

IMPACT OF ACID ADDITIVES ON ELASTIC MODULUS OF VISCOELASTIC
SURFACTANTS

A Thesis

by

WAQAR AHMAD KHAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Petroleum Engineering

Impact of Acid Additives on Elastic Modulus of Viscoelastic Surfactants

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ABSTRACT

Impact of Acid Additives on Elastic Modulus of Viscoelastic Surfactants.

(December 2011)

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Chair of Advisory Committee: Dr. Hisham Nasr-El-Din

In live acid solutions at concentrations of HCl namely 15-20 wt% HCl, elastic modulus remained quite low as compared to 10-12 wt% HCl concentrations. At 10 wt% HCl concentration, elastic modulus was 3.4 Pa observed whereas at 20 wt% HCl concentration, elastic modulus was 0.03 Pa. 0.5- 1.0 wt% concentrations of NaCl and CaCl₂ showed negligible effect on the elastic modulus while 3-10 wt % concentrations, substantially reduced the elastic modulus. As little as 0.5 wt% Fe (III) concentration reduced elastic modulus quite significantly. In live acids, increase in temperature resulted in viscous modulus dominating the elastic modulus. Corrosion inhibitor reduced values of elastic modulus significantly, at 10 wt% HCl concentration elastic modulus dropped from 5.1 Pa to 3.4 Pa. Preparation of acid solution with sea water showed negligible effect at higher concentrations of HCl (> 10 wt% HCl) whereas at lower concentrations of HCl the elastic modulus fell sharply.

For spent acid solutions, the elastic modulus at room temperature was quite low.

Increase in temperature resulted in the increase in elastic modulus up to 130 F after

which it decreased. At 190 - 205F and 18.8 rad/s, elastic modulus for 12 wt% HCl concentrations was 0.4 Pa whereas at 130 F, it was 2.25 Pa. At high temperatures (>130 F), the maximum elastic modulus shifted to higher concentrations of HCl namely 20 wt% HCl concentration. At 160 F, elastic modulus of 20 wt% HCl concentration at 18.8 rad/s was observed to be 2.6 Pa, whereas for 12 wt% HCl concentrations, it was 1.27 Pa. Throughout the HCl concentration and temperature range tested, viscous modulus dominated the elastic modulus for spent acid solutions.

The effects of organic acids namely, formic and acetic acid, on the elastic modulus of viscoelastic surfactants have also been investigated.

DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor Prof. Dr. Hisham Nasr- El- Din for the continuous support of my Master's study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my master's study.

I thank my fellow lab mates in Texas A&M University, for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last two years.

Last but not the least; I would like to thank my family: my parents Prof. Dr. Khalil Ahmad Khan and Naseem Khalil, for and supporting me spiritually throughout my life.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Carbonate reservoirs are heterogeneous, with large variations in rock permeability. When carbonate hydrocarbon bearing formations are acidized by hydrochloric acid (HCl), stimulation fluids will flow through the path of the least resistance where the permeability is high or the damage (skin) is low. A few dominating channels in the matrix are created and the majority of the treatment acid will flow along the channels, leaving the rest of the rock untreated. This phenomena is undesirable, particularly when long vertical sections or horizontal open holes are to be acidized. Therefore, a diverting agent is often, if not always, needed. Polymer gels, foams or rock salt are commonly used as diverting agents during matrix acidizing of carbonates. Effective diversion is the key for the success of carbonate matrix stimulation treatments, especially for long wells.

Various systems were introduced to enhance diversion by increasing the viscosity of the injected acid. Depending on the viscosifying agent, these systems can be divided into two main categories: polymer-based acids and surfactant-based acids.

Acid-soluble polymers have been used to increase the viscosity of HCl, and to improve its performance. As the viscosity of the acid increases, the rate of spending

This thesis follows the style of *SPE Journal*.

decreases and as a result deeper acid penetration can be achieved.

Cross linked acids were introduced in the mid '70s as cited by (Metcalf et al. 2000). As compared to uncrosslinked polymers or regular acids, crosslinked polymer based acids have much higher viscosity. The first type of cross-linked acid is cross-linked on the surface and reaches the formation already in the form of a gel. It consists of a polymer, a crosslinker, and other acid additives (Johnson et al. 1988). The second type of crosslinked acid forms the gel insitu. The acid in this case reaches the formation uncrosslinked, and the crosslinking reaction occurs in the formation (Saxon et al. 2000; Taylor and Nasr-El-Din 2002).

In the current market, the in situ gelled acid is prepared by gelling the HCl acid with a polymer and adding a crosslinker and an internal breaker. When the acid spends upon dissolving carbonate, the increase of pH causes the crosslinker to activate and the gelled acid becomes crosslinked. This crosslinked gel temporarily blocks the wormholes being created and diverts acid elsewhere. Any further increase of pH by complete spending of the acid causes the breaker to activate, and the in situ gelled acid hence breaks down to near water-like viscosity to assist easy flow back.

However, several concerns have been expressed regarding the use of polymer based fluids in matrix acidizing treatments (Lynn and Nasr-El-Din 2001; Nasr-El-Din et al. 2002). Since the system contains polymers, and the bulk fluid viscosity is dramatically

reduced, there is still polymer residue which can plug the face of the wormholes. (Lynn and Nasr-El-Din 2001) noted precipitation of the crosslinker Fe(III) when in-situ gelled acids were used to enhance the permeability of tight carbonate cores at high temperature. (Nasr-El-Din et al. 2002) showed that the crosslinker (Fe (III)) may precipitate in sour environments.

To overcome some problems encountered with polymer-based fluids, viscoelastic surfactant-based acid systems were developed. These systems are easy to mix in the field, and use fewer additives than those utilized in polymer based acids. Unlike the polymer based gelled acid systems, the new material does not leave any residue once it has broken (Chang et al. 2001) nor does it require any metallic crosslinker.

Viscoelastic based acids have performed successfully in high permeability contrast formations where polymer based acids have failed (Al-Mutawa et al. 2005; Al-Nakhli, Ayman R. et al. 2008). More than 250 wells (oil, gas, water injectors and disposal wells) have been successfully treated with viscoelastic surfactants (Nasr-El-Din and Samuel 2007). Viscoelastic surfactants have also proven to be effective in sour environments where hydrogen sulfide levels reached nearly 10 mol%. The fluid has been termed as non-damaging in terms of clean-up efficiency and permeability (Kreh 2009). Unlike conventional crosslinked fluids, this fluid does not contain any metallic crosslinkers, such as iron or zirconium. This feature is particularly advantageous in sour gas wells in which there are concerns of hydrogen sulfide (H_2S) reacting with an iron crosslinker

producing insoluble iron sulfide. When the acid spends, these metals can also precipitate as hydroxides. The tendency of damage cause by precipitation of metal hydroxides and sulfides is eliminated because metals are not used with this VES system. Viscoelastic based acids have also been utilized effectively as a foam to enhance acid diversion in a vertical, perforated oil producer (Nasr-El-Din et al. 2005).

Viscoelastic surfactant-based systems are gelling systems that use surfactants as their gelling agents. Surfactants are made of two parts: a hydrophilic group called the head, and a lipophilic group called the tail. The hydrophilic group is water soluble while the lipophilic group is oil soluble.

A surfactant's preference to oil or water-based systems is determined by the size of its head and tail. Surfactants with larger heads are water soluble and surfactants with larger tails are oil soluble. There are five different types of surfactants namely anionic, cationic, nonionic, amphoteric and zwitterionic. Anionic surfactants have a negatively charged head. Cationic surfactants have a positively charged head. Nonionic surfactants have no charge. Amphoteric surfactants are pH sensitive and have a positively charged head for acidic pH, no charge for neutral pH and a negative charge for alkaline pH.

Carbonate formations are positively charged and sandstone formations are negatively charged. Because of these charges, anionic surfactants will oil-wet carbonates and water-wet sandstones, cationic surfactants will water-wet carbonated and oil-wet sandstones, nonionic surfactants will water-wet both carbonates and sandstones and amphoteric

surfactants will both water-wt and oil-wet carbonates and sandstones depending on the pH of the fluid.

When surfactants are used as gelling agents they are added at much larger loadings than normal. When surfactants are added to water-based fluids they like to expel their lipophilic tails from the surface of the fluid. As more and more surfactants are added, they line up along the fluid's edge until no more can fit. When no more surfactants can expel their lipophilic tails, they start to form spherical aggregates called micelles. This concentration is usually around 0.5% by volume. The surfactants in these micelles group together with their lipophilic tails to the inside and their hydrophilic heads to the outside. This is in an effort to protect their lipophilic tails from the water-based fluids they are mixed into.

As the concentration of surfactants is increased even further, the spherical micelles become long worm-like micelles similar to polymer strings. These long worm-like micelles are what give the system its viscosity. When many worm-like micelles form, they tangle together, helping build viscosity.

As the concentration of surfactants is increased even further, the spherical micelles become long worm-like micelles similar to polymer strings. In dilute solution, the preferred self-assembled geometry may be spherical micelles, but as surfactant concentration increases, it often becomes more energetically favorable for micelles to grow axially into rodlike micelles (Kumar et al. 2007; Schubert et al. 2003). The linear

growth of these micelles can eventually result in overall contour lengths of micrometers (Kumar et al. 2007). These “wormlike” or “threadlike” micelles typically become entangled into a transient network, thereby imparting viscoelastic properties to the solution. While polymers are held by strong covalent bonds that are not easily broken, wormlike micelles are held by weak, physical bonds that continuously break and reform. There is thus a continuous exchange for surfactant unimers between the micelles, and the micellar breaking dynamics influences the rheological properties of the fluid (Kumar et al. 2007).

The main advantage of using a viscoelastic surfactant-based gelling system is the ease of cleanup. As the pH of the system approaches neutral, the micelles start to break. This means as the acid spends; the gelling agents naturally break down. This is a very handy characteristic of viscoelastic systems: they essentially break themselves. The system is also broken down by hydrocarbons. As hydrocarbons mix with the fluid, they start to attract the lipophilic tails of the surfactants. The micelles are essentially turned inside, out breaking the gel’s viscosity in the process. So if not all the acid is spend when the well is ready to be flowed back, the formation fluid will break whatever viscosity is left. If the well is a dry gas well, a chemical breaker can be included or a preflush with a solvent can be performed. If a solvent is used in the preflush, it will be the first thing that contacts the gelled system when flowing back and will break it as if the well were an oil producing zone.

From a rheological standpoint, wormlike micelles typically exhibit a viscoelastic response with a finite relaxation time. It is well known that viscoelastic surfactant solutions can behave, under certain conditions, like an ideal Maxwell material with a single characteristic relaxation time, λ , for the whole system. Deviations from the monoexponential relaxation behavior are observed at high frequencies due to Rouse-like behavior of the micellar segments. However, the linear rheological properties of wormlike micellar solutions depend on the ratio of breaking and reputation times, denoted

$$\zeta = \frac{\lambda_{br}}{\lambda_{rep}}$$

where the weak micellar structures break and recombine on an individual timescale denoted λ_{br} .

Since G' and G'' represent the elastic and viscous components of viscoelasticity, it has been suggested that the inverse of the frequency at which G' and G'' intersects is the characteristic relaxation time of the polymer solution (Delshad et al. 2008). This intersection has also been described as an indication of the onset of a phenomenon called entanglement coupling. This is a phenomenon whereby there is a strong coupling of neighboring molecules to a molecular motion along the chain. This relaxation time is in turn used to calculate the Deborah number, defined as “ratio of magnitude of the elastic forces to that of the viscous forces”.

The two main types of viscoelastic surfactants that have been used in the industry are amphoteric and cationic. Our study involves amphoteric surfactants, namely, amidoamine oxide surfactant. The basic structure was shown by Cawiezel et al. (2007). At low pH, the surfactant is protonated and the net charge of the molecule is positive. (Li et al. 2010) reported its rheological properties in water, live acids and spent acids. One of the results showed that the addition of iron control agents could reduce the apparent viscosity of spent acids. They also studied the organic acids/ chelating agents on the viscosity of amidoamine oxide surfactant. It was shown that the addition of organic acids / chelating agents to the spent acid reduces its apparent viscosity, thus organic acids can be used to break the VES acid. In order to compensate for the reduced viscosity cause by organic acids or chelating agents, more concentrated surfactant should be added to the acid system.

(Al-Nakhli, Ayman R. et al. 2008) noted that amphoteric and cationic surfactants contained functional groups that can interact in concentrated HCl acid solutions with Fe (III). Viscoelastic surfactants can form a complex with iron (III) which precipitates at high iron (III) concentrations. It is observed that temperature, pH, shear conditions and acid additives have a profound influence on the apparent viscosity of the surfactant- acid system (Al-Nakhli, Ayman Raja et al. 2008).

CHAPTER II

EXPERIMENTAL PROCEDURE/ METHODS

Acid Preparation

Live Surfactant-Based Acid: Two acid formulas were used in this work: For surfactant A (AROMAX APA-T), 5 wt% of amidoamine oxide was used with different concentrations of HCl, whereas for surfactant B (AROMAX APA-TW), 6.2 wt% of amidoamine was used with different concentrations of HCl. The difference in surfactant concentrations was because of the different activity coefficients of the two surfactants. Regular acid solutions were prepared by mixing the corrosion inhibitor and HCl acid with water. The solutions were stirred using a magnetic stirrer using a Teflon agitator. Every effort was made not to contaminate the acid with iron.

Spent Surfactant-Based Acid: Calcium carbonate was obtained by crushing limestone cores. It was carefully added to neutralize the acid until pH was 4 to 5. Corrosion Inhibitor and other additives were then added to the spent acid. A blender was used to mix these solutions; the viscoelastic surfactant was added quickly as the last additive to the spent-acid mixture. The whole mixture was blended at a high shear rate (approximately 4,000 rev/min) for 1 to 2 minutes.

Removal of Air Bubbles: A substantial amount of air bubbles were generated in both live acid and spent acid solutions. The samples were centrifuged at 3500 rpm for approximately 15 minutes for the removal of the air bubbles.

Materials: The viscoelastic surfactant (amidoamine oxide) used was a mixture of an amphoteric surfactant and solvent. Hydrochloric acid (ACS reagent grade, 36.8 wt% and deionized water (resistivity = 18.2 M Ω .cm) were used to prepare the solutions. Acid concentration was determined by titration using 1N sodium hydroxide solution. Acid additives examined included: Corrosion Inhibitor, Sodium Chloride, Calcium Chloride, and Ferric Chloride and Organic acids. Seawater was also used to prepare the acid, in order to observe its effect on the elastic modulus. Its composition is given in Table 1. Calcium chloride dehydrate was purchased from VWR, Anhydrous ferric chloride and Sodium chloride was obtained from Sigma-Aldrich.

Table 1: Composition of Seawater.

Ions	Concentration mg/l
Na ⁺	16,877
Ca ²⁺	664
Mg ²⁺	2,279
Si ²⁺	0
Cl ⁻	31,107
HCO ₃ ⁻	193
SO ₄ ²⁻	3,560
TDS, mg/l	54,680

Measurements: Live acids were mixed using a magnetic stirrer. For spent acids, a blender was used at high shear rate (approximately 4,000 rev/min) for 1 to 2 minutes. Acid concentration and pH values for the collected samples were measured using Orion 370 PerpHecT Ross Electrode. Elastic modulus measurements were carried out on Grace M5600 rheometer.

CHAPTER III

EFFECT OF HCL CONCENTRATION AND ADDITIVES ON LIVE VISCOELASTIC ACID SYSTEM FOR AROMAX APA-T

Effect of HCl Concentration on VES

Fig. 1 shows the effect of HCl concentration on the elastic modulus. A maximum elastic modulus in the vicinity of 10% HCl concentration is observed followed by a steep decline. At high concentrations of HCl (15wt% to 20 wt%) the elastic modulus has a significantly lower value than that observed at 10 wt% HCl concentration, i.e. solution is no longer exhibiting elastic properties.

Effect of Corrosion Inhibitor on VES

In order to assess the effect of corrosion inhibitor concentration on elastic moduli of viscoelastic surfactant solutions, two concentrations of corrosion inhibitor were tested. One was at 0.1%, whereas the second concentration was at 1% (recommended by the chemical provider). The addition of 1 wt% corrosion inhibitor significantly lowers the magnitude of elastic modulus as compared to 0.1% corrosion inhibitor. In the case of 10 wt% HCl concentration, where a maximum in elastic modulus was observed, the difference is almost twice. **Fig. 2** shows the difference in magnitude of elastic modulus with the increase of corrosion inhibitor concentration.

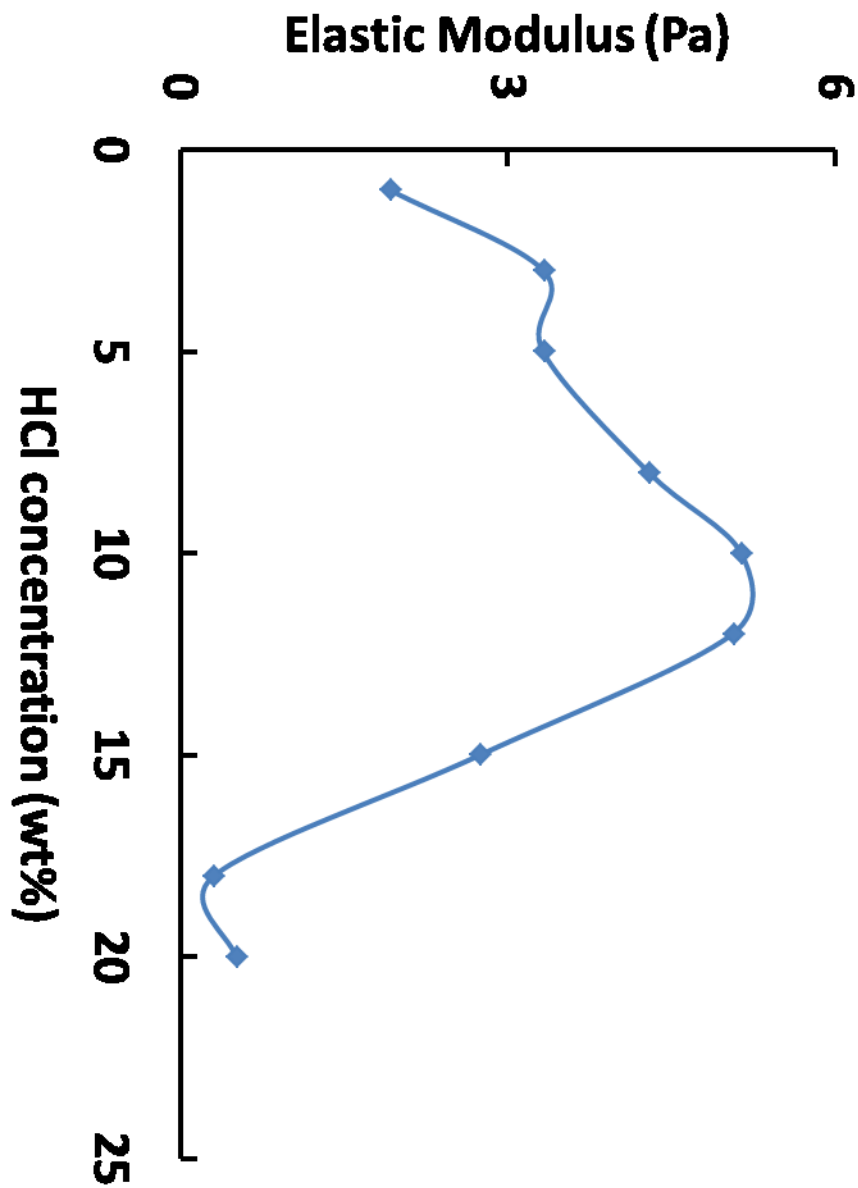


Figure 1-- Elastic modulus increases with increasing HCl concentration until 10 wt% HCl concentrations after which a sharp decline is observed. The readings are noted at 18.8 rad/s at corrosion inhibitor concentration of 0.1 wt%.

