

Dynamic NMR Study of Model CMP Slurry Containing Silica Particles as Abrasives

In memory of Professor Yuzhuo Li

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Abstract: Chemical mechanical planarization (CMP) should provide a good surface planarity with minimal surface defectivity. Since CMP slurries are multi-component systems, it is very important to understand the various processes and interactions taking place in such slurries. Several techniques have been employed for such task, however, most of them lack the molecular recognition to investigate molecular interactions without adding probes which in turn increase complexity and might alter the microenvironment of the slurry. Nuclear magnetic resonance (NMR) is a powerful technique that can be employed in such study.

The longitudinal relaxation times (T_1) of the different components of CMP slurries were measured using Spin Echo-NMR (SE-NMR) at a constant temperature. The fact that NMR is non-invasive and gives information on the molecular level gives more advantage to the technique. The model CMP slurry was prepared in D_2O to enable monitoring of T_1 for the various components' protons. SE-NMR provide a very powerful tool to study the various interactions and adsorption processes that take place in a model CMP silica based slurry which contains BTA and/or glycine and/or Cu^{+2} ions. It was found that BTA is very competitive towards complexation with Cu^{+2} ions and BTA-Cu complex adsorbs on silica surface.

1. Introduction:

Silica slurries are of great importance in applications ranging from computer industry to medical fields [1, 2]. However, their use in microelectronic industry is considered one of the most important achievements, specifically in the chemical mechanical planarization (CMP). Several processes take place in CMP including physical and chemical processes [3]. A good understanding of these physicochemical processes associated with CMP (such as surface kinetics, complexation, and corrosion) is critical [4]. This understanding is not also essential for the CMP itself, but is also crucial for post CMP operations such as cleaning and environmental effect of discharged slurries [5]. A wide range of physical and spectroscopic techniques have been applied for the characterization of these slurries such as dynamic [6] and static light scattering [7], scanning tunneling microscope (STM) [8], x-ray photoemission spectroscopy



(XPS) [9], UV- photoemission spectroscopy (UPS) [10], low-energy electron diffraction (LEED) [11], electrochemical impedance spectroscopy [12] and FTIR [13].

Slurries used in CMP are multi-component systems. In such slurries different compounds will be present such as the oxidizing agents and anticorrosion agents. In Cu-CMP silica based slurries in particular, there will be an oxidizing agent (e.g. H_2O_2), complexing agent (e.g. glycine) and anticorrosion agent (e.g. benzotriazole (BTA)) in addition to silica particles and the solvent (water). Due to presence of the oxidizing copper ions (Cu^{+1} and Cu^{+2}) will also be in the slurry. These copper ions will form complexes with the various components. Probable complexes presents are Cu- H_2O , Cu-BTA, and Cu-glycine in addition to copper oxides [4]. The free and complex components will also be available to adsorb on silica surface. This adsorption will modify the silica particles' surface by changing the charge, hydrophobicity and size among other changes. These changes will modify the polishing characteristics of these particles. In addition to changing the surface nature, adsorption might also affect the amount available of these components for action in the CMP process. An understanding of these interactions on the molecular level will provide valuable information about the different components involved in the Cu-CMP process and enables huge advancements in the CMP field.

Nuclear magnetic resonance (NMR) provides a very powerful tool for studying interactions and other dynamic properties on the molecular level. One of the most advantages of NMR is that it is not invasive which is important in keeping number of components in the system low and no disturbances to the present equilibria will happen due to introduction of probe molecules. Also NMR is flexible and can cover a wide spectrum of atoms that can be studied depending on the system under study. For example it can be used to observe ^1H , ^{13}C , ^{29}Si and many other different nuclei in the system. Therefore, valuable information about the type and strength of interactions and conformations present in the system will be gained according to the nucleolus observed. Another big advantage for NMR is there are so many different types of experiments that can be performed ranging from simple 1D experiments to 3D ones, and from decoupling experiments to coupling ones, and the coupling between various types of nuclei. Dynamic NMR experiments using Spin Echo (SE-NMR) add to this wide range of different experiments [14]. Since the development of SE-NMR spectroscopy, valuable information were obtained such as solvation effects and solvent-solute interactions [15], internal hydration in proteins [16], probing active sites in enzymes and binding modes [17], interactions in biological systems [18, 19], pharmaceutical and drug release [20] and study of self assembly and organized structures [21, 22].

