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**Investigation of Oil Recovery Improvement by Coupling  
An Interfacial Tension Agent and a Mobility Control Agent  
in Light Oil Reservoirs**

**Annual Report for the Period  
October 1992 to September 1993**

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## Abstract

Investigation of Oil Recovery Improvement by Coupling an Interfacial Tension Agent and a Mobility Control Agent in Light Oil Reservoirs will study two major areas concerning co-injecting an interfacial tension reduction agent(s) and a mobility control agent. The first area defines the interactions of alkaline agent, surfactants, and polymers on a fluid-fluid and a fluid-rock basis. The second area concerns the economic improvement of the combined technology.

This report examines the interactions of different alkaline agents, surfactants, and polymer combinations on a fluid-fluid basis. Alkali and surfactant combine to reduce the interfacial tension between a low acid number, 42 API gravity crude oil and the aqueous solution to values lower than either agent alone. Surfactant structure can vary from linear chain sulfonates to alkyl aryl sulfonates to produce low interfacial tension values when combined with alkali. However as a class, the alkyl aryl sulfonates were the most effective surfactants. Surfactant olefinic character appears to be critical in developing low interfacial tensions. For the 42 API gravity crude oil, surfactants with molecular weights ranging from 370 to 450 amu are more effective in lowering interfacial tension. Ultra low interfacial tensions were achieved with all of the alkaline agents evaluated when combined with appropriate surfactants. Different interfacial tension reduction characteristics with the various alkali types indicates alkali interacts synergistically with the surfactants to develop interfacial tension reduction. The solution pH is not a determining factor in lowering interfacial tension. Surfactant is the dominate agent for interfacial tension reduction.

Increasing the temperature up to 170°F did not significantly alter the interfacial tension reducing capability of an alkaline-branched alkyl aryl sulfonate solution but changed interfacial tension for linear alkyl aryl sulfonates. Shifts in the alkali concentration and/or the range of alkali concentrations which produce the ultra low interfacial tension values were observed consistent with the change in surfactant solubility. The alkyl surfactants which did not produce low interfacial tension at 72°F were still not effective as the temperature increased.

Increasing the salinity of the surfactant and alkaline plus surfactant solutions demonstrates that the interfacial tension reduction synergism is not the result of changing salinity for the range tested. Ultra low interfacial tension values for surfactant plus alkali solutions could not be achieved with surfactant plus sodium chloride before alkyl-aryl surfactants precipitated from solution. The alkali plus surfactant solutions with the more water soluble surfactants gave lower interfacial tension values than surfactant plus sodium chloride at the tested salt concentrations. For alkaline plus surfactant solutions which produce ultra low interfacial tensions, an increase of the solution salinity shifted the surfactant which was most effective to a slightly more water soluble type. Also, an increase in temperature increased the salinity at which the minimum interfacial tension occurred for alkyl aryl surfactants. For non-optimum surfactants, increasing the temperature did not change the salinity effects with any consistent trend.

Addition of alkali to the surfactant solutions decreased the critical micelle concentration. Polymer addition to the alkyl aryl sulfonates increased the critical micelle concentration while polymer addition to a linear alkyl sulfonate solution caused the critical micelle concentration to decrease.

For alkaline plus surfactant plus polymer solutions exhibiting minimum interfacial tension, polymer increases the interfacial tension. The increase is independent of polymer type. With solutions which have not achieved a minimum interfacial tension, the interfacial tension will continue to decline with polymer addition.

Alkali addition to xanthan gum, hydroxyethyl cellulose, and partially hydrolyzed polyacrylamide polymer solutions reduces solution viscosity, intrinsic viscosity and polymer hydrodynamic radius in a similar manner as sodium chloride. Alkali addition to the polymer solutions reduces the pseudoplastic character of the solution considerably, especially for polyacrylamide solutions. Surfactant addition to polymer solutions either has little effect or increases the solution viscosity, intrinsic viscosity, and hydrodynamic radius of the polymer. Surfactant addition to polymer solutions containing alkali results in a decrease of the property values initially but as surfactant concentration becomes greater the property values increase. Addition of surfactant to the polymer solutions regains some of the pseudoplastic character for xanthan gum and hydroxyethyl cellulose but results in a continued decline for polyacrylamide.

### **Executive Summary**

The co-injection of an interfacial tension agent(s) such as an alkaline agent or a surfactant and a mobility control agent or polymer has the potential to recover an equivalent amount of tertiary oil as demonstrated by the micellar-polymer technology but at substantially lower costs. Chemical costs can be as low as \$2 per barrel of incremental oil. However, for the co-injection of an interfacial tension agent(s) and a mobility control agent to be economically utilized in a wide variety of oil reservoirs, the mechanism of incremental oil production must be defined as well as the limitations of the technology.

A low acid number, 42 API gravity oil from the Adena Field, a DOE class I, fluvial dominated deltaic reservoir located in Colorado, was used to evaluate the fluid-fluid interactions of potential interfacial tension agent plus mobility control solutions. The observations from the fluid-fluid evaluations were as follows:

- Alkali and surfactant can be mixed together to synergistically produce ultra low interfacial tension. Low interfacial tension is not dependent on alkali type nor pH. Surfactant is the dominating component for developing the low interfacial tension. The surfactant structure does not appear to be significant but olefinic character does.
- The alkali and surfactant synergism which results in ultra low interfacial tensions is not a simple salinity or saponification effect.
- Polymer interacts with the alkali and surfactant in solution. Interfacial tension of alkaline plus surfactant solutions change when polymer is added to the solution. Polymer rheological characteristics are altered when combined with alkali and surfactant.
- Changes of solution salinity alter the alkali and surfactant interaction.
- Increasing temperature up to 170°F alters the alkali and surfactant interactions for the alkyl aryl sulfonates but has a minimal effect on the alkyl sulfonates surfactants.

From a technical point of view, a design of an alkaline-surfactant-polymer solution for injection into an oil reservoir requires the understanding of how each component will effect the solution properties. Alkyl aryl sulfonate surfactants would be the recommended surfactant class for initial design screening. The type of alkali is not as important. Polymer type is not a critical design criteria. However, from an economic point of view, chemical type does become important, ie when water salinity dictates selection of more brine tolerant polymer or more water soluble surfactant.

### **Introduction**

The co-injection of an interfacial tension agent(s) and a mobility control agent has demonstrated laboratory oil recoveries equivalent to the micellar-polymer technology.<sup>1-3</sup> Micellar-polymer field projects were technically successful, producing 0.15 PV of tertiary oil and reducing the oil field residual oil saturation to less than 20% PV. However, the chemical cost of the recovered oil ranged from \$10 to \$45 per incremental barrel of oil.<sup>4-5</sup> A current project in the West Kiehl Minnelusa "B" Field which co-injected interfacial tension and mobility control agents will recover approximately 0.15 PV of incremental oil at about \$2 per incremental barrel.<sup>6</sup>

The improved oil recovery due to the co-injection of an interfacial tension agent(s) with a mobility control agent can be divided into two stages. The first stage is the mobilization of residual crude oil by the interfacial tension agent(s). The second stage is the displacement of the mobilized oil to the producing well.

The combination of alkali and surfactant has been demonstrated to be more effective in mobilizing oil than either agent alone.<sup>7-10</sup> The mechanism of this synergism and polymer addition effects on the synergism have not been defined. Also, the mechanism of the improved oil displacement efficiency from porous media by the combination of chemicals is not understood.

The objective of this project is to define:

- Mechanisms and limitations of the technology of co-injection of an interfacial tension reduction agent(s) and a mobility control agent to recover incremental oil.
- An evaluation of the economics of the combination technology and a series of studies to investigate methods to make the process more profitable.

This first yearly report will focus on the mechanisms of the fluid-fluid interactions: 1) the alkali-surfactant interfacial tension synergism, 2) the effect of polymer on the alkali-surfactant interfacial tension synergism, and 3) the effect of alkali and surfactant on the polymer solution characteristics.

## **Discussion of Evaluations**

### **Crude Oil**

A fluvial deltaic dominated reservoir crude oil was selected for use in the study. The crude oil was from the Adena Field in Morgan County, Colorado.<sup>11</sup> The Adena crude oil is a 42 API gravity crude oil with a dead oil viscosity of 3.8 cp at 72°F and 1.3 cp at the 180°F (reservoir temperature). Live oil viscosity at 180°F and 1,150 psi was 0.42 cp. Acid number was <0.002 mg KOH/g crude oil.

### **Water**

All chemicals are dissolved in 1,000 mg/l NaCl unless designated differently. Divalent cations were not added to the water for two reasons. First, in a field application, water is softened to dissolve alkali if divalent cations are present in quantities large enough to cause precipitation. Second, precipitation of alkali by divalent cations will alter the concentrations of alkali in solution which may alter conclusions.

## **Chemicals and Procedures**

Interfacial tension measurements were performed using either a DuNouy ring tensiometer<sup>12</sup>, a constant rate spinning drop tensiometer,<sup>13</sup> or a University of Texas, Model 300 variable rate spinning drop tensiometer using the method of Cayias et.al.<sup>14</sup> Surface

tension measurements were performed using a DuNouy ring tensiometer.<sup>15</sup> The lowest interfacial tension value reported is 0.001 mN/m.

Viscosities were determined using either a Brookfield LVT viscometer equipped with a UL adaptor or using an Ubbelohde four bulb viscometer.

Alkaline agents selected for the study were NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, and Na<sub>2</sub>HPO<sub>4</sub>. Surfactants used in the study and a structural description are listed in the following table. All surfactant concentrations are active concentrations. Surfactants were obtained from a variety of surfactant manufacturers. All surfactants are sodium salts. Surfactant selection was based on commercial availability and structure. Surfactant concentrations were equal to or less than 0.2 wt% active and alkaline agent concentrations were equal to or less than 2.0 wt% so the chemical blends would have the potential to be economic at a crude price of \$15/bbl.

<u>Surfactant</u>	<u>Structure</u>
<b>Linear Alkyl Group</b> <b>- Alkyl Aryl Surfactants</b>	
Naccanol 90-F	linear alkyl benzene sulfonate - molecular weight 341, 11 carbon side chain
Polystep A7	linear alkyl benzene sulfonate - molecular weight 348, 12 carbon side chain
LXS 370	linear xylene sulfonate molecular weight 370, 11 to 12 carbon side chain
Petrostep B-120	linear alkyl aryl sulfonate molecular weight 370, 13 to 14 carbon side chain
LXS 395	linear xylene sulfonate molecular weight 395, 13 to 14 carbon side chain
LXS 420	linear xylene sulfonate molecular weight 420, 15 to 16 carbon side chain
TRS 10-410	linear alkyl aryl sulfonate molecular weight 423, 17 to 18 carbon side chain
LTS 18	linear toluene sulfonate molecular weight 446, 18 carbon side chain
Petrostep B-105	linear alkyl aryl sulfonate molecular weight 465, 20 to 21 carbon side chain

<u>Surfactant</u>	<u>Structure</u>
<b>Linear Alkyl Group</b>	
- Internal Bond to Aryl Functionality	
- Alkyl Aryl Surfactant	
Petrostep H67	linear alkyl aryl sulfonate, alkyl group bonded to aryl group internally to give dialkyl side chain - molecular weight 415, total side chain 17 carbons
<b>Branched Alkyl Group</b>	
- Alkyl Aryl Surfactants	
Petrostep B-100	branched alkyl aryl sulfonate molecular weight 410, 16 to 17 carbon side chain
Chaser XP-100	branched toluene sulfonate molecular weight 430, 16 to 17 carbon side chain
Petrostep B-110	branched alkyl aryl sulfonate molecular weight 495, 23-24 carbon side chain
<b>Internal Olefin Sulfonates</b>	
Neodol IOS 1517	internal olefin sulfonate molecular weight 328, 15 to 17 carbon chain
Neodol IOS 1720	internal olefin sulfonate molecular weight 363, 17 to 20 carbon chain
<b>Alpha Olefin Sulfonates</b>	
AOS 12	alpha olefin sulfonate molecular weight 270, 12 carbon chain
Bioterge AS-40	alpha olefin sulfonate molecular weight 314, 14 to 16 carbon chain
<b>Sulfonated Linear Alkane</b>	
Bioterge PAS 8S	1 octane sulfonate - molecular weight 216, 8 carbon chain
<b>Sulfonated Ethoxylated Linear Alkane</b>	
Avanel S-30	sulfonated ethoxylated alkane, 3 moles ethylene oxide - molecular weight 383, 12 to 15 carbon chain
<b>Sulfated Linear Alkane</b>	
Stepanol WAC	sodium laurel sulfate - molecular weight 288, 12 carbon chain
<b>Sulfated Ethoxylated Linear Alkane</b>	
Neodol 25-3S	sulfated ethoxylated alcohol molecular weight 399, 12 to 15 carbon chain

Three types of polymers, xanthan gum (X7D-226), hydroxyethyl cellulose (Natrosol 210HHR), and partially hydrolyzed polyacrylamide (Alcoflood 1175, Alcoflood 1135 and Cyanatrol 750) were used in the study. Polyacrylamides used in the study were approximately 30% hydrolyzed. All polymers used in the study were dry products.

### Alkali and Surfactant Interaction

**Interfacial Tension with Alkali** - The interfacial tension reductions by the alkalis alone are shown in Figure 1. Only  $\text{Na}_3\text{PO}_4$  reduced the interfacial tension to low levels. Figures 2 through 4 depict the low interfacial tension achieved by  $\text{Na}_3\text{PO}_4$  and blends of  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$ , and  $\text{Na}_2\text{CO}_3$  and blends of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ . Figures 3 and 4 indicate interfacial tension reduction to low values is not simply a pH phenomenon. Valence of the alkaline anion being related to the  $\text{Na}_3\text{PO}_4$  low interfacial tension values is not apparent. Mono-valent  $\text{NaOH}$  has lower interfacial tension values than di-valent  $\text{Na}_2\text{CO}_3$  with tri-valent  $\text{Na}_3\text{PO}_4$  having very low interfacial tension values.

**Surfactant Structure Effect on Interfacial Tension** - The interfacial tension was determined for each of the surfactants at 0.1 wt% and 0.2 wt%. The data are listed in the following table.

Surfactant	Interfacial Tension at 72°F (mN/m)	
	0.1 wt%	0.2 wt%
<b>Linear Alkyl Group</b>		
<b>-Alkyl Aryl Sulfonates</b>		
Naccanol 90-F	0.475	0.340
Polystep A7	0.369	0.655
LXS 370	0.172	0.100
Petrostep B-120	0.230	0.530
LXS 395	0.590	0.836
LXS 420	0.217	0.016
TRS 10-410	1.476	0.659
LTS 18	13.2	12.0
Petrostep B-105	4.5	5.1
<b>Linear Alkyl Group</b>		
<b>- Internal Bond to Aryl Functionality</b>		
<b>- Alkyl Aryl Sulfonates</b>		
Petrostep H67	0.108	1.002
<b>Branched Alkyl Group</b>		
<b>- Alkyl Aryl Sulfonates</b>		
Petrostep B-100	0.034	0.335
Chaser XP-100	0.012	0.006
Petrostep B-110	0.791	0.951

<u>Surfactant</u>	Interfacial Tension at 72°F (mN/m)	
	<u>0.1 wt%</u>	<u>0.2 wt%</u>
<b>Internal Olefin Sulfonates</b>		
Neodol IOS 1517	0.9	0.597
Neodol IOS 1720	2.0	1.8
<b>Alpha Olefin Sulfonates</b>		
AOS 12	1.879	1.673
Bioterge AS-40	1.006	1.414
<b>Sulfonated Linear Alkane</b>		
Bioterge PAS 8S	0.767	1.649
<b>Sulfonated Ethoxylated Linear Alkane</b>		
Avanel S-30	0.403	0.532
<b>Sulfated Linear Alkane</b>		
Stepanol WAC	0.681	0.712
<b>Sulfated Ethoxylated Linear Alkane</b>		
Neodol 25-3S	0.629	0.581

In the above table, the interfacial tension increases when Polystep A7 and LXS 370 are compared with AOS 12. This demonstrates that removing the aromatic group from the linear chain and attaching the sulfonate group to the linear chain of the same number of carbons increased the interfacial tension. Comparing Bioterge AS-40 and LXS 420, Neodol IOS 1517 and either TRS 10-410, Chaser XP-100 or Petrostep B-100 gives the same conclusion.

Molecular weight is not the key factor when evaluating the interfacial tension trends in the above table with Polystep A7 < Neodol IOS 1517, and LXS 370 and Petrostep B-120 < Neodol IOS 1720. Adding ethylene oxide to the linear chain to increase the molecular weight, as with Avanel S-30, did not result in low interfacial tensions. Increasing the olefinic character of the surfactant by adding an aromatic group to the molecule is the significant parameter which decreased the interfacial tension. However, if the molecule is made too hydrophobic in character (extending the alkyl group chain length beyond 17 carbons), the interfacial tension becomes greater. A similar change of interfacial tension with an increase hydrophobic character is observed with the alpha olefin sulfonates.

When the alkyl group is branched instead of linear, the interfacial tensions decrease to lower values. LXS 370, LXS 395, LXS 420, and Petrostep B-120 have higher interfacial tension values than either Petrostep B-100 or Chaser XP-100 and Petrostep B-105 has higher interfacial tension values than Petrostep B-110. In each comparison, the interfacial tension difference is an order of magnitude.

Sterically hindering the alkyl group by attaching one or more methyl groups to the aromatic functionality did not alter the interfacial tension values with any trend. LXS 370 gave lower interfacial tensions than Polystep A7 while LXS 395 gave higher interfacial tension values than Petrostep B-120. Chaser XP-100 produced lower interfacial tension than Petrostep B-100.

The difference in interfacial tension between sulfonated and sulfated surfactants is minimal.

**Surfactant Structure Effect on Alkali plus Surfactant Interaction** - Addition of alkali to the surfactant solutions decreased the interfacial tensions to lower values than either the alkaline agent or the surfactant alone. The data are depicted for each surfactant as listed in the following table.

<u>Surfactant</u>	<u>Figure Number</u>
<b>Linear Alkyl Group</b>	
<b>-Alkyl Aryl Sulfonates</b>	
Naccanol 90-F	5
Polystep A7	6
Petrostep B-120	7
LXS 370	8
LXS 395	9
LXS 420	10
TRS 10-410	11
LTS 18	12
Petrostep B-105	13
<b>Linear Alkyl Group</b>	
<b>- Internal Bond to Aryl Functionality</b>	
<b>- Alkyl Aryl Sulfonates</b>	
Petrostep H67	14
<b>Branched Alkyl Group</b>	
<b>- Alkyl Aryl Sulfonates</b>	
Petrostep B-100	15
Chaser XP-100	16
Petrostep B-110	17
<b>Alpha Olefin Sulfonates</b>	
AOS 12	18
Bioterger AS-40	19
<b>Internal Olefin Sulfonates</b>	
Neodol IOS 1517	20
Neodol IOS 1720	21

<u>Surfactant</u>	<u>Figure Number</u>
<b>Sulfonated Ethoxylated Linear Alkane</b> Avanel S-30	22
<b>Sulfonated Linear Alkane</b> Bioterge PAS 8S	23
<b>Sulfated Linear Alkane</b> Stepanol WAC	24
<b>Sulfated Ethoxylated Linear Alkane</b> Neodol 25-3S	25

NaOH, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub> either gave lower interfacial tension values or achieved ultra low interfacial tension values at lower alkali concentrations than NaHCO<sub>3</sub> and Na<sub>2</sub>HPO<sub>4</sub> with every surfactant tested. Surfactants with molecular weights in the 370 to 420 range (Chaser XP-100, LXS 370, LXS 395, and LXS 420) performed best with the lower pH alkalis. The ranges of pH observed for each alkaline agent with the different surfactant and alkali concentrations are:

<u>alkaline agent</u>	<u>pH range</u>
NaOH	11.9-13.5
Na <sub>2</sub> CO <sub>3</sub>	10.2-12.0
Na <sub>3</sub> PO <sub>4</sub>	11.6-12.8
NaHCO <sub>3</sub>	8.6-9.4
Na <sub>2</sub> HPO <sub>4</sub>	8.3-9.3

The data indicates that pH is a factor in the alkali-surfactant interaction which produces low interfacial tension. However, the data indicate that pH itself does not determine the interfacial tension.

Surfactant addition to an alkaline solution resulted in a decrease in interfacial tension for Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaHCO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub>. However, addition of surfactant to a Na<sub>3</sub>PO<sub>4</sub> solution increased the interfacial tension for a majority of the surfactants at high concentrations of Na<sub>3</sub>PO<sub>4</sub> but not at low concentrations of Na<sub>3</sub>PO<sub>4</sub>. Figures 26 through 28 for Bioterge AS-40 showing the interfacial tension values as a function of alkali and surfactant concentration is typical of the trend for surfactants which did not result in ultra low interfacial tension values when combined with alkali (ie Naccanol 90-F, Polystep A-7, Enordet AOS 12, Neodol IOS 1517, Neodol IOS 1720, Avanel S-30, Stepanol WAC, Neodol 25-3S). Note in Figure 27 that high interfacial tensions were observed for the Na<sub>3</sub>PO<sub>4</sub> plus Bioterge AS-40 solutions even though the solution pH approached 12 and the interfacial tension with alkali alone is low. This suggests that pH is not a dominating factor in producing ultra low interfacial tension values when alkali and surfactant are mixed and that the surfactant dominates the alkali-surfactant synergism.

Figures 29 through 31 depicting the same plots for Petrostep B-100 is typical for surfactants which produce ultra low interfacial tension values (LXS 370, LXS 395, LXS 420, Petrostep B-120, TRS 10-410, Chaser XP-100, LTS-18, Petrostep B-105, Petrostep H-67, and Bioterge PAS 8S). These types of surfactants lower the interfacial tension to minimum values over a limited range of alkali concentration as shown for 0.75 to 1.25 wt% NaOH and Petrostep B-100 in Figure 29 or a minimum interfacial tension plane between alkali and surfactant concentrations as shown by 0.75 to 2.0 wt% Na<sub>2</sub>CO<sub>3</sub> and 0.1 to 0.2 wt% Petrostep B-100 in Figure 30. The level of interfacial tension reduction did vary with each surfactant and alkaline agent as shown earlier in Figures 5 through 25.

For alkaline solutions, surfactant type was significant in lowering the interfacial tension. However, the interfacial tension data for the Adena crude oil suggests this is more a function of molecular weight and, therefore, olefinic character of the surfactant than it is a function of surfactant structure. Figure 32 depicts the minimum interfacial tension versus sulfonated surfactant molecular weight for 0.1 wt% surfactant. The minimum interfacial tension occurred at different alkali concentrations. 0.2 wt% surfactant shows an identical trend. The 216 amu Petrostep PAS-8S linear alkyl sulfonate is an exception. The dialkylate sulfonate (Petrostep H67), the ethoxylated sulfate and sulfonate (Neodol 25-3S and Avanel S-30), and sulfated linear alkane (Stepanol WAC) are consistent. A similar conclusion was reached by Salager et. al.<sup>16</sup> who demonstrated that the optimal salinity of the surfactant solution was a function of surfactant structure and hydrophilic-lipophilic balance number for blending micellar solutions.

Figure 33 shows the minimum interfacial tension versus molecular weight for the branched and linear alkyl aryl sulfonates. The poorer interfacial tension reduction capability of the low pH alkaline agents with the linear alkyl aryl sulfonates. The branched alkyl aryl sulfonates demonstrate little difference between the high and low pH alkaline agents.

In summary, the surfactant-alkali interfacial tension reduction synergism is controlled by the surfactant. For the Adena crude oil, only specific surfactants in a molecular weight range of 370 to 450 were effective in lowering the interfacial tension. Surfactants with lower and higher molecular weight with the same alkaline agents produced higher interfacial tensions. Similarly, addition of the surfactant to the Na<sub>3</sub>PO<sub>4</sub> solutions with ultra low interfacial tension without surfactant resulted in increased interfacial tensions for the majority of surfactants.

**Temperature Effect on Alkali plus Surfactant Interaction** - An increase in temperature from 72°F to 170°F changed the interfacial tensions differently for the various surfactants and alkaline agents. The low molecular weight alkyl surfactants capability to reduce the interfacial tension did not change significantly with temperature. Low interfacial tensions were not developed at 72°F or at elevated temperatures. Figure 34 depicting the change of interfacial tension for alkaline-surfactant (IOS 1517) solutions as a function of NaOH and Na<sub>2</sub>CO<sub>3</sub> concentration and temperature is typical for this class of surfactant.

This was not true of the higher molecular weight alkyl aryl sulfonates. The linear alkyl aryl sulfonates plus alkali interfacial tension reduction capability was temperature dependent. Figure 35 depicts LXS 370 and LXS 420 combined with NaOH interfacial tension values as a function of temperature and alkali concentration and Figure 36 is the same except with Na<sub>2</sub>CO<sub>3</sub>. Both figures demonstrate that the interfacial tension reduction is dependent on temperature and this dependency is unique for each surfactant. The topology of the interfacial tension-alkali concentration-temperature plot is generally consistent with each surfactant, regardless of alkali type, agreeing with the prior conclusion that surfactant is the dominate component in the interfacial tension reduction synergism.

Solutions of branched alkyl aryl sulfonates (Petrostep B-100 and Chaser XP-100) plus alkali agents interfacial tensions were not effected with a change of temperature. Figure 37 shows the data for Petrostep B-100 and Chaser XP-100 and NaOH while Figure 38 depicts the temperature changes with Na<sub>2</sub>CO<sub>3</sub>. A trend toward the higher molecular weight surfactant producing lower interfacial tensions is suggested with both alkaline agents as the temperature increases. The trend of ultra low interfacial tensions being produced with the higher molecular weight surfactants as the temperature increases is consistent with phase theory and the change of solubility of surfactants with temperature.

The alkali concentration(s) which produced the lowest interfacial tension changed with temperature not only for the branched alkyl aryl surfactants but the linear alkyl aryl surfactants as well. The data for 0.1 wt% alkyl aryl surfactants are listed in the following table. The alkyl surfactants are not listed since ultra low interfacial tensions were not observed and the interfacial tension minimum may not have been measured over the limited alkali concentration evaluated.

Surfactant	Alkali	Concentration Range of Alkali (wt%) at Minimum Interfacial Tension		
		72°F	125°F	170°F
<b>Linear Alkyl Aryl Sulfonates</b>				
LXS 370	NaOH	0.75-1.00	2.00	1.00
	Na <sub>2</sub> CO <sub>3</sub>	1.00-1.25	2.00	2.00
	NaHCO <sub>3</sub>	2.00	2.00	0.75-2.00
	Na <sub>3</sub> PO <sub>4</sub>	0.50-1.50	2.00	1.50
	Na <sub>2</sub> HPO <sub>4</sub>	0.75	2.00	2.00
LXS 420	NaOH	0.50	0.50	0.50
	Na <sub>2</sub> CO <sub>3</sub>	0.50	0.50-0.75	0.50
	NaHCO <sub>3</sub>	0.50	0.50-0.75	0.50-1.25
	Na <sub>3</sub> PO <sub>4</sub>	0.50	0.50	0.50-1.25
	Na <sub>2</sub> HPO <sub>4</sub>	0.50	0.50-0.75	0.50-2.00
LTS 18	NaOH	1.50-2.00	0.50-0.75	0.50
	Na <sub>2</sub> CO <sub>3</sub>	1.25	0.50-1.00	0.50-1.00
	NaHCO <sub>3</sub>	2.00	0.50-1.00	1.25-2.00
	Na <sub>3</sub> PO <sub>4</sub>	2.00	0.50-0.75	0.75-2.00
	Na <sub>2</sub> HPO <sub>4</sub>	2.00	0.50-1.25	0.75-1.00

<u>Surfactant</u>	<u>Alkali</u>	Concentration Range of Alkali (wt%) at Minimum Interfacial Tension		
		<u>72°F</u>	<u>125°F</u>	<u>170°F</u>
<b>Branched Alkyl Aryl Sulfonates</b>				
Petrostep B-100	NaOH	0.50-1.50	0.50-2.00	0.75-2.00
	Na <sub>2</sub> CO <sub>3</sub>	0.50-2.00	0.50-2.00	1.00-2.00
	NaHCO <sub>3</sub>	1.25-2.00	1.25-2.00	1.25-2.00
	Na <sub>3</sub> PO <sub>4</sub>	0.50-2.00	1.00-2.00	1.00-2.00
	Na <sub>2</sub> HPO <sub>4</sub>	1.50-2.00	1.00-2.00	1.00-2.00
Chaser XP-100	NaOH	0.50-2.00	1.00-1.50	0.50-2.00
	Na <sub>2</sub> CO <sub>3</sub>	0.50-1.25	0.50-2.00	1.25-2.00
	NaHCO <sub>3</sub>	1.00-2.00	1.00-2.00	1.25-2.00
	Na <sub>3</sub> PO <sub>4</sub>	0.75-2.00	0.50-2.00	0.75-2.00
	Na <sub>2</sub> HPO <sub>4</sub>	0.50-1.50	0.75-2.00	1.25-2.00

The most notable difference between the two surfactant groups is the interfacial tension minimums occur over a broader range of alkali concentrations with the branched alkyl aryl sulfonates than the linear alkyl aryl sulfonates at the three temperatures. A trend toward higher alkali concentrations is observed with increasing temperature. At 0.2 wt% surfactant, the minimum interfacial tension occurs over essentially the same alkali concentration range. If a change does occur with 0.2 wt% surfactant, the alkali concentration range generally gets broader. The alkali range expansion was not consistent toward either lower or higher alkali concentrations.

**Critical Micelle Concentration** - To determine if the synergistic interfacial tension effect of combining the surfactant with the various alkaline agents is due to increasing the free surfactant concentration, the critical micelle concentration was determined at 72°F for five of the surfactants of different structure with each of the alkaline agents. The data are listed in the following table. Critical micelle concentration was determined using solution conductivity, surface tension, and interfacial tension measurements. The critical micelle concentration range measured by the three techniques are listed below.

<u>Surfactant</u>	<b>Critical Micelle Concentration (wt% x 10<sup>3</sup>)</b>					
	<u>0.5 wt% NaOH</u>	<u>0.5 wt% Na<sub>2</sub>CO<sub>3</sub></u>	<u>2.0 wt% NaHCO<sub>3</sub></u>	<u>0.5 wt% Na<sub>3</sub>PO<sub>4</sub></u>	<u>2.0 wt% Na<sub>2</sub>HPO<sub>4</sub></u>	<u>no alkali</u>
<b>Linear Alkyl Aryl Sulfonate</b>						
LXS 420	1 - 5	1 - 10	4 - 5	1 - 6.5	1 - 10	20 - 40
Petrostep B-105	10 - 16	10 - 20	10 - 16	10 - 20	10 - 20	20 - 100
<b>Branched Alkyl Aryl Sulfonate</b>						
Petrostep B-100	10 - 16	10 - 20	10 - 24	10 - 20	10 - 24	40 - 60
<b>Alpha and Internal Olefin Sulfonate</b>						
Bioterge AS-40	1 - 20	10 - 40	20 - 40	10 - 40	10 - 40	40 - 60
Neodol IOS 1518	20 - 40	10 - 40	40 - 100	20	40	60 - 200

The surfactant monomer concentration decreases with alkali addition.

**Salinity Effect on Alkali plus Surfactant Interaction** - The effect of increasing salinity on the interfacial tension between Adena crude oil and alkaline plus surfactant solutions are depicted in Figures 39 through 43 as a function of temperature. Salinity of each solution was increased by addition of NaCl. Each figure depicts surfactant and surfactant plus NaOH dissolved in waters of varying sodium chloride concentration. For the alkyl sulfonate class of surfactant, Neodol 1517 is typical. Figure 39 demonstrates these low molecular weight surfactants' interfacial tensions do not change significantly with increasing salinity. Comparing Figure 39 with Figure 34 demonstrates that alkali addition to the surfactant solution decreases the interfacial tension to lower values than sodium chloride addition over the range tested.

The linear alkyl aryl sulfonate class is characterized by LXS 370 in Figure 40 and LXS 420 in Figure 41. Addition of NaCl to the LXS 370-NaOH solution has made the solution more optimum (lower interfacial tension) while for the LXS-420-NaOH solution the solution was made less optimum. A trend of lower molecular weight surfactants becoming over optimum with increasing salinity is consistent with phase theory and the changing solubility of surfactants. Figure 35 and 36 compare with Figures 40 and 41 in showing the interfacial tension reduction by alkali addition and by NaCl addition to the surfactant solution. Again, alkali addition to the LXS 370 and LXS 420 give lower interfacial tension values than NaCl addition.

Figures 42 and 43 depict the effect of NaCl addition on surfactant and surfactant plus NaOH solutions for the branched alkyl aryl sulfonates. These figures compare with Figures 37 and 38 for alkali addition. Like the linear alkyl aryl sulfonates, the branched alkyl aryl sulfonates have lower interfacial tension values with alkali than NaCl. Both branched alkyl aryl sulfonates demonstrate optimum surfactant plus alkali solution becoming less optimum with NaCl addition.

The minimum interfacial tension and the concentration of NaCl required to achieve the minimum interfacial tension for Bioterge AS-40, Neodol IOS 1517, LTS 18, LXS 370, LXS 420, Chaser XP-100, and Petrostep B-100 are summarized in the following table. The alkali concentrations varied for each surfactant. Bioterge AS-40 and Neodol IOS 1517 represent the alkyl sulfonates; LXS 370, LXS 420 and LTS 18 represent the linear alkyl aryl sulfonates; and Chaser XP-100 and Petrostep B-100 represent the branched alkyl aryl sulfonates. Alkali concentrations correspond to the minimum interfacial tension at 72°F for each surfactant and alkali combination.

Surfactant	Alkali	Minimum Interfacial Tension (mN/m)			NaCl Concentration (mg/l)		
		72°F	125 °F	170°F	72°F	125 °F	170°F
<b>Alkyl Sulfonates</b>							
Bioterge AS-40	no alkali	0.229	0.504	0.496	30,000	30,000	30,000
	2.0 wt% NaOH	0.108	0.095	0.103	20,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> CO <sub>3</sub>	0.120	0.103	0.216	5,000	1,000	1,000
	2.0 wt% NaHCO <sub>3</sub>	0.443	0.418	0.310	20,000	30,000	1,000
	1.25 wt% Na <sub>3</sub> PO <sub>3</sub>	0.162	0.154	0.108	1,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.497	0.448	0.463	20,000	30,000	30,000
Neodol IOS 1517	no alkali	0.319	0.305	0.284	30,000	30,000	30,000
	2.0 wt% NaOH	0.067	0.072	0.060	30,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> CO <sub>3</sub>	0.128	0.156	0.191	1,000	1,000	30,000
	2.0 wt% NaHCO <sub>3</sub>	0.202	0.159	0.186	30,000	1,000	30,000
	1.25 wt% Na <sub>3</sub> PO <sub>3</sub>	0.117	0.141	0.078	1,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.275	0.228	0.227	30,000	1,000	30,000
<b>Linear Alkyl Aryl Sulfonates</b>							
LXS 370	no alkali	0.004	0.007	0.014	5,000	10,000	10,000
	0.5 wt% NaOH	0.002	0.004	0.002	20,000	30,000	10,000
	0.5 wt% Na <sub>2</sub> CO <sub>3</sub>	0.004	0.003	0.002	1,000	5,000	10,000
	0.5 wt% NaHCO <sub>3</sub>	0.007	0.005	0.001	30,000	5,000	10,000
	0.5 wt% Na <sub>3</sub> PO <sub>3</sub>	0.002	0.006	0.014	1,000	10,000	5,000
	0.75 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.003	0.006	0.001	1,000	5,000	10,000
LXS 420	no alkali	0.166	0.038	0.008	5,000	5,000	5,000
	0.5 wt% NaOH	0.002	0.014	0.001	1,000	1,000	1,000
	0.5 wt% Na <sub>2</sub> CO <sub>3</sub>	0.003	0.001	0.001	1,000	1,000	1,000
	0.5 wt% NaHCO <sub>3</sub>	0.013	0.001	0.001	1,000	1,000	1,000
	0.5 wt% Na <sub>3</sub> PO <sub>3</sub>	0.015	0.001	0.001	1,000	1,000	1,000
	0.75 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.053	0.002	0.001	1,000	1,000	1,000
LTS 18	no alkali	3.0	0.058	0.001	5,000	15,000	5,000
	1.0 wt% NaOH	0.105	0.019	0.014	1,000	1,000	1,000
	1.25 wt% Na <sub>2</sub> CO <sub>3</sub>	0.037	0.024	0.069	1,000	1,000	1,000
	2.0 wt% NaHCO <sub>3</sub>	0.045	0.017	0.003	1,000	1,000	1,000
	2.0 wt% Na <sub>3</sub> PO <sub>3</sub>	0.088	0.136	0.025	1,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.019	0.006	0.007	1,000	1,000	1,000

Surfactant	Alkali	Minimum Interfacial Tension (mN/m)			NaCl Concentration (mg/l)		
		72°F	125 °F	170°F	72°F	125 °F	170°F
<b>Branched Alkyl Aryl Sulfonates</b>							
Chaser XP-100	no alkali	0.012	0.001	0.001	1,000	15,000	20,000
	1.0 wt% NaOH	0.008	0.001	0.001	1,000	1,000	1,000
	1.25 wt% Na <sub>2</sub> CO <sub>3</sub>	0.001	0.001	0.001	1,000	1,000	1,000
	2.0 wt% NaHCO <sub>3</sub>	0.001	0.001	0.002	1,000	1,000	1,000
	2.0 wt% Na <sub>3</sub> PO <sub>3</sub>	0.002	0.001	0.001	1,000	1,000	1,000
	2.0 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.004	0.001	0.001	1,000	1,000	1,000
<b>Petrostep B-100</b>							
	no alkali	0.015	0.006	0.002	15,000	15,000	15,000
	0.75 wt% NaOH	0.001	0.001	0.001	1,000	1,000	10,000
	1.0 wt% Na <sub>2</sub> CO <sub>3</sub>	0.001	0.001	0.001	1,000	1,000	1,000
	1.25 wt% NaHCO <sub>3</sub>	0.003	0.001	0.002	1,000	1,000	5,000
	1.0 wt% Na <sub>3</sub> PO <sub>3</sub>	0.006	0.001	0.001	1,000	1,000	10,000
	2.0 wt% Na <sub>2</sub> HPO <sub>4</sub>	0.008	0.001	0.001	1,000	1,000	1,000

The tabular and graphic data indicate the decrease of interfacial tension by the addition of alkali alone to surfactant solutions is not simply a salinity effect. The interfacial tensions were lower for the alkali plus surfactant solutions than surfactant solutions with corresponding NaCl concentrations. The magnitude of interfacial tension reduction which occurs as either alkali or NaCl are added to the surfactant solutions is different for each surfactant.

No consistent trend was observed with the salinity at which the minimum interfacial tension occurred as the temperature changed.

### **Polymer, Surfactant and Alkali Interaction**

**Effect of Alkali and Surfactant on Polymer Solution Characteristics** - The effect of alkali and surfactant on the polymer solution characteristics were determined by monitoring the apparent viscosity using Brookfield and Ubbelohde viscometers. Xanthan gum, hydroxyethyl cellulose and partially hydrolyzed polyacrylamide polymers were mixed with Bioterge AS-40, Petrostep B-100, and LXS 420 which were representative of the alkyl sulfonates, the branched alkyl aryl sulfonates, and the linear alkyl aryl sulfonates, respectively.

**Effect of Alkali and Surfactant on Apparent Viscosity** - Brookfield viscosities were measured to determine the solution characteristics when various alkaline agents and surfactants are added to the polymer solutions. The data are summarized in the following table.

1,200 mg/l Polymer Solution  
 -----Brookfield Viscosity (cp)-----  
 Hydroxyethyl

<u>Surfactant</u>	<u>Alkali</u>	<u>wt%</u>	<u>Xanthan Gum</u>		<u>Cellulose</u>		<u>Polyacrylamide</u>	
			<u>70°F</u>	<u>180°F</u>	<u>70°F</u>	<u>180°F</u>	<u>70°F</u>	<u>180°F</u>
None	none	0.00	59.6	2.2	5.8	1.2	45.8	17.1
	NaOH	1.25	40.6	5.4	2.2	0.8	11.7	4.0
	Na <sub>2</sub> CO <sub>3</sub>	2.00	46.3	6.1	3.1	0.9	9.6	5.6
	NaHCO <sub>3</sub>	2.00	57.4	7.4	3.0	1.1	9.8	4.9
	Na <sub>3</sub> PO <sub>4</sub>	2.00	44.5	5.9	2.7	1.0	9.8	3.9
	Na <sub>2</sub> HPO <sub>4</sub>	2.00	44.3	6.2	3.2	1.1	10.3	4.9
Bioterge AS-40 0.1 wt%	none	0.00	60.6	2.6	5.9	1.2	44.1	22.4
	NaOH	1.25	----	---	3.4	0.7	11.6	4.9
	Na <sub>2</sub> CO <sub>3</sub>	2.00	48.8	6.6	6.1	1.1	9.6	4.6
	NaHCO <sub>3</sub>	2.00	----	---	6.1	0.8	10.9	4.9
	Na <sub>3</sub> PO <sub>4</sub>	2.00	----	---	5.2	0.9	10.3	5.4
	Na <sub>2</sub> HPO <sub>4</sub>	2.00	----	---	5.9	1.0	9.3	4.8
LXS 420 0.1 wt%	none	0.00	61.3	2.6	4.8	0.9	41.6	26.8
	NaOH	1.25	44.3	6.2	3.7	1.1	9.9	5.3
	Na <sub>2</sub> CO <sub>3</sub>	2.00	49.3	6.9	5.5	1.2	10.1	5.7
	NaHCO <sub>3</sub>	2.00	62.6	8.0	5.6	1.2	11.6	5.2
	Na <sub>3</sub> PO <sub>4</sub>	2.00	48.3	7.4	4.7	1.1	10.8	5.7
	Na <sub>2</sub> HPO <sub>4</sub>	2.00	63.6	8.1	5.4	1.4	11.4	4.3
Petrostep B-100 0.1 wt%	none	0.00	62.8	3.0	5.6	0.8	44.8	18.3
	NaOH	1.25	----	---	3.8	0.8	9.5	4.9
	Na <sub>2</sub> CO <sub>3</sub>	2.00	46.9	6.9	5.3	0.8	9.7	5.2
	NaHCO <sub>3</sub>	2.00	----	---	4.9	0.7	10.6	3.7
	Na <sub>3</sub> PO <sub>4</sub>	2.00	----	---	4.6	1.0	11.3	4.1
	Na <sub>2</sub> HPO <sub>4</sub>	2.00	----	---	3.9	0.7	10.8	2.6

The viscosity changes of the polymer solutions with alkali are consistent with prior researchers.<sup>17</sup> The effect of surfactant and alkali on the polymer solution varied with polymer type and temperature. Alkali addition increased the xanthan gum viscosity at 180°F but not at 70°F. Hydroxyethyl cellulose and polyacrylamide solution viscosities were decreased by alkali addition. Alkali type was not significant in defining the alteration of polymer solution apparent viscosity.

Surfactant addition to xanthan gum solutions resulted in solution viscosity increases of approximately 3% without alkali and 5.2% with alkali at 70°F while at 180°F viscosity increases of 24% without alkali and 16.3% with alkali were observed. Figures 44 and 45 demonstrate the increase in xanthan gum solution viscosities at 70°F and 180°F. The

viscosity decrease due to alkali addition is evident at 70°F while at 180°F xanthan gum plus surfactant viscosities increase with alkali addition.

Hydroxyethyl cellulose apparent viscosities were essentially unchanged by surfactant addition at 180°F either with or without alkali. At 70°F, hydroxyethyl cellulose viscosity was unchanged with surfactant addition but increased by an average 74% with alkali. Surfactant structure was not significant in the viscosity alteration of either xanthan gum or hydroxyethyl cellulose.

Surfactant addition to polyacrylamide solutions did demonstrate a difference with surfactant structure. The linear chain surfactants (with and without aryl group) generally increased the solution viscosity at 70°F and at 180°F. The branched alkyl aryl group surfactant essentially had no effect on the apparent viscosity. Addition of alkali to the surfactant solutions negated the increase in apparent viscosity observed with the linear alkyl group surfactants. Figures 46 and 47 are typical of alkali on polyacrylamide plus surfactant solutions. In both cases, the apparent viscosity decreases significantly with Na<sub>2</sub>CO<sub>3</sub> and the solution viscosity difference with polymer concentration is less. The increase in viscosity of the polymer solution and the alkali plus polymer solution with LXS 420 addition is evident but not with Petrostep B-100.

**Pseudoplastic Characteristics of Alkaline-Surfactant-Polymer Solutions** - To further investigate the change in surfactant-polymer interaction with alkali addition, the apparent viscosity as a function of shear rate was studied using four bulb Ubbelohde viscometers at 72°F. Figures 48 through 50 depict the apparent viscosity versus shear rate for polymer dissolved in water, surfactant, alkali, and alkali plus surfactant for xanthan gum, polyacrylamide, and hydroxyethyl cellulose, respectively. Each of the polymers show a decrease in apparent viscosity as well as a loss of pseudoplastic character when alkali is added to the polymer or surfactant plus polymer solutions. For the solutions depicted, surfactant addition demonstrated slight increases in apparent viscosities with imperceptible changes in pseudoplastic character.

For the range of shear rates used, the solutions exhibit pseudoplastic character that can be modeled with a power law such as

$$\mu = K\dot{\gamma}^{n-1}$$

where  $\mu$  is viscosity, K is consistency index, and n is the power law exponent.

The power law constant for the polymer solutions with alkali, surfactant, and alkali plus surfactant are documented in the following table for 800 mg/l polymer solutions.