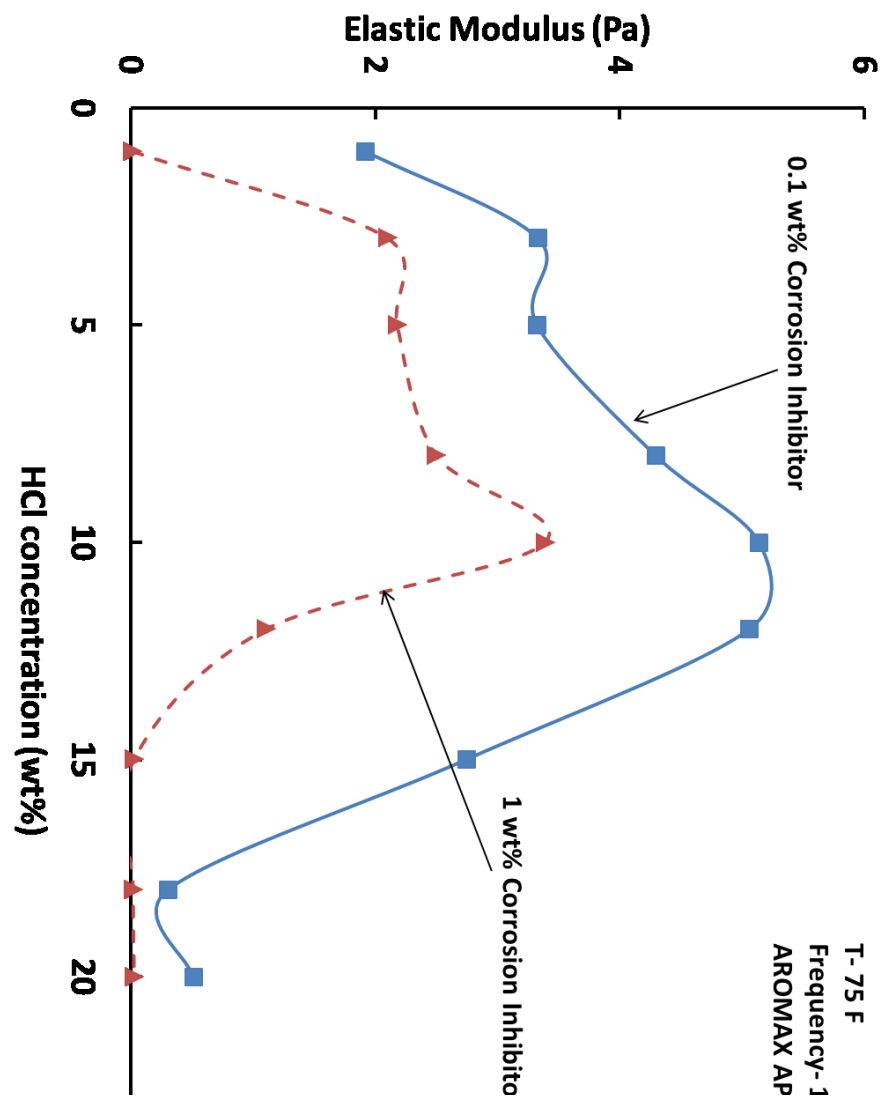


Figure 2 -- Elastic modulus is significantly reduced with the increase in corrosion inhibitor concentration. At concentrations above 15 wt% HCl at 1 wt% corrosion inhibitor concentration, elastic modulus is negligible.

Effect of Monovalent Cations on VES

The impact of monovalent cations on viscoelastic based surfactant solutions was studied by the addition of NaCl. In the case of 20 wt% HCl solutions, the salt was found to not dissolve completely. **Fig. 3** and **Fig. 4** compare the effect of NaCl concentrations on elastic modulus at 10 wt% HCl concentration and 20 wt% HCl concentrations respectively with respect to frequency. NaCl shows no effect at 20 wt% HCl concentration on the elastic modulus. The effect of NaCl concentration with 1 wt% corrosion inhibitor concentration is observed as expected. As shown in **Fig. 5**, the addition of 3 wt% NaCl shows the elastic modulus to be higher at high frequencies which is expected since the maximum elastic modulus is observed at a value slightly higher than 10 wt% HCl concentration, whereas further increase of NaCl concentration to 10 wt% reduced the elastic modulus significantly. As explained later in the discussion, this is believed to be due to the increase in Cl^- ion concentration.

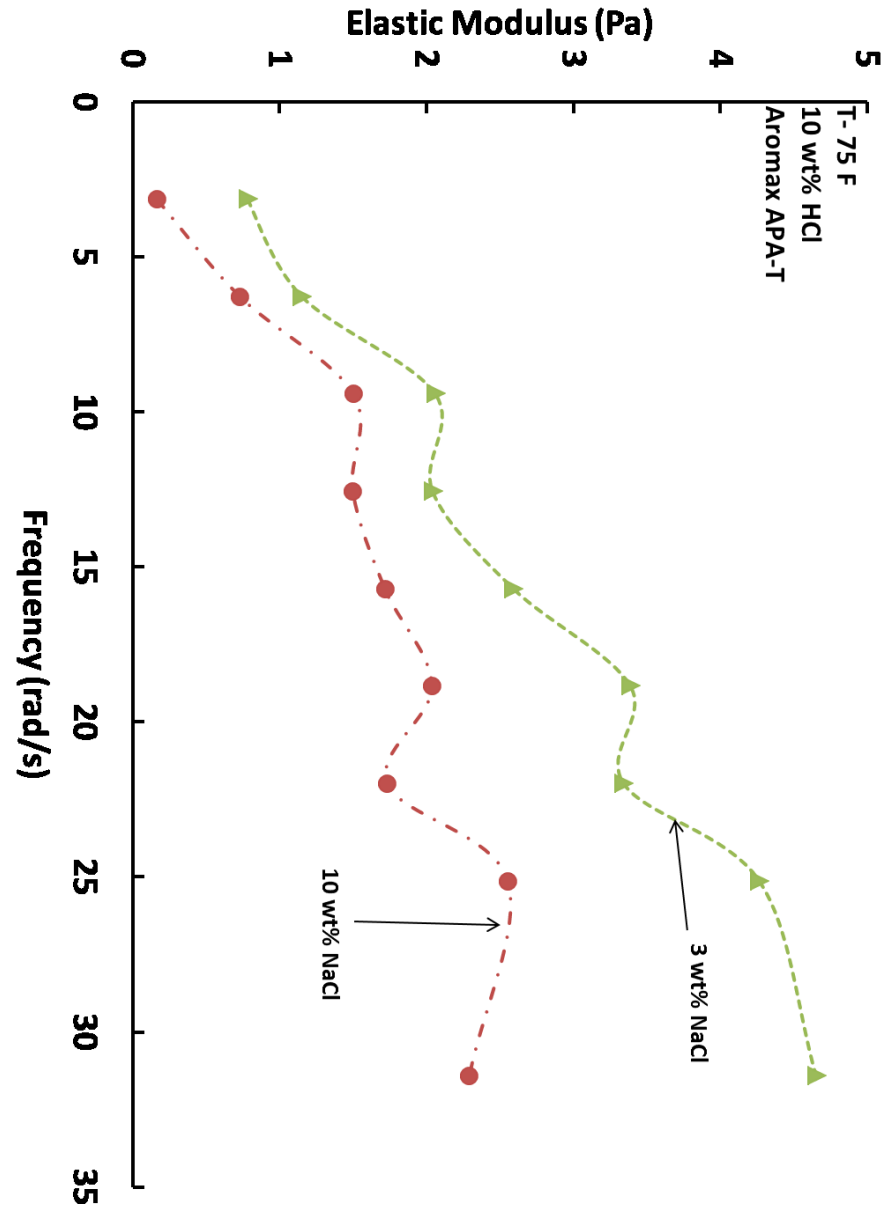


Figure 3-- Addition of 10wt% NaCl to 10 wt % HCl with 1 wt% corrosion inhibitor is found to reduce the elastic modulus significantly. 3 wt% NaCl shows negligible effect on elastic modulus. At 10 wt% NaCl, salt was found not to dissolve completely.

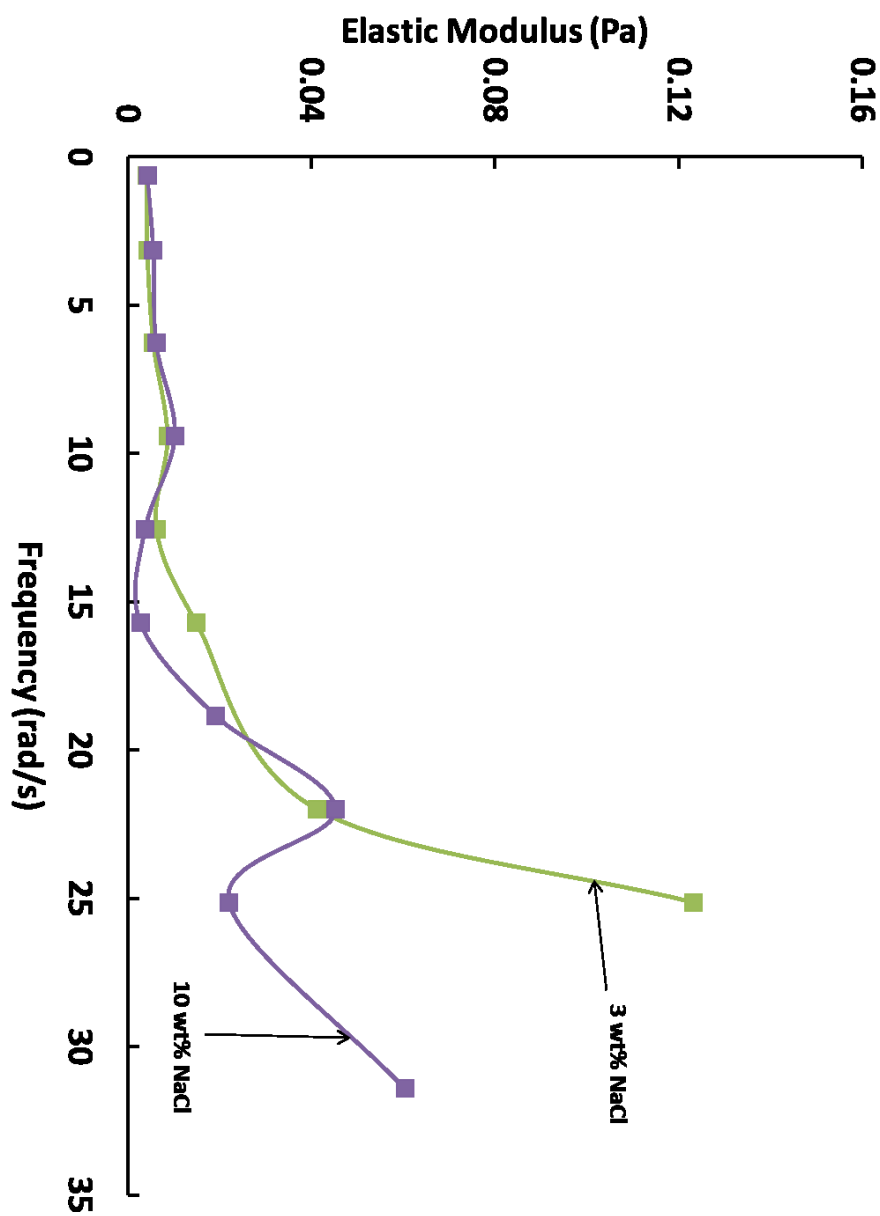


Figure 4 – Addition of 10wt% NaCl to 20 wt % HCl with 1 wt% corrosion inhibitor is found to reduce the elastic modulus. 3 wt% NaCl shows negligible effect on viscous modulus. At 10 wt% NaCl, complete dissolution did not occur. Magnitude of elastic modulus is significantly lower than what was observed at 10 wt% HCl.

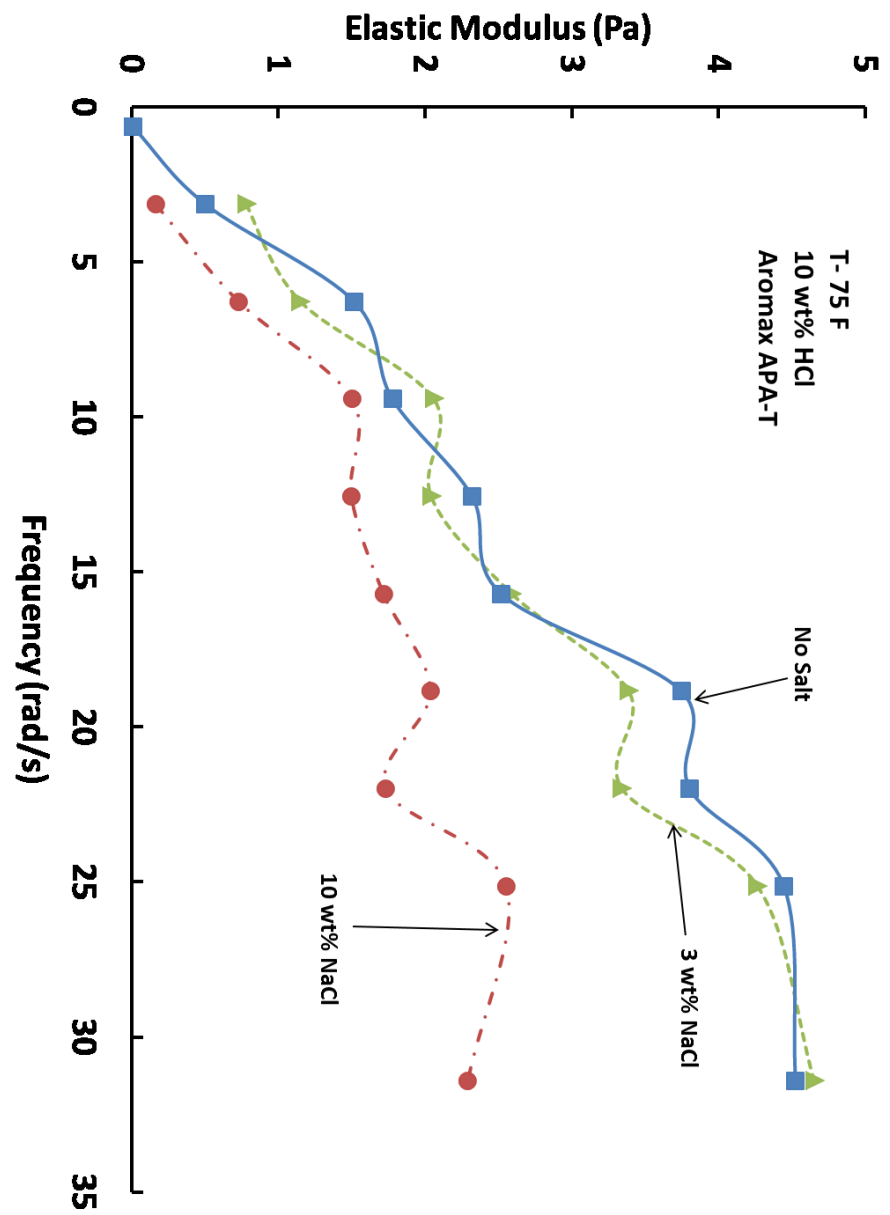


Figure 5 --When compared with 0 wt% NaCl concentration, slight addition of NaCl does not impact the elastic modulus whereas further addition reduces the elastic modulus significantly.

Effect of Divalent Cations on VES

The impact of divalent cations on viscoelastic based surfactant solutions was studied by the addition of CaCl_2 . The addition of 0.5 -1.0 wt% CaCl_2 to viscoelastic surfactant based acid showed little or no impact on the elastic modulus whereas further increase decreased the elastic modulus significantly.

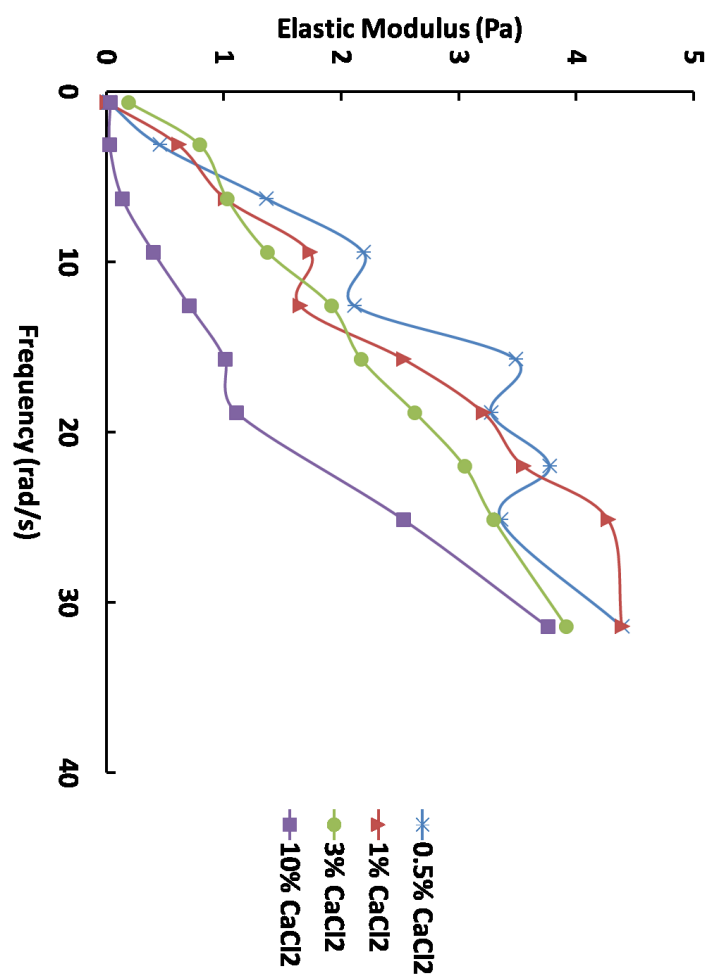


Figure 6 -- Addition of 0.5-1 wt% CaCl_2 does not seem to affect the elastic modulus whereas further increase reduces the elastic modulus significantly.

