DOE/BC/14886-9
Distribution Category UC-122

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

Second Annual Report
October 1993-September 1994

By
Malcolm J. Pitts

April 1995

Work Performed Under Contract No. DE-AC22-92BC14886

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Jerry Casteel, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005

Prepared by
Surtek, Inc.
Golden, CO 80401

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table of Contents
List of Illustrations

Table of Contents
List of Illustrations
page 2

Table of Contents
List of Illustrations
page 3

Abstract

"Investigation of Oil Recovery Improvement by Coupling an Interfacial Tension Agent and a Mobility Control Agent in Light Oil Reservoirs" is studying 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 agents, 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 continues the fluid-fluid interaction evaluations and begins the fluid-rock studies. Fluid-fluid interfacial tension work determined that replacing sodium ion with either potassium or ammonium ion in solutions with interfacial tension reduction up to 19,600 fold was detrimental and had little or no effect on alkali-surfactant solutions with interfacial tension reduction of 100 to 200 fold. Reservoir brine increases interfacial tension between crude oil and alkaline-surfactant solutions. Na_2CO_3-surfactant solutions maintained ultra low and low interfacial tension values better than NaOH-surfactant solutions.

The initial phase of the fluid-rock investigations was adsorption studies. Surfactant adsorption is reduced when co-dissolved with alkali. Na_2CO_3 and Na_3PO_4 are more efficient at reducing surfactant adsorption than NaOH. When polymer is added to the surfactant solution, surfactant adsorption is reduced as well. When both polymer and alkali are added, polymer is the dominate component, reducing the Na_2CO_3 and NaOH effect on adsorption. Substituting sodium ion with potassium or ammonium ion increased or decreased surfactant adsorption depending on surfactant structure with alkali having a less significant effect. No consistent change of surfactant adsorption with increasing salinity was observed in the presence or absence of alkali or polymer.

Na_2CO_3 consistently was adsorbed the least with Na_3PO_4 adsorption being the greatest. Surfactant addition to an alkaline solution reduced alkali adsorption by 1.4 to 6.8%. Variances were surfactant specific. Substituting potassium and ammonium ion for sodium ion increased alkali adsorption with the differences between carbonate and hydroxide salt being maintained. Polyacrylamide and xanthan gum addition to an alkaline solution increased alkali consumption. When surfactant is added to the alkaline-polymer solution, alkali adsorption is either reduced or does not change. Polymer again is the dominate component. Increasing salinity did not alter alkali consumption significantly.

Polyacrylamide adsorbs at a greater rate than xanthan gum. Mixing Na_2CO_3 with both polymer types either reduced polymer adsorption or did not change adsorption. NaOH increased both polyacrylamide and xanthan gum adsorption. Surfactant addition to the polymer solutions increased xanthan gum adsorption and decreased polyacrylamide adsorption. Adding surfactant to the alkaline-polymer solutions did not change Na_2CO_3-polymer adsorption but decreased polymer adsorption with NaOH. Polymer adsorption generally decreased with increasing salinity.

Temperature increases generally did not affect the surfactant or polymer adsorption. Alkali adsorption rates were essentially constant up to 100°F but increased at 150°F.

Relative permeability determinations indicate that alkaline-surfactant solutions changed the relative permeability curve primarily by increasing the water relative permeability with a small change in oil saturation. Mobility ratio for aqueous phase displacing crude oil increases from 0.5 to 3.9. The largest increase of mobility ratio occurred with the alkaline-surfactant solution with the greatest interfacial tension reduction. Polymer addition to the alkaline-surfactant decreased the mobility ratio even though the water relative permeability continued to increase. Significant incremental oil was produced only with alkaline-surfactant-polymer solutions having ultra low interfacial tension values.

The importance of mobility control on oil recovery was also demonstrated by injecting into radial core alkaline-surfactant-polymer solutions of varying polymer concentration. Incremental oil increased from less than 5% of the initial oil saturation to over 20% of the initial oil saturation as the polymer concentrations were increased. Once the oil recovery maximum was reached, incremental oil did not increase with increasing polymer concentration. Injection of water prior to an alkaline-surfactant-polymer solution did not alter the oil recovery efficiency.

The importance of the fluid-rock interaction in oil recovery was demonstrated by performing radial corefloods with three alkaline-surfactant-polymer solutions, all with ultra low interfacial tension values. Incremental oil recovery varied from 7 to 20% of the initial oil saturation.

Executive Summary

The co-injection of an interfacial tension agent(s) such as an alkaline agent or a surfactant and a mobility control agent such as a 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 this co-injection 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 and fluid-rock interaction of interfacial tension agent plus mobility control solutions. Fluid-fluid evaluations were a continuation of previous work while the fluid-rock evaluations were initiated in this fiscal year. The conclusions of current evaluations are as follows:

- Substituting sodium ion with either potassium or ammonium ion increased interfacial tension of solutions initially showing ultra low values. Substitution of alternate cations did not decrease adsorption of either surfactant or polymer when alkali is present. No advantage of using either a potassium or ammonium based system over a sodium based system was determined.

- Na_2CO_3 dissolved in an alkaline-surfactant solution is better at preventing interfacial tension increases when mixed with produced water than NaOH. Na_2CO_3 is also better at reducing surfactant and polymer adsorption onto rock.

- When alkali, surfactant, and polymer are dissolved in the same solution, polymer is the dominate component altering alkali and surfactant adsorption. Polymer adsorption is affected primarily by surfactant.

- Increases in salinity changed surfactant adsorption specific to the solution composition but increased alkali and decreased polymer adsorption.

- Temperature increases did not affect surfactant and polymer adsorption significantly but increased alkali adsorption.

- Alkaline-surfactant solution injection increases the mobility ratio for aqueous phase displacing oil compared to water. The lower the interfacial tension the greater the increase of mobility ratio. Polymer addition is required at sufficient levels to reduce the mobility ratio and produce incremental oil.

- A specific concentration of polymer is required to give maximum incremental oil recovery with an alkaline-surfactant-polymer solution. Increases of polymer concentration above that required to give the maximum incremental oil recovery does not produce additional oil.

- Interfacial tension reduction measurements alone are not sufficient to produce incremental oil. Incremental oil recovery with three alkaline-surfactant-polymer solutions each having interfacial tensions of 0.001 mN/m varied from 7 to 20% of the initial oil saturation.

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.[1-3] 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.[4-5] 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 from the gross swept area for less than $2 per incremental barrel.[6]

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 processes. The first process is the mobilization of residual crude oil by the interfacial tension agent(s). The second process 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.[7-10] The mechanism of this synergism and how polymer addition effects 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 second yearly report completes the study of the fluid-fluid interactions and begins the fluid-rock studies. The continuation of the fluid-fluid studies include the effect of cation on the alkali-surfactant interfacial tension synergism and the effect of brine composition on the alkali-surfactant interfacial tension synergism. Fluid-rock studies include relative permeability determinations and radial corefloods with fluids of different mobilities.

Discussion of Evaluations

Materials and Procedures

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.[11] 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. The live oil viscosity at 180°F and 1,150 psi is 0.42 cp. The 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.

Core - Core is either Berea sandstone available from Cleveland Quarries in Ohio or Adena Core from well Glenn "F" #3.

Chemicals and Procedures - Chemicals and procedures for interfacial tension measurements were described previously.[12] NaOH and Na_2CO_3 concentration of the aqueous solutions were determined by titration with HCl to a phenolphthalein end point.[13] Alcoflood 1175 and Alcoflood 1135 concentration was determined using a starch-triiodide technique.[14-15] Anionic surfactant concentrations were determined using a dual phase Hyamine titration.[16] Chemicals used are described within each section as appropriate.

Adsorption studies were performed by crushing Berea sandstone and sieving the crushed sandstone to -20 and +100 mesh. 100 g of dried crushed sandstone mixed with 100 g of aqueous solution. Sand-solution mixtures were incubated in sealed containers at 72, 100 and 150°F with 5 ml aliquots taken at 0, 1, 3, 10, and 20 days. Aliquots were analyzed for alkali, surfactant, and polymer as appropriate.

A positive displacement pump, pressure transducers, Hassler type linear core holders and radial core holders were used to perform corefloods. Berea linear corefloods used 1 inch diameter by 6 inch long core plugs. Linear corefloods with Adena core were with 2 inch diameter by 6 inch long core plugs. Radial corefloods were performed with Berea sandstone of dimensions 2 inches high by 6 inches diameter. Corefloods were performed at 150°F with a back pressure of 50 psi.

Fluid-Fluid Interaction

A series of evaluations on the fluid-fluid interactions with alkali, surfactants, and polymer has been performed and reported as part of this study.[12] The earlier portion of the work focused on interfacial tension studies investigating the surfactant structure, alkali-

surfactant combinations, temperature, critical micelle concentration, and polymer addition to alkaline-surfactant solutions (interfacial tension changes, intrinsic viscosity, and solution rheology). This report will not duplicate the prior research narrative.

Ion Composition Effect on Interfacial Tension

Alternate Cations - The effect of the type of cation in solution on alkaline-surfactant combinations was studied by measuring the interfacial tension. The cation was replaced in the brine, alkali and surfactant if possible. For example, alkali and surfactant were dissolved in 1,000 mg/l KCl rather than NaCl. Substitute alkalis were potassium or ammonium hydroxide and carbonate. Substitute surfactants and sodium based surfactants utilized are listed in Table 1. If a sodium based surfactant was used, no attempt was made to replace the surfactant sodium ion. Surfactant concentrations were 0.2 wt% active.

Table 1

Sodium, Potassium and Ammonium Surfactant Descriptions

Surfactant	Structure
Linear Alkyl Group - Alkyl Aryl Surfactants	
Polystep A7	linear alkyl benzene sulfonate sodium salt - molecular weight 348, 12 carbon chain
Polystep A 15-30K	linear alkyl benzene sulfonate potassium salt - molecular weight 364, 12 carbon chain
LXS 420	linear xylene sulfonate sodium salt - molecular weight 420, 15 to 16 carbon chain
Ninate 411	linear alkyl aryl sulfonate isopropyl amine salt - molecular weight 411, 13 carbon chain
Branched Alkyl Group - Alkyl Aryl Surfactants	
Petrostep B-100	branched alkyl aryl sulfonate sodium salt - molecular weight 410, 16 to 17 carbon chain
Alpha Olefin Sulfonates	
Bioterge AS-40	alpha olefin sulfonate sodium salt - molecular weight 314, 14 to 16 carbon chain
Sulfated Linear Alkane	
Stepanol WAC	sodium lauryl sulfate - molecular weight 288, 12 carbon chain
Polystep B7	ammonium lauryl sulfate - molecular weight 288, 12 carbon chain
Sulfated Ethoxylated Linear Alkane	
Neodol 25-3S	sodium sulfated ethoxylated alcohol - molecular weight 399, 12 to 15 carbon chain, 3 moles ethylene oxide
Steol CA-460	sulfated ethoxylated alcohol ammonium salt (ammonium laureth ethoxy sulfate) - molecular weight 460, 11 carbon chain, 4 to 5 moles ethylene oxide

Replacing sodium with potassium in alkaline-surfactant solutions containing sodium based surfactants increased interfacial tension by 2 orders of magnitude for the solutions with ultra low interfacial tensions (Petrostep B-100 and LXS-420). Alkaline-surfactant solutions without ultra low interfacial tensions (Bioterge AS-40) showed no effect of changing the cation. Figure 1 shows the data. Sodium based surfactants were not soluble with ammonia salts. Replacing the cation of the surfactant with either potassium or ammonium ion renders the same conclusion as with sodium based surfactants, as shown in Figures 2 and 3.

Replacing sodium ion with potassium or ammonium ion indicates the synergistic relationship between the sodium based alkali and the surfactant is not simply due to ionic strength changes. The ionic strengths of the potassium alkalis are 77% of the corresponding sodium alkalis. If the synergistic effect was due to ionic strength, an interfacial tension minimum should be shifted for the potassium salts. pH is not the cause of the interfacial tension synergism since pH values are similar at equivalent concentrations for the potassium and sodium salts.

Figure 4 shows that as the temperature increases, the concentration at which ultra low interfacial tension values are developed by alkali and Petrostep B-100 increases. Figures 5 and 6 show the same trend with ammonium and potassium based surfactants. Figure 5 and 6 also demonstrate that ammonium ion increases interfacial tension values relative to potassium ion. Similar trends were observed for Ninate 411.

Increasing the potassium or ammonium chloride concentration increased the interfacial tensions of the less brine tolerant alkyl aryl sulfonates as shown in Figure 7. The difference between cation type is minimized. Solubility of the surfactants were reduced relative to the corresponding sodium solutions. With the more brine tolerant surfactants, the interfacial tension values continued to decline as the solution salinity increased (See Figure 8).

Interfacial tension data suggests the cation type does effect interaction between crude oil and alkaline-surfactant solutions. No advantage was observed for substituting potassium or ammonium ion for sodium in the solutions on an interfacial tension basis.

Reservoir Brine Composition - 0.1 wt% surfactants dissolved with either 1.25 wt% NaOH or 2.0 wt% Na_2CO_3 were blended with four reservoir produced waters to determine how the interfacial tension changes. Reservoir brines were selected so the total dissolved solids and divalent cation content increased. Two "J" sand reservoir brines were used as well as two brines from other formations in proximity to the Adena Field. The brine compositions are listed in Table 2.

Table 2

Reservoir Brine Compositions

Ion	Singleton	Adena	Jumper Creek	Sleepy Hollow
	Ion Concentration mg/l			
Calcium	13	18	900	2,230
Magnesium	2	8	150	376
Strontium	0	1	14	264
Barium	0	0	60	64
Sodium	111	2,700	16,400	14,200
Potassium	1	6	37	72
Chloride	18	2,750	20,100	31,750
Sulfate	8	23	10	0
Total Dissolved Solids	349	6,500	34,000	60,300
pH	8.0	8.5	7.0	7.6

Figures 9 through 11 show the interfacial tension changes as an alkaline-surfactant solution is diluted with reservoir brine. Lower total dissolved solids-fresher waters resulted in minimal increase of interfacial tension and higher total dissolved solids-harder waters resulted in significant increases of interfacial tension. Ultra low interfacial tension solutions (Petrostep B-100 with alkali, Figure 9) demonstrate this clearly. As the interfacial tension of the solutions increase, the effect is less pronounced, especially with more water brine tolerant surfactants (Bioterge AS-40, Figure 11). The decline of the interfacial tension of the LXS 420 solutions with Singleton water (Figure 10) suggests the solution concentrations were not optimum to achieve maximum interfacial tension reduction. Figures 9 through 11 indicate Na_2CO_3 blended with surfactant is a better agent for maintaining low interfacial tension values as alkaline-surfactant solutions are diluted with produced water than NaOH.

Rock-Fluid Interaction

Chemical Adsorption

Surfactant Adsorption - The adsorption of alkali, surfactants, and polymer onto crushed Berea sandstone were studied. The surfactants, alkaline agents, and polymers studied were described previously.[12] Potassium and ammonium surfactants are listed in Table 1.

Adsorption of 0.2 wt% active surfactants dissolved in 1,000 mg/l NaCl with and without 2.0 wt% alkali are summarized in Table 3. The table shows surfactant adsorption onto crushed Berea sandstone at 100°F and 30 days. "MW" in Table 3 refers to molecular weight.

Table 3

Surfactant Adsorption with Alkali onto Berea Sandstone

	Surfactant Adsorption - - - - - - - 30 day mg/100 g rock at 100°F - - - - - -				
Surfactant Type	No Alkali	Na_2CO_3	NaOH	Na_3PO_4	MW
Linear Alkyl Aryl Sulfonates					
Polystep A-7	13.6	14.3	17.2	37.5	348
LXS-395	148.6	98.8	162.0	70.0	395
LTS-18	93.9	39.2	62.8	38.3	446
Linear Alkyl Aryl Sulfonates - Alkyl Internally Bonded to Aryl Functionality					
Petrostep H-67	145.3	47.9	54.0	48.4	415
Branched Alkyl Aryl Sulfonates					
Petrostep B-100	133.7	19.4	78.2	51.7	410
Chaser XP-100	38.5	69.2	96.3	59.3	430
Internal Olefin Sulfonates					
Neodol IOS 1517	15.9	17.8	68.0	34.0	328
Neodol IOS 1720	23.7	13.0	40.6	35.7	363
Alpha Olefin Sulfonates					
AOS 12	35.6	12.9	32.9	12.3	270
Bioterge AS-40	11.3	10.7	30.2	16.8	314
Sulfonated Liner Alkane					
Bioterge PAS 8S	12.6	12.8	8.2	9.9	216
Sulfonated Ethoxylated Linear Alkane					
Avanel S-30	30.2	67.4	36.2	54.2	383
Sulfated Ethoxylated Linear Alkane					
Neodol 25-3S	31.0	8.9	20.8	9.0	399
Average	56.5	33.3	54.4	36.7	

Adsorption of surfactants dissolved without alkali was highest for alkyl aryl sulfonates. Surfactant consumption increased with molecular weight. The exceptions are Neodol 25-3S and Chaser XP-100. Figure 12 shows the trend at 72, 100 and 150°F.

The inverse of the surfactant concentration remaining in the aqueous phase as a function of time is shown in Figure 13. Inverse concentration is plotted to give a straight line during aqueous phase concentration changes. Primary adsorption kinetics is demonstrated by the linear decline of the aqueous surfactant concentration. Petrostep B-100 was selected since it is typical of the alkyl aryl sulfonates which are most beneficial for oil recovery. Surfactant removal from the aqueous phase shows an inverse decline to a stable value. The stable value occurs when the rock adsorption is satiated. For Petrostep B-100 dissolved without alkali or polymer, a secondary adsorption was observed at 72°F and 100°F but not at 150°F.

Na_2CO_3, NaOH, or Na_3PO_4 addition to the surfactant solutions showed a distinct reduction in surfactant consumption for surfactants with molecular weights 395 or greater. Below 395, Na_2CO_3 did not alter surfactant consumption while NaOH and Na_3PO_4 increased consumption at 72 and 100°F. At 150°F, only NaOH caused increased surfactant adsorption. The data are shown in Figure 12.

The change of surfactant adsorption by alkali addition is consistent with alkali type. Some exceptions exist such as Chaser XP-100. However, the general trend suggests that alkali will dominate surfactant consumption if present. NaOH is least beneficial to surfactant consumption causing it to increase below molecular weight 395 and reduces it the least for surfactants with molecular weight 395 or greater.

pH is a factor affecting surfactant adsorption. The NaOH, Na_2CO_3, and Na_3PO_4 plus surfactant solutions evaluated had pH values of 12.2 to 13.7, 10.7 to 11.7, and 11.8 to 12.8, respectively. The surfactant solutions with no alkali have pH values of 6 to 9 with the exception of Petrostep H-67 which is an acidic surfactant with a pH of 2.4. Surfactant consumption is higher for surfactants of lower molecular weight and lower for higher molecular weight surfactants at the more neutral pH values. Figure 14 shows the adsorption of the alkyl aryl sulfonates, alkyl sulfonates and alkyl sulfates as a function of pH. Surfactant adsorption go through a minimum at pH 11 to 12 and increase as the pH exceeds 12.5.

The change in adsorption of surfactant without alkali with temperature was minimal. As the temperature increased, the difference between the reduction of surfactant consumption of the higher molecular weight surfactants when dissolved with NaOH, Na_2CO_3, and Na_3PO_4 is minimized. Below molecular weight 395, NaOH effect on surfactant consumption does not change while Na_2CO_3 and Na_3PO_4 effects are reduced and become essentially equal. Figure 12 shows the adsorption of the different molecular weight surfactants with temperature.

Addition of 1,000 mg/l polymer to the surfactant solution either with or without alkali was evaluated for a single higher adsorbing alkyl aryl sulfonate (Petrostep B-100) and a low adsorbing alpha olefin sulfonate (Bioterge AS-40). Xanthan gum and polyacrylamide (Alcoflood 1135) were also added. The data at 100°F are shown in the following table.

Table 4

Surfactant Adsorption with Polymer onto Berea Sandstone

Surfactant Type	Surfactant Adsorption - - - - 30 day mg/100 g rock at 100°F - - - - - No Polymer	Polyacrylamide	Xanthan Gum
No Alkali			
Bioterge AS-40	11.3	12.1	11.2
Petrostep B-100	133.7	80.1	96.1
With Na_2CO_3			
Bioterge AS-40	10.7	13.5	18.1
Petrostep B-100	19.4	79.6	95.3
With NaOH			
Bioterge AS-40	30.2	15.8	15.1
Petrostep B-100	78.2	117.9	122.5

Polymer addition to the surfactant solutions alters the adsorptive characteristics of Petrostep B-100 but not Bioterge AS-40. Addition of Na_2CO_3 to the surfactant plus polymer solutions showed a small reduction of surfactant consumption for Petrostep B-100 but not with Bioterge AS-40. Surfactant adsorption with NaOH addition continues to decrease with polymer in solution. Polymer is the dominant component affecting surfactant adsorption when surfactant, alkali, and polymer are mixed together. Alkali effect on adsorption continues to be expressed, however.

Figures 15 and 16 show the surfactant adsorption as a function of temperature. Increasing temperature does not alter the effect of polymer and alkali on surfactant adsorption. Figure 15 shows alkyl aryl sulfonate (Petrostep B-100) adsorption generally decreases with temperature but the alkali and polymer effects remain consistent. Alpha olefin sulfonate (Bioterge AS-40) adsorption was unchanged with temperature with the effect of alkali and polymer being unchanged. The effect of alkali and temperature on Petrostep B-100 adsorption as well as other surfactants is clearly demonstrated in Figure 12 as well. Polymer type does not alter the surfactant adsorption significantly.

The effect of replacing sodium ion with potassium or ammonium ion on adsorption of surfactant was determined by dissolving the chemicals in KCl and NH_4Cl and using either potassium or ammonium based alkalis and surfactants. No attempt was made to replace the sodium ion of sodium salt surfactants when dissolved in KCl or NH_4Cl. The adsorption data at 100°F are summarized in Table 5. The alkali designation XOH are NaOH, KOH, or NH_4OH as appropriate for the surfactant or brine cation. A similar designation for carbonates is used. Na designation next to the surfactant indicates a sodium based solution. A K designates potassium and NH_4 designates ammonium based solutions.

Table 5

Surfactant Adsorption with Different Cations onto Berea Sandstone

Surfactant Type	Cation	Surfactant Adsorption - - - - 30 day mg/100 g rock at 100°F - - - - No Alkali	X_2CO_3	XOH
Linear Alkyl Aryl Sulfonates				
Polystep A-7	Na	13.6	14.3	17.2
Polystep A-15-30K	K	26.3	54.9	67.6
Linear Alkyl Sulfonates				
Polystep B-7	NH_4	50.6	6.0	19.6
Branched Alkyl Aryl Sulfonate				
Petrostep B-100	Na	133.7	19.4	78.2
Petrostep B-100	K	48.8	63.5	86.5
Petrostep B-100	NH_4	54.0	41.4	33.7
Alpha Olefin Sulfonate				
Bioterge AS-40	Na	11.3	10.7	30.2
Bioterge AS-40	K	20.0	21.3	25.7
Bioterge AS-40	NH_4	11.6	11.4	18.2

Potassium and ammonium ion replacement reduced the adsorption of the branched alkyl aryl sulfonates but the effect is negated by alkali addition. Linear alkyl aryl sulfonate adsorption increased with potassium ion addition in the presence and absence of alkali. Bioterge AS-40 adsorption was not affected by replacement of sodium ion. Data are consistent with 72°F and 150°F data.

