizer and atomic absorption spectrometric detection (CVG-AAS). Details of the apparatus are reported elsewhere [5]. Sample and reductant solution flow rates are 4 and 2 mL $min^{-1}$, respectively. Two different the reaction loop volumes, 500 µL (Teflon PFA, 0.8 mm i.d.) and 3.9 mL (Teflon PFA, 1.5 mm i.d.), were employed. The absorbance, $S_0$, obtained by reduction of 0.2 mg $L^{-1}$ $Se^{IV}$ in 5 mol $L^{-1}$ HCl with 0.2 mol $L^{-1}$

THB was taken as reference signal in consideration that $^{75}Se$ radiotracer studies indicated an almost quantitative conversion (>95%) of selenite to hydrogen selenide [16]. The absorbance ratio $S/S_0$ was taken as a measure of the generation efficiency of hydrogen selenide.

Determination of selenium in natural waters was performed by a more sensitive laboratory assembled CVG atomic fluorescence detector (CVG-AFS). The continuous flow hydride generator reactor, using a 500 μL sample volume, coupled with the miniature hydrogen diffusion flame atomizer were the same as those described above for CVG-AAS. The only difference was that but the AAS detection was replaced by AFS detection. More details on AFS detector are reported elsewhere [17].

### 2.2.2. Rate of hydrogen gas evolution

The rate of hydrogen gas generated by the hydrolysis of borane complexes was measured by monitoring the pressure, P, in the headspace of reaction cell used for hydrolysis. Measurements were performed by using a modified version of the laboratory made thermostated cell (25°C) described previously [5] . The modified cell (see Figure 1) was realized in borosilicate glass (17.5 mL total volume) and was equipped with and injection port and pressure sensor (DS Europe, model LP625-1, 3.5 bar full scale). The measurements were performed by placing 2.0 mL of aqueous solution at different acidities and composition (0.1, 0.5, 5.0 mol $L^{-1}$ HCl or $HClO_4$, 0.1 mol $L^{-1}$ acid + 0.1 mol $L^{-1}$ L-cysteine) in the cell. A 1 mL plastic syringe was loaded with 0.5 mL of water followed by 0.5 mL of amine borane solution (0.2 mol $L^{-1}$ for both AB and TBAB, and 1 mol $L^{-1}$ for DMAB, all prepared in 0.05 mol $L^{-1}$ NaOH). This particular loading sequence allows complete and reproducible injections, avoiding that an uncontrolled amount of solution containing the borane remained in the injection port. Then the syringe was placed into the injection port, which comprised a manual on-off valve (Hamilton, small body) to avoid pressure losses. The solution was left under magnetic stirring for 5 min., the pressure signal acquisition was then started and, after baseline

stabilization, the amine borane solution was injected under constant stirring, and the valve was immediately turned in the off position. The pressure signal was acquired for 1800 s at 10 $s^{-1}$ . The maximum, steady pressure level $P_{\infty}$, was reached in 5 mol $L^{-1}$ acid solution at reaction times of about 100, 180 and 500 s for AB, TBAB and DMAB, respectively. The pressure was corrected for a blank that is due to pressure increase caused by the contraction of the headspace volume following the 1 mL injection. The blank was measured by placing 2 mL of $H_2O$ in the reaction cell and injecting 1 mL of $H_2O$.

## 2.3. Kinetic calculations

Amine boranes undergo acid hydrolysis according a second order kinetic:

$$-\frac{d[XBH_3]}{dt} = k_{H^+}[XBH_3][H_3O^+] \qquad (4)$$

(X = $NH_3$, *tert*butyl$NH_2$, $Me_2NH$,)

At constant acidity the pseudo first order approximation gives the kinetic of hydrolysis of amine borane, $C_t = C_0 e^{-k_{H^+}[H^+]t}$, where $C_t$ and $C_0$ are the borane concentrations at time $t$ and $t$=0, respectively.

Expected rates of hydrogen evolution were calculated only in those case in which the acidity of the solution can be considered almost constant during the early stage of hydrolysis, namely with 5 mol $L^{-1}$ acid and with cysteine buffer. In this cases, the pseudo first order approximation applies to equation 4. The relation between the kinetic of hydrogen evolution and the kinetic of amine borane hydrolysis is given by $x(t)= 1 - y(t)$, where $x(t)$ is the fraction amount of hydrogen evolved, and $y(t) = C_t/C_0$ is the fraction amount of amine borane hydrolyzed at time t. It follows that $x(t) = 1 - e^{-k_{H^+}[H^+]t}$ where $k_H^+$ is the second order rate constant of hydrolysis. The values of $k_H^+$ employed, 6 L $mol^{-1}$ $s^{-1}$ for AB[14], 0.87 L $mol^{-1}$ $s^{-1}$ for TBAB [12] and $9.7\times10^{-3}$ L $mol^{-1}$ $s^{-1}$ for DMAB [12], are the only reported in the available literature. Assuming an ideal gas behavior for

hydrogen $x(t) = P/P_\infty$, where P is the pressure measured at time t and $P_\infty$ is the maximum pressure measured after complete hydrolysis of amine boranes (reaction 3), we obtained:

$$\frac{P}{P_\infty} = 1 - e^{-k_{H^+}[H^+]t} \qquad (5)$$

which allows the comparison between experimental and calculated rate of hydrogen generated during the hydrolysis of the investigated amine boranes.

Concentration of $H^+$ was considered equal to the stoichiometric concentration of the acid. The initial acid concentration after the reagent mixing (2 mL acid + 1mL borane solution, section 2.2.1.) is 3.33 mol $L^{-1}$ for experiments with 5 mol $L^{-1}$ acid. For cysteine buffer, considering that the reported value of $pK_{a3}$ span from about 1.7 to 2.4 at 25°C [18], the concentration of $H^+$ were calculated at two different values of $pK_{a3}$, 1.9 and 2.0.