Polymer	Surfactant	Surfactant Concentration		Alkali Concentration		
		wt%	Alkali	wt%	K	n
xanthan gum 800 mg/l	none	0.0	none	0.0	96.4	0.489
	LXS 420	0.1	none	0.0	92.8	0.493
		0.2		0.0	94.3	0.491
		0.5		0.0	91.4	0.494
	Petrostep B-100	0.1	none	0.0	87.9	0.529
		0.2		0.0	99.5	0.494
	none	0.0	NaOH	1.25	58.5	0.562
	LXS 420	0.1	NaOH	1.25	54.3	0.580
		0.2		1.25	57.8	0.578
		0.5		1.25	57.8	0.579
	Petrostep B-100	0.1	NaOH	1.25	57.6	0.574
		0.2		1.25	58.1	0.573
	none	0.0	Na <sub>2</sub> CO <sub>3</sub>	2.00	57.7	0.570
	LXS 420	0.1	Na <sub>2</sub> CO <sub>3</sub>	2.00	57.5	0.574
		0.2		2.00	60.7	0.567
		0.5		2.00	61.9	0.573
	Petrostep B-100	0.1	Na <sub>2</sub> CO <sub>3</sub>	2.00	65.6	0.558
		0.2		2.00	64.8	0.561
	none	0.0	NaHCO <sub>3</sub>	2.00	90.9	0.490
	LXS 420	0.1	NaHCO <sub>3</sub>	2.00	91.4	0.495
		0.2		2.00	86.7	0.506
		0.5		2.00	91.3	0.502
	none	0.0	Na <sub>3</sub> PO <sub>4</sub>	2.00	62.6	0.555
	LXS 420	0.1	Na <sub>3</sub> PO <sub>4</sub>	2.00	57.9	0.577
		0.2		2.00	57.7	0.578
		0.5		2.00	56.2	0.581

Polymer	Surfactant	Surfactant Concentration		Alkali Concentration		
		wt%	Alkali	wt%	K	n
<b>xanthan gum</b> 800 mg/l	none	0.0	Na <sub>2</sub> HPO <sub>4</sub>	2.00	98.2	0.475
	LXS 420	0.1	Na <sub>2</sub> HPO <sub>4</sub>	2.00	91.0	0.498
		0.2		2.00	88.0	0.506
		0.5		2.00	91.9	0.502
<b>polyacrylamide</b> 800 mg/l	none	0.0	none	0.0	75.5	0.579
	LXS 420	0.1	none	0.0	63.9	0.614
		0.2		0.0	64.2	0.610
		0.5		0.0	61.4	0.619
	Petrostep B-100	0.1	none	0.0	68.9	0.598
		0.2		0.0	68.4	0.594
	none	0.0	NaOH	1.25	9.8	0.822
	LXS 420	0.1	NaOH	1.25	10.3	0.831
		0.2		1.25	11.7	0.810
		0.5		1.25	11.6	0.814
	Petrostep B-100	0.1	NaOH	1.25	11.2	0.813
		0.2		1.25	12.7	0.793
	none	0.0	Na <sub>2</sub> CO <sub>3</sub>	2.00	10.5	0.818
	LXS 420	0.1	Na <sub>2</sub> CO <sub>3</sub>	2.00	9.9	0.834
		0.2		2.00	9.6	0.840
		0.5		2.00	9.1	0.851
	Petrostep B-100	0.1	Na <sub>2</sub> CO <sub>3</sub>	2.00	9.7	0.833
		0.2		2.00	9.4	0.838
	none	0.0	NaHCO <sub>3</sub>	2.00	12.0	0.800
	LXS 420	0.1	NaHCO <sub>3</sub>	2.00	10.7	0.831
		0.2		2.00	10.8	0.826
		0.5		2.00	10.2	0.838

Polymer	Surfactant	Surfactant Concentration		Alkali Concentration			
		wt%	Alkali	wt%	K	n	
<b>polyacrylamide</b> 800 mg/l	none	0.0	Na <sub>3</sub> PO <sub>4</sub>	2.00	9.8	0.824	
	LXS 420	0.1	Na <sub>3</sub> PO <sub>4</sub>	2.00	8.5	0.854	
		0.2		2.00	8.5	0.858	
		0.5		2.00	8.3	0.856	
		none		0.0	Na <sub>2</sub> HPO <sub>4</sub>	2.00	11.2
	LXS 420	0.1	Na <sub>2</sub> HPO <sub>4</sub>	2.00	9.3	0.837	
		0.2		2.00	11.2	0.810	
		0.5		2.00	11.0	0.821	
		<b>hydroxyethyl cellulose</b> 800 mg/l		none	0.0	none	0.0
	LXS 420		0.1	none	0.0	3.2	0.954
			0.2		0.0	3.2	0.956
			0.5		0.0	3.6	0.940
			none		0.0	NaOH	1.25
	LXS 420		0.1	NaOH	1.25	1.9	1.000
			0.2		1.25	1.9	0.997
0.5			1.25		2.0	0.998	
none			0.0		Na <sub>2</sub> CO <sub>3</sub>	2.00	2.9
LXS 420	0.1		Na <sub>2</sub> CO <sub>3</sub>	2.00	2.8	0.979	
	0.2			2.00	2.7	0.988	
	0.5			2.00	3.2	0.961	
	none			0.0	NaHCO <sub>3</sub>	2.00	1.5
LXS 420	0.1		NaHCO <sub>3</sub>	2.00	1.9	0.965	
	0.2			2.00	2.0	0.957	
	0.5	2.00		1.5	0.995		
	none	0.0		Na <sub>3</sub> PO <sub>4</sub>	2.00	1.5	0.996
LXS 420	0.1	Na <sub>3</sub> PO <sub>4</sub>	2.00	1.4	0.997		
	0.2		2.00	1.4	0.992		
	0.5		2.00	1.3	0.975		

Polymer	Surfactant	Surfactant Concentration		Alkali Concentration		K	n
		wt%	Alkali	wt%			
hydroxyethyl cellulose 800 mg/l	none	0.0	Na <sub>2</sub> HPO <sub>4</sub>	2.00		1.4	1.00
	LXS 420	0.1	Na <sub>2</sub> HPO <sub>4</sub>	2.00		1.9	0.951
		0.2		2.00		1.5	0.990
		0.5		2.00		1.4	0.997

The effect of alkali on the pseudoplastic character of xanthan gum solutions depends on the type of alkali. Loss of pseudoplastic character is less for Na<sub>2</sub>HPO<sub>4</sub> and NaHCO<sub>3</sub> than for NaOH, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub>. Polyacrylamide and hydroxyethyl cellulose did not show a difference with alkali type. Hydroxyethyl cellulose dissolved with alkali essentially behaves like a newtonian fluid as demonstrated by the power law exponents near 1.0.

Addition of surfactant to the alkaline-polymer solutions returned some of the pseudoplastic character to the xanthan gum solutions. For polyacrylamide plus alkali solutions, pseudoplastic character continued to decrease with surfactant addition. Hydroxyethyl cellulose plus alkali solutions demonstrated further decrease of slope followed by an increase at the higher surfactant concentrations. Both surfactants interact with each of the three polymers dissolved with alkali and without alkali to affect solution rheology.

**Intrinsic Viscosity of Alkaline-Surfactant-Polymer Solutions** - Solution viscosity is useful to measure the polymer molecular weight, size and extension in space.<sup>18</sup> Intrinsic viscosity was calculated from the solution viscosity versus shear rate data according to

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c)$$

where  $[\eta]$  is the intrinsic viscosity,  $\eta_s$  is the specific viscosity and  $c$  is the polymer concentration.

The molecular weight of the polymers was calculated using the Mark-Hank equation<sup>18</sup>

$$[\eta] = K'M^a$$

where  $K'$  and "a" are constants specific for each polymer and  $M$  is the molecular weight. Constants<sup>19</sup> used were:

	$K'$	a
Polyacrylamide	$3.73 \times 10^{-4}$	0.66
Hydroxyethyl Cellulose	$0.95 \times 10^{-5}$	0.87
Xanthan Gum	$1.18 \times 10^{-5}$	0.85

Molecular weights calculated for polyacrylamide (Alcoflood 1175), hydroxyethyl cellulose (Natrosol 210HHR), and xanthan gum (X7D-226) dissolved in 1,000 mg/l NaCl were  $16.6 \times 10^6$ ,  $1.54 \times 10^6$ , and  $5.54 \times 10^6$  amu, respectively.

Hydrodynamic radius was calculated from the intrinsic viscosity according to the Fox-Flory equation<sup>18</sup>

$$[\eta] = \frac{\phi(\overline{r^2})^{1.5}}{M}$$

where  $\phi$  is a universal constant ( $2.1 \times 10^{21}$ ) and  $r$  is the hydrodynamic radius.

The molecular weight calculated from the polymer dissolved in 1,000 mg/l NaCl was used in the Fox-Flory equation to calculate all hydrodynamic radii. The intrinsic viscosity of the polymer solutions dissolved with surfactant, alkali, and alkali plus surfactant and the calculated hydrodynamic radius of the polymer are listed in the following table.

<u>Polymer</u>	<u>Alkali - wt%</u>	<u>Surfactant - wt%</u>	<u>Intrinsic Viscosity ml/g</u>	<u>Hydrodynamic Radius microns</u>
<b>xanthan gum</b>	none	none	6,370	0.256
		LXS 420 0.1	7,969	0.276
		0.2	10,801	0.305
		0.5	10,134	0.299
		B-100 0.1	5,300	0.241
		0.2	10,316	0.301
	1.25 wt% NaOH	none	7,676	0.273
		LXS 420 0.1	2,738	0.193
		0.2	2,174	0.179
		0.5	3,012	0.200
		B-100 0.1	5,364	0.242
		0.2	5,591	0.245
	2.00 wt% Na <sub>2</sub> CO <sub>3</sub>	none	8,535	0.282
		LXS 420 0.1	3,117	0.202
		0.2	2,287	0.182
		0.5	3,457	0.211
		B-100 0.1	3,156	0.203
		0.2	6,101	0.252
	2.00 wt% NaHCO <sub>3</sub>	none	6,696	0.260
		LXS 420 0.1	5,304	0.241
0.2		6,257	0.255	
0.5		6,851	0.262	

<u>Polymer</u>	<u>Alkali - wt%</u>	<u>Surfactant - wt%</u>	<u>Intrinsic Viscosity ml/g</u>	<u>Hydrodynamic Radius microns</u>	
<b>xanthan gum</b>	2.00 wt% Na <sub>3</sub> PO <sub>4</sub>	none	6,342	0.256	
		LXS 420 0.1	2,560	0.189	
		0.2	3,325	0.206	
		0.5	6,523	0.258	
	2.00 wt% Na <sub>2</sub> HPO <sub>4</sub>	none	6,566	0.258	
		LXS 420 0.1	1,356	0.153	
		0.2	2,254	0.181	
		0.5	2,675	0.192	
	<b>polyacrylamide</b>	none	none	21,710	0.556
			LXS 420 0.1	15,621	0.498
			0.2	12,290	0.460
			0.5	12,208	0.459
B-100 0.1			18,072	0.523	
0.2			20,696	0.547	
1.25 wt% NaOH		none	4,252	0.323	
		LXS 420 0.1	3,189	0.293	
		0.2	2,871	0.283	
		0.5	3,511	0.303	
		B-100 0.1	3,181	0.293	
		0.2	3,970	0.315	
2.00 wt% Na <sub>2</sub> CO <sub>3</sub>		none	4,685	0.333	
		LXS 420 0.1	3,137	0.292	
		0.2	3,118	0.291	
		0.5	3,726	0.309	
		B-100 0.1	2,694	0.277	
		0.2	3,096	0.290	
2.00 wt% NaHCO <sub>3</sub>		none	6,751	0.376	
		LXS 420 0.1	3,470	0.302	
		0.2	3,029	0.288	
		0.5	4,114	0.319	
2.00 wt% Na <sub>3</sub> PO <sub>4</sub>		none	3,988	0.316	
		LXS 420 0.1	3,475	0.302	
	0.2	3,372	0.299		
	0.5	3,511	0.322		
2.00 wt% Na <sub>2</sub> HPO <sub>4</sub>	none	5,629	0.354		
	LXS 420 0.1	3,057	0.289		
	0.2	2,156	0.257		
	0.5	3,544	0.304		

<u>Polymer</u>	<u>Alkali - wt%</u>	<u>Surfactant - wt%</u>	<u>Intrinsic Viscosity ml/g</u>	<u>Hydrodynamic Radius microns</u>
<b>hydroxyethyl cellulose</b>	none	none	2,293	0.119
		LXS 420 0.1	2,025	0.114
		0.2	2,144	0.116
		0.5	2,269	0.118
	1.25 wt% NaOH	none	619	0.077
		LXS 420 0.1	598	0.076
		0.2	622	0.077
		0.5	692	0.080
	2.00 wt% Na <sub>2</sub> CO <sub>3</sub>	none	1,376	0.100
		LXS 420 0.1	1,067	0.092
		0.2	1,162	0.095
		0.5	1,259	0.097
	2.00 wt% NaHCO <sub>3</sub>	none	536	0.073
		LXS 420 0.1	410	0.067
		0.2	446	0.069
		0.5	481	0.071
	2.00 wt% Na <sub>3</sub> PO <sub>4</sub>	none	509	0.072
		LXS 420 0.1	450	0.069
		0.2	475	0.070
		0.5	510	0.072
	2.00 wt% Na <sub>2</sub> HPO <sub>4</sub>	none	379	0.065
		LXS 420 0.1	299	0.060
		0.2	461	0.070
		0.5	406	0.067

The intrinsic viscosity data leads to the same conclusions as the apparent viscosity data. Alkali has a significant effect on polymer solution rheology. Xanthan gum viscosity and molecular size increased with alkali addition while polyacrylamide and hydroxyethyl cellulose decreased. Surfactant addition to the polymer solutions either dissolved with or without alkali produced a polymer-surfactant interaction. Intrinsic viscosity values either increased or initially decreased with the lowest surfactant concentration followed by an increase at higher surfactant concentrations.

**Effect of Polymer on Alkali plus Surfactant Interactions** - To define the effect of polymer on the alkali plus surfactant interactions, interfacial tension and critical micelle concentrations were determined. Xanthan gum and polyacrylamide were added to Petrostep

B-100, LXS 420 and Bioterge AS-40 solutions dissolved with a single concentration of each of the five alkaline agents taken from prior evaluations. For these evaluation, representative surfactants from the different classes of sulfonate structures were selected. A second criteria was selecting solutions which produced high as well as ultra low interfacial tensions.

**Effect of Polymer on Alkali plus Surfactant Interfacial Tension** - The interfacial tension data are depicted in Figure 51 for xanthan gum and Figure 52 for partially hydrolyzed polyacrylamide. The two polymers increased the interfacial tensions in an identical manner, regardless of alkali. LXS 420 was not tested with polyacrylamide because the xanthan gum behavior was similar to Bioterge AS-40. Interfacial tension increased with surfactant-alkali combinations which produced ultra low interfacial tensions as well as those with higher values. For a few of the alkali plus surfactant combinations, interfacial tensions decreased; LXS 420 with  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{NaHCO}_3$ , and Bioterge AS-40 plus  $\text{NaHCO}_3$ .

Figure 53 depicts the interfacial tensions of Petrostep B-100 dissolved with either  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  and either polyacrylamide and xanthan gum. Again interfacial tension values increase with polymer addition. However, ultra low interfacial tension values can be produced in the presence of polymer by proper alkali concentration selection.

Increasing the polymer concentration greater than 400 mg/l did not change the interfacial tensions for those solutions which increased in interfacial tension. However, increasing the polymer concentration in those solutions showing a decrease continued to decrease the interfacial tension.

**Effect of Polymer on Surfactant Critical Micelle Concentrations** - To further investigate the effect of polymer addition on the surfactant and alkali interaction, the critical micelle concentrations of Petrostep B-100, LXS 420, and Bioterge AS-40 were determined with added polymer. 1,000 mg/l polyacrylamide (Alcoflood 1135, PHPA) was added to the surfactant alkali solutions and the critical micelle concentration determined. Again, critical micelle concentration was determined using solution conductivity, surface tension, and interfacial tension measurements. The critical micelle concentration range measured by the three techniques are listed below.

<u>Surfactant</u>	<b>Critical Micelle Concentration (wt% x 10<sup>3</sup>)</b>					
	0.5 wt% <u>NaOH</u>	0.5 wt% <u>Na<sub>2</sub>CO<sub>3</sub></u>	2.0 wt% <u>NaHCO<sub>3</sub></u>	0.5 wt% <u>Na<sub>3</sub>PO<sub>4</sub></u>	2.0 wt% <u>Na<sub>2</sub>HPO<sub>4</sub></u>	<u>no alkali</u>
<b>Linear Alkyl Aryl Sulfonate</b>						
LXS 420	1 - 5	1 - 10	4 - 5	1 - 6.5	1 - 10	20 - 40
LXS 420 with PHPA	10 - 40	5 - 60	20	10 - 20	10	20 - 60

<u>Surfactant</u>	<b>Critical Micelle Concentration (wt% x 10<sup>3</sup>)</b>					
	<u>0.5 wt% NaOH</u>	<u>0.5 wt% Na<sub>2</sub>CO<sub>3</sub></u>	<u>2.0 wt% NaHCO<sub>3</sub></u>	<u>0.5 wt% Na<sub>3</sub>PO<sub>4</sub></u>	<u>2.0 wt% Na<sub>2</sub>HPO<sub>4</sub></u>	<u>no alkali</u>
<b>Branched Alkyl Aryl Sulfonate</b>						
Petrostep B-100	10 - 16	10 - 20	10 - 24	10 - 20	10 - 24	40 - 60
Petrostep B-100 with PHPA	10 - 40	20	10 - 40	20 - 40	40	20 - 60
<b>Alpha Olefin Sulfonate</b>						
Bioterge AS-40	1 - 20	10 - 40	20 - 40	10 - 40	10 - 40	40 - 60
Bioterge AS-40 with PHPA	5 - 20	1 - 10	1 - 40	5 - 40	1 - 20	40

For the two alkyl aryl sulfonates, critical micelle concentration increased with polymer addition dissolved either with or without alkali. The linear alkyl sulfonate showed a decrease of critical micelle concentration dissolved either with or without alkali. Alkali type was not a factor with any of the surfactants.

### Conclusions

1. Blending alkaline agents and low concentrations of surfactants synergistically reduces the interfacial tension between the aqueous solutions and crude oil. Ultra low interfacial tension generation is not dependent on alkali type or pH. Surfactant is the dominating component relative to interfacial tension reduction. Olefinic character of the surfactant is the critical parameter defining ultra low interfacial tension reduction, not surfactant structure. However as a class, the alkyl aryl sulfonates performed best.
2. Altering the temperature did not significantly alter the interfacial tension for branched alkyl aryl sulfonates but did change the interfacial tension values with linear alkyl aryl sulfonates. Temperature did alter concentration at which the interfacial tension minimums occurred and the range of alkali concentration over which low interfacial tension values were observed.
3. The alkali and surfactant interfacial tension synergism which results in ultra low interfacial tension values is not a simple salinity or saponification effect.
4. Alkali addition decreased surfactant critical micelle concentration. Addition of polymer to the alkaline-surfactant solutions increased the critical micelle concentration for alkyl aryl surfactant and decreased critical micelle concentration for alpha olefin sulfonates.
5. Polymer addition to the alkaline-surfactant solutions increased interfacial tension, regardless of polymer type. Ultra low interfacial tensions can still be achieved with an alkaline-surfactant-polymer solution by altering the alkali concentration.

6. Polymer solution rheology is altered by alkali in the same manner as with changes in salinity. Linear alkyl and linear alkyl aryl surfactant addition to polymer and polymer plus alkali solutions altered solution rheology. At low concentrations of surfactant, solution viscosity decreased while at high concentrations solution viscosity increased. Branched alkyl aryl surfactants effect on polymer solution rheology was minimal.
7. Pseudoplastic behavior of polymer solutions are minimized with alkali addition. Surfactants at higher concentrations increased the pseudoplastic character of the solutions.
8. The inter-dependance between alkali, surfactant, and polymer to produce desirable solution characteristics must be considered in any design for a field application. Testing to define the optimum solution is required for a reservoir application. Alkali type is not critical on a technical basis.
9. Branched alkyl aryl sulfonate surfactants appear to be the best class of surfactants to begin any evaluation.

### References

1. Surkalo, H., Pitts, M.J., and Wyatt, K.: "Design and Field Implementation of Alkaline-Surfactant-Polymer Chemical Enhanced Oil Recovery Systems," Proceedings, 7th European Improved Oil Recovery Symposium, Moscow, Russia, October 27-29, 1993.
2. Schuler, P.J., Kuehne, D.L., and Lerner, R.M.: "Improving Chemical Flood Efficiency with Micellar/Alkaline/Polymer Processes," J. Pet. Tech., vol 41, pages 80-88 (1989).
3. Ball, J. And Surkalo, H.: "Alkaline-Surfactant-Polymer Process Makes EOR Economic," Amer. Oil Gas Reporter, 1988, vol 31, pages 46-48.
4. Hartshorne, J.M. and Nonchick, J.S.: "Micellar/Polymer Flood Shows Success in Bell Creek Field," SPE 13122, Presented at the 60th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Las Vegas, Nv, Sept 22-25, 1985.
5. Hause, W.: "Wilmington Micellar/Polymer Project," Soc. Pet. Eng. J., 213-218 (1984).
6. Meyers, J., Pitts, M.J. and Wyatt, K.: "Alkaline-Surfactant-Polymer Flood of the West Kiehl Unit," SPE 24144, presented at the SPE/DOE Eight Symposium on Enhanced Oil Recovery, Tulsa, Ok, April 22-24, 1992.
7. Hawkins, B., Taylor, K. and Nasr-El-Din, H.: "Mechanisms of Surfactant and Polymer Enhanced Alkaline Flooding: Application to David Lloydminster and Wainwright Sparky Fields," CIM/AOSTRA 91-28, Proceedings of the 1991 CIM Annual Technical Conference, April 21-24, 1991.

8. Clark, S.R., Pitts, M.J. and Smith, S.M.: "Design and Application of an Alkaline-Surfactant-Polymer Recovery System to the West Kiehl Field," SPE Advanced Technology Series, 1993, Volume 1, pages 172-179.
9. Lin, F.J., Besserer, G.J. and Pitts, M.J.: "Laboratory Evaluation of Crosslinked Polymer and Alkaline-Polymer-Surfactant Flood," Can. J. Pet. Tech., 1987, vol 27, pages 49-55.
10. French, T.R. and Josephson, C.B.: "Alkaline Flooding Injection Strategy," NIPER-563, Department of Energy, March 1992.
11. Holm, L.W.: "Propane-Gas-Water Miscible Floods in Watered-Out Areas of the Adena Field, Colorado," J. Pet. Tech., October 1972, pages 1264 to 1270.
12. American Standard Testing Method ASTM D971, Annual Book of ASTM Standards, 1985, Petroleum Products and Lubricants, Volume 05.01, pages 435-437.
13. Gash, B. and Parrish, D.R.: "A Simple Spinning-Drop Interfacial Tensiometer," J. Pet. Tech., January 1977, pages 30-31.
14. Cayias, J.L., Schechter, R.S. and Wade, W.H.: "The Measurement of Low Interfacial Tension via the Spinning Drop Technique," Adsorption at Interfaces, ACE Symposium Series, No. 8, page 234-247 (1975).
15. American Standard Testing Method ASTM D1590, Annual Book of ASTM Standards, 1985.
16. Salager, J. L., Morgan, J.C., Schechter, R.S., Wade, W.H. and Vasques, E.: "Optimum Formulation of Surfactant/Water/Oil Systems for Minimum IFT or Phase Behavior," Soc. Pet. Eng. J., vol 19, no. 2, April 1979, pages 107-115.
17. Nasr-El-Din, H.A., Hawkins, B.F., and Green, K.A.: "Viscosity Behavior of Alkaline, Surfactant, Polyacrylamide Solutions Used for Enhanced Oil Recovery," SPE 21028, presented at the SPE International Symposium on Oilfield Chemistry held in Anaheim, California, February 20-22, 1991.
18. Billmeyer, F.W. Jr.: Textbook of Polymer Science, Wiley-Interscience, New York, 1971, pages 84-90.
19. Unsal, Esref, Duda, J.L. and Elmer, K.: "Comparison of Solution Properties of Mobility Control Polymers," Chemistry of Oil, American Chemical Society, Washington D.C., 1978, Chapter 8, pages 141-170.

Figure 1

Interfacial Tension Between Aqueous Alkali  
Dissolved in 1000 mg/l NaCl  
and Adena Crude Oil at 72°F

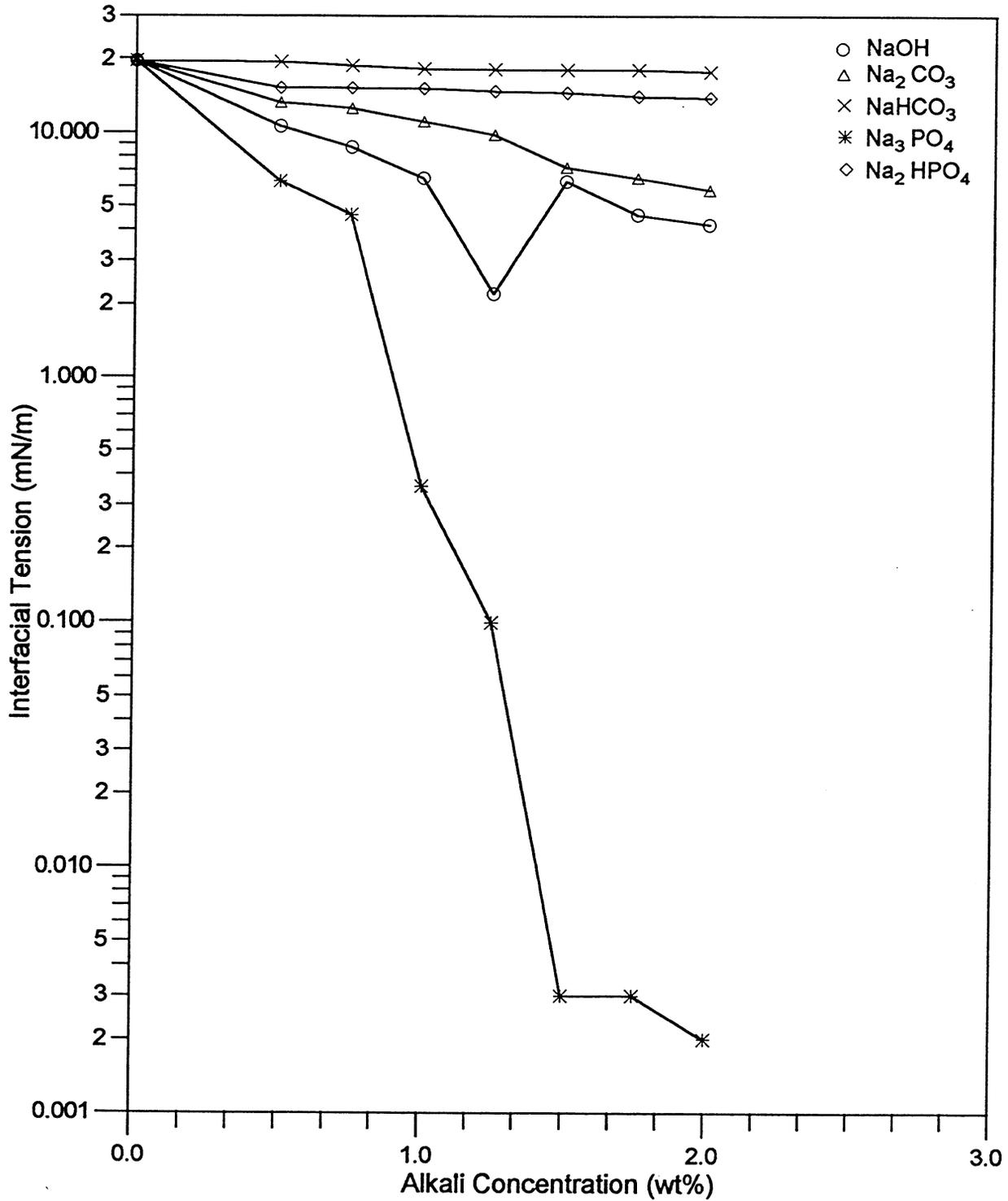


Figure 2

Interfacial Tension Between Aqueous Carbonate-Bicarbonate  
Dissolved in 1000 mg/l NaCl  
and Adena Crude Oil at 72° F

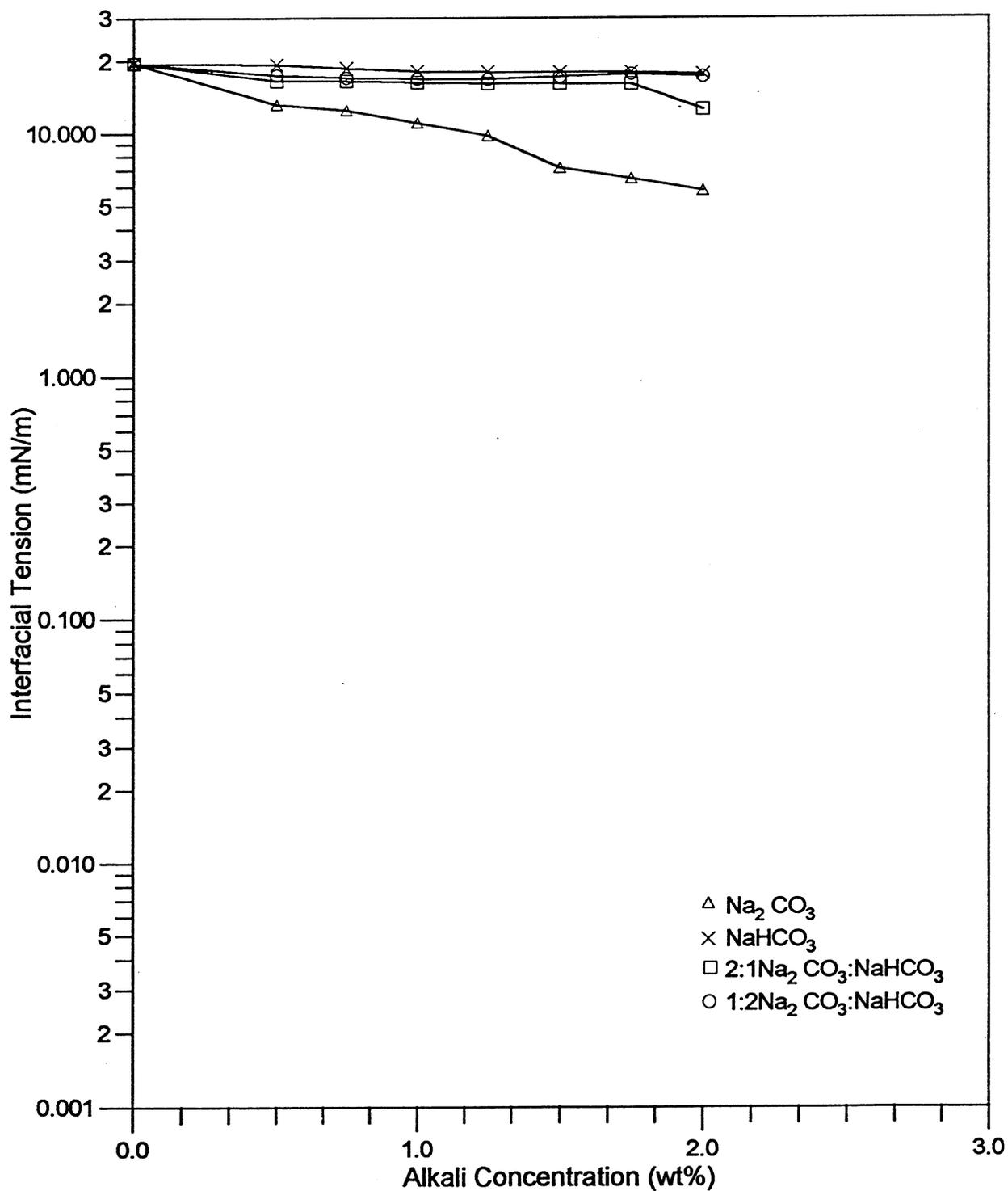


Figure 3

Interfacial Tension Between Aqueous Phosphate-Debasic Phosphate  
Dissolved in 1000 mg/l NaCl  
and Adena Crude Oil at 72° F

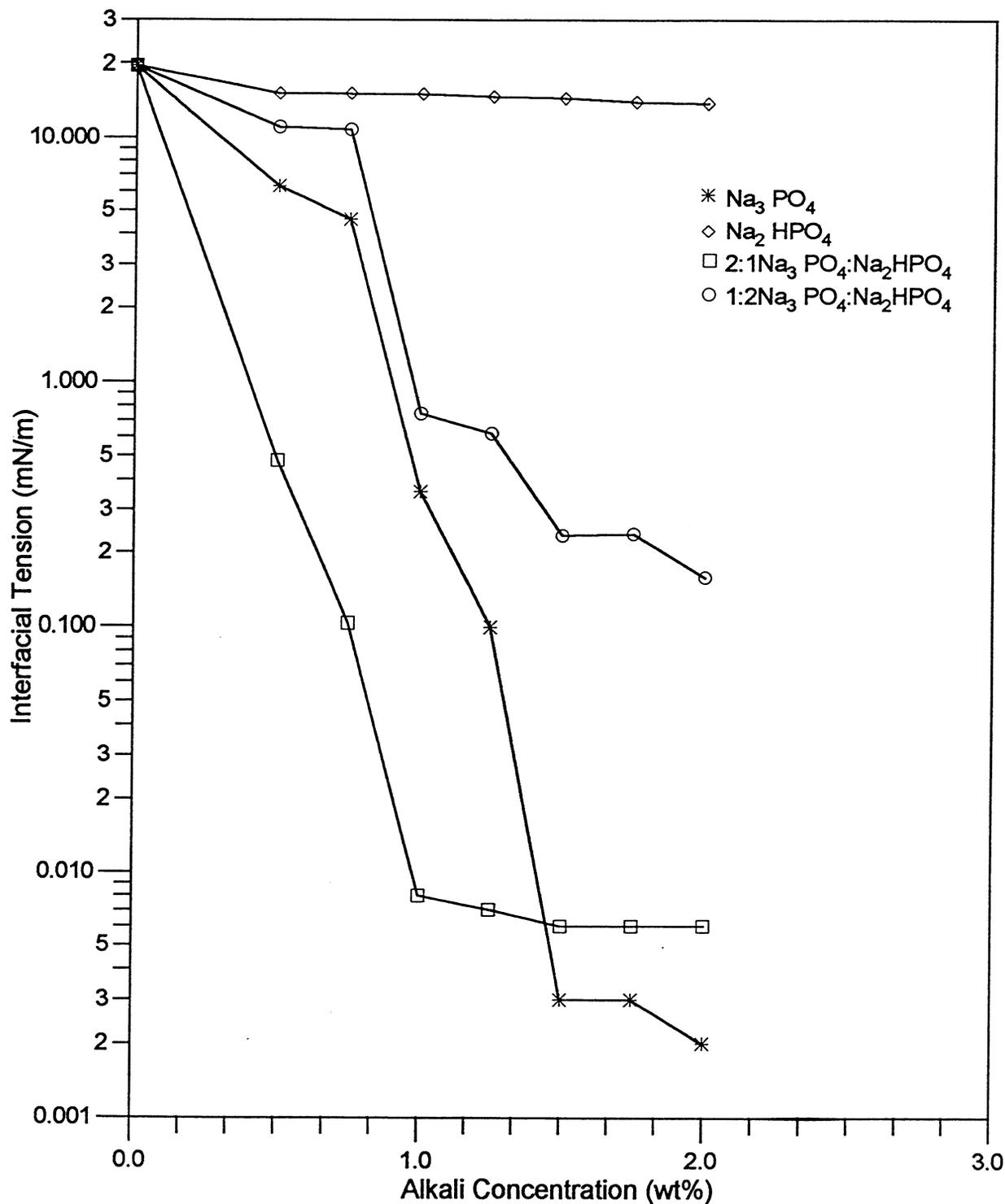


Figure 4

Interfacial Tension Reduction of Adena Crude Oil  
with 2.0 wt% Alkali as a function of pH

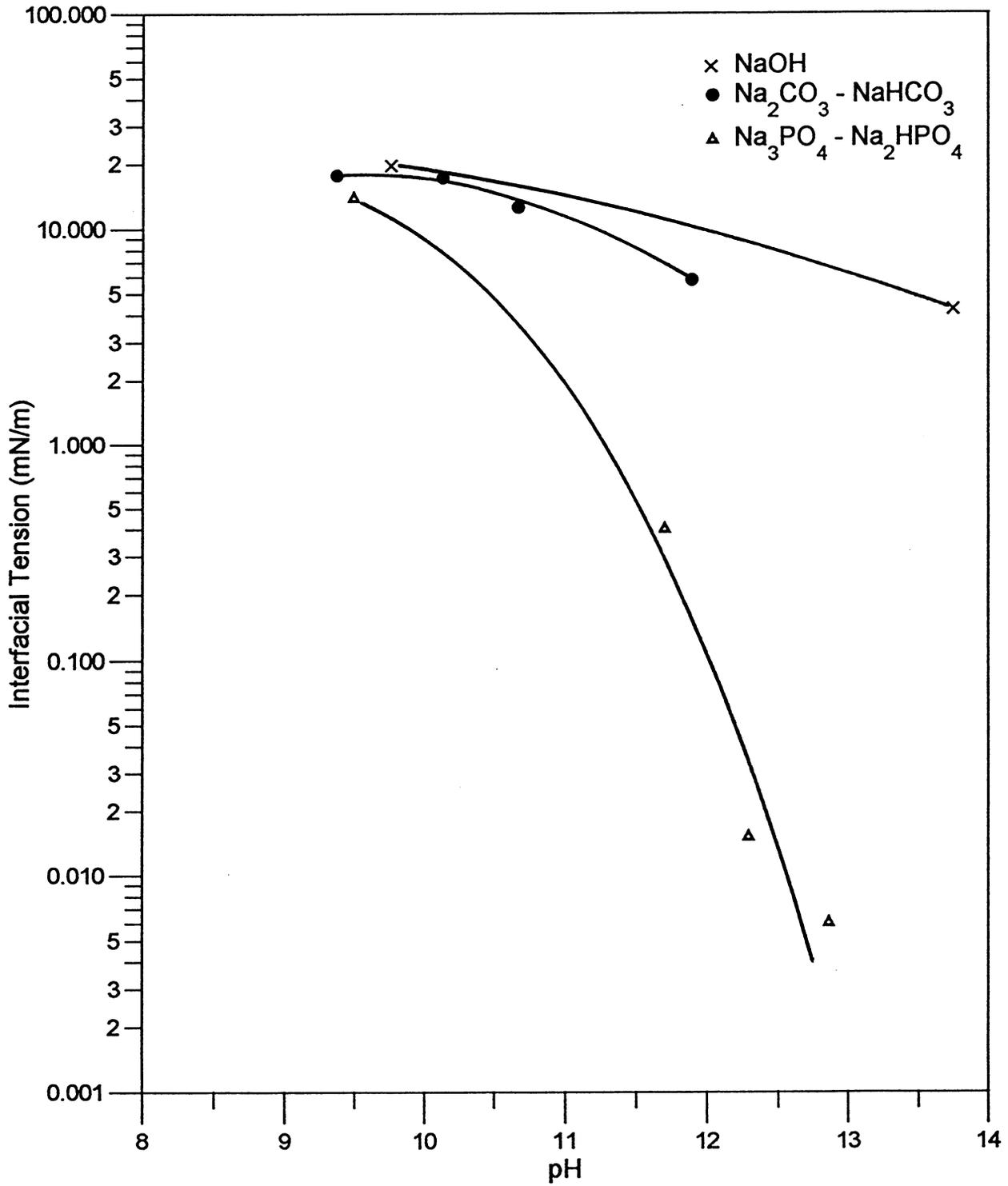


Figure 5

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

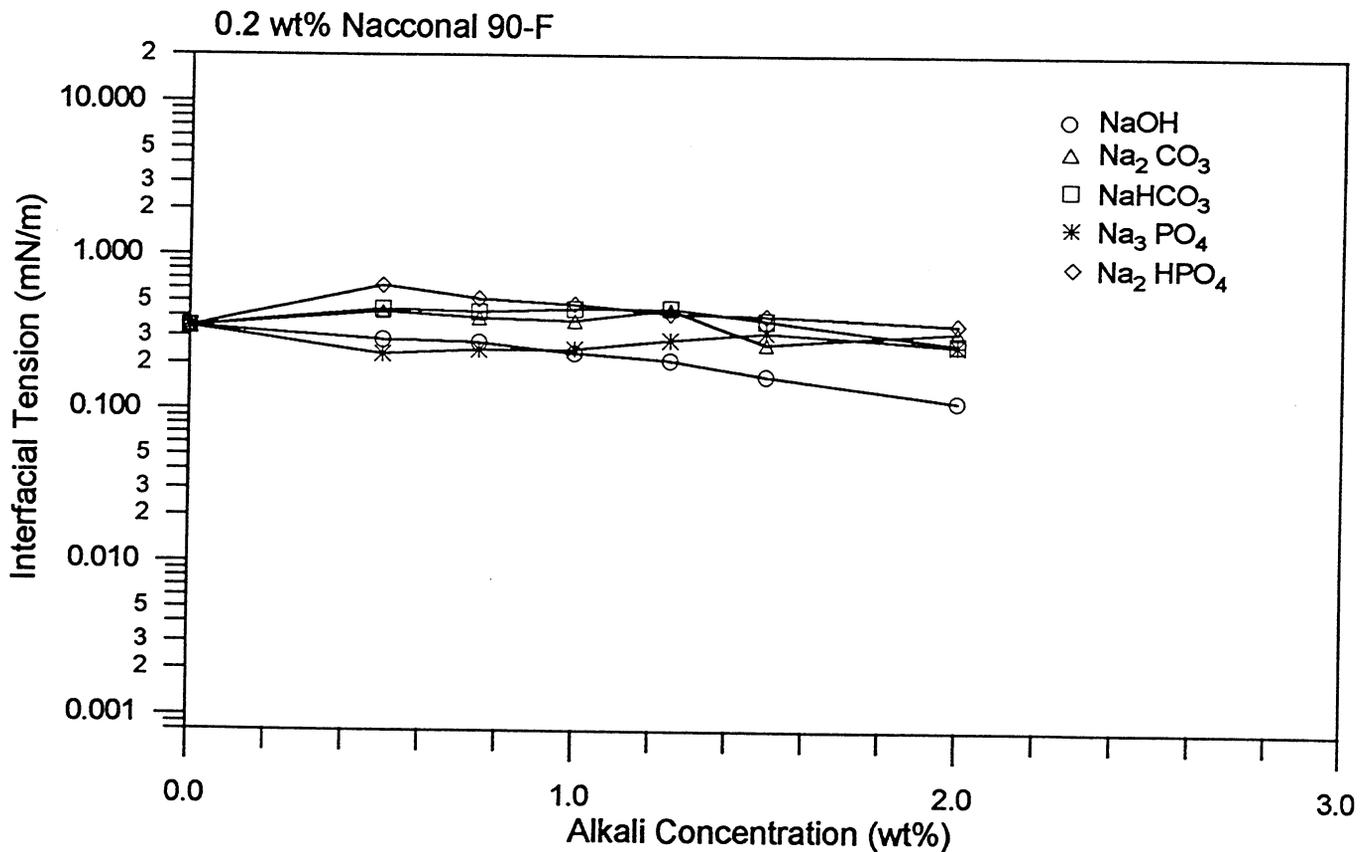
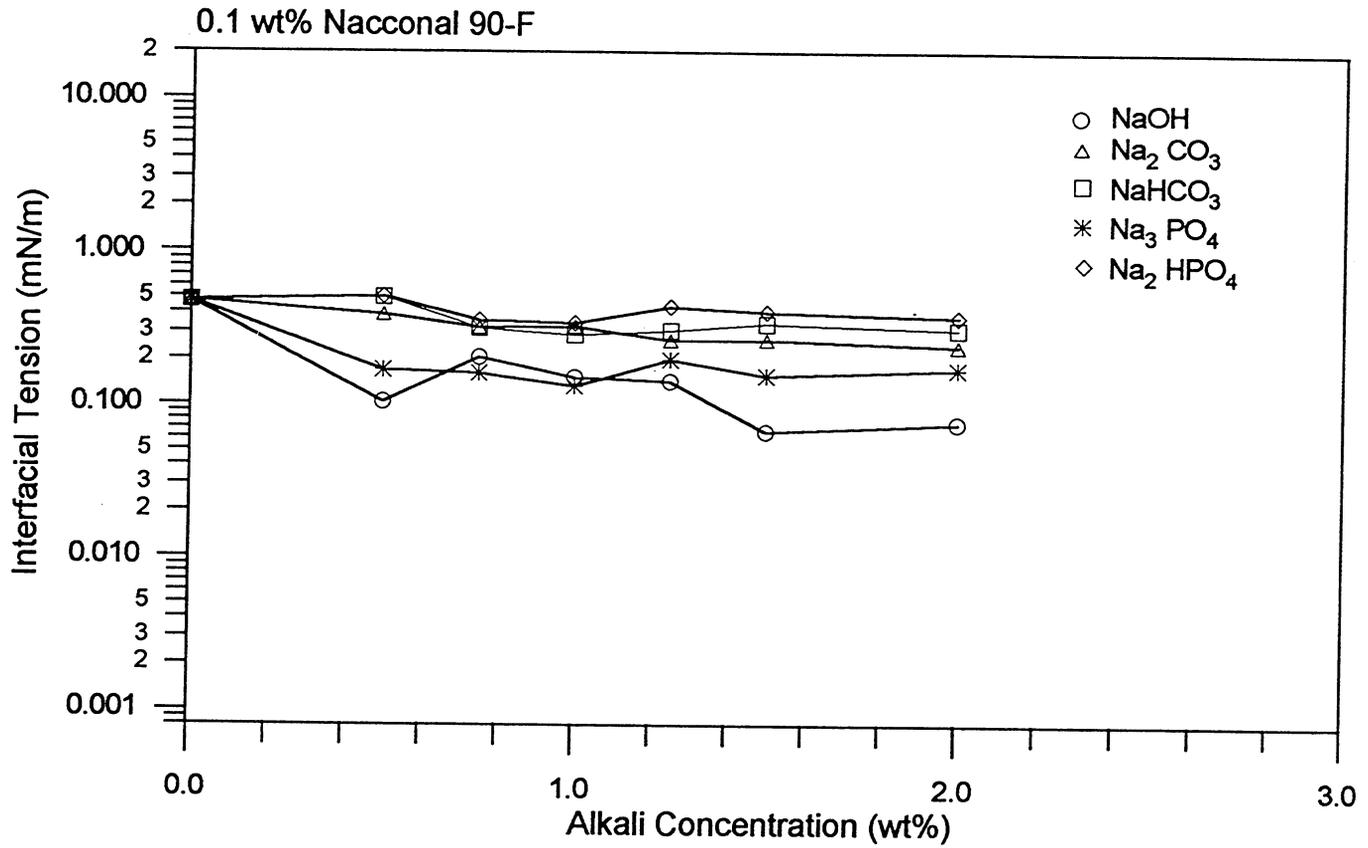