Sodium chloride was added to the alkaline plus surfactant plus polymer solutions to determine the effect of increasing salinity on alkali adsorption. Sodium chloride concentrations were increased up to 20,000 mg/l and adsorption was monitored at 72°F. The surfactants, alkaline agents, and polymer used were Bioterge AS-40 (alpha olefin sulfonate) and Petrostep B-100 (branched alkyl aryl sulfonate), Na_2CO_3, NaOH, and polyacrylamide (Alcoflood 1175). Petrostep B-100 plus alkali and Petrostep B-100 plus alkali plus polymer were not stable above 10,000 mg/l NaCl. Figure 17 indicates that adsorption of Bioterge AS-40 did not increase until the salinity was above 10,000 mg/l. Petrostep B-100 adsorption decreased with salt addition initially and then increased as the NaCl concentration reached 20,000 mg/l. Petrostep B-100 adsorption increased with the initial salinity change when polymer was added to the solution. When hydroxide was dissolved with Petrostep B-100, surfactant adsorption increased with salinity while surfactant adsorption decreased with salinity when Petrostep B-100 was dissolved with no other additives or with Na_2CO_3. The effect of salinity on the adsorption of surfactant is dependent on surfactant type. No consistent trend was observed with either polymer or alkali addition.

Alkali Adsorption - Alkali adsorption onto crushed Berea sandstone shows a distinctly different adsorption pattern than surfactant. Figure 18 depicts the inverse of alkali concentration versus time. Adsorption to an asymptote is very rapid, suggesting primary adsorption is neutralization of rock. Little difference is observed between Na_2CO_3 and NaOH. Na_3PO_4 displayed an identical trend. Alkali adsorption dissolved with the surfactants listed in Table 3 are listed in Table 6.

Table 6

Alkali Adsorption with Surfactant onto Berea Sandstone

	Alkali Adsorption - 30 day mg/100 g rock at 100°F -		
Surfactant Type	Na_2CO_3	NaOH	Na_3PO_4
No Surfactant	61.0	84.7	186.6
Linear Alkyl Aryl Sulfonates			
Polystep A-7	74.4	119.0	222.2
LXS-395	53.8	71.3	106.3
LTS-18	88.7	60.4	116.4
Linear Alkyl Aryl Sulfonates - Alkyl Internally Bonded to Aryl Functionality			
Petrostep H-67	55.6	30.1	160.7
Branched Alkyl Aryl Sulfonates			
Petrostep B-100	130.3	100.2	138.2
Chaser XP-100	41.0	70.7	192.5
Internal Olefin Sulfonates			
Neodol IOS 1517	85.4	185.5	147.3
Neodol IOS 1720	209.4	139.0	185.6
Alpha Olefin Sulfonates			
AOS 12	74.3	69.9	111.2
Bioterge AS-40	77.5	115.1	153.5
Sulfonated Liner Alkane			
Bioterge PAS 8S	98.9	73.7	128.0
Sulfonated Ethoxylated Linear Alkane			
Avanel S-30	91.3	58.3	175.8
Sulfated Ethoxylated Linear Alkane			
Neodol 25-3S	110.8	78.3	222.7
Average	89.5	89.7	160.5

Na_2CO_3 consistently had the lowest consumption with Na_3PO_4 having the greatest. Surfactant addition to the alkaline solution increased average consumption by 1.4 to 6.8%. Variances in consumption were surfactant specific, varying within each class. Changing the temperature did not alter either Na_2CO_3 or Na_3PO_4 adsorption either with or without surfactant but NaOH adsorption increased with increasing temperature in the presence and absence of surfactant. Figure 19 shows some of the data. Surfactant structure had no apparent effect on alkali adsorption.

The failure of Na_2CO_3 to be removed from the aqueous phase at a greater quantity than either NaOH or Na_3PO_4 is interesting when considering that Na_2CO_3 is better at reducing surfactant adsorption. Carbonate ion is interacting with the surfactant to reduce surfactant adsorption since the aqueous phase carbonate ion concentration is not decreased. The fact that polymer will negate or reduce the alkali effect on surfactant suggests polymers affinity for surfactant is greater. Carbonate ion may form coordinate covalent bonds with surfactant to alter adsorption.

The effect of replacing sodium ion with potassium or ammonium ion on adsorption of alkali was identical to the procedure for surfactant adsorption. Table 7 compares the different alkali adsorption at 100°F.

Table 7

Alkali Adsorption with Different Cations onto Berea Sandstone

	Alkali Adsorption					
	- - - - - - 30 day mg/100 g rock at 100°F - - - - - - -					
Alkali Type	No Surfactant	Polystep A-7	Polystep A-15-30K	Polystep B-7	Petrostep B-100	Bioterge AS-40
Sodium Salts						
Na_2CO_3	61.0	74.4			130.3	77.5
NaOH	84.7	119.0			100.2	115.1
Potassium Salts						
K_2CO_3	154.3		134.6		81.2	93.2
KOH	171.6		62.0		51.4	63.1
Ammonium Salts						
$(NH_4)_2CO_3$	32.0			81.8	18.8	48.0
NH_4OH	148.2			90.0	124.3	111.9

Potassium and ammonium alkaline agents adsorption are greater than the sodium alkaline agents without surfactant. Higher adsorption of hydroxide ion relative to carbonate ion is maintained with potassium and ammonium alkaline agents. When surfactant is added to the alkaline solutions, hydroxide consumption decreased with both potassium and

ammonium ions but increased with the sodium ion. Carbonate ion consumption showed a consistent decrease with potassium ion and a consistent increase with the sodium ion. Surfactant type again showed no consistent effect on alkali adsorption. The adsorption trends were consistent with changes in temperature as shown in Figure 20 for the potassium alkalis and Figure 21 for the ammonium alkalis.

Bioterge AS-40, Petrostep B-100, Polyacrylamide, or Xanthan Gum were added to Na_2CO_3 and NaOH solutions to study adsorption with all three components. The following table shows the alkali adsorption at 100°F as polymer and surfactant are blended into the solution.

Table 8

Alkali Adsorption with Polymer onto Berea Sandstone

	Alkali Adsorption		
	- - - - - - - 30 day mg/100 g rock at 100°F - - - - -		
Alkali Type	No Polymer	Polyacrylamide	Xanthan Gum
No Surfactant			
Na_2CO_3	61.0	89.5	66.8
NaOH	84.7	72.3	46.2
With Bioterge AS-40			
Na_2CO_3	77.5	99.7	94.7
NaOH	115.1	55.9	61.4
With Petrostep B-100			
Na_2CO_3	130.2	83.4	88.1
NaOH	100.2	45.7	25.9
Average with Added Surfactant	94.8	74.4	63.8

Addition of either polyacrylamide or xanthan gum to NaOH and Na_2CO_3 solutions increased adsorption except for Na_2CO_3 dissolved with a surfactant whose adsorption is reduced by carbonate ion addition (Petrostep B-100). Petrostep B-100 addition reduced Na_2CO_3 adsorption when blended with polymer. Polymer type has a minimal effect on alkali adsorption.

Figure 22 shows the effect of temperature on alkali adsorption. Polymer addition to the alkaline or alkaline-surfactant solutions did not alter the adsorption characteristics of alkali with temperature. The exception is NaOH adsorption without polymer or surfactant which increased at 150°F.

Na_2CO_3 and NaOH adsorption onto Berea core increased with increasing salinity as shown in Figure 23. Increasing salinity increased alkali adsorption with the exception of NaOH with Petrostep B-100.

Polymer Adsorption - Figure 13 shows the inverse aqueous polyacrylamide concentration versus time. Polymer adsorption increased rapidly to an asymptote. Xanthan gum showed similar adsorption characteristics except the increase in polyacrylamide adsorption at 10 days with NaOH. Polyacrylamide and xanthan gum loss from the aqueous phase were similar to Figure 13 at 100 and 150°F.

Polymer adsorption onto crushed Berea sandstone as NaOH, Na_2CO_3, Petrostep B-100 and Bioterge AS-40 are blended into the solution are shown in the following table.

Table 9

Adsorption of Polymer with Surfactant onto Berea Sandstone

	Polymer Adsorption - - - 30 day mg/100 g rock at 100°F - - -		
Polymer Type	No Alkali	Na_2CO_3	NaOH
No Surfactant			
Polyacrylamide	21.5	11.5	38.4
Xanthan Gum	3.4	9.3	21.7
With Bioterge AS-40			
Polyacrylamide	16.9	13.7	9.2
Xanthan Gum	10.4	6.8	9.9
With Petrostep B-100			
Polyacrylamide	17.1	19.1	10.0
Xanthan Gum	19.4	6.0	33.6
Average with Added Surfactant	14.8	11.1	20.5

NaOH and Na_2CO_3 addition decreased or did not change polymer adsorption when surfactant was dissolved in the solution. NaOH alone increased polymer adsorption while Na_2CO_3 decreased or did not alter polymer adsorption. When polymer was dissolved with only surfactant, a difference in polymer type was observed; surfactant increased xanthan gum adsorption and decreased polyacrylamide adsorption.

Polymer adsorption decreased with increases in salinity up to 10,000 mg/l NaCl. Polymer dissolved with the alkyl aryl sulfonate (Petrostep B-100) and either alkaline agent is the only exception. Polymer adsorption with no other additive increased at 20,000 mg/l

NaCl while polyacrylamide dissolved with either surfactant or alkaline agent showed a decreased adsorption. Figure 24 shows the data.

Polymer adsorption characteristics generally did not change with increasing temperature, the exception being Na_2CO_3 plus surfactant addition to polyacrylamide solutions. Figure 25 shows the polyacrylamide adsorption as temperature increases.

Relative Permeability Change with Alkali-Surfactant-Polymer

Unsteady state water-oil relative permeability studies at 150°F were performed in Berea sandstone linear core, 1 inches diameter by 6 inches long. Relative permeability data were developed according to Jones and Roszelle[17] with the injection rate calculated according to Batycky et.al.[18] Solutions for displacing Adena crude oil from the core were:

- 1,000 mg/l NaCl - interfacial tension between crude oil and water is 19.6 mN/m
- 1.0 wt% Na_2CO_3 plus 0.2 wt% Petrostep B-100 - interfacial tension between crude oil and solution is 0.001 mN/m
- 1.0 wt% Na_2CO_3 plus 0.2 wt% Bioterge AS-40 - interfacial tension between crude oil and solution is 0.130 mN/m

Injected solution viscosities were 0.5 cp at the 150°F. Figure 26 depicts the relative permeability curves. Please note that the relative permeabilities are calculated by dividing by the effective permeability to oil at immobile water. The effective permeability to oil a immobile water is one third to one fourth absolute permeability values, allowing relative permeability values to approach a value of 4. Effective permeability to oil at immobile water was used as the base to better illustrate the relative permeability curves.

Interfacial tension (alkali-surfactant) agents added to the displacing aqueous phase effects the relative permeability curves in the following manner:

- a small shift in the oil saturation waterflood end point
- a significant increase in water relative permeability
- the solution with the greatest interfacial tension reduction has the greatest increase in water relative permeability
- a shift of the point at which k_{ro} equals k_{rw} to a lower water saturation

The oil recoveries and mobility ratios for each solution are summarized in the following table. Mobility ratio was calculated according to Smith.[19]

Table 10

Oil Recovery and Mobility Ratios for Water and Alkali plus Surfactant Solutions

Injected Solution	Initial Oil Saturation (PV)	Final Oil Saturation (PV)	Oil Recovery $\%S_{oi}$	Mobility Ratio
water	0.687	0.354	48.5	0.6
Na_2CO_3-Petrostep B-100	0.669	0.301	55.5	3.9
Na_2CO_3-Bioterge AS-40	0.699	0.424	39.3	1.0

Mobility ratio increased with the addition of a reduced interfacial tension solution in agreement with Bentsen.[20] Mobility ratio increased greater for the solution with the greatest interfacial tension reduction. Oil recovery increased only for the solution with a 19,600 fold interfacial tension reduction but decreased with a 130 fold decrease of interfacial tension. The Na_2CO_3-Bioterge AS-40 capillary number change is insufficient to produce incremental oil according to Tabor[21] and the increase in mobility ratio decreased oil recovery efficiency. With the Na_2CO_3-Petrostep B-100 solution, the capillary number increase was sufficient to produce additional oil even with the mobility ratio increase.

Mobility Control Effect on Alkaline-Surfactant-Polymer Oil Recovery

Two series of experiments were performed to evaluate the effect of improving the mobility ratio by the addition of polymer to the injected solution. First, a series of relative permeability determinations were made using Berea core and core from the Adena Field in which polymer was added to the alkaline-surfactant solution. Second, a series of radial corefloods were performed in which polymer concentration of the injected alkaline-surfactant-polymer solution was varied.

Figure 27 depicts the relative permeability for the Na_2CO_3-Petrostep B-100 and Na_2CO_3-Bioterge AS-40 solutions, each with 250 mg/l Flopaam 3330S. Injected viscosities for the two solutions are 1.2 and 1.1 cp at 150°F, respectively. Changes in the relative permeability curves with polymer addition are:

- The oil saturation end point is reduced for the Petrostep B-100-Na_2CO_3-Flopaam 3330S solution with an ultra low interfacial tension but is not changed as significantly for the Bioterge AS-40-Na_2CO_3-Flopaam 3330S solution with only a 130 fold interfacial tension reduction.

- The water relative permeability increases to larger values at the final oil saturations but are lower for alkaline-surfactant-polymer solutions at identical water saturations than the corresponding solutions with no polymer.

- The solution with the greatest interfacial tension reduction has the greatest increase in water relative permeability.

- The point at which k_{ro} equals k_{rw} has shifted to a higher water saturation relative to an alkaline-surfactant solution.

The injection of an alkaline-surfactant-polymer solution makes Berea sandstone more water-wet according to the criteria of Honarpour et.al.[22]

The oil recoveries and mobility ratios for each alkaline-surfactant and alkaline-surfactant-polymer solution are summarized in the following table.

Table 11

Oil Recovery and Mobility Ratios of Alkaline plus Surfactant and Alkaline plus Surfactant plus Polymer Solutions

Injected Solution	Initial Oil Saturation (PV)	Final Oil Saturation (PV)	Oil Recovery $\%S_{oi}$	Mobility Ratio
Na_2CO_3-Petrostep B-100	0.669	0.301	55.5	3.9
Na_2CO_3-B-100-3330S	0.633	0.080	87.4	3.3
Na_2CO_3-Bioterge AS-40	0.699	0.424	39.3	1.0
Na_2CO_3-AS-40-3330S	0.606	0.276	54.5	0.5

In both cases, the mobility ratio decreased with added polymer addition even with the increase of water relative permeability due to the reduction of oil saturation. Increasing the polymer concentration to 500 mg/l and the injected viscosity to 1.6 cp at 150°F, decreased relative water permeability at all oil saturations, as shown in Figure 28. The mobility ratio declined to 2.5. Essentially no further decrease in oil saturation occurred with increasing polymer concentration.

When a 1.2 cp 125 mg/l Flopaam 3330S solution was injected, the relative permeability characteristics changed in a similar manner relative to water. The water relative permeability end point decreased to 0.18 to give a mobility ratio of 0.2, one third the water value. The polymer residual oil saturation was 0.306 PV from an initial oil saturation of 0.567 PV giving a polymer flood recovery of 46% S_{oi}. Waterflood recovery was 48.5% S_{oi} with a final oil saturation of 0.354 PV.

Changing the porous matrix from Berea sandstone to Adena sandstone had a pronounced effect on the relative permeability with water or a Na_2CO_3-Petrostep B-100-250 mg/l Flopaam 3330S solution. Two inch diameter by six inch long Adena core were used

in the evaluations. Figure 29 depicts the relative permeability curves. Less oil was produced with Adena core using water injection or alkaline-surfactant-polymer solution injection; 33.5% S_{oi} versus 48.5% S_{oi} for water and 64.8% S_{oi} versus 87.4% S_{oi} for Na_2CO_3-Petrostep B-100-Flopaam 3330S solution. Mobility ratio changes with alkaline-surfactant-polymer solution relative to water were similar as well as the shapes of the curves. Mobility ratio in Berea sandstone increased from 0.5 for water to 3.3 for alkaline-surfactant-polymer solution and in Adena core mobility ratio increased from 0.2 to 3.7.

The second series of corefloods to define the effect on oil recovery of changing the injected solution viscosity and, therefore, the mobility ratio, was a series of radial corefloods using Berea sandstone. Different concentrations of polyacrylamide polymer were added to an alkaline-surfactant solution. Each core was waterflooded to an average residual oil saturation of 0.315 PV. 0.300 PV of 1.0 wt% Na_2CO_3 plus 0.2 wt% Petrostep B-100 plus varying concentrations of Flopaam 3330S was injected followed by injection of 0.300 PV of polymer. A water flush of 1.5 PV followed chemical injection. The incremental oil as a function of initial oil saturation is plotted against polymer concentration in Figure 30. Incremental oil production reaches an asymptote as the concentration of polymer increases. For the 500 mg/l Flopaam 3330S alkaline-surfactant-polymer solution studied, the alkaline-surfactant-polymer viscosity was approximately half the viscosity value required to achieve a mobility ratio of 1 based on Brookfield viscometer measurements. The corresponding polymer drive solution calculated mobility ratio is about 1. Radial corefloods in which a limited volume of chemical solutions were injected indicate that addition of 150 to 250 mg/l polymer to an alkaline-surfactant-polymer solution will not recover the same volume of incremental oil as solutions with 500 mg/l polymer, a different a different result than the linear coreflood.

Figure 31 demonstrates that a prior waterflood does not alter the total oil recovery of an alkaline-surfactant-polymer solution. An identical procedure as listed for the previous series of corefloods except the 0.300 PV of 1.0 wt% Na_2CO_3 plus 0.2 wt% Petrostep B-100 plus 500 mg/l Flopaam 3330S was injected without a waterflood. Radial Berea sandstone corefloods using different core discs were performed. Total oil recovery is 54% OOIP in both cases. The tertiary flood shows the alkaline-surfactant-polymer solution contributed 20% OOIP. Waterflood oil recovery was increased by 60% when an alkaline-surfactant-polymer was injected.

Alkaline-Surfactant Composition Effect on Oil Recovery

Different alkaline-surfactant-polymer solutions with identical ultra low interfacial tension values were injected into separate Berea sandstone radial core discs after a waterflood following the same injection procedure outlined for the previous radial corefloods. Figure 32 shows the results. Even though all the solutions had ultra low interfacial tension values, incremental oil varied from 7% OOIP to 20% OOIP. Therefore, the rock-fluid interaction is an important aspect in determining which system should be considered for a field project. Fluid-fluid determinations alone are not sufficient.

Tables 3 and 6 explain the difference in oil recovery. NaOH plus surfactant systems adsorb more heavily than Na_2CO_3 plus surfactant combinations by an average of 63%. Chaser XP-100 adsorption is 3.5 times greater than Petrostep B-100 when dissolved with Na_2CO_3. NaOH and Na_2CO_3 adsorption are about equal.

Conclusions

1. No advantage was demonstrated for substituting potassium or ammonium ion for sodium ion in an alkaline-surfactant-polymer solution either from an interfacial tension or reduced chemical adsorption basis.

2. Sodium carbonate is the best alkali at preventing the interfacial tension increases when an alkaline-surfactant-polymer solution contacts reservoir brine and is the best alkali at reducing polymer and surfactant adsorption onto rock.

3. Polymer is the dominate component altering the adsorption of alkali and surfactant onto reservoir rock when the three components are mixed together. Polymer adsorption is primarily effected by surfactant.

4. Salinity increases will increase alkali and decrease polymer adsorption with any change of surfactant adsorption being specific to solution composition.

5. Polymer addition to alkaline-surfactant solutions is required to achieve maximum incremental oil recovery. Addition of alkali and surfactant to the injection water will result in an increase in the mobility ratio which can be prevented with polymer addition.

6. As the polymer concentration of an alkaline-surfactant-polymer solution is increased, incremental oil reaches an asymptote. The most economic system will contain the minimum concentration of polymer required to recover the maximum incremental oil.

7. Interfacial tension reduction measurements alone are not sufficient to produce maximum incremental oil recovery. Different alkaline-surfactant-polymer solutions, all with ultra low interfacial tension values, have incremental oil recovery which varied from 7 to 20% of the initial oil saturation.

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. Pitts, M.J.: "Investigation of Oil Recovery Improvement by Coupling an Interfacial Tension Agent and a Mobility Control Agent in Light Oil Reservoirs," June 1994, DOE/BC/14886-6, Annual Report for the Period October 1992 to September 1993.

13. Skoog, D.A. and West, D.M.: Fundamentals of Analytical Chemistry, 2nd Edition, Holt, Rinehart, and Winston, Inc., New York, 1969, pages 310-313.

14. Taylor, K.D.: "Spectrophotometric Determination of Acrylamide Polymers by Flow Injection Analysis," SPE 21007.

15. Scoggins, M.W. and Miller, J.W.: "Determination of Water-Soluble Polymer Containing Primary Amide Groups Using Starch-Triiodide Method," Soc. Pet. Eng. J., 1979, volume 20, pages 151-154.

16. Epton, S.R., Analytical Chemistry, 1948, vol 44, pages 66-71.

17. Jones, S.C. and Roszelle, W.O.: "Graphical Techniques for Determining Relative Permeability from Displacement Experiments," J. Pet. Technology, May 1978, page 807-817.

18. Batycky, J.P., McCaffery, F.G., and Hodgins, P.K.: "Interpreting Capillary Pressure and Rock Wetting Characteristics From Unsteady-State Displacement Measurements," SPE 9403.

19. Smith, R.S.: Mechanisms of Secondary Oil Recovery, Robert E. Drieger Publishing Co, Inc., Huntington, New York, 1966, pages 74-75.

20. Bentsen, R.G.: "A New Approach to Instability Theory in Porous Media", Soc. Pet. Eng. J., volume 25, pages 765-779 (1985).

21. Taber, J.J.: "Research on Enhanced Oil Recovery: Past, Present, and Future," presented at the Symposium on Surface Phenomenon in Enhanced Oil Recovery, Stockholm, Sweden (August 20-25, 1979).