## 3. Results and discussion

### 3.1. CVG of hydrogen selenide

The evidences reported in a previous paper on the CVG of both inorganic $Hg^{II}$ and $Sb^{III}$ in 1 mol $L^{-1}$ HCl media [4] indicate that the reaction efficiencies linearly correlates with the logarithm of the second order rate constant of boranes (THB = $1.0\times10^6$ L $mol^{-1}$ $s^{-1}$ [19], AB = 6 L $mol^{-1}$ $s^{-1}$ [14], TBAB = 0.87 L $mol^{-1}$ $s^{-1}$ [12]). In other terms, the reaction efficiency of Hg° and $SbH_3$ generation follow the trend THB > AB> TBAB.

In the case presented in this paper, namely generation of $H_2Se$ from $Se^{IV}$, the reduction curves (relative absorbance signal, $S/S_0$, *vs* borane concentration at a given acid concentration) obtained with different acids ( $[H^+]$= 5 mol $L^{-1}$) and using THB, AB and TBAB as the reductants, are reported in Figure 2. DMAB was not reported because it gave poor or no signals (maximum $S/S_0$ values observed at around 0.1 mol $L^{-1}$ DMAB, $S/S_0$=12, 5, <1, and <1 % in $HClO_4$, $H_2SO_4$, $HNO_3$

and HCl, respectively). The reduction curves of Figure 2 were found interesting both for the reactivity of aqueous boranes and from the analytical point of view. Whereas DMAB gave the expected much lower sensitivity than THB, the other amine boranes AB and TBAB exhibited an unexpected behavior compared to that observed for Hg° and $SbH_3$ generation. In the lower concentration range of borane reagent (<0.005 mol $L^{-1}$ borane for HCl media, < 0.05 mol $L^{-1}$ borane for both $HClO_4$ and $H_2SO_4$ media) the correlation between reaction efficiency of $H_2Se$ and the hydrolysis rate constant of borane follows an opposite trend (TBAB > AB > THB) compared to the one observed for Hg° and $SbH_3$ generation. Although concentrated nitric acid is not the appropriated reaction media for CVG of selenium using THB, the reaction efficiencies maintain the same trend and amine boranes, in particular TBAB seems to work better than THB. The different trends of the reduction curves for HCl reaction medium with respect to $HClO_4$ and $H_2SO_4$ could be the due to chloride, which can form complexes that modify the structure of both analytical substrate and borane [10]. On the contrary sulfate, nitrate and, in particular, perchlorate anions, which can be considered as non-complexing anions, do not show such a behavior. It is interesting to note that chloride exhibits the well-known catalytic effect with THB [20,21], whereas it depletes the generation efficiency for AB > 0.01 mol $L^{-1}$ and TBAB > 0.005 mol $L^{-1}$. This effect, not easy to explain, manifests itself as an interference ~~which~~ that occurs at concentrations above a given threshold (0.01 mol $L^{-1}$ and 0.005 mol $L^{-1}$ for AB and TBAB, respectively). A reasonable hypothesis is that the hydrolysis of amine boranes in HCl media forms chloride-modified borane intermediates, which are efficient in the generation of $H_2Se$ at concentration lower than the threshold. On the other hand, at higher concentrations, the formation of non-volatile complex species between $H_2Se$ and the chloride-modified borane intermediates might hinder the release of the volatile hydride.

The generation efficiency of hydrogen selenide was further investigated under reaction conditions that are much closer to analytical CVG for $Se^{IV}$determination, namely 1 mol $L^{-1}$ acid and 500 µL reaction loop. The results are reported in Figures 3a and 3b for borane concentration of 0.01 and

0.05 mol $L^{-1}$, confirm the evidence obtained at 5 mol $l^{-1}$ $H^+$ (Figure 2): at the low millimolar level of reductant, both TBAB and AB are much more efficient than THB in generating $H_2Se$. Hydrochloric acid confirms to be not suitable for CVG of $H_2Se$. On the contrary, the generation efficiency in nitric acid media improved dramatically with 0.05 mol $L^{-1}$ reductant, where the generation efficiency obtained by TBAB is about 4.5 times higher than that obtained by THB reduction.

From the analytical point of view, for determination of $Se^{IV}$ the most appropriate acids are $HClO_4$ $H_2SO_4$ and interesting reaction curves are obtained at 0.5 mol $L^{-1}$ acid concentration using 500 µL reaction loop (Figure 4). Also, under these reaction conditions the reaction efficiencies follow the same trend observed above, TBAB >AB >THB, with the maximum efficiency of about 75% in the range of 0.01-0.02 mol $L^{-1}$ TBAB.

The behavior of TBAB under mild acidity appears also to be interesting for analytical application. Quantification of $Se^{IV}$ in natural waters was performed by using CVG-AFS (sample volume and reaction loop both 500 µL) using 0.5 mol $L^{-1}$ $H_2SO_4$ and 0.01 mol $L^{-1}$ TBAB. The determination of selenium in NIST 1640a (Trace Element in Natural Water) was performed by the analyte addition technique, and gave a value opf 19.57 ± 0.24 ng $mL^{-1}$ ($n$ = 3), which is in good agreement with the certified value of 20.13 ± 0.17 ng $mL^{-1}$. In SLRS-6, (River Water Certified Reference Material for Trace Metals and other Constituents) the level of selenium was below the detection limit of CVG-AFS apparatus (0.1 ng $mL^{-1}$). The slope of the calibration curve obtained by spiking SLRS-6 river water with $Se^{IV}$ (0.5 – 2 ng $mL^{-1}$) was (93.7 ± 2.8) % of the slope of the calibration curve obtained from $Se^{IV}$ in aqueous solution of 0.5 mol $L^{-1}$ $H_2SO_4$.

The anomalous behavior of $Se^{IV}$ in CVG, apart from its possible analytical applications, open news question on the mechanism of CVG because it cannot be explained in the light of the current knowledge on the mechanisms of CVG by aqueous borane complexes. In order to clarify this point a series of dedicated experiments were performed on the kinetic of hydrolysis of amine boranes under reaction conditions that are typically employed in CVG.