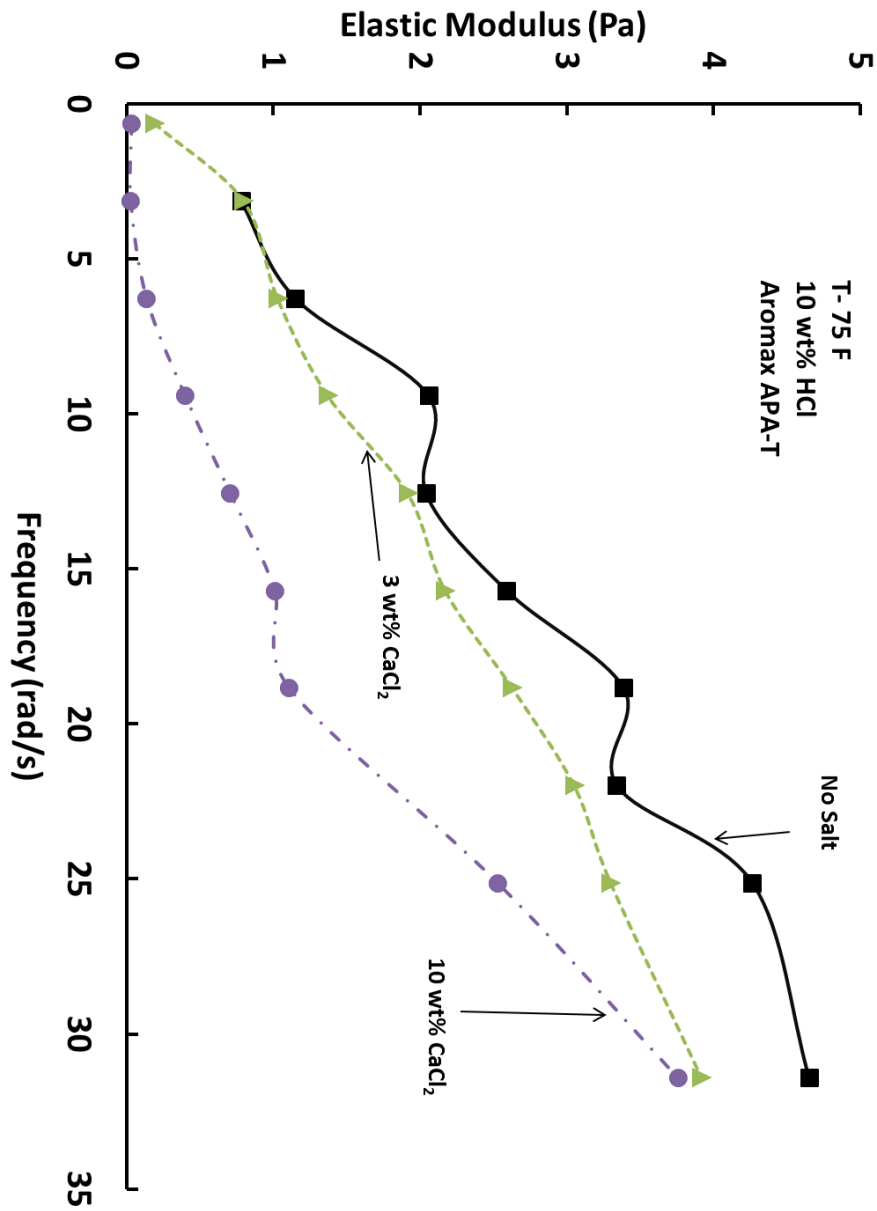


Figure 7--Comparison of the effects of addition of CaCl₂ with 0 wt% CaCl₂ solution. 0.5 -1 wt% shows little effect on elastic modulus whereas further increase reduces the elastic modulus significantly.

Effect of Trivalent Cations on VES

The impact of trivalent cations on viscoelastic based surfactant solutions was studied by the addition of FeCl_3 . Fe (III) ions were observed to affect the elastic modulus with as little as 0.5 wt% affecting the elastic modulus significantly. At 3 wt% and 10 wt% FeCl_3 concentration, precipitation was observed.

Effect of Seawater on VES

In place of de-ionized water, sea water was used to prepare live VES solutions. In all the 3 concentrations tested i.e. 3 wt%, 10wt% and 20 wt% HCl, elastic modulus was observed to decrease, particularly sharply for 3 wt% HCl solution.

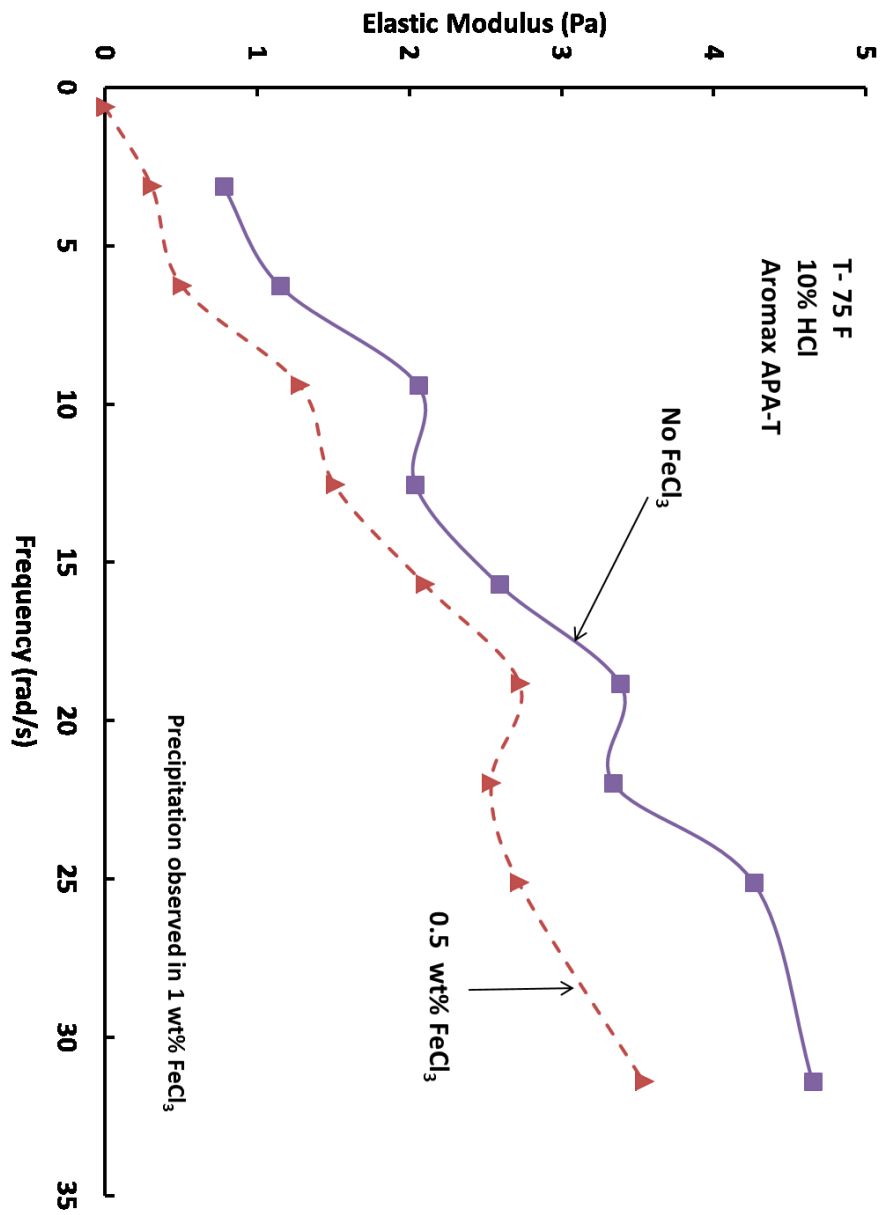


Figure 8--Addition of Fe (III) ions reduces the elastic modulus significantly. At 3 wt% an emulsion was observed after which the elastic modulus was found to reduce quite significantly.

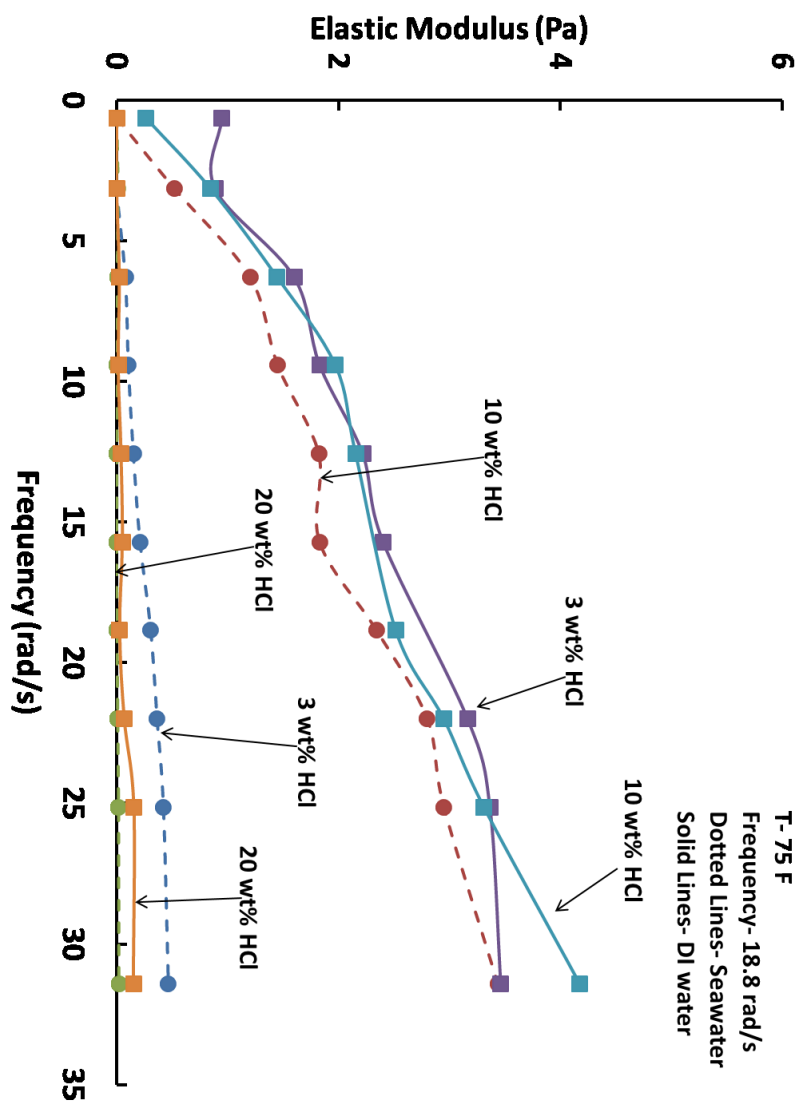


Figure 9 -- Elastic modulus was observed to decrease with the usage of sea-water to prepare the acid solutions in place of de-ionized water.

Effect of Temperature on VES

Because 10 wt% HCl showed the highest elastic modulus, to ascertain the effect of temperature on elastic modulus, readings were taken at 100 F, 130 F and 150 F. Elastic

modulus was observed to decrease with the increase of temperature. A significant drop in elastic modulus was observed at 130 F.

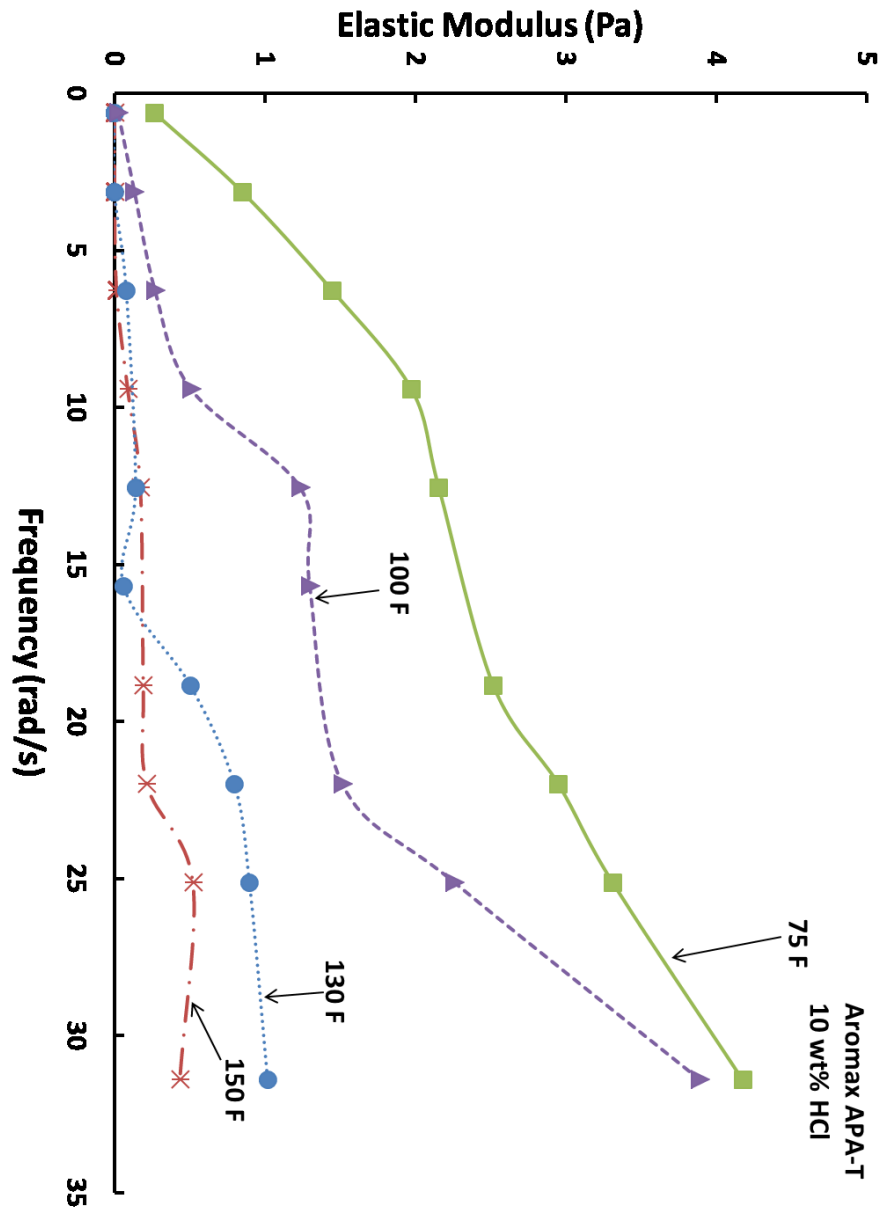


Figure 10-- At 150 F, elastic modulus has decreased quite significantly when compared with room temperature.

CHAPTER IV

EFFECT OF HCL CONCENTRATION AND ADDITIVES ON LIVE
VISCOELASTIC ACID SYSTEM FOR AROMAX APA-TW**Effect of HCl Concentration on VES**

Fig. 11 shows the effect of HCl concentration on the elastic modulus. A maximum elastic modulus in the vicinity of 5% HCl concentration is observed followed by a steep decline. At high concentrations of HCl (15wt% to 20 wt%) the elastic modulus has a significantly lower value than that observed at 10 wt% HCl concentration, i.e. solution is no longer exhibits elastic properties.

Fig. 12 compares the elastic modulus of AROMOX APA-TW with AROMOX APA-T. It was observed, elastic modulus achieves a maximum at a lower concentration of 5 wt% HCl concentration with AROMOX APA-TW as opposed to the 10wt% HCl concentration observed with AROMOX APA-T. It was also observed at room temperature for AROMAX APA-T, at concentrations 3 wt%, 10 wt% and 12 wt% HCl, elastic modulus was observed to overcome the viscous modulus i.e. fluid behaved as a viscoelastic material. At all other concentrations tested, the viscous modulus dominated the elastic modulus over the range of frequencies, i.e. fluid behaved as a liquid rather than a viscoelastic material. For AROMAX APA-TW, the elastic modulus was observed to overcome the viscous modulus at 5 wt% and 12 wt% HCl concentrations.

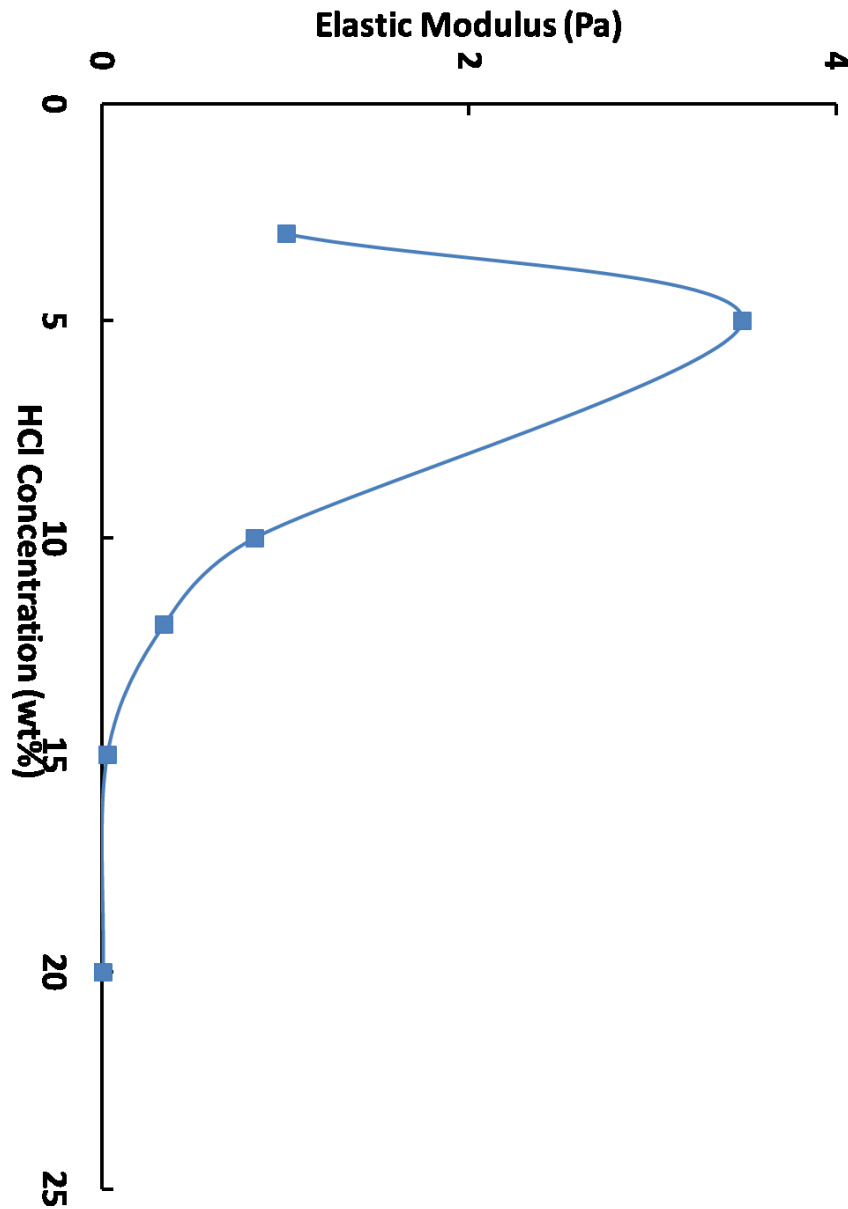


Figure 11 -- Elastic Modulus increases with increasing HCL concentration until 5 wt% HCl concentration, after which a sharp decline is observed. The readings are taken at 18.8 rad/ s at a corrosion inhibitor concentration of 1 wt%

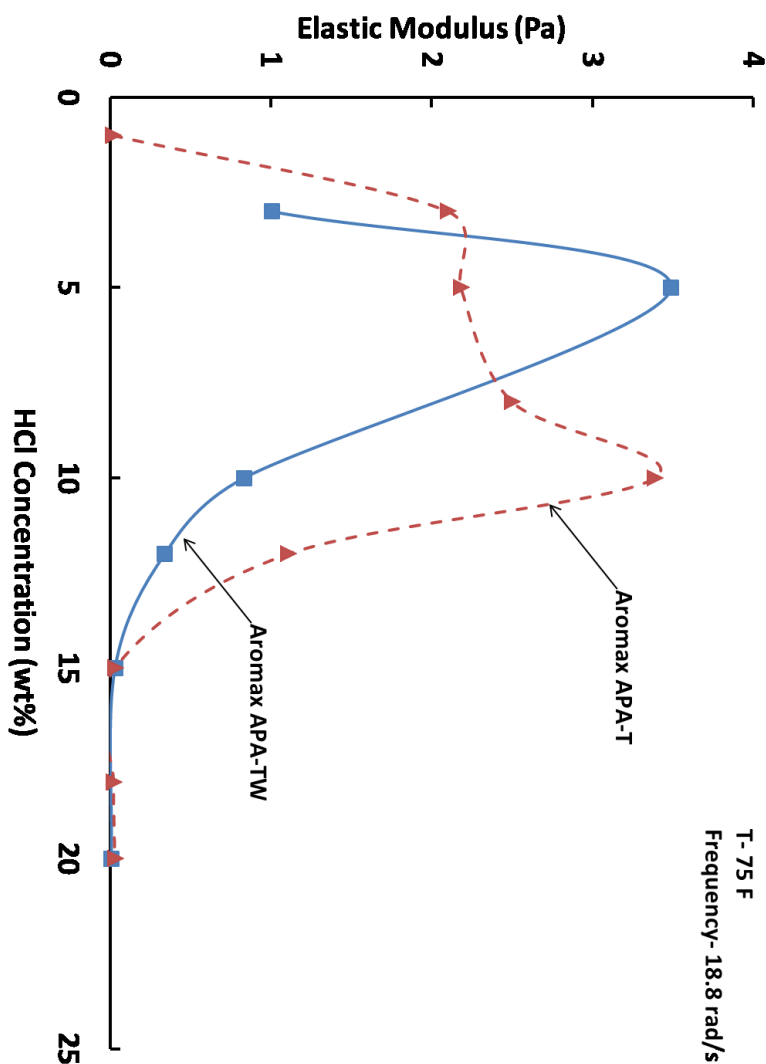


Figure 12 --Maximum for AROMOX APA-TW was observed at a lower HCl concentration as opposed to AROMOX APA-T (5 wt% HCl as opposed to 10 wt% HCl concentration)

Effect of Temperature on VES

Fig. 13 shows the effect of temperature on elastic modulus of AROMOX APA-TW with HCl concentration. Elastic modulus falls sharply with the increase in temperature while maintaining the maximum elastic modulus at 5wt% HCl concentration, however, at

220F, the maximum elastic modulus was observed at 15 wt% HCl concentration. It was also observed, at room temperature, the elastic modulus overcame the viscous modulus at 5 wt% and 12 wt% HCl concentrations, whereas at 130 F, elastic modulus overcame the viscous modulus at 3 wt% HCl concentration, at 180 F, it overcame at 5 wt% HCl concentration and at 220 F, elastic modulus dominated the viscous modulus over the entire range of frequencies at 15 wt% HCl concentration i.e. fluid behaved as a gel at 15 wt% HCl concentration at 220 F.