22. Honarpour, M., Koederitz, L. and Harvey, A.H.: Relative Permeability of Petroleum Reservoirs, CRC Press Inc., Boca Raton, Florida, 1986, page 67

Figure 1

Potassium Ion Effect on the Interfacial Tension between Adena Crude Oil at 72°F and Alkyl Aryl Sulfonates

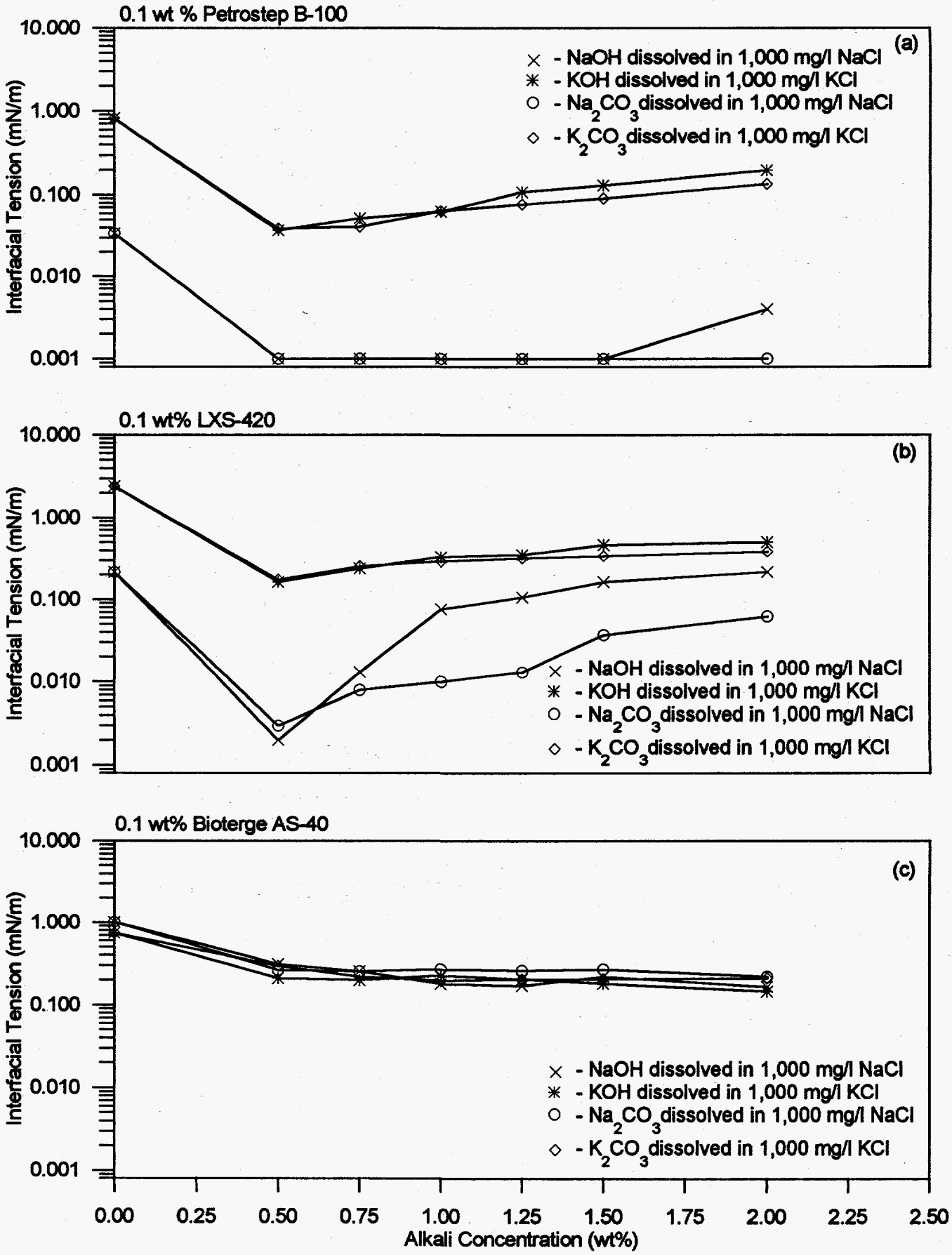
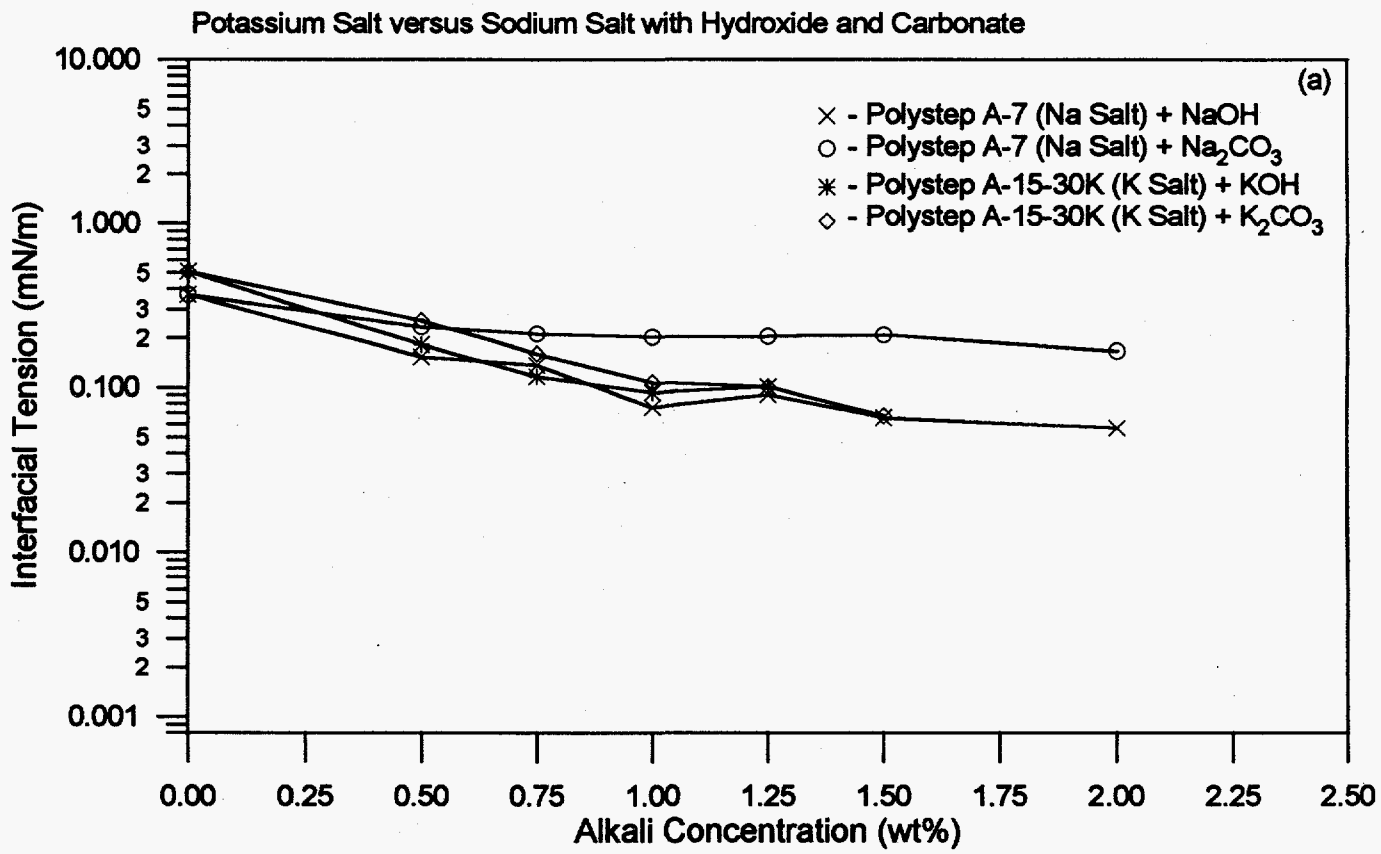


Figure 2

Ammonium Ion Effect on the Interfacial Tension Between Adena Crude Oil at 72°F and Alkyl Aryl Sulfonates



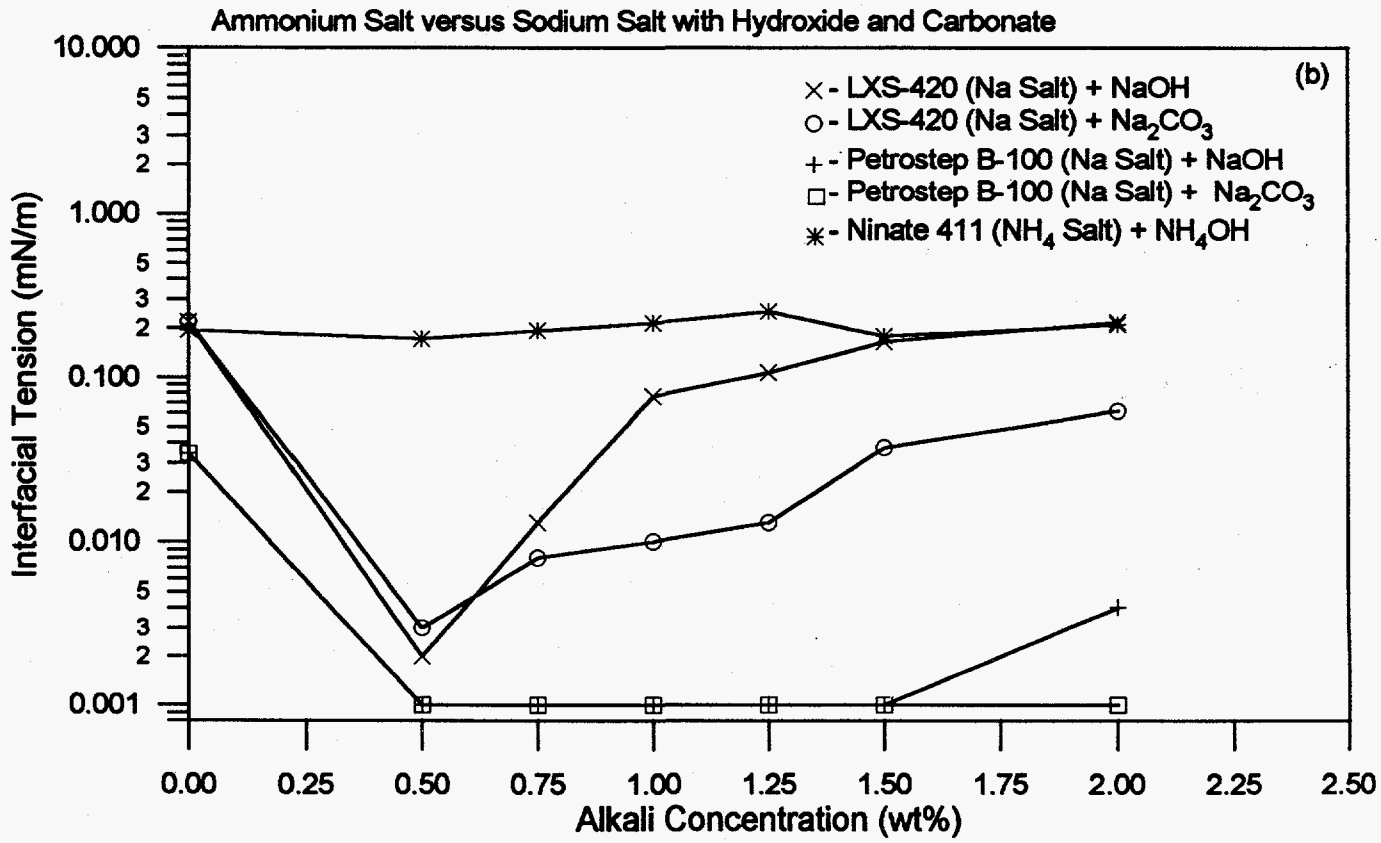
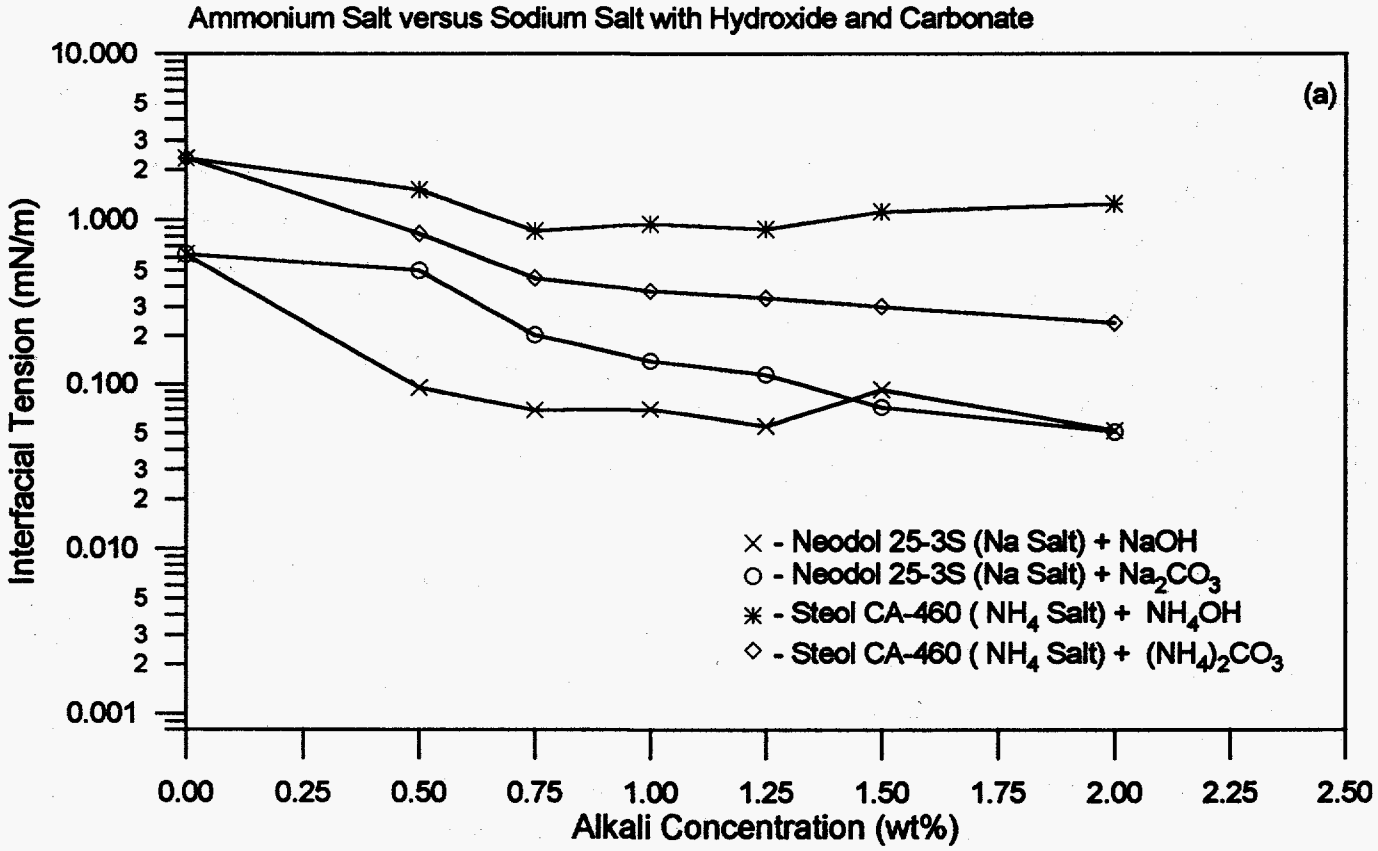


Figure 3

Ammonium Ion Effect on the Interfacial Tension Between Adena Crude Oil at 72°F and Alkyl Sulfonates and Alkyl Ethoxy Sulfates



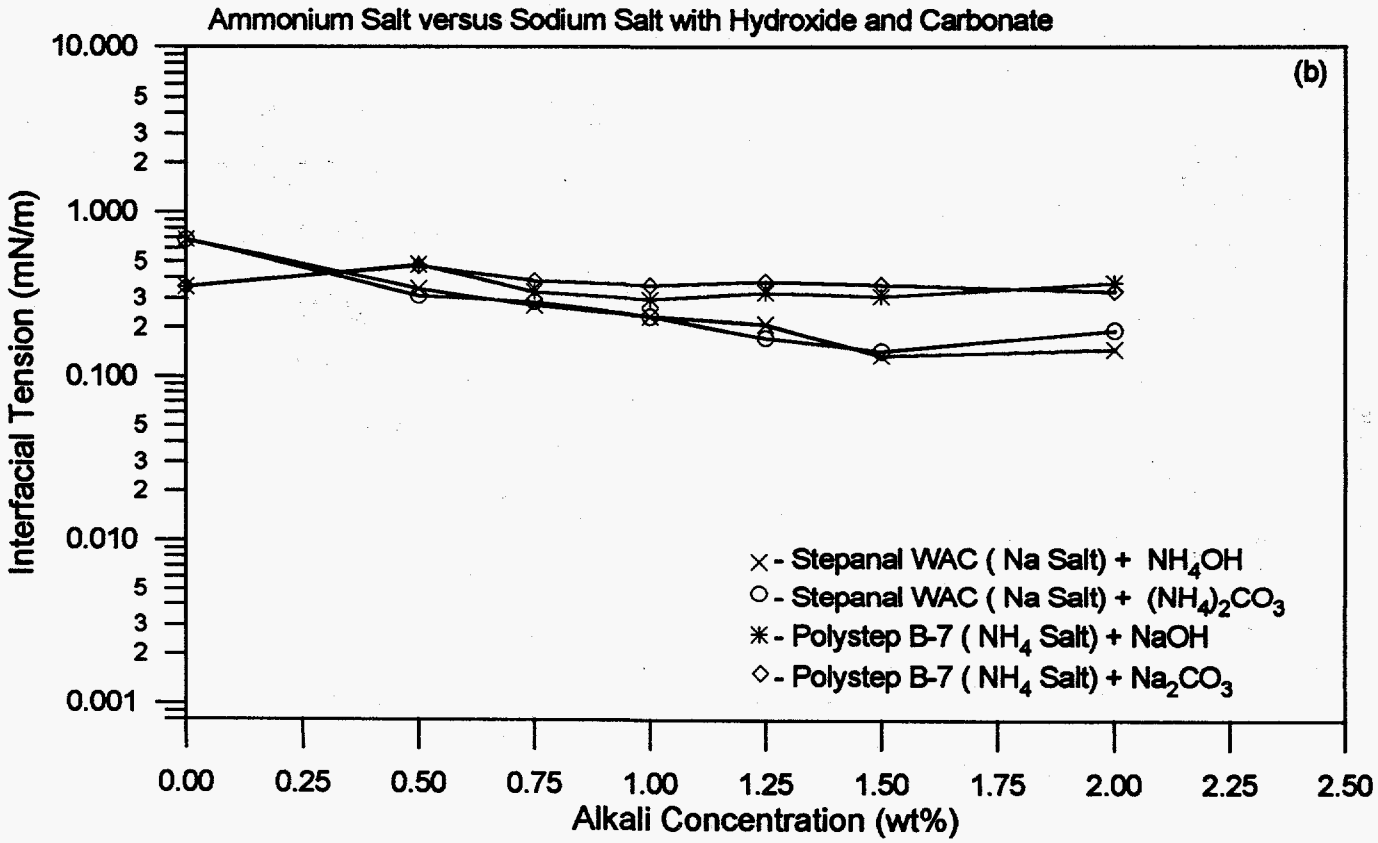
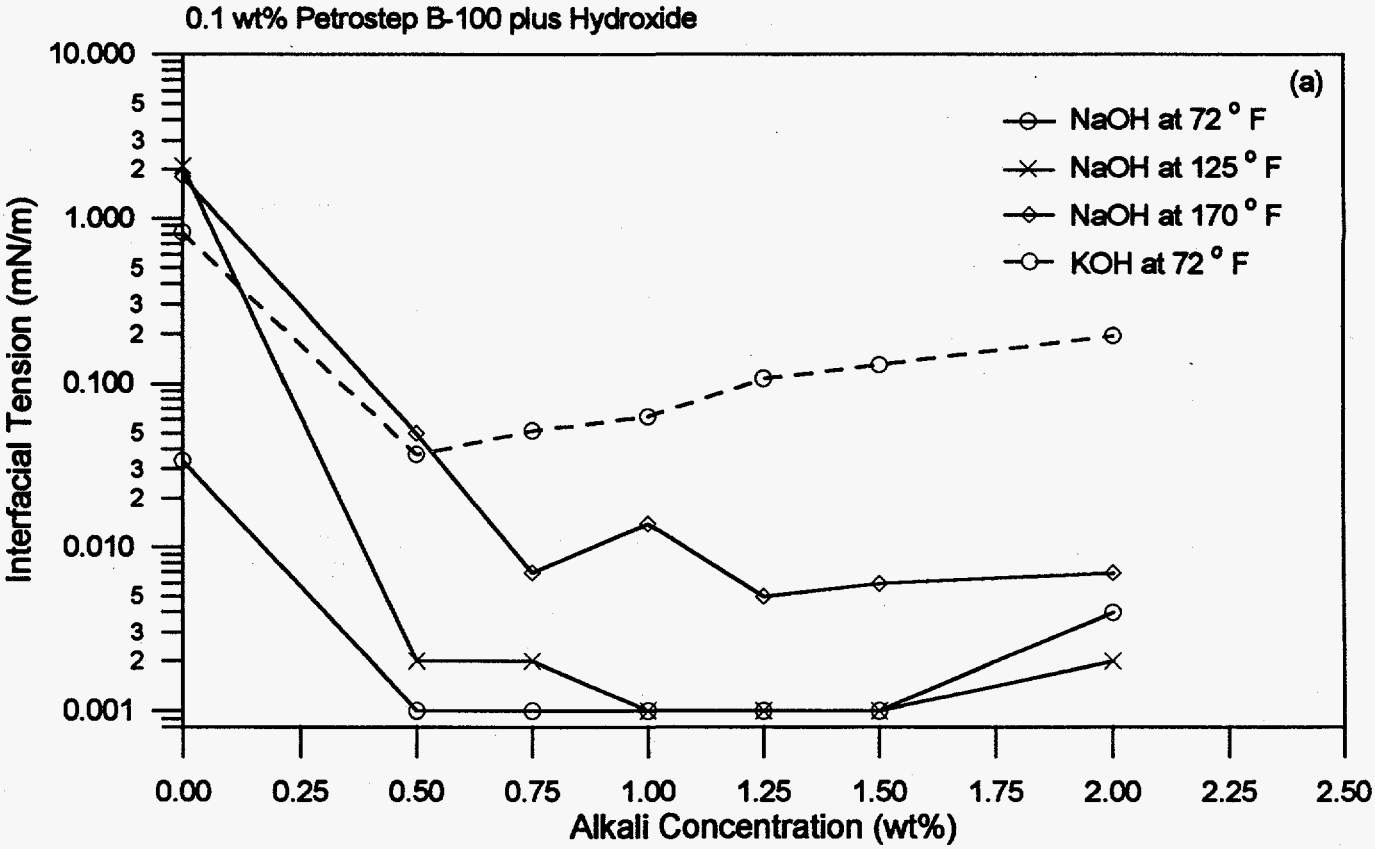


Figure 4

Temperature Effect on the Interfacial Tension between Adena Crude Oil and Sodium and Potassium Alkaline-Alkyl Aryl Sulfonate Solutions