## 3.2. Rate of hydrogen generation by hydrolysis of amine boranes

The behavior of aqueous boranes in acid media was investigated by monitoring the rate of evolution of the hydrogen gas that is formed during the borane hydrolysis. The study was performed on AB, TBAB and DMAB that were hydrolyzed in the acid media typically employed in CVG. The choice of HCl and $HClO_4$ as acid media allows to verify the complexing effects of chloride on the hydrolysis rate of boranes, whereas the non-complexing feature of perchlorate ion does not introduce any perturbation. The results are reported in Figure 5 for AB, TBAB and DMAB. The expected rates of hydrogen evolution calculated by equation 5 and by using the hydrolysis rate constants reported in the literature are shown in Figure 6.

Dramatic differences among the experimental and the calculated rates of hydrogen evolution are well evident by comparison of Figure 5 and Figure 6. In the case of AB it is evident the anomalous rate of hydrogen evolution from 0.1 mol $L^{-1}$ $H^+$ medium, which is comparable or faster than the rate observed in 0.5 and 5 mol $L^{-1}$ $H^+$ media. With 5 mol $L^{-1}$ acid, the concentration of $H^+$ remains almost constant during reaction (from about 3.33 to 3.16 mol $L^{-1}$), but it can be observed that hydrogen evolution takes place in two steps. In the first step a significant fraction of hydrogen, from about $P/P_\infty = 0.22$ to about $P/P_\infty = 0.38$, is quickly generated, while the remaining fraction is released much slower. Considering that the maximum relative pressure of hydrogen, $P/P_\infty = 1$, corresponds to the release of three moles of hydrogen, at $P/P_\infty \cong 0.33$ we have the release of the first mole of hydrogen. The fact that the change of the slope reported for 5 mol $L^{-1}$ reaction media takes place at $0.22 < P/P_\infty < 0.38$ is an evidence that about one mole of hydrogen (0.67 – 1.15 moles) is fast released at the beginning of the hydrolysis, similarly to the process described by reaction 3. The formed solvated borane cation $[(R_2NH)(H_2O)BH_2]^+$ (R=H or Alkyl) could undergo hydrolysis at a slower rate, as these type of compounds are more resistant to hydrolysis than their amine borane precursors [22]. At high acidities, similarly to the hydrolysis of THB [5,9,11] in

strongly acidic conditions, the decreased rate of hydrolysis for amine boranes can be addressed to the formation of amine borane cations. The kinetic of hydrogen generation is also affected by the type of hydrolyzing acid. As it is shown in Figure 5, significant differences can be observed for the kinetics of hydrogen evolution between HCl and $HClO_4$ media at the same concentration. This support the hypothesis of formation of chloride modified borane intermediates which can also play a role in the reactivity of $Se^{IV}$ in CVG, as it has been discussed in section 3.1.

With 5 mol $L^{-1}$ acid and 0.1 mol $L^{-1}$ cysteine buffer, the pseudo first order approximation is applied to the expected rate of hydrogen evolution (see section 2.3.), in consideration that $H^+$ concentration remains constant for most of reaction time.

The experimental rates of hydrogen evolution with cysteine buffer are reported in Figure 7 for AB, TBAB and DMAB. The expected rate of hydrogen evolution are in good agreement with the experimental results for TBAB and DMAB. For AB the observed discrepancies could be addressed to the formation of thiolate complexes of the borane substrate with cysteine, which undergo slower hydrolysis than AB. However, both experimental rates reported in Figure 7 for AB are almost perfectly fitted by assuming a $pK_{a3}$=2.4. In general, the results obtained with cysteine buffer confirm that at higher pH values the kinetic data reported in the literature for amine boranes are able to explain the experimental data, within the relatively high uncertainty of $pK_{a3}$ values reported in the literature [18]. This also confirm the validity of the approach to investigate the kinetic of hydrolysis of amine boranes by measuring the rate of hydrogen evolution.

At extremely high concentration of $H^+$ (Figure 8) the dramatic discrepancies among expected and experimental rate of hydrogen evolution indicated that the mechanism of hydrolysis of amine boranes takes place at least in two steps and is different from the mechanism followed under moderate acidic conditions as depicted in Scheme 1.

## 3.3. Considerations on the mechanism of hydrolysis of amine boranes and the formation of hydrogen selenide

The experimental evidences reported in section 3.2 at 5 mol $L^{-1}$ acid concentration support a mechanism of hydrolysis of amine boranes that started with the release of a first mole of hydrogen (reaction 3). Considering that the hydrolysis rate constants for the investigated amine boranes span over three orders of magnitude, the above conclusions have a more general validity than previously observed for AB only [5] (reaction 3). Moreover it is interesting to underline that this stepwise mechanism for amine boranes starts in a similar way of hydrolysis of THB:

$$R_2NHBH_3 + H_3O^+ \rightarrow [(H_2O)R_2NHBH_2]^+ + H_2 \quad (R = \text{alkyl, H}) \qquad (6)$$

$$BH_4^- + H_3O^+ \rightarrow (H_2O)BH_3 + H_2 \qquad (7)$$

As discussed in section 3.2., the agreement of the kinetic of hydrolysis of ammonia boranes (cysteine buffer, pH=2) with the kinetic data reported in the literature, indicates that under moderate acidic conditions the dissociative mechanism (Scheme 1) takes place. In the intermediate range of acidities, obtained in 0.1 and 0.5 mol $L^{-1}$ acid-concentrations, the kinetics of hydrolysis are much slower than those predicted by the literature data (compare Figures 5 and 6), but no evidence of the mechanism described by reaction 3 is apparent from the kinetic of hydrogen evolution (Figure 5).

A reasonable conclusion is that in the hydrolysis of amine boranes the "dissociative" mechanism proposed by Kelly et al. [12,14] and Ryschkewitsch [13] (Scheme 1) and the stepwise "THB" like mechanism proposed here, can coexist in relatively wide range of acidity and the passage from one to the other occurs gradually when the acidity is increased.