One of the most important values studied for a system is the relaxation of the observed nucleus in a compound at a certain environment. Relaxation processes are caused by interaction of the magnetic dipole of the nuclear spins with neighboring nuclei [23]. These interactions are stochastic in nature and are modulated by molecular tumbling and translation and dependent on several factors such as intermolecular collisions, Van der Waals binding, and proton exchange with other molecules. there are two pathways for relaxation, longitudinal (spin-lattice relaxation T_1) and transvers (spin-spin relaxation T_2). Longitudinal relaxation time is mainly affected by fast motion at ω_0 and $2\omega_0$ frequency orders (ω_0 is Larmor frequency of the proton in the NMR instrument), whereas T_2 additionally sensitive to slow motions near zero frequency components resulting on the fast loss of the transverse magnetization without affecting the populations of the spin states. T_1 is the time required for a nucleus to relax from the excited state (after excitation by a pulse of energy) to its ground state. T_1 occurs by getting rid of the excess energy to the lattice (or the environment) through radiationless processes (e.g. heat). The values of T_1 are very

sensitive to any changes of the nucleus environment; these changes could be due to molecular interactions such as adsorption, H-bonding or complexation or to micro-environmental ones such as temperature, pH and ionic strength. It is more convenient to calculate relaxation rate R_1 ($1/T_1$). Relaxation times have been used as an analytical and probing tool in many fields [22, 25-28].

In this paper, a systematic study for the effect of each component in model CMP slurries will be studied using SE-NMR as an attempt to better understand most aspects affecting the CMP process.

2. Experimental:

2.1 General:

Deuterium oxide (CIL D, 99.9%) was used for all experiments and was used without any further treatment. The silica used was Aerosil 200 (Degussa). Silica dispersions were prepared from a stock solution and sonicated for at least 30 minutes. The stock solution was prepared as 10% in D_2O then it was sonicated for at least one hour in a water sonicator to have a homogenous and stable suspension. The Cu^{+2} solution (1000 ppm) was prepared using Copper (II) nitrate, 2.5-hydrate (J.T. Baker) in D_2O . 1H-Benzotriazole (ACROS), Glycine (Fisher) were of general laboratory grade and used as purchased and were prepared as stock solutions of 1% and 10% respectively. All solutions prepared were in weight percentages unless it was indicated otherwise.

2.2 NMR measurements:

The relaxation time T_1 was measured using Bruker 400 AVANCE with a BBO probe equipped with z-gradient and the temperature was controlled using a VTU and held constant at 300 °K, the relaxation delay used varied from 10 seconds (in presence of 100 ppm Cu^{+2} ions in the solutions) to 60 seconds depending on the relaxation time of the solution's components. Each sample was prepared and measured at least three times, and the T_1 for each sample was repeated at least three times. The standard deviation was measured for all data presented in the work and was 0.98%.

All samples for the T_1 experiments were prepared by placing the solutions to be studied into NMR (5 mm) tubes. The parameters used to obtain T_1 were the same for all samples. A relaxation delay of 60 seconds was used for all samples that does not contain Cu^{+2} ions with 12 delay times in the t_1 -delay list ranging from 0.01 sec to 120 seconds and number of scans ranging from 4 to 16 according to the sample's concentration and receiver gain (rg) values ranging from 64 to 512 also depending on the sample's concentration. The spectral width used was 12 ppm and was not optimized to shorter spectral width to minimize the time for each T_1 -experiment.

