DYNAMIC ADSORPTION ISOTHERM MEASUREMENTS APPLIED TO KNOWN ORGANIC PRECIPITATION INHIBITORS AND SCALE CONTROL STUDIES

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Abstract

Scaling of metallic surfaces in contact with supersaturated solutions follows a fairly general pattern where an induction period as well as a growth period are observed. The induction period, which can last more than one hundred hours in the Bayer process, corresponds to a very slow surface coverage where nuclei start to appear on the surface. The kinetics during this induction period is governed mostly by the metal/solution interactions. The growth region is the period during which the scale thickness increases more rapidly, and is governed by scale/solution interactions. In gibbsitic scale formation, this region is comparable to gibbsite precipitation.

A large variety of organic gibbsite precipitation inhibitors has been identified in the literature. During the induction period, the efficiency of these precipitation/scale inhibitors can be related to their adsorption ability to the metallic surface. During the gibbsite growth period, it can be correlated to the inhibitor adsorption strength onto the gibbsite.

A method to study adsorption strengths of organics, which is particularly well suited to this process, has been improved over the past years in our laboratory. The method consists of determination of the dynamic adsorption isotherm by high-pressure liquid chromatography. With this highly sensitive technique, the adsorption strength of a compound is quantified.

In this paper, adsorption results of known organic precipitation/scale inhibitors, obtained with gibbsite and metallic surfaces in caustic solutions, were correlated to their inhibition effect for both the induction and the growth regions.

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1. Introduction

Gibbsite scaling of metallic surfaces in contact with supersaturated Bayer liquor takes place according to two well-known steps: nucleation of the first gibbsite nuclei (induction period), followed by growth of gibbsite crystals (Figure 1). Nucleation is a very slow surface coverage that happens directly on to the metallic surface. Growth is a rapid crystallisation of gibbsite occurring on the already deposited gibbsite. Thus, there are two ways that inhibitors can be used. Some molecules may adsorb directly on to the metallic surface, avoiding nucleation and completely inhibiting scaling (Rossiter et al. 1998). Some may adsorb on to the gibbsite crystals and halt the growth process. It is important for the precipitation inhibition effect of these molecules to be verified because they may be found later in the Bayer process, particularly at the precipitation stage.
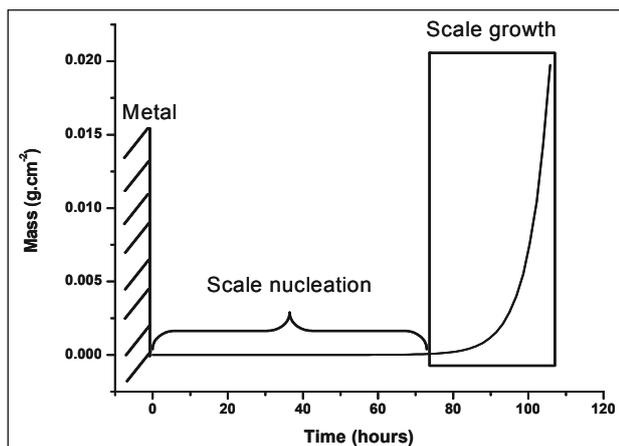

Figure 1. Scale growth typical curve

Therefore, it is extremely interesting to use an analytical technique to discriminate which molecules are potentially adsorbed on to a metallic surface and which on to gibbsite. In our laboratory,

we use adsorption isotherm measurements to calculate the adsorption strength of organic compounds on a given support for a given medium. Adsorption isotherms are determined from the quantity of product adsorbed on the support for solutions with different concentrations of adsorbant.

While several types of isotherms (Brunauer et al. 1940) are known, the most commonly used are Langmuir and Henry isotherms. Langmuir isotherm (Eq. 1) is typical of concentrated solutions.

$$Q_e = \frac{Q_{max}KC_e}{1+KC_e} \quad (1)$$

$$Q_e = k_H C_e \quad (2)$$

$$C_e = \frac{n_i h_{max}}{\omega I_2} = \frac{n_i h_{max}}{\omega \int_{\tau_1}^{\tau_2} h d\tau} \quad (3)$$

$$Q_e = \frac{n_i I_1}{m I_2} = \frac{n_i \int_0 (\tau_r - \tau_0) dh}{m \int_{\tau_1}^{\tau_2} h d\tau} \quad (4)$$