About the efficient formation of hydrogen selenide with amine boranes at elevated acidities, the above conclusion implies that $H_2Se$ is formed by reaction of the $Se^{IV}$ substrates with intermediates boranes, the amine borane cations and or their derivatives. These intermediates, are formed during

the hydrolysis of amine boranes, according to a mechanism in which the amine ligand remains bound to boron.

On the contrary, the hydrolysis products which are formed by amine boranes according the dissociative mechanism (Scheme 1) are the same obtained by THB hydrolysis, $(H_2O)BH_3$ $(H_2O)BH_2OH$, $[(H_2O)_2BH_2]^+$, $(H_2O)BH(OH)_2$ etc [9,10,11], and they cannot account for the improved efficiency of the amine boranes with respect to THB.

## 4. Conclusions

In CVG of $H_2Se$, at elevated acidities (0.5-5 mol $L^{-1}$ $H^+$), the higher reaction yields obtained with AB and TBAB in comparison to THB in the millimolar range (TBAB > AB > THB), diverges from the trends already observed for $Hg^0$ and $SbH_3$ generation (THB > AB >TBAB ). This anomalous behavior, while can be usefully employed for analytical applications of CVG to determination of trace selenium in natural waters, has even more interesting implications on the reactivity of amine boranes.

The mechanism of acid-catalyzed hydrolysis of amine boranes depends on the acidity. At moderate acidities it takes place according to kinetics and mechanism proposed in the literature by Kelly *et al.* [12, 14] and Ryschkewitsch [13] (Scheme 1). At elevated acidities amine boranes hydrolyze, similarly to THB [9,10,11], according to a stepwise mechanism where the first step is the generation of hydrogen and the formation an amine borane cation (reaction 3). Similarly to THB, increased of acidity of the hydrolysis medium promotes the formation of intermediate amine borane cations, which are more resistant to hydrolysis [22]. The mechanisms taking place at moderate and elevated acidities can coexist in relatively wide range of acidity and the passage from one to the other occurs gradually when the acidity is increased.

The anomalous behavior observed in CVG of $H_2Se$ can be, in part, explained by the different mechanism of hydrolysis of amine boranes at elevated acidities leading to formation of borane

intermediates, amine borane cations and their derivatives, which possess a different reactivity compared to those borane intermediates formed by THB hydrolysis in the same reaction conditions.

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## Figure Captions

Figure 1 – Thermostated cell employed for pressure measurements for the kinetics of hydrogen evolution

Figure 2 – Reduction curves of $Se^{IV}$ (0.2 mg $L^{-1}$) to $H_2Se$ by aqueous $NaBH_4$ (THB), borane ammonia (AB) and borane *tert*-butylamine (TBAB) using different inorganic acids. (a) HCl = 5 mol $L^{-1}$; (b) $H_2SO_4$ 2.5 mol $L^{-1}$; (c) $HNO_3$ 5 mol $L^{-1}$ and (d) $HClO_4$ 5 mol $L^{-1}$. Continuous flow reaction system coupled with AAS. Reaction loop 3.9 mL. Borane concentration varied in the range from $10^{-5}$ to 0.2 mol $L^{-1}$..

Figure 3 – Effect of different acids on the generation efficiency of $H_2Se$ using a continuous flow reaction system coupled with AAS. (a) Borane concentration 0.01 mol $L^{-1}$; (b) Borane concentration 0.05 1 mol $L^{-1}$. Other conditions: $Se^{IV}$ 0.2 mg $L^{-1}$, acid concentration 1 mol $L^{-1}$, reaction loop 500 μL.

Figure 4 – Reduction curves of $Se^{IV}$ (0.2 mg $L^{-1}$) to $H_2Se$ by aqueous $NaBH_4$ (THB), borane ammonia (AB) and borane *tert*-butylamine (TBAB) using using a continuous flow reaction system coupled with AAS: (a) 0.5 mol $L^{-1}$ $HClO_4$; (b) 0.5 mol $L^{-1}$ $H_2SO_4$. Borane concentration varied in the range from $10^{-3}$ to 0.2 mol $L^{-1}$. Reaction loop 500 μL.

Figure 5 – Relative pressure increase monitored during acid hydrolysis of AB, TBAB and DMAB at +25 °C in HCl and $HClO_4$ media in various acid conditions. For AB and TBAB the [Acid]/[Borane] molar ratios are 2, 10, 100 for acid concentration of 0.1, 0.5 and 5.0 M, respectively. For DMAB the [Acid]/[Borane] molar ratios are 0.4, 2, 20 for acid concentration of 0.1, 0.5 and 5.0 mol $L^{-1}$, respectively

Figure 6 – Rates of hydrogen evolution calculated from equation 5 and rate constants reported in the literature for: (a) AB; (b) TBAB and (c) DMAB. T = +25 °C. The initial $H^+$ concentrations used in the computation are 3.33, 0.33, 0.066 and 0.01 mol $L^{-1}$ for experiments using sample acidity of 5, 0.5, 0.1 and 0.01 mol $L^{-1}$ acid concentration (2 : 3 dilution factor).

Figure 7 – Relative pressure increase due to hydrogen evolution arising from acid hydrolysis in 0.1 mol $L^{-1}$ HCl+0.1 mol $L^{-1}$ Cys, and 0.1 mol $L^{-1}$ $HCO_4$ + 0.1 mol $L^{-1}$ Cys of (a) AB; (b) TBAB and (c) DMAB. T = +25 °C Comparison of experimental data with the relative pressure calculated by equation 5 at pH=1.9 and 2.0 Cys buffer.