3. Results and Discussion:

3.1 Effect of D_2O/H_2O changing ratio on T_1 of water:

The relaxation time (T_1) of water is a very useful marker of the environment it is present in. It has been used to study many microenvironments [22, 25, 28], All our measurements were performed in deuterated water to enable the measurements of T_1 for the different components of the model CMP slurry at their respective chemical shift (δ). Hence, it was important to study the relaxation time of water and the effect of increasing percentages of the deuterated form on the relaxation time of these mixtures. A series of samples were prepared with increasing amounts of D_2O and were studied for the relaxation time of the water signal at 4.78 ppm, results are shown in Figure 1. From the data listed below we observe (as expected) that increasing the ratio of D_2O

will increase the relaxation time. This is expected since we are reducing the effective relaxation by adding D atoms instead of protons. Protons relax in a totally different way than D atoms. Also this study is essential to see the effect of the protons added with the various components such as glycine and BTA and not confuse any changes in T_1 due to H-exchange with adsorption or complexation processes. However, T_1 values were smaller than expected for samples with more H_2O ratio. This is caused by the presence of dissolved oxygen in the samples, and since oxygen is paramagnetic it result in a sharp drop of T_1 values [29]. By examining the data in Figure 1 we see that only when $H_2O\%$ is more than 20% that T_1 drops to less than 15 seconds and R1 is less than one second. Since the maximum amount of glycine added is 1% and BTA is 0.1%, it is not probable that H-exchange is the cause of any drop in T_1 observed in this study. So Figure 1 can be used effectively to distinguish between T_1 drop due to proton exchange or other processes present.

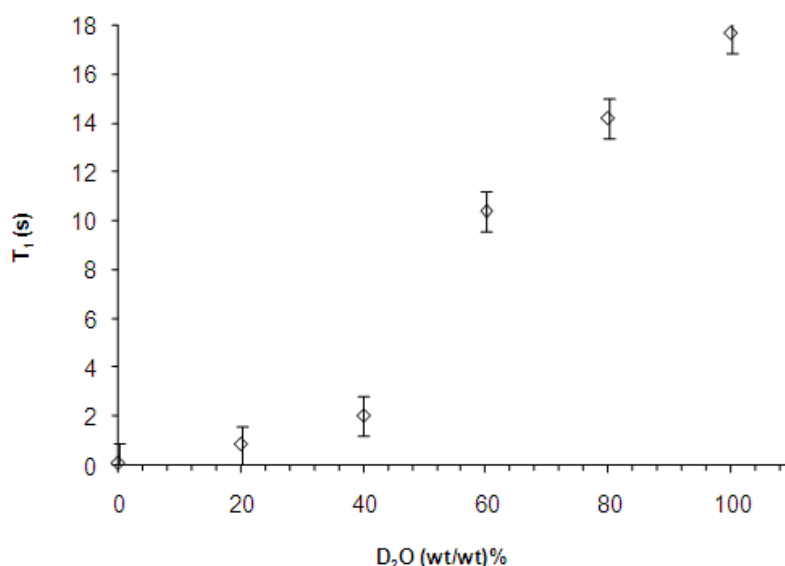


Figure 1: The effect of increasing amounts of D_2O on the relaxation time of water at 300° K.

3.2 Effect of changing silica ratio on T_1 of water:

The relaxation time of water in a series of samples with increasing amounts of silica was measured at a constant temperature of 300 °K (Figure 2). Our analysis of water-silica interaction was based on a two-site exchange model. A fast exchange between surface-bound water and bulk water was assumed since no trace of confined water signal was observed at this temperature. Studies using 1H - and 2H -NMR spin-lattice relaxation studies (T_1) at various magnetic fields and much lower temperatures have been performed [30]. These studies anticipated the presence of a three site exchange between protein and water, bound and free water (bulk), but in general a fast-exchange is seen between bound and free water. Such behavior can also be attributed to the interaction between water and silica particles. Increasing silica leads to a decrease in T_1 of water via two pathways of interactions. Firstly, increase of adsorption of water on silica surface due to increase in surface area available for adsorption. The observed T_1 values are the average of T_1 of adsorbed and T_1 of bulk water. Since we are working on a constant magnetic field, the deciding factor affecting T_1 observed is the population of each state. Increasing the surface area available

for adsorption by increasing silica% will increase the population of adsorbed water and therefore the observed T_1 will decrease. Secondly, the interaction between water protons and silanol group protons ($-\text{Si}-\text{OH}$) on the silica particle's surface [26, 27]. From Figure 1, it can be concluded that adsorption to silica particle's surface and not the exchange between hydroxyl groups of silica and D_2O is the main source for T_1 drop since the amount of protons added due to the addition of silica is less than 10% and 20% proton exchange is needed to drop T_1 of water to less than 15 seconds. These results are in agreement with previous studies of the water structure and dynamics in presence of silica particles conducted using both solution and solid NMR [31] were the contribution of H-bonding contributed less to T_1 decrease than adsorption on silica. These conclusions were supported by a recent NMR study of the orientation of water near silica surfaces [32].