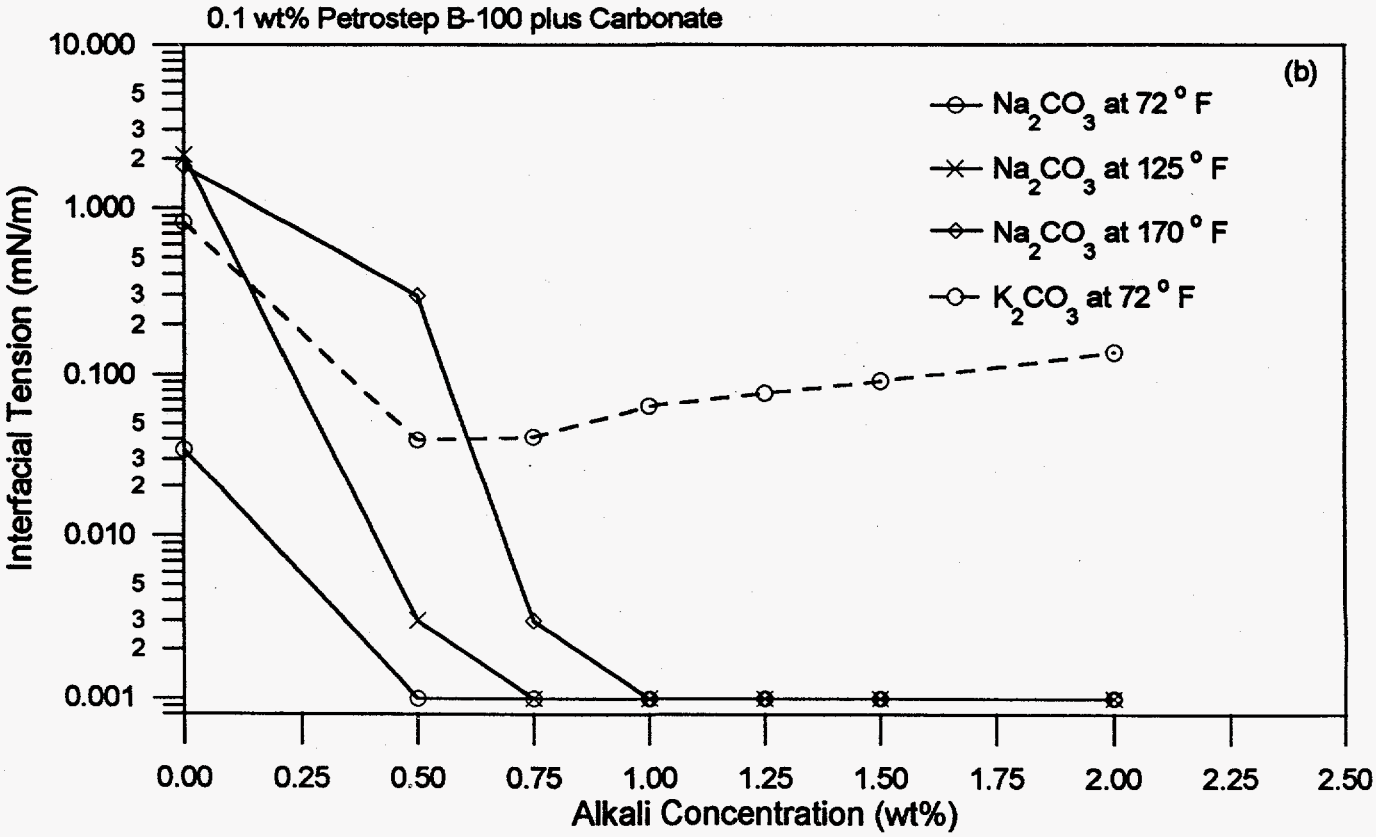
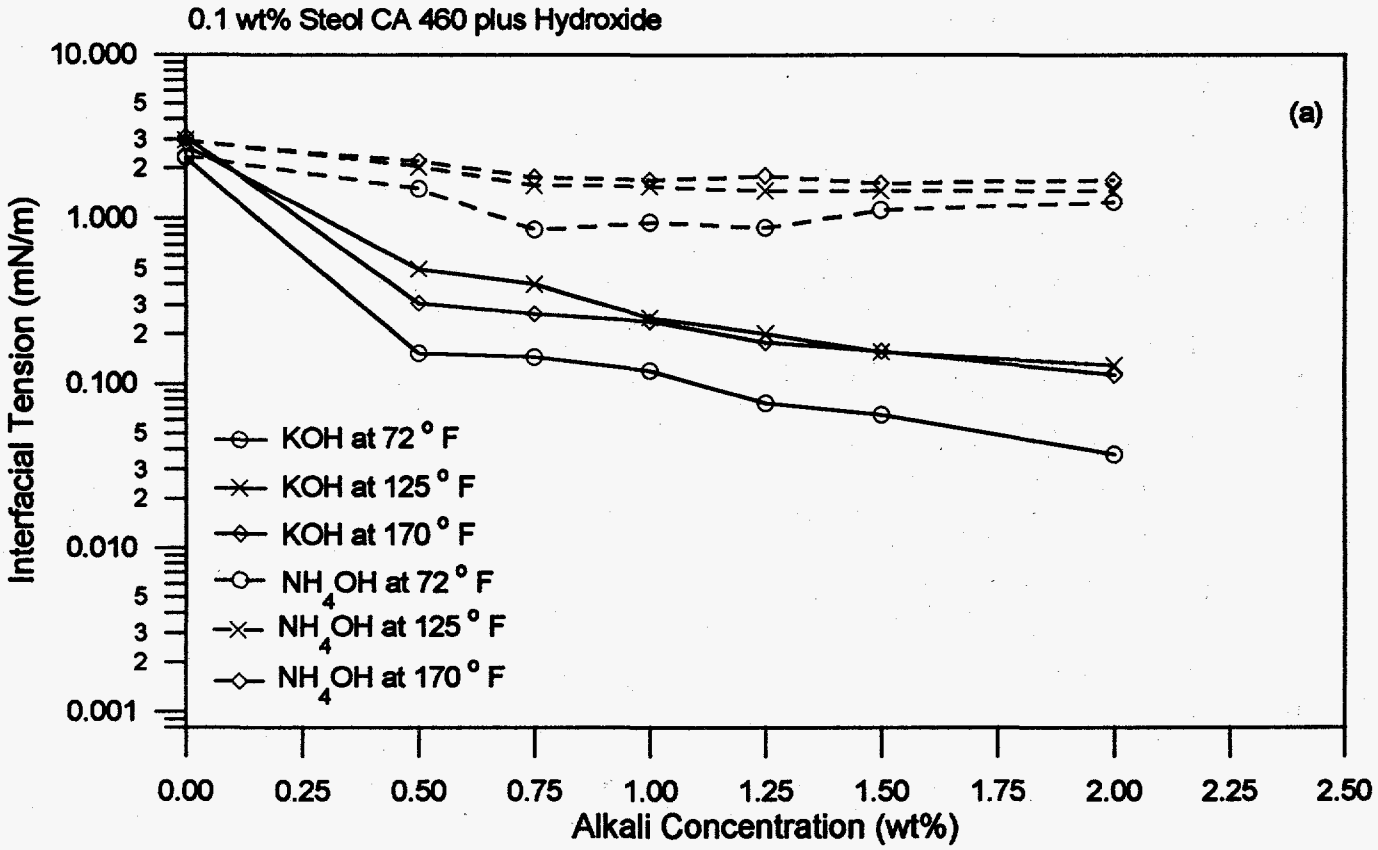


Figure 5

Temperature Effect on the Interfacial Tension between Adena Crude Oil and Potassium and Ammonium Alkyl Ethoxy Sulfate Solutions



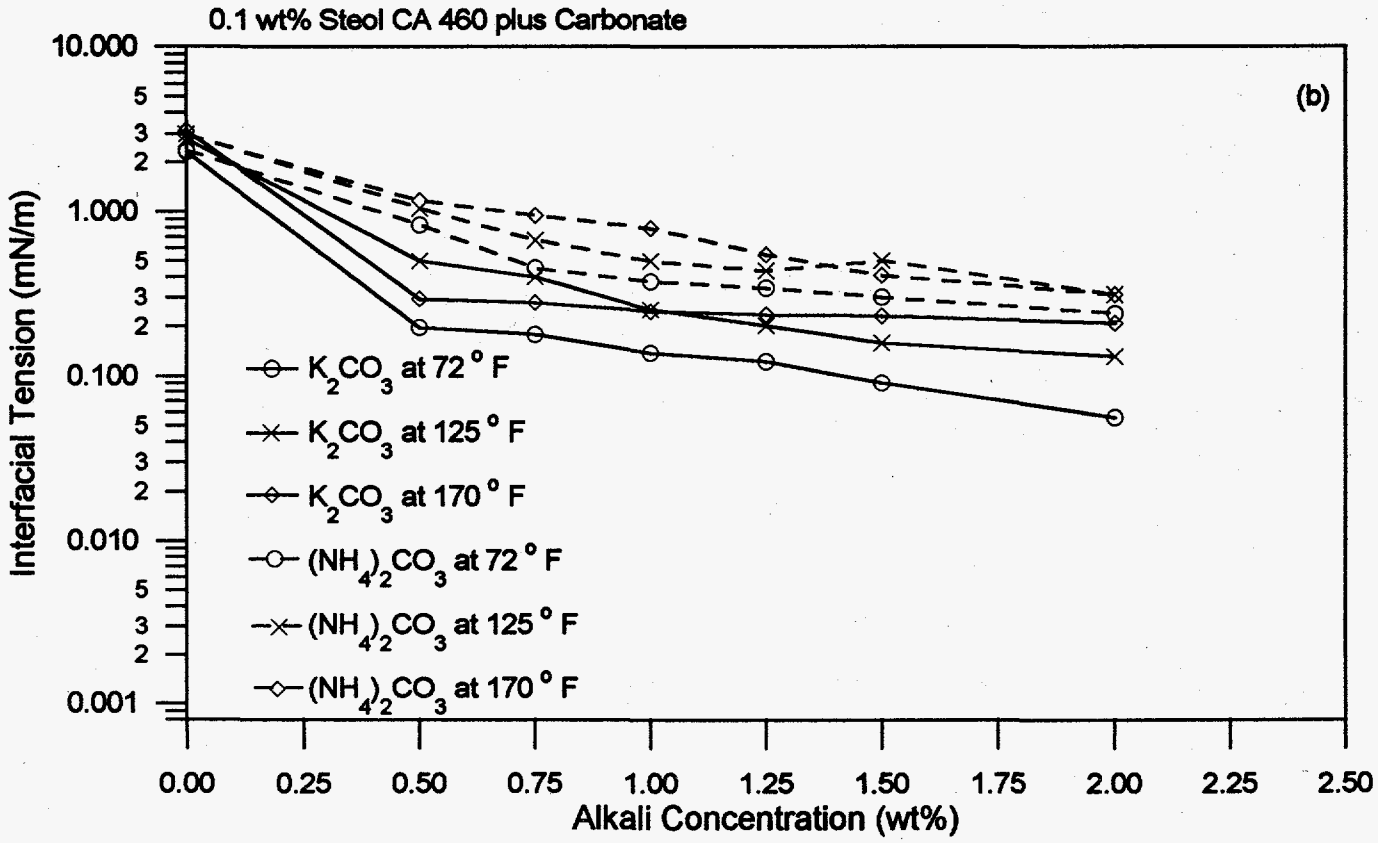
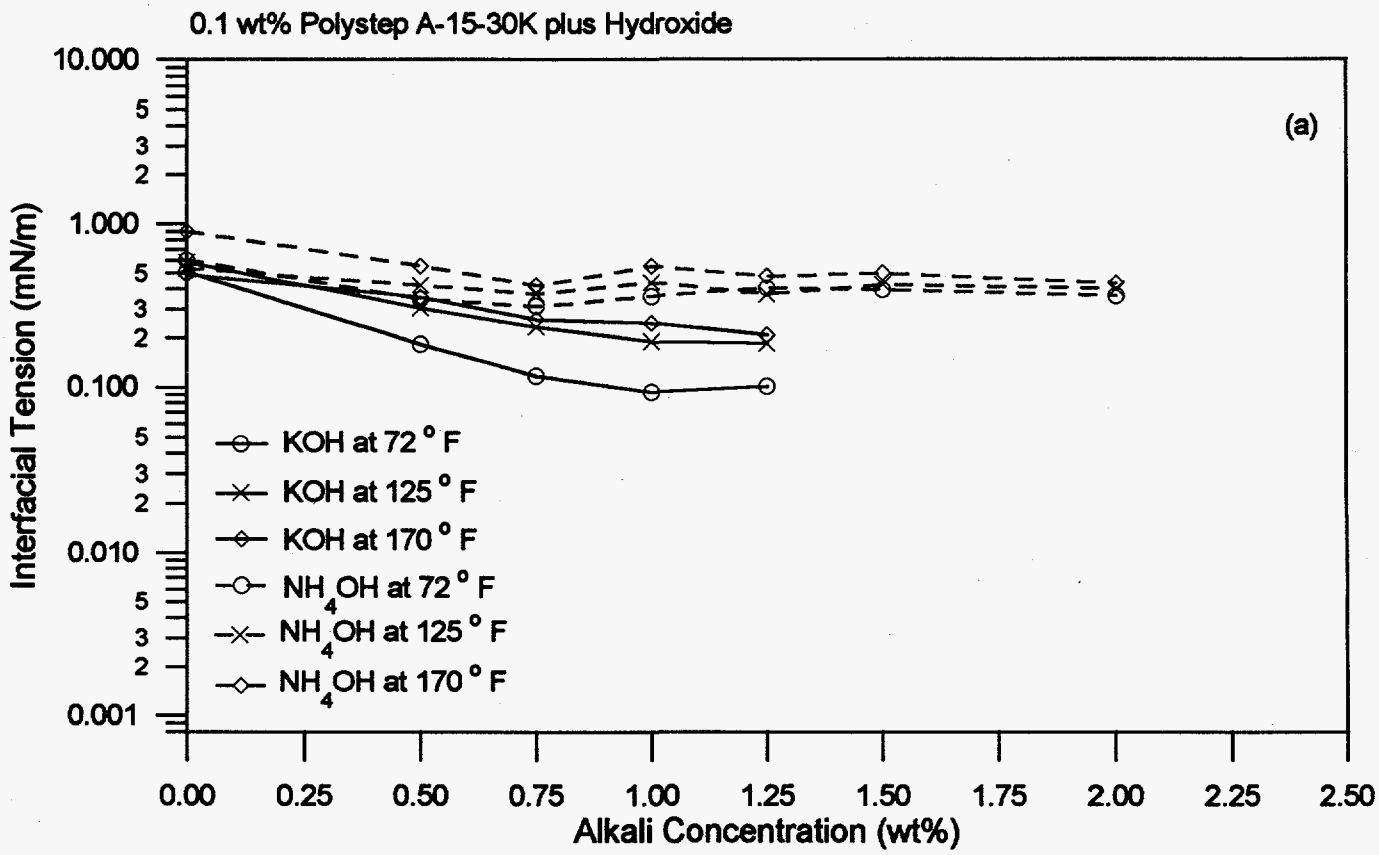


Figure 6

Temperature Effect on the Interfacial Tension between Adena Crude Oil and Potassium and Ammonium Alkyl Aryl Sulfonate Solutions



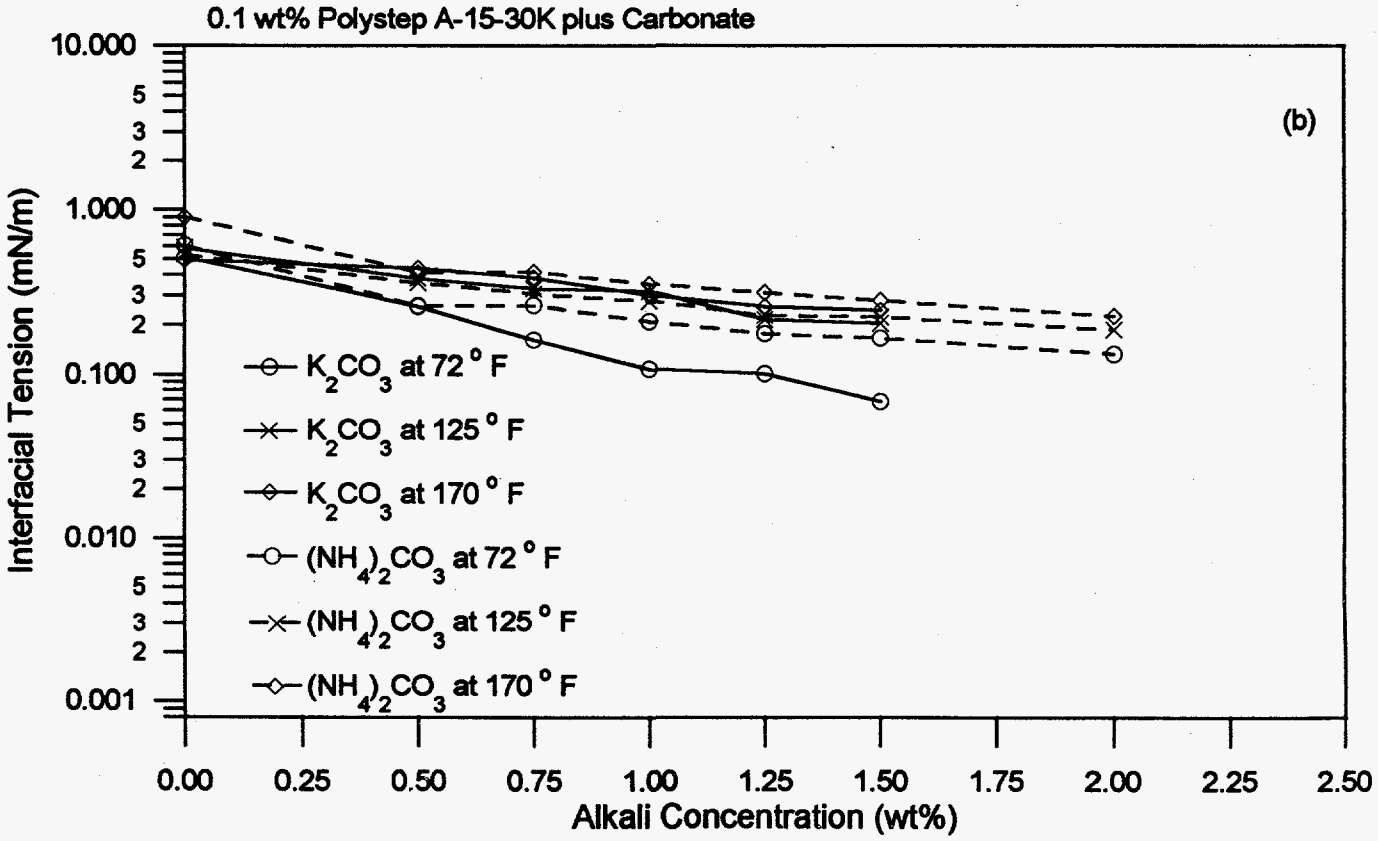
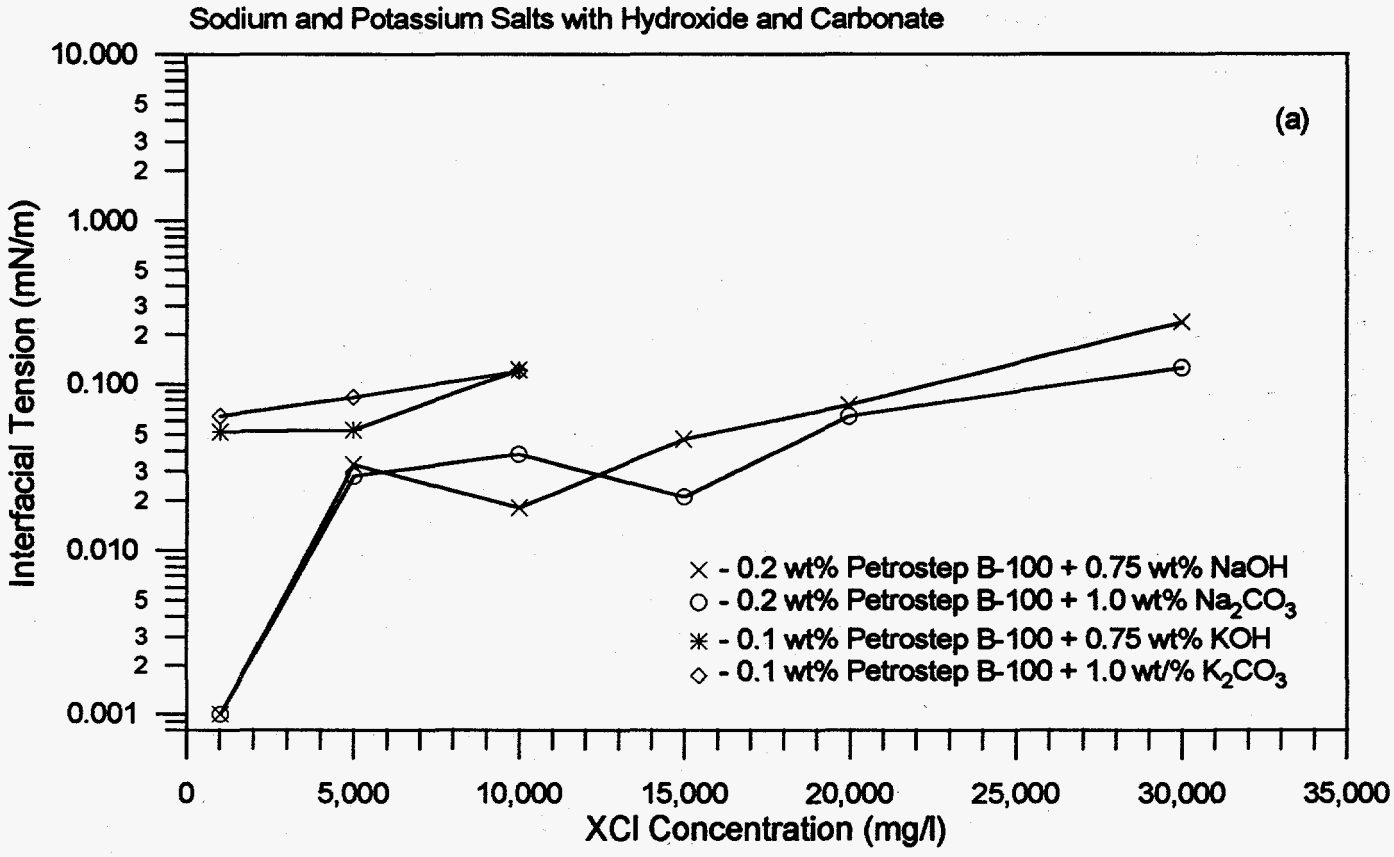


Figure 7

Increasing Salinity Effect on the Interfacial Tension between Adena Crude Oil at 72°F and Alkaline-Alkyl Aryl Sulfonate Solutions with Different Cations