Figure 8 – Relative pressure increase due to hydrogen evolution arising from acid hydrolysis in in 5 mol $L^{-1}$ HCl and 5 mol $L^{-1}$ $HClO_4$ of : (a) AB; (b) TBAB and (c) DMAB. T = +25 °C. Comparison of experimental data with the pressure expected according the kinetic law of hydrolysis at the calculated initial and final acidities

FIGURE 1

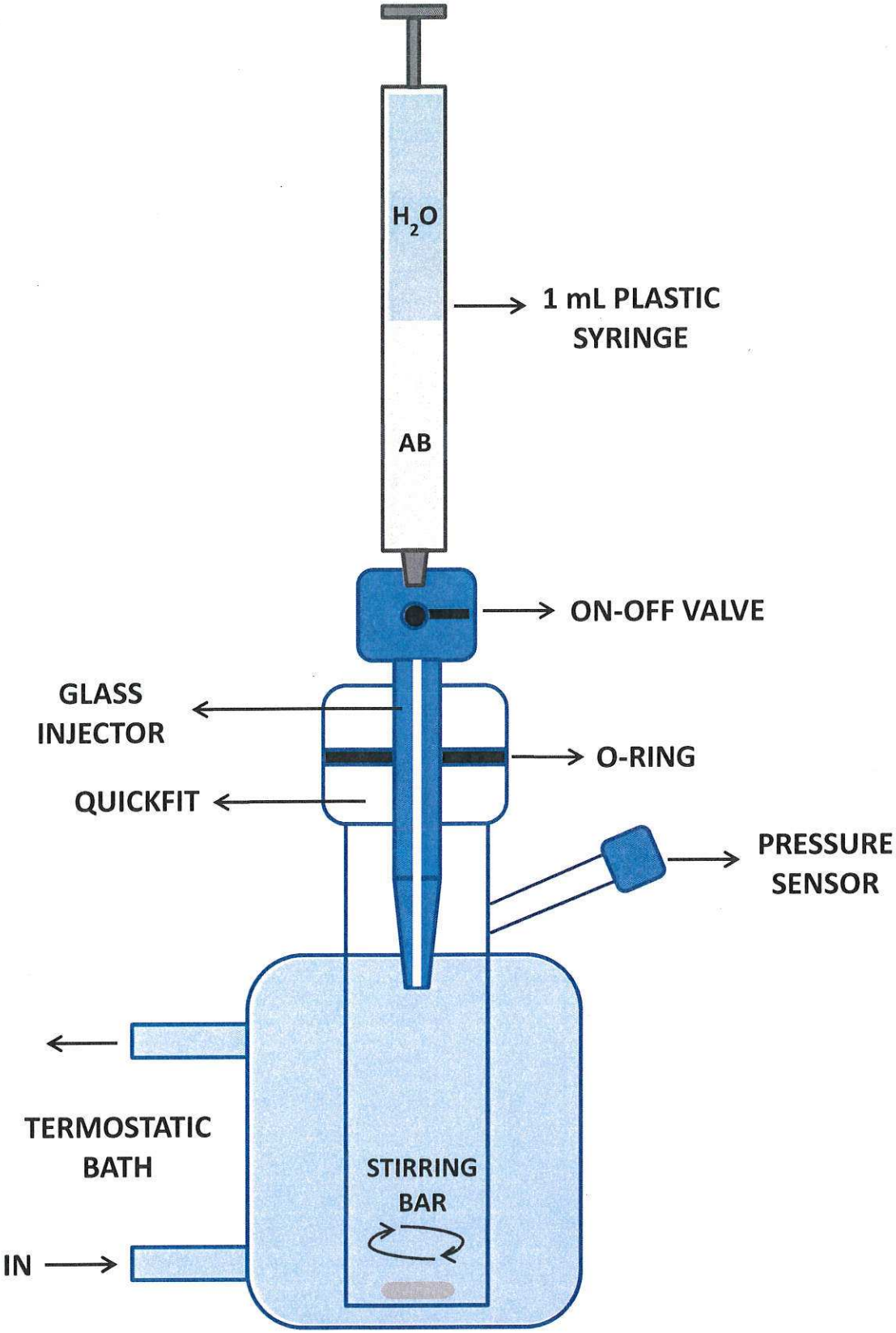

$H_2O$
1 mL PLASTIC SYRINGE
AB
ON-OFF VALVE
GLASS INJECTOR
O-RING
QUICKFIT
PRESSURE SENSOR
TERMOSTATIC BATH
STIRRING BAR
IN