In this case, a rapid increase of adsorption occurs, followed by saturation of the surface, its behaviour graphically characterised by an asymptote. Qmax is the maximal concentration adsorbed and K is the adsorption coefficient. Henry isotherm is valid for very small concentrations of product and presents a linear behaviour (Eq. 2). The Henry constant (k_H) represents the volume of eluant needed to desorb one molecule for a given quantity of support. Therefore, it is expressed in volume unit per mass or surface unit. High k_H means high adsorption. However, no information about the maximal quantity adsorbed is available with this method, so only a comparison between several isotherm adsorption curves

is significant. For the experiments reported here, we used a static adsorption method for the Langmuir part and a dynamic method to determine the Henry part. In particular, the dynamic determination, which is a very fast and sensitive quantification method, uses high-performance liquid chromatography, a powerful technique for small amounts of product when used with sensitive detectors (Brisach-Wittmeyer *et al.* 2006; Chuduk, Eltekov, & Kiselev 1981; Cirtiu *et al.* 2006; Laplante *et al.* 2003). It requires filling a chromatographic column with the desired powder support and using the solution of interest as the eluant. Several concentrations of product are injected into the column. The recorded chromatograms allow extracting the calculation parameters (Figure 2): concentration of molecules in solution at the equilibrium (Ce Eq. 3), and quantity adsorbed on to the support (Q_e Eq. 4). n_i is the injected amount in moles, h_{max} is the peak height in arbitrary units, ω is the flow rate in the column expressed in litre per second, and m is the mass of support packed into the column in grams. It is important that if one wants to express Q_e in mole per surface unit, the mass of support to surface unit must be converted. This conversion is recommended to enable comparison of the adsorption of molecules on different supports. I_1 is the integral represented by the area ABCD where curve AB is connecting the points of peak maxima. I_2 is the peak area integrated from the chromatogram of each amount injected (Figure 2). It can be seen that the retention time (τ_r) is a function of the adsorption capacity for the molecule of interest on to the support: it will shift to the smaller values when concentration increases. Q_e is then drawn as a function of C_e and the resulting curve is called the "adsorption isotherm".
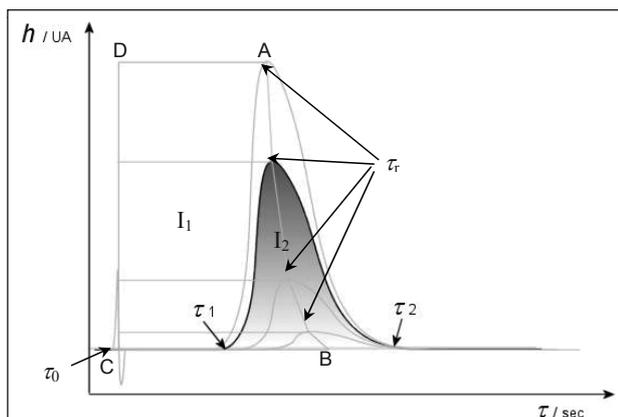

Figure 2. Chromatographic curves for adsorption isotherm measurement

We used the adsorption isotherms as a sensor to compare the adsorption strength of several organic molecules known to be gibbsite precipitation inhibitors (sodium gluconate, catechol) or organic compounds found in the Bayer liquor (phenol, hydroxybenzoic acids, phtalic acid, benzentricarboxylic acids, etc). This technique permits anticipation of the reactivity of molecules regarding precipitation, scaling or its adhesion to a surface. Indeed, it has been shown that the growth inhibiting effect is related to the adsorption power of the molecules (Coyne *et al.* 1994; Tran *et al.* 1996; Watling 2000; Watling, Loh, & Gatter 2000; Watling, Townsend, & Loh 1999). To verify the effect induced by the molecules under investigation, we used gibbsite precipitation tests in the presence or absence of inhibitor (Bouchard N.A. *et al.* 2005; Bouchard N.A. *et al.* 2007). These results showed that the more the inhibitor is adsorbed on gibbsite (alumina hydrate), the more the gibbsite precipitation yield decreases. We also used balances to test scale growth tests. In this paper, we present the correlation between new adsorption isotherm measurements and scale growth measurements carried out on mild steel.