Figure 6

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

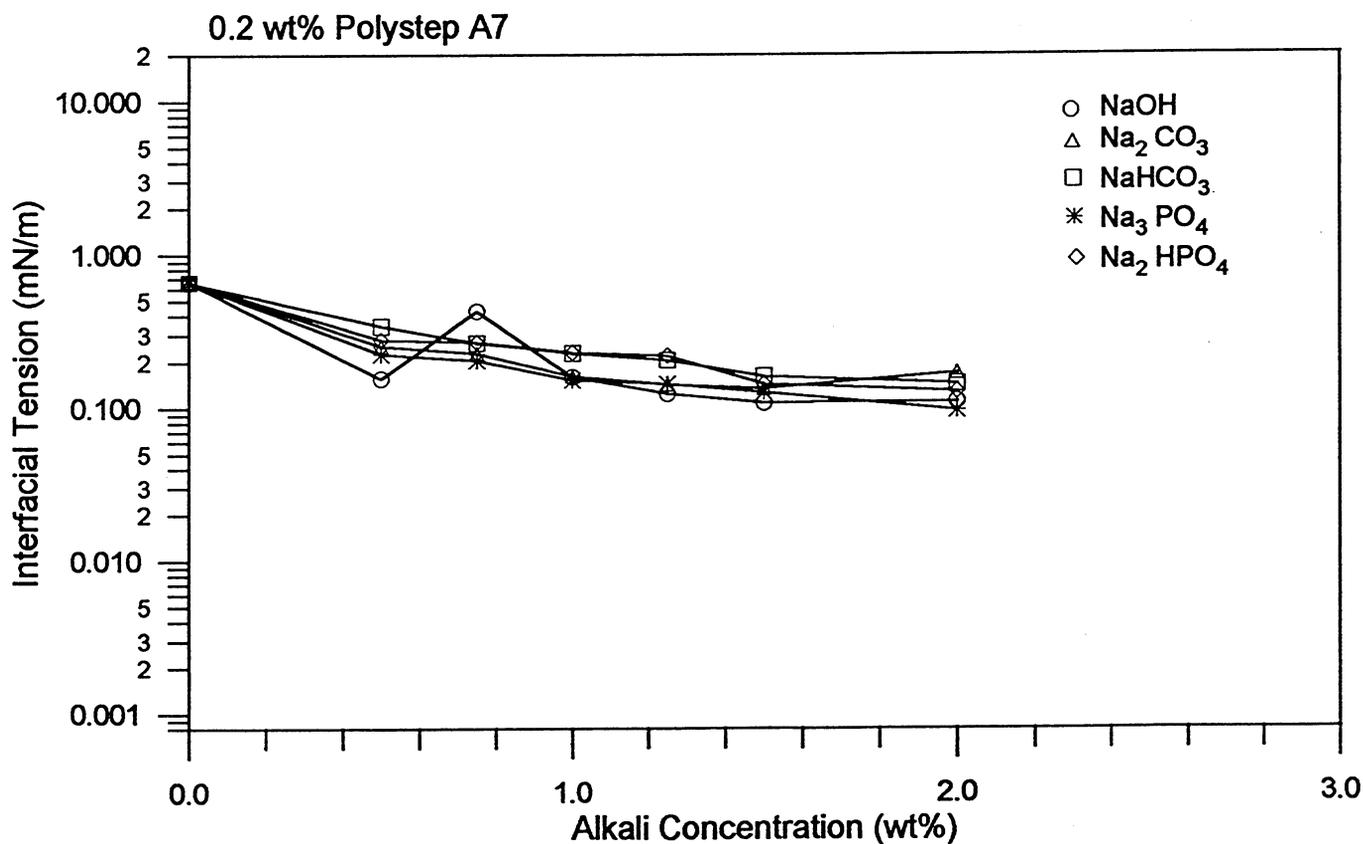
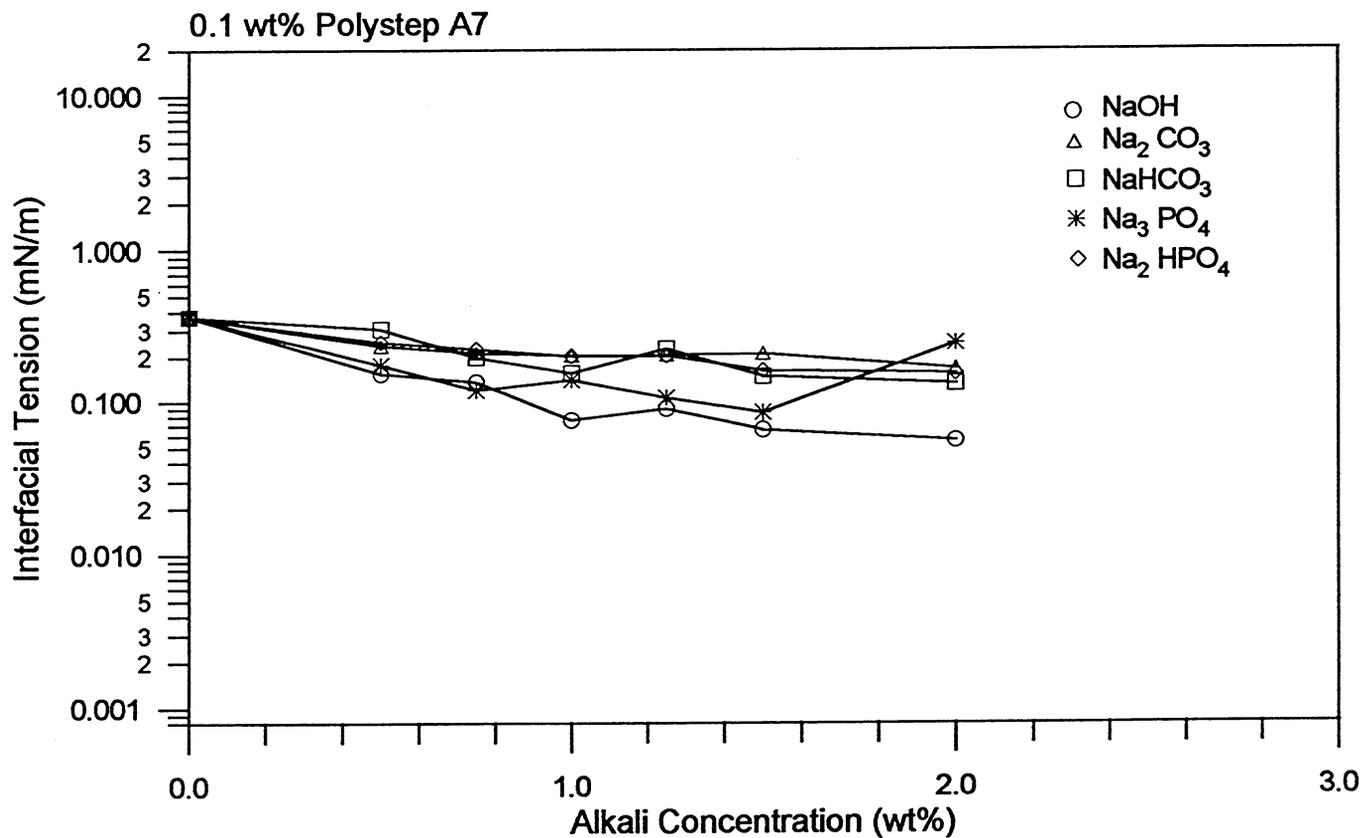


Figure 7

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

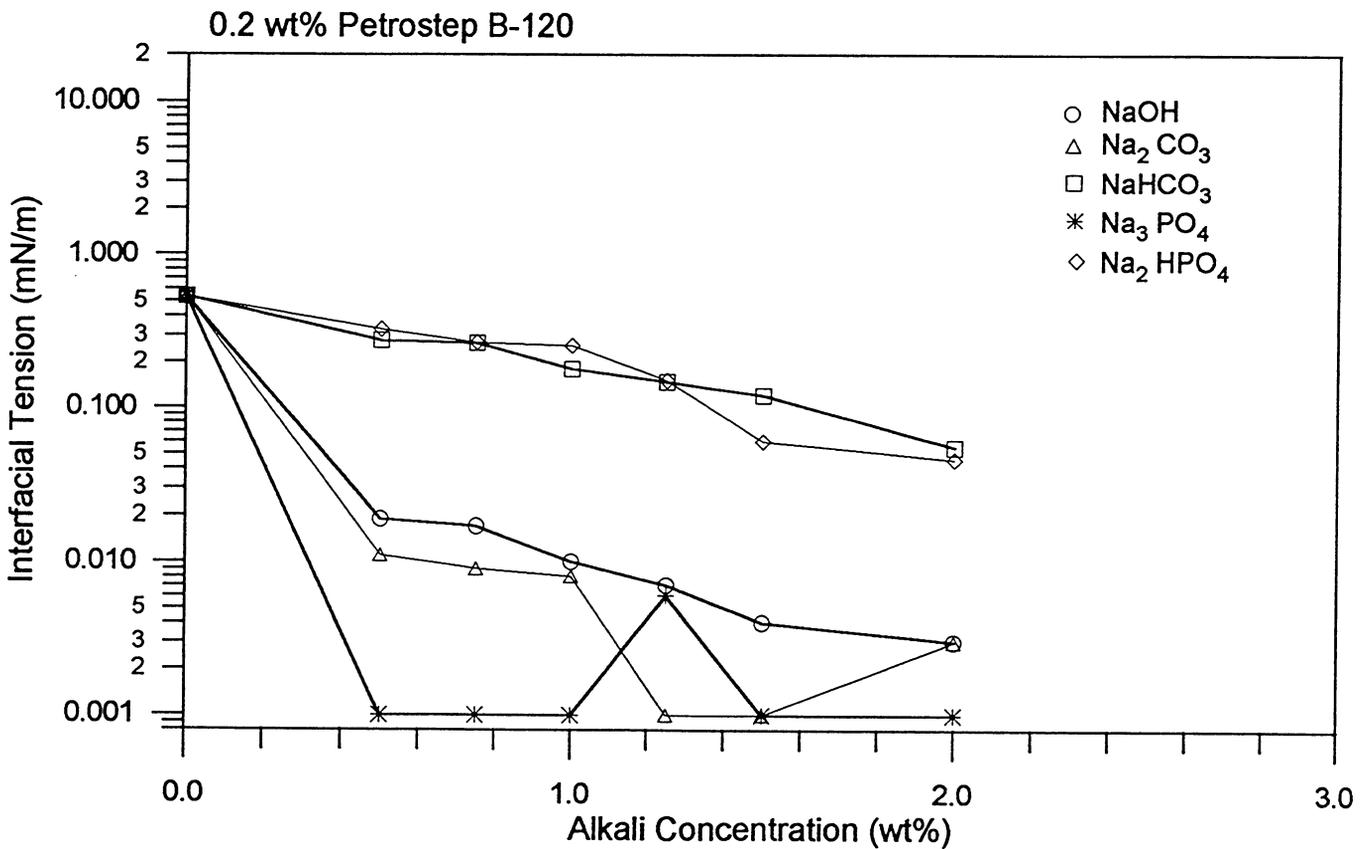
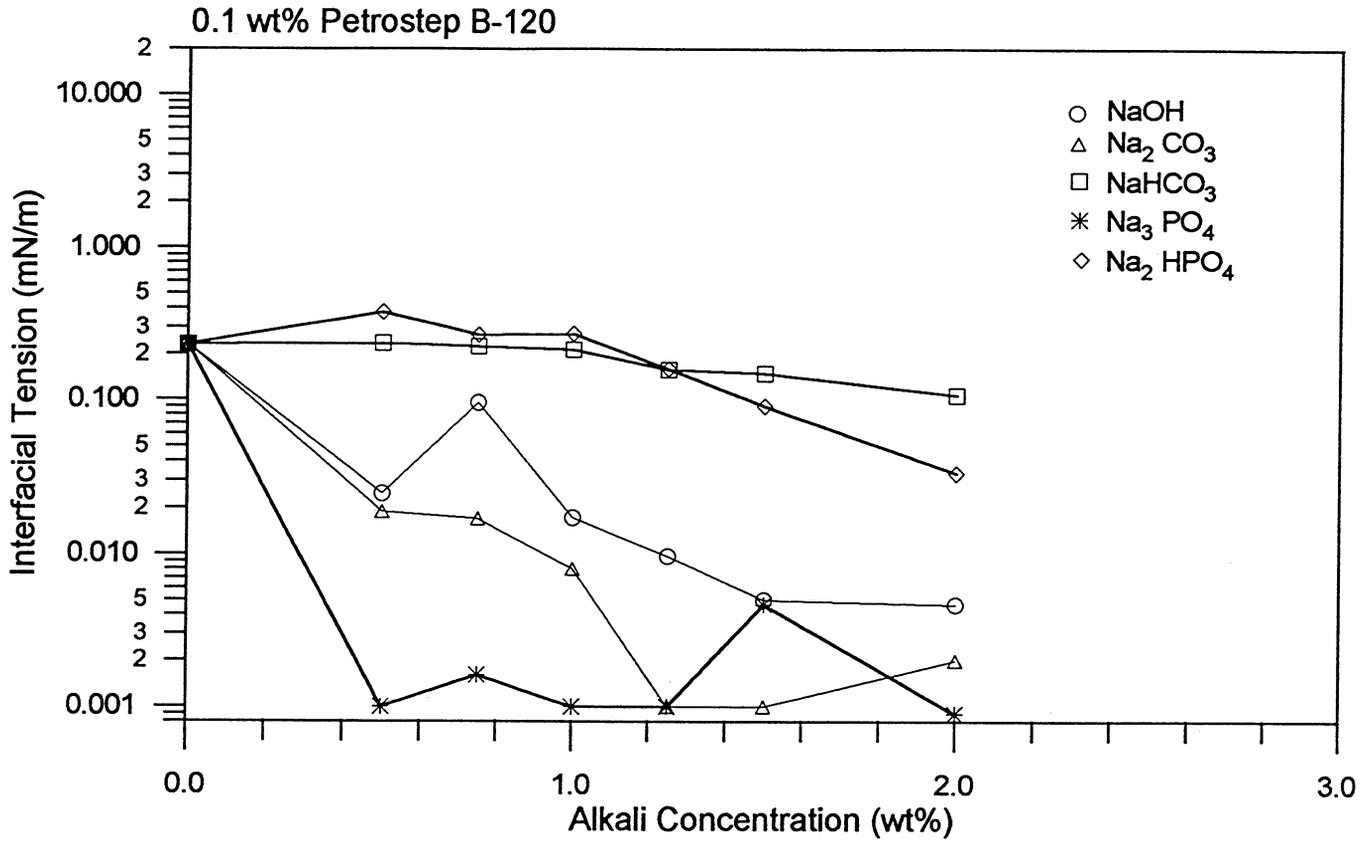


Figure 8

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

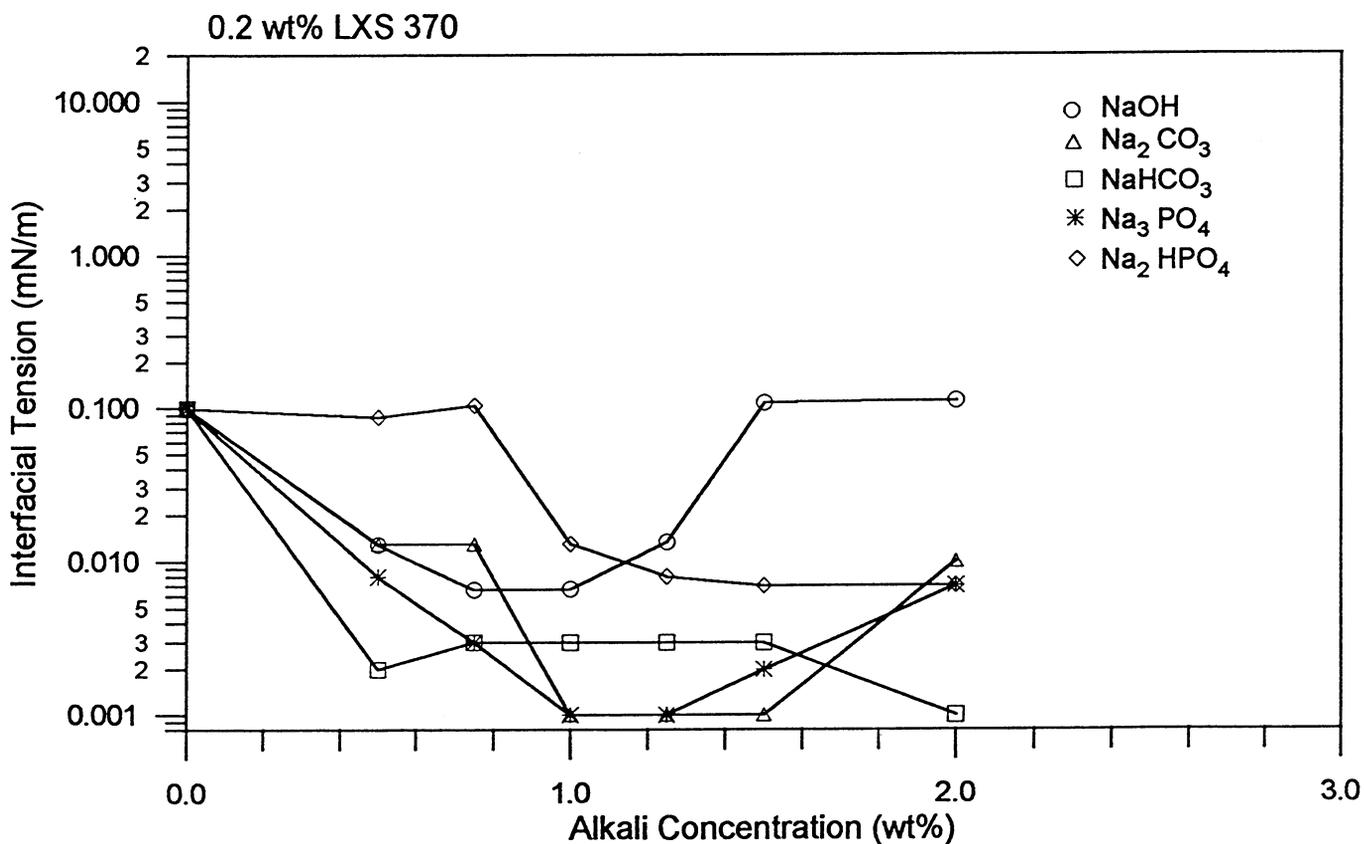
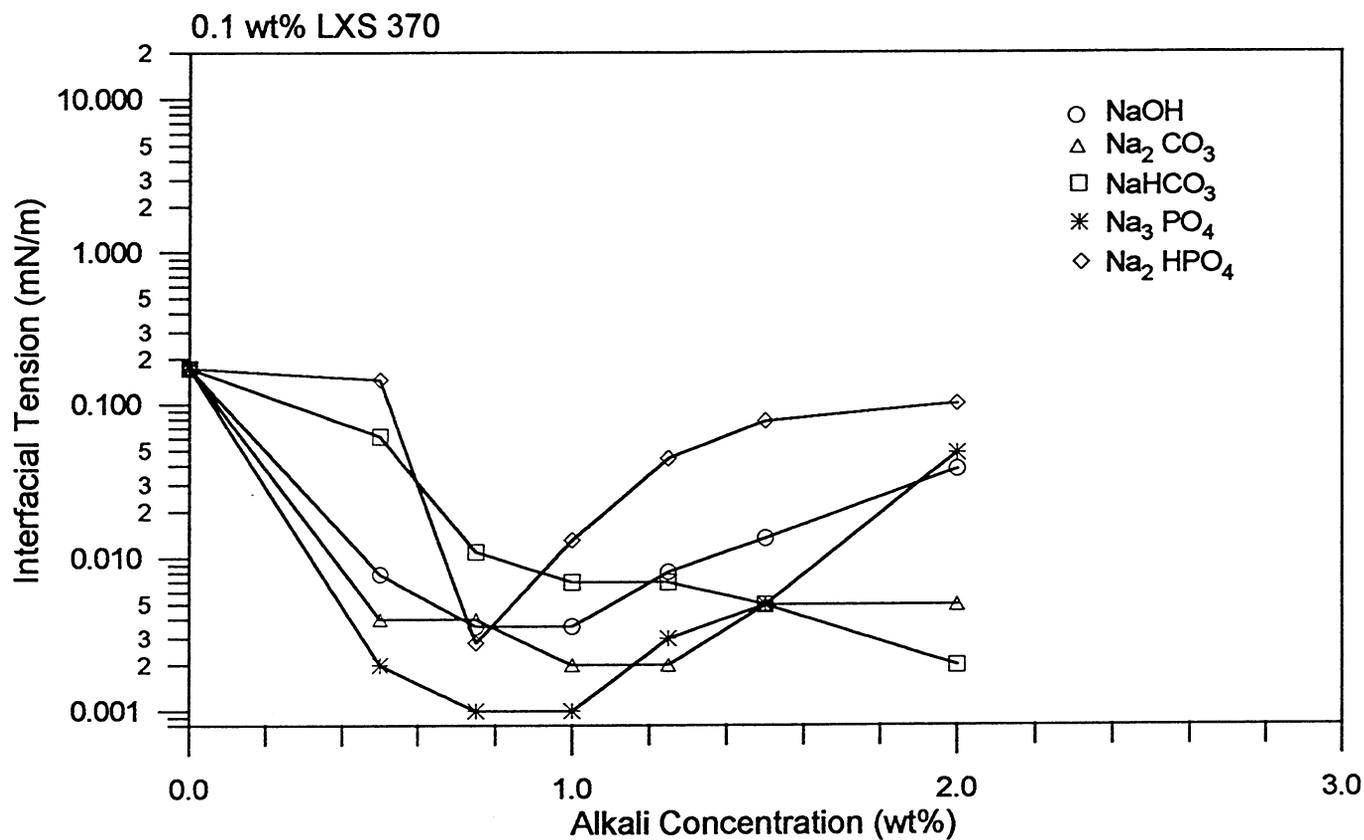
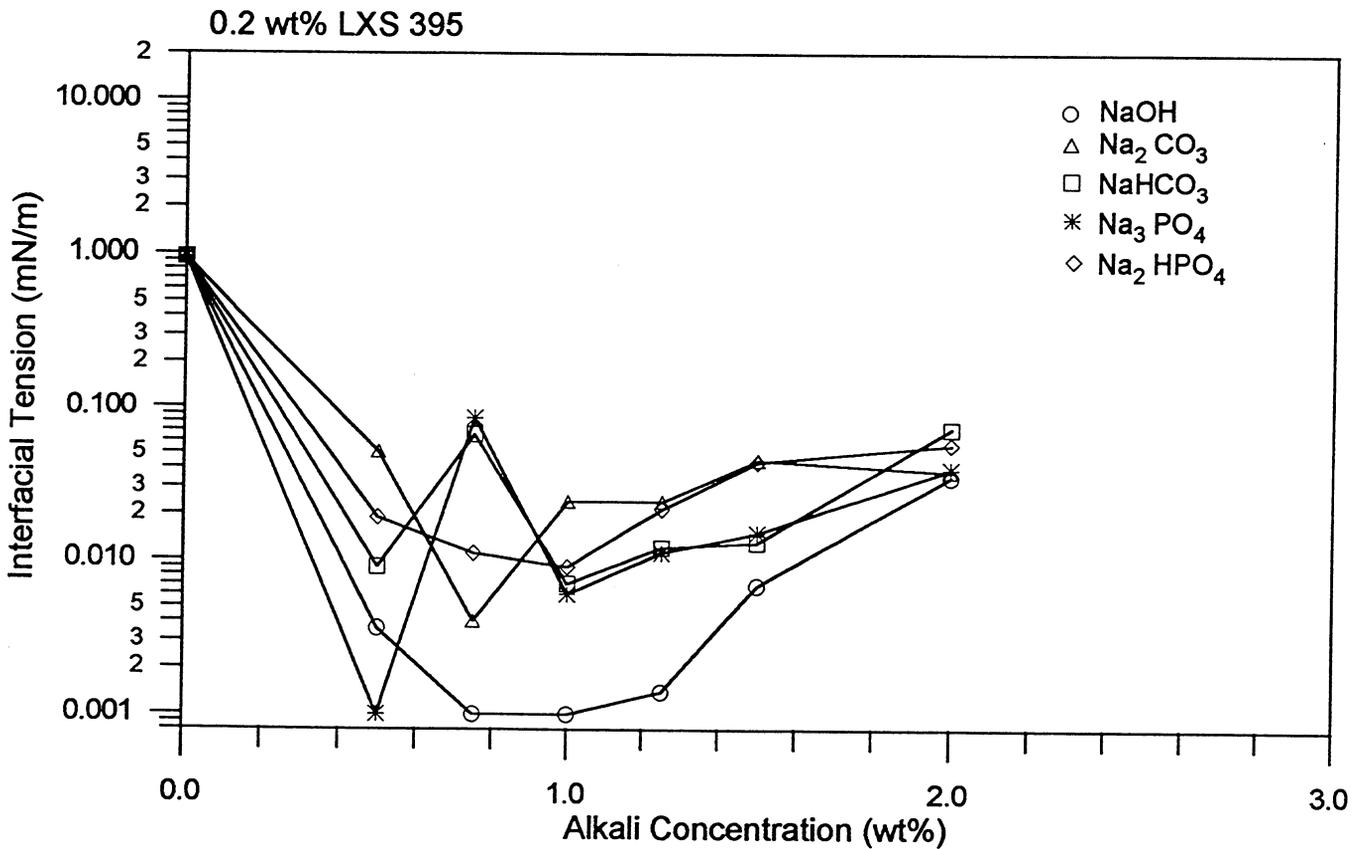
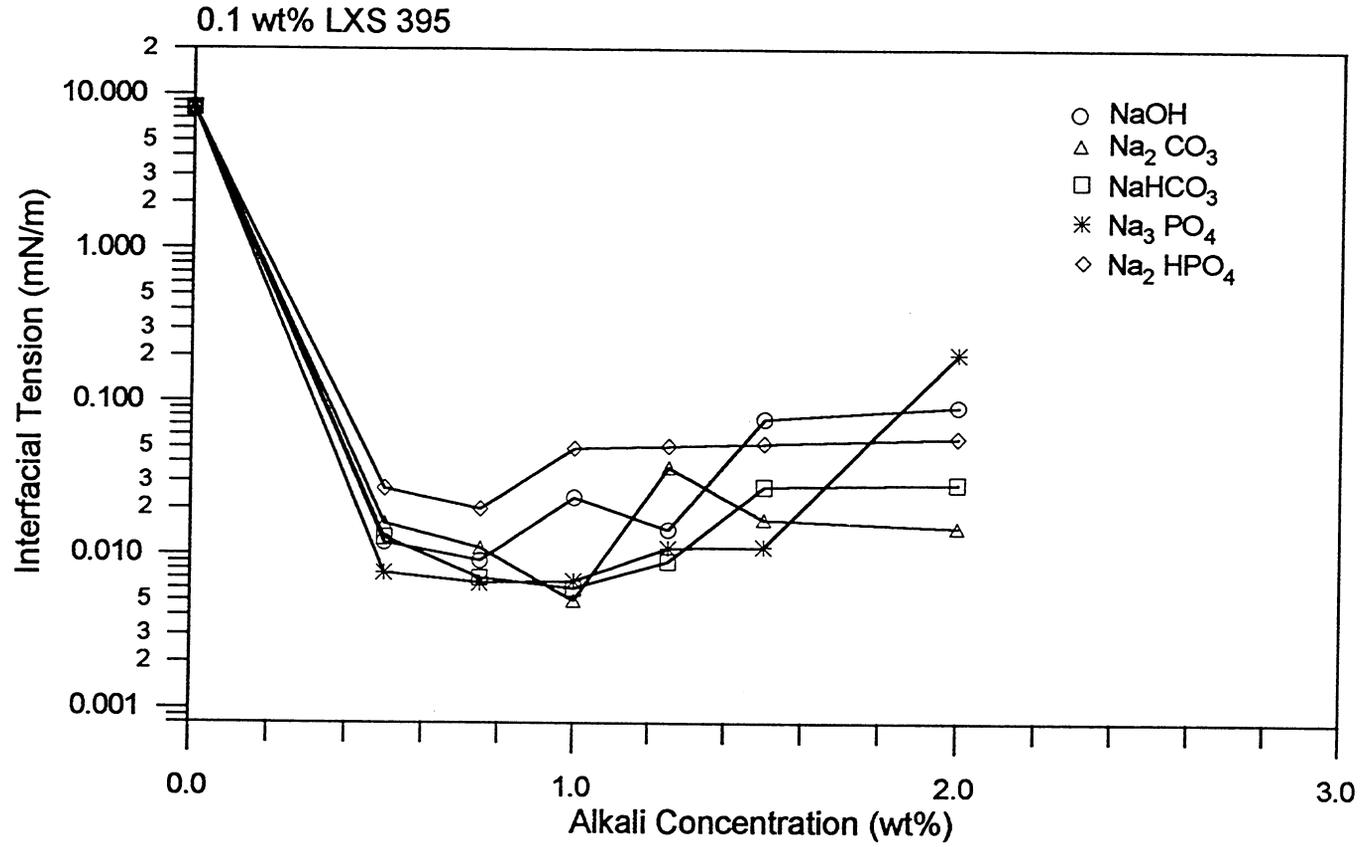
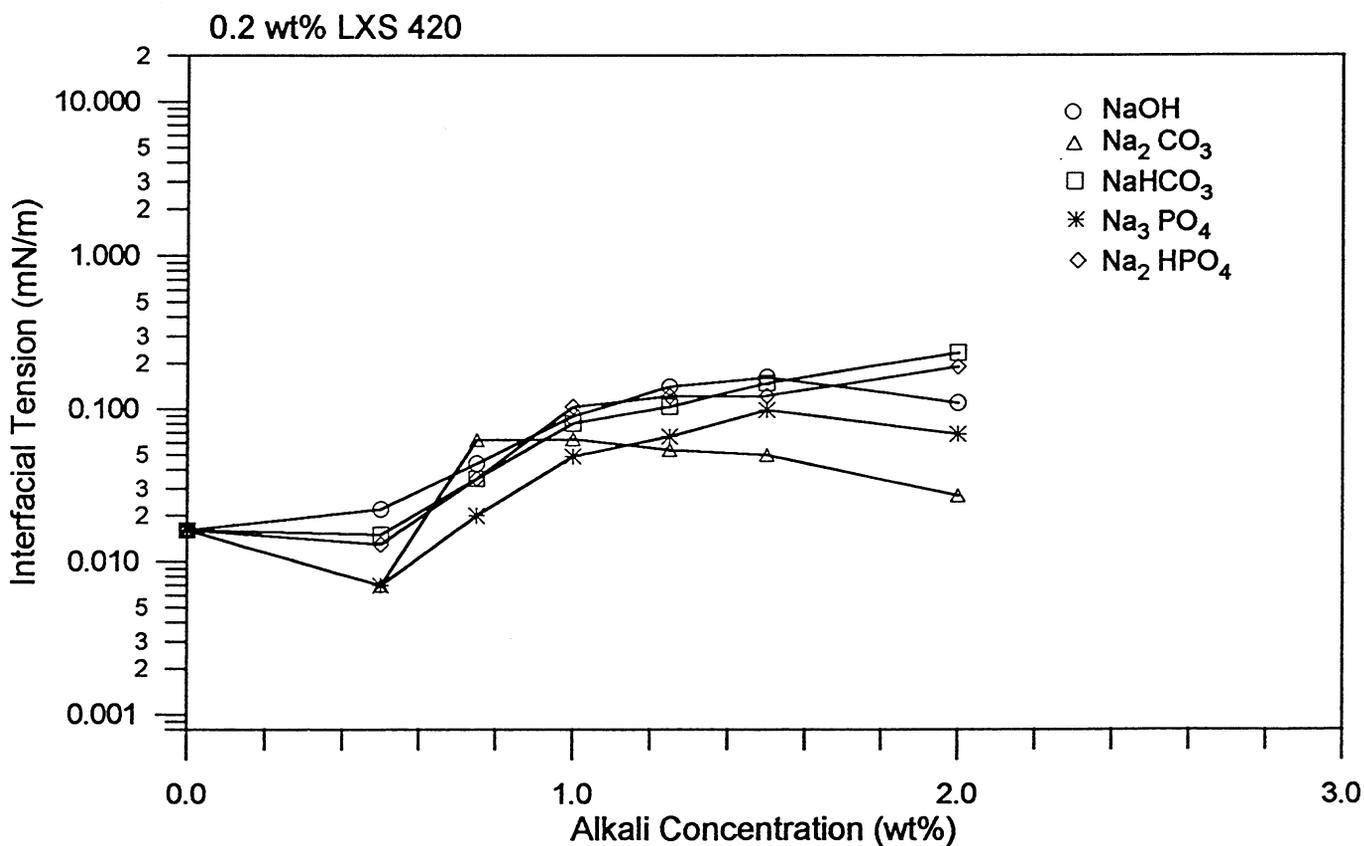
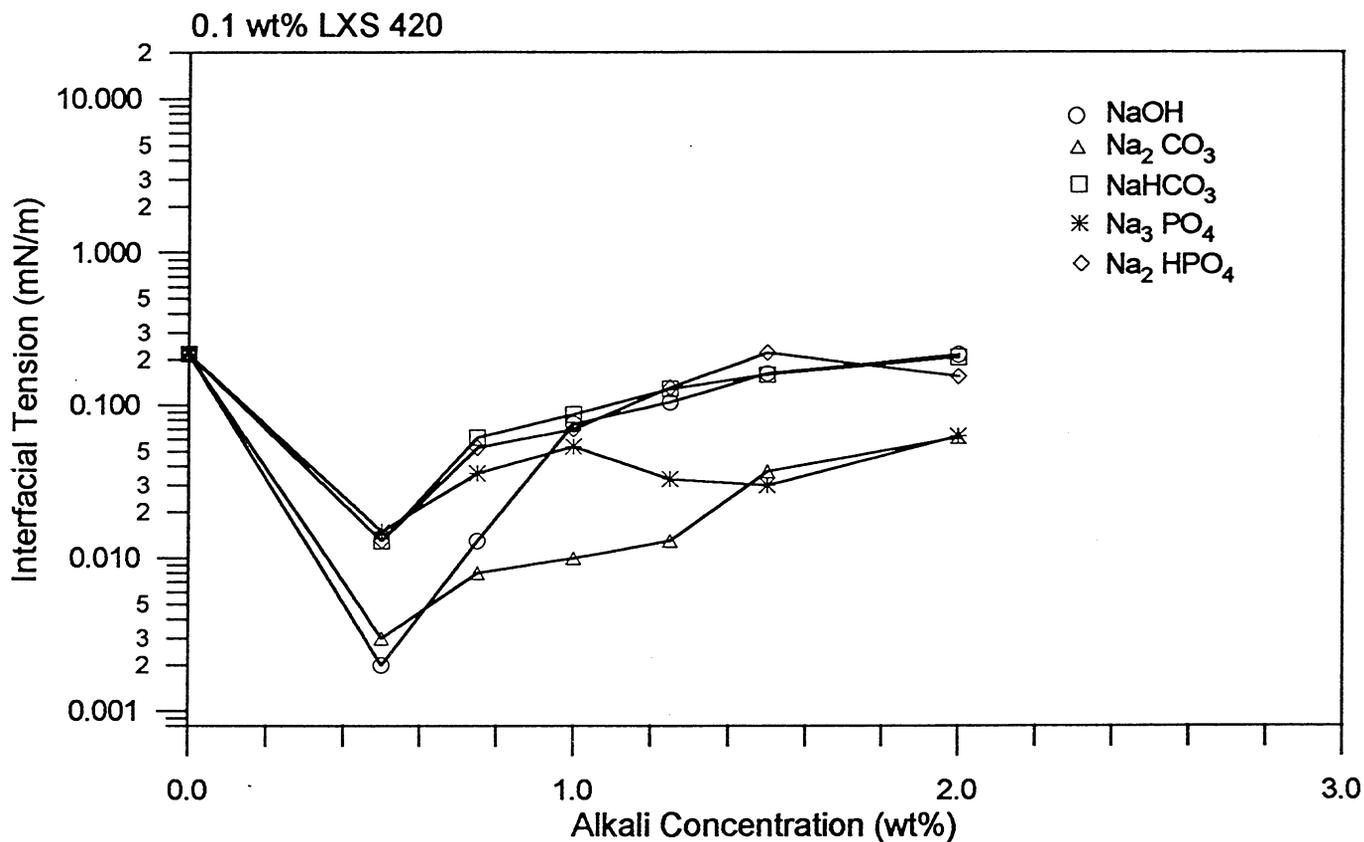


Figure 9

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

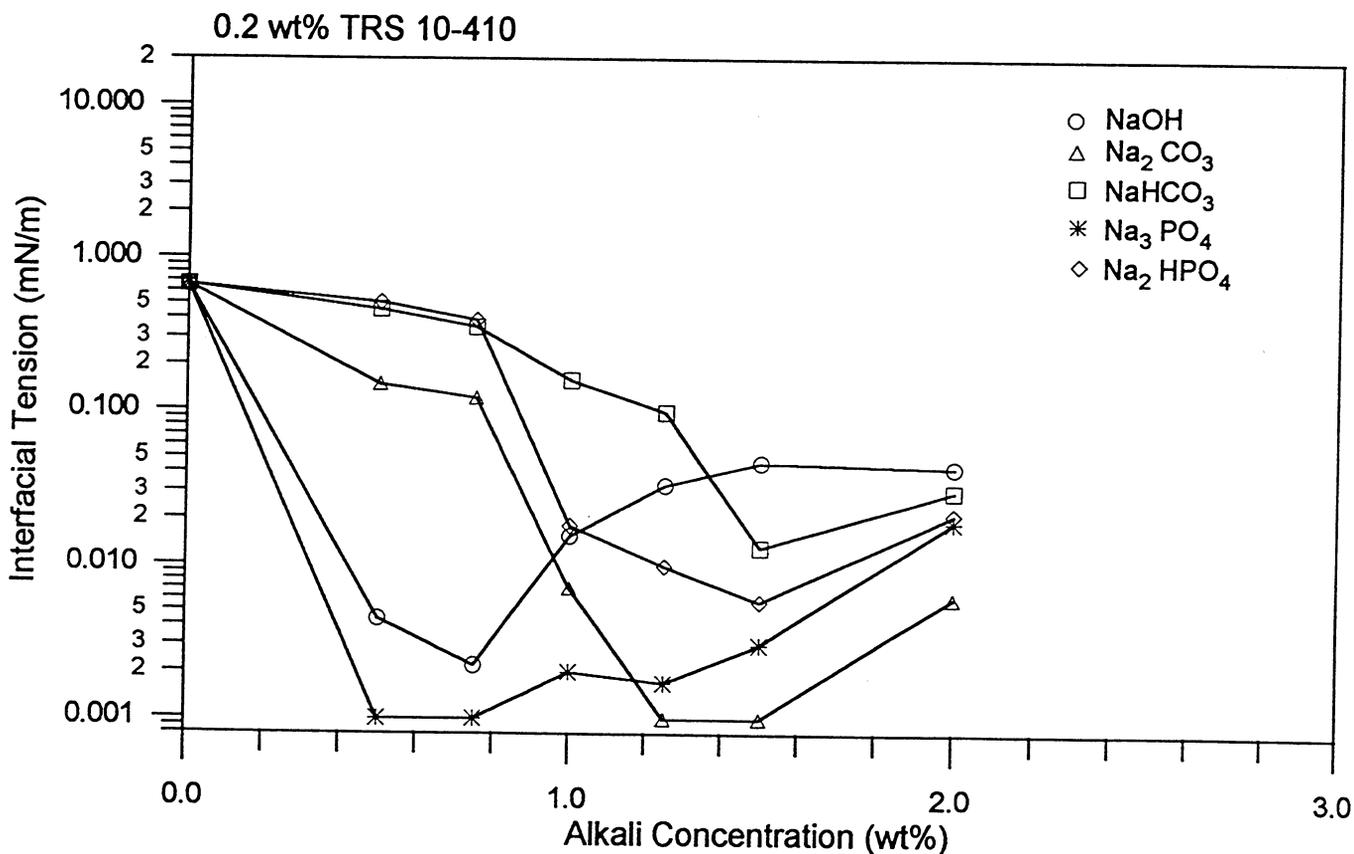
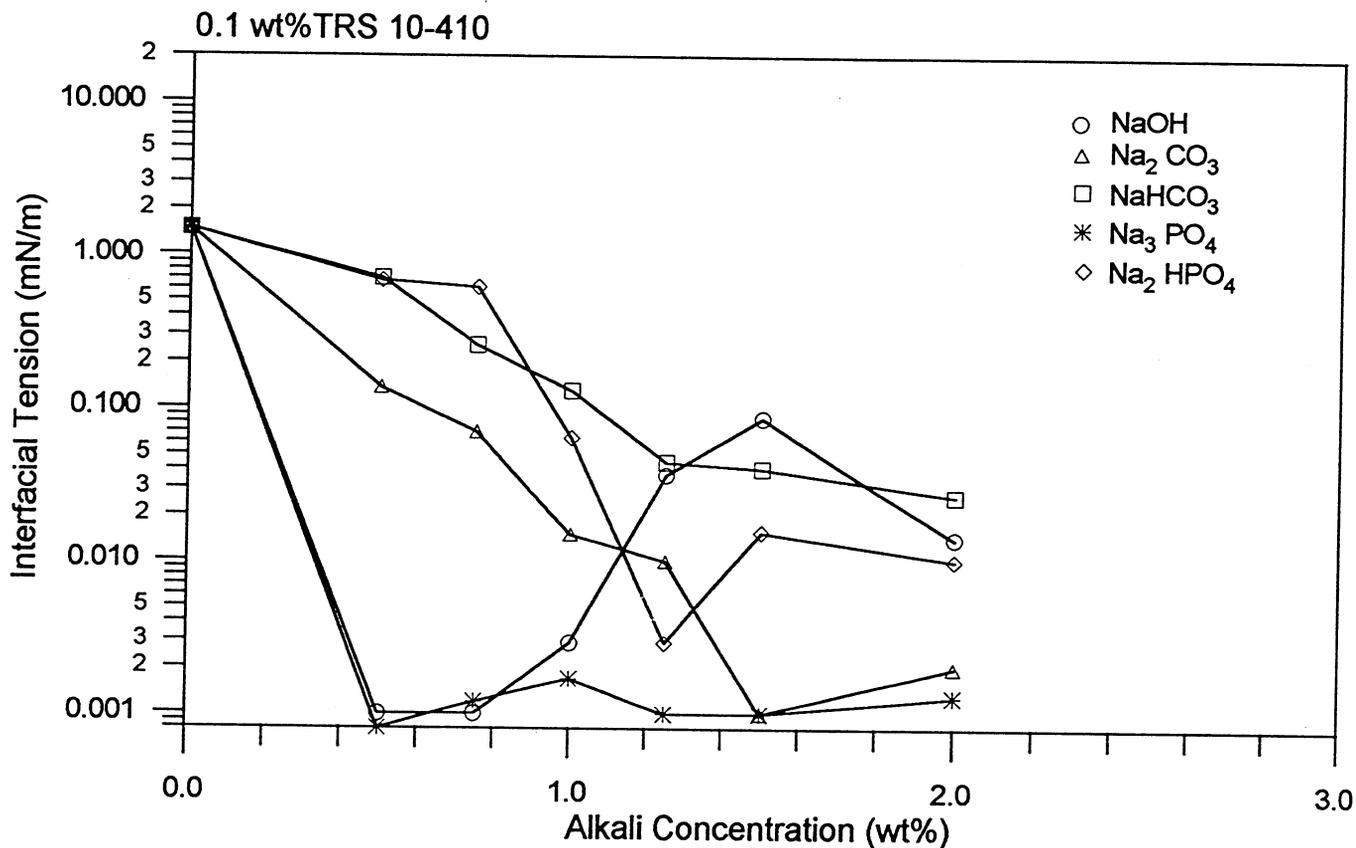