FIGURE 2

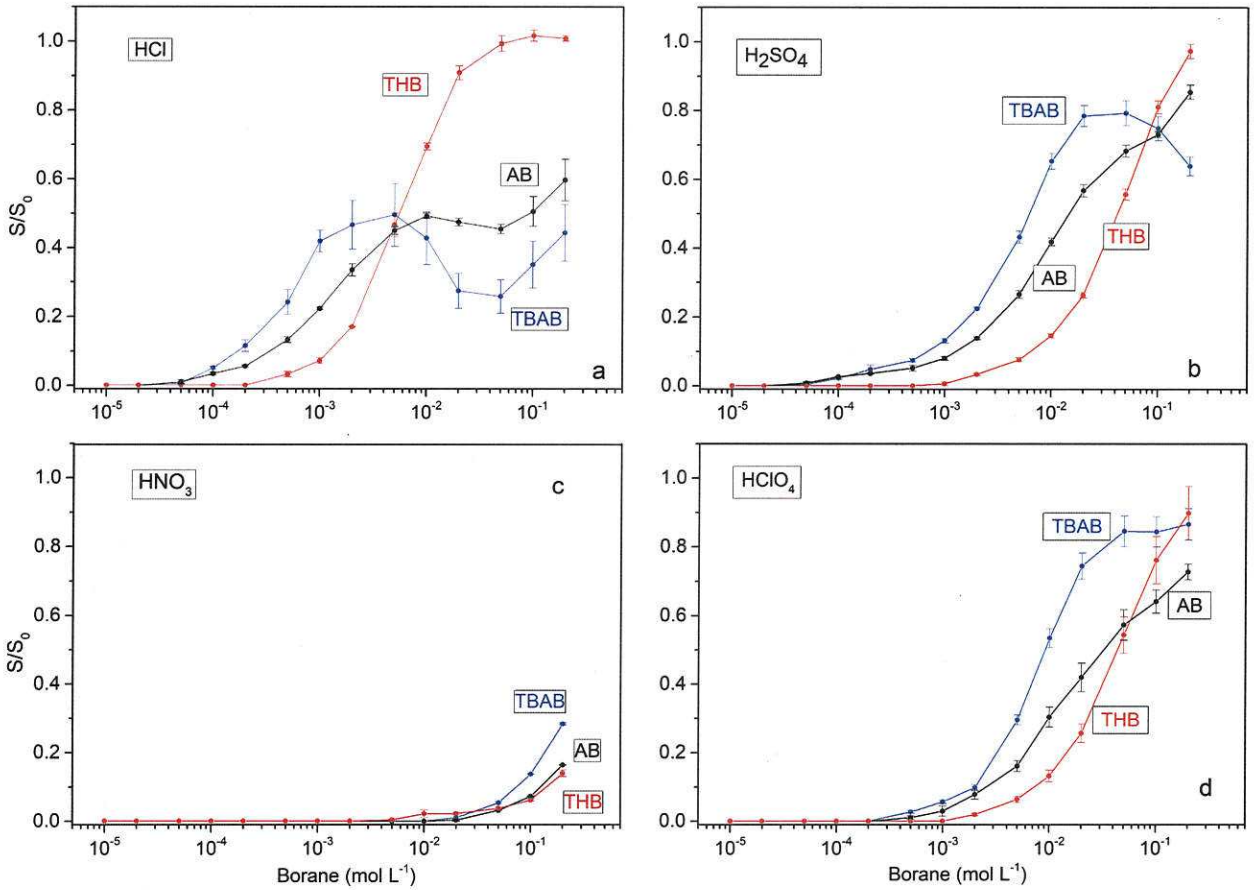

HCl
THB
AB
TBAB
a
$H_2SO_4$
TBAB
THB
AB
b
$HNO_3$
c
TBAB
AB
THB
$HClO_4$
TBAB
AB
THB
d
S/S$_0$
Borane (mol L$^{-1}$)