2. Experimental

2.1 Chemicals

HLPC grade (Fisher Scientific) water was used to prepare the eluants. NaOH 10N (Fisher Scientific), NaOH pellets 99% puriss. (Fisher Scientific), Na2CO3 (Fisher Scientific) and organic molecules (Aldrich) were used as received. Gibbsite supplied by Rio Tinto Alcan was used as received to prepare synthetic Bayer liquor and to pack the HPLC columns. Iron powder 325 mesh, reduced, 98% was purchased from Alfa Aesar. Mild steel coupons (1 cm diameter) used for the growth measurements were of 1018 type and treated by mechanical or electrochemical polishing. Preparation of synthetic Bayer liquor is described elsewhere (Bouchard *et al.* 2005).

2.2 Adsorption isotherms

Chromatographic parameters were obtained using Dionex GP 50 equipped with a UV detector, model UVD340U. Dead volume (τ_0) was determined by injecting 10 μL deuterium oxide D_2O. The mobile phases were 0.001 M, 0.01 M, 0.1 M or 1 M of NaOH prepared with HPLC grade water. The molecules injected were prepared directly in the eluant at concentrations between 0.0005 M and 0.1 M. The flow rate was 1.00 mL/min. The columns (15 cm) were filled with gibbsite or iron powder, whose average particle size was between 25 μm and 45 μm. The parameters used to determine the dynamic adsorption isotherms were collected from the HPLC elution chromatograms, and the Henry constants were calculated from the well-known equation $Q_e = k_H C_e$.

2.3 Growth measurements

Mild steel coupons (1 cm diameter) were treated mechanically or electrochemically. The mechanical treatment used three different polishing grains (120 grit, 400 grit and diamond powder 1 μm) at 120 rpm with a pressure of 15 lb during 10 minutes at clockwise and counter-clockwise rotation. The electrochemical polishing was accomplished in a perchloric acid solution 20% in methanol. Temperature was maintained at 28°C during the processes. The working electrode was a steel coupon, the counter electrode was a steel grid and the reference electrode was Ag/AgCl. The coupons were then fixed to a microbalance (weight capacity of micrograms) and plunged in synthetic Bayer liquor (A/C ratio = 0.62). The mass variations were measured as a function of time.

3. Results and discussion

Dynamic adsorption isotherm measurements render fast screening of the adsorption power of molecules of potential interest. We are able to rapidly evaluate their effect on different supports and for different eluants. To avoid nucleation initiation, the most interesting molecule was strongly adsorbed on to a metallic support, covered the surface completely and would not allow gibbsite adsorption. To halt growth of gibbsite on to gibbsite, the most interesting molecule would adsorb on to gibbsite, even slightly. Because under plant conditions one cannot exclude the possible mechanical attachment of a gibbsite particle to the surface, the most efficient scale inhibitor would be one that adheres to both the metallic surface and the gibbsite, in order to prevent immediate scale formation during the induction period. Thus, we had to determine if a molecule adsorbs on the metallic surface in order to be efficient during the induction period, and to verify the adsorption of these molecules on to gibbsite. The required conditions should be attainable because some similarities in the structure of the surfaces in these two kinds of supports were observed, inducing some similar adsorption modes. Indeed, gibbsite and iron present –OH groups and oxides at their surface. It is well known that on gibbsite, the adsorption of an organic molecule is favoured by the presence of two adjacent –OH groups through hydrogen bridges with the bridging oxygen

in gibbsite (van Bronswijk, Watling, & Yu 1999). The presence of one –OH group and an adjacent acid group can also form a complex with gibbsite, as depicted in Figure 3a. Indeed, it is also known that acidic functions adsorb well on alumina hydrate (Madsen & Blokhus 1994) due to an esterification reaction (Figure 3b) (Karaman, Antelmi, & Pashley 2001). Moreover, it is also possible to observe a complexation between the acid –OH group of the acid function and aluminium, replacing a hydroxyl group on the surface of gibbsite (ligand exchange) (Kummert & Stumm 1980; Rosenqvist *et al.* 2003) (Figure 3).

Figure 3. Possible adsorption mechanisms on gibbsite.
(a) H bridging and ligand exchange
(b) esterification with an acid

This new link can even lead to redissolution of gibbsite (Molis *et al.* 2000). On iron, the metal used to model mild steel, it has been shown that some organic molecules with two acidic adjacent functions can replace the –OH groups in $Fe(OH)_2$ by forming a complex (Figure 4a) (Abd El-Maksoud *et al.* 2005). Literature also records that aromatic organic molecules can adsorb via the aromatic ring on to iron oxides, and that the carboxylate can form a bond with the oxide surface (Figure 4b) (Bandara, Mielczarski, & Kiwi 2001).