Figure 12

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

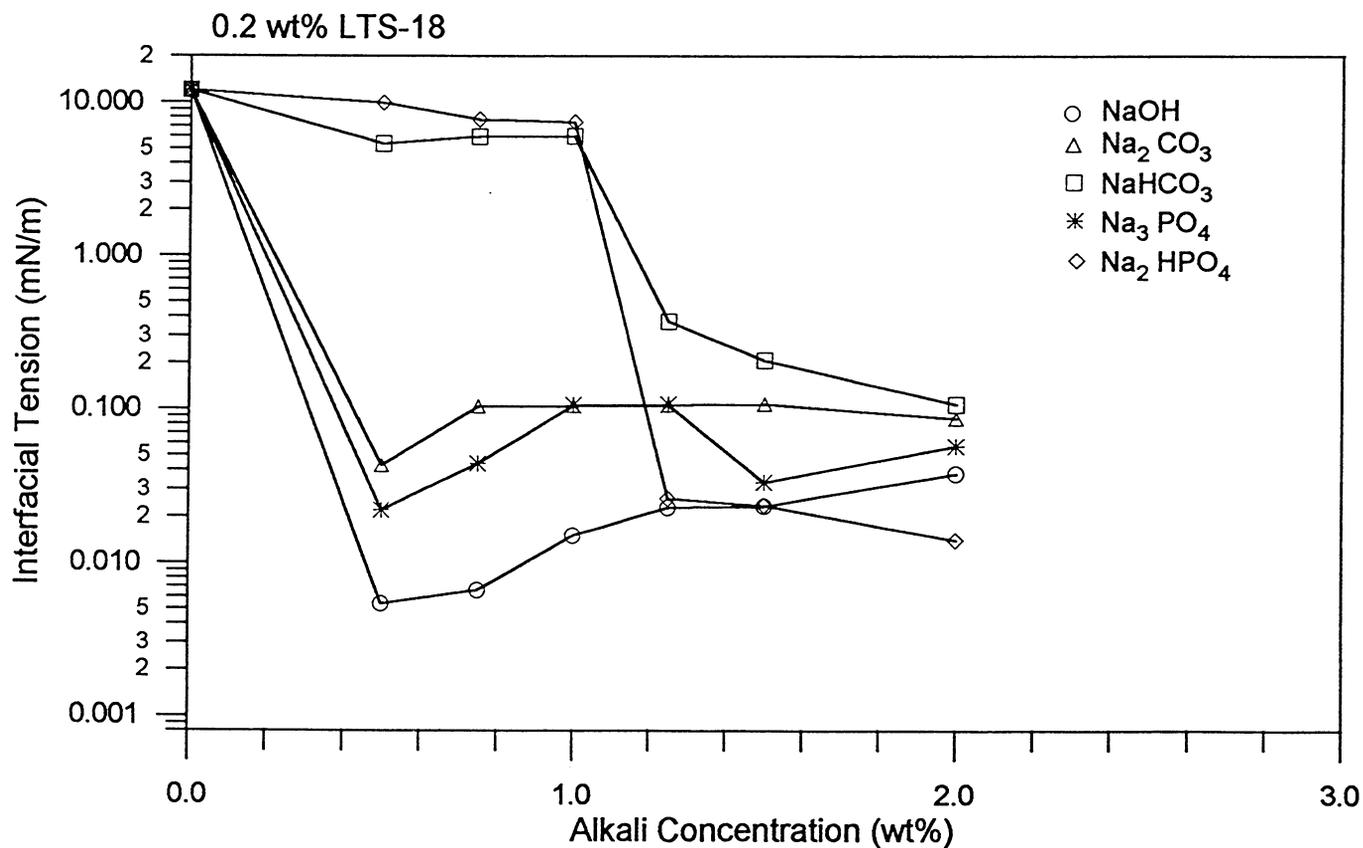
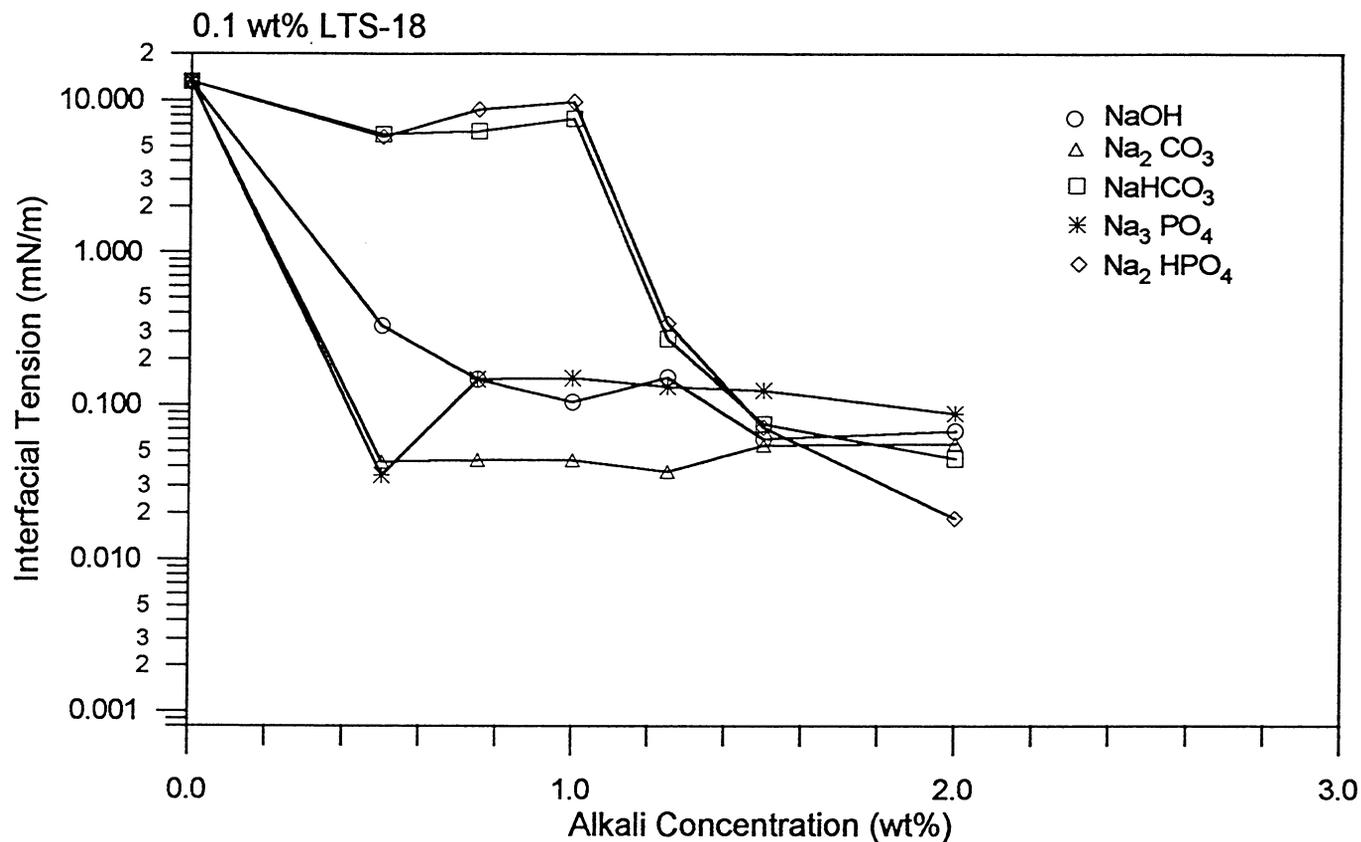
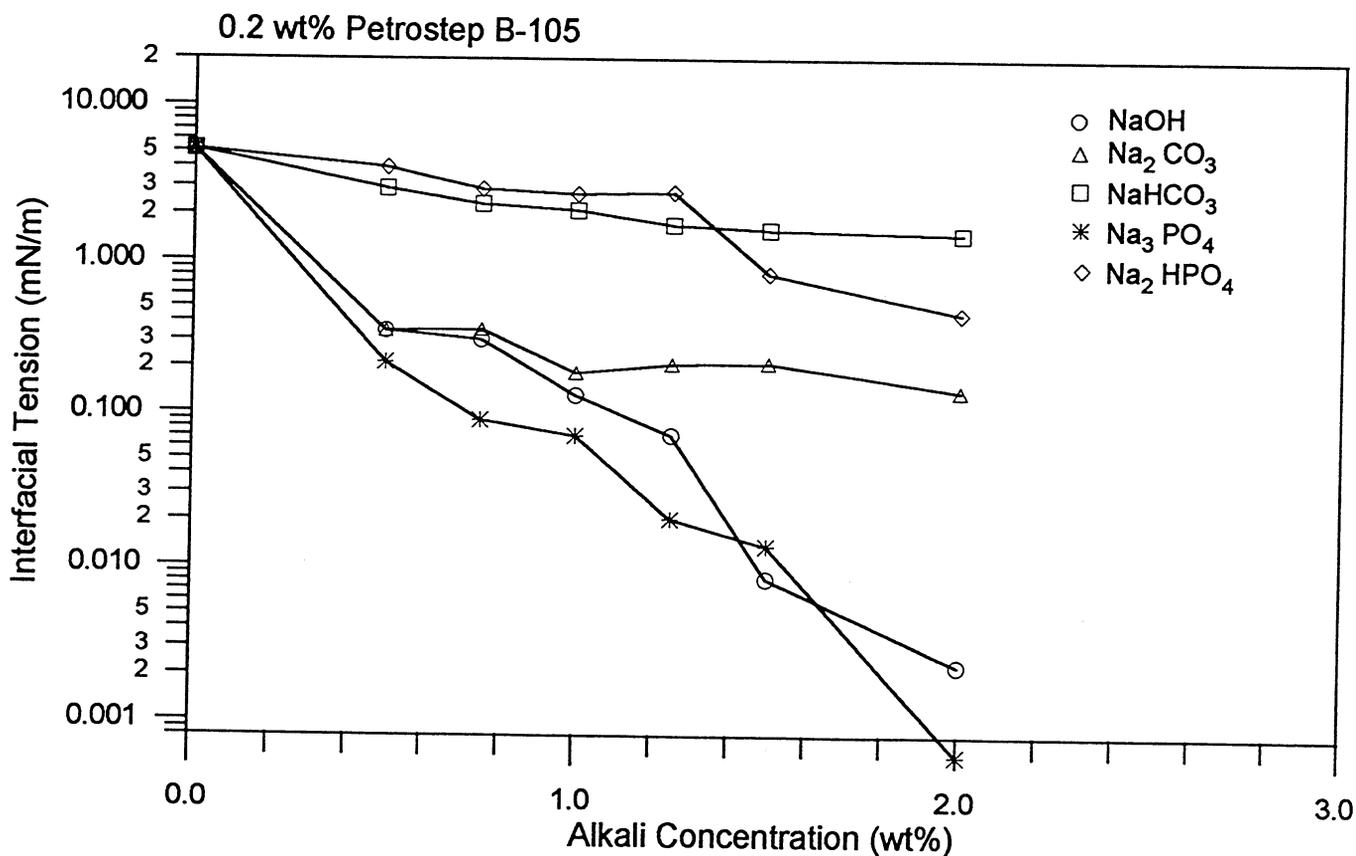
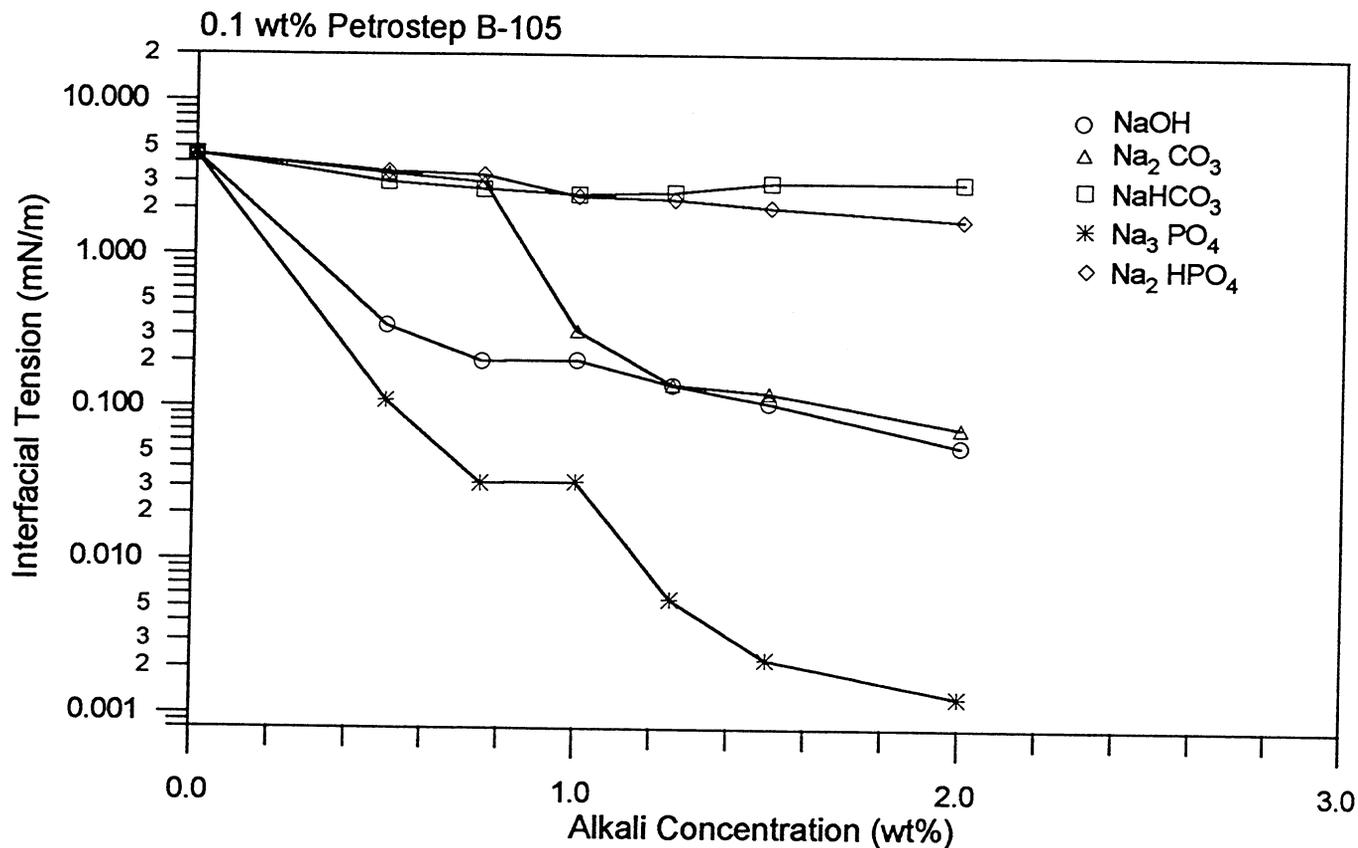


Figure 13

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

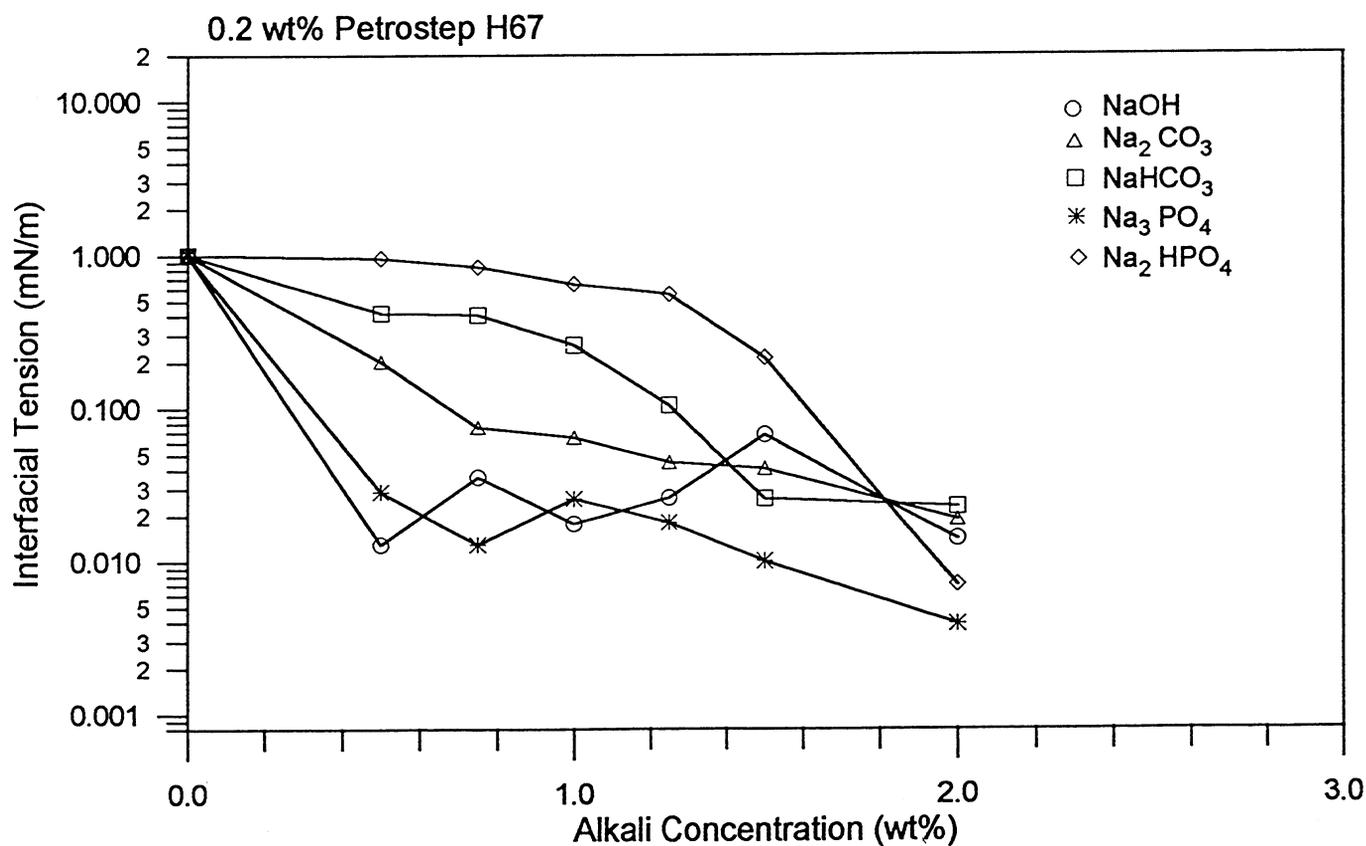
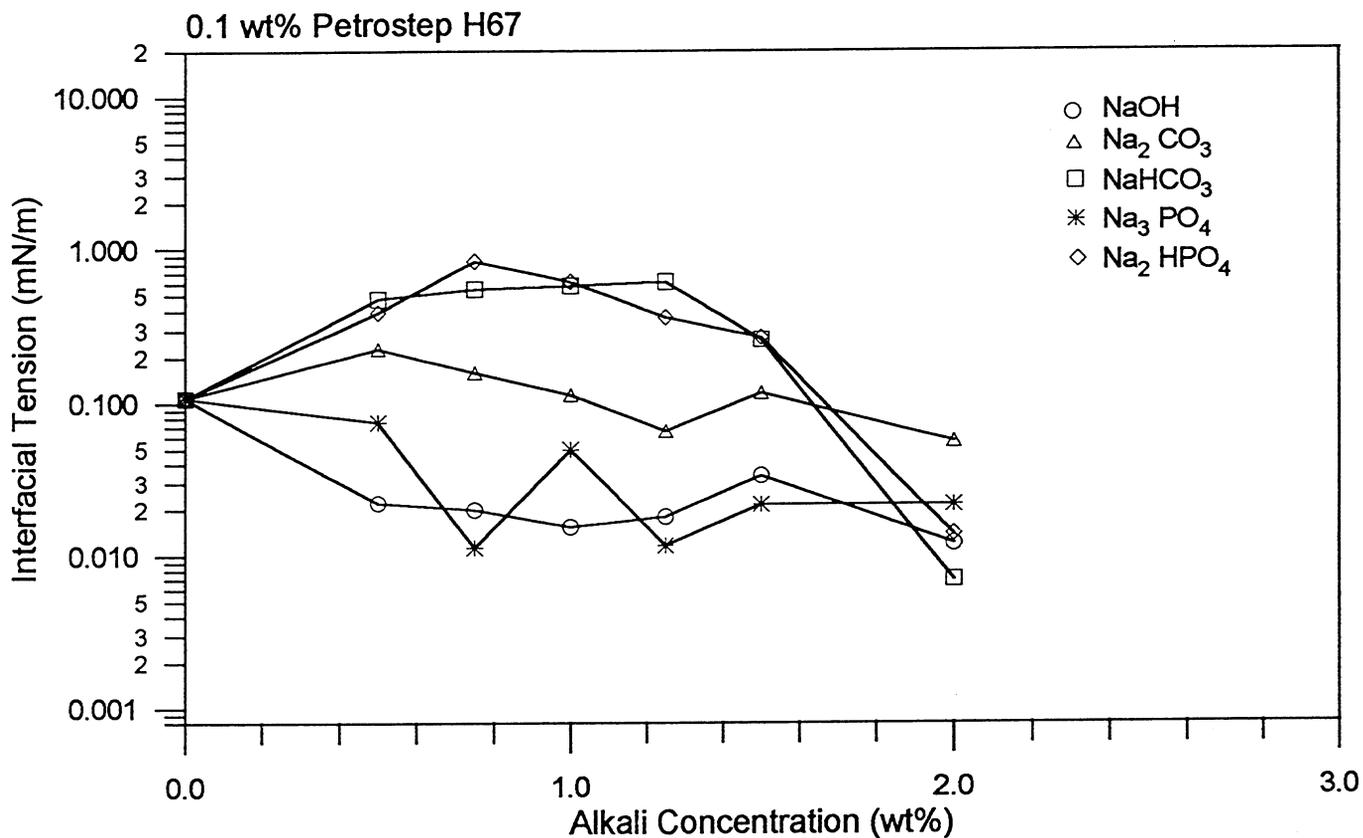


Figure 15

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

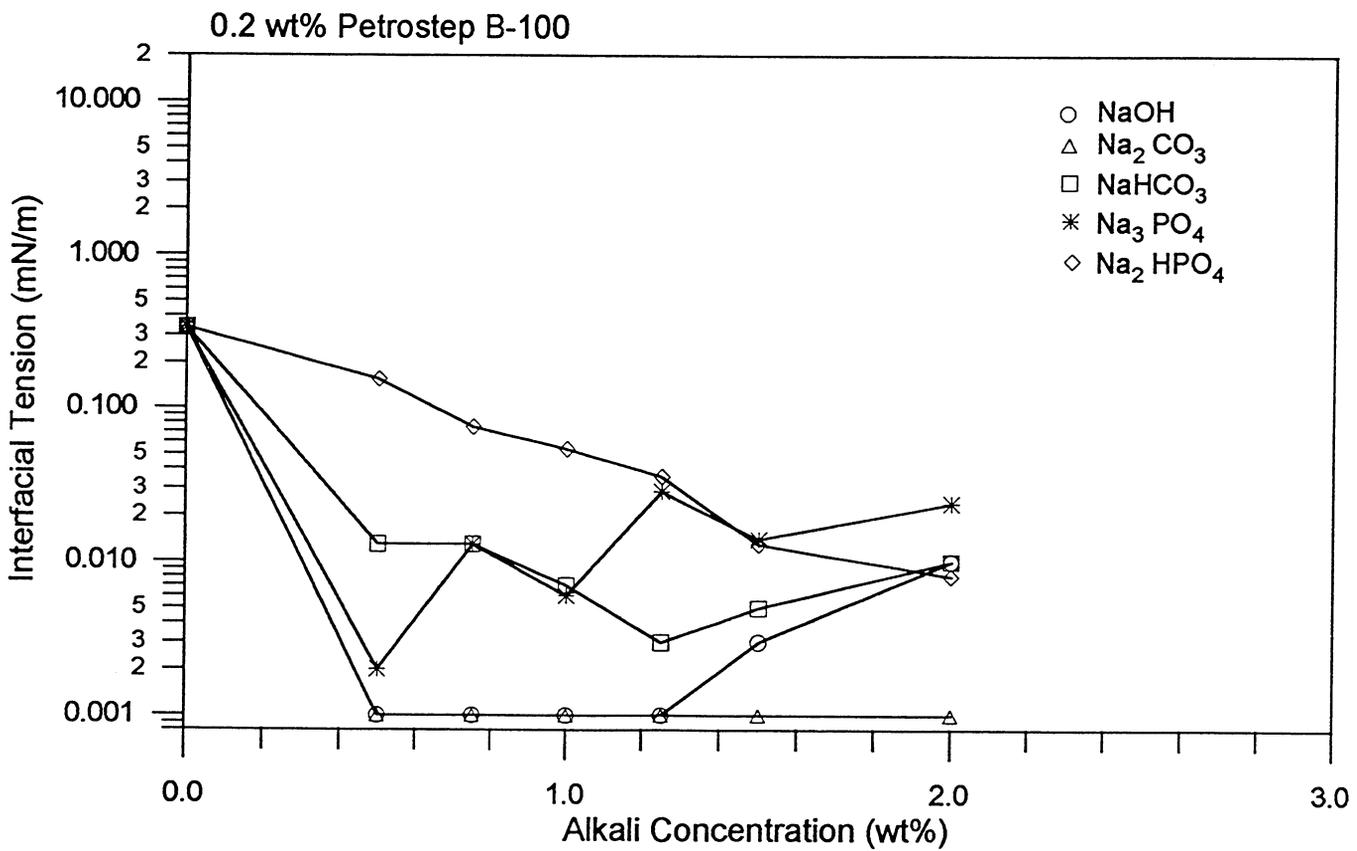
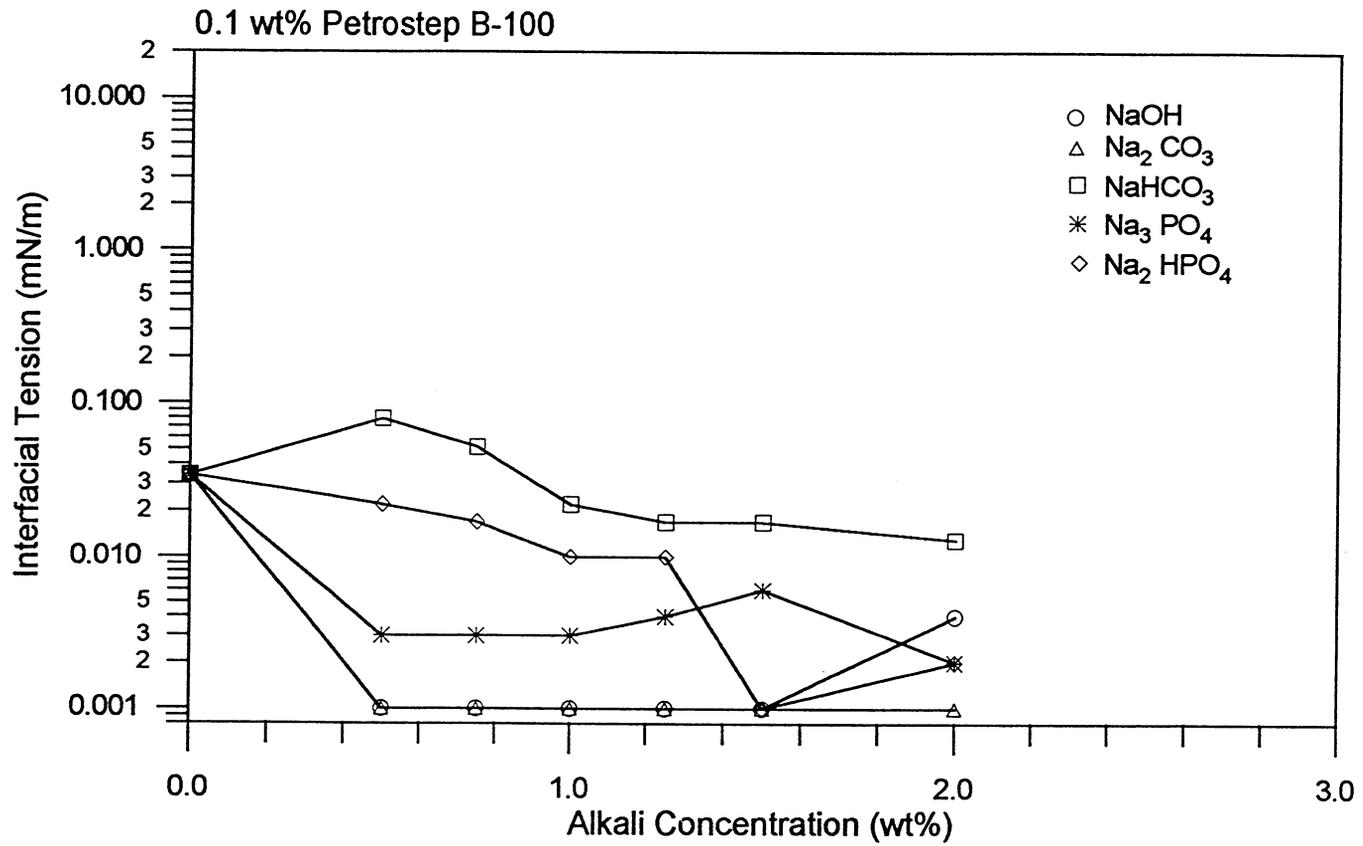


Figure 16

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

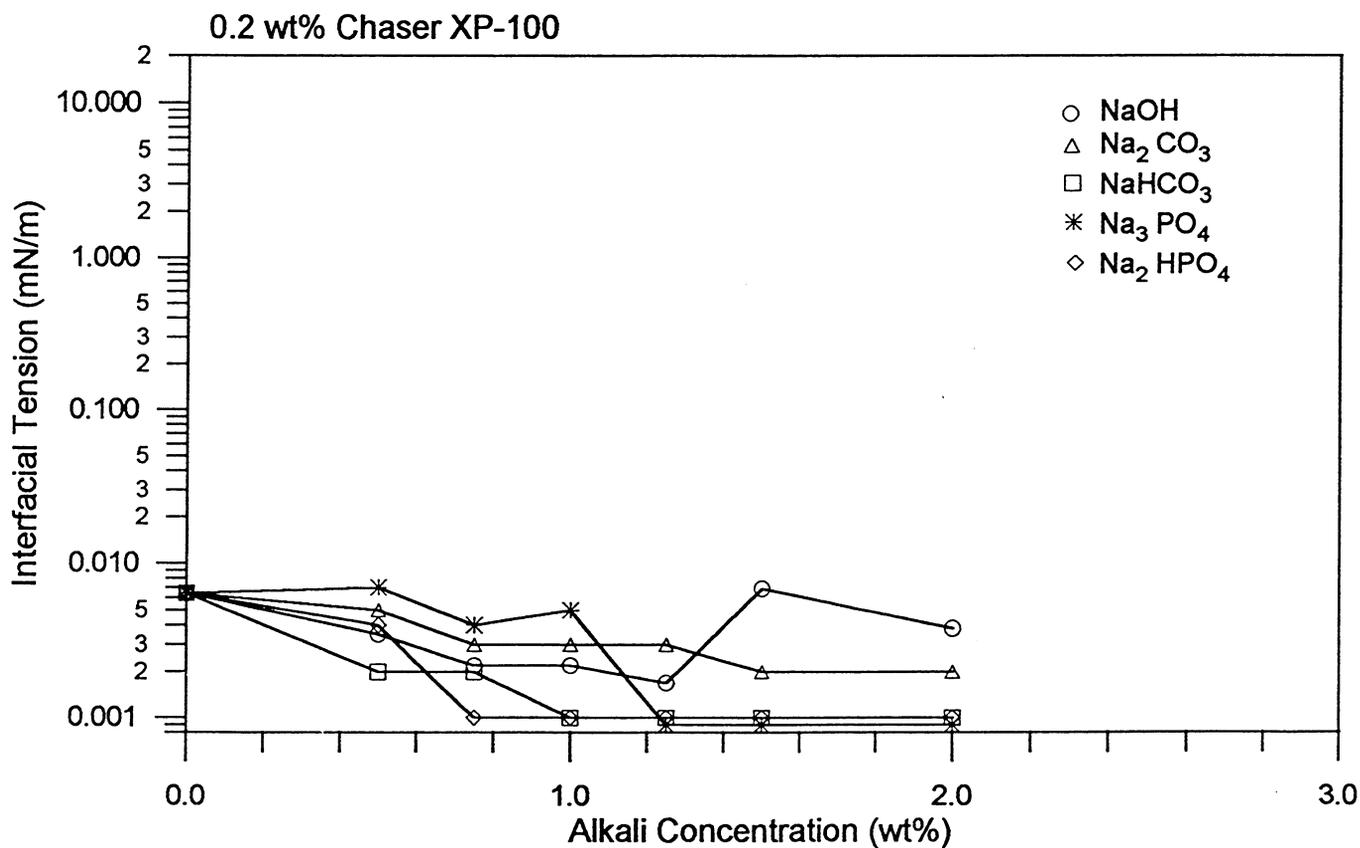
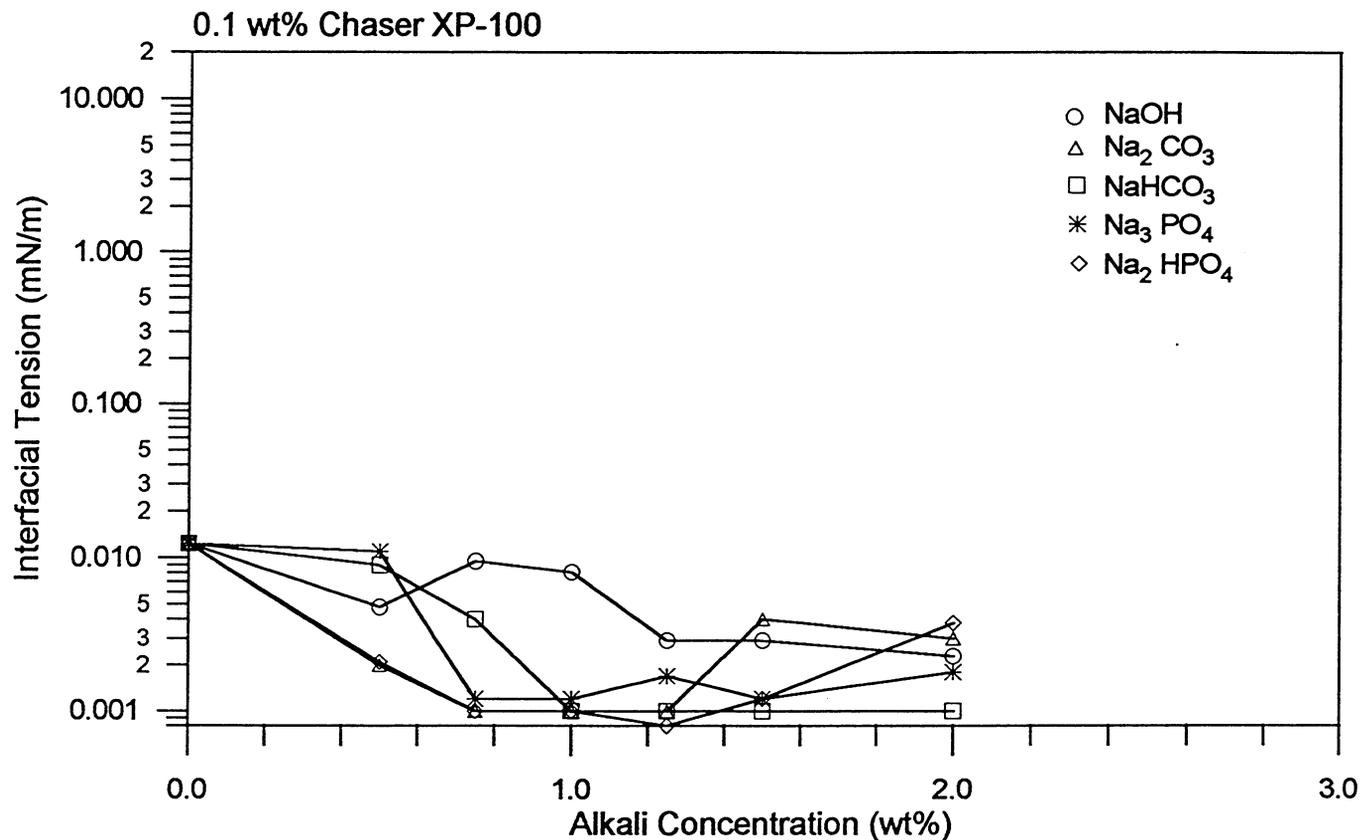
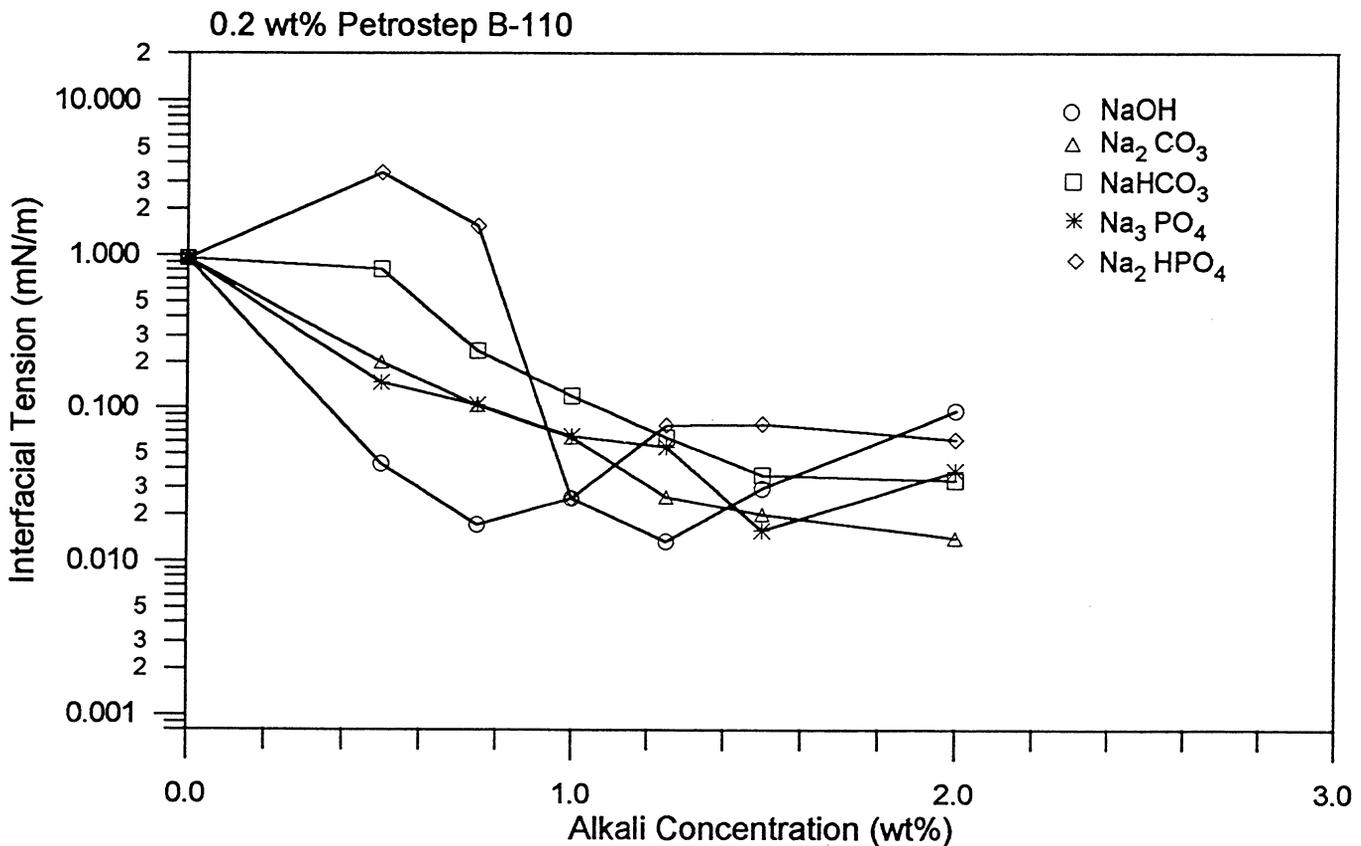
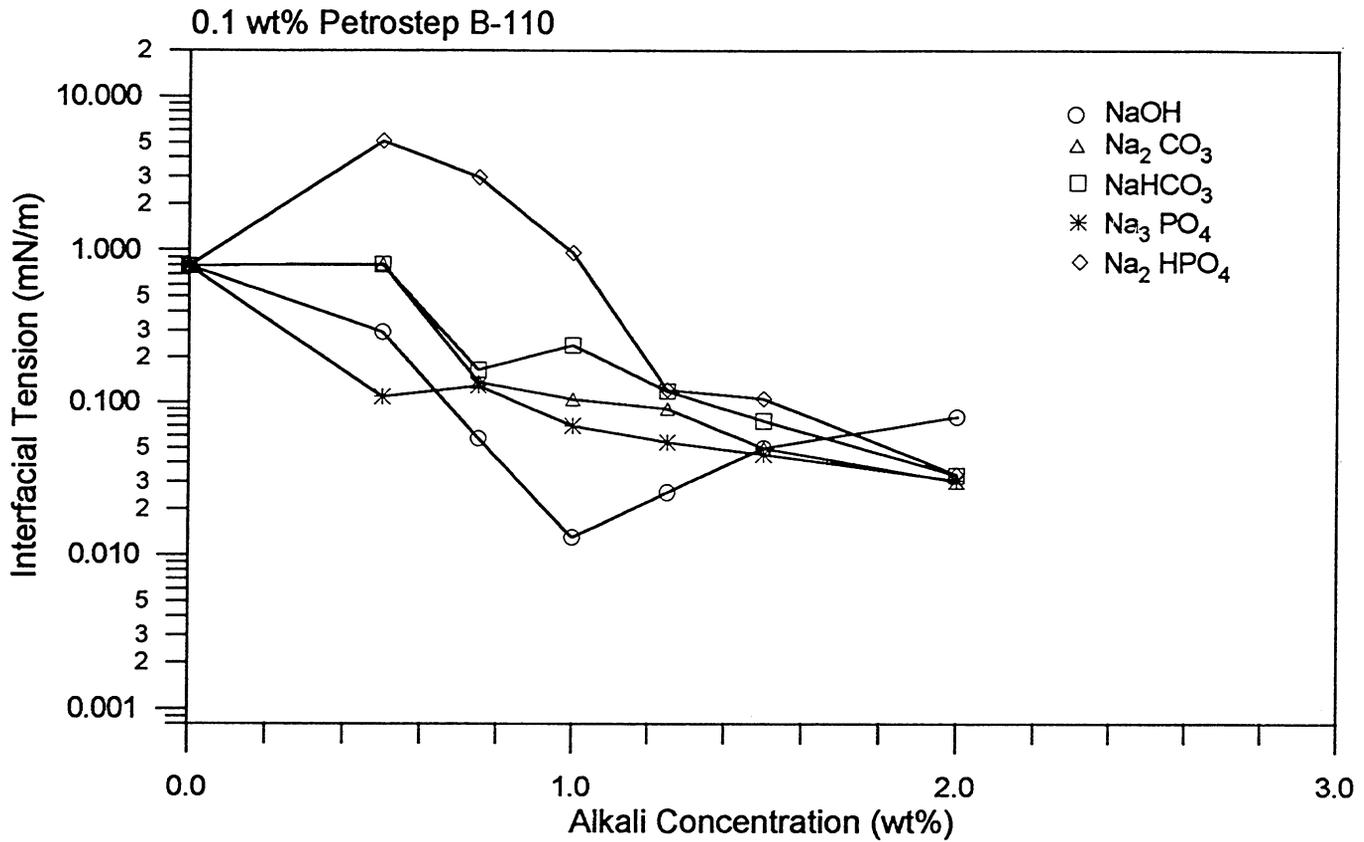


Figure 17

Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

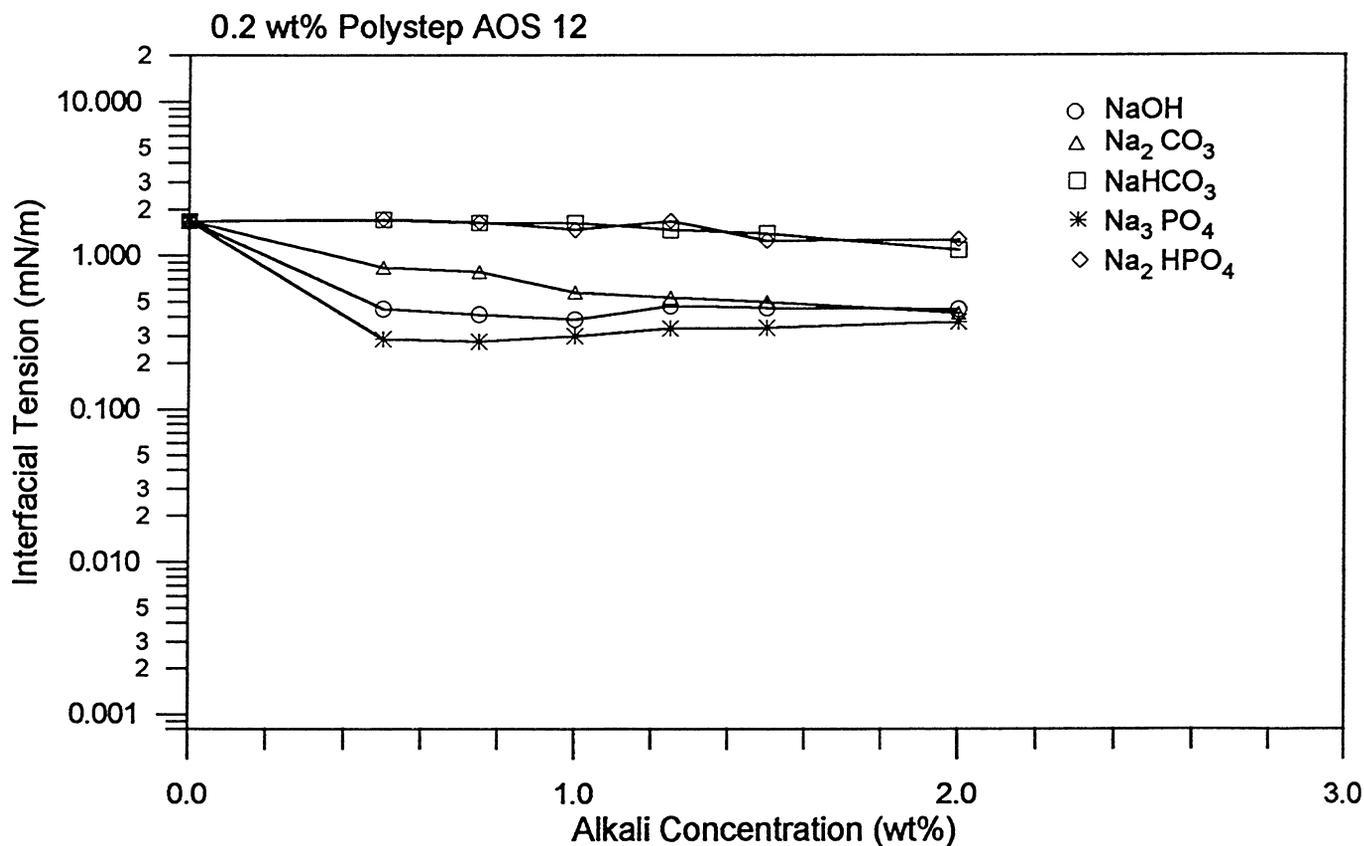
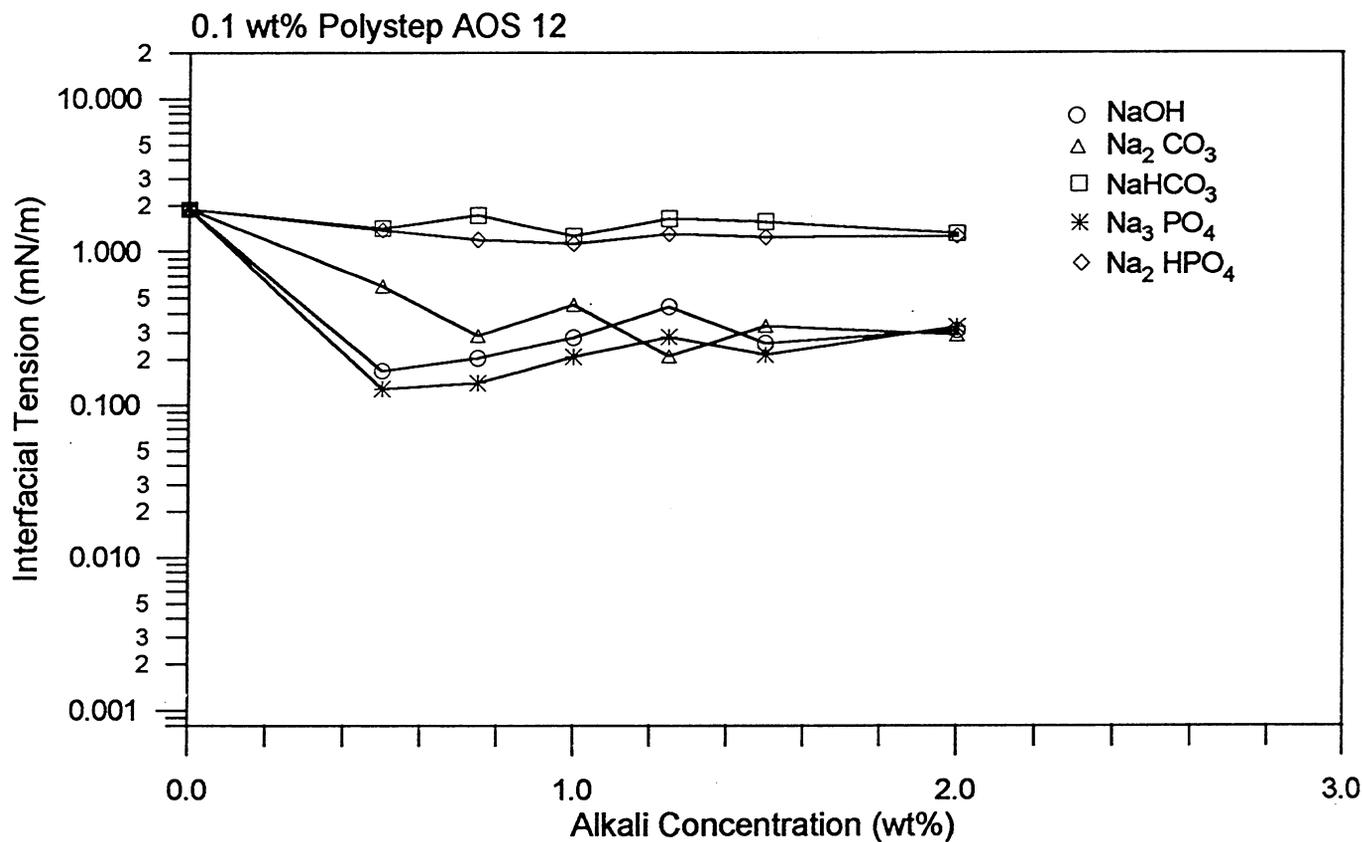
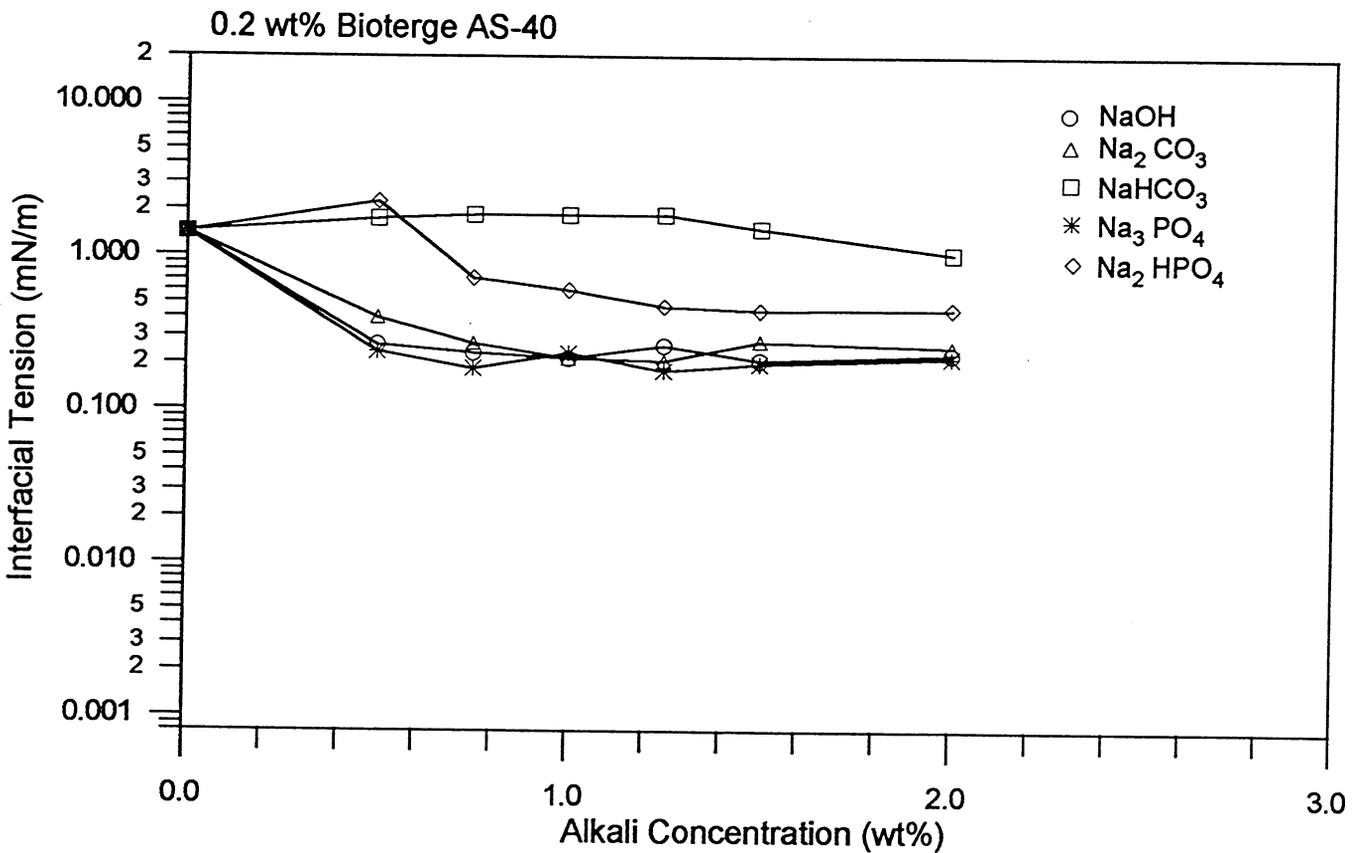
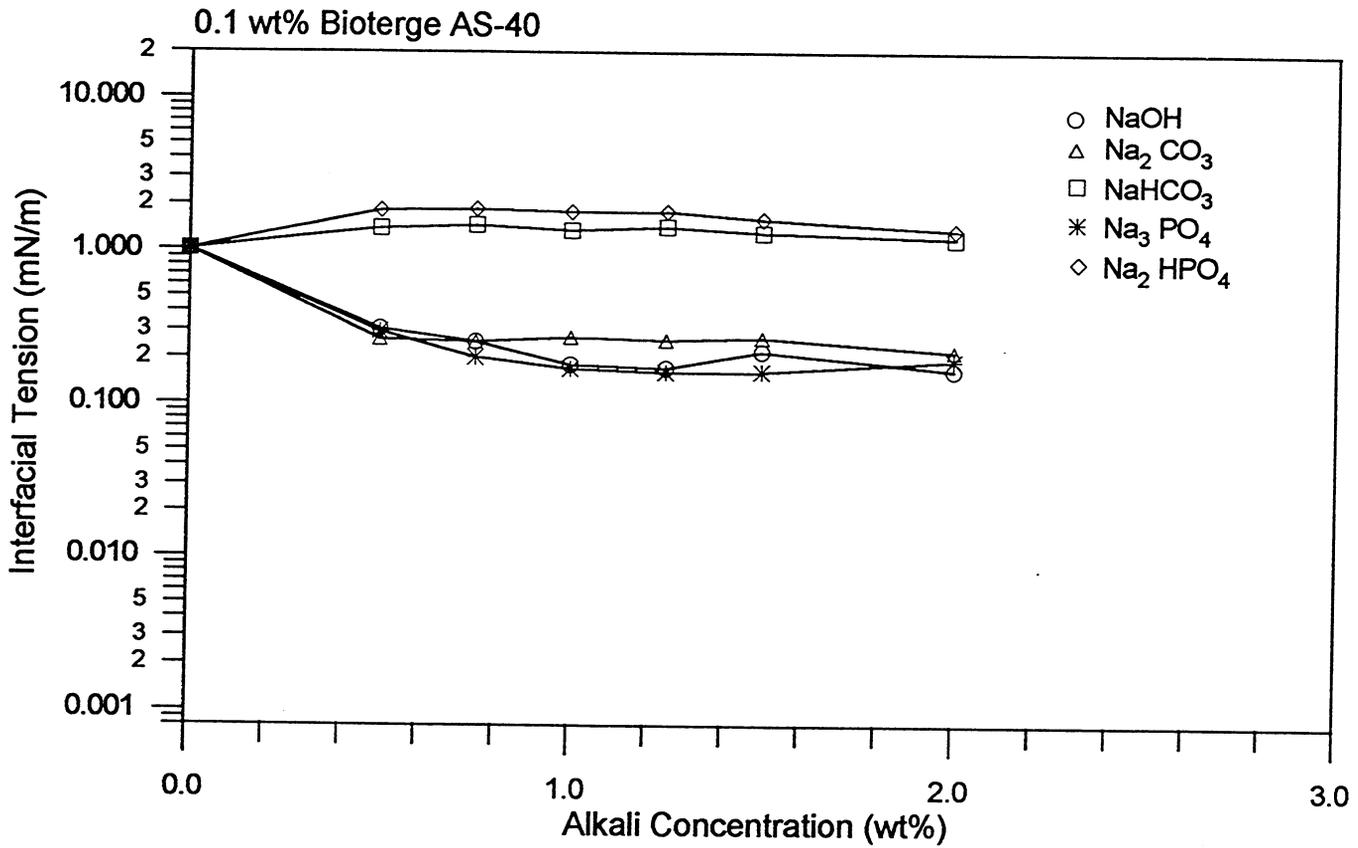
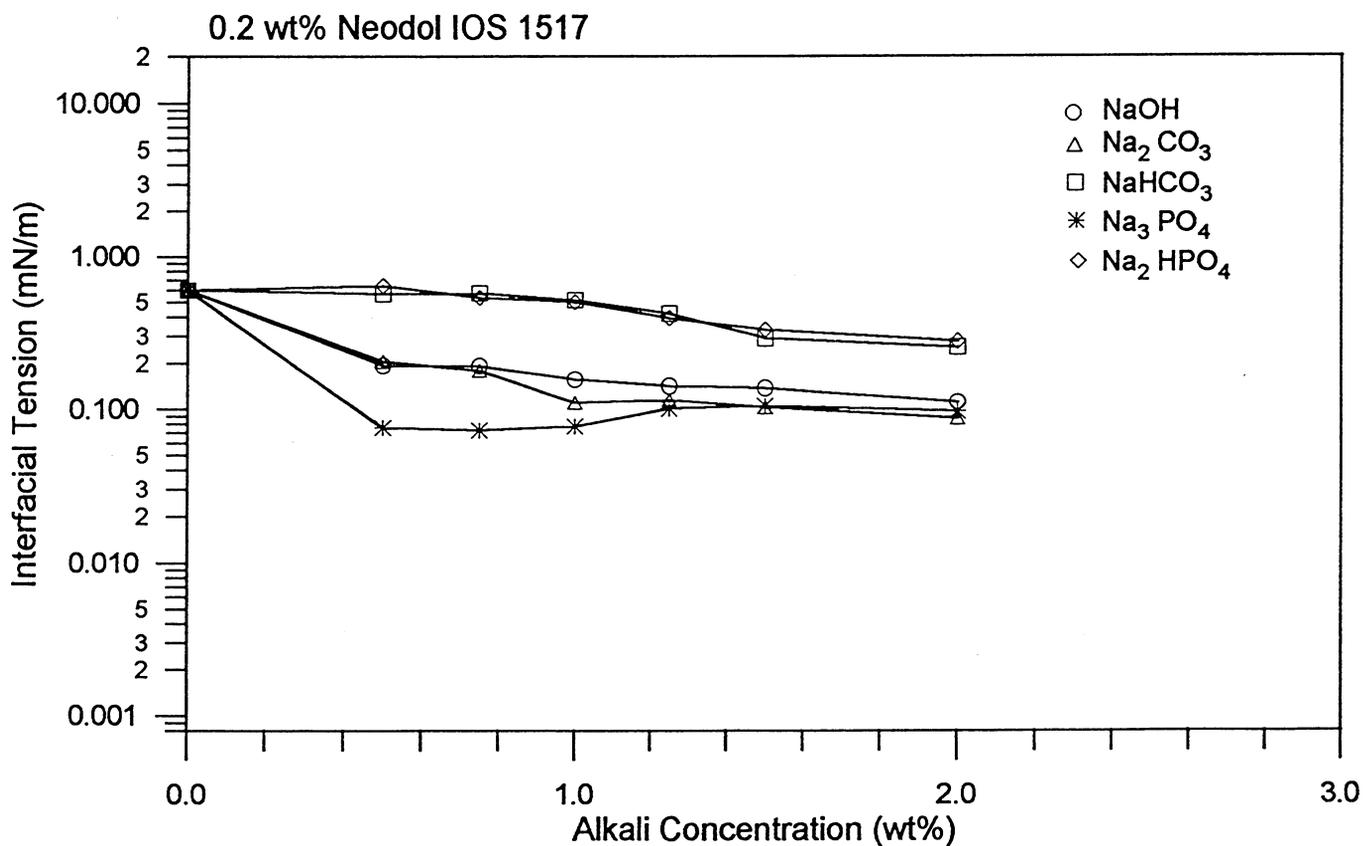
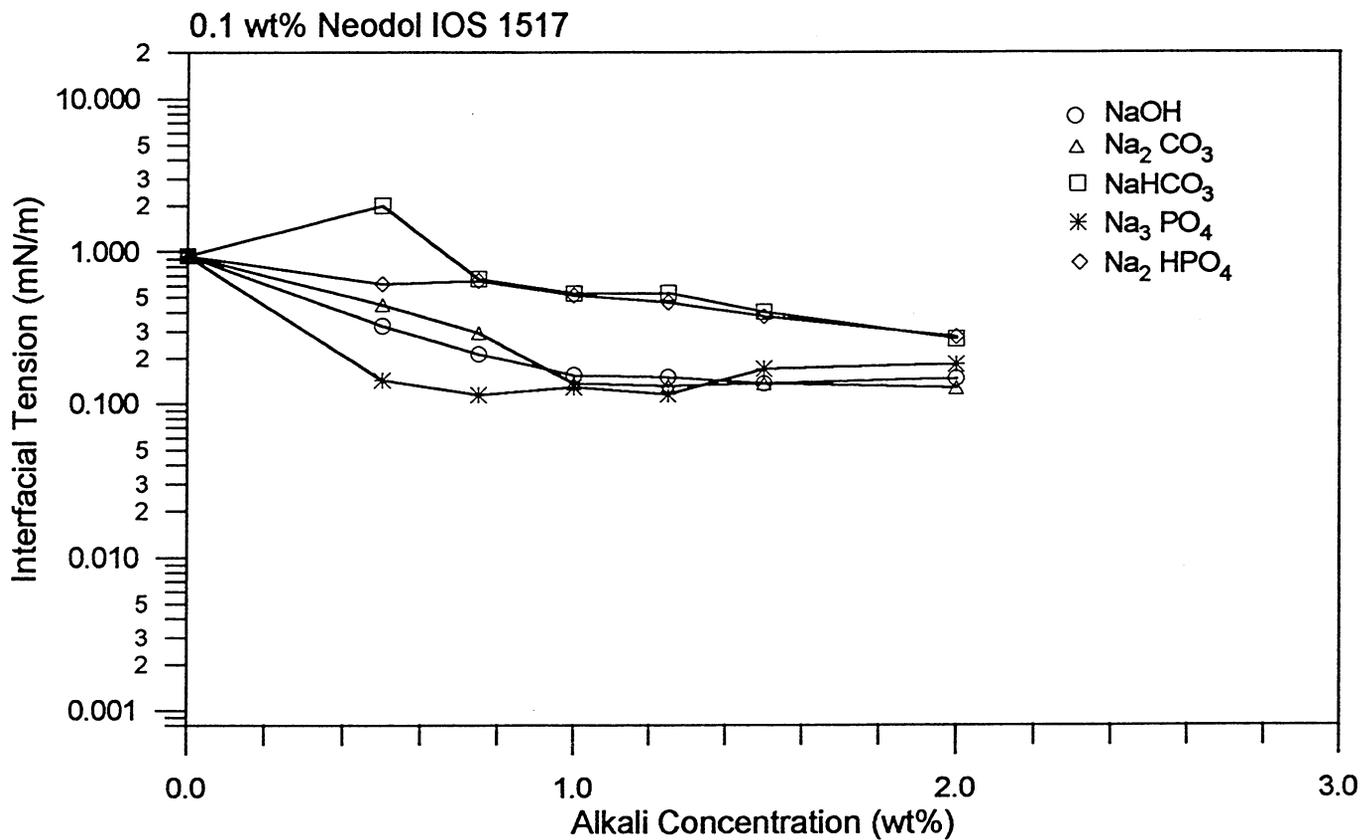