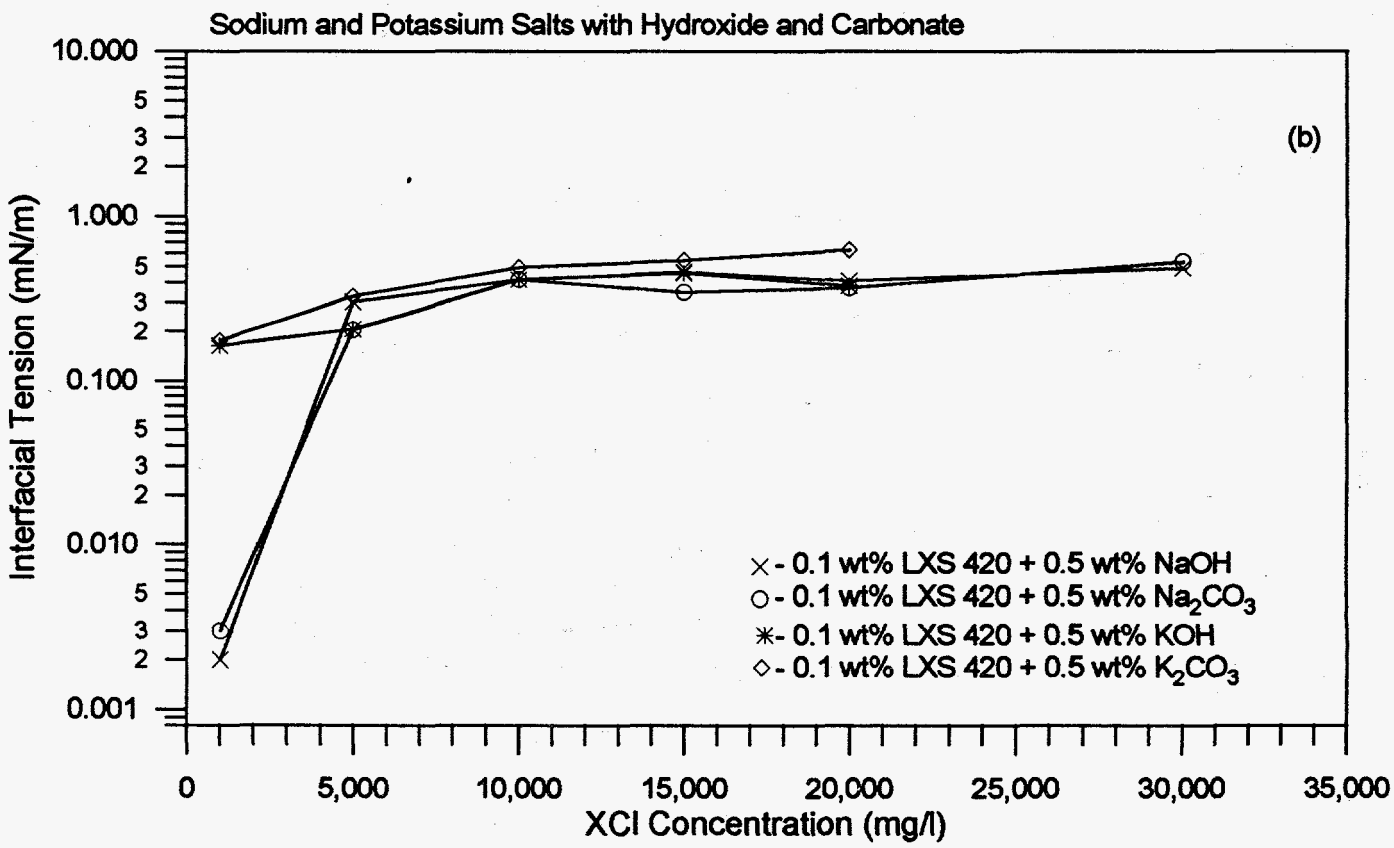
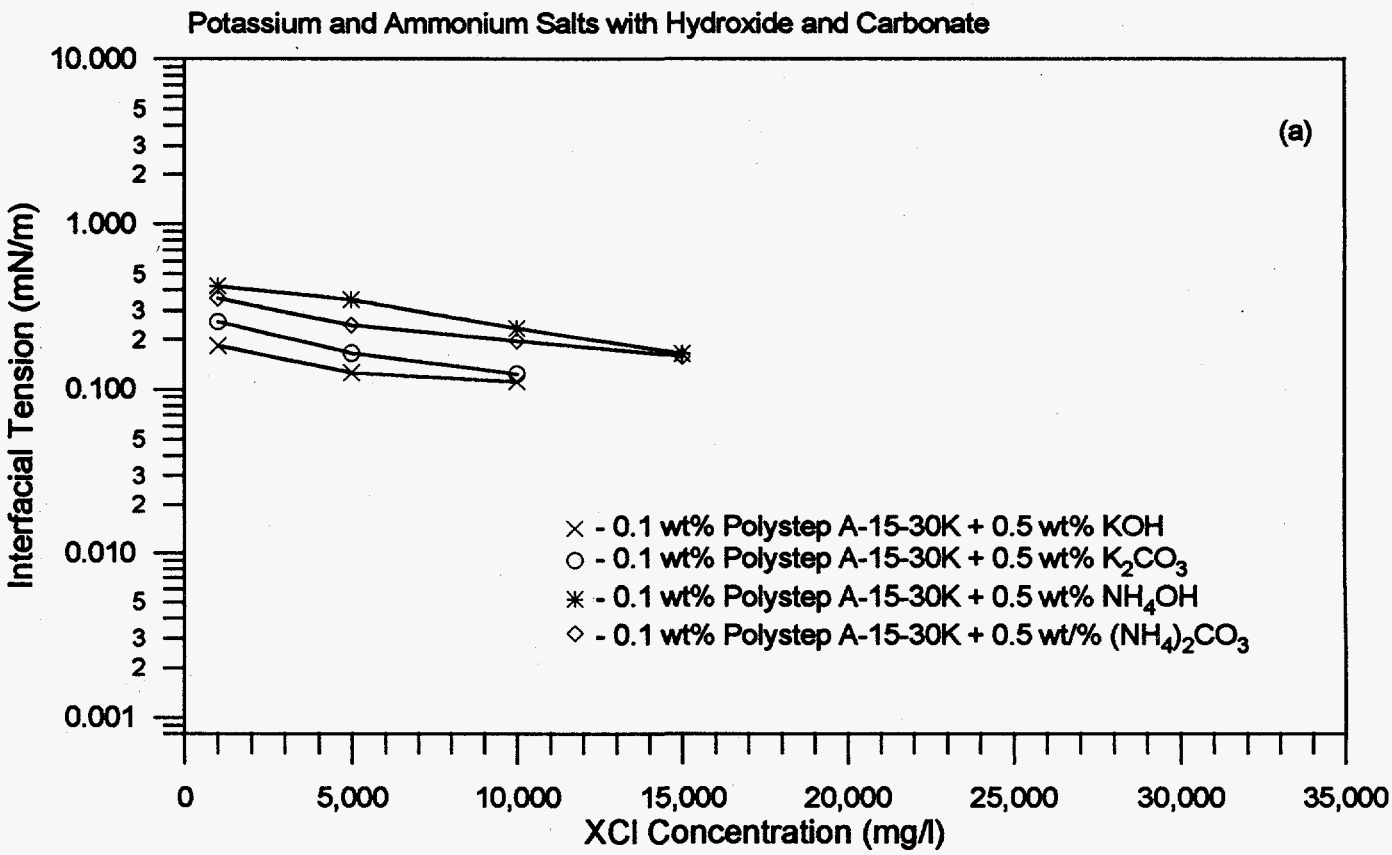


Figure 8

Increasing Salinity Effect on the Interfacial Tension between Adena Crude Oil at 72°F and Alkaline-Surfactant Solutions with Different Cations



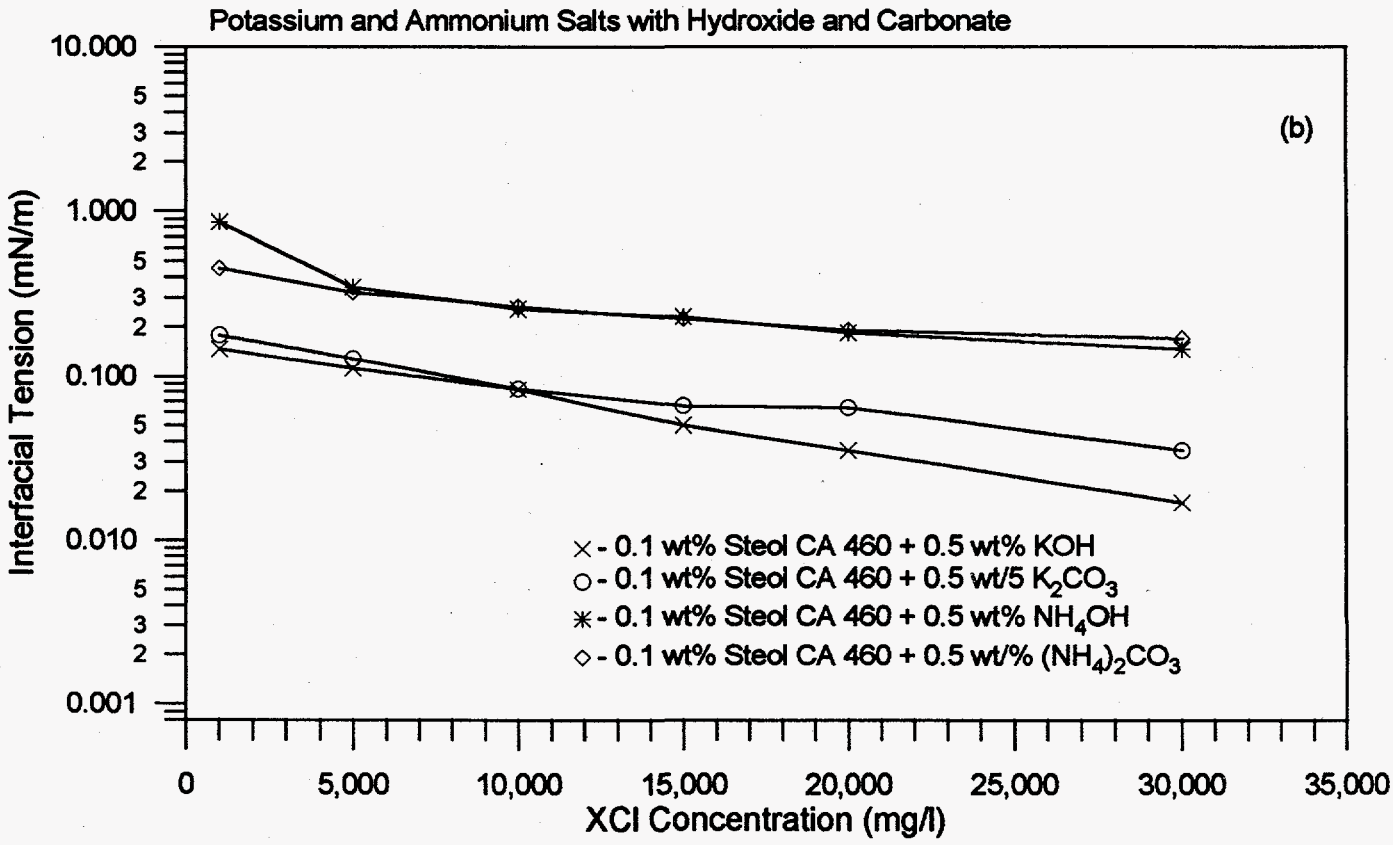
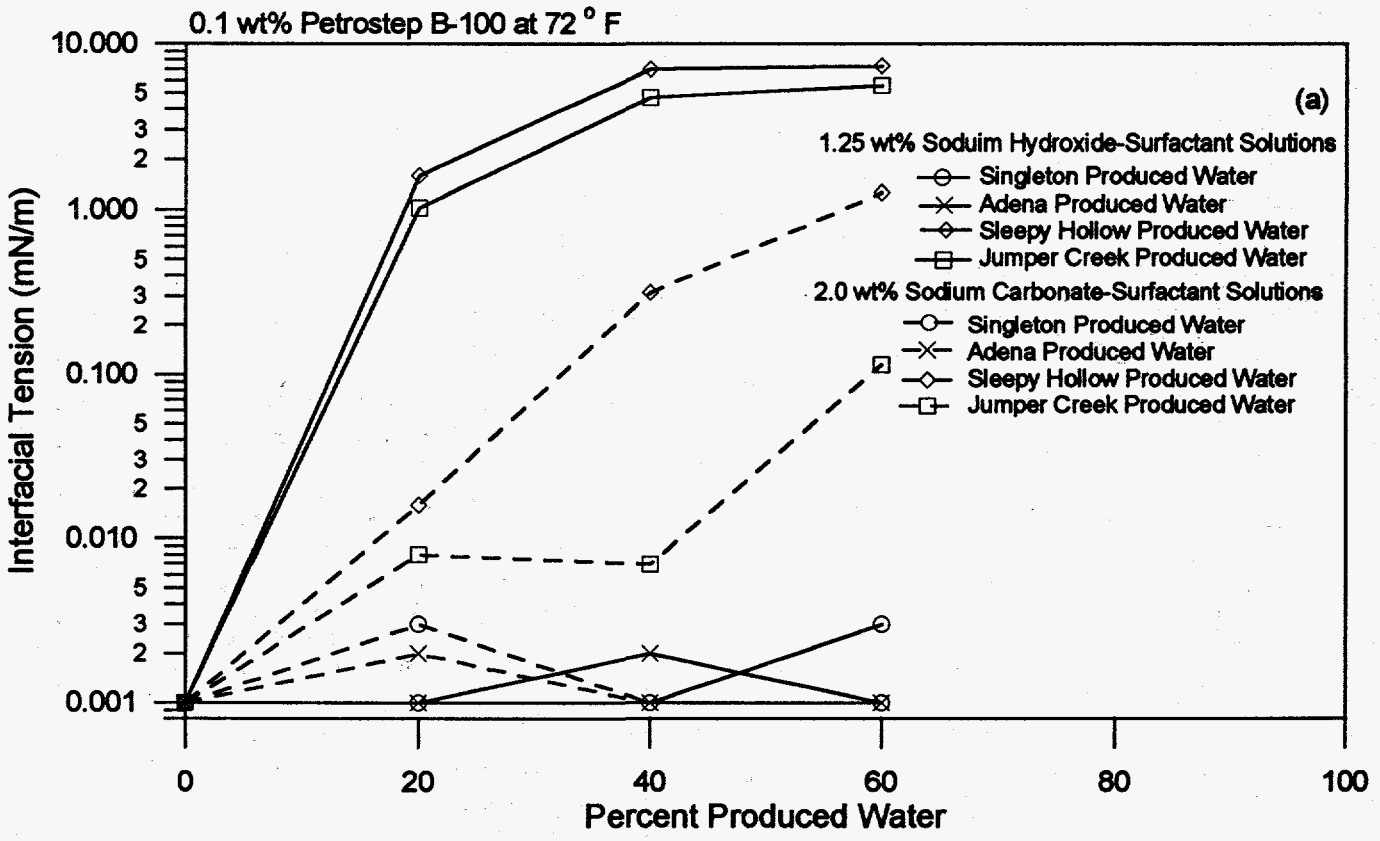


Figure 9

Produced Water Effect on the Interfacial Tension between Adena Crude Oil and Alkaline-Surfactant Solutions at 72°F and 170°F



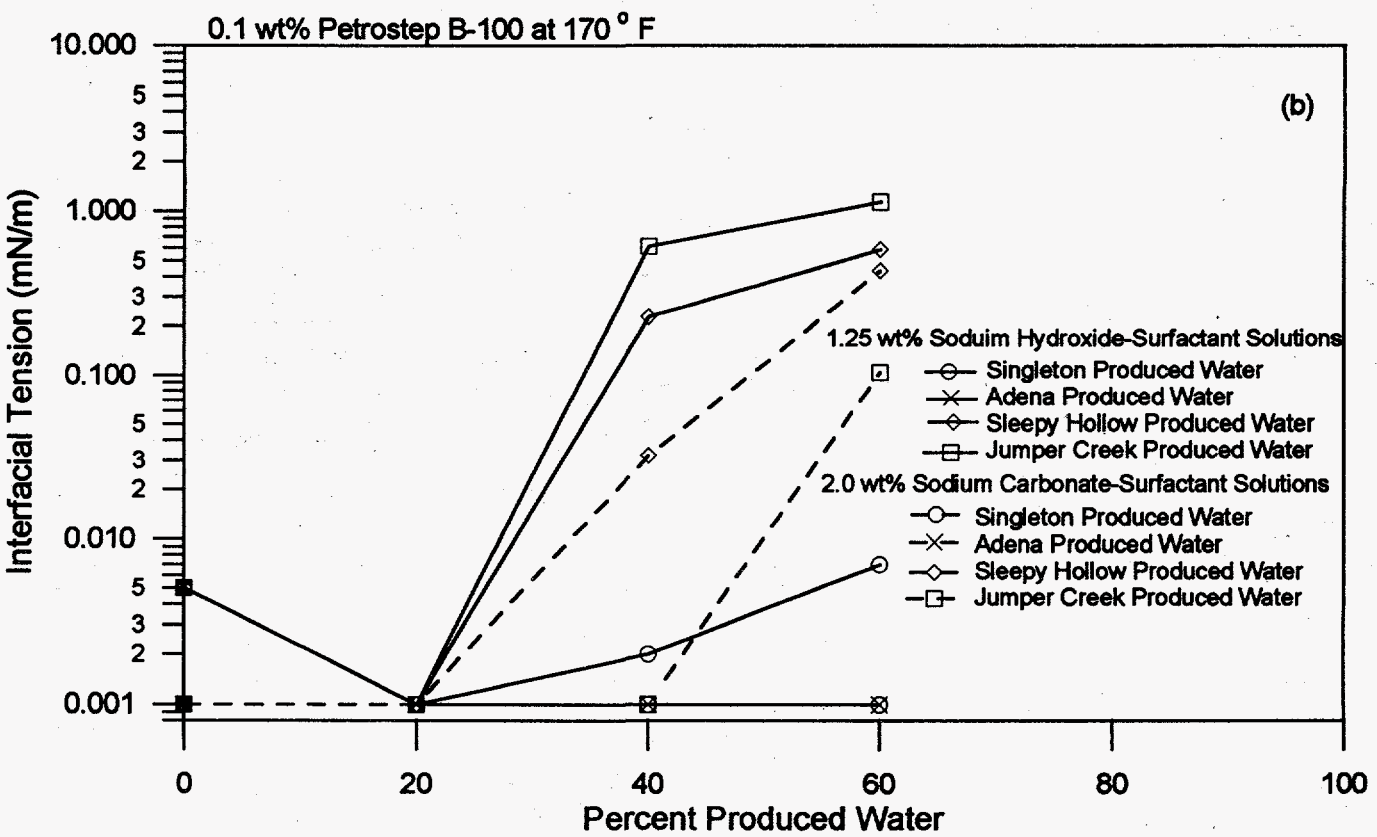
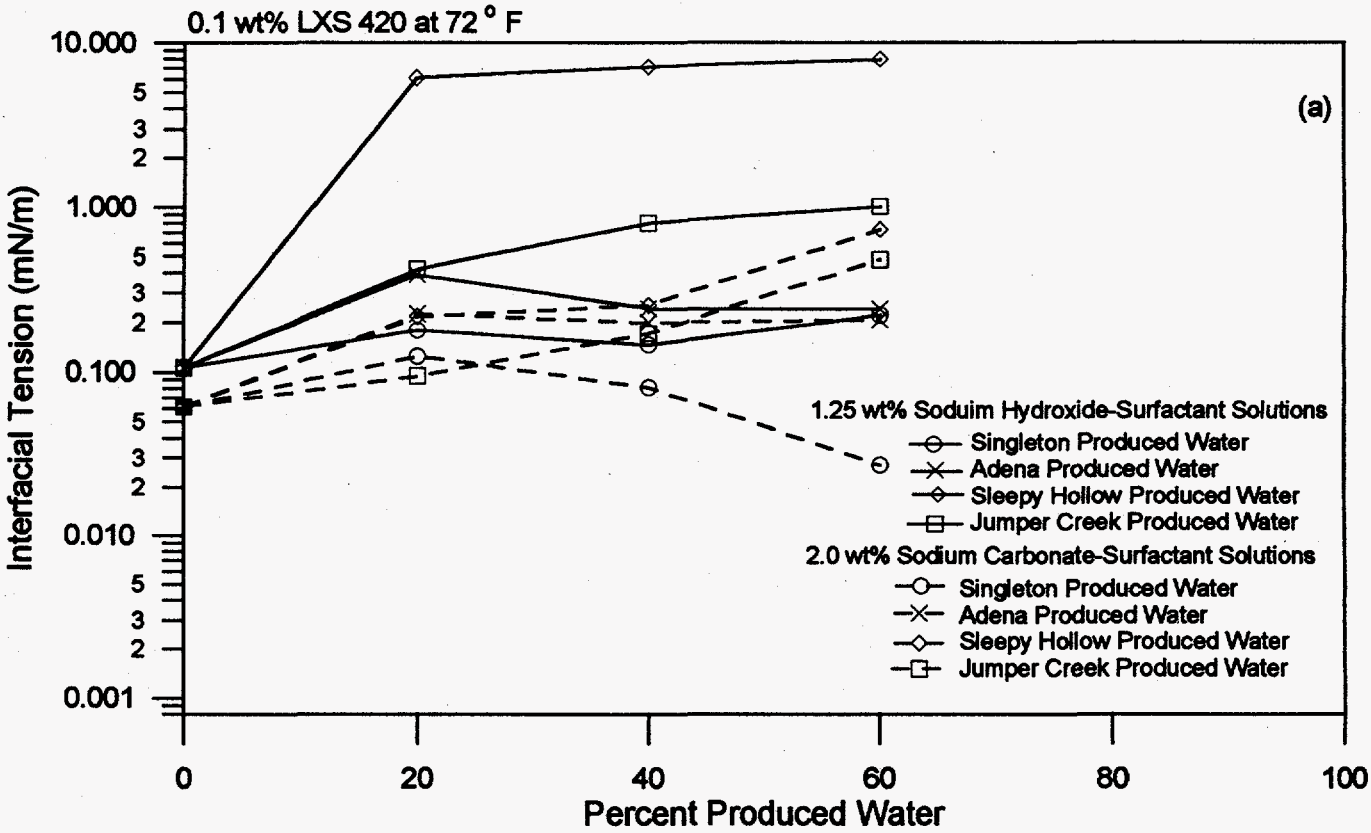


Figure 10

Produced Water Effect on the Interfacial Tension between Adena Crude Oil and Alkaline-Surfactant Solutions at 72°F and 170°F