Figure 4. Possible adsorption mechanisms on: (a) iron hydroxides, (b) iron oxides

Figure 5 shows the adsorption curves for six different organic molecules drawn for two supports, gibbsite and iron, with the same concentration of NaOH (0.01 M). Table 1 shows the Henry constants for all the molecules studied. We observed that for gibbsite, all the constants are in the same range.

The slight differences observed in the adsorption tendency (3-hydroxybensoic acid = 1,3,5-benzenetricarboxylic acid <1,2,3-benzenetricarboxylic acid <phthalic acid <isophthalic acid <salicylic acid) (Figure 5a) are due to the structure of the molecules (Table 1). Indeed, in 3- hydroxybensoic acid and 1,3,5-benzenetricarboxylic acid, the two –OH groups are far away from one another. In 1,2,3-benzenetricarboxylic acid and phthalic acid, the functional groups are adjacent, but present steric hindrances; isophthalic acid adsorbs a little better because there are fewer steric hindrances and it contains two acidic functions.

Figure 5. Effect of molecule structure on adsorption on: (a) gibbsite with NaOH 0.01 M, (b) iron with NaOH 1 M for (-■-)1,2,3-benzenetricarboxylic acid, (-♦-) 1,3,5-benzenetricarboxylic acid, (-▲-) Salicylic acid, (-●-) Phthalic acid, (-○-) Isophthalic acid, (-x-) 3-hydroxybensoic acid, (-Δ-) Benzoic acid and (-□-)Phenol.

Finally, salicylic acid presents a good adsorption power because there is a –OH group at the ortho position of the acid (Das *et al.* 2004; Szekeres *et al.* 1998). Figure 5b shows the adsorption isotherms measured on iron. We observed that the presence of only one hydroxyl or acidic group on the aromatic ring is not sufficient to properly adsorb, and that these two functions are not distinguishable regarding adsorption, as phenol and benzoic acid present a similar Henry constant. Indeed, at NaOH concentration ≥ 0.001 M, pH is ≥ 11.3, both phenol and benzoic acids are deprotonated (see pK_a values in Table 1) and their reactivity is similar. As well, we observed that the adsorption tendency for the four other molecules studied (phthalic acid <1,3,5-benzenetricarboxylic acid < 1,2,3-benzenetricarboxylic acid <salicylic acid) indicates that:

1) on this support, the greater the number of acidic groups, the greater the adsorption;
2) the closer the acidic functions, the greater the adsorption;
3) the presence of one –OH and one –COOH group at the same time is the most favourable configuration for adsorption on iron.

However, we can observe that the four common molecules for both supports, gibbsite and iron, do not present exactly the same adsorption tendency (Figure 5, a and b) from one support to another. Phthalic acid is less adsorbed than other molecules onto iron, whereas onto gibbsite, it is the opposite. We also observed that all the molecules are much better adsorbed onto iron than onto gibbsite. For example, the adsorption of salicylic acid is approximately 28 times more important on iron than on gibbsite for the same concentration of NaOH (Table 1). Nevertheless, adsorption onto gibbsite is not negligible. These behaviours are attributed to the different adsorption modes for the two supports and indicate that all the molecules studied are good candidates as scale inhibitors.

Table 1. Henry constants for several organic molecules on gibbsite and iron

Molecule	Formula	pKa	Henry constants (L.m^{-2})			
			Gibbsite	Iron		
			0.01 M NaOH	0.001 M NaOH	0.01 M NaOH	1 M NaOH
1,2,3-benzenetricarboxylic acid		(1) 2.50	0.0012	0.42	0.13	0.036
1,3,5-benzenetricarboxylic acid		(1) 3.50	0.0011	-	-	0.028
Salicylic acid		(1) 2.97	0.0018	0.029	0.051	0.064
Phthalic acid		(1) 2.98 (2) 5.28	0.0015	0.017	-	0.013
Isophthalic acid		(1) 3.46 (2) 4.46	0.0016	-	-	-
3-hydroxybensoic acid		(1) 4.08	0.0011	-	-	-
Benzoic acid		(1) 4.17	-	0.025	-	0.0083
Phenol		(1) 9.98	-	0.0048	0.012	0.0085
Catechol		(1) 9.45 (2) 12.8	0.0015	-	-	-
Sodium D-gluconate		-	0.0018	0.063	-	0.068