Figure 19

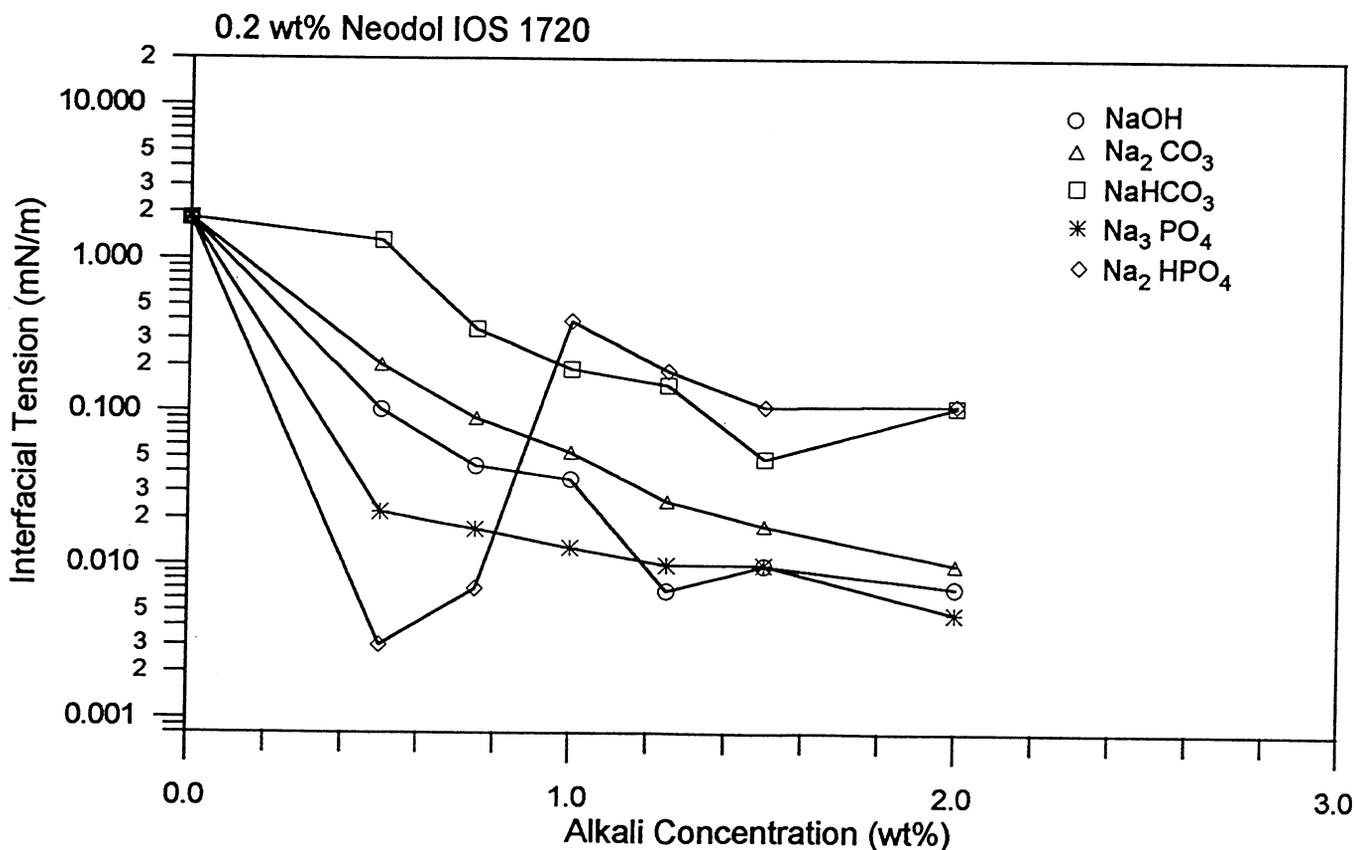
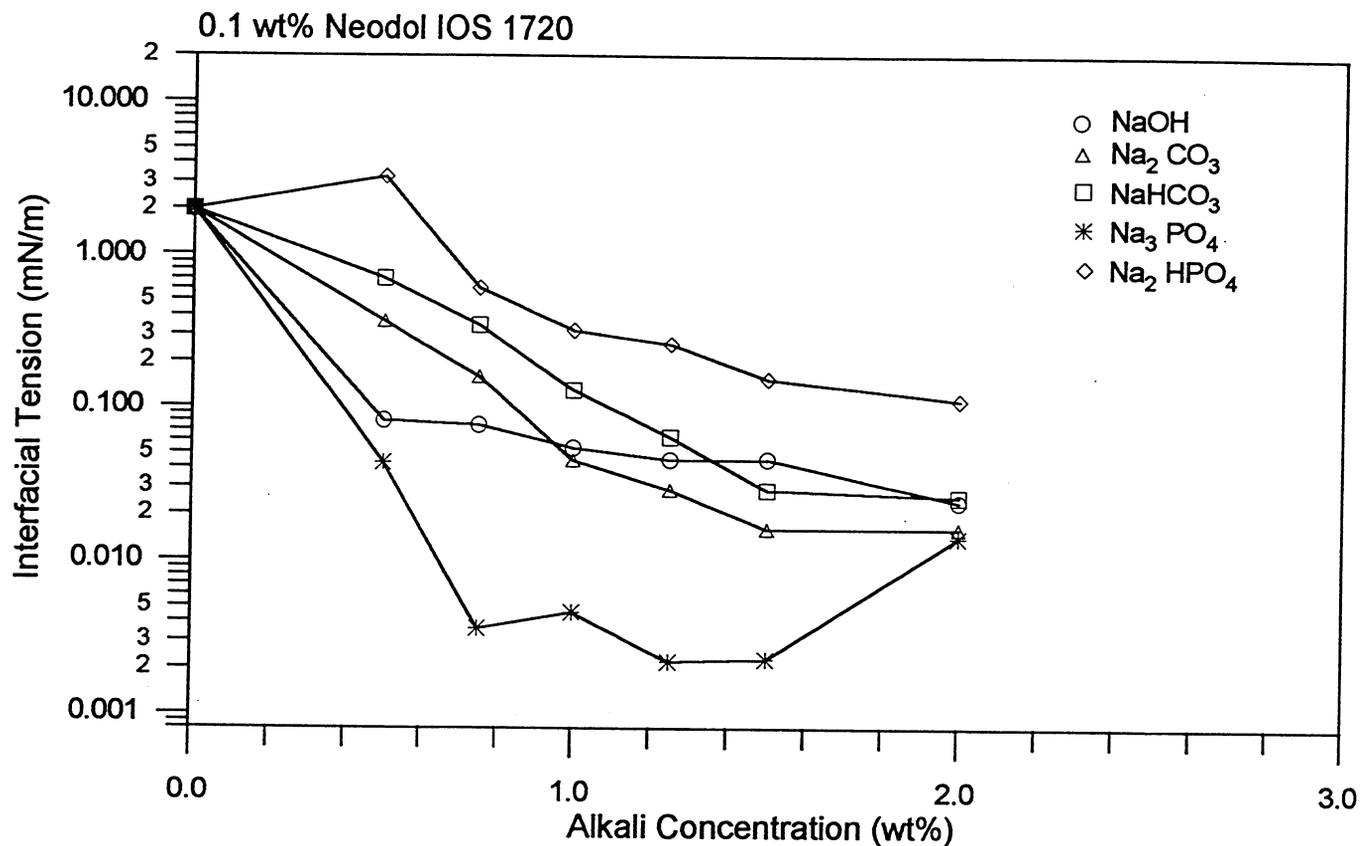
Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



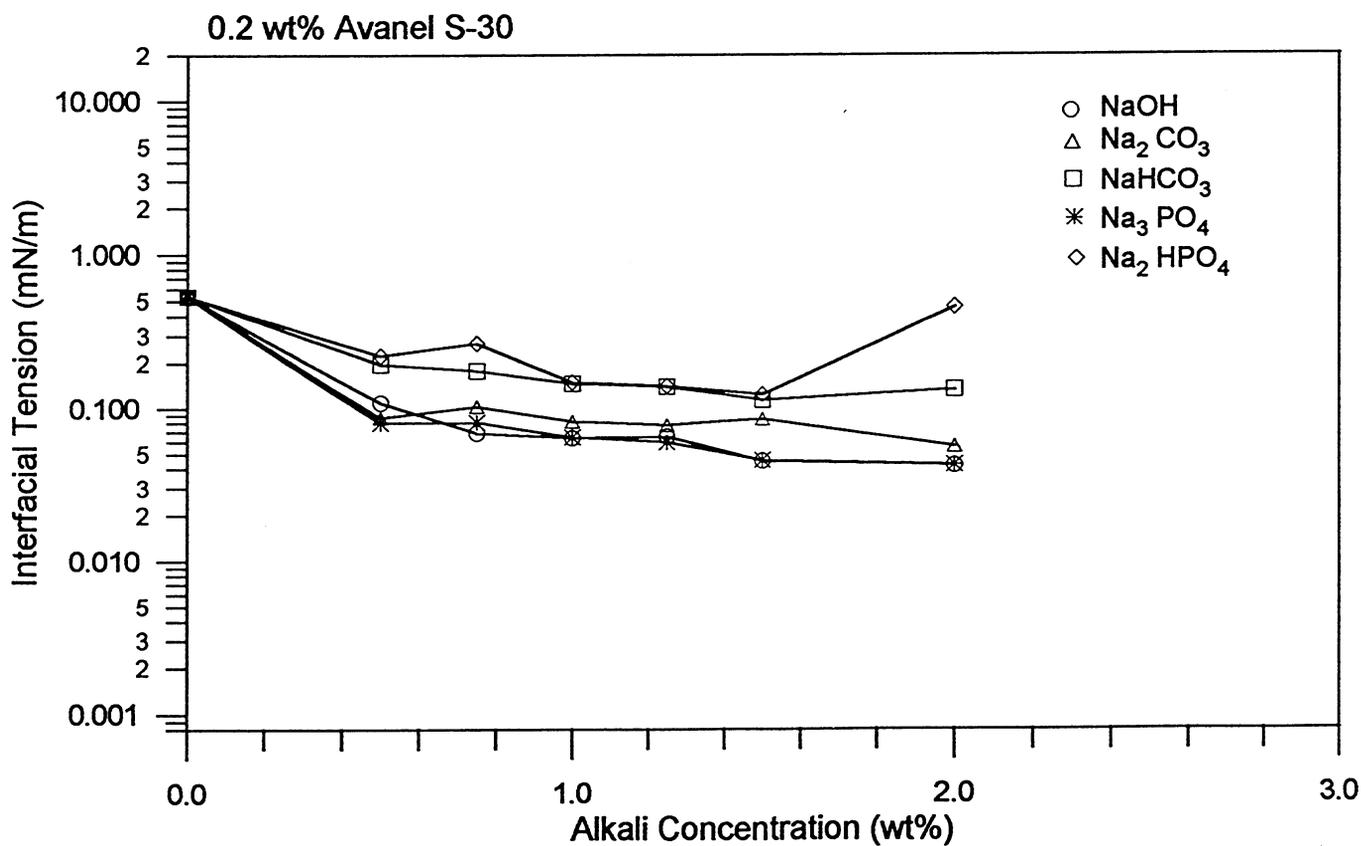
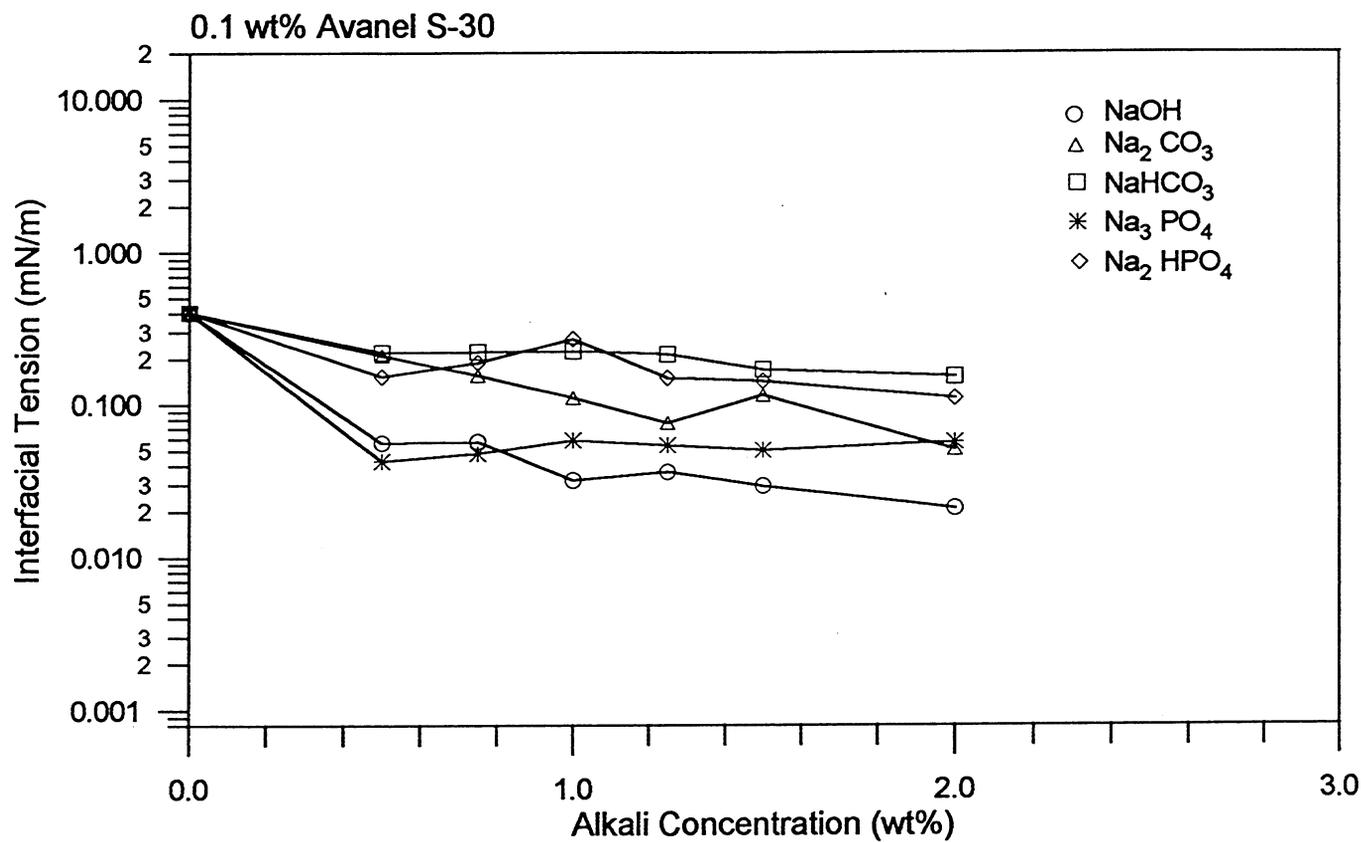
Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



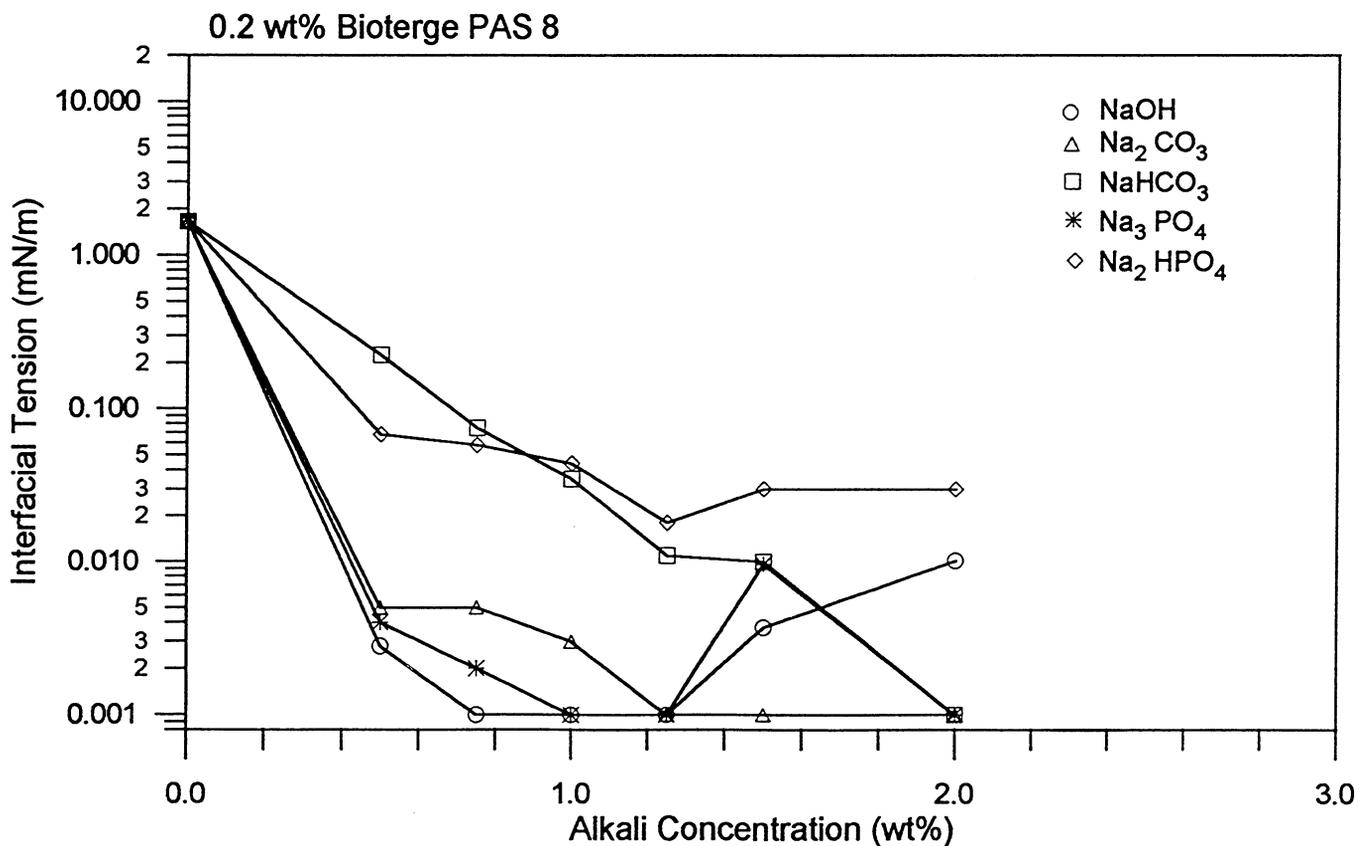
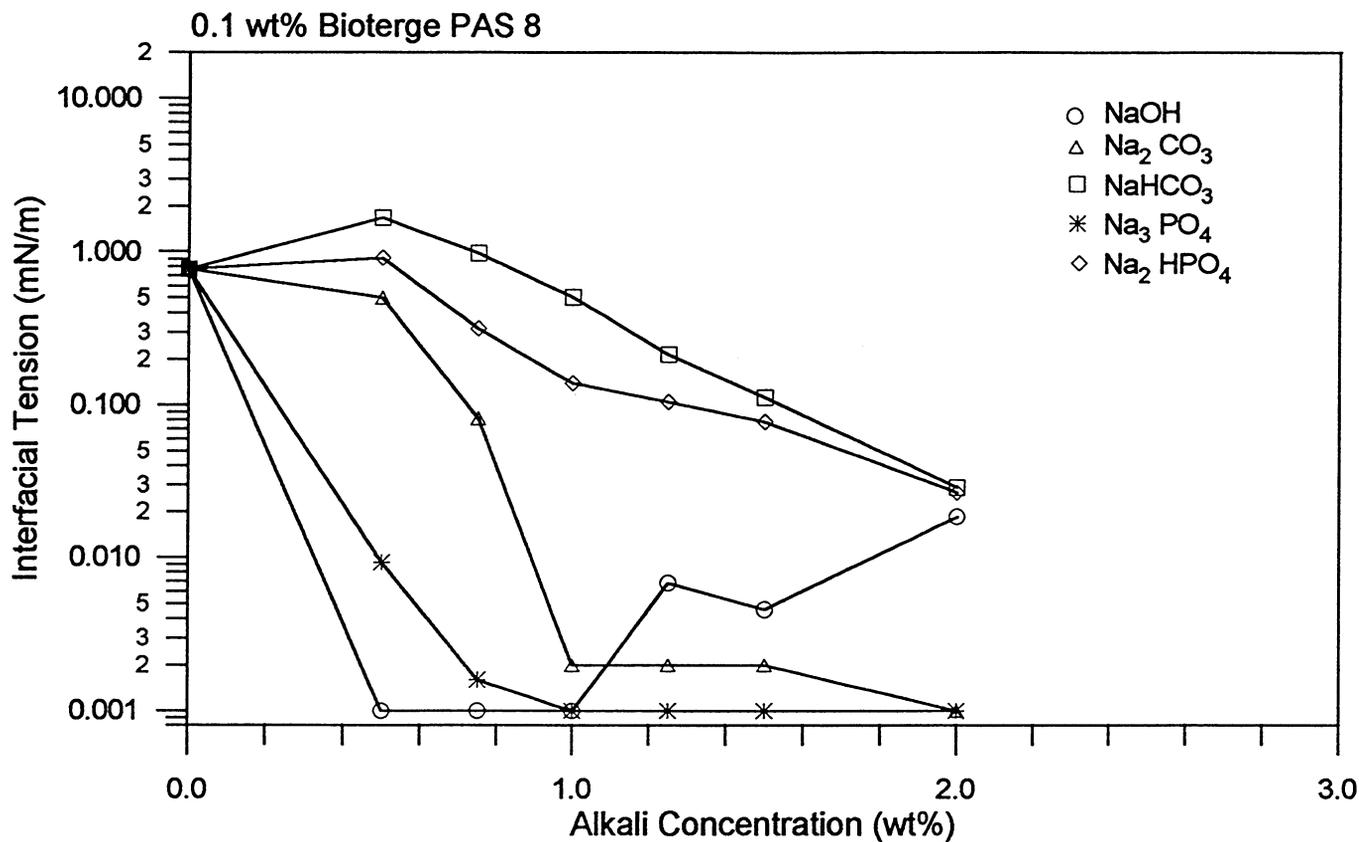
Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



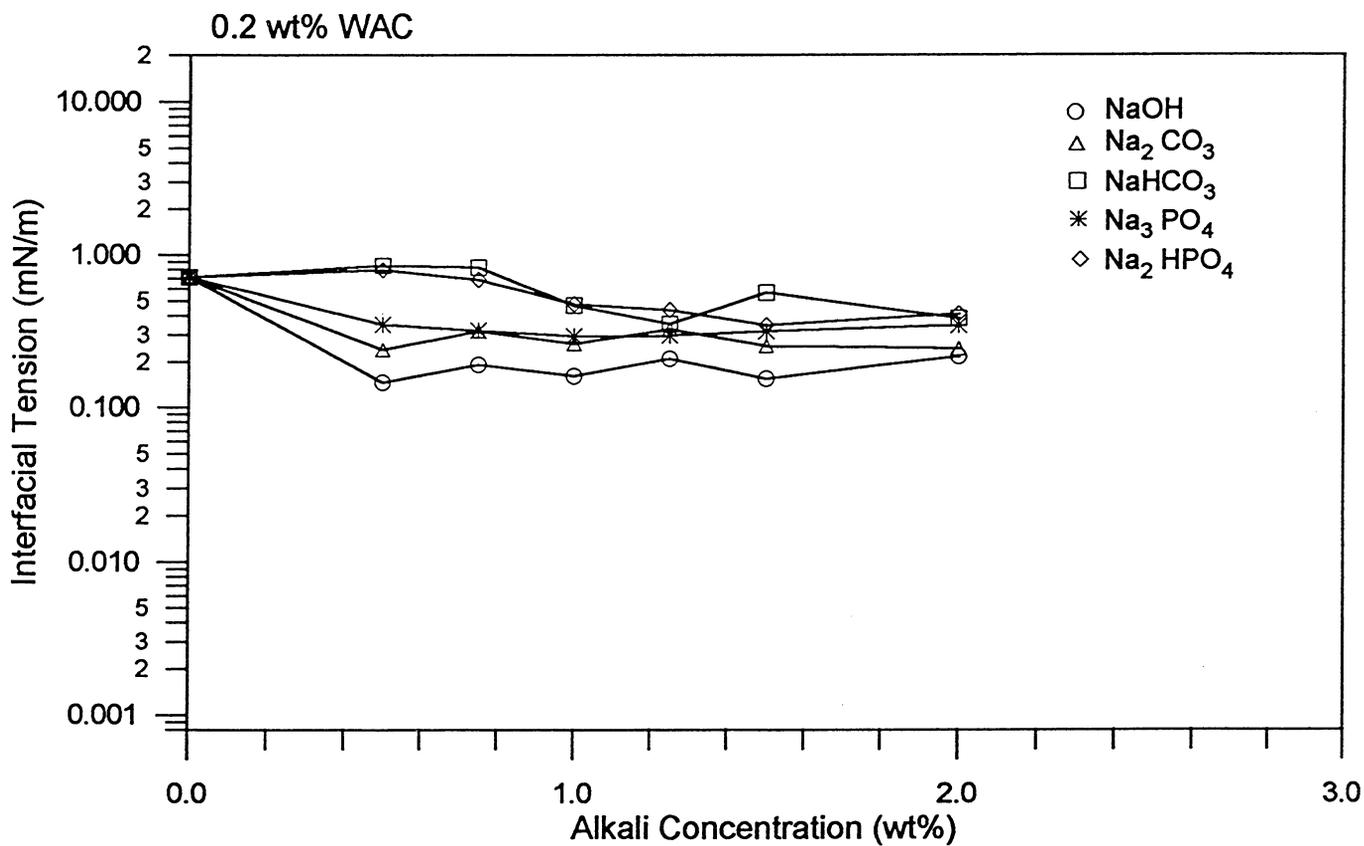
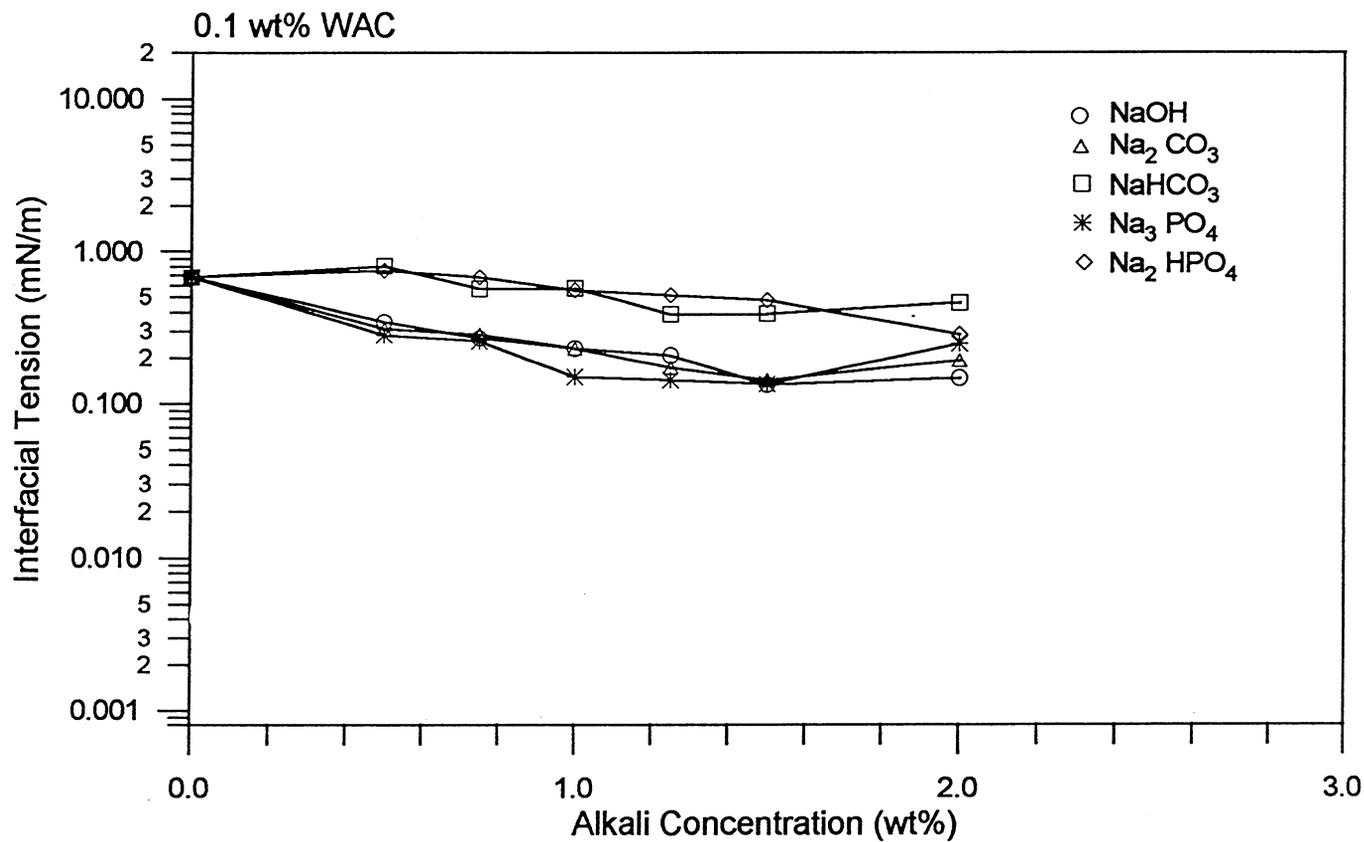
Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration



Interfacial Tension Between Adena Crude Oil at 72°F  
and Alkaline-Surfactant Solutions versus Alkali Concentration

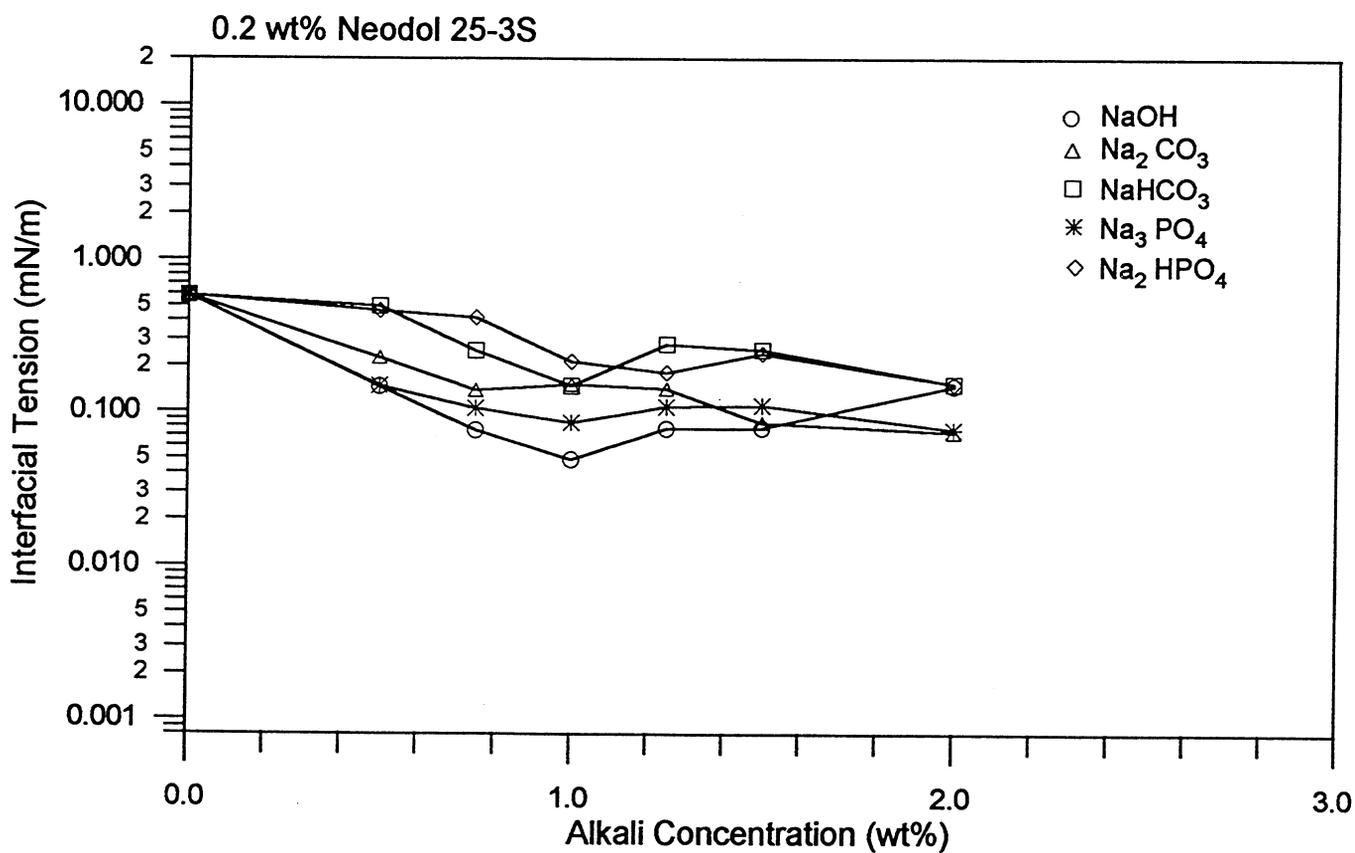
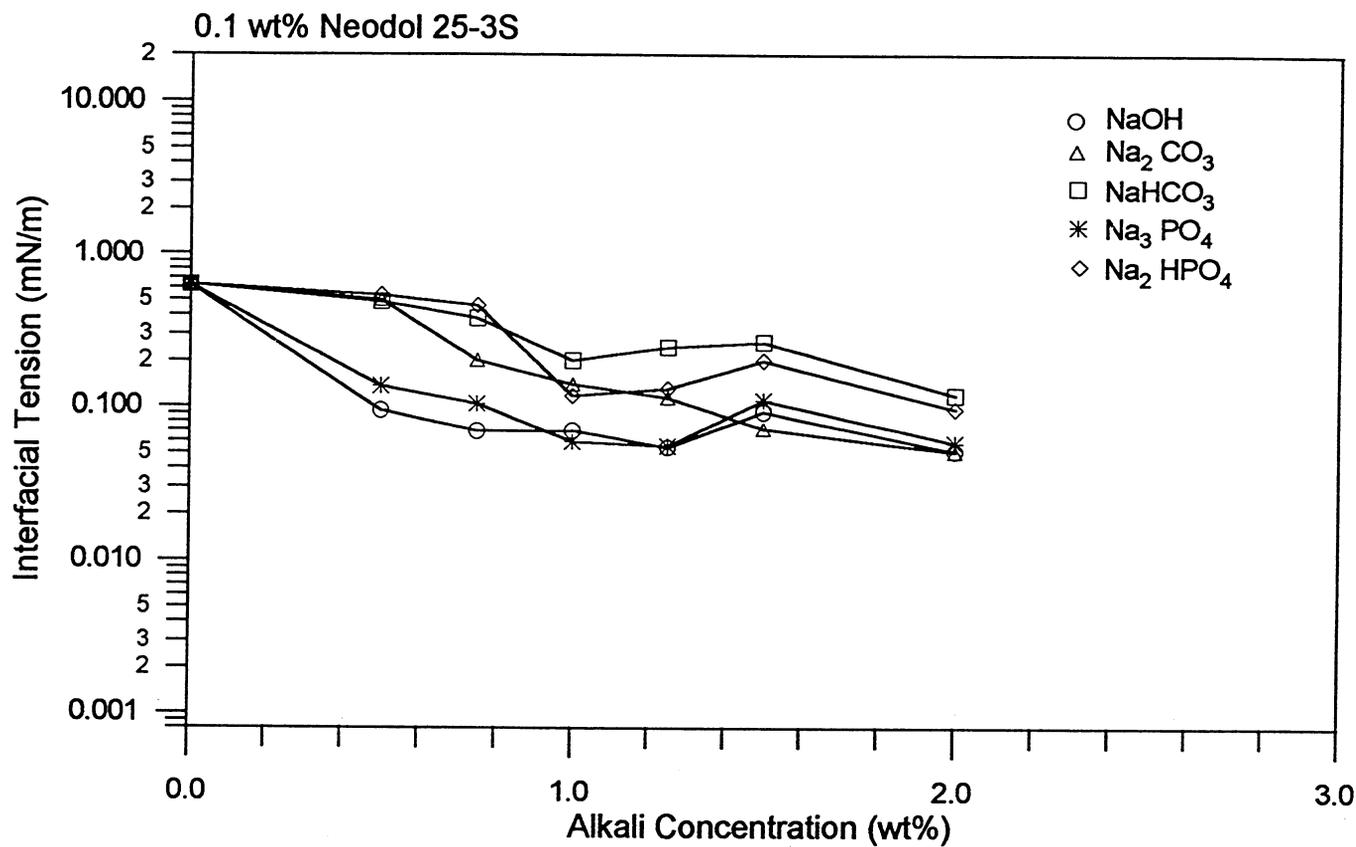