FIGURE 3

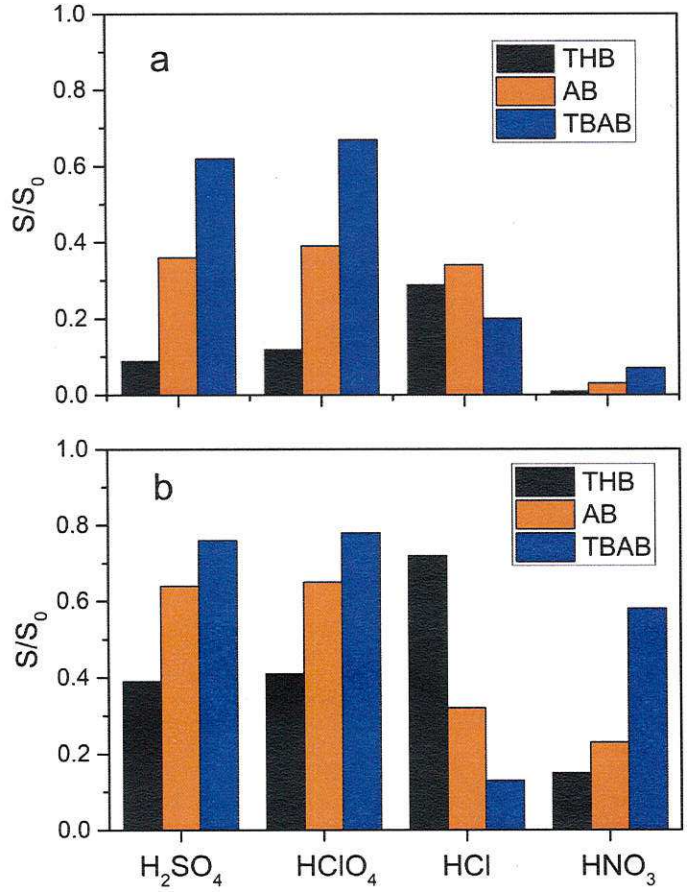


FIGURE 4

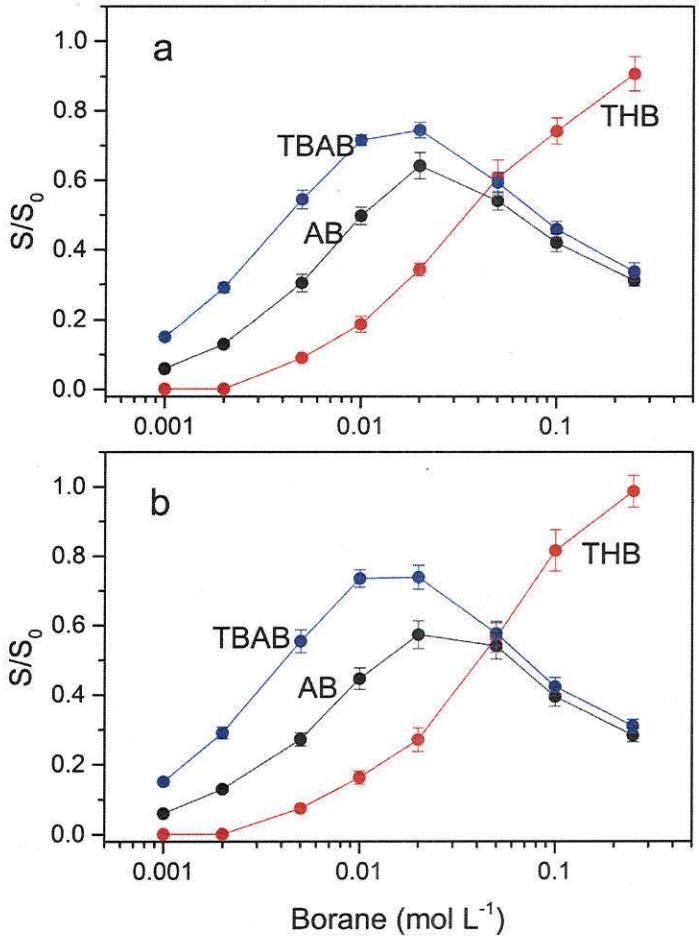


FIGURE 5

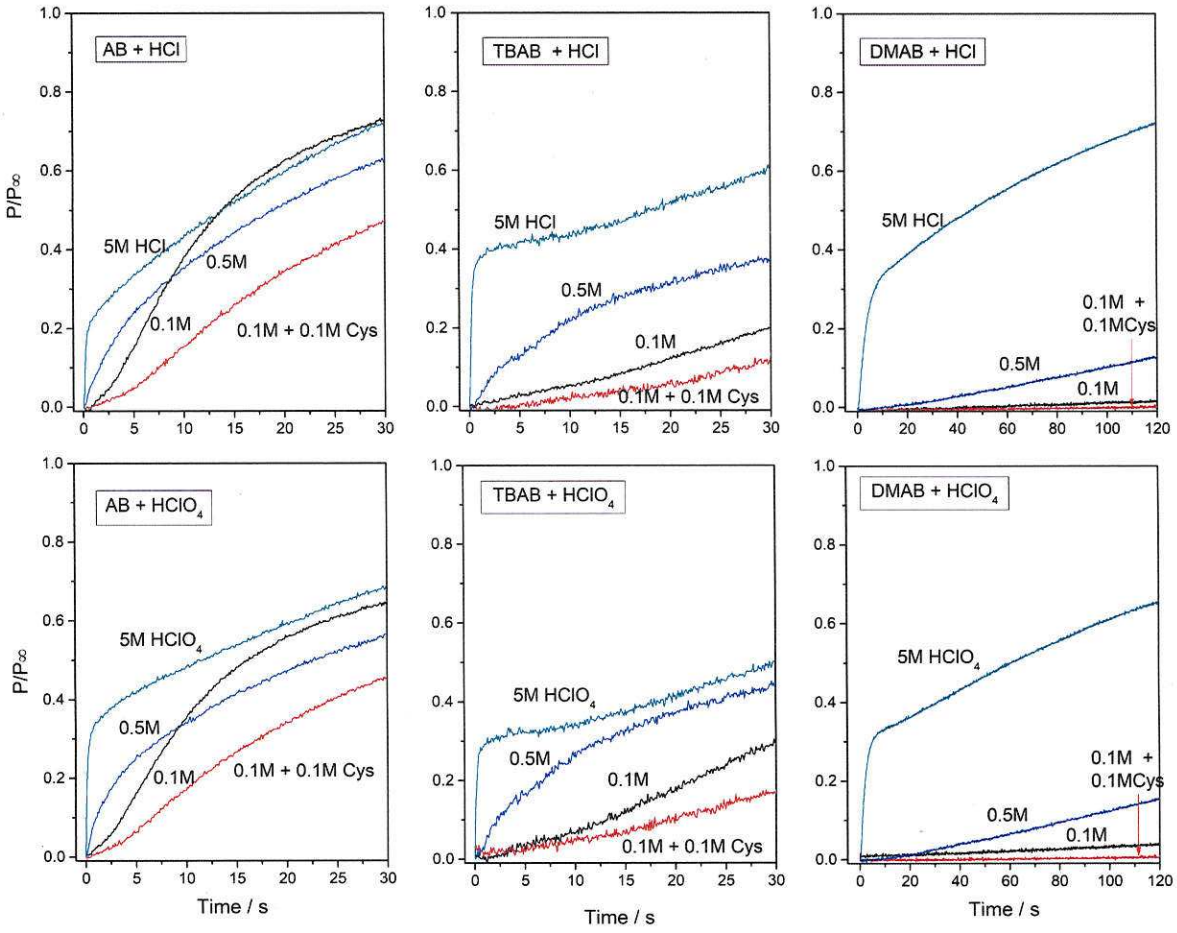

AB + HCl
TBAB + HCl
DMAB + HCl
AB + HClO4
TBAB + HClO4
DMAB + HClO4
5M HCl
0.5M
0.1M
0.1M + 0.1M Cys
5M HClO4
0.1M + 0.1MCys
P/P∞
Time / s

FIGURE 6

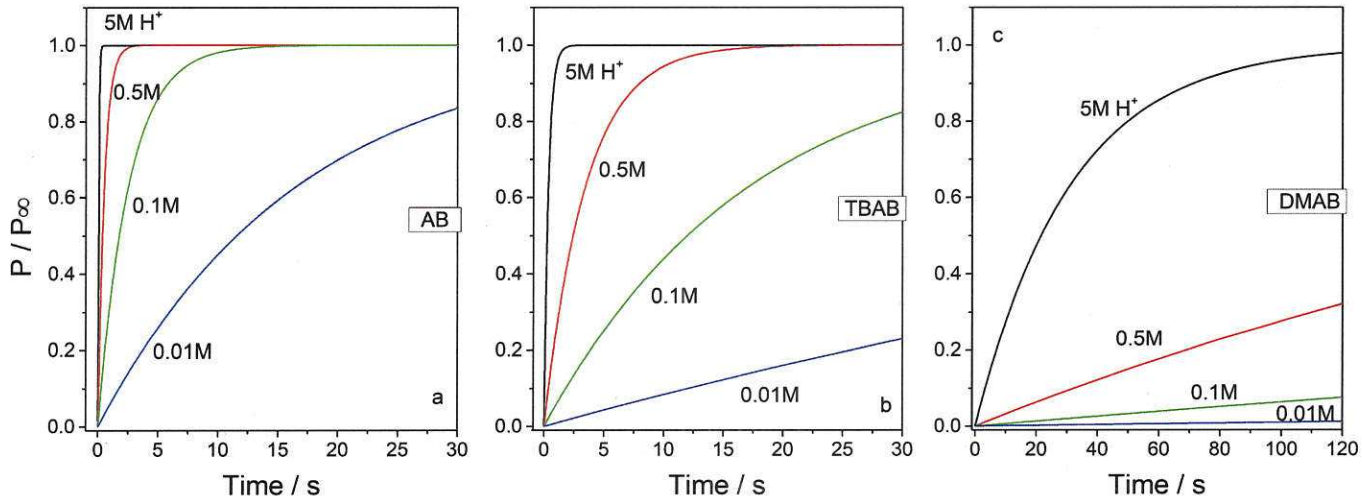

5M H+
0.5M
0.1M
0.01M
AB
a
P / P∞
Time / s
5M H+
0.5M
0.1M
0.01M
TBAB
b
Time / s
c
5M H+
DMAB
0.5M
0.1M
0.01M
Time / s