Afterwards, we studied the effect of caustic concentration on adsorption (Figure 6) for the same two molecules on iron. 1,2,3-benzenetricarboxylic acid is better adsorbed than salicylic acid for concentrations of NaOH at 0.001 M and 0.0 1M. For 1 M of NaOH, salicylic acid is the best adsorbed, but the Henry constants are in the same range for both molecules. The adsorption tendencies as a function of caustic concentration are inversed from 1,2,3-benzenetricarboxylic acid (Figure 6a) to salicylic acid (Figure 6b). As the first pKa of the molecules are similar (Table 1), we cannot attribute the differences to the form of the molecule as a function of pH. However, pH and temperature can influence the nature of the metallic surface, favouring the presence of iron oxides or hydroxides (Kiyama 1974; Tolchev et al. 2002). At room temperature, no distinction can be made for the abundance of one or the other species at our working pH (11 <pH <13). Therefore, we can conclude that 1,2,3-benzenetricarboxylic acid adsorption is favoured over salicylic acid adsorption on to iron at pH values between 11 and 13 because of the presence of an additional acidic function. However, at high temperature, the presence of iron oxides is favoured (Tolchev, Kleschov, Bagautdinova, & Pervushin 2002) and organic molecules must then be chosen in order to adsorb preferably on these sites.
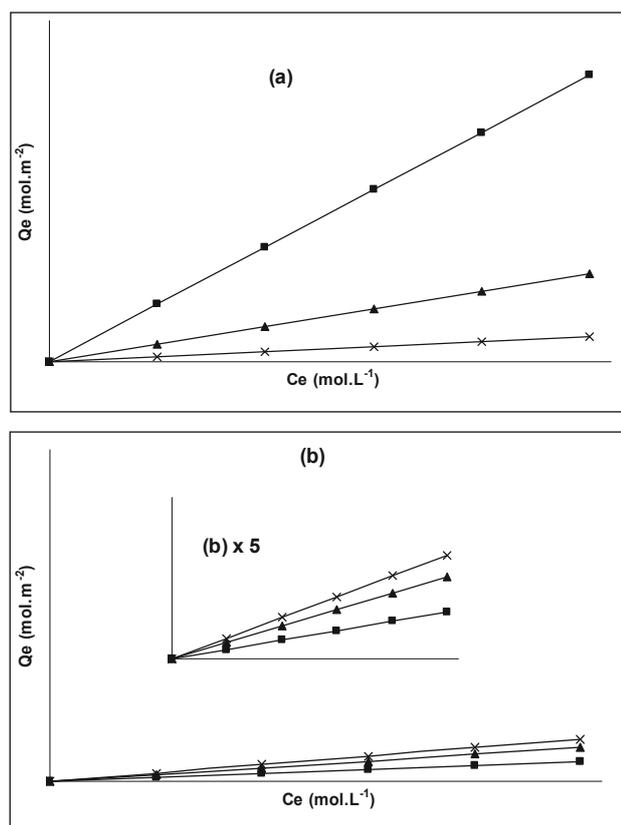
Figure 6. Effect of NaOH concentration on adsorption on iron for: (a) 1,2,3-benzenetricarboxylic acid, (b) salicylic acid with NaOH (-■-) 0.001 M, (-▲-) 0.01 M and (-x-) 1 M.

To improve the adsorption tendencies observed with isotherm measurements, we tested scale growth. Our tests involve putting a metallic coupon in synthetic Bayer liquor and measuring the mass gain as a function of time. When no inhibitor was added to the solution, we observed a nucleation period between 120 and 160 hours. The nucleation period represents the time necessary for a complete coverage of the surface with nuclei, i.e. first aggregates of gibbsite (Figure 1). Nucleation was followed by the growth period during which the gibbsite crystal growth occurs. When we added sodium D-gluconate as an inhibitor (Figure 7a), we observed two distinct behaviours. When the molecule was added before plugging the coupon into the solution, the nucleation time was lengthened. When it was added after the crystal growth had begun, growth of gibbsite ceased and a mass