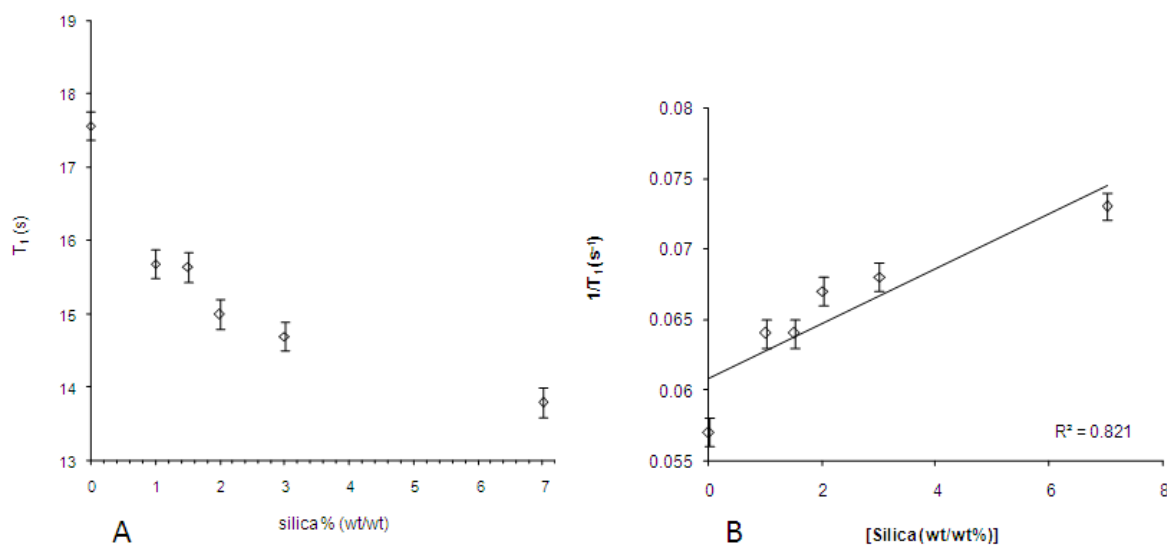


Figure 2: The effect of increasing amounts of silica on (A) the relaxation time and on (B) relaxation rate of water at 300° K.

3.3 Effect of Cu^{+2} on T_1 of water:

The addition of increasing amounts of Cu^{+2} ions to D_2O samples is expected to decrease the values of T_1 of water sharply. This is due to interaction with the paramagnetic ion in two ways. The first way is through short range interactions when water molecules are in the inner-sphere of the complex (very short T_1); the second way is by a long range interaction of water molecules with the metal ion if these molecules are in the outer-sphere of the complex [33]. However, in both cases we have a very fast equilibrium between these sites and the averaged signal is observed by NMR. In this study, constant and increasing amounts of Cu^{+2} were added to D_2O samples and T_1 was measured at a constant temperature of 300 °K. The data are shown in Figure 3, the relaxation time of water dropped sharply from a value of 17.5 s to less than one second when a total final concentration of 100 ppm of Cu^{+2} was reached. This huge effect was anticipated due to the complexation of water molecules with the Cu^{+2} ions, which will eventually decrease T_1 .