Figure 26

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

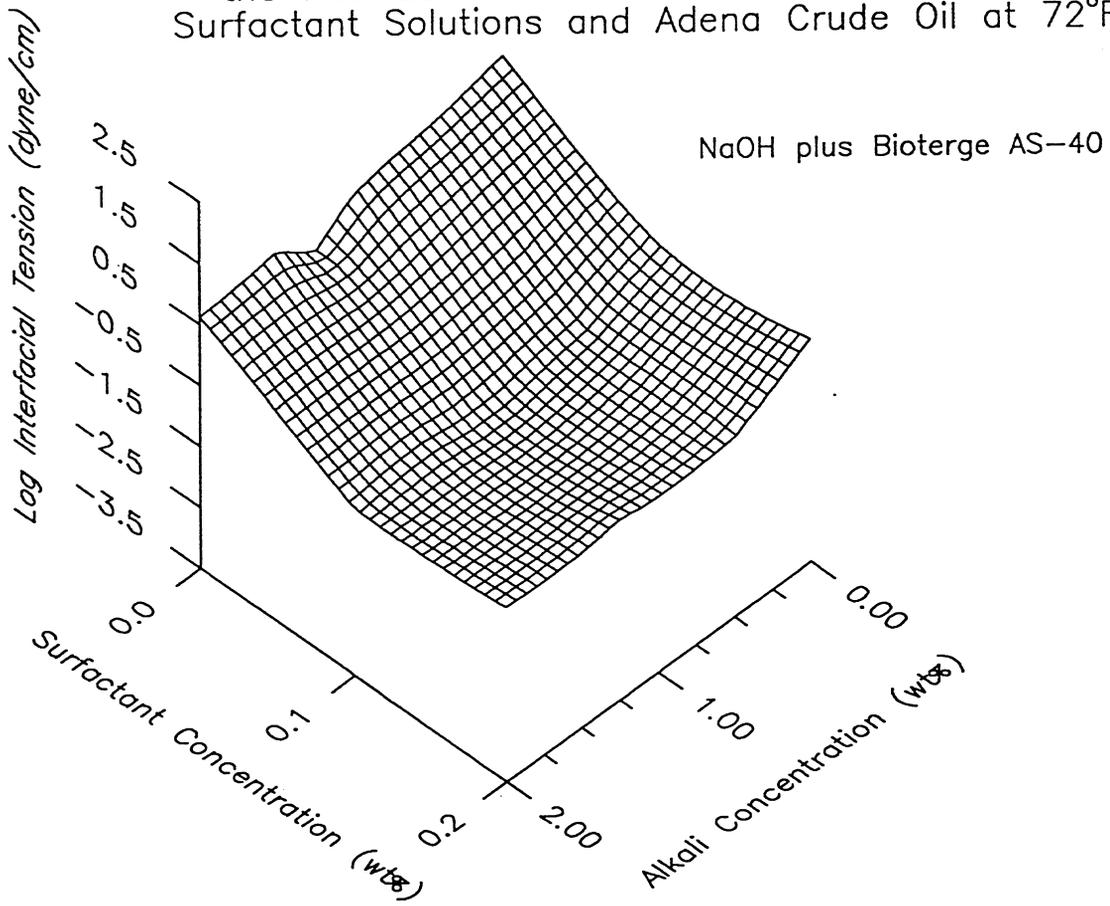


Figure 27

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

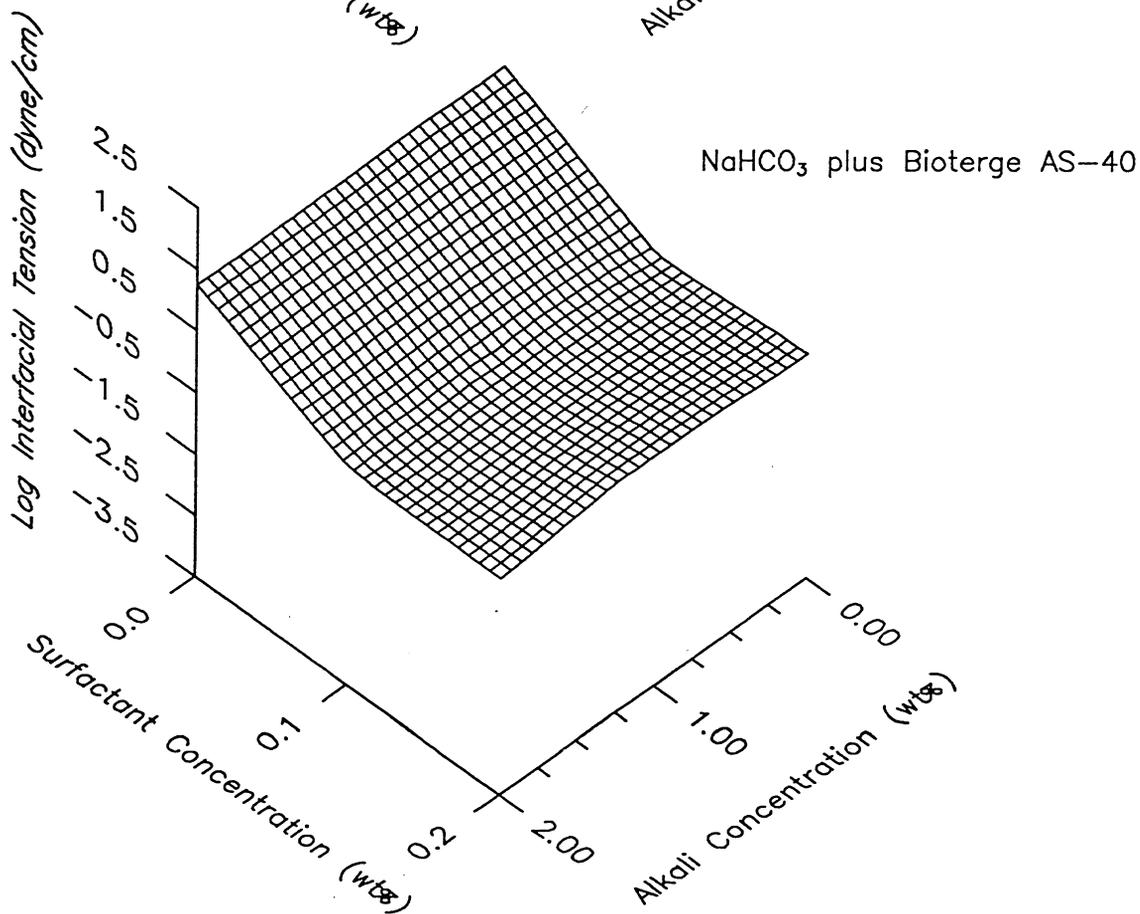
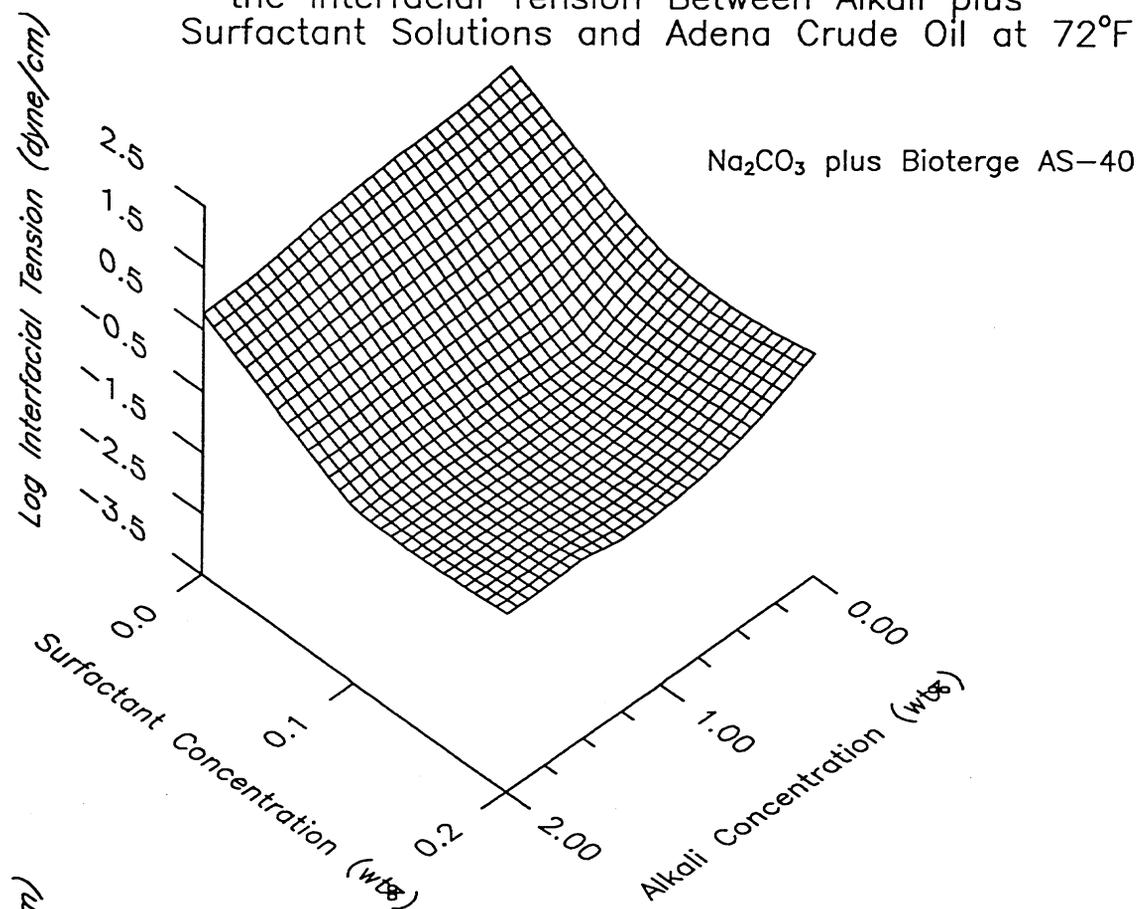


Figure 28

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

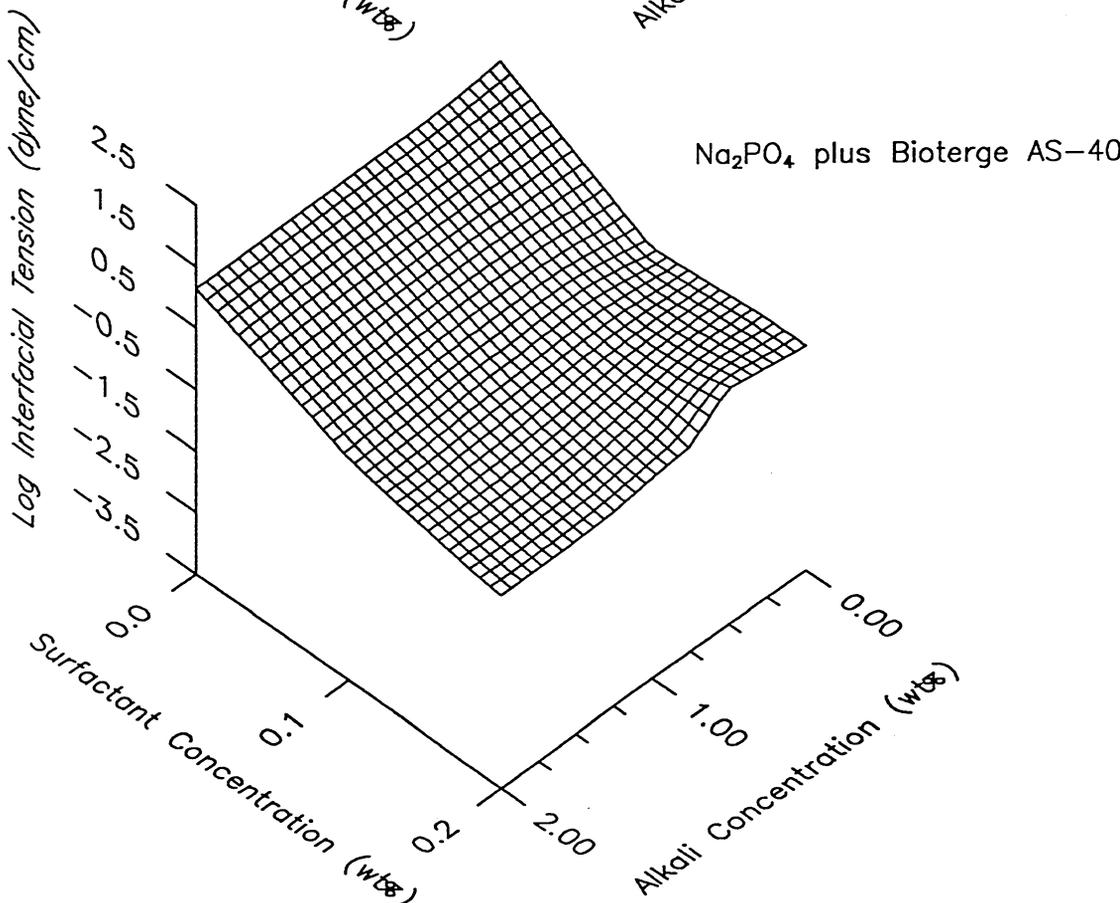
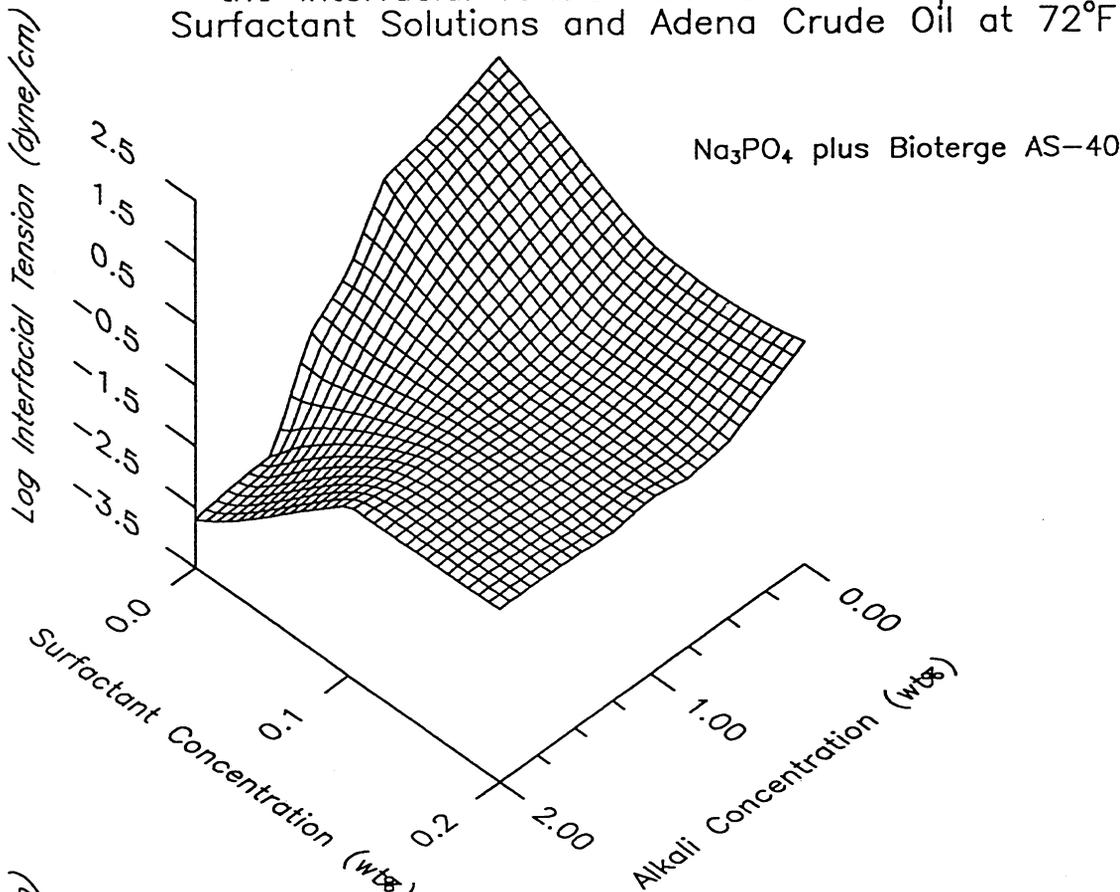


Figure 29

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

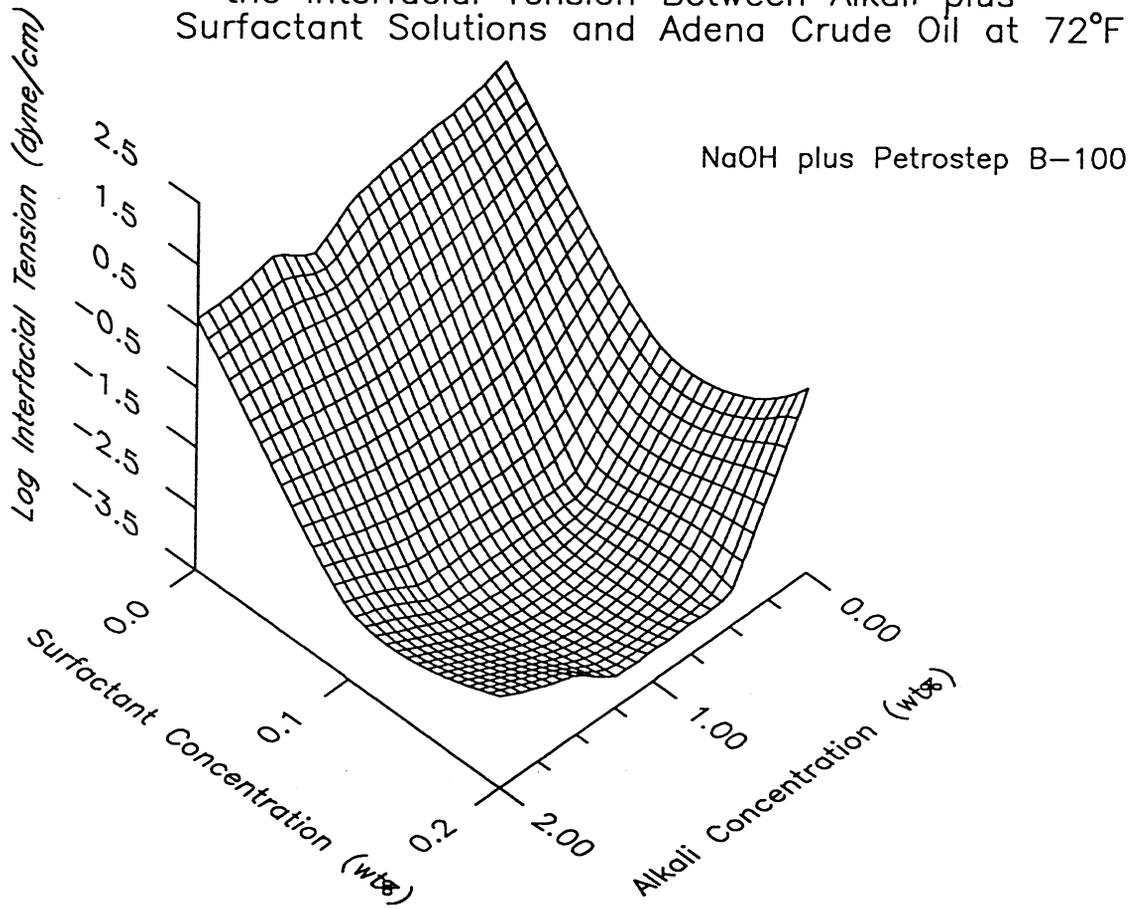


Figure 30

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

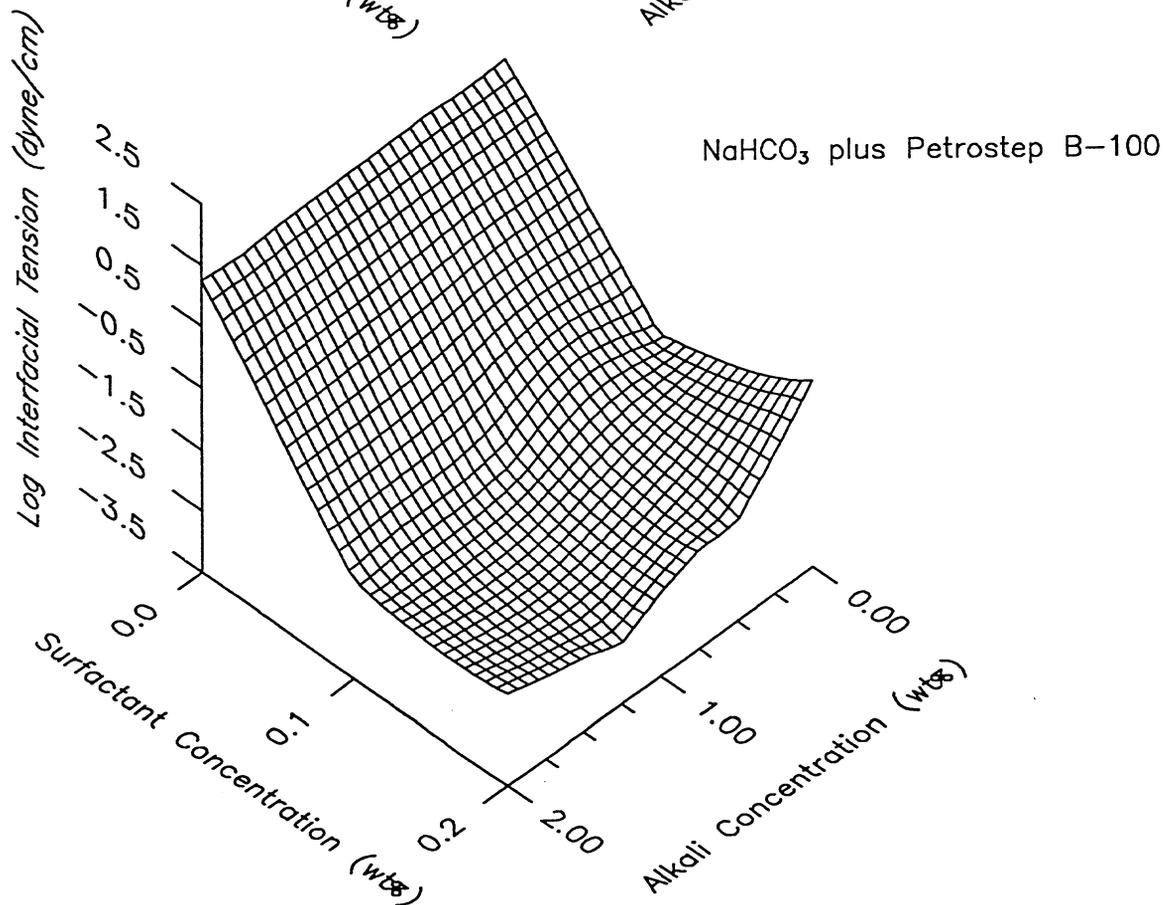
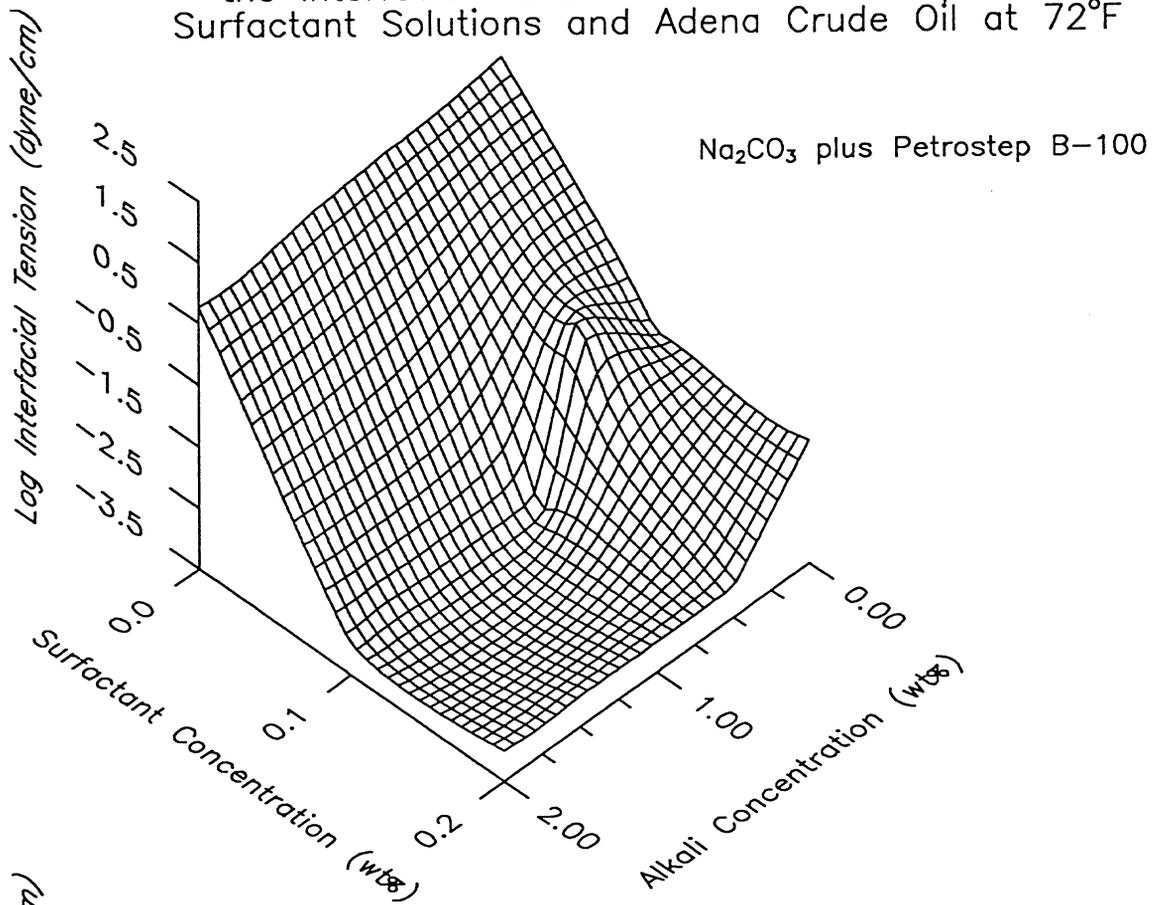


Figure 31

Effect of Alkali and Surfactant Concentration on the Interfacial Tension Between Alkali plus Surfactant Solutions and Adena Crude Oil at 72°F

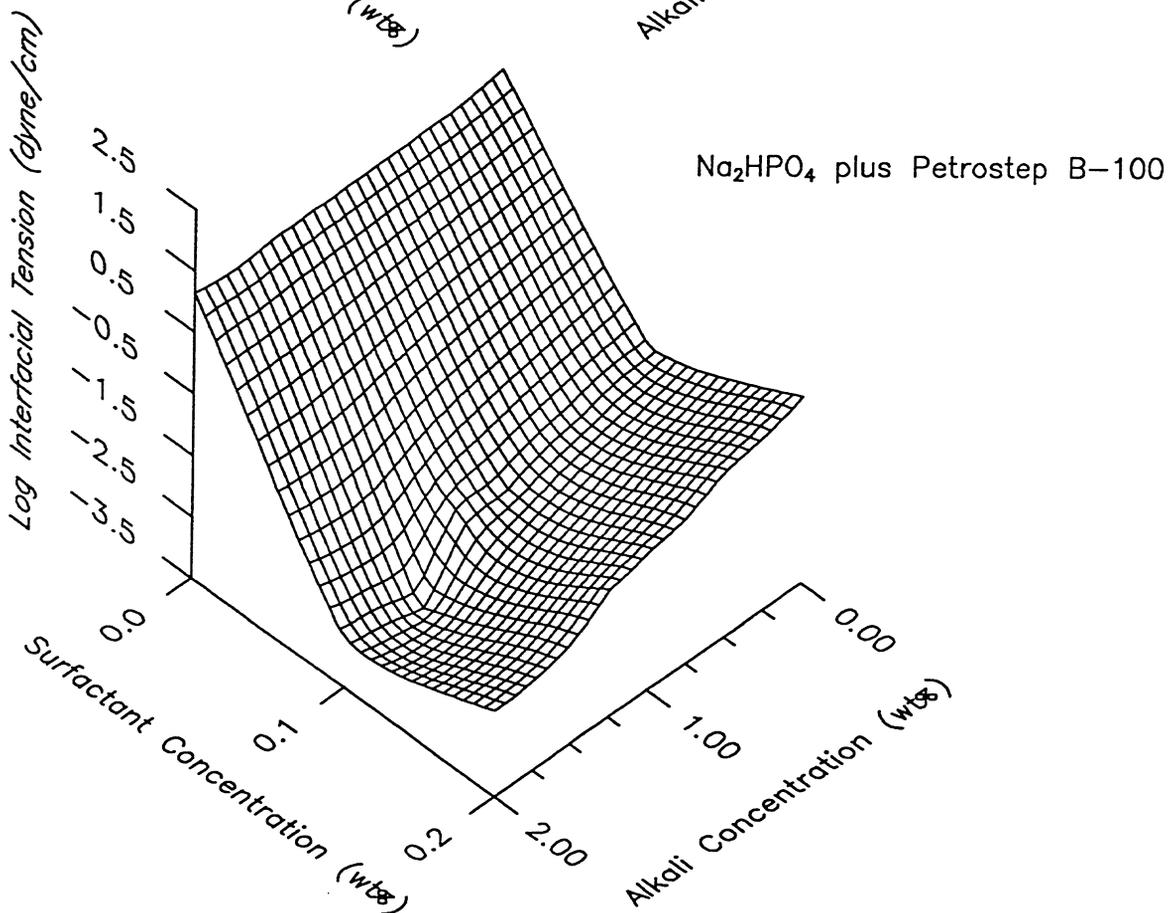
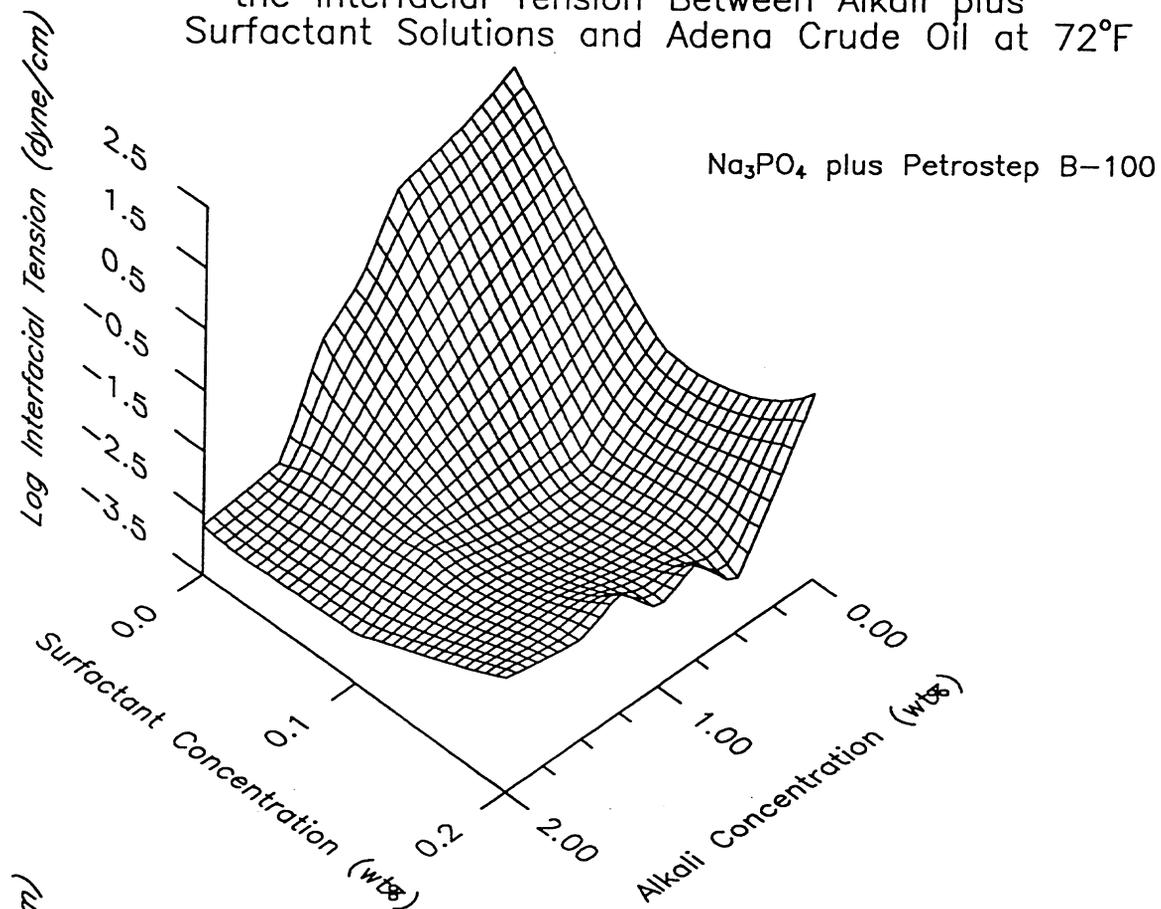
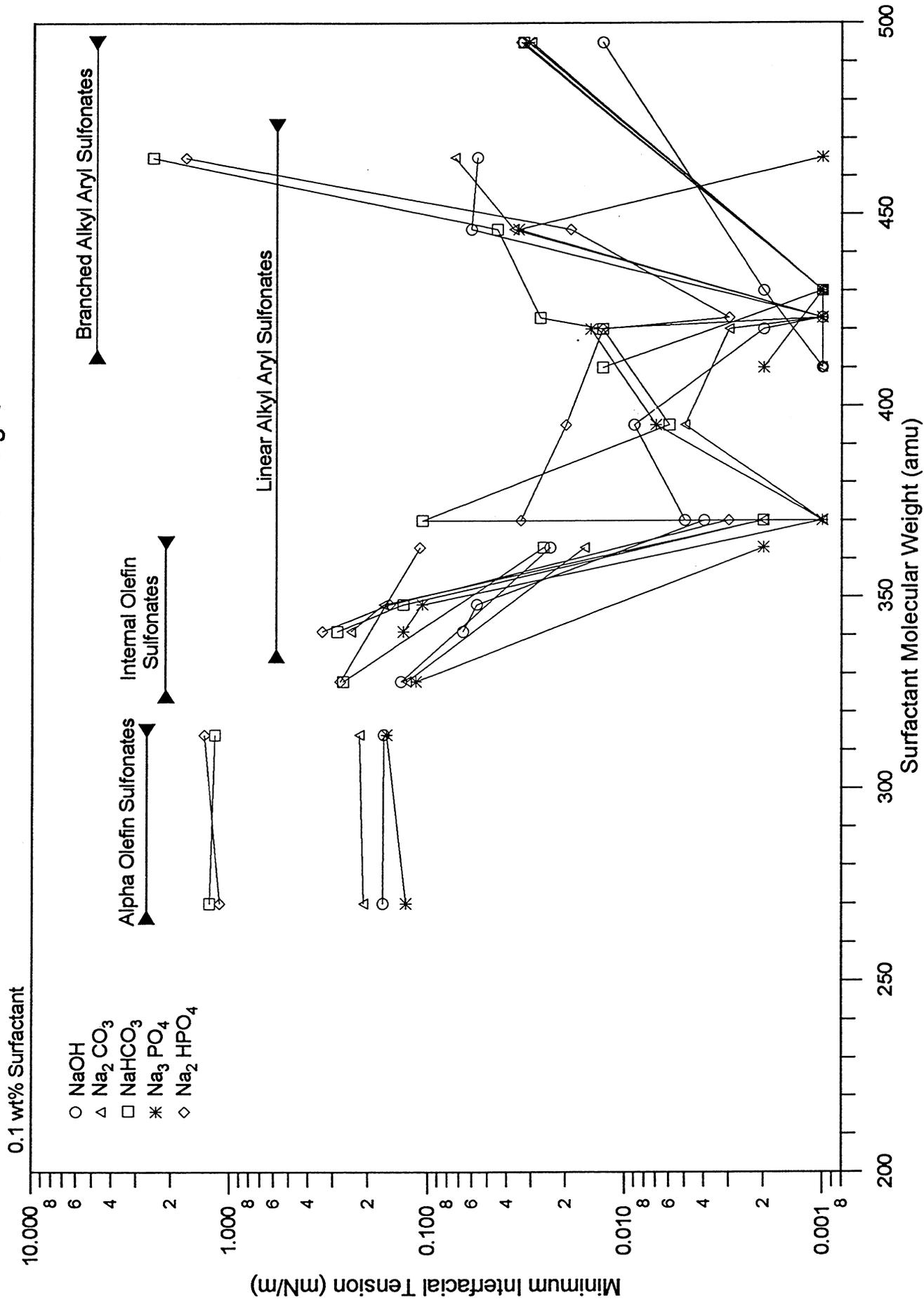


Figure 32

Minimum Interfacial Tension of Alkali plus Surfactant Solutions  
versus Surfactant Molecular Weight



Minimum Interfacial Tension of Alkali plus Surfactant Solutions  
versus Surfactant Molecular Weight

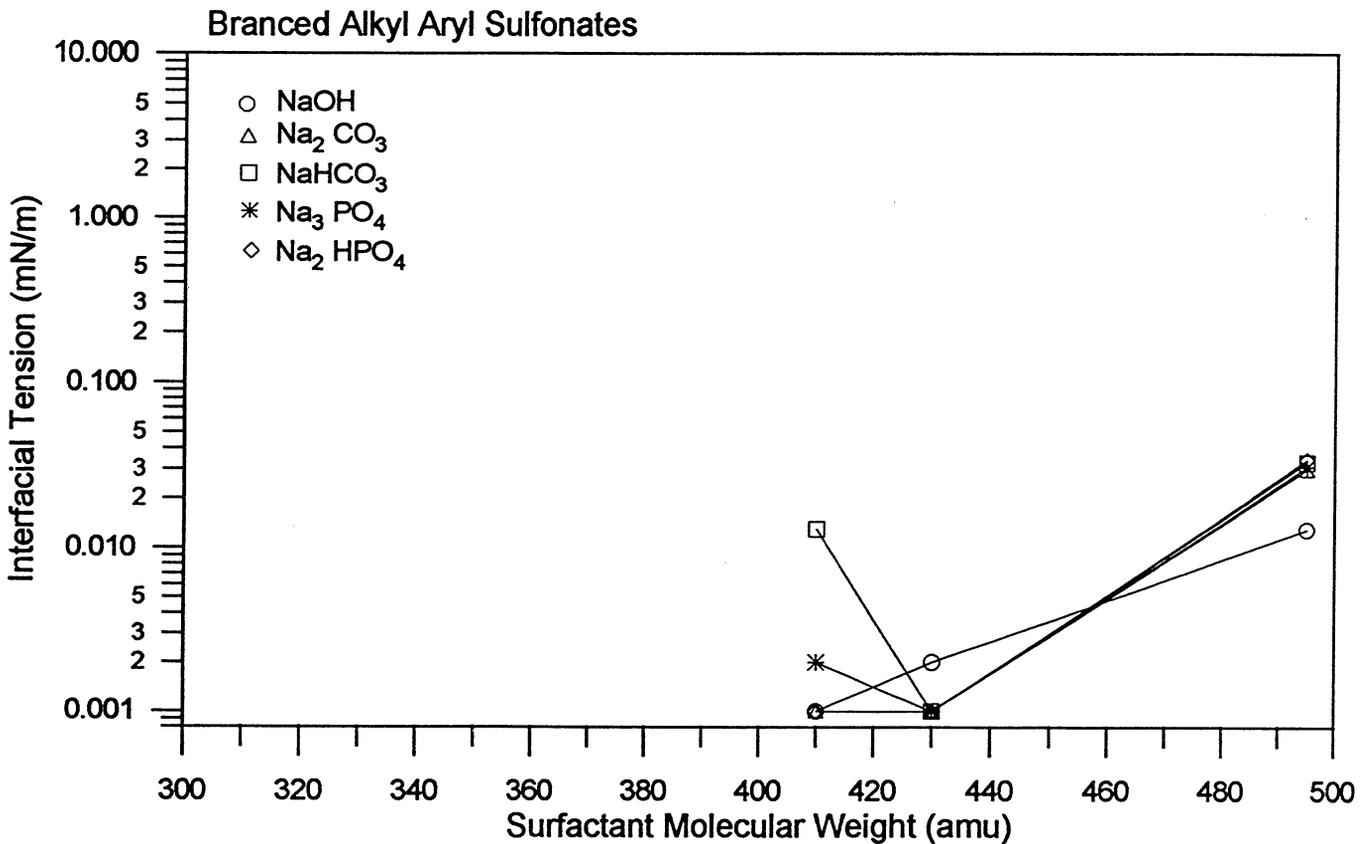
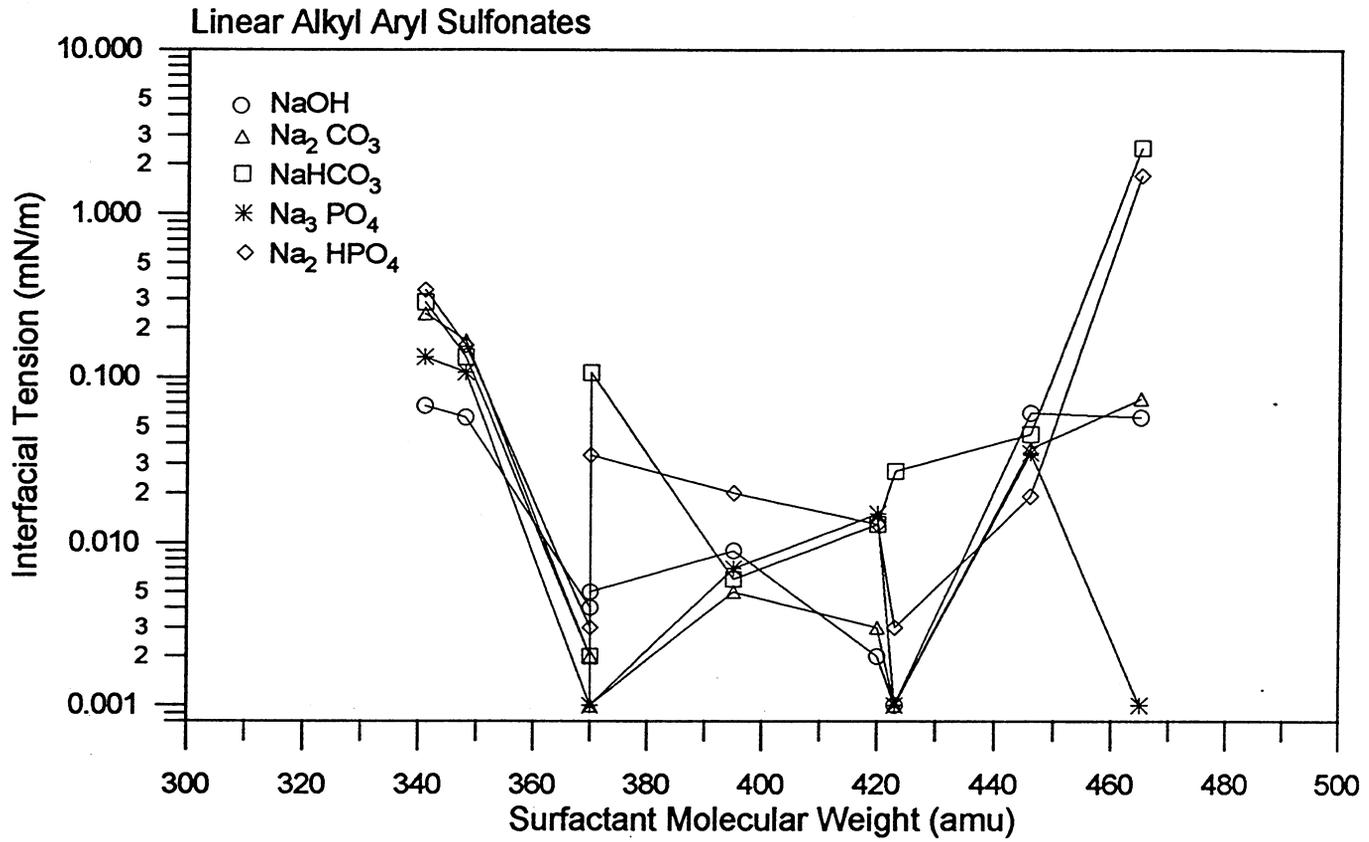


Figure 34

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different Alkali Concentrations

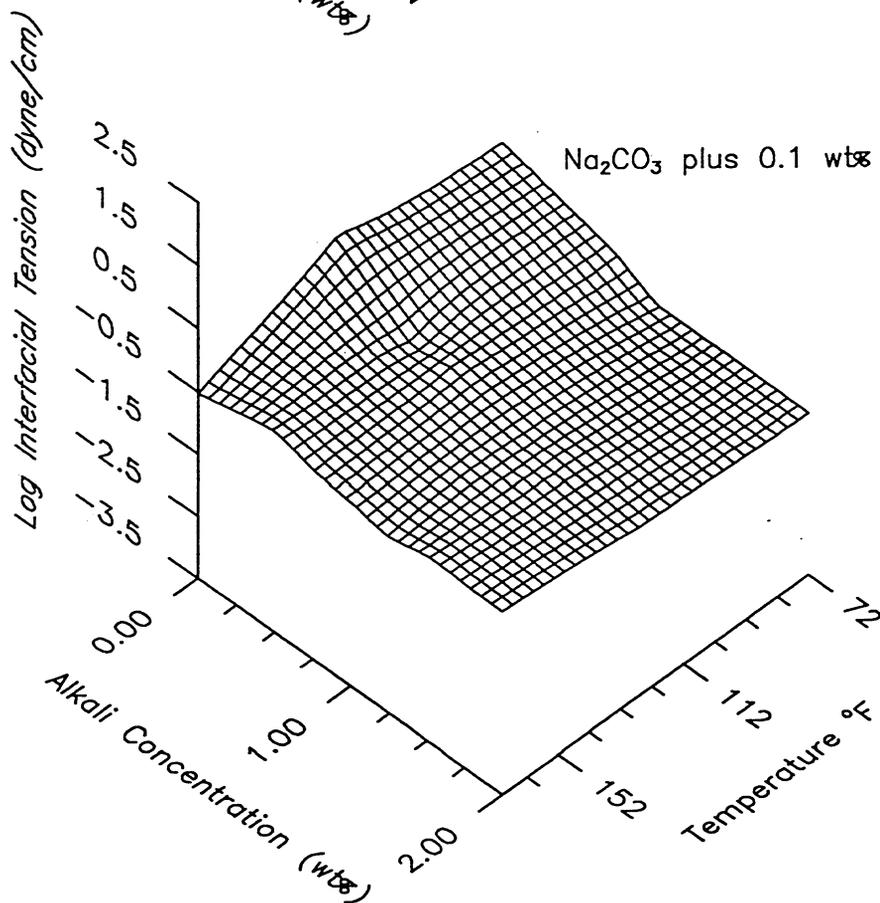
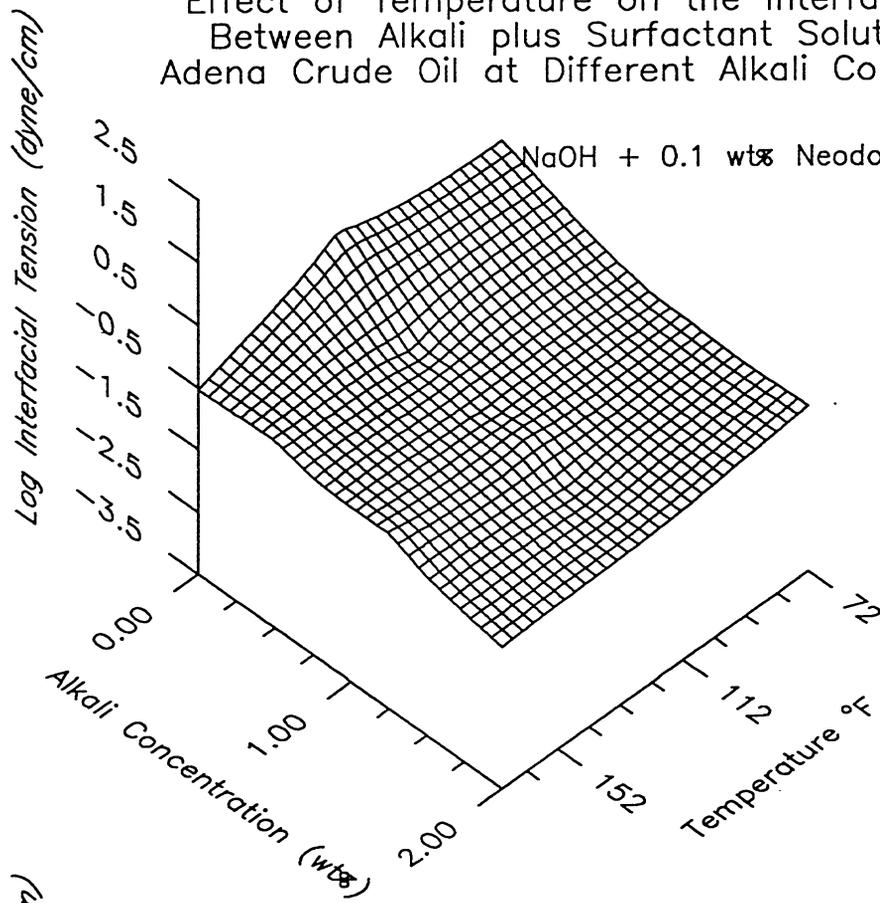