FIGURE 7

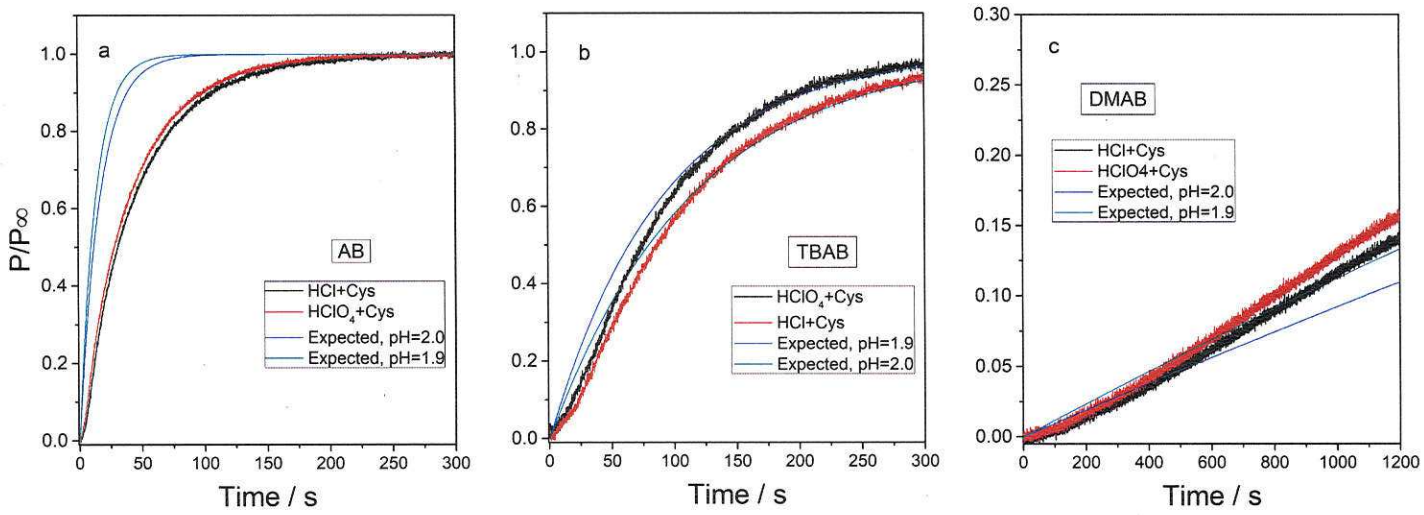
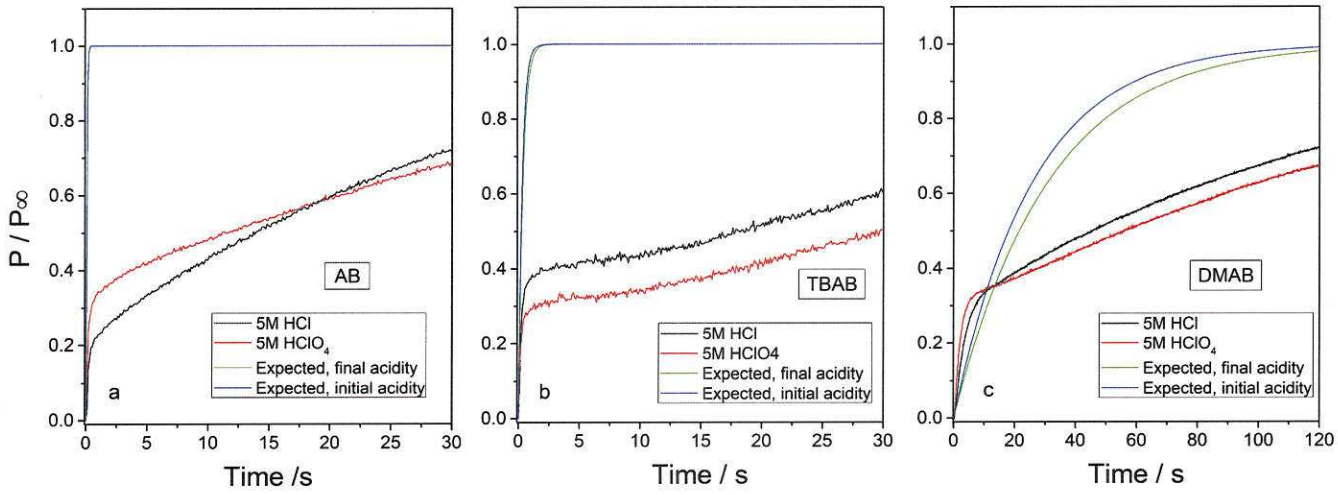

a
AB
HCl+Cys
HClO4+Cys
Expected, pH=2.0
Expected, pH=1.9
P/P∞
Time / s
b
TBAB
HClO4+Cys
HCl+Cys
Expected, pH=1.9
Expected, pH=2.0
Time / s
c
DMAB
HCl+Cys
HClO4+Cys
Expected, pH=2.0
Expected, pH=1.9
Time / s

Figure 8


P / P∞
Time /s
AB
5M HCl
5M HClO4
Expected, final acidity
Expected, initial acidity
a
Time / s
TBAB
5M HCl
5M HClO4
Expected, final acidity
Expected, initial acidity
b
Time / s
DMAB
5M HCl
5M HClO4
Expected, final acidity
Expected, initial acidity
c