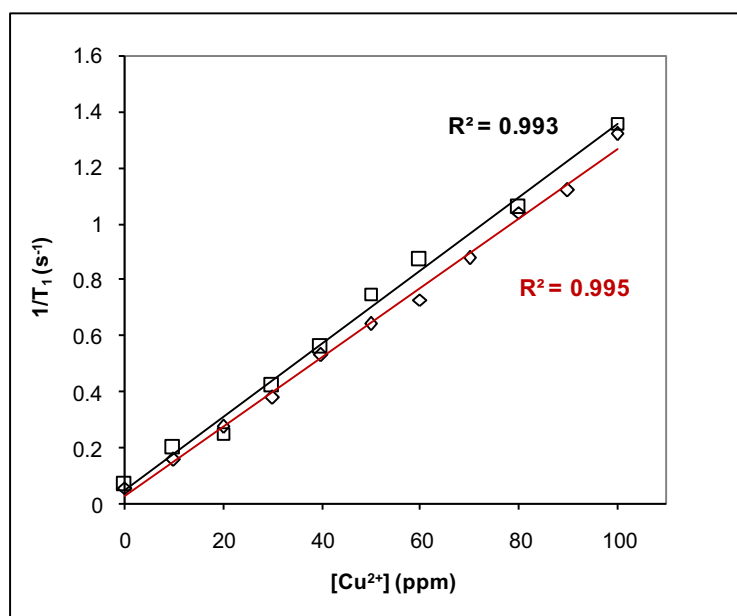


Figure 3: The effect of increasing amounts of Cu^{+2} on the relaxation time of water at 300° K in D_2O (◇) and in 3%Silica (□).

The effect of Cu^{+2} ions was also studied in 3% Silica dispersions, which is the silica ratio that will be used throughout this study in the model silica-based dispersions (Figure 3); indicate that complexation with Cu^{+2} ions cause a large drop in T_1 . There was no big difference in presence or absence of silica on T_1 of water in these samples which is a further proof of a complexation mechanism. The addition of transition metal ions to solid surfaces has been the focus of many studies especially in presence of silica particles and many methods were used such as titration methods [33] and ESR [34]. It was found that Cu^{+2} adsorb on oxide surfaces via coordination with the oxygen of the silanol groups but this interaction is weakest if the ligand available was water, while in presence of other ligands chelating to Cu^{+2} ions, the adsorption of these Cu-complexes on the silica surface tend to be stronger. This is very important since the presence of Cu^{+2} ions will participate in occupying some of the adsorption sites on the silica surface but even though, the relaxation time of water is expected to decrease due to the paramagnetic nature of the Cu^{+2} ions. In addition, the fact that relaxation time (T_1) of water is very sensitive to the presence of Cu^{+2} ions is very useful in determining fate of these ions in CMP slurries [5].

3.4 Effect of glycine and benzotriazole on T_1 of water:

It is known that glycine is very soluble in water and can form H-bonding with it, so it is expected to have a decrease in T_1 of both water and glycine which is exactly what we observed (Figure 4A). Addition of Glycine to D_2O causes a moderate decrease in T_1 for both water and glycine indicating the formation of H-bonding between glycine and water as expected. Also the addition of glycine causes changes in the pH of the solutions (more acidic). However, such changes in pH have small effect on T_1 [31]. The addition of glycine to 3% Silica solution was also studied (Figure 4B). By examining the data obtained we see a very small change in T_1 of both water and glycine upon addition of glycine compared to the case in absence of silica particles. This could suggest that adsorption of water and/or glycine to silica particles is more effective than the H-bonding and other interactions between glycine and water.