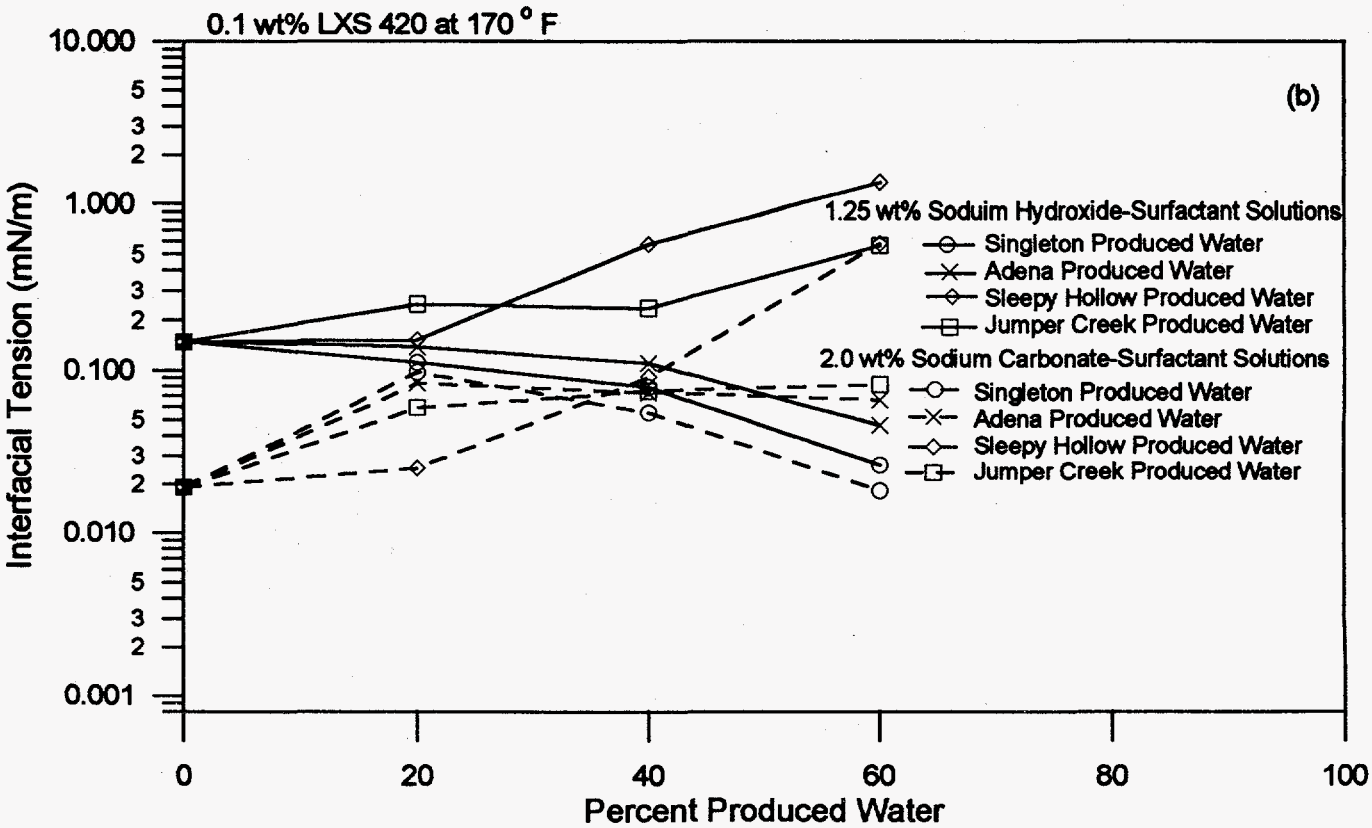
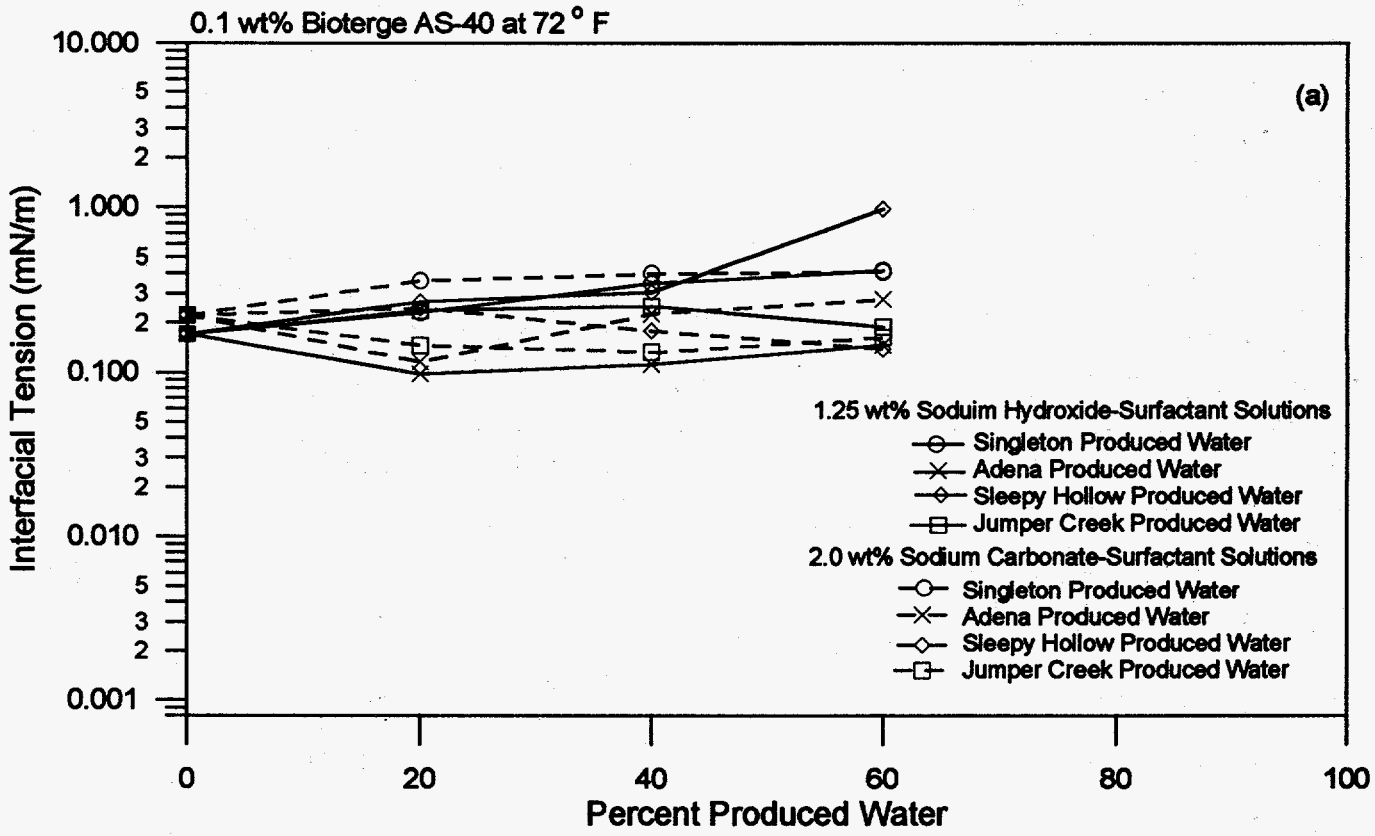


Figure 11

Produced Water Effect on the Interfacial Tension between Adena Crude Oil and Alkaline-Surfactant Solutions at 72°F and 170°F



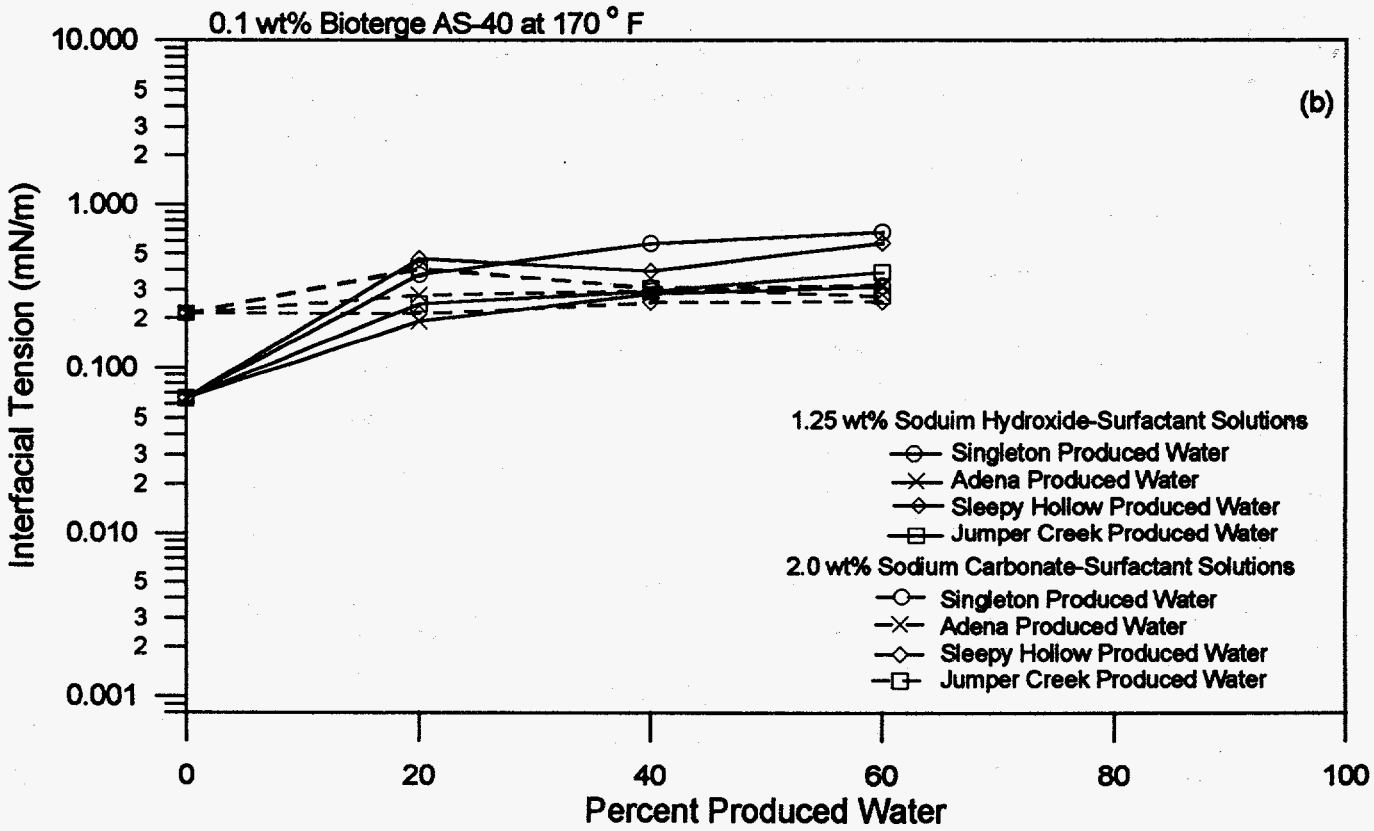


Figure 12

Alkali Effect on Surfactant Adsorption onto Crushed Berea at 30 Days versus Surfactant Molecular Weight

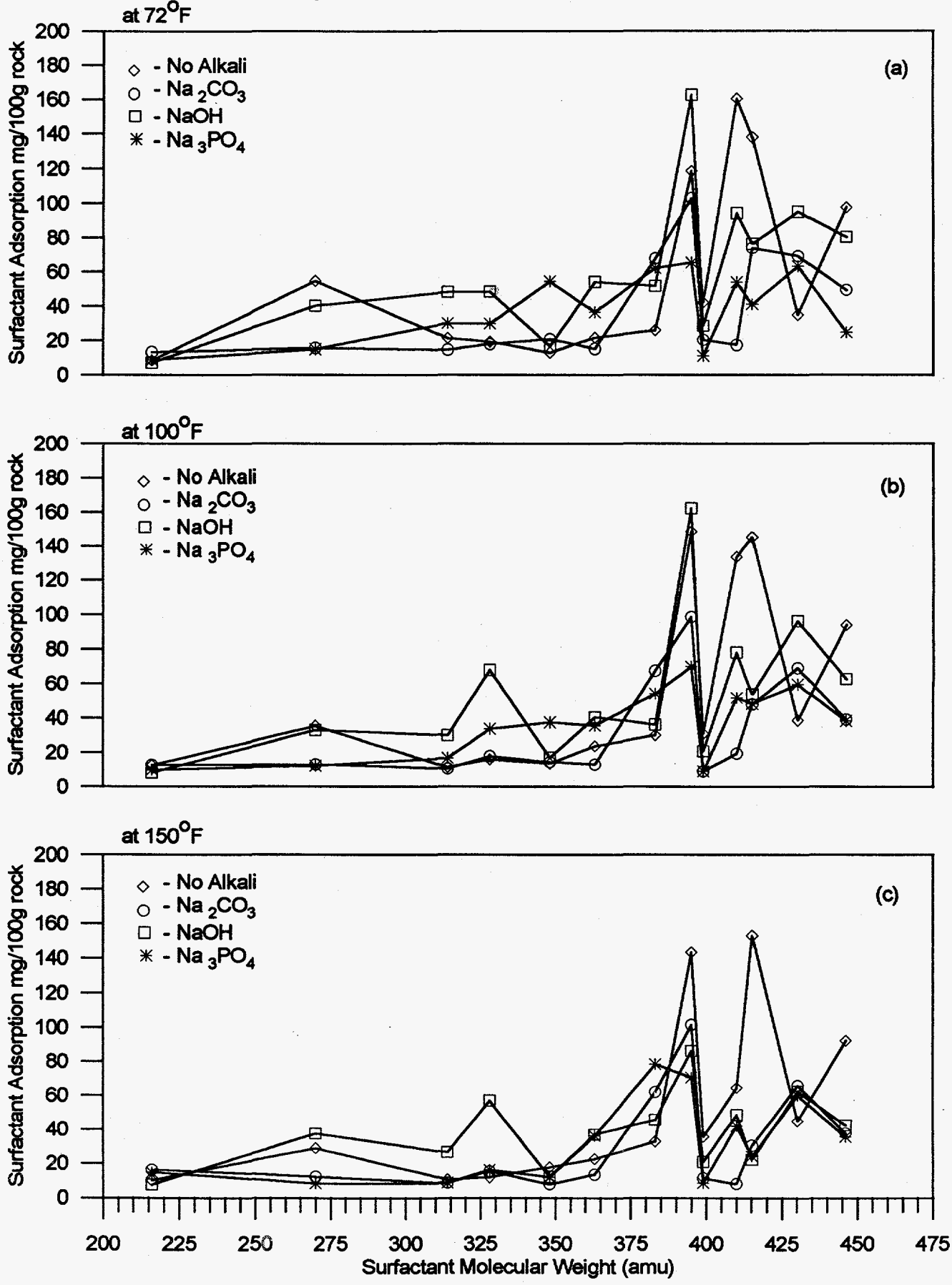
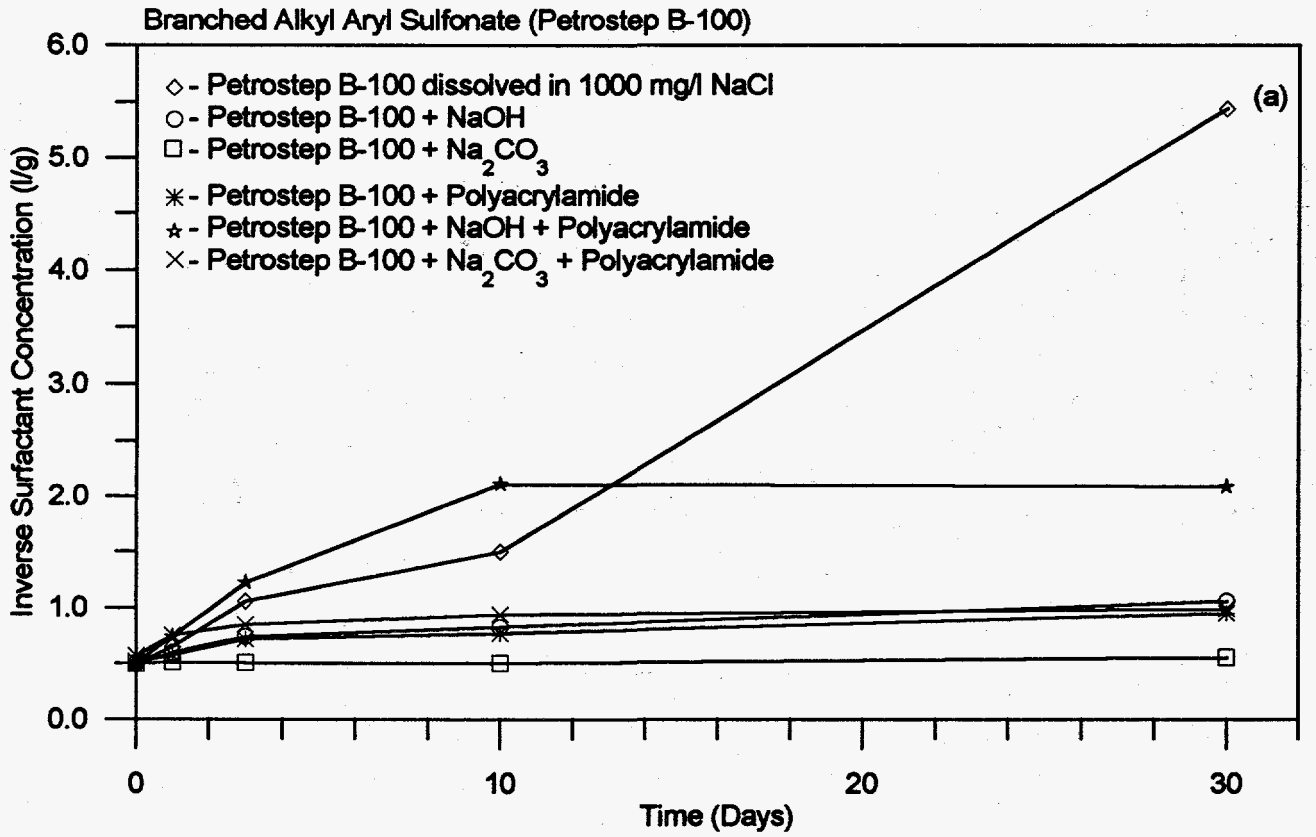


Figure 13

Inverse Surfactant and Polymer Concentration versus Time



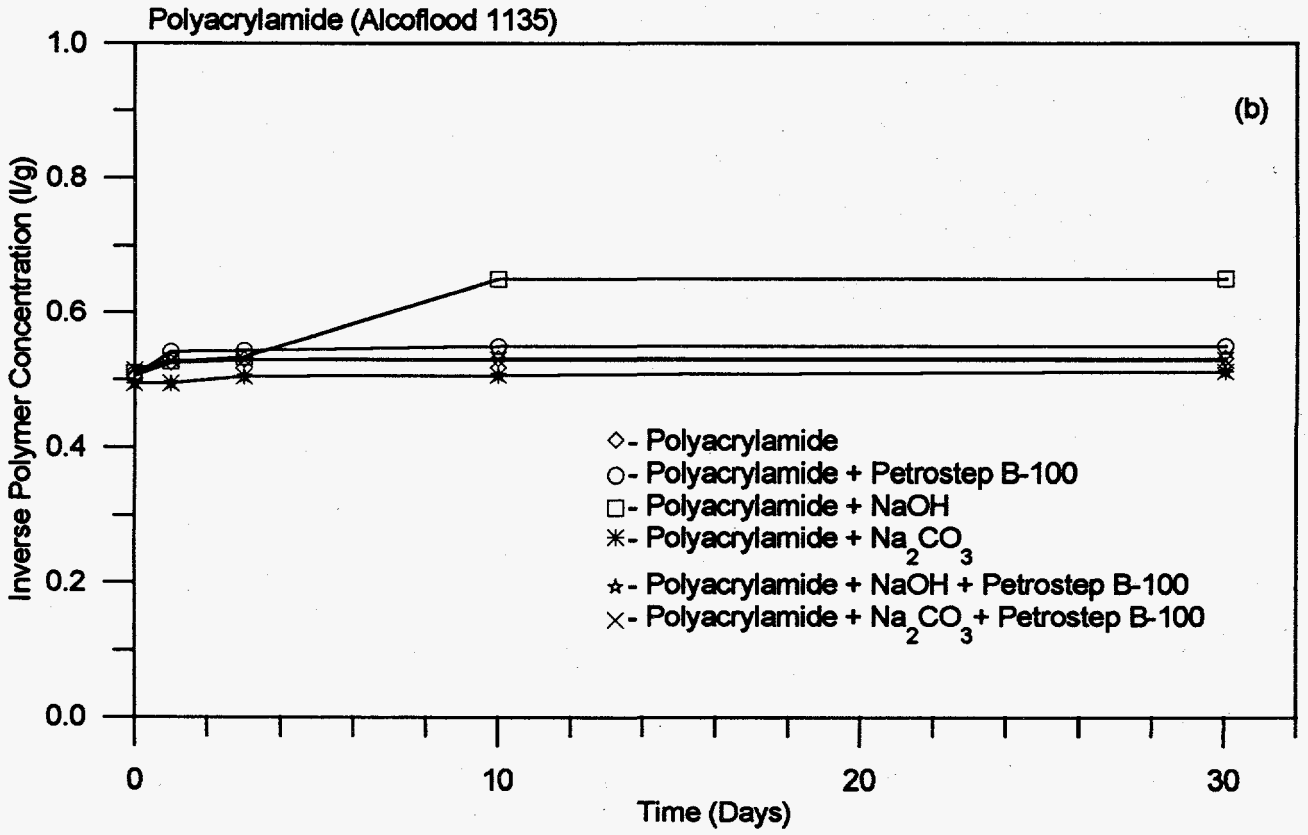
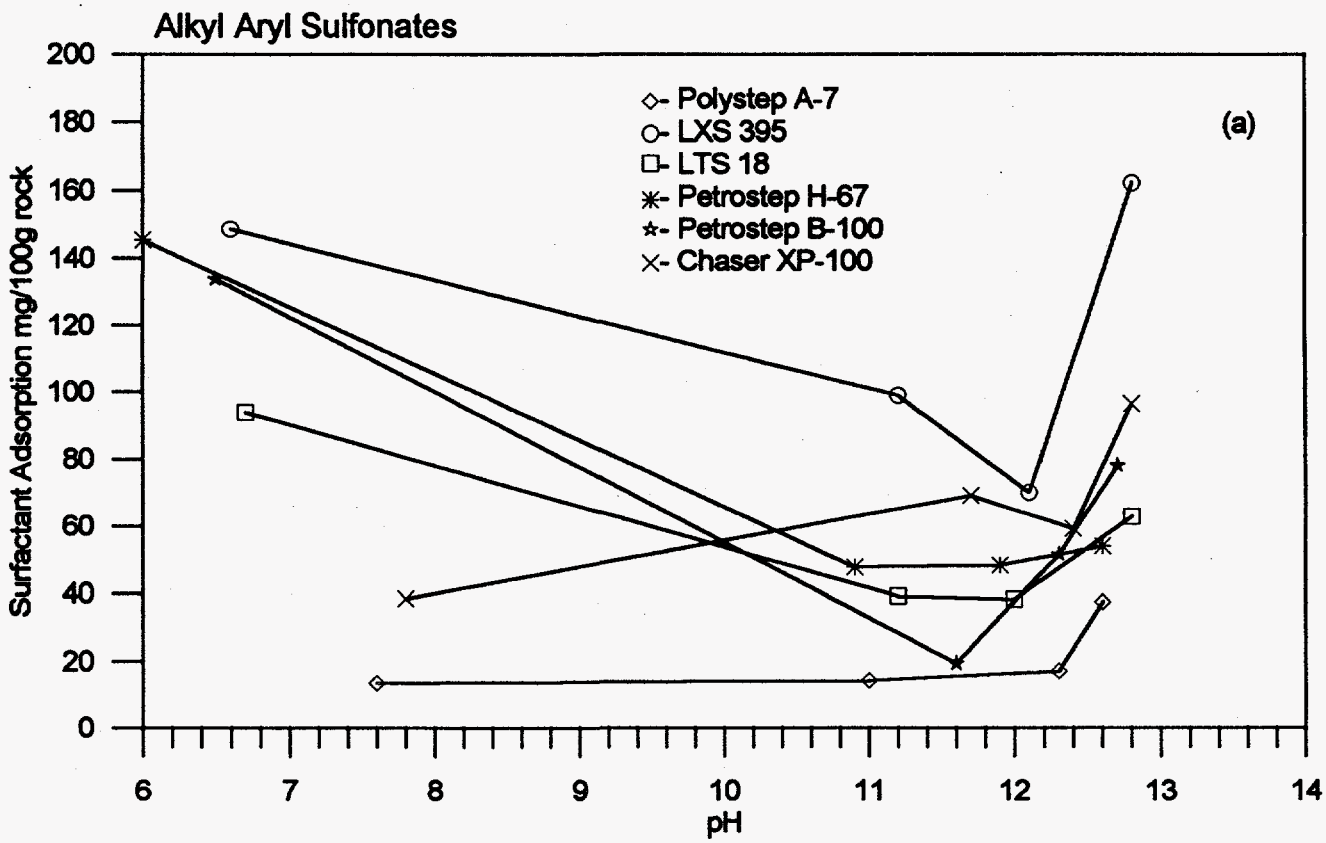