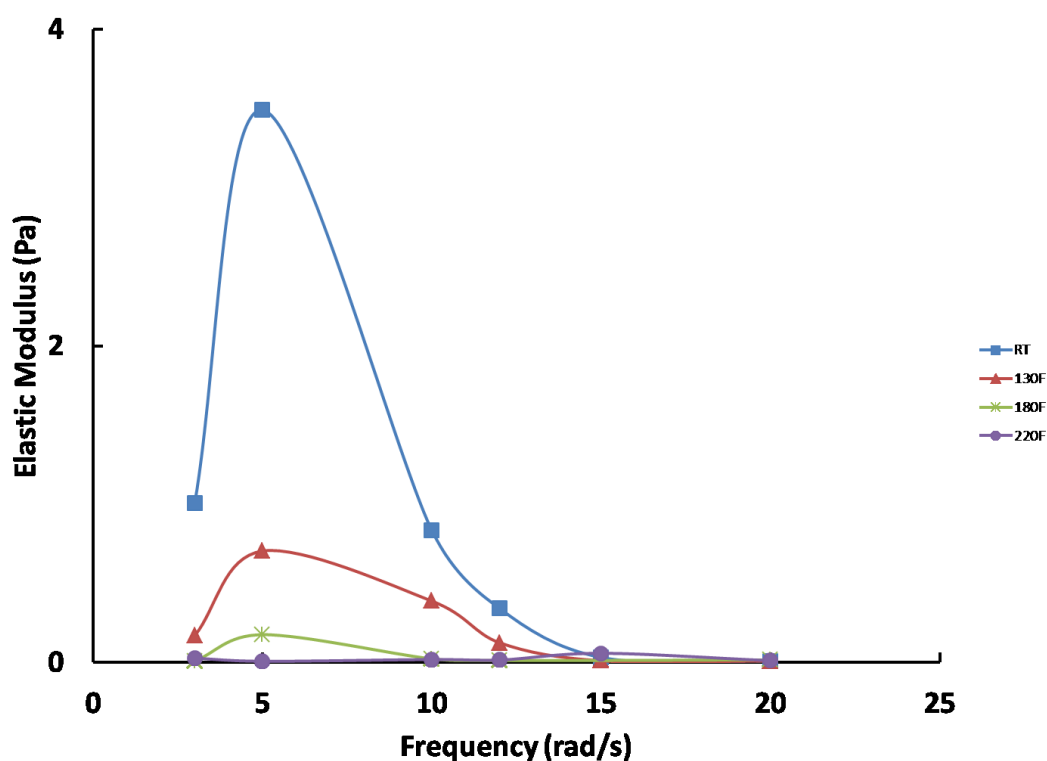


Figure 13 -- Increase in temperature results in the elastic modulus decreasing. At 220 F, maximum elastic modulus shifts from 5 wt% HCl concentration to 15 wt% HCl concentrations. The readings were measured at 18.8 rad/s.

CHAPTER V

EFFECT OF HCL CONCENTRATION AND ADDITIVES ON SPENT
VISCOELASTIC ACID SYSTEM FOR AROMAX APA-T

Fig. 14 shows the effect of HCl concentration on the elastic modulus of spent acid at room temperature. Compared to the values observed for the elastic modulus in live VES solutions at room temperature, the values are quite low. The elastic modulus overcomes the viscous modulus at high frequencies at all concentrations, indicating the entanglement of wormlike micelles.

Fig. 15 shows the effect of temperature on the elastic modulus of spent acid at 130 F. As opposed to live VES acid solutions, where the elastic modulus was observed to decrease rapidly with temperature, the elastic modulus was observed to increase substantially at 130 F. The viscous modulus dominates the elastic modulus at all frequencies at 130 F, indicating the absence of worm entanglements.

Fig. 16 shows the effect of temperature on the elastic modulus of 10 wt% HCl spent acid solution. The elastic modulus appears to be decreasing with temperature, but at 130 F, it increases rapidly. (Li 2009) showed the viscosity for spent acid system at 20 wt% HCl solution to be a maximum at 130 F.

Fig. 17 compares the effect of temperature on elastic modulus at room temperature and 130 F. The elastic modulus is significantly higher at 130 F as opposed to elastic modulus at room temperature. It was observed, throughout the frequency range tested at 130 F, viscous modulus dominated the elastic modulus at all frequencies, i.e. fluid is not behaving as viscoelastic.

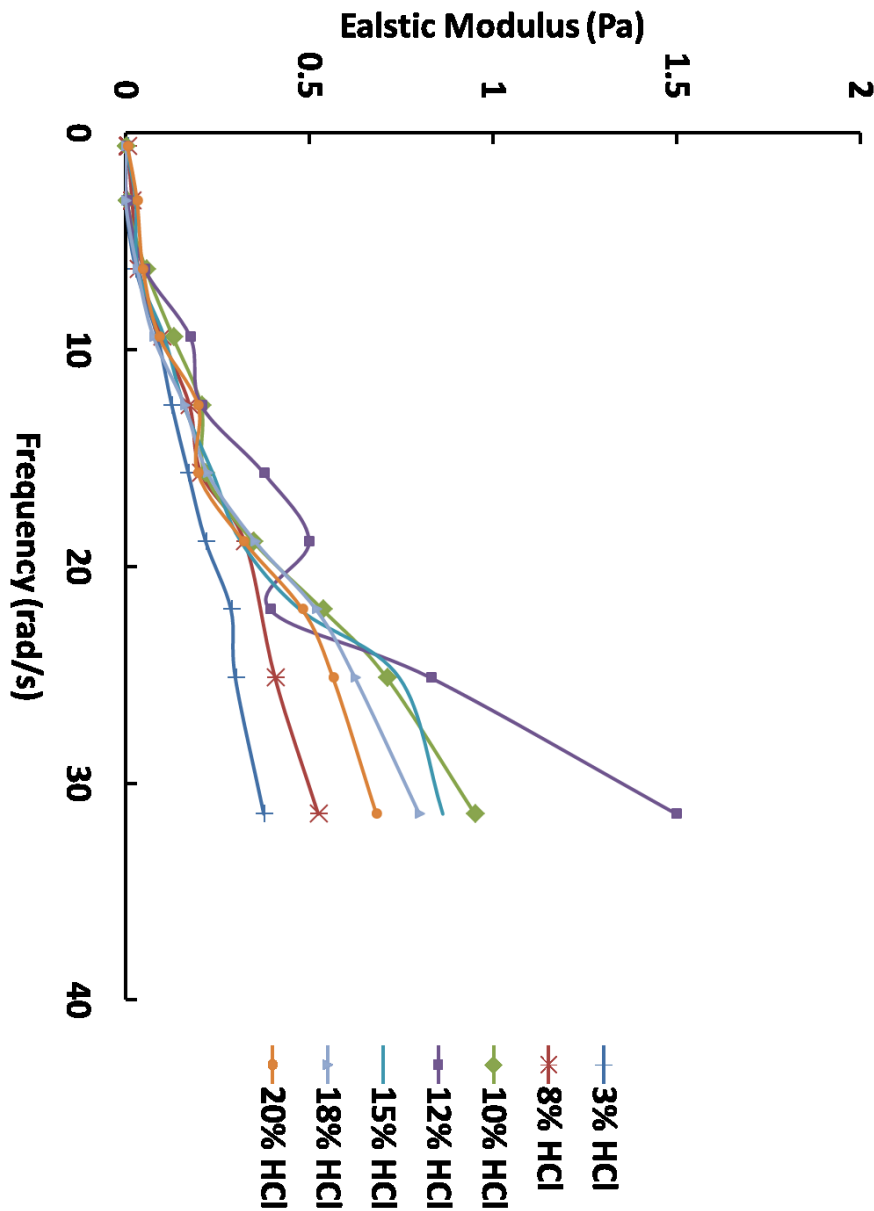


Figure 14 -- Elastic modulus increases with increasing HCl concentration till 12 wt% HCl concentration after which it is observed to decrease with decreasing HCl concentration.

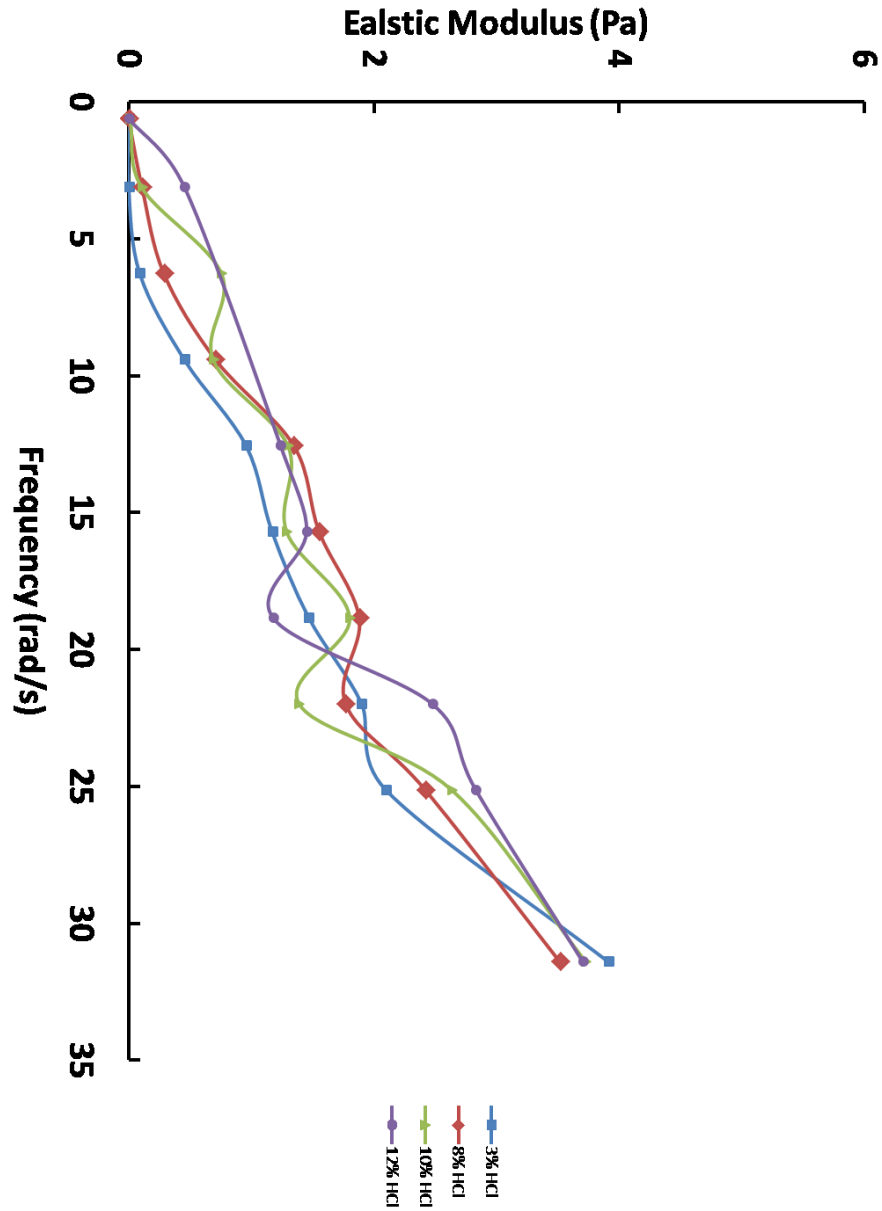


Figure 15 -- Elastic modulus is found to be independent of HCl concentration at 130 F.

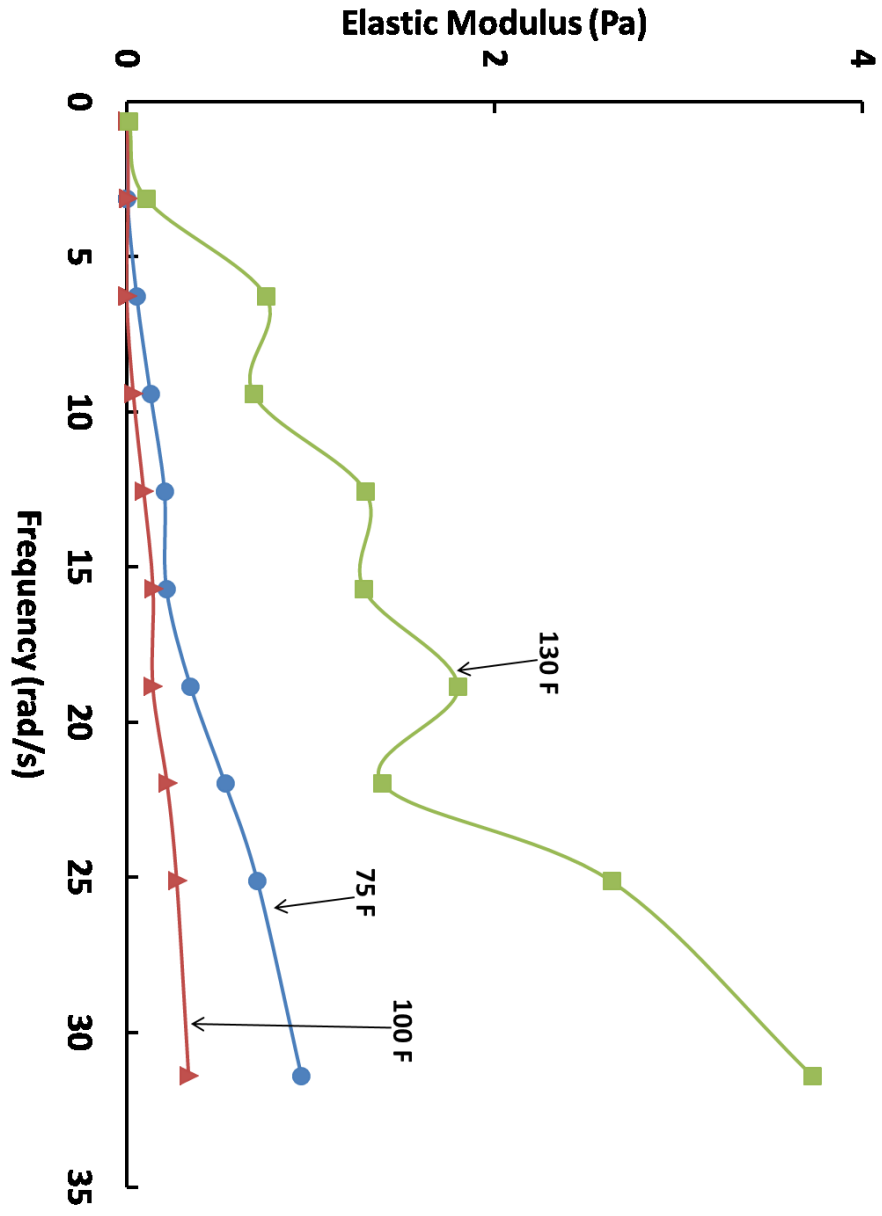


Figure 16 --Impact of temperature on elastic modulus of 10 wt% HCl spent acid solution.