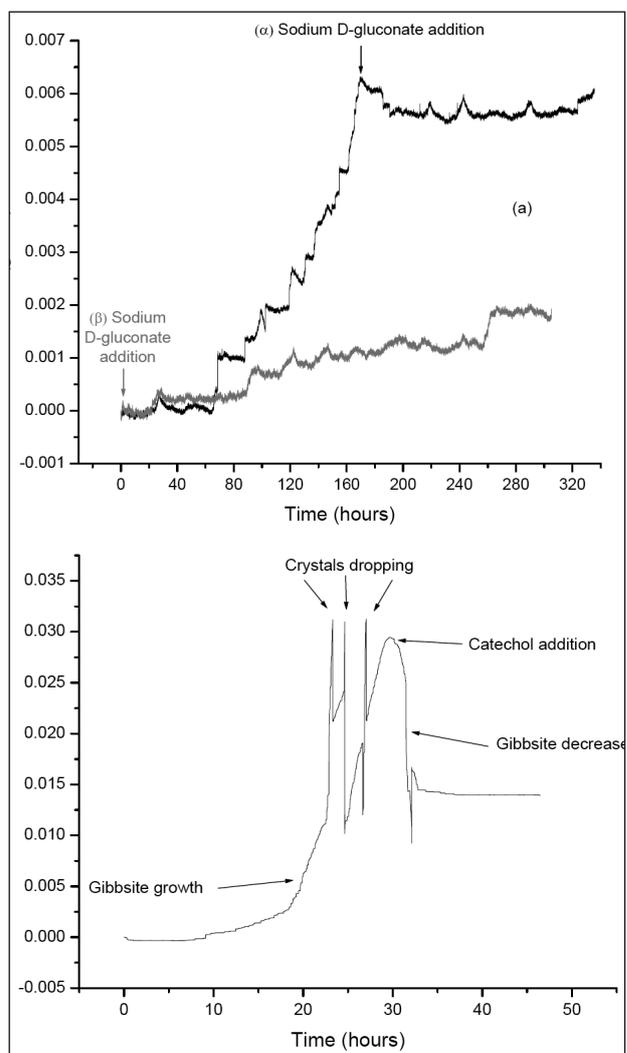plateau appeared on the curve, indicating that no mass loss occurred.

Figure 7. Scale growth tests in synthetic Bayer liquor. Addition of growth inhibitors: (a) sodium D gluconate (α) before plugging the plate into the solution (β) after the crystal growth had begun (b) catechol after the crystal growth had begun. For (b), the coupon was previously treated in Bayer liquor during 95 hours.

Therefore, the behaviour observed during growth tests is consistent with the adsorption constants measured for this molecule on iron and gibbsite supports. In fact, we observed that the adsorption of sodium D-gluconate is approximately 35 times more important on iron than on gibbsite (Table 1). We also noticed that the adsorption of sodium D-gluconate on iron is independent of caustic concentration. We can then assume that the adsorption onto iron in Bayer liquor, where the caustic concentration is around 4 M, is at least as strong as those measured in the adsorption isotherms experiments. Unfortunately, we were not able to determine the Henry constants at high caustic concentration onto gibbsite because this support is rapidly solubilised. However, when sodium D-gluconate is added before starting mass measurements, it strongly adsorbs onto iron and avoids further gibbsite adsorption. When it is added after growth has started, its adsorption on gibbsite is strong enough to cover the surface and, consequently, further growth of gibbsite cannot occur.

When we added catechol to the solution after approximately 120 hours of growth, we observed that this well-known gibbsite precipitation inhibitor leads not only to a ceasing of growth, but also to a decrease in the scale mass deposited on the coupon (Figure 7b). Since catechol's Henry constant values on gibbsite

are similar to those of sodium D-gluconate, there must be an additional effect causing a solubilisation of gibbsite.

Regarding the structure of catechol and sodium D-gluconate (Table 1), we propose that, in both cases, the adsorption phenomena is due to the complexation effect between gibbsite and the "grip" formed by two hydroxyl groups (in catechol) or one hydroxyl and the acid group (in sodium D-gluconate). In the first case, this effect can even induce dissolution of gibbsite.

4. Conclusions

Adsorption depends on several parameters: nature of molecules, surface and eluant. The eluant can also modify the surface composition of the metallic support. Thus, caustic concentration is an important parameter that will play a key role on the nature of the groups present on mild steel. So, the ideal scale inhibitor at high temperature will be chosen as a good adsorbent on iron oxides and on gibbsite. In general, the inhibitor must properly adsorb on to iron and also adsorb, although to a lesser degree, onto gibbsite. Salicylic acid is a well-known inhibitor, but molecules like 1,2,3-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid or Sodium D-gluconate are also potential candidates.

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