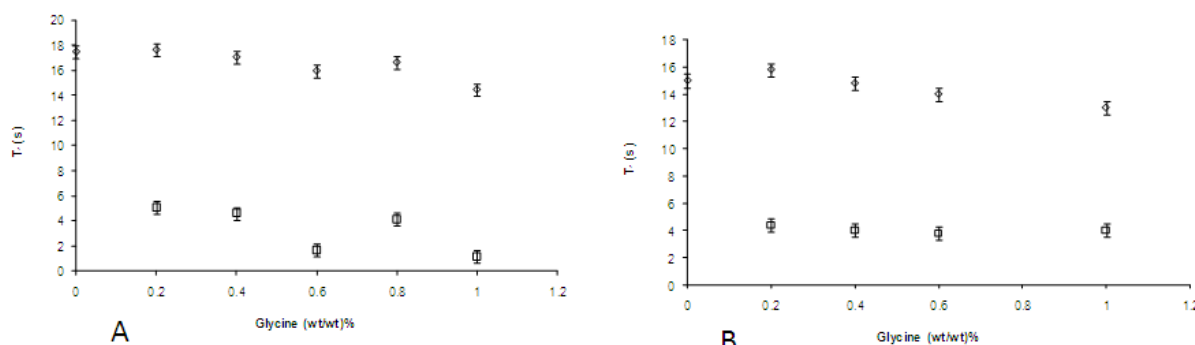


Figure 4: The effect of increasing amounts of glycine on the relaxation time of glycine ($\square$) and water ($\diamond$) at 300 °K in (A) D_2O and (B) 3% silica.

The addition of benzotriazole (BTA) to water was not expected to have a large impact on the relaxation time of both. Although BTA has N-H bond and a triazole ring which might interact with water through H-bonding but on the overall BTA is a hydrophobic compound and moderately soluble in water. In Figure 6, the relaxation data for both water and BTA protons (BTA1 at δ 7.9 ppm, BTA2 at δ 7.6 ppm, the third proton in BTA which is NH appeared at δ 16 ppm but was not monitored due to its broad and labile signal) are summarized. When BTA was first added to water in small quantities, no big change was observed. However, when the amount of BTA reached more than 0.2%, T_1 for both BTA and water protons start to decrease suddenly then reached a constant value. Since T_1 reached a steady state even though BTA was still being added, H-bonding was not thought to be the main cause. The cause of this change is most probably due to BTA-BTA interaction and the formation of some sort of aggregation in the BTA system [Figure 5] which was studied in more details by this group [21, 31].

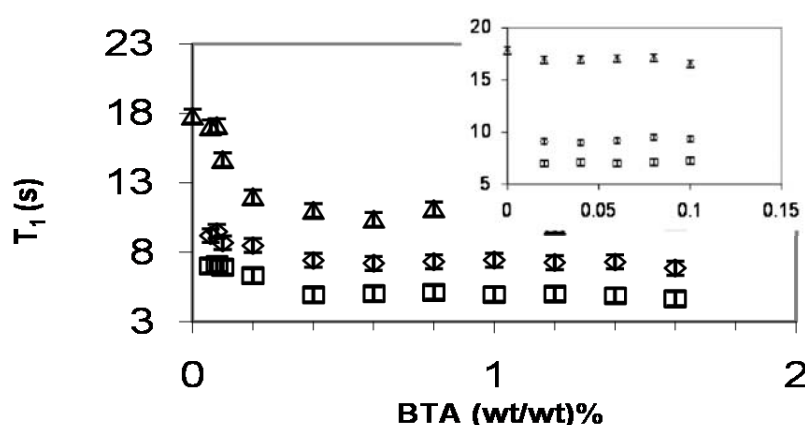


Figure 5: The effect of increasing amounts of BTA in D_2O on the relaxation time of BTA ($\diamond$ BTA1, $\square$ BTA2) and water (Δ) protons (A) over a large concentration range, (B) a clearer plot over the small concentration range of BTA at 300 °K.

The behavior of BTA in 3% silica dispersions was also studied. In presence of silica particles (Figure 6), the relaxation time of both BTA protons started to increase and for water protons, it was an increase upon the first introduction of BTA then it was stable through out the whole additions. This behavior was rather strange since a drop was expected due to adsorption of BTA molecules on silica surface and some sort of interaction (even small) with water. This could be explained by strong adsorption of BTA and forming a film at the same time covering the adsorption sites, hence any further addition of BTA will be marked with increase in T_1 (averaged) but still lower than T_1 for BTA in D_2O solutions. This assumption is strengthened by the way T_1 was changing for BTA1 and BTA2 protons. In D_2O , the BTA protons behaved differently and usually BTA1 (at ~7.9 ppm) has a higher T_1 value than BTA2 (at ~7.6 ppm). However, when BTA was present in silica dispersion, both protons had the same T_1 value indicating very similar effect on both of them which might be an indication of flat adsorption of BTA on silica surface.