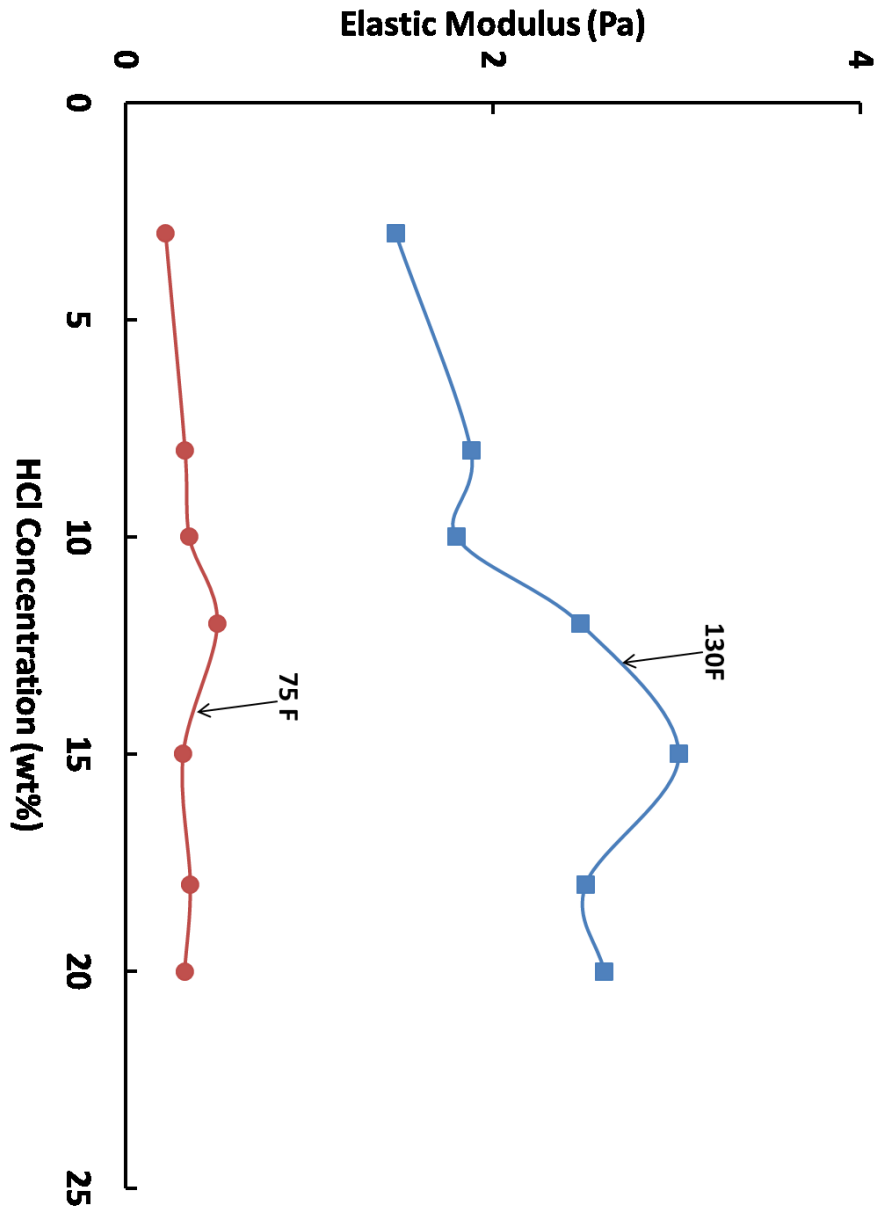


Figure 17 -- Impact of temperature on elastic modulus of spent acid at 18.8 rad/s. The elastic modulus at 130 F is significantly higher than at room temperature, but viscous modulus was observed to dominate the elastic modulus at all frequencies

CHAPTER VI

EFFECT OF HCL CONCENTRATION AND ADDITIVES ON SPENT

VISCOELASTIC ACID SYSTEM FOR AROMAX APA-TW

Fig. 18 shows the effect of HCl concentration on the elastic modulus of spent acid at different temperatures. At room temperature the elastic modulus remains quite low, rises significantly as temperature reaches 130 F and falls sharply at temperatures in the range of 200 F.

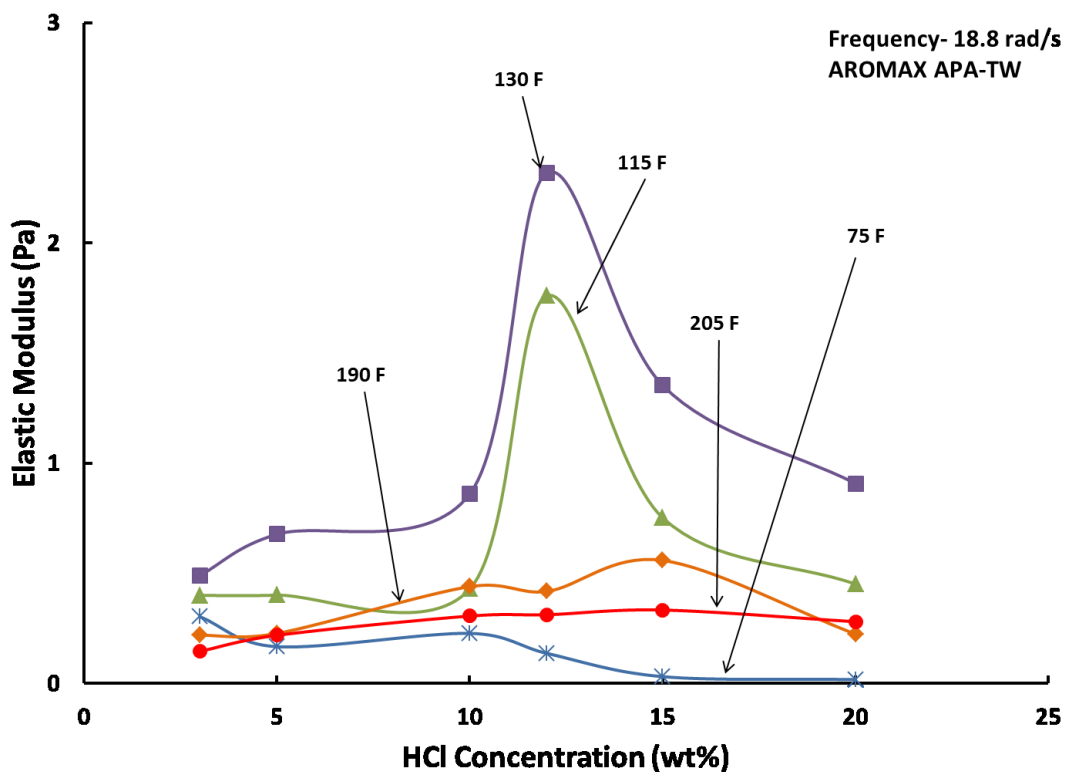


Figure 18 --Maximum elastic modulus is observed at 130 F. The readings are taken at 18.8 rad/s.

Effect of Temperature on VES

Fig. 19- 27 shows the effect of temperature at varying HCl concentrations on the elastic modulus of spent acid. At room temperature the maximum elastic modulus is observed at 12 wt% HCl concentration. At temperatures in the range of 100- 130 F, maximum elastic modulus remains at 12 wt% HCl concentration, after which it starts shifting to higher HCl concentrations. At 145 F, maximum elastic modulus is observed at 15 wt% HCl concentration, whereas further increasing the temperature to 160 F and beyond shifts the maximum elastic modulus to 20 wt% HCl concentration.

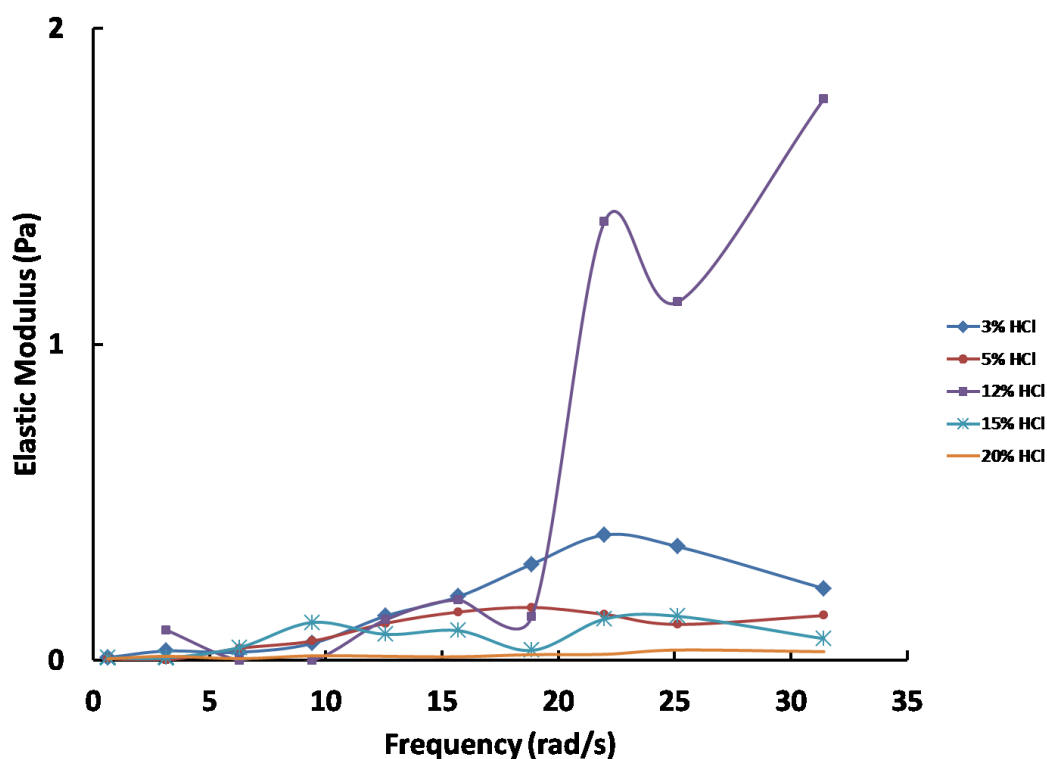


Figure 19 -- Maximum elastic modulus is observed to be at 12 wt% HCl concentration at room temperature.

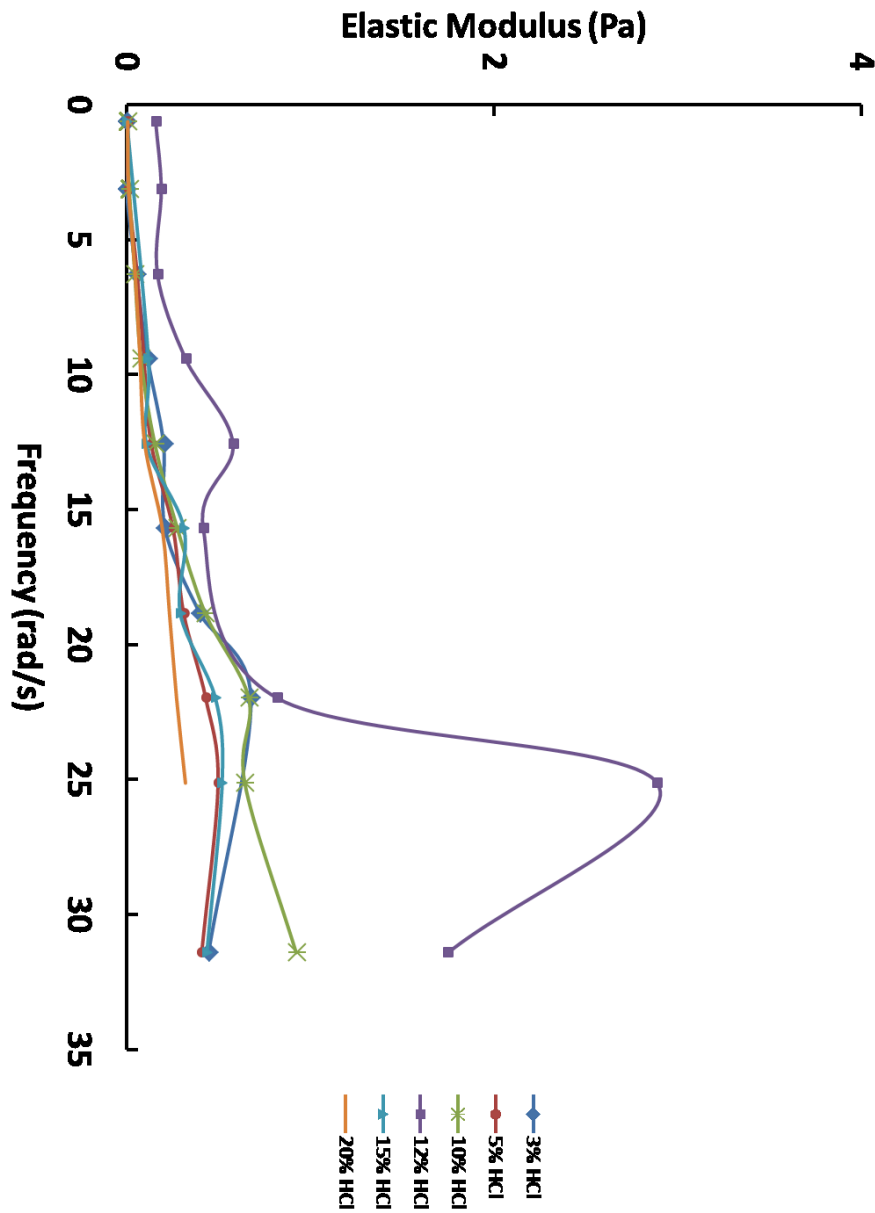


Figure 20 -- Maximum elastic modulus is observed at 12 wt% HCl concentration at 100 F.

The elastic modulus is higher than that observed at room temperature.

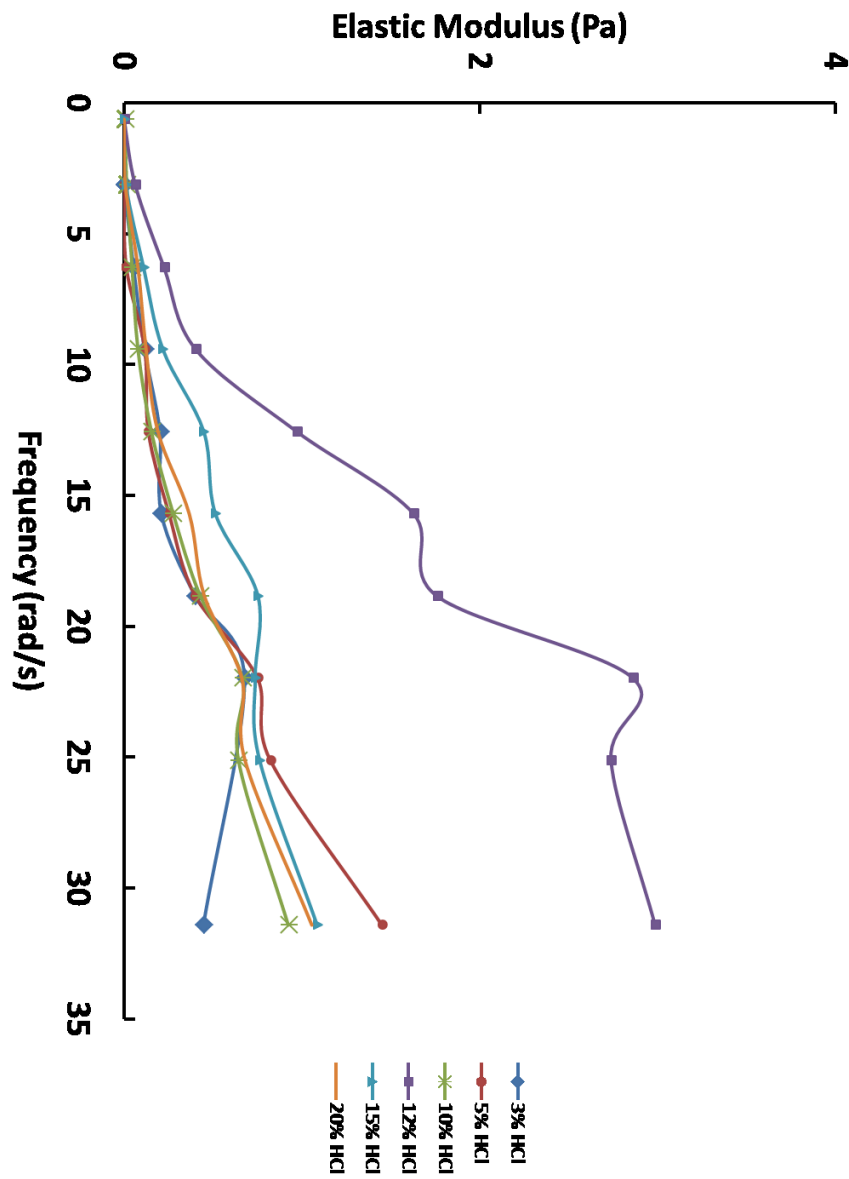


Figure 21 -- Maximum elastic modulus is observed at 12 wt% HCl concentration at 115 F. The elastic modulus is higher than that observed at 100 F.

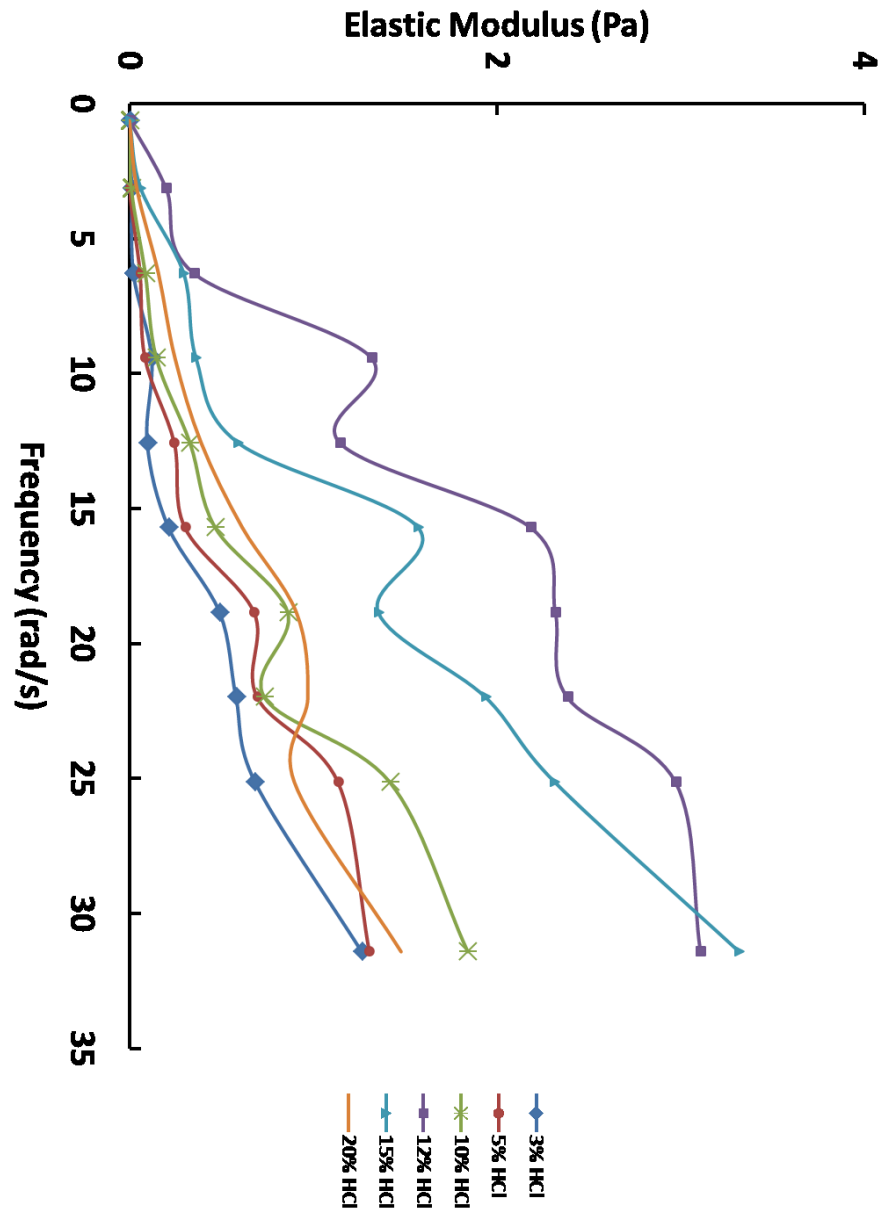


Figure 22 -- Maximum elastic modulus remains at 12 wt% HCl concentration at 130 F.