Figure 35

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different Alkali Concentrations

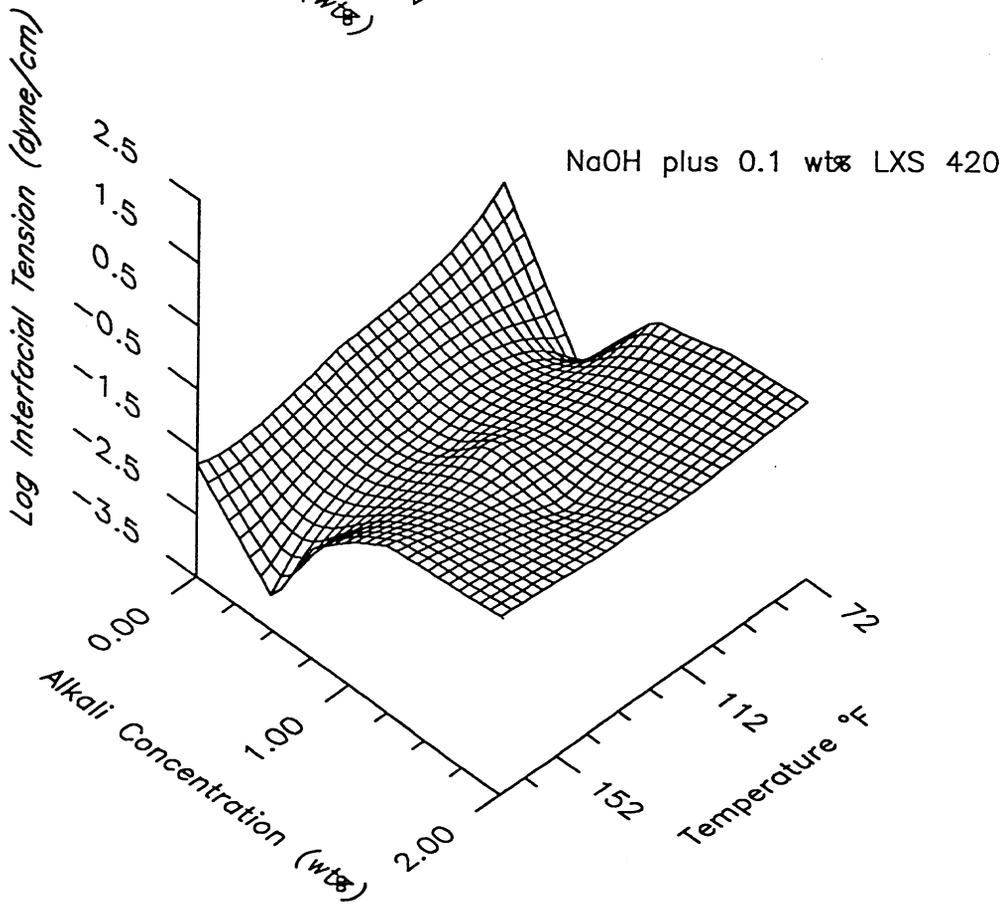
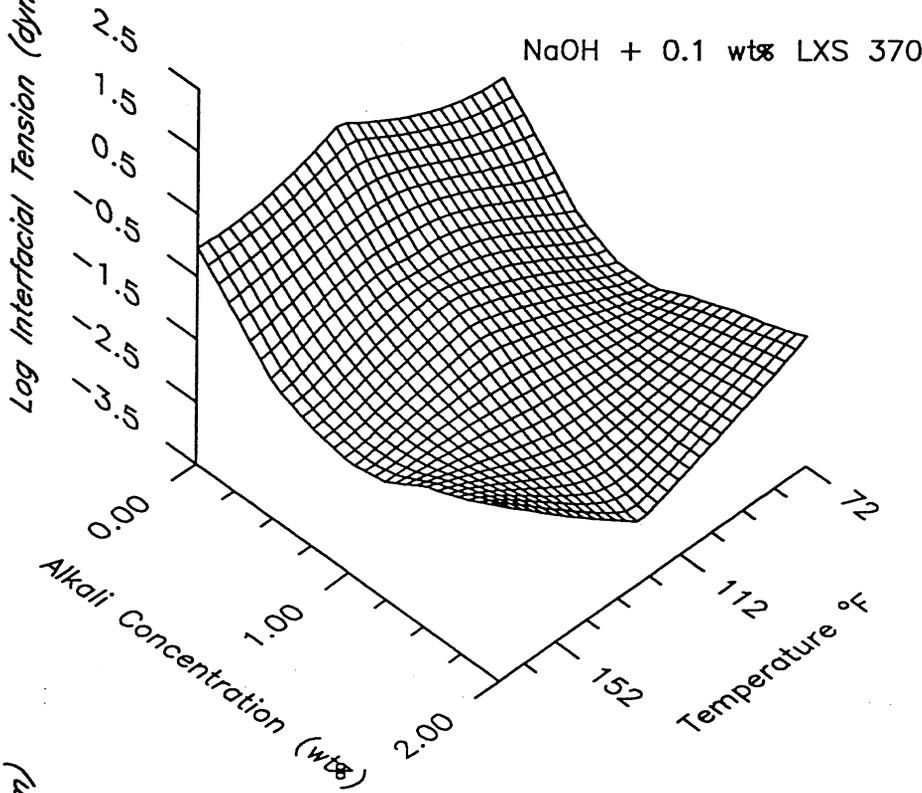


Figure 36

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different Alkali Concentrations

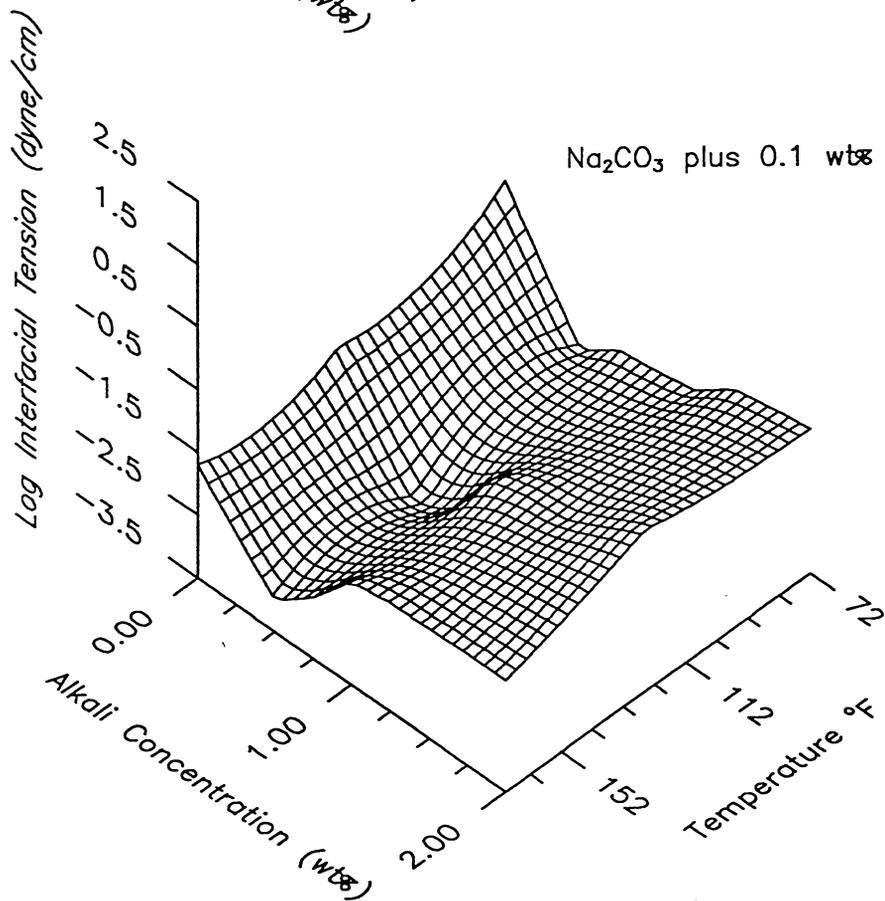
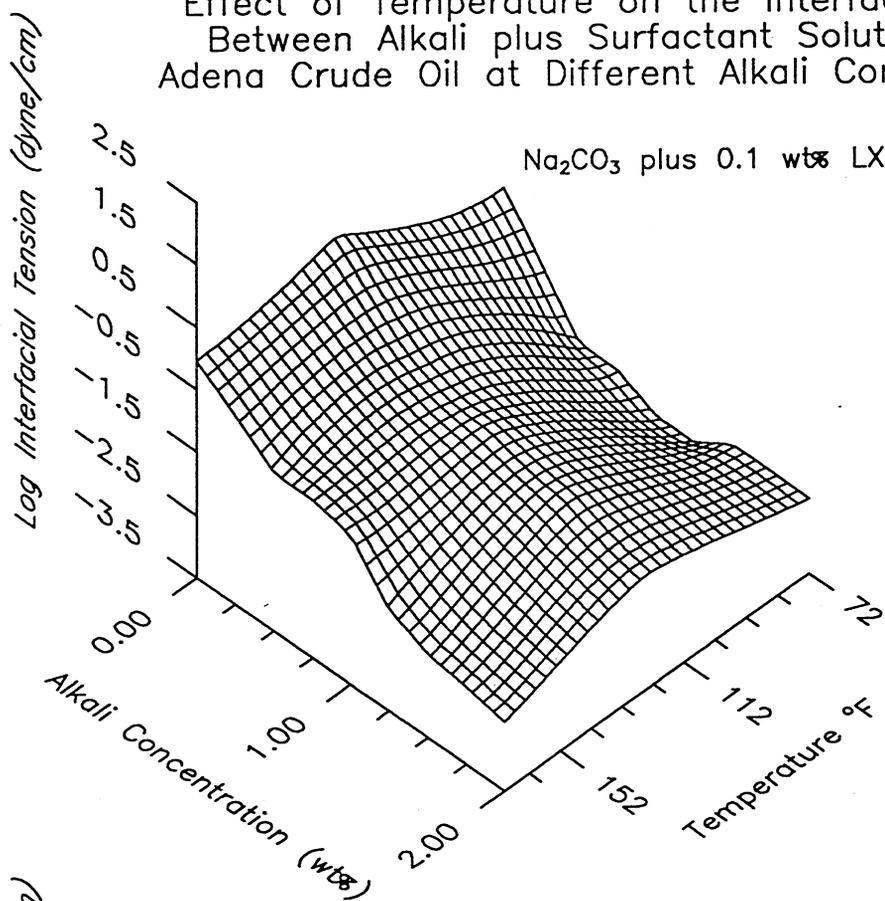


Figure 37

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different Alkali Concentrations

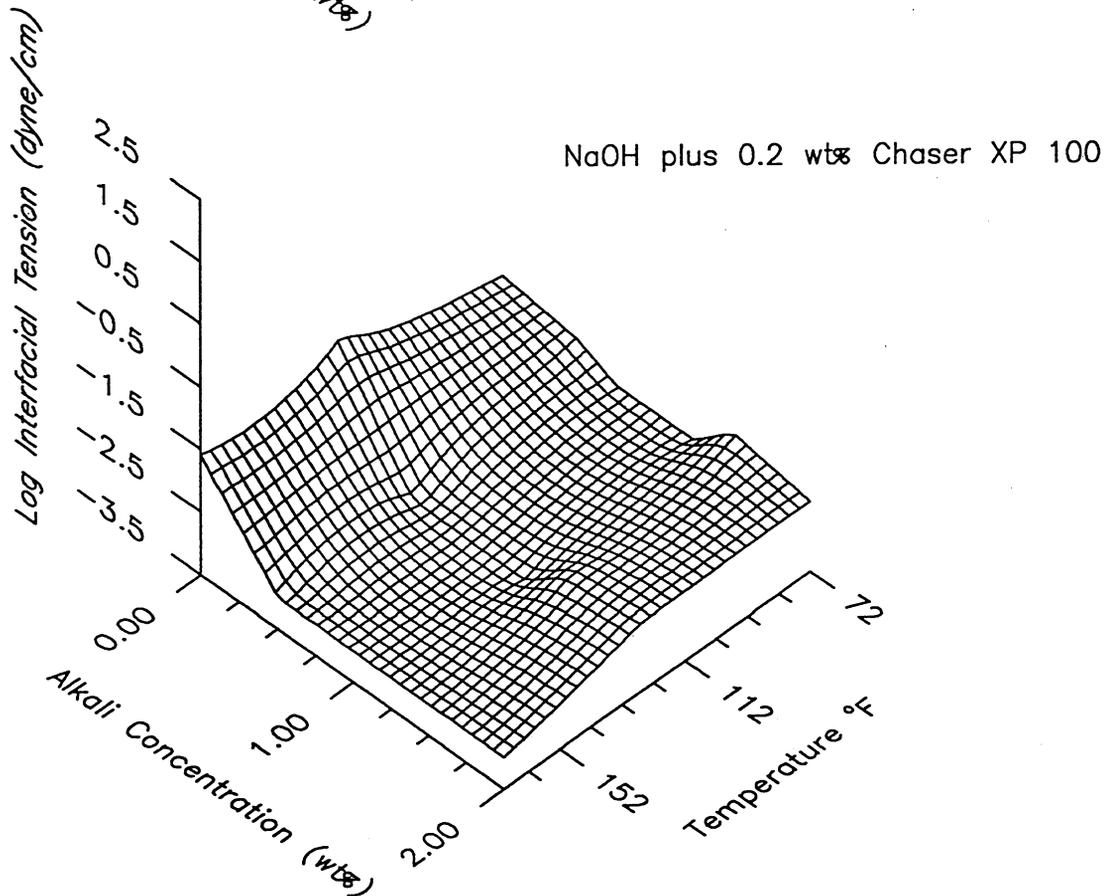
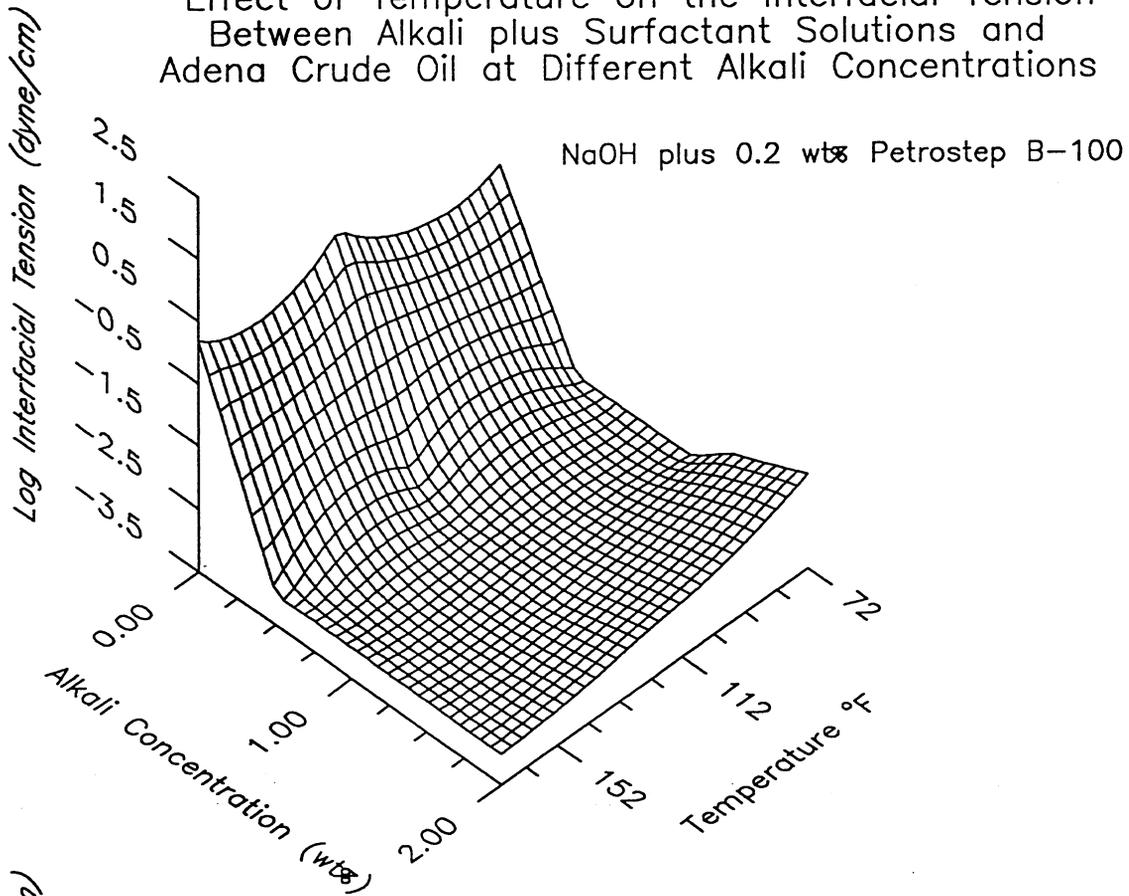


Figure 38

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different Alkali Concentrations

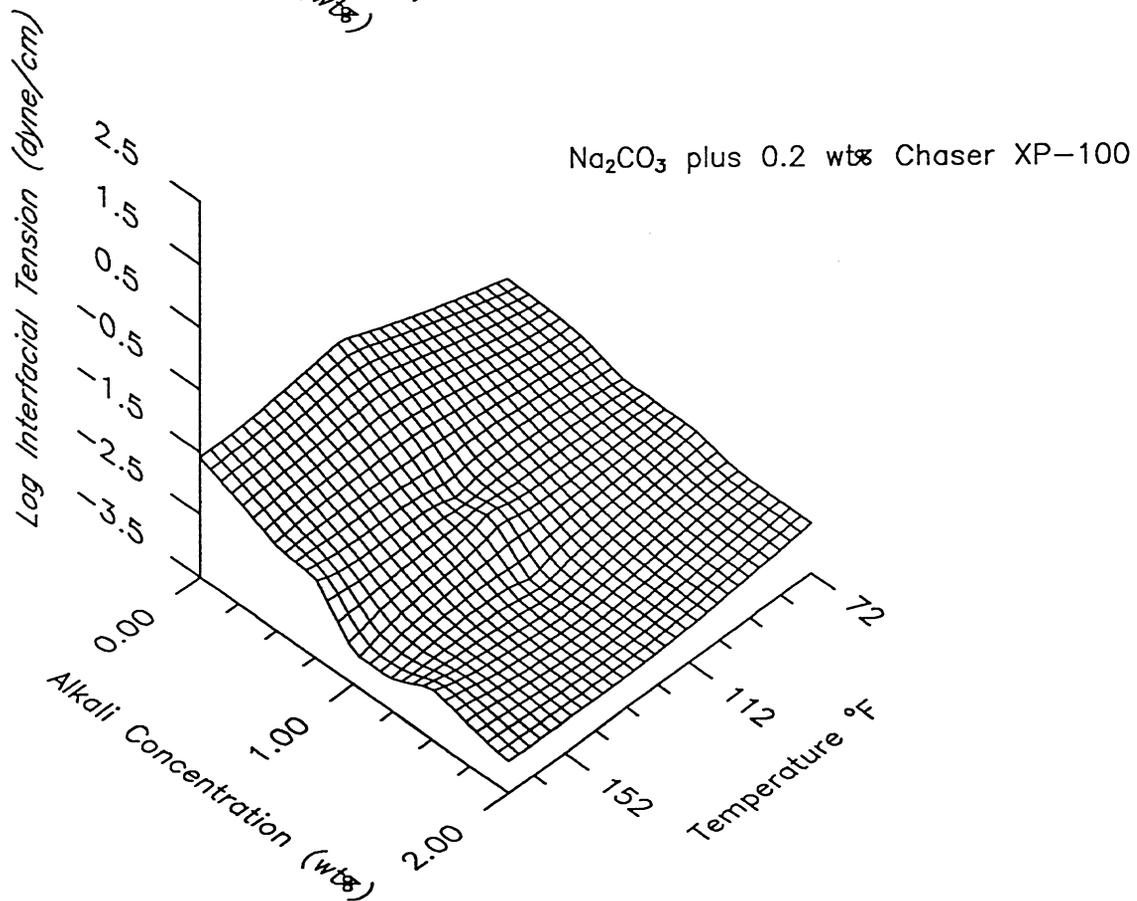
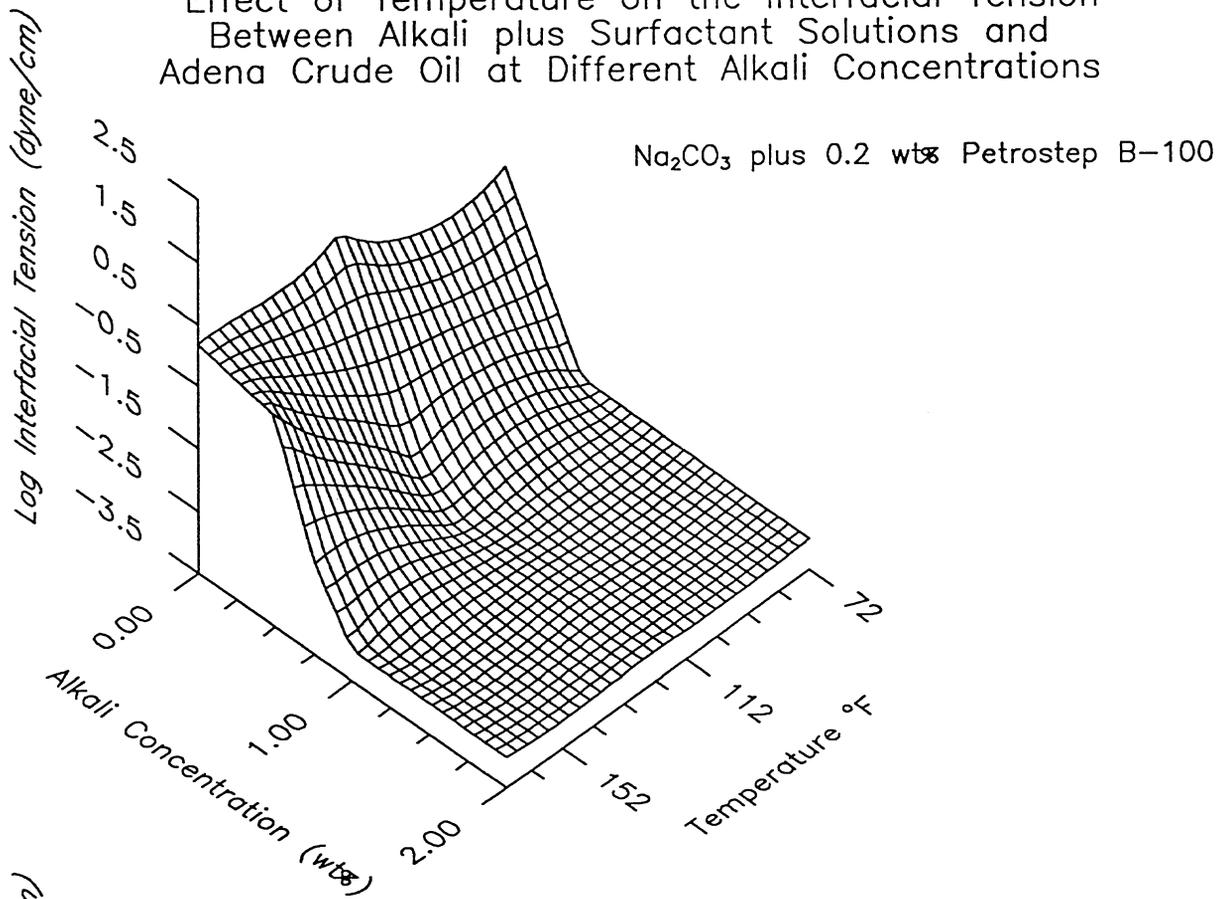


Figure 39

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different NaCl Concentrations

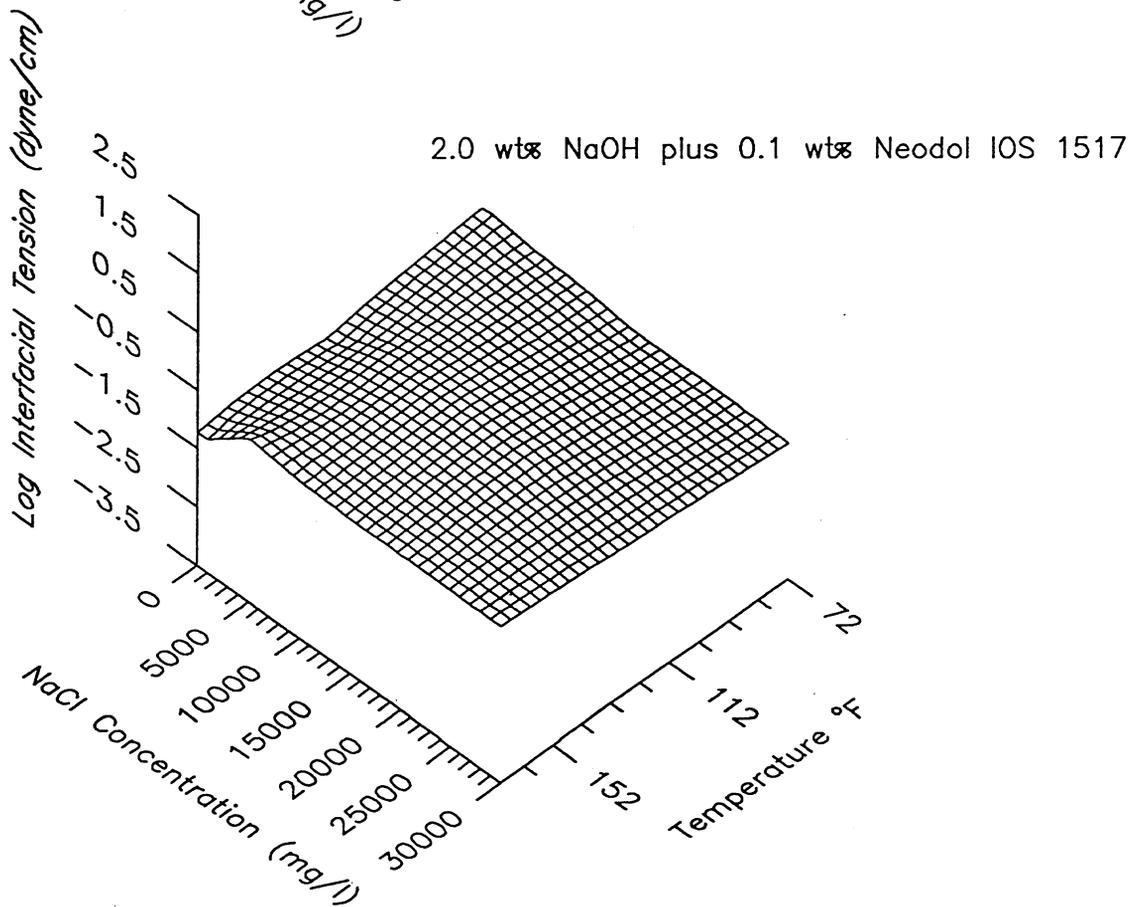
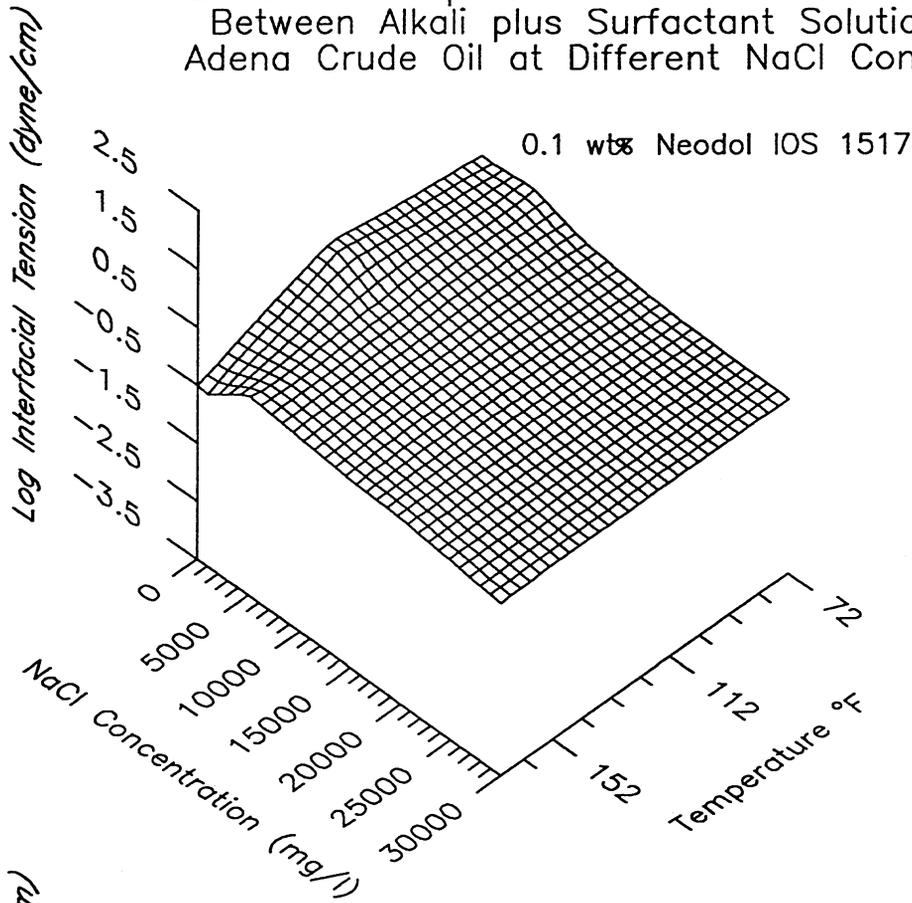


Figure 40

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different NaCl Concentrations

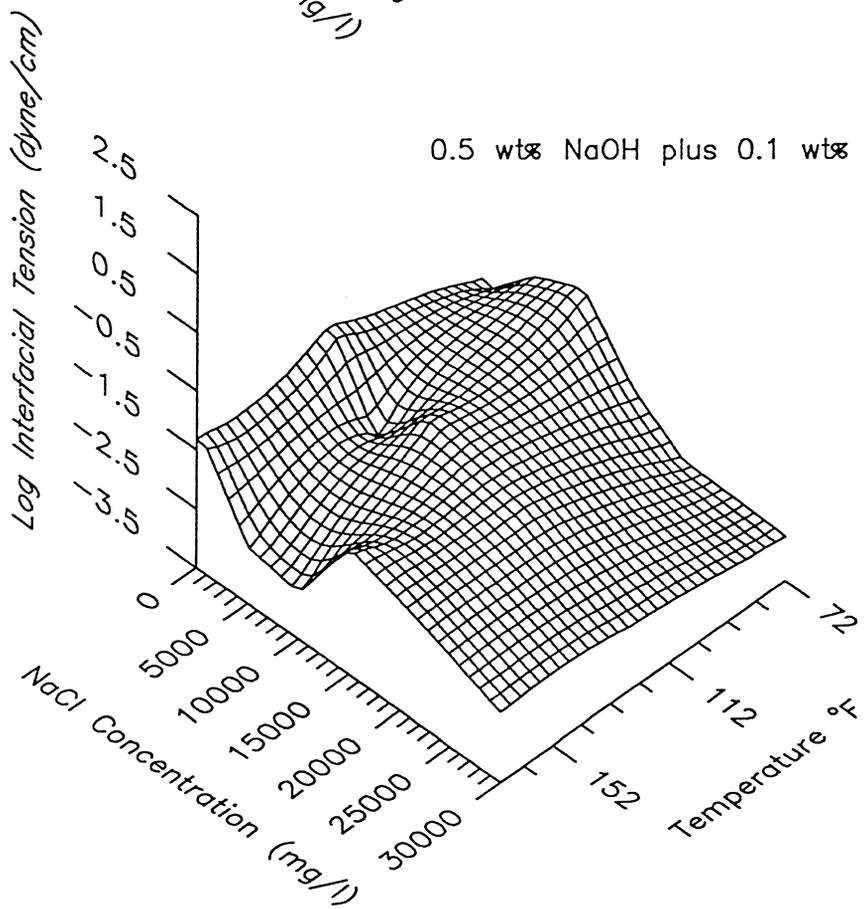
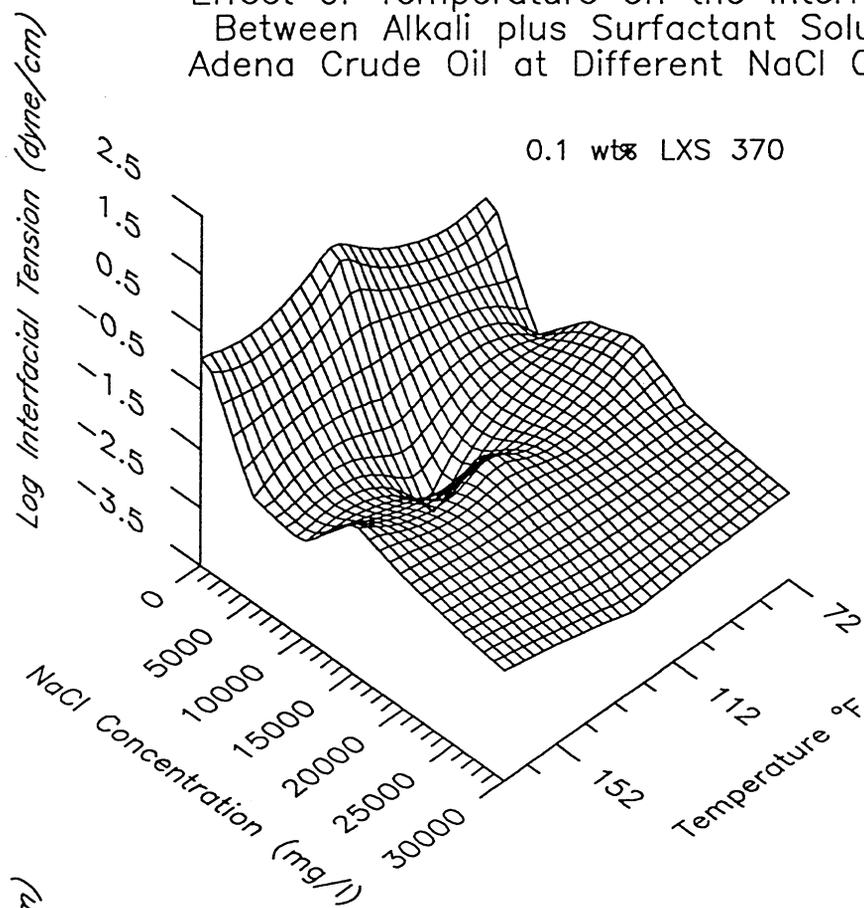


Figure 41

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different NaCl Concentrations

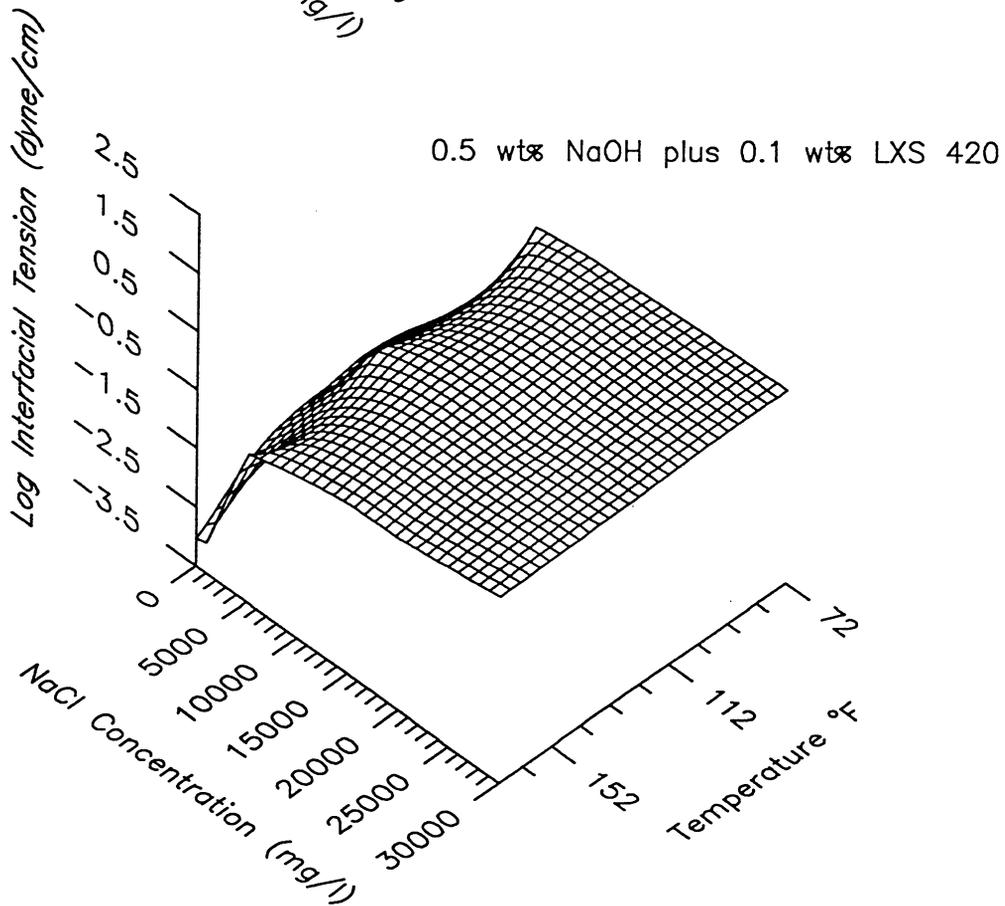
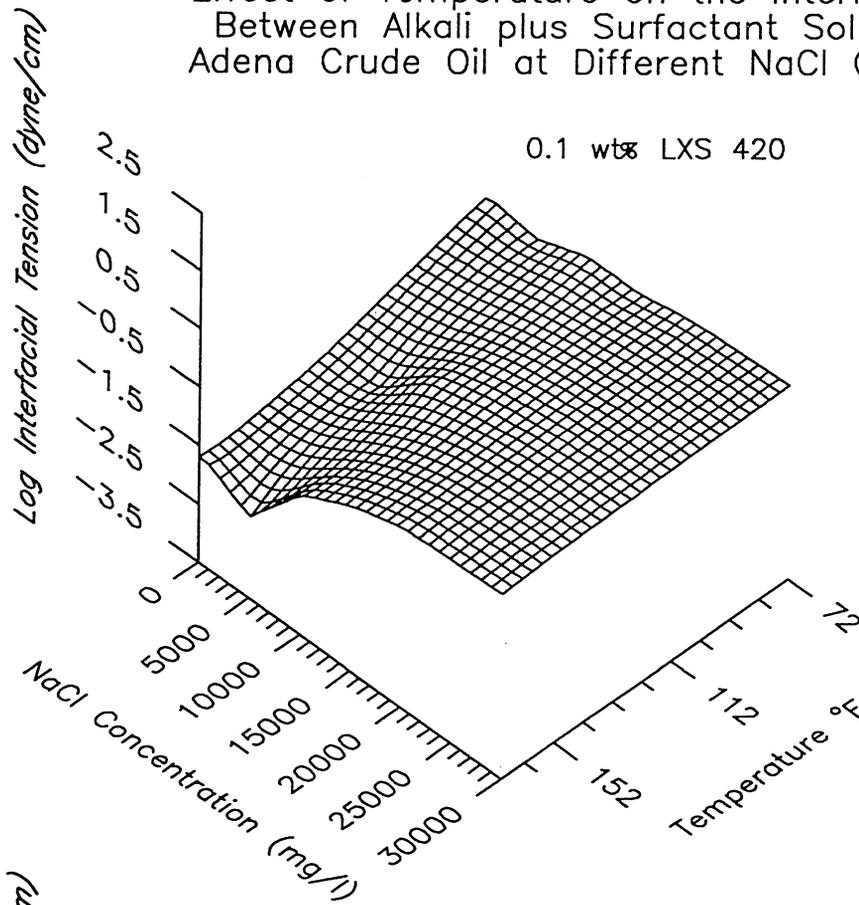


Figure 42

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different NaCl Concentrations

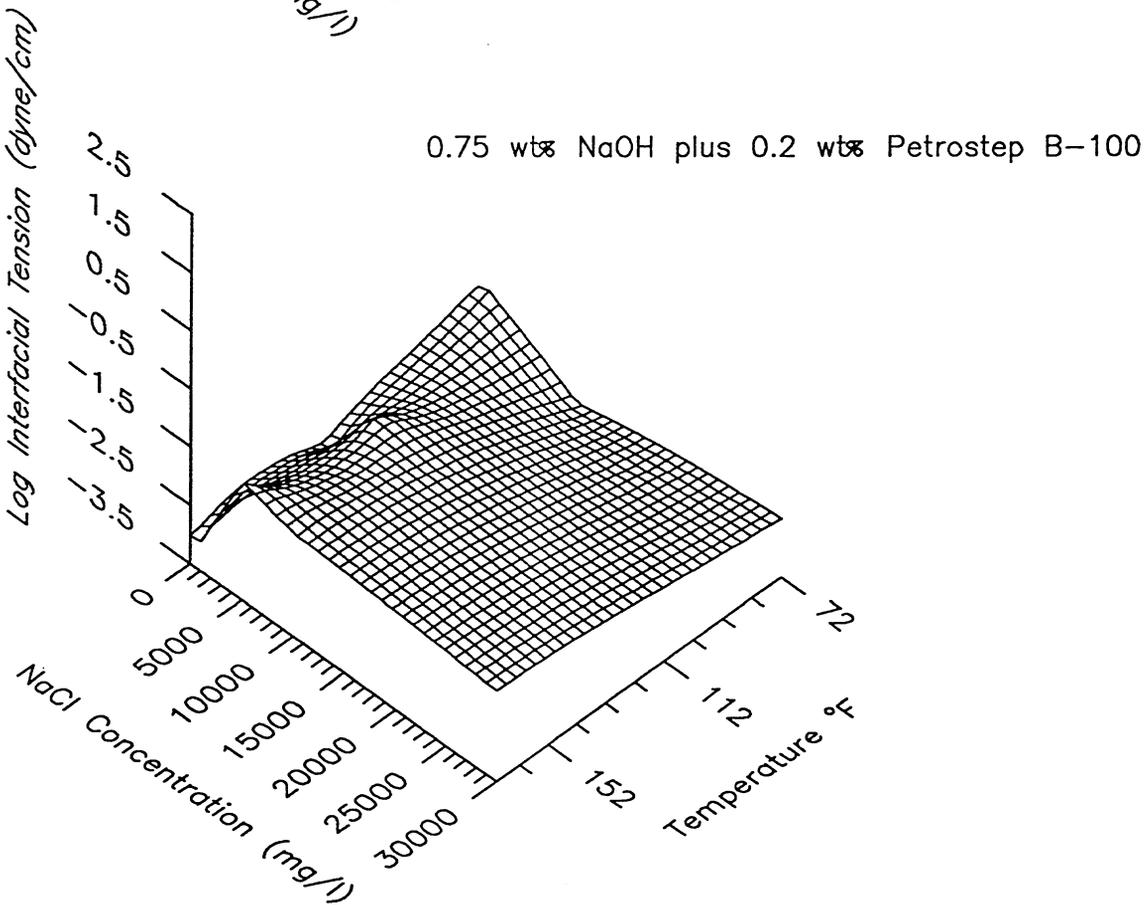
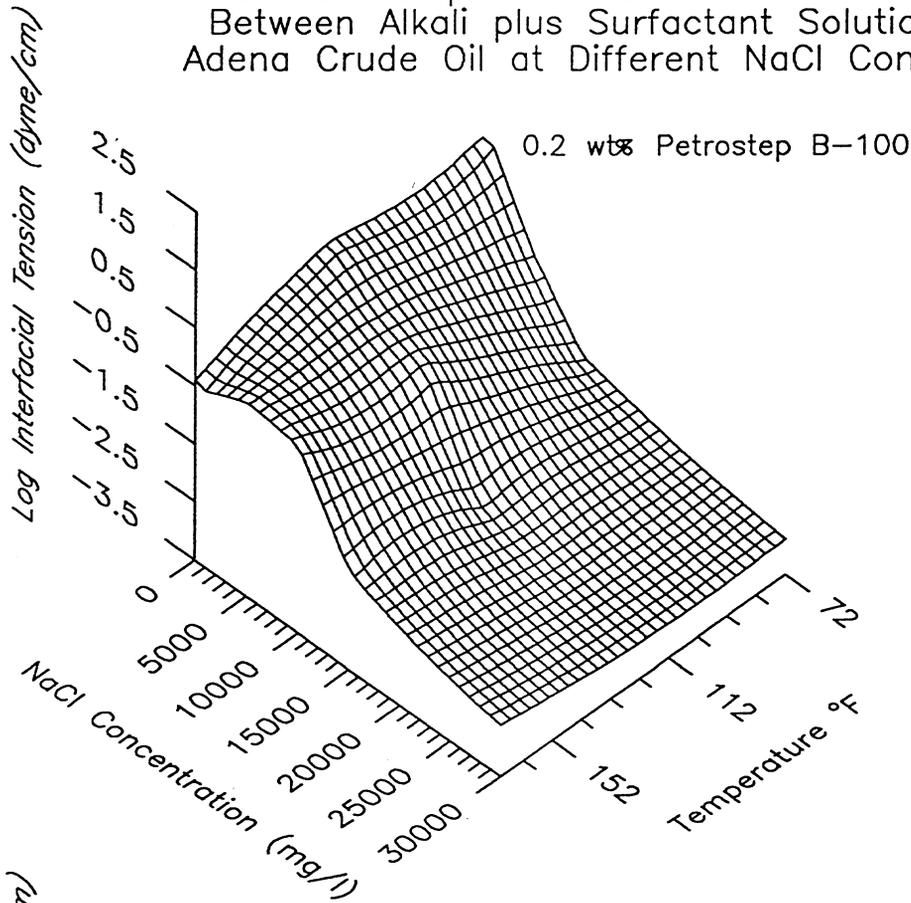
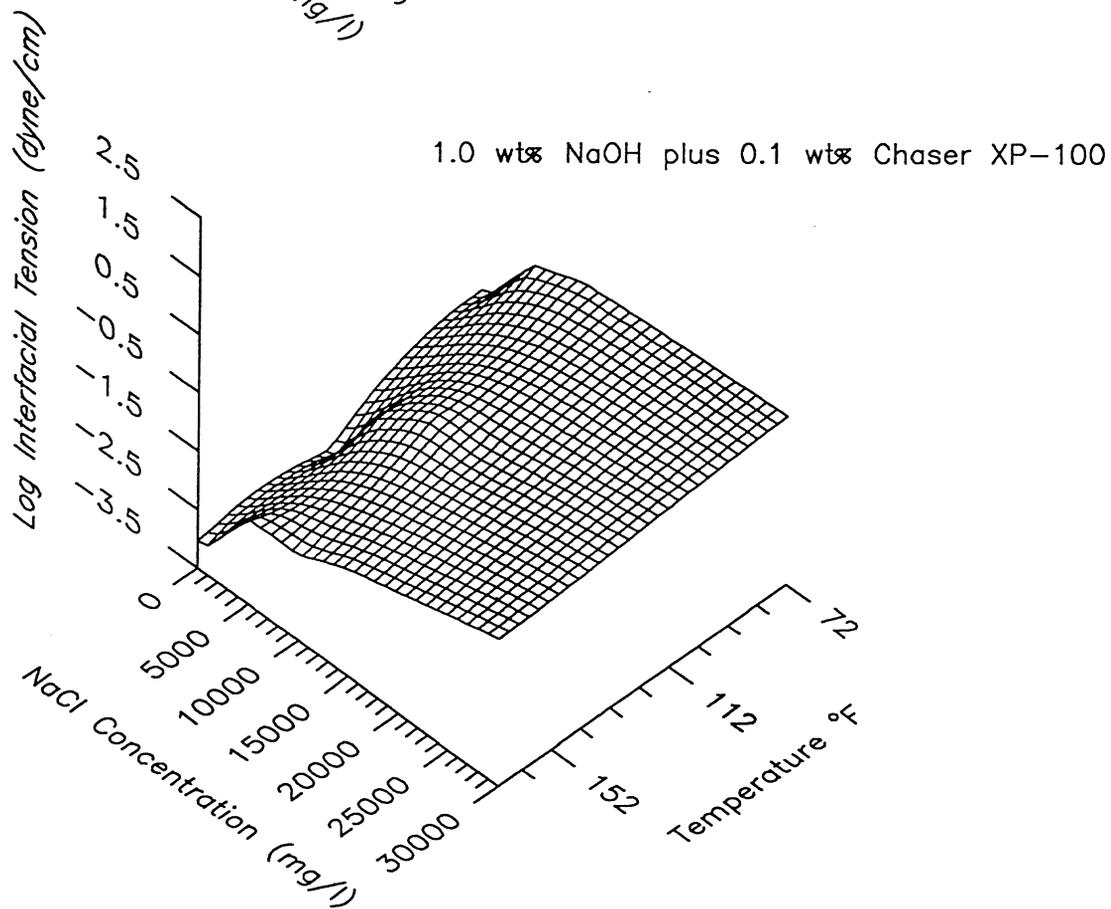
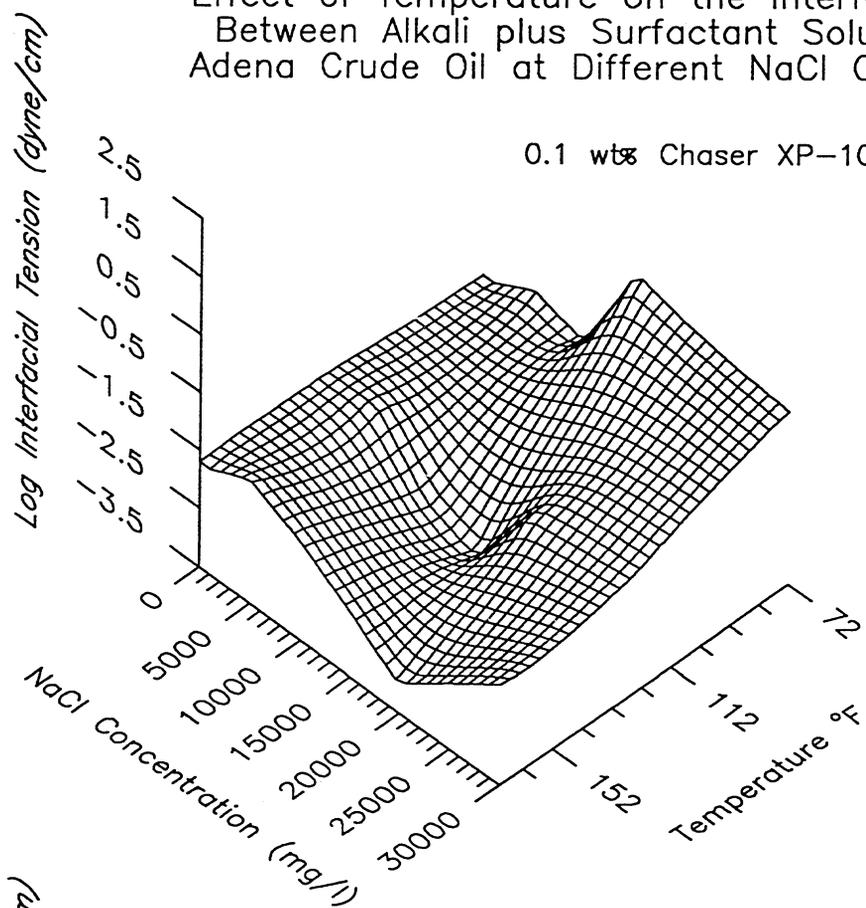