Figure 14

Surfactant Adsorption at 100°F versus pH



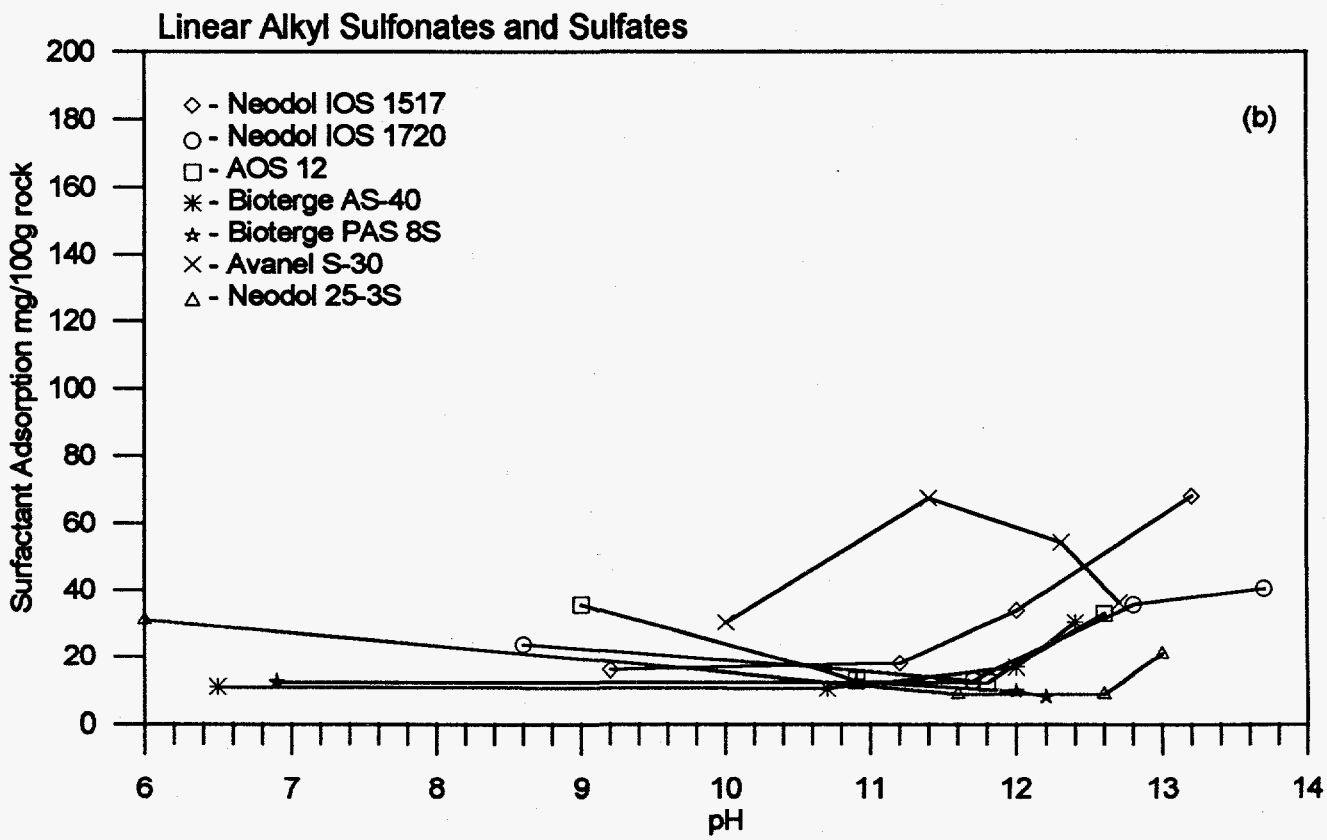
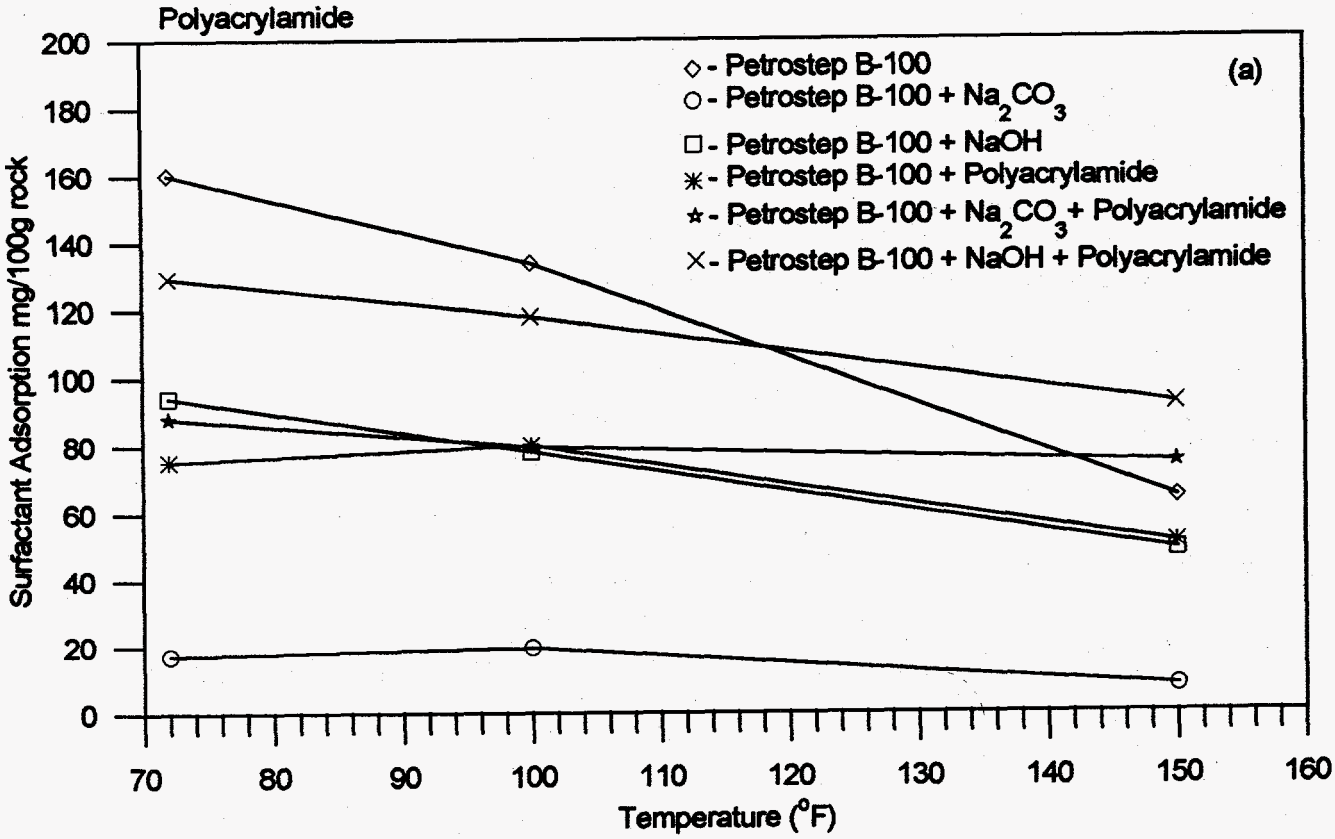


Figure 15

Temperature Effect on Alkyl Aryl Sulfonate Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Alkali and Polymer



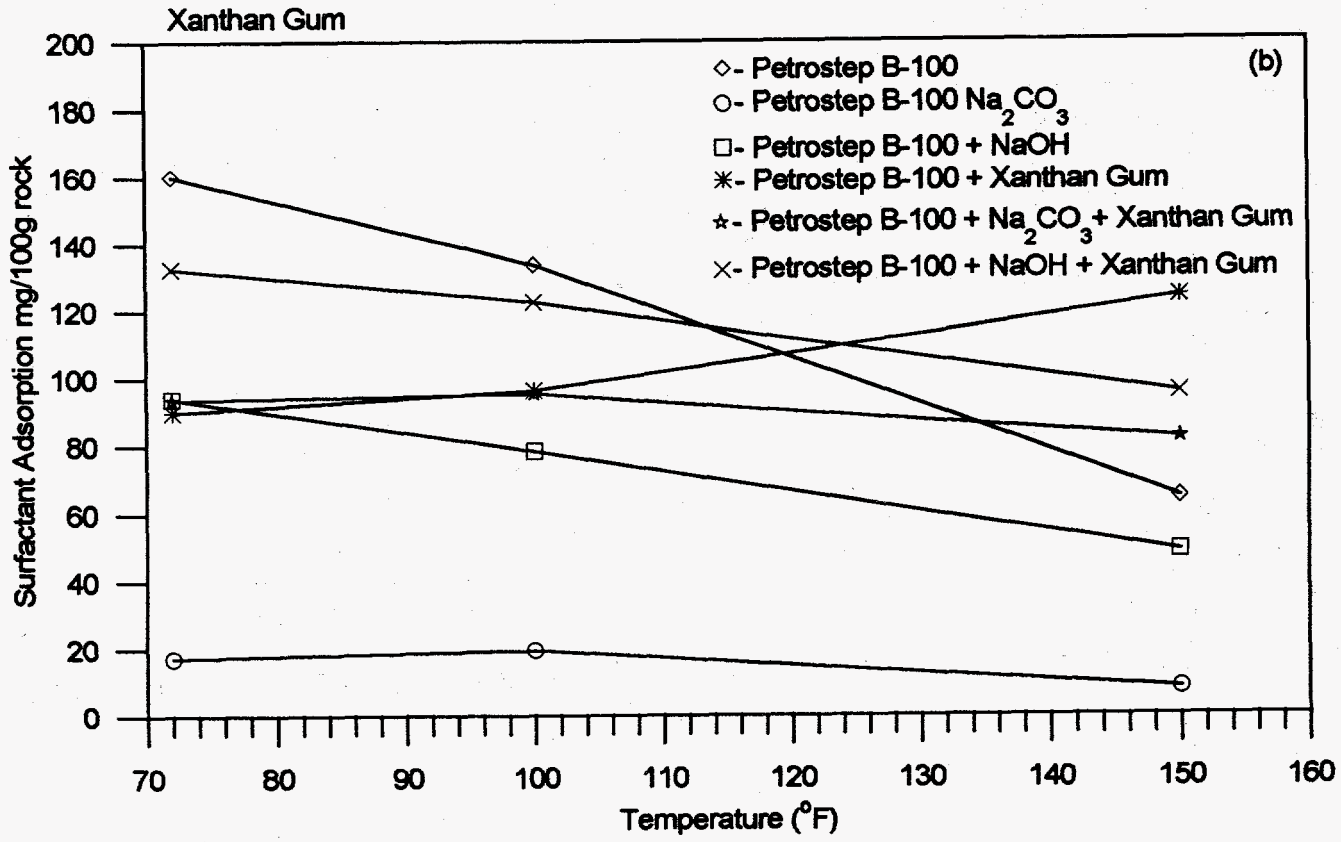
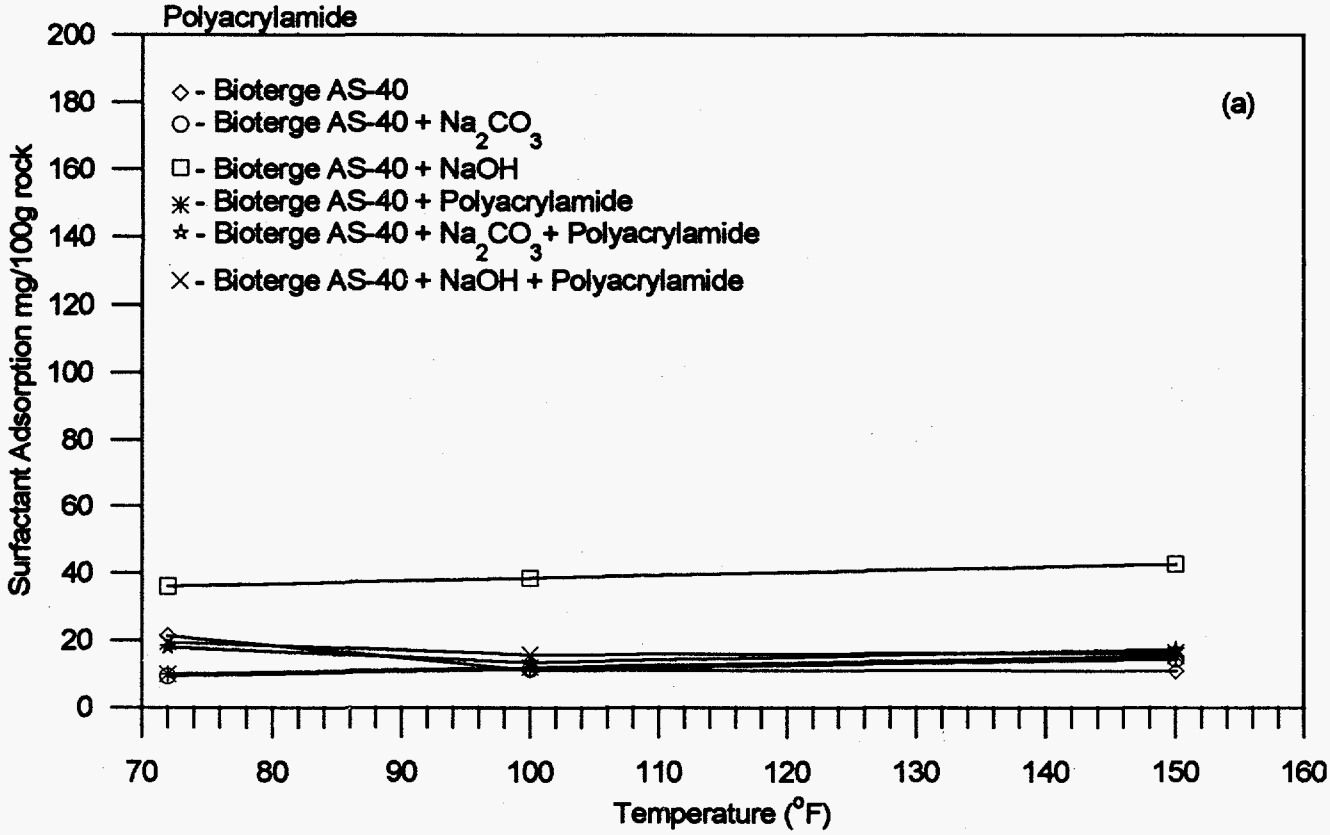


Figure 16

Temperature Effect on Alpha Olefin Sulfonate Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Alkali and Polymer



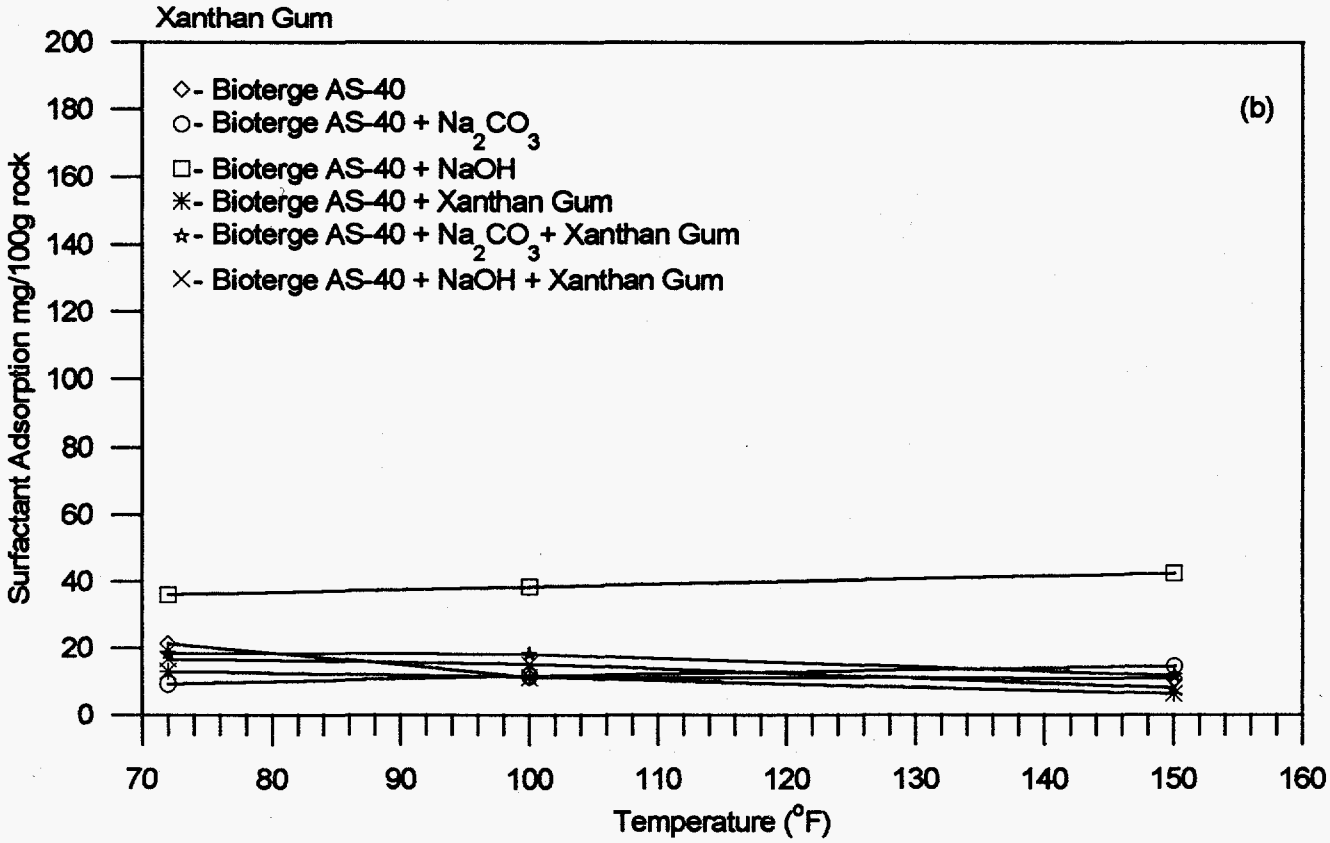
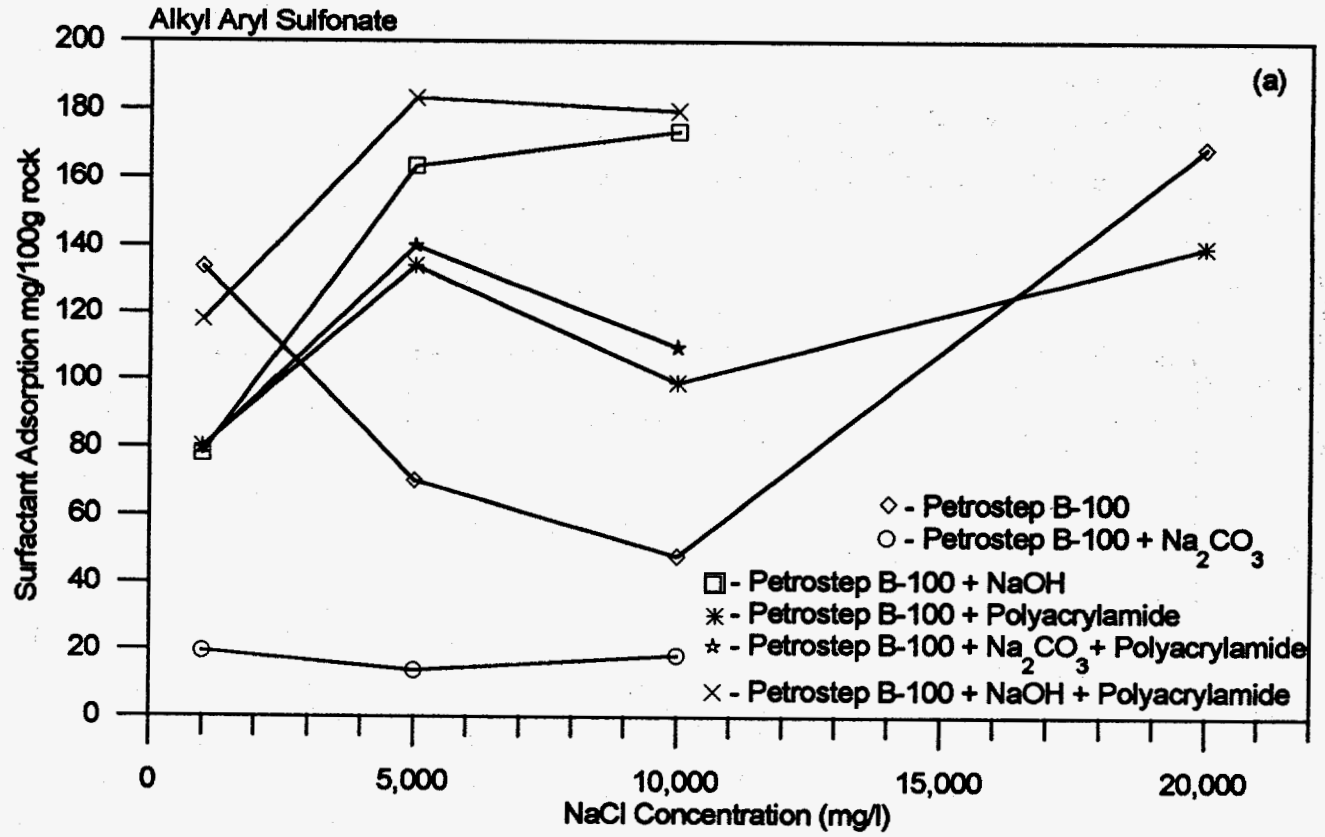