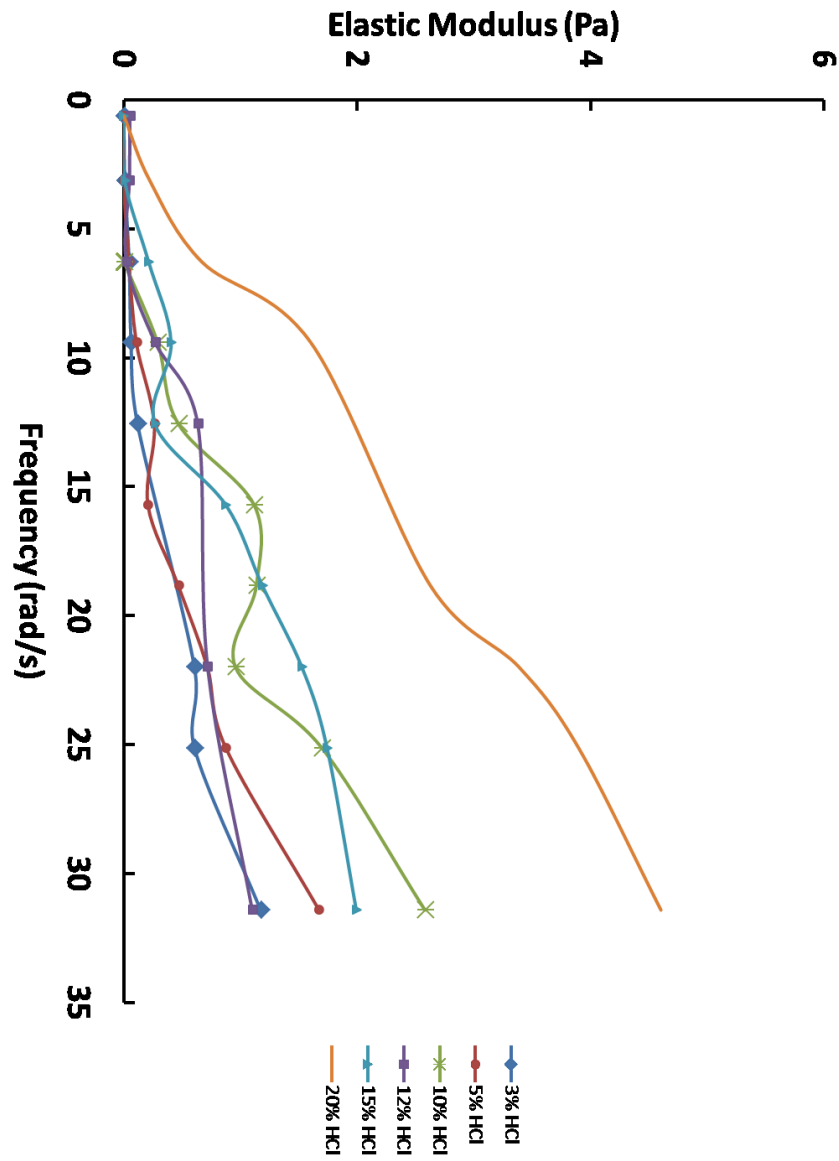


Figure 23 -- Maximum elastic modulus continues to shift to higher HCl concentration values, and is observed at (15- 20 wt%) HCl concentrations at 160 F

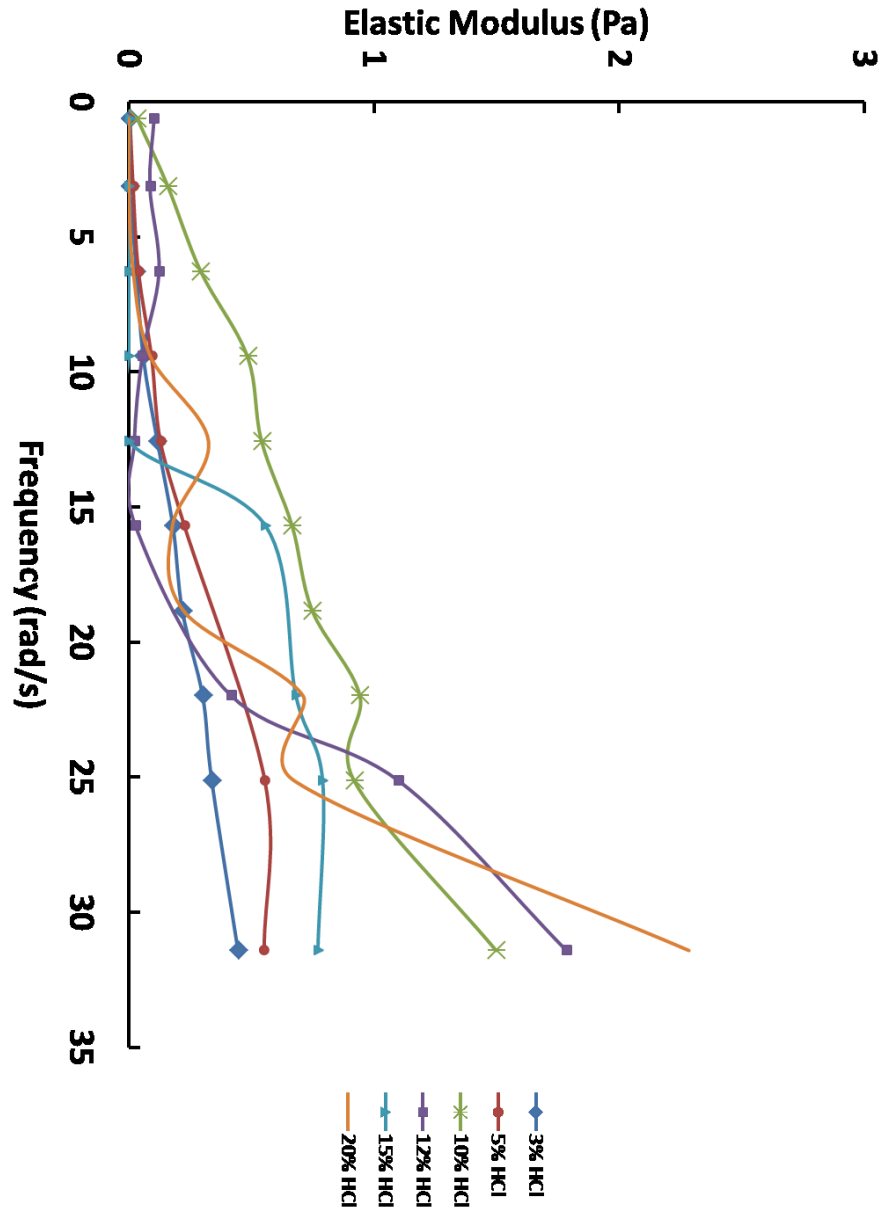


Figure 24 -- Maximum elastic modulus is observed at 20 wt% HCl concentration at 190 F

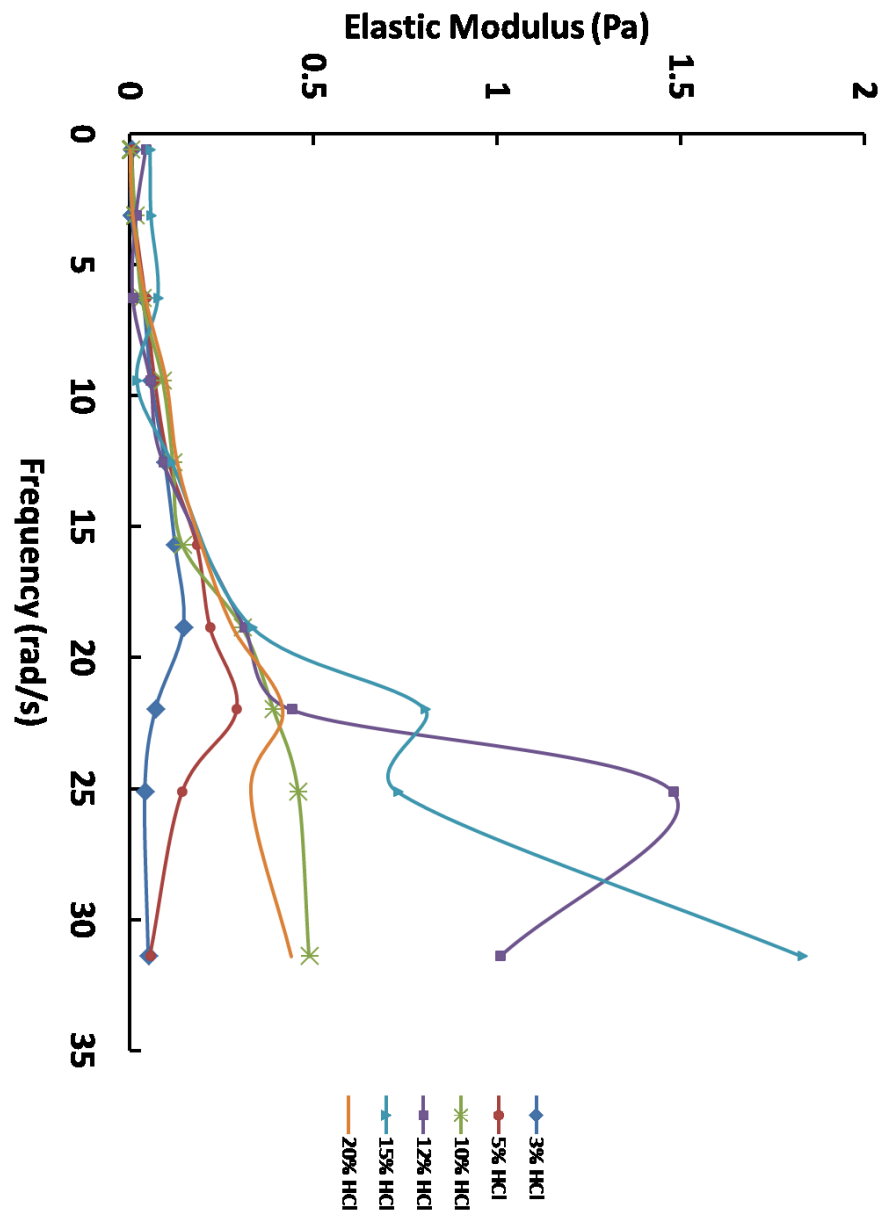


Figure 25 -- At 205 F, maximum elastic modulus is observed at 15 wt% HCl concentration, whereas, at 20 wt% HCl concentrations, the elastic modulus remains quite low.

CHAPTER VII

EFFECT OF ORGANIC ACIDS ON SPENT VISCOELASTIC ACID SYSTEM

The impact of the addition of organic acid along with HCl was studied for two different acid systems, namely

1. Formic Acid
2. Acetic Acid

The two acid systems were investigated at two concentrations, 0.025 mol and 0.05 mol.

Effect of Temperature on Addition of Organic Acids

Fig. 27-28 shows the effect of HCl concentration on elastic modulus at two frequencies, 18.8 rad/s and 31.4 rad/s respectively. The maximum elastic modulus was observed at room temperature whereas further increase in temperature resulted in a drop in elastic modulus. At relatively low temperature, the maximum elastic modulus was observed at 15 wt% HCl concentration, whereas at high temperatures, it shifts to 20 wt% HCl concentration.

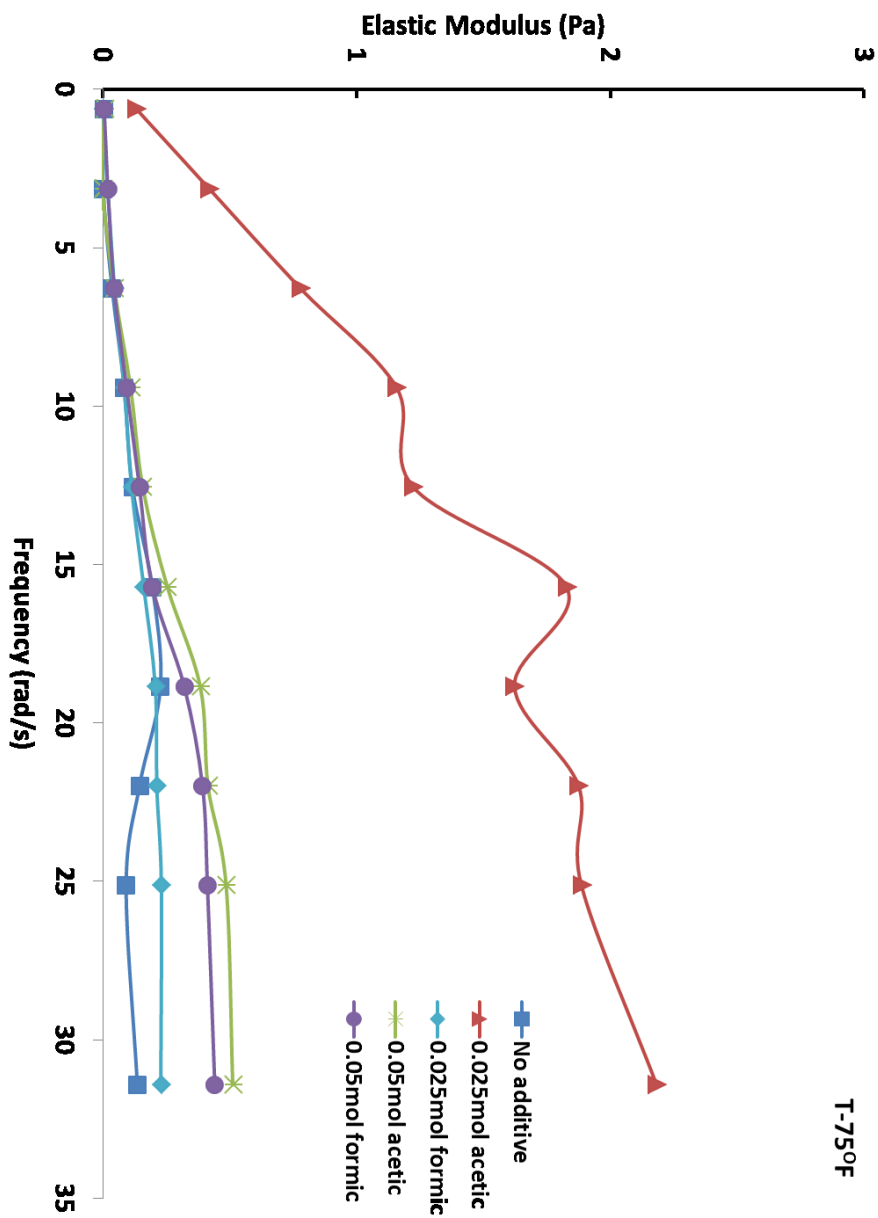


Figure 26 -- Addition of 0.025mol to 10 wt% HCl increases the elastic modulus significantly.

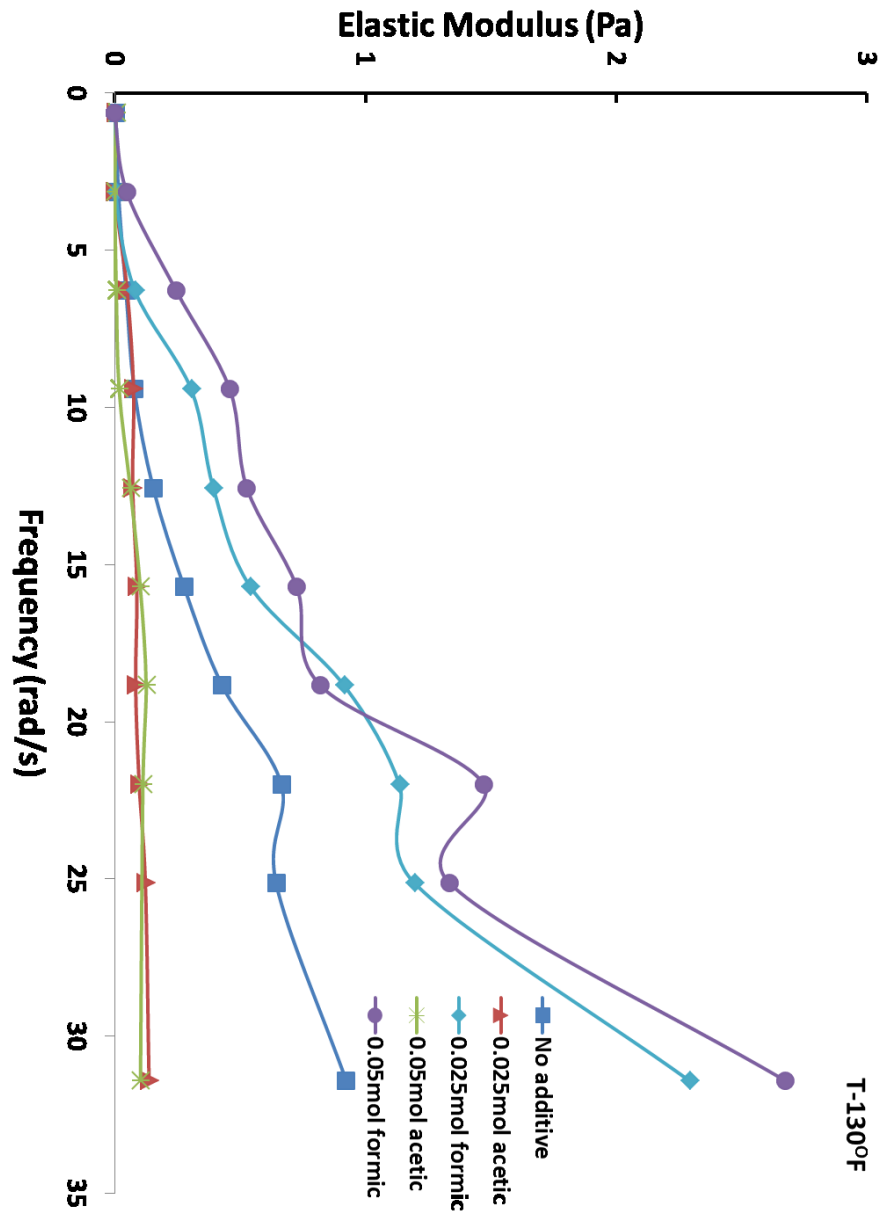


Figure 27 -- At 130 F, 0.05 mol formic acid shows higher elastic modulus for 10 wt% HCl

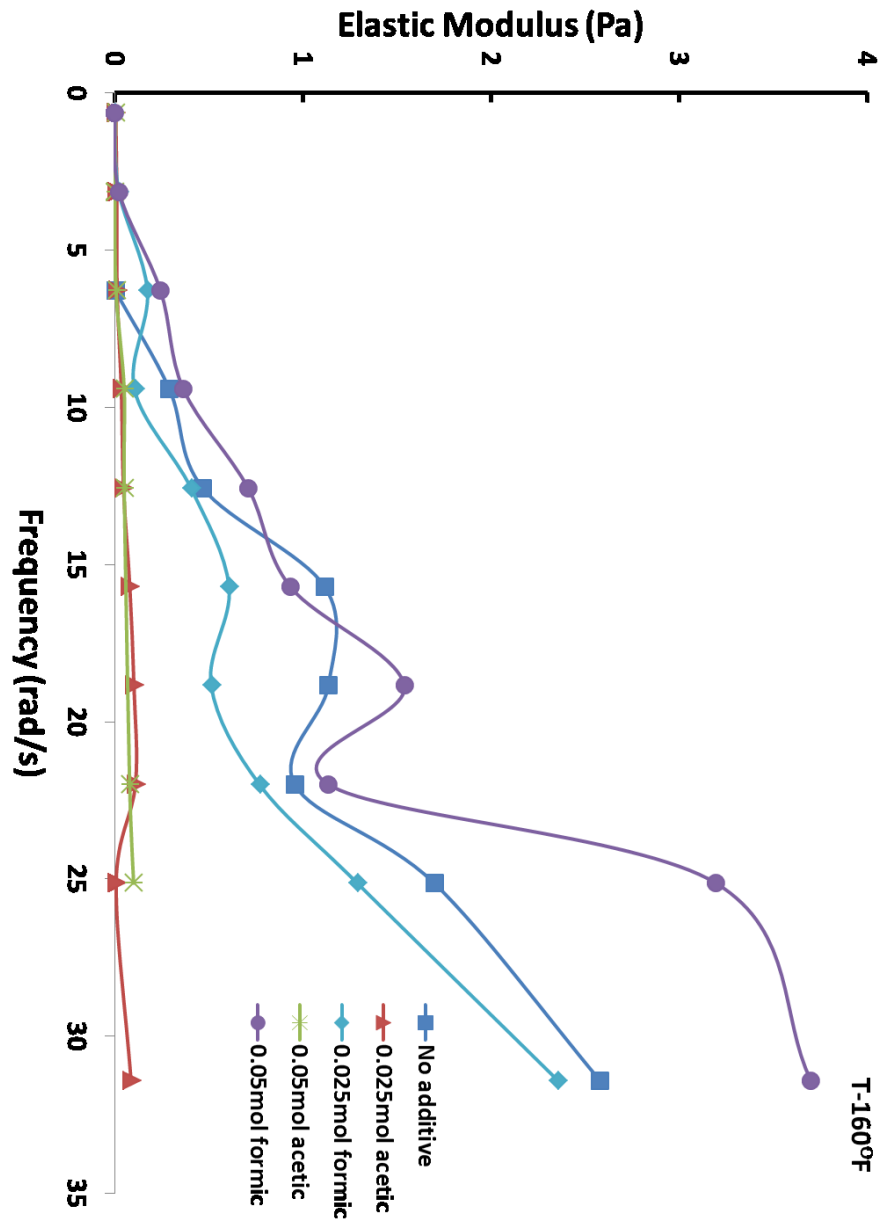


Figure 28 -- At 160 F, addition of 0.05 mol formic acid to 10 wt% HCl solutions still shows the highest elastic modulus