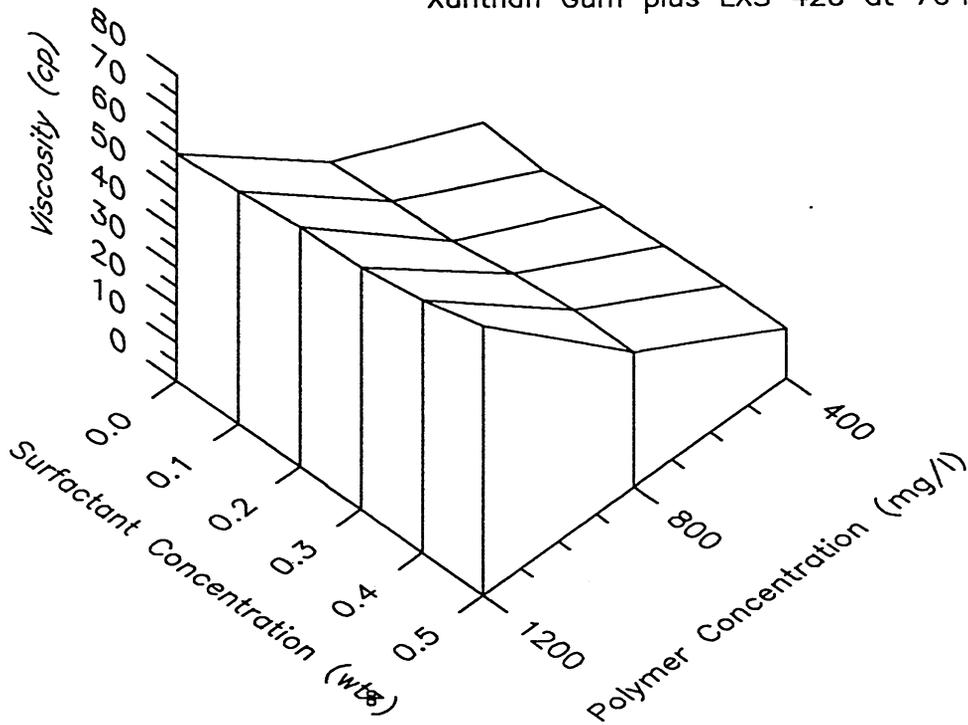
Figure 43

Effect of Temperature on the Interfacial Tension  
Between Alkali plus Surfactant Solutions and  
Adena Crude Oil at Different NaCl Concentrations



Effect of Surfactant Concentration on Polymer Solution Viscosity

Xanthan Gum plus LXS 420 at 70°F



Xanthan Gum plus LXS 420 plus 2.0 wt% Na<sub>2</sub>CO<sub>3</sub> at 70°F

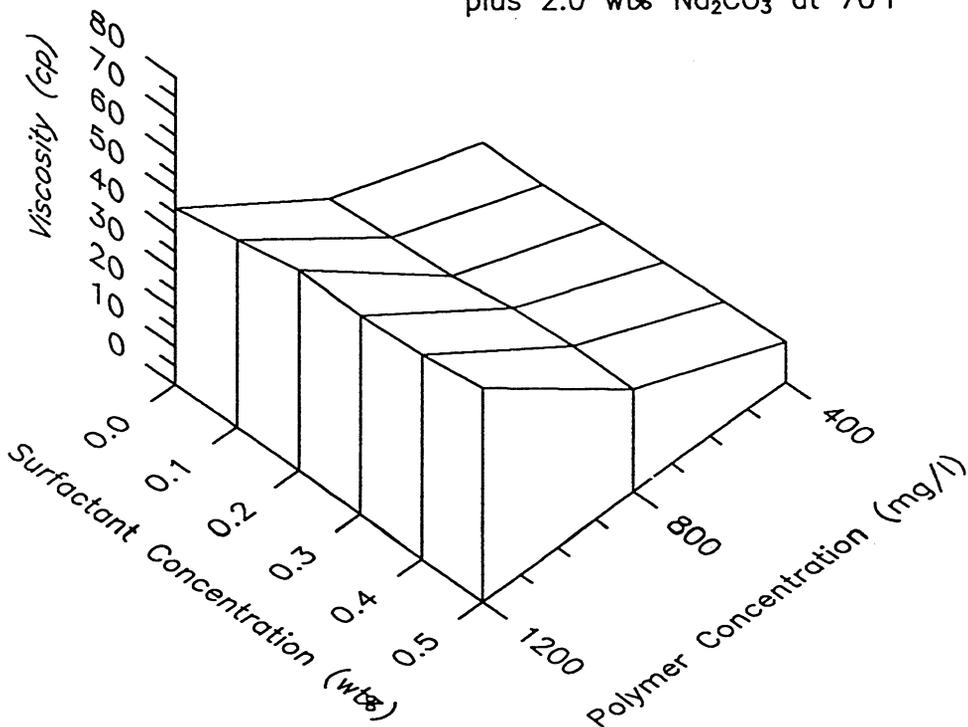


Figure 45

Effect of Surfactant Concentration on Polymer Solution Viscosity

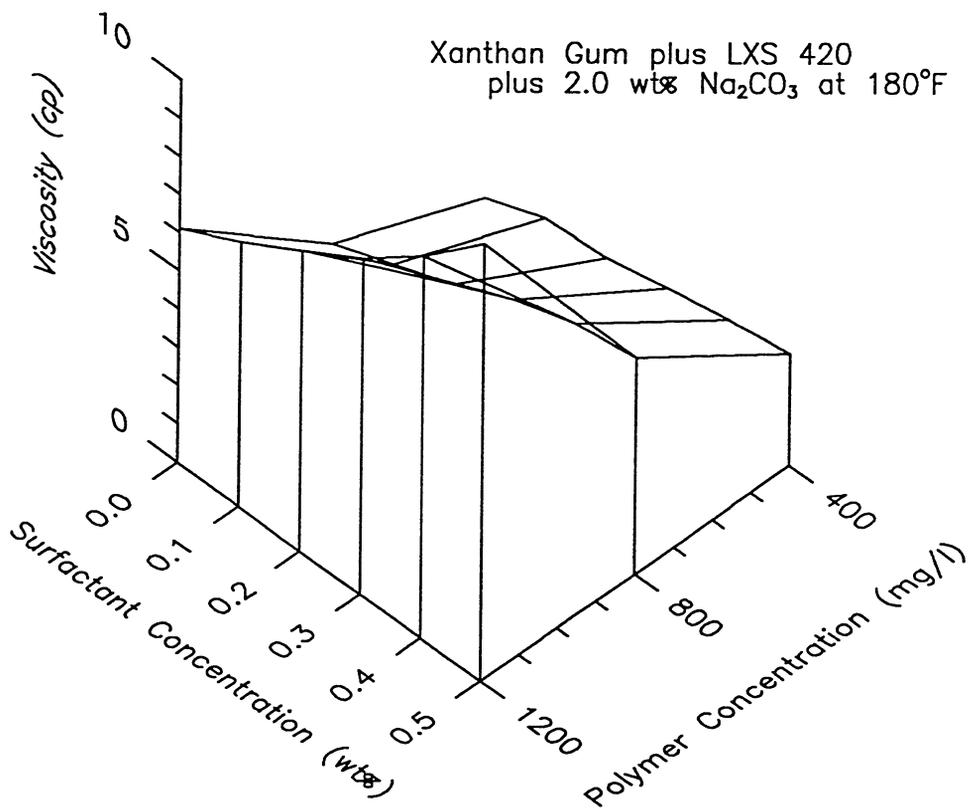
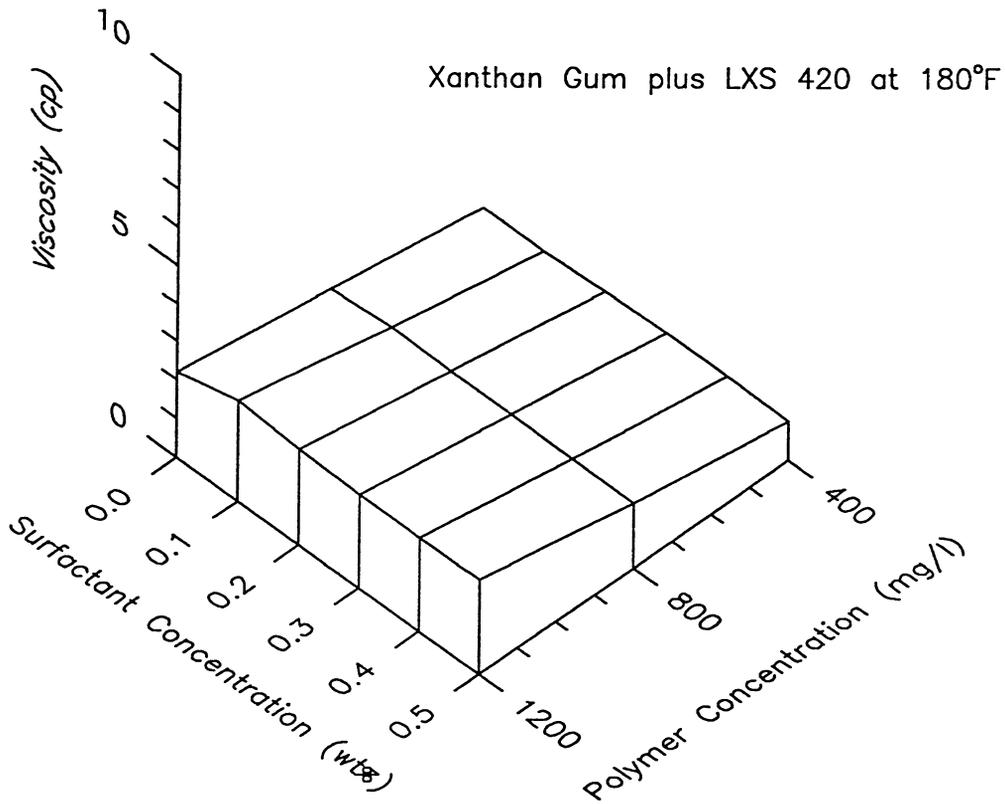


Figure 46

### Effect of Surfactant Concentration on Polymer Solution Viscosity

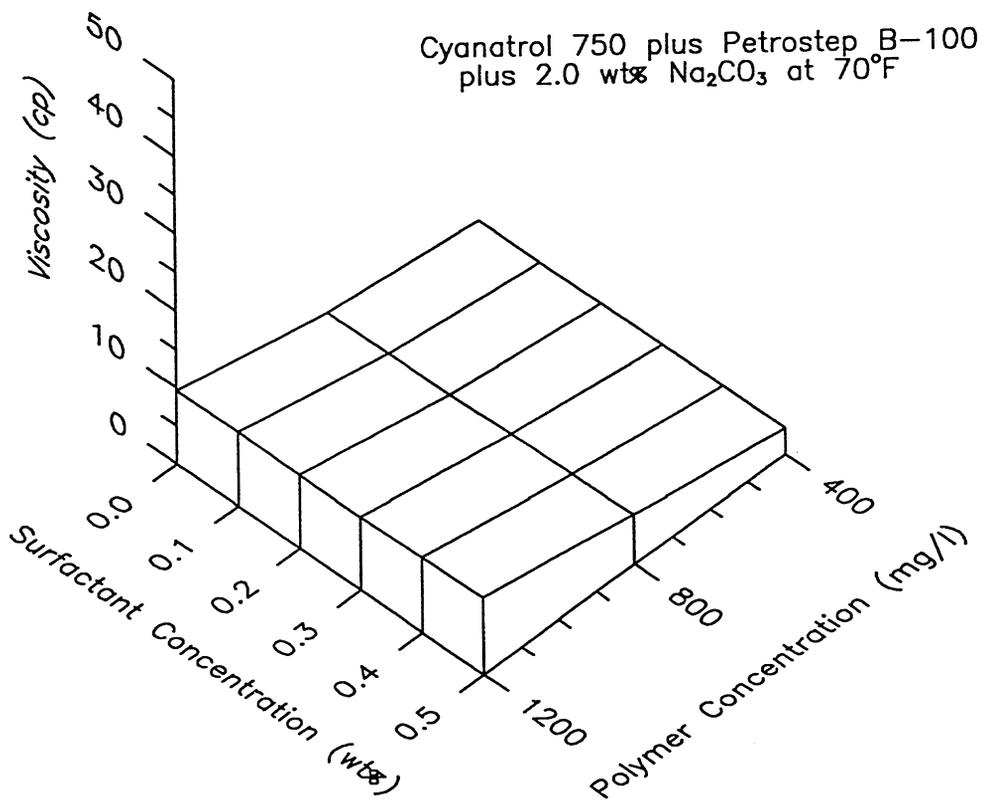
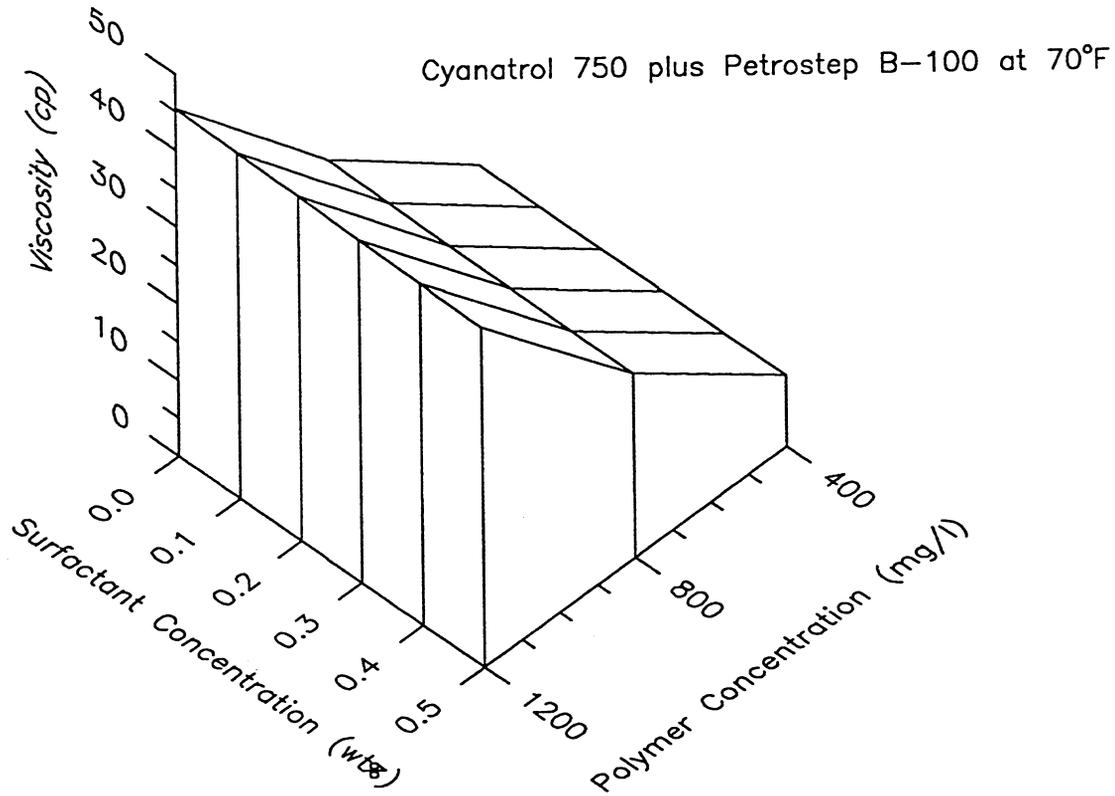
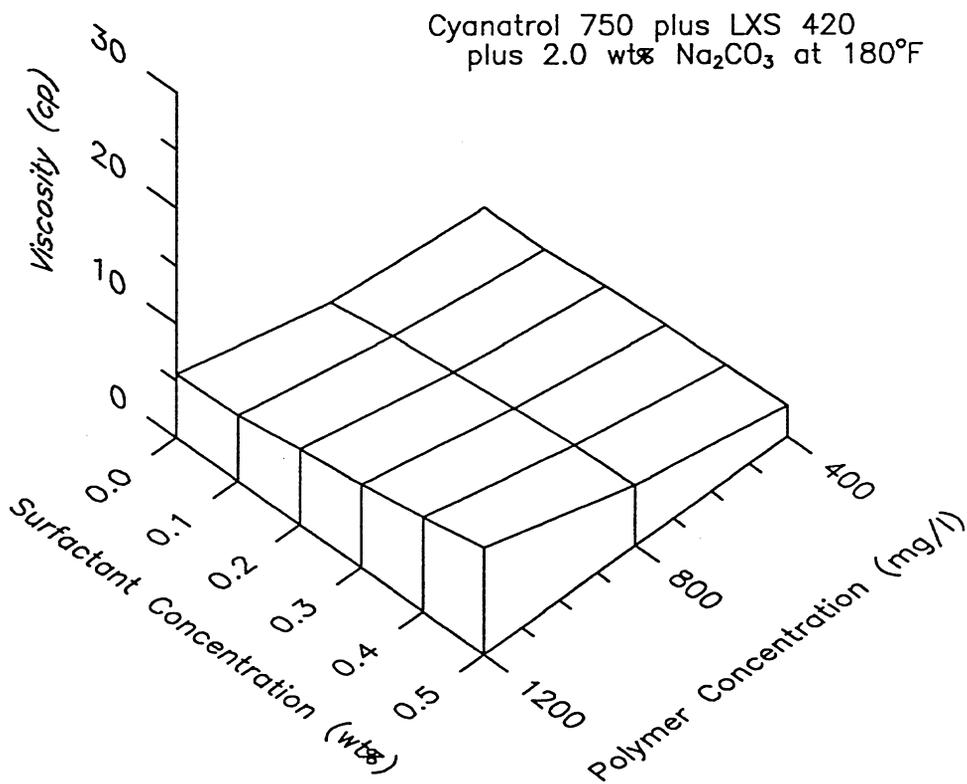
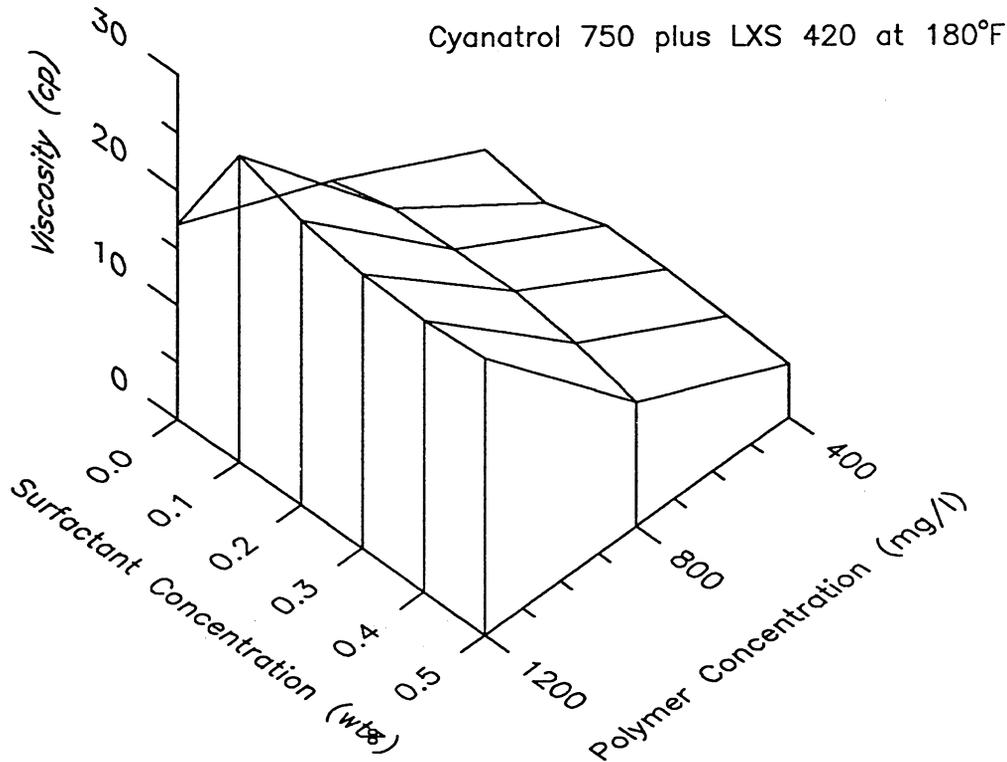


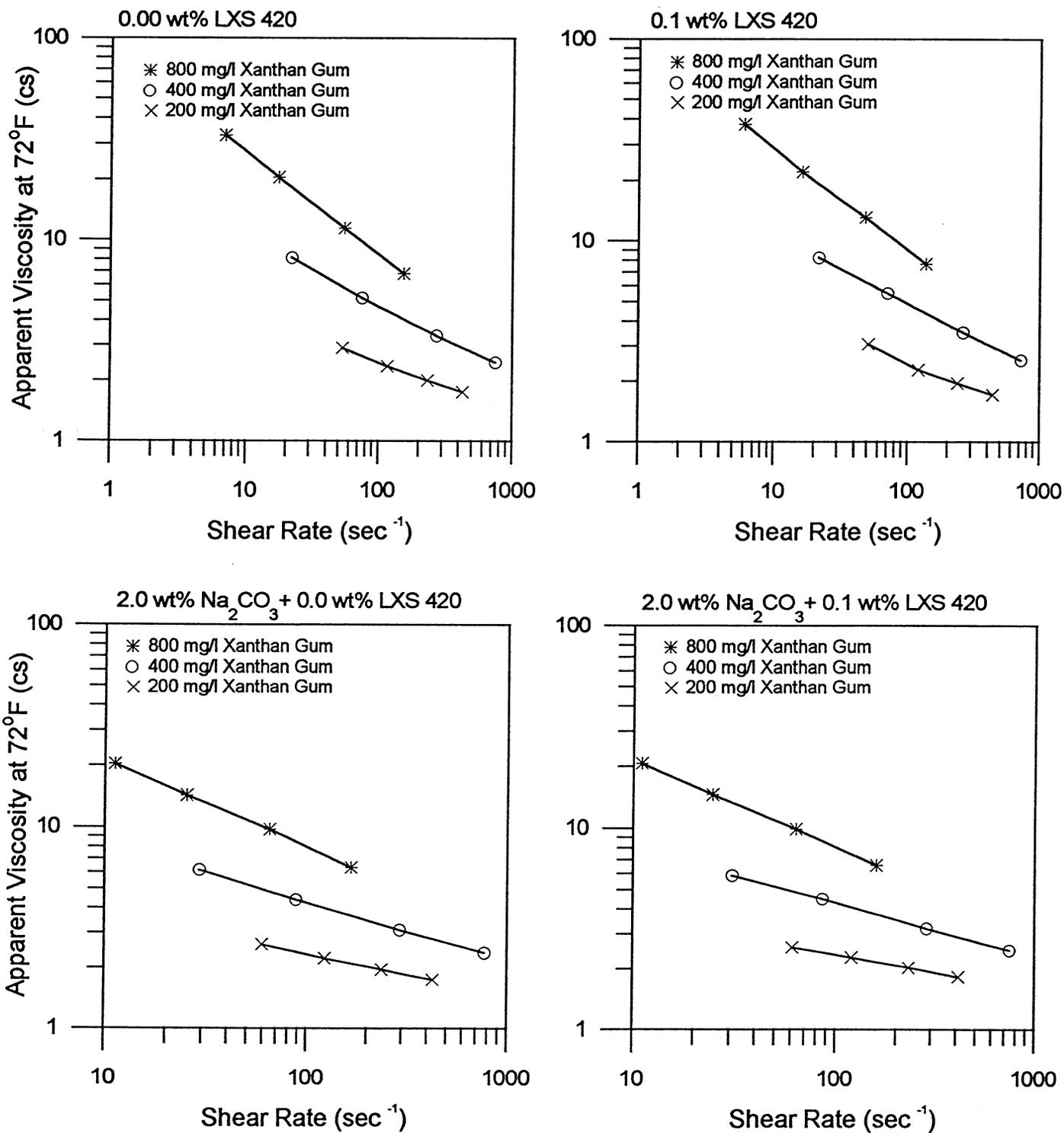
Figure 47

### Effect of Surfactant Concentration on Polymer Solution Viscosity



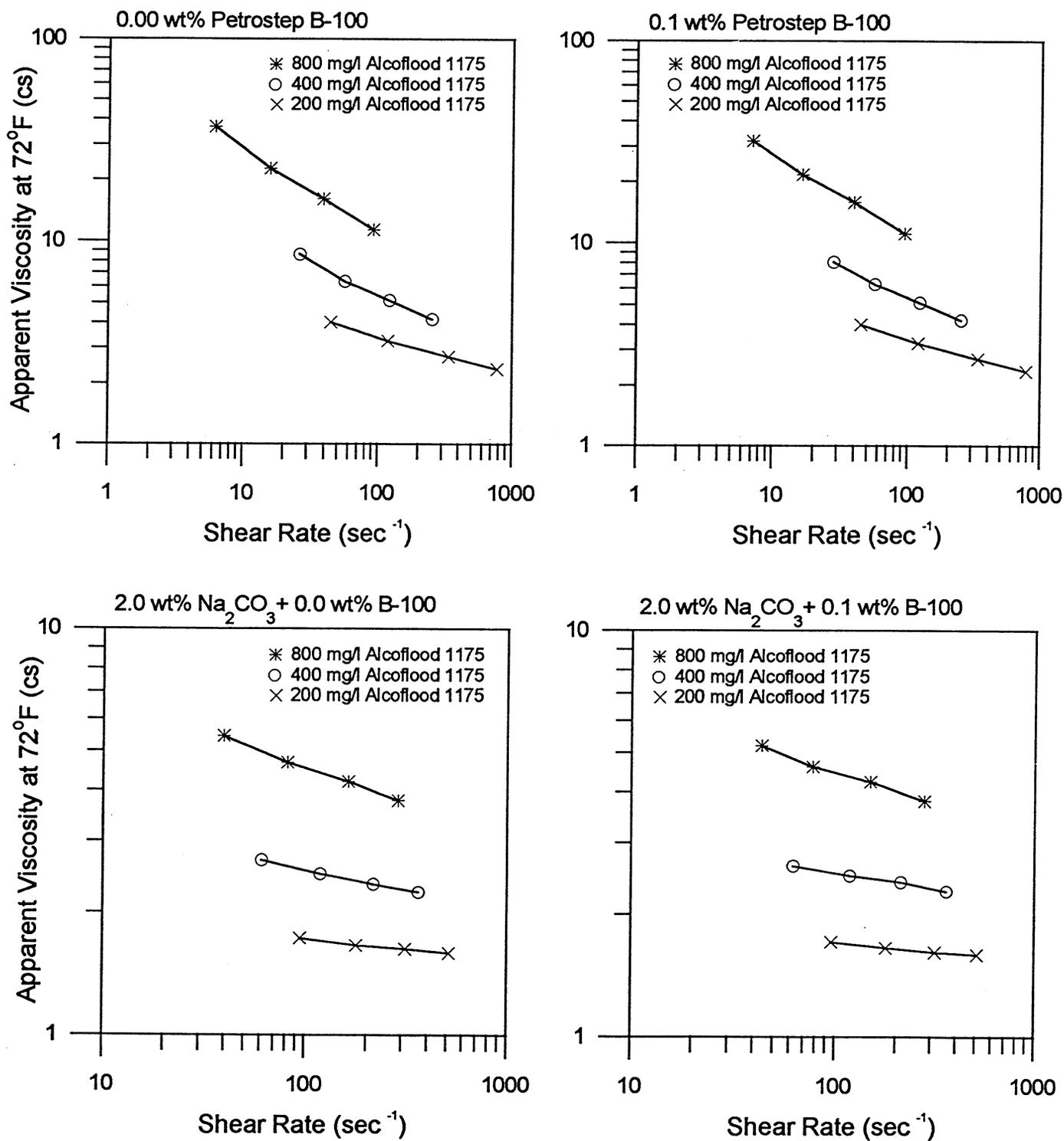
Apparent Viscosity versus Shear Rate

LXS 420 plus Xanthan Gum



### Apparent Viscosity versus Shear Rate

#### Petrostep B-100 plus Alcoflood 1175



Apparent Viscosity versus Shear Rate  
LXS 420 plus Hydroxyethyl Cellulose

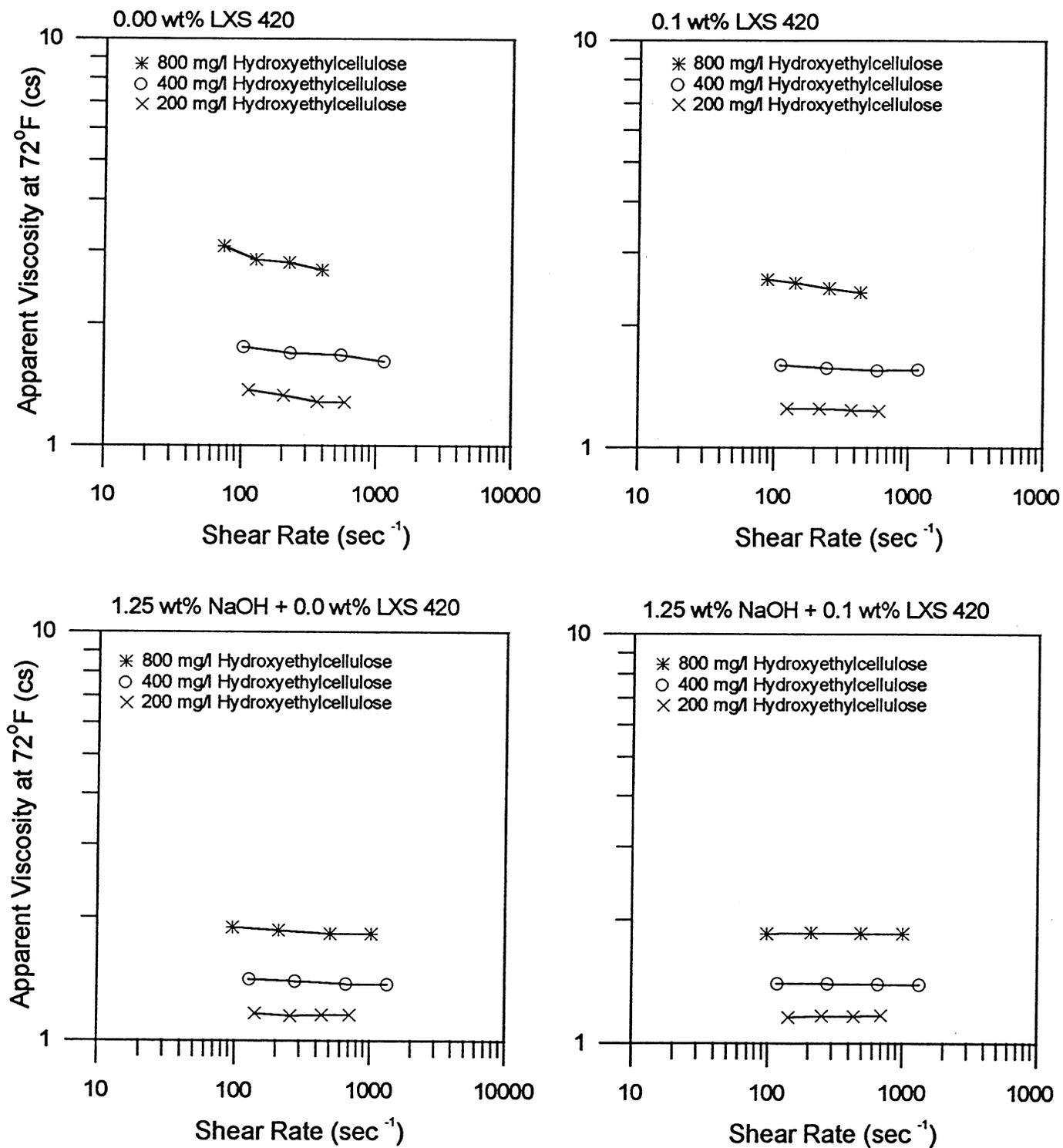
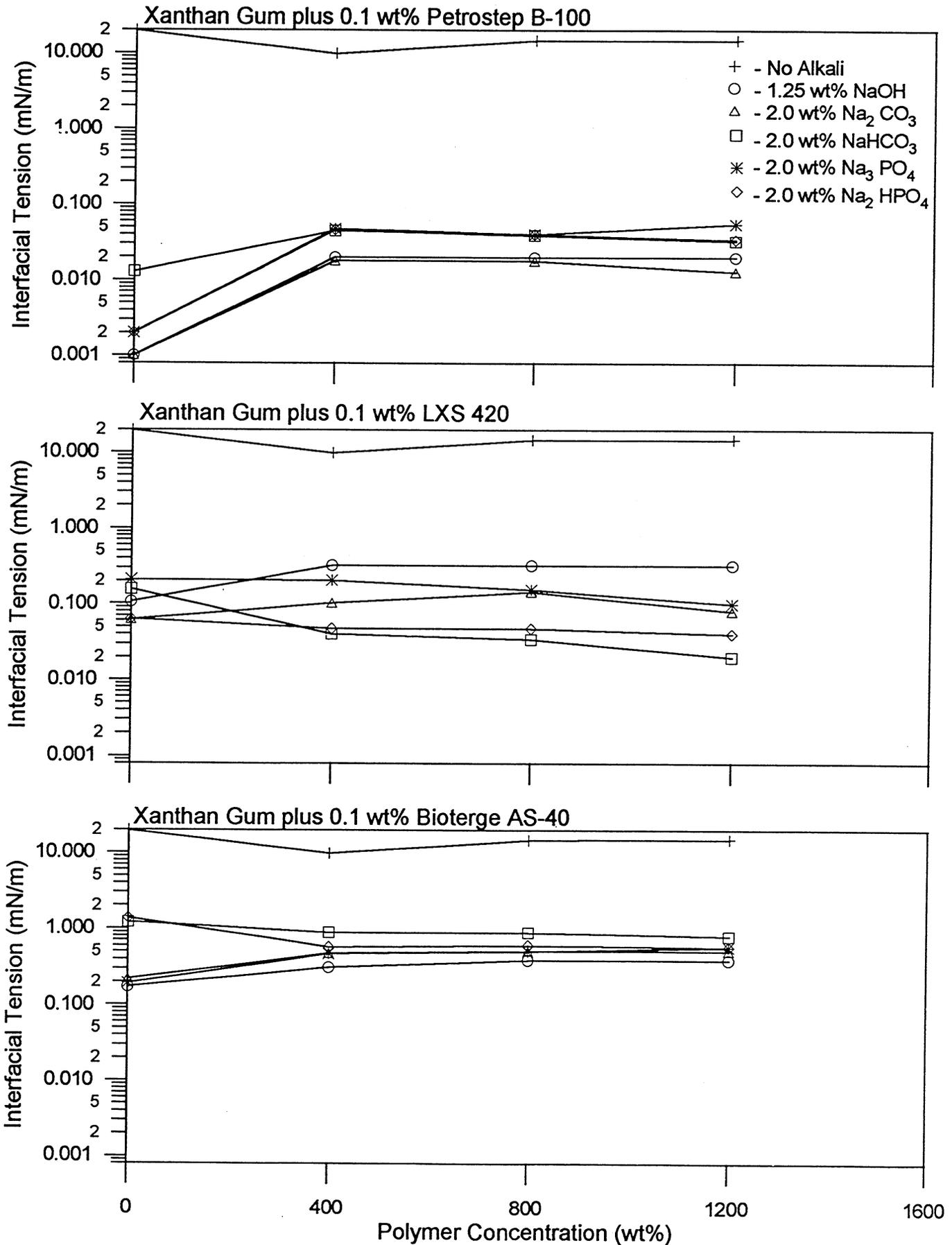


Figure 51

Effect of Polymer Concentration on the Interfacial Tension  
Between Aqueous Alkali plus Surfactant plus Polymer Solutions



Effect of Polymer Concentration on the Interfacial Tension  
Between Aqueous Alkali plus Surfactant plus Polymer Solutions

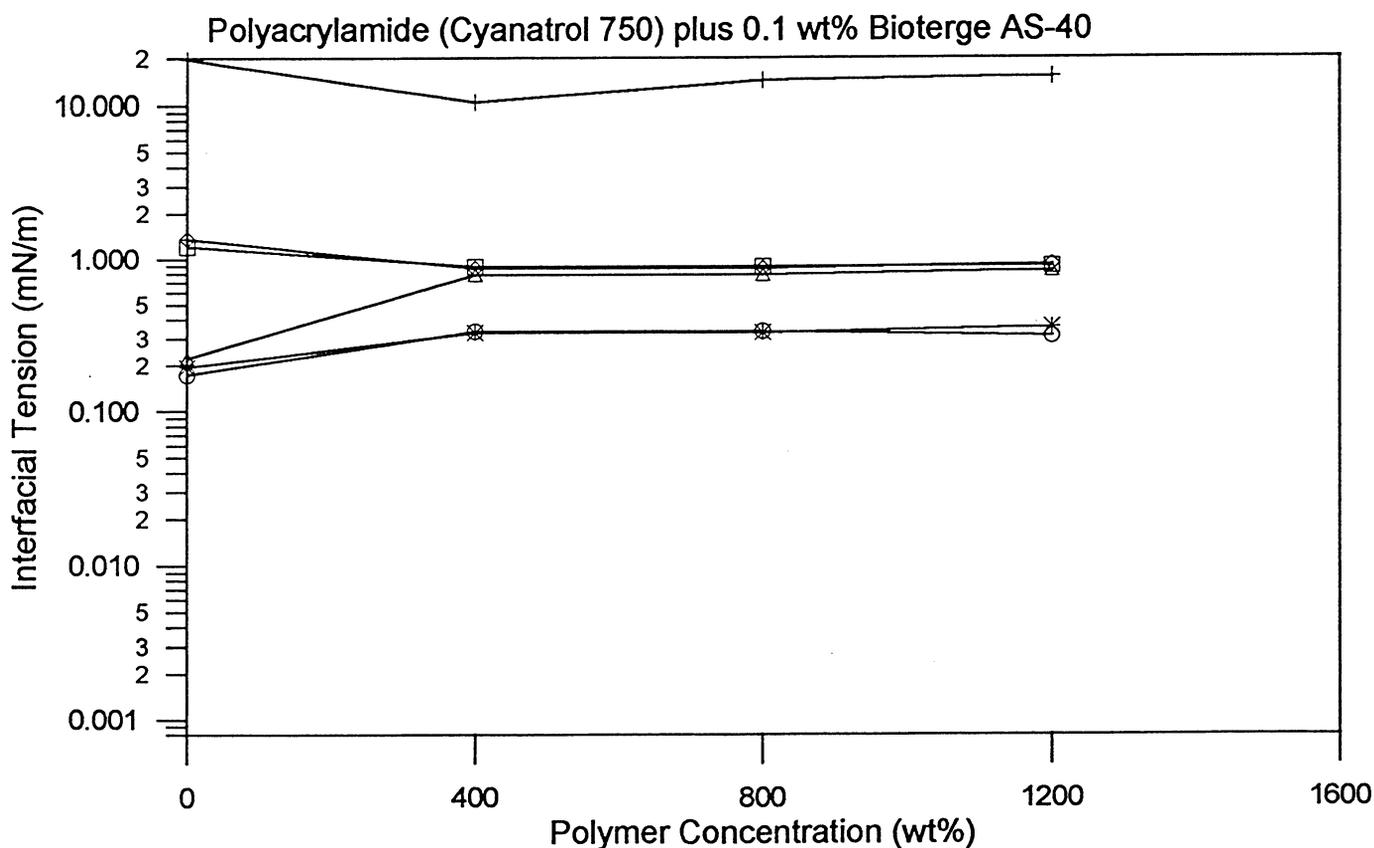
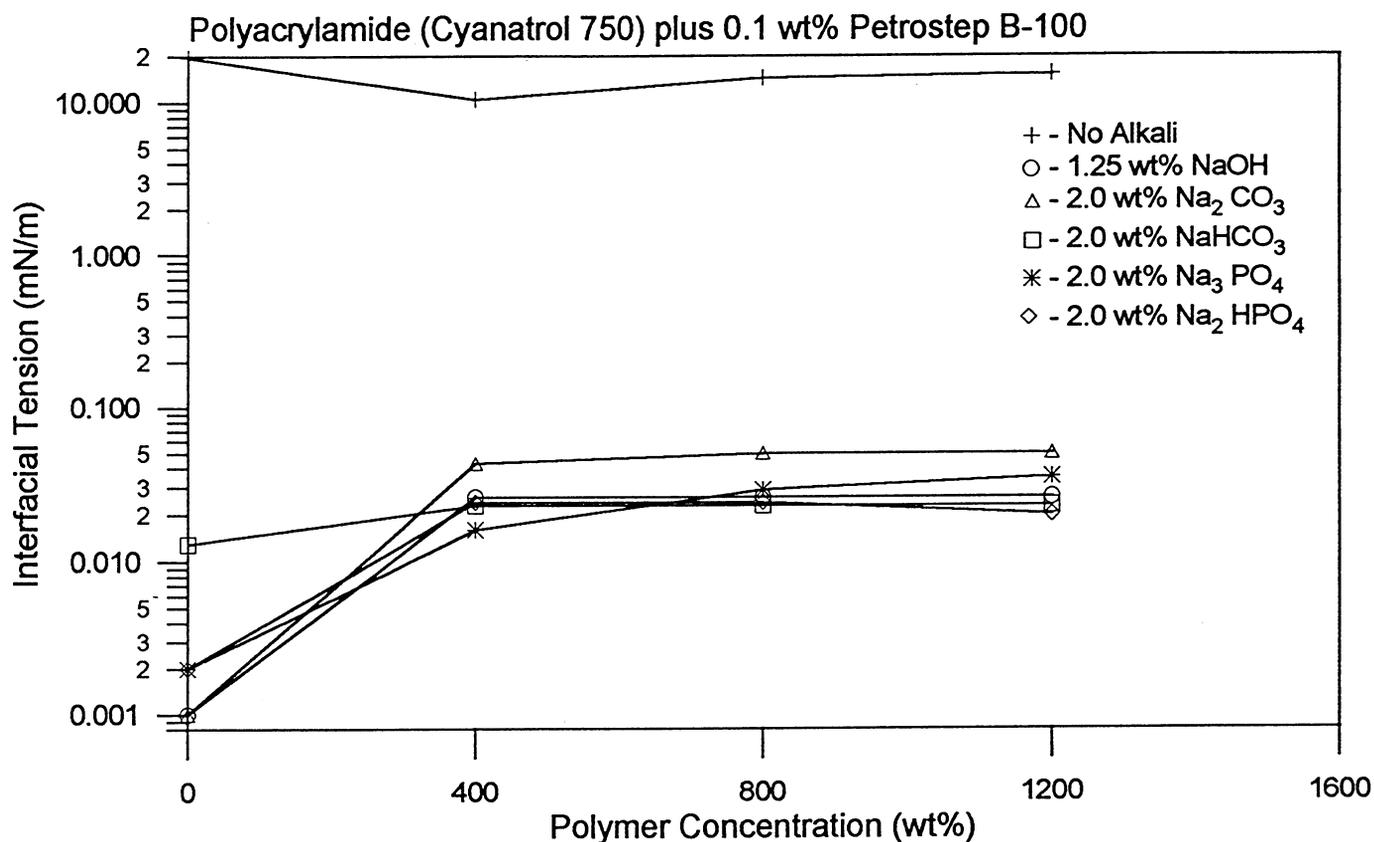


Figure 53

### Interfacial Tension Between Alkali plus Petrostep B-100 plus Polymer Solutions and Adena Crude Oil versus Alkali Concentration