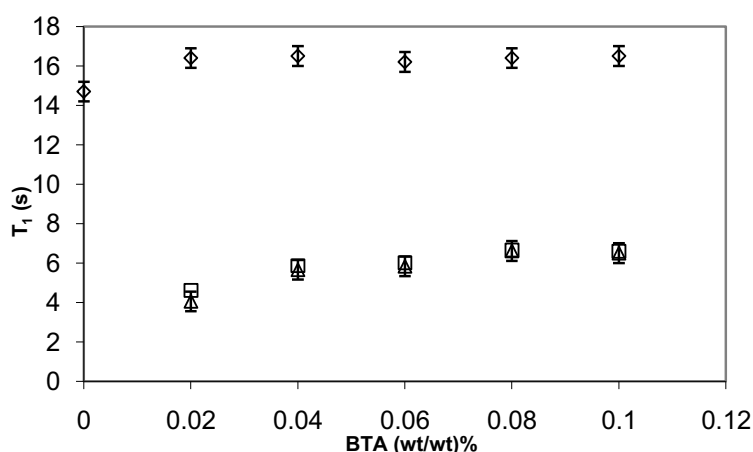


Figure 6: The effect of increasing amounts of BTA on the relaxation time of BTA ($\square$ is BTA1), (Δ is BTA2) and water ($\diamond$) at 300 °K in 3% silica.

In presence of Cu^{+2} ions, the relaxation time of glycine, BTA and water dropped significantly (Figure 7) in presence and absence of silica. As was expected, Cu^{+2} ions caused a sharp drop in T_1 values for all components but with different extents. The largest drop was in BTA1 protons (~6 seconds) which is understandable since BTA1 protons are close to the chelating centers in BTA molecule so they will be closer to Cu^{+2} ion. For BTA2, they were a little far away on the edge of BTA molecule. Glycine was also affected by Cu^{+2} ions presence and experienced a drop of ~3.5 seconds in T_1 values. The effect on water was less due to the high competition from BTA and glycine molecules. BTA and glycine are very strong complexing agents compared to water and any drop of T_1 of water is mainly due to its partial participation in the Cu-Gly complex and occupying the axial positions.

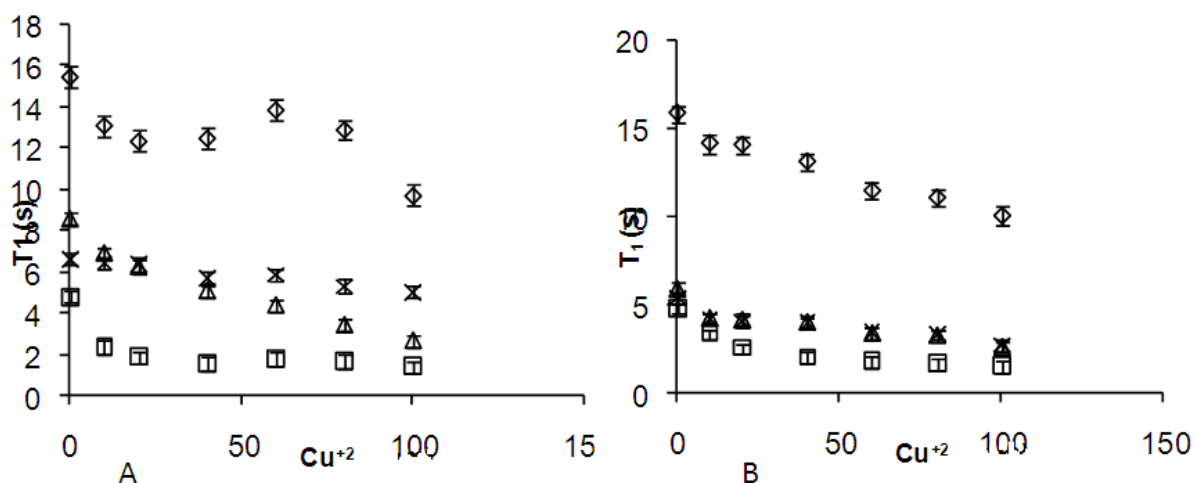


Figure 7: The effect of increasing amounts of Cu^{+2} to D_2O solutions containing BTA (0.1%) and glycine (1.0%) on the relaxation time of BTA (Δ BTA1, $\times$ BTA2), glycine ($\square$) and water ($\diamond$) in (A) D_2O and (B) 3% silica at 300 °K.