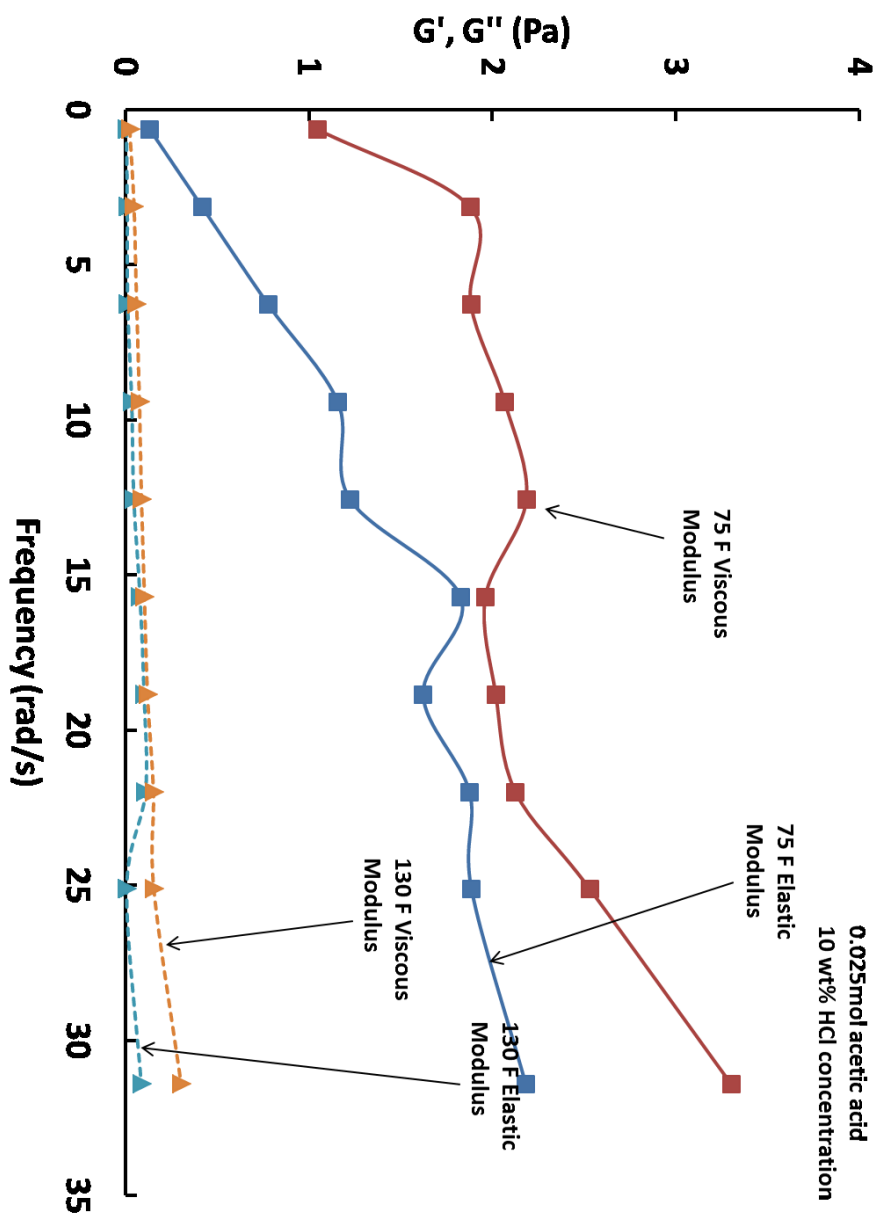


Figure 29 -- No cross-over point observed, fluid is behaving as a viscous fluid rather than a viscoelastic fluid.

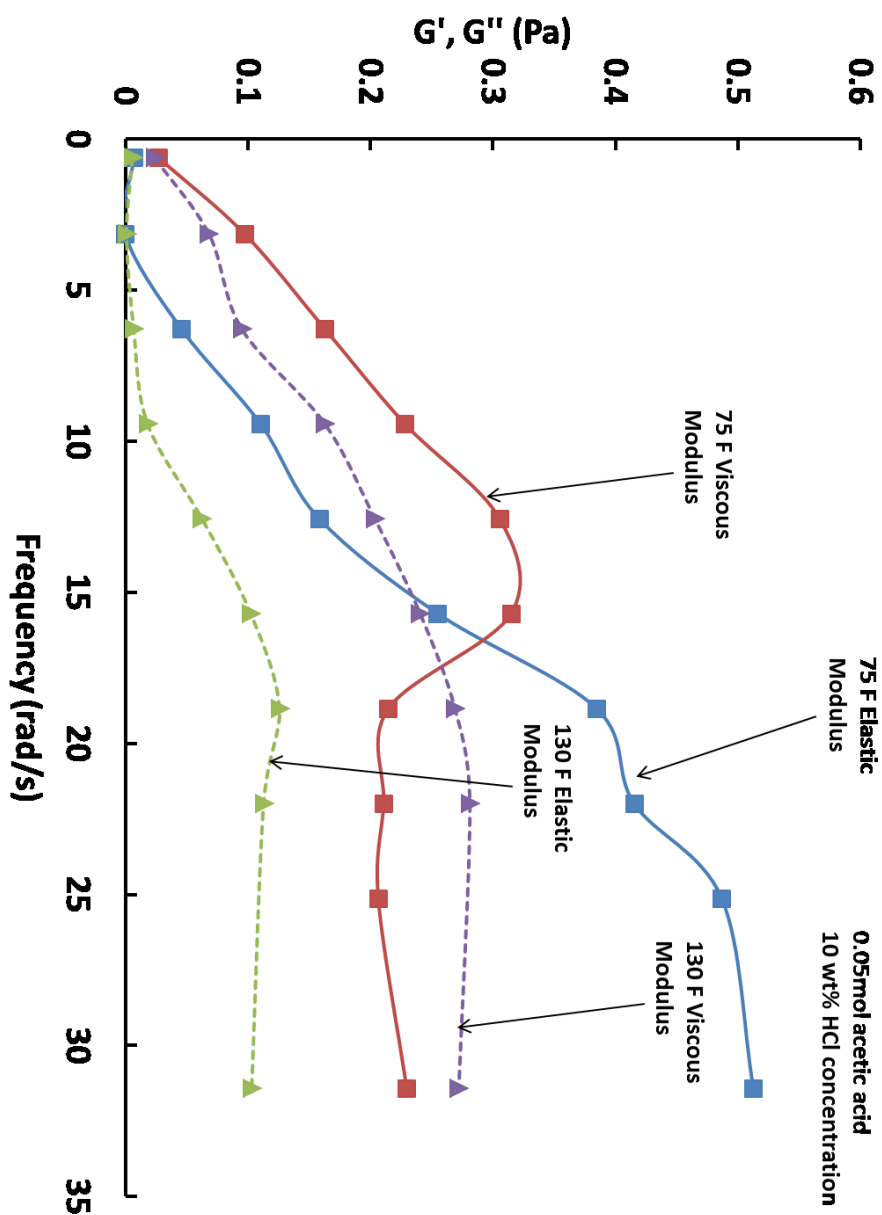


Figure 30 -- Increase in acetic acid concentration to 0.05 mol shows a cross-over point at 75 F, i.e. entanglement of micelles is taking place. The elastic modulus values are quite low as compared to formic acid samples.

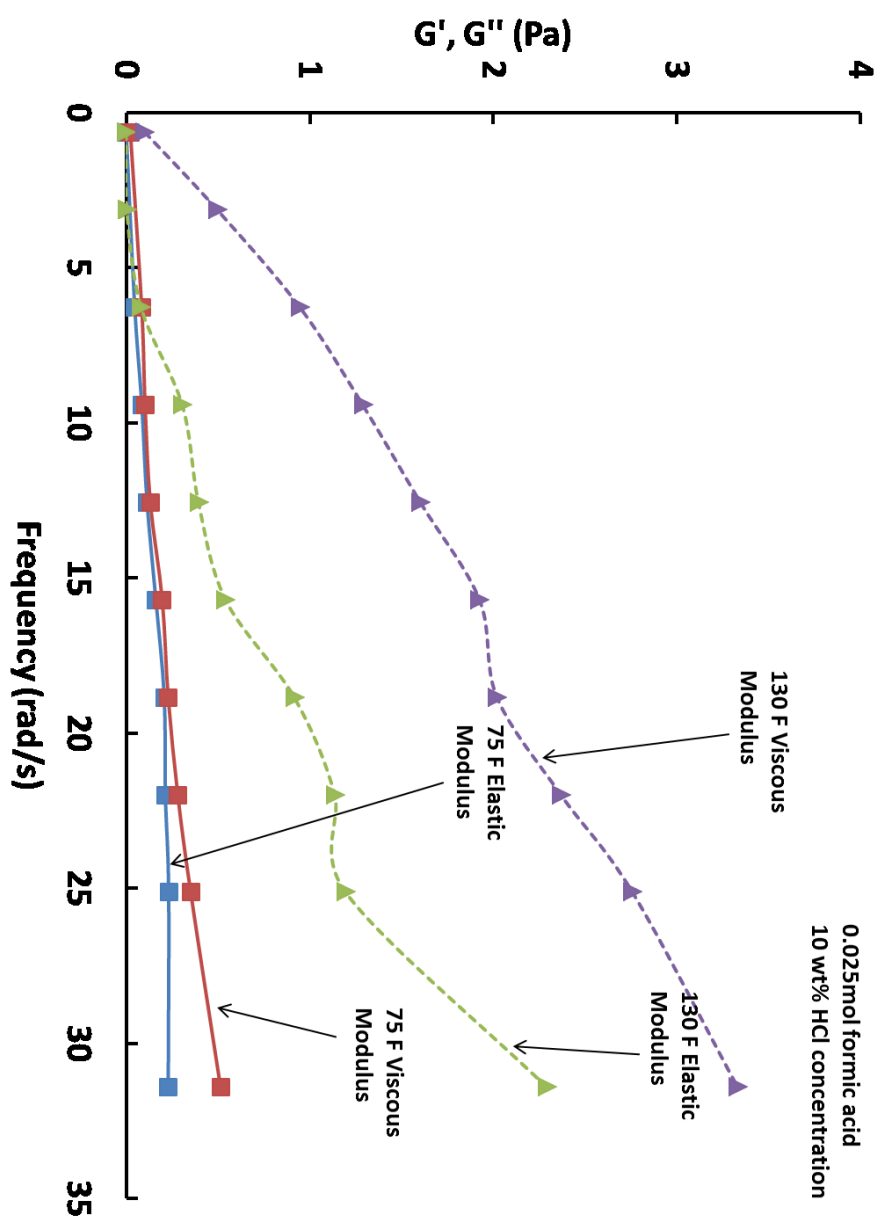


Figure 31-- No cross-over point observed, i.e. entanglement of micelles is not occurring

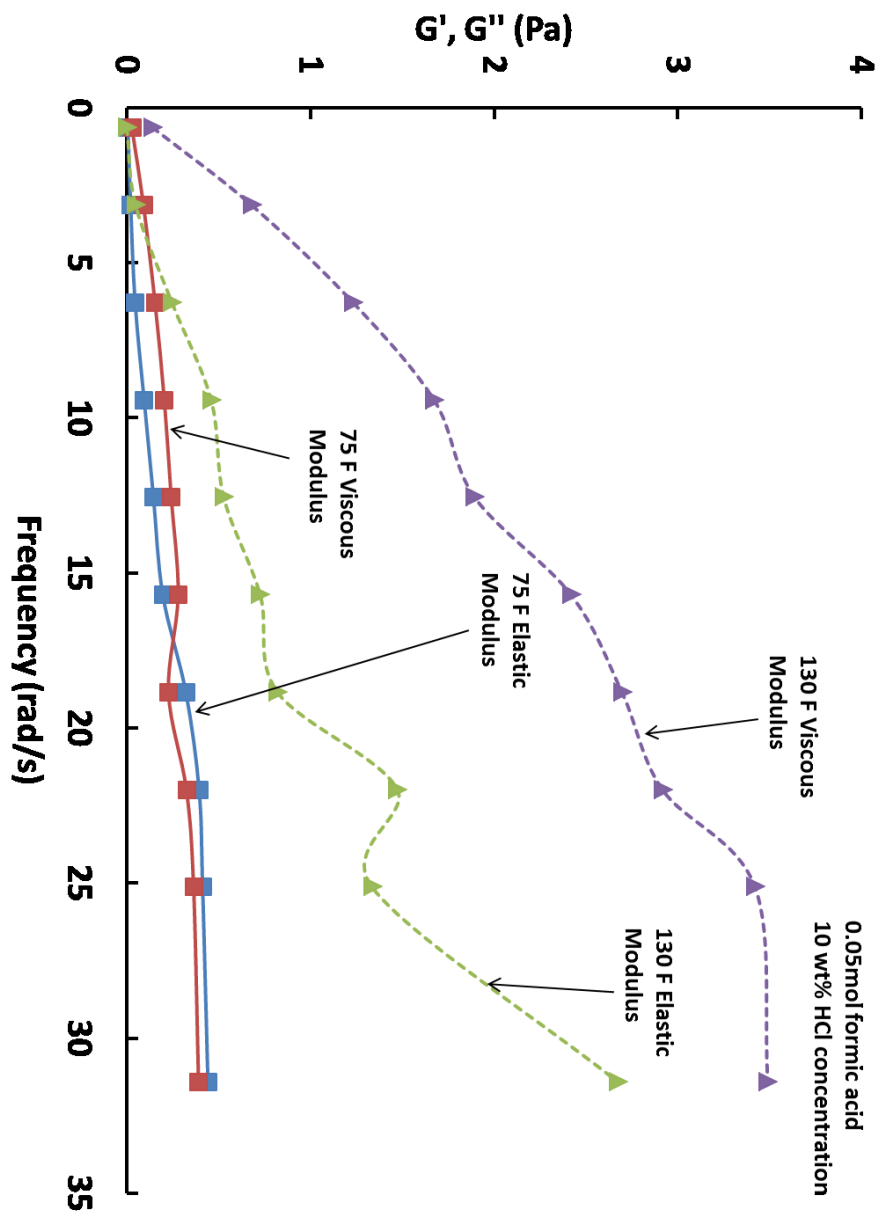


Figure 32 -- Increasing formic acid concentration to 0.05 mol, cross-over point is observed at 75 F

CHAPTER VIII

EFFECT OF TIME AND HYSTERESIS ON LIVE VISCOELASTIC ACID SYSTEM

Fig. 38-40 shows the effect of time on viscoelastic properties of 10 wt% HCl live VES acid system. The elastic modulus is observed to decrease with time and eventually diminish.

Fig. 41 shows the impact of hysteresis on 10 wt% HCl live acid VES solution. The difference b/w the elastic modulus with increasing and decreasing shear is not substantial.

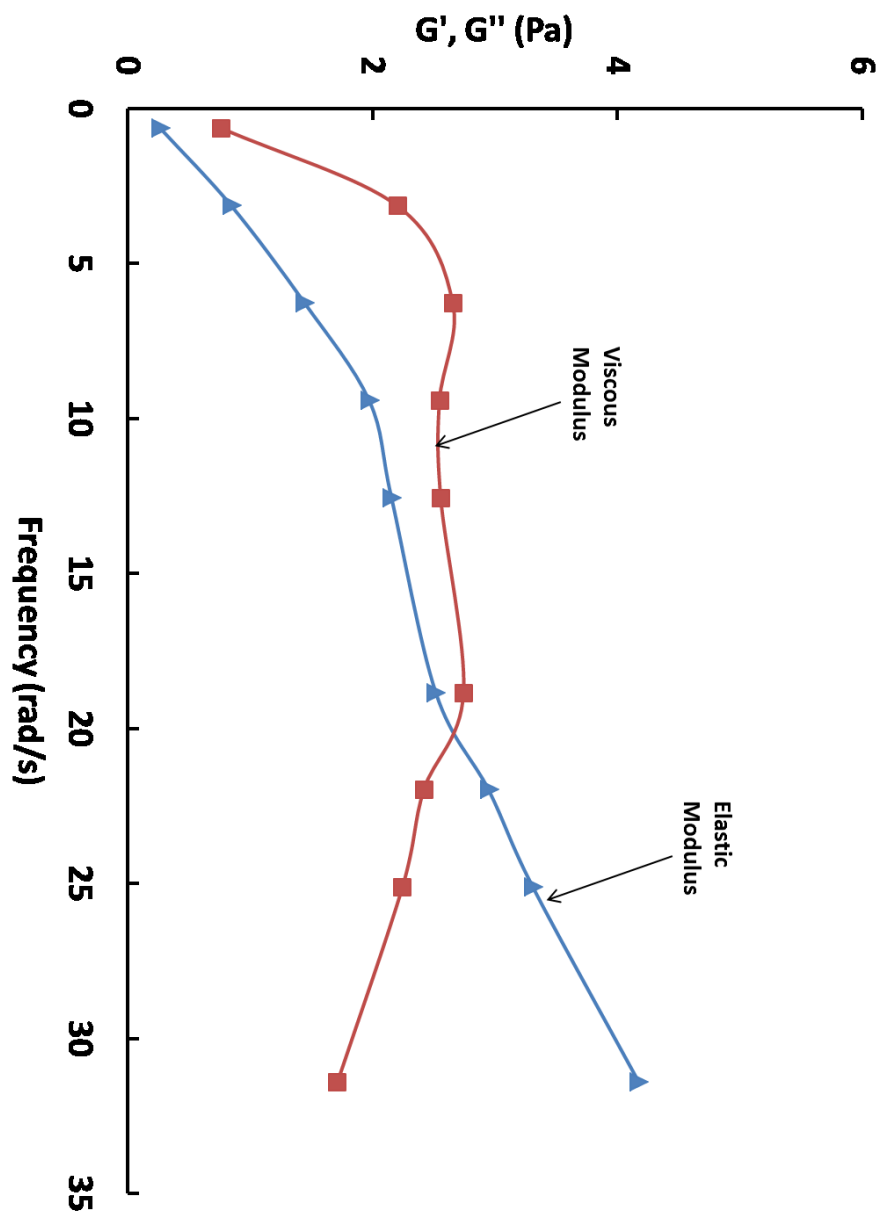


Figure 33 – Readings taken immediately after sample preparation for 10 wt% live acid solution