Figure 17

Increasing Salinity Effect on Surfactant Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Alkali and Polymer



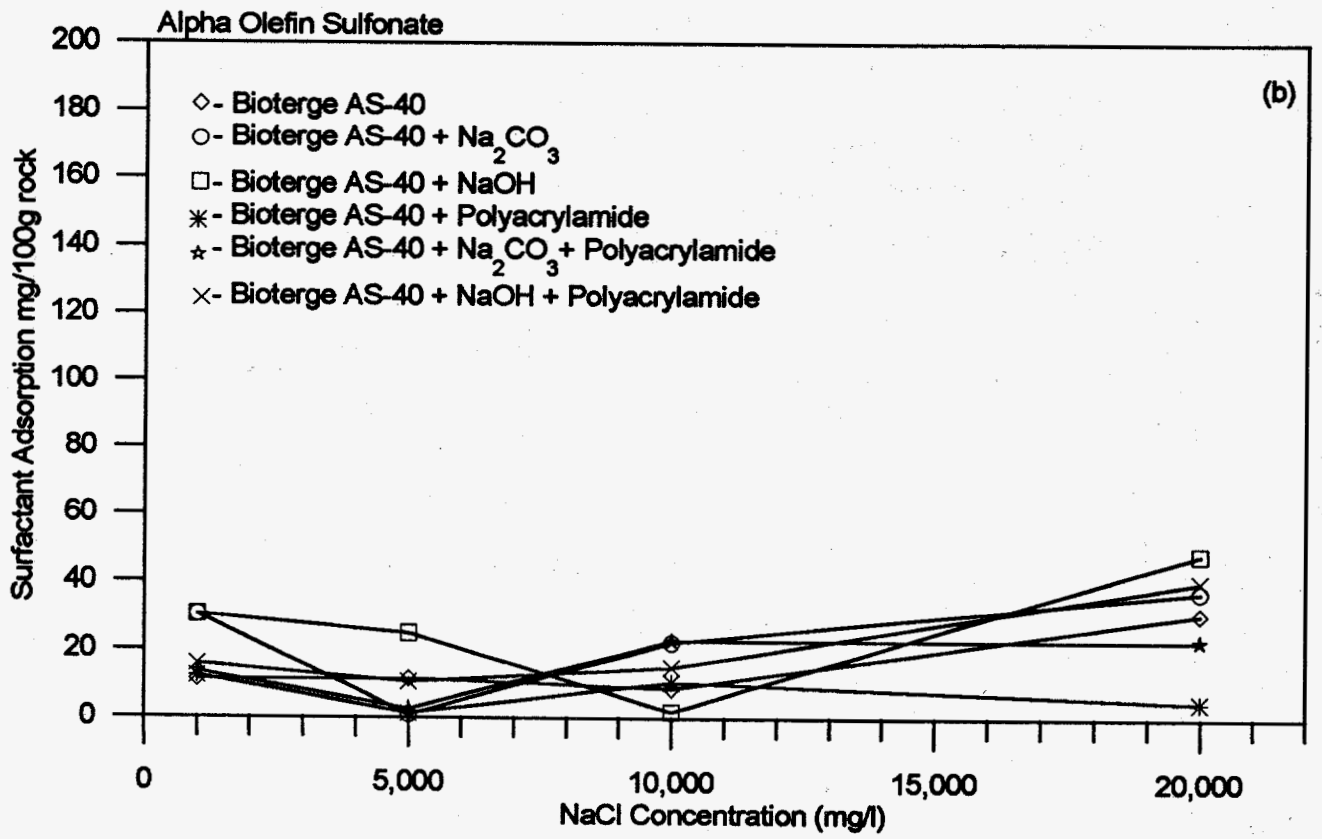
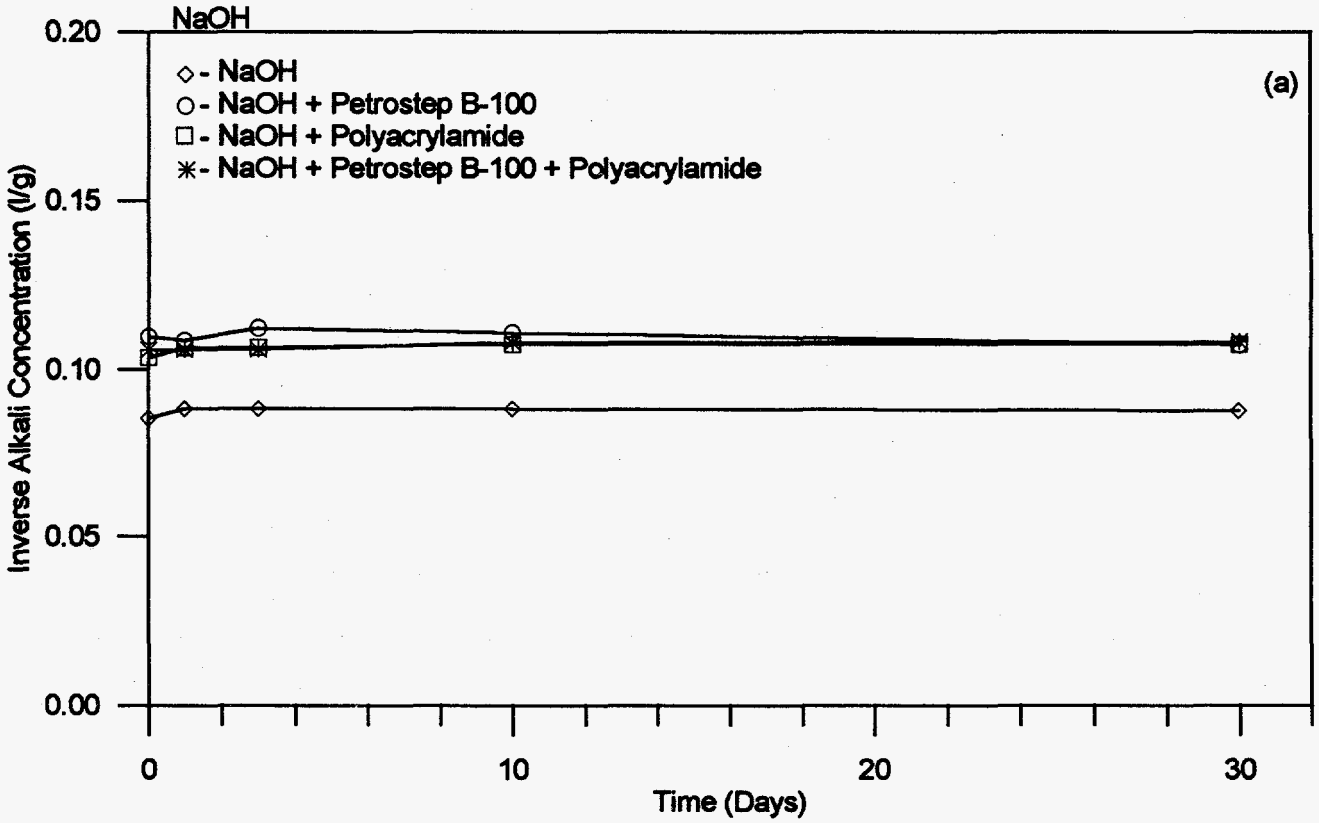


Figure 18

Polymer and Surfactant Effect on Inverse Alkali Concentration versus Time



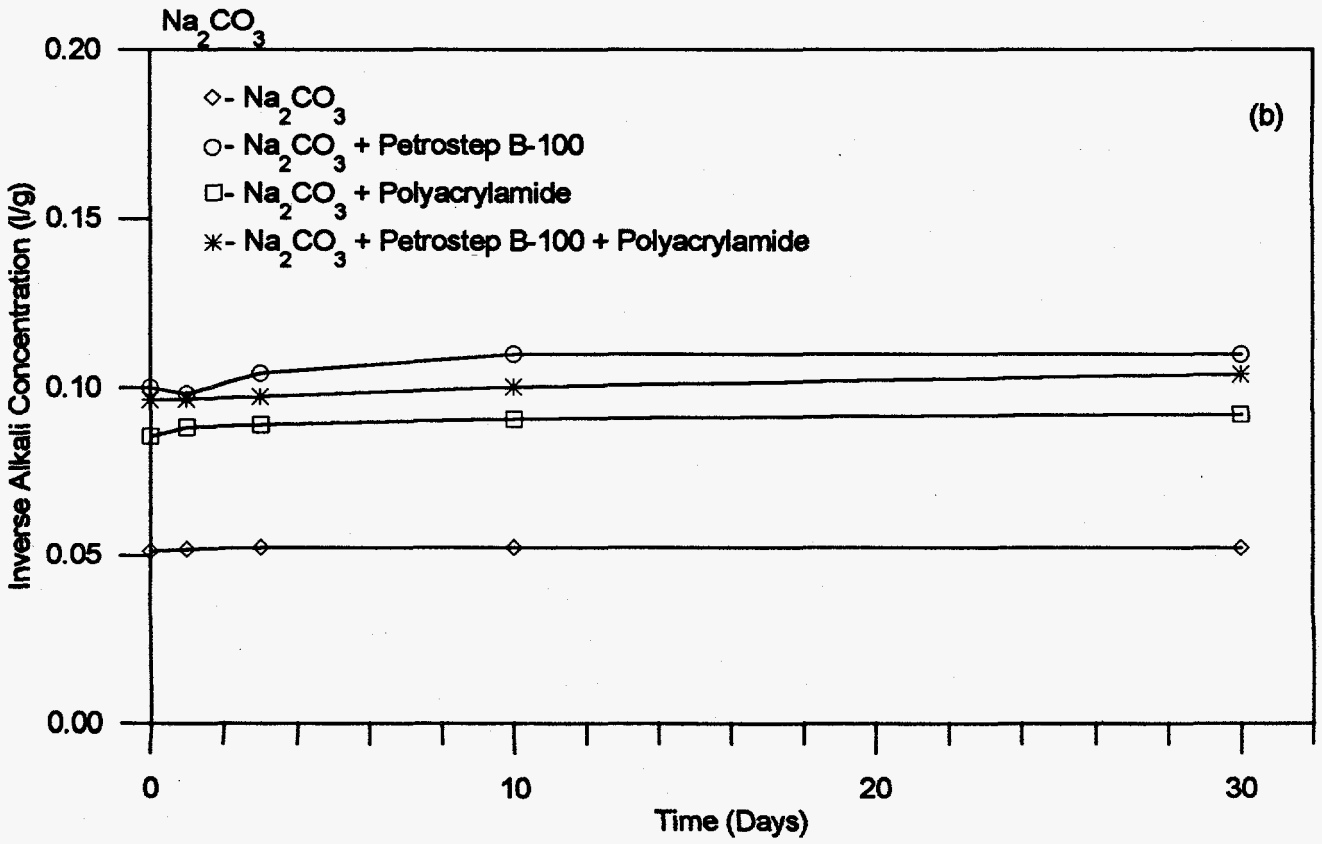


Figure 19

Surfactant Effect on Alkali Adsorption onto Crushed Berea versus Temperature

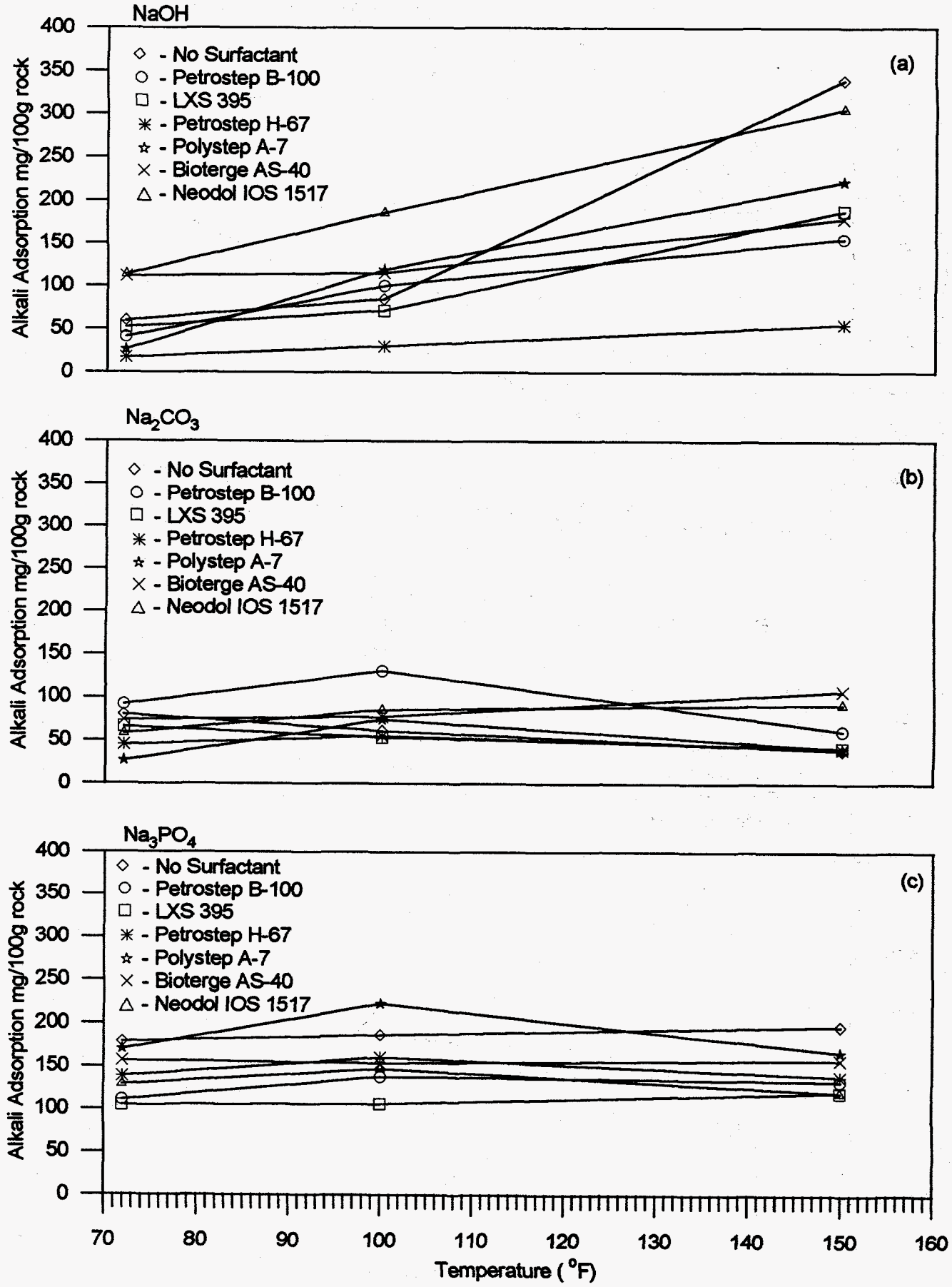
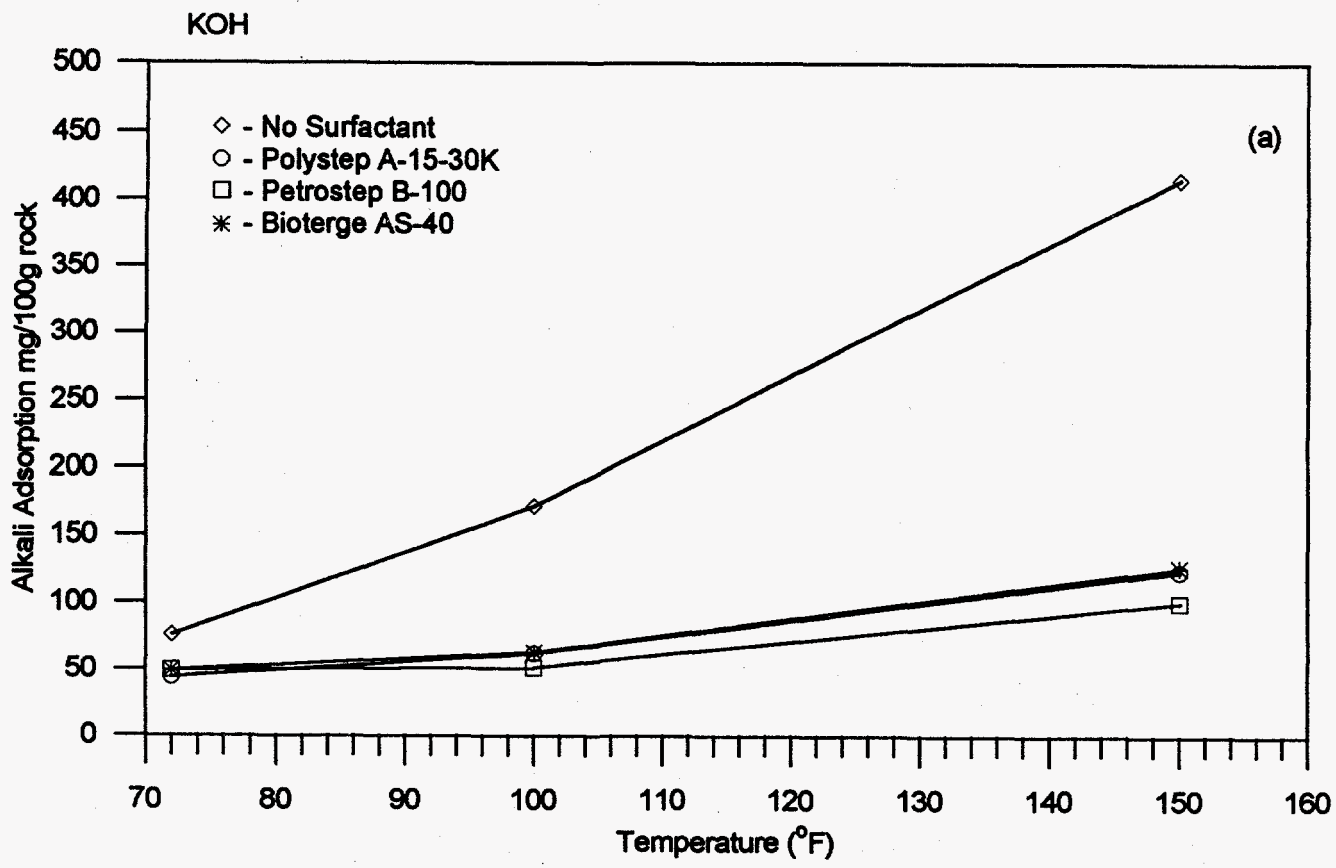


Figure 20

Surfactant Effect on Potassium Alkali Adsorption onto Crushed Berea at 30 Days versus Temperature



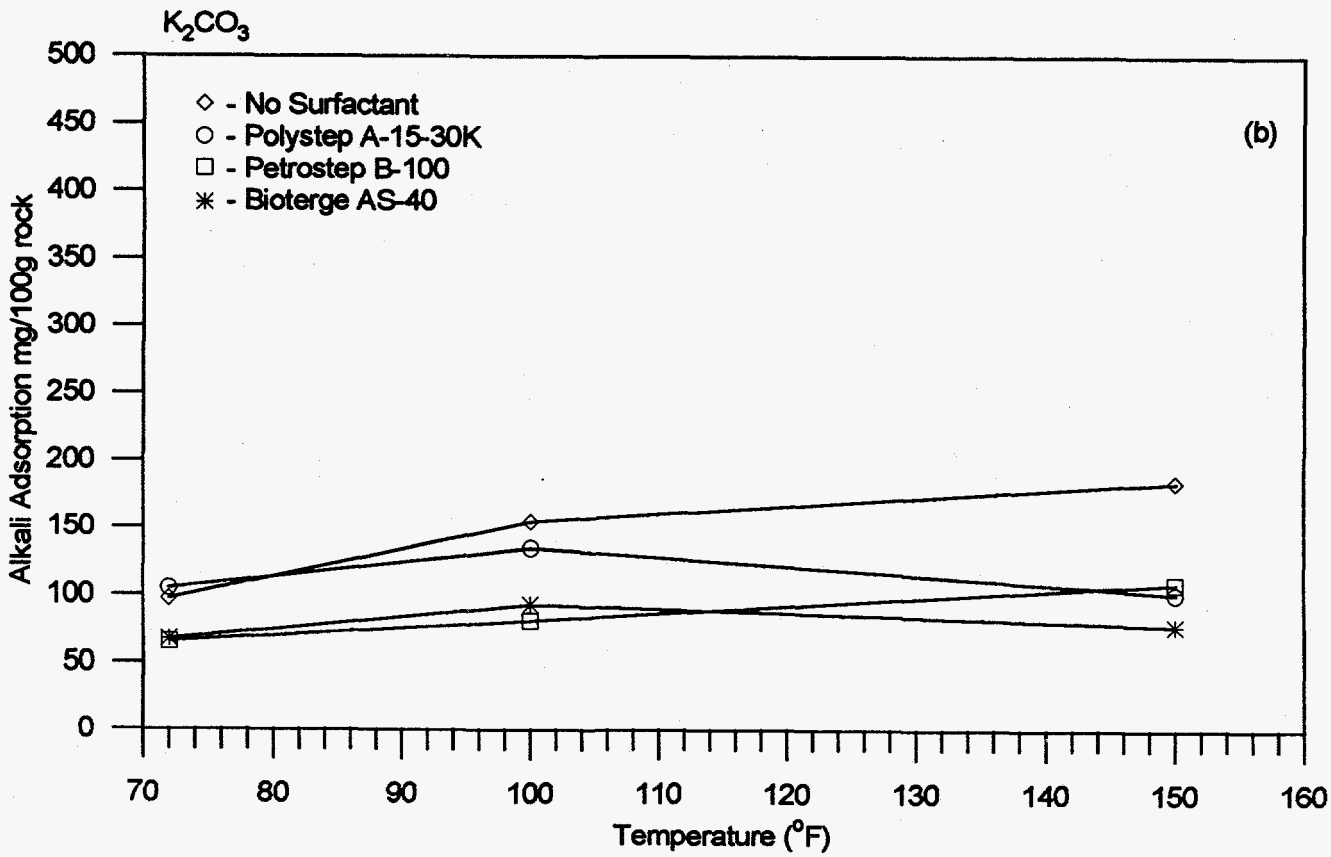