In order to understand the competition between BTA and glycine over complexation with Cu^{+2} ions, BTA was added to solutions containing glycine and Cu^{+2} in presence and absence of silica particles. The results are shown in Figure 8. BTA molecules were able to react with Cu^{+2} ions and remove both glycine and water from their complexes with Cu^{+2} in D_2O at 300 °K (Figure 8A); this is clearly seen from the T_1 data obtained after adding increasing amounts of BTA to prepared solutions containing glycine and Cu^{+2} ions. This addition caused the T_1 for both water and glycine to increase.

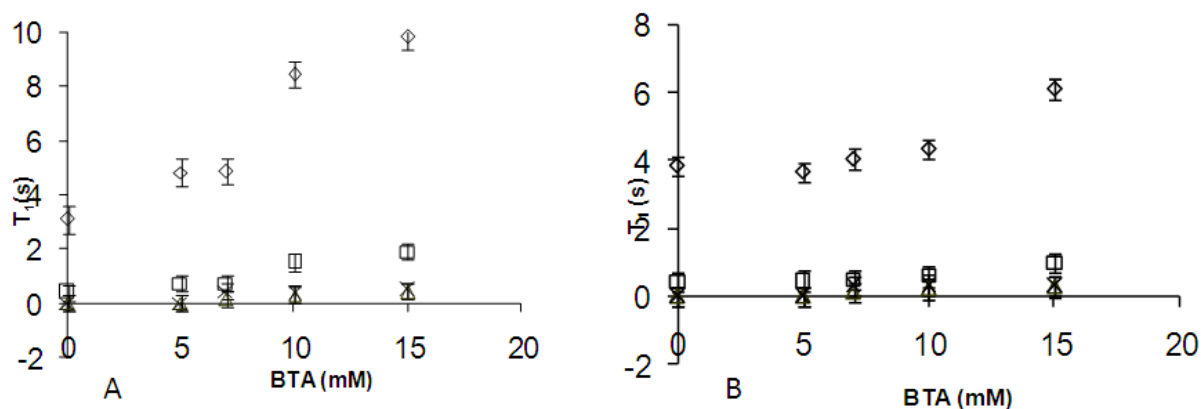


Figure 8: The effect of increasing amounts of BTA to samples containing BTA glycine (20 mM) and Cu^{+2} (1.0 mM) in D_2O on the relaxation time of BTA (Δ BTA1, $\times$ BTA2), glycine ($\square$) and water ($\diamond$) in (A) D_2O and (B) 3% silica at 300 °K.

The same controlled study was performed in a silica dispersion to see the effect of silica particles on these equilibria. Figure 8B summarizes the data obtained. The same behavior was observed, when BTA was added to a silica dispersion containing 20 mM of glycine and 1 mM of Cu^{+2} ions.

T_1 values for both glycine and water were increased while T_1 for BTA protons were very small and comparable with BTA-Cu complex values obtained earlier.

4. Conclusions:

From the data shown above, we see that BTA behavior has many consequences on the dynamics of these systems in presence and absence of silica particles. The presence of silica particles make BTA's behavior more smooth which is clear from T_1 values of both BTA protons compared to their values in D_2O solutions. This is an indication of both complexation and adsorption when both silica and Cu^{+2} ions are present; several studies mentioned an increased adsorption tendency of Cu^{+2} ions on metal oxide surfaces in presence of ligands other than water. For glycine behavior, although it forms well known and stable complexes with Cu^{+2} , but the competition of BTA towards complexation with Cu^{+2} is very high and since glycine is added to silica based Cu-CMP slurries for chelation with Cu^{+2} ions produced from the oxidation reaction, its role should be studied more. Even though BTA is highly competitive towards complexation but the BTA-Cu complex itself adsorbs strongly on the silica surface and also adsorbs on the Cu surface giving BTA its famous anticorrosion behavior.

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