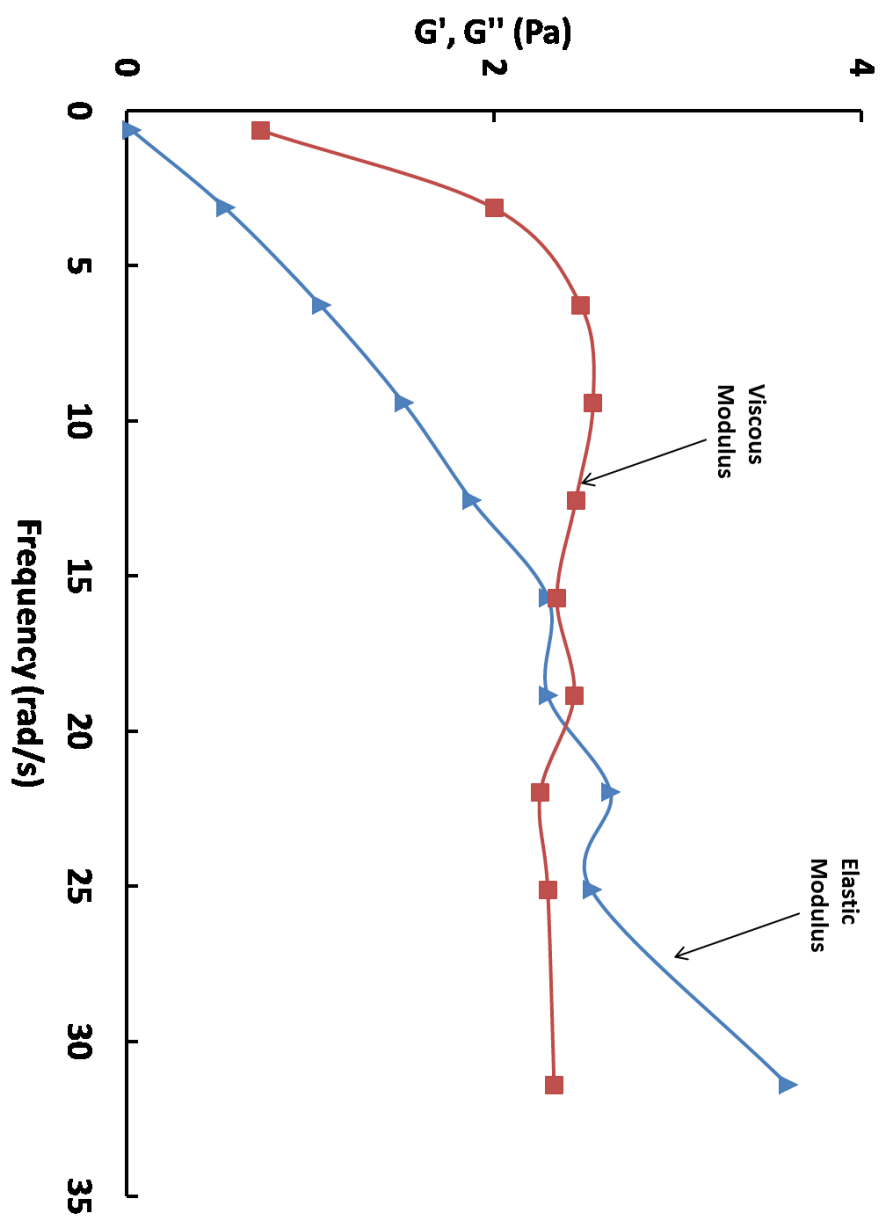


Figure 34-- Readings taken 1 day after sample preparation for 10 wt% live acid solution

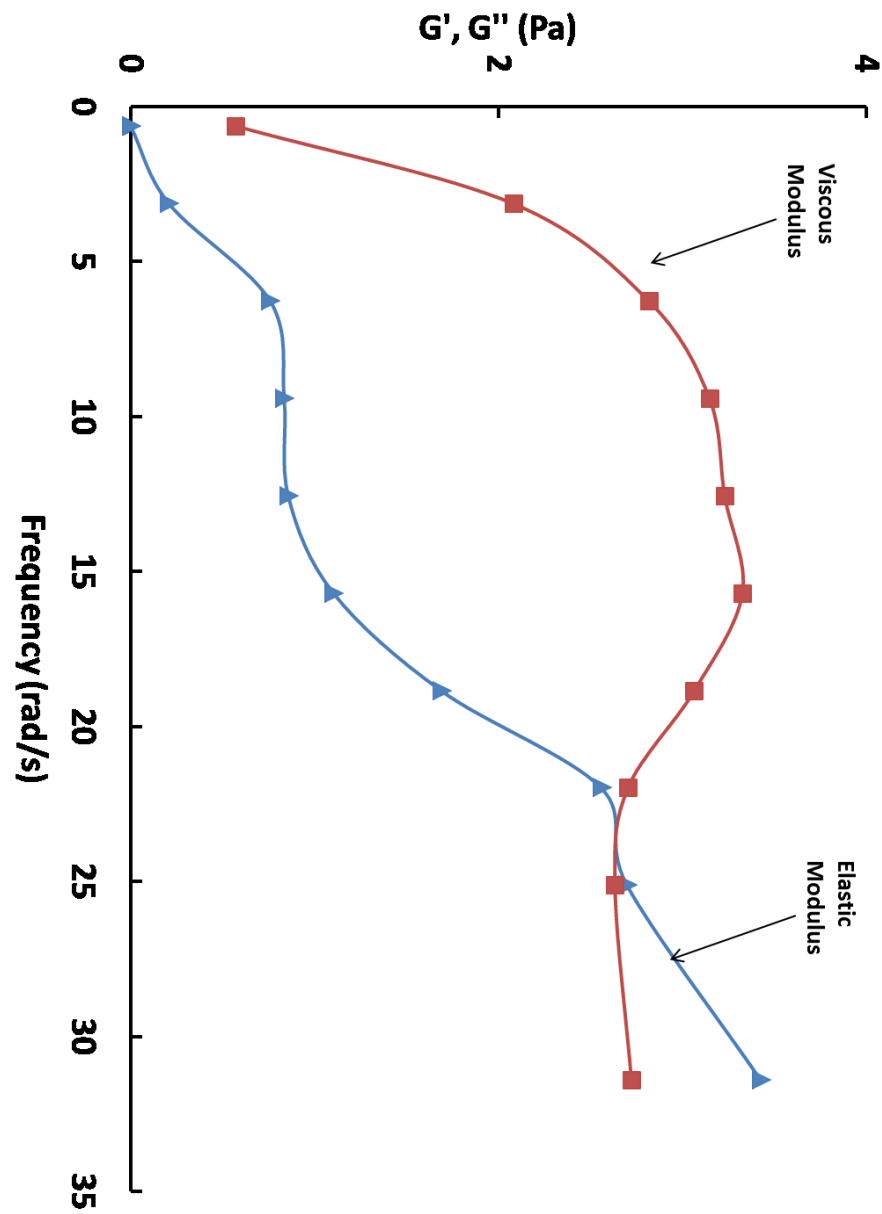


Figure 35 -- Readings taken 5 days after sample preparation for 10 wt% live acid solution. A slight reduction in elastic modulus is observed.

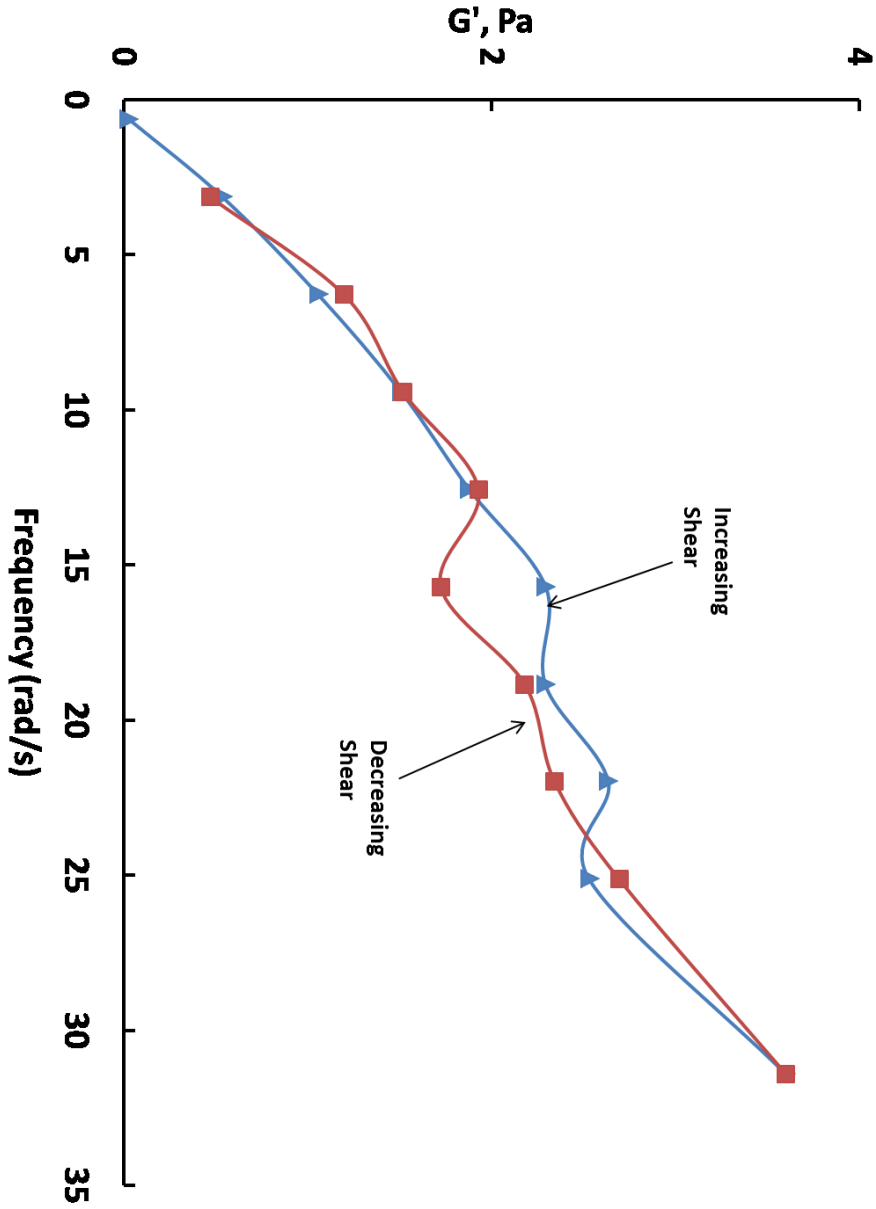


Figure 36 – There seems to be negligible hysteresis impact on 10 wt% HCl live acid solution.

CHAPTER IX

DISCUSSION OF RESULTS

At low pH, materials containing carboxyl and amine groups act as cationic surfactants, while at high pH, the activity would be anionic (Berg 1989) due to protonation of the surfactant head group. In our analysis, since we are dealing with live acid, maximum pH observed was 1.0 for 1 wt% HCl solution so it can safely be said: amidoamine oxide though being zwitterionic behaves as a cationic surfactant in our samples. A peculiar behavior observed during the experiments is the behavior of elastic modulus by varying the concentration of HCl. As concentration of HCl is reduced from 20 wt%, the elastic modulus increases until the concentration reaches 10 wt%, after which the elastic modulus decreases. This peculiar behavior was also reported by (Li 2009) when she observed the viscosity behavior of amidoamine oxide with HCl concentration.

Since at low pH values, amidoamine oxide is behaving as a cationic surfactant due to their charge, repulsion amongst the surfactant particles is expected. (Zhu and Rosen 1985) noted the increase of Cl^- ions compresses the electrical double layer thus rendering stability to the solution by suppressing the repulsion. She noted with the addition of Cl^- ions by adding HCl, no effect on the minimum surface area/molecule (A_{\min}) at the aqueous solution/air interface. Due to protonation of the betaine molecule in her study, A_{\min} would be expected to increase, due to mutual repulsion of the positively charged cationic protonated betaine. It was concluded the simultaneous increase in the

concentration of protonated betaine and decrease in the thickness of the electrical double layer apparently keeps the value of A_{\min} constant. This explains the increase in elastic modulus with HCl concentration.

The increase and then a sudden decrease in elastic modulus were also observed by (Lin 1996; Raghavan et al. 2002; Rehage and Hoffmann 1988). If $\tau_{\text{rept}} < \tau_{\text{break}}$, reptation is the rate-determining step of stress relaxation; the dynamic properties vary with the concentration. From a geometrical point of view, the crosslinks and entanglement points contribute equally to the crossings of the network, but it is sensible to expect that the proportion of cross links and entanglement points will have a strong influence on the dynamic properties of the micellar networks. This self-assembly into aggregates of different morphologies is explained in terms of a preferred curvature for the surfactant monolayer (Khatory et al. 1993). Elongated micelles thus correspond to locally cylindrical aggregates, their two free ends are generally thought to be closed by globular endcaps and the driving force for the micellar growth is then the difference in the free energy of surfactants in the cylindrical of globular environment; a larger difference leads to longer micelles in order to diminish the number of surfactants in the “unfavorable” globular surroundings (with a larger curvature than the cylinder). (Khatory et al. 1993) postulated of another way to suppress the free ends of locally cylindrical micelles: to connect the cylinders in which case the unfavorable surroundings (the connection point) correspond to smaller curvatures than the cylinder. The solution adopted by a particular system will depend on the respective energies to form globular endcaps or connection

points. If the increase of a given parameter (addition of salt, acid etc) triggers the elongation of micelles, it implies that it decreases the optimal curvature of the surfactant monolayer so that the formation energy of connection points will decrease. Thus in a given system it is possible to imagine that the increase of such a parameter promotes the elongation of micelles with endcaps and upon further increase promotes the connection (cross-linking) of cylindrical micelles. (Lin 1996) showed Cryo-TEM images of branched worm-like micelles and how they resulted in the sharp decrease in viscosity with the increase of Cl^- ions.

In our case, the above discussion explains the observations. By increasing the HCl concentration, we are essentially increasing Cl^- ions, since acid is live, pH remains at 0. (Khatory et al.) suggested a network of branched worm-like micelles that were interconnected as opposed to an entangled network. In viscous flow, the branched micelle can slide the crosslink points along the micelle to respond to the flow. This will give a very fluid solution and allow the solution to have a faster relaxation of stress than disentanglement of breaking of worm-like micelles.

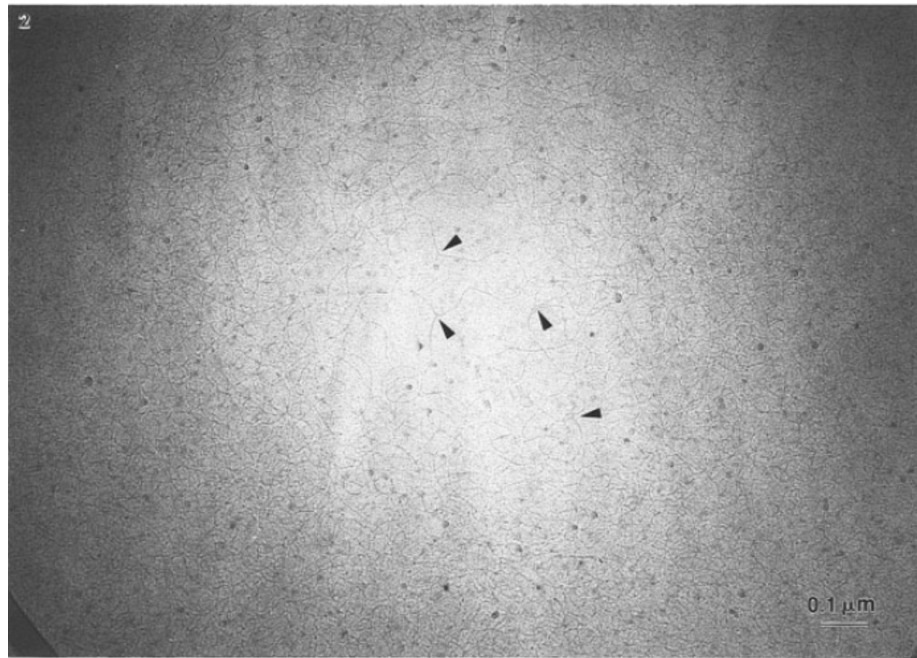


Figure 37 -- Wormlike micelles observed to have crosslink points rather than entanglement

Figure 45 shows a cryo-TEM image of a VES based solution. Due to higher mean inner electron potential, micelles appear darker than the surrounding media. If two micelles are entangled or simply overlap, the entanglement point or overlapping point would appear darker. If the micelles are branched, the branching point should have the same appearance as the regular micelles.

This change in structure explains the decrease in elasticity observed after a certain HCl concentration.

Since corrosion inhibitors used with HCl always contain short chain alcohols, these alcohols can impact the elasticity of surfactant solutions adversely. Hence, increase in corrosion inhibitor concentration results in a decrease in elasticity.

In the limit of high salt concentration, it has been suggested that intermicellar branching might occur. This results in a change in the relaxation mechanism. The boundary between the high and moderate salt content regimes depends on the material. Thus increase in monovalent and divalent cations results in the changing of structure from entanglement to intermicellar branching. Owing to this change in structure, elasticity is observed to decrease with the increase of monovalent and divalent cations concentration. Ferric species are suitable to complex with VES at low pH values by forming ligands with $-N$ and/or $-COO$. Furthermore, (Nasr-El-Din et al. 2002) showed the precipitate resulting in the presence of Fe(III) ion concentrations as low as 1 wt% to contain both iron and VES. He also showed the supernatant of acid did not form gel upon neutralization. For this reason, it is essential to pickle the tanks prior to the treatment. Elasticity was observed to decrease with the increase of temperature. For micellar solutions, increasing temperature is accompanied by a large decrease of the average micellar length. This result, according to Cates model, is predicted by the scaling theory applied to semi-dilute solutions of elongated micelles.

CHAPTER X

CONCLUSIONS

The following are the main conclusions from this research project:

1. At the maximum concentration of 20 wt% HCl, both the elastic and the viscous moduli are significantly lower than the rest of the samples.
2. The maximum elastic modulus is observed at 12 wt% HCl and 10 wt% HCl whereas the maximum viscous modulus is observed at 5 wt% HCl.
3. Increase in concentration of NaCl results in a slight increase in elastic modulus after which it falls sharply.
4. Fe (III) ions effect the elastic modulus sharply with concentrations as low as 0.5 % results in a significant reduction in elastic modulus.
5. High concentrations of Fe (III) (>3wt %) results in phase separation.
6. Low concentrations of CaCl₂ (0.5-1 wt %) do not have an effect on elastic modulus whereas further increase results in a drop in elastic modulus.
7. At high temperature (100F-150F), 10 wt% HCl no longer exhibits elastic properties, viscous modulus dominates over the range of frequency.
8. Using seawater in place of deionized water results in a decrease of elastic modulus at all concentrations of HCl tested.
9. Elastic modulus of spent acid solutions increases with the increase of HCl concentration till 12 wt% HCl solution, after which it is observed to decrease.
10. At 130 F, elastic modulus of spent acid solutions is found to be independent of HCl concentration

11. Time has an impact on elastic modulus of live acid solutions.
12. There seems to be no impact of hysteresis on elastic modulus of live acid solutions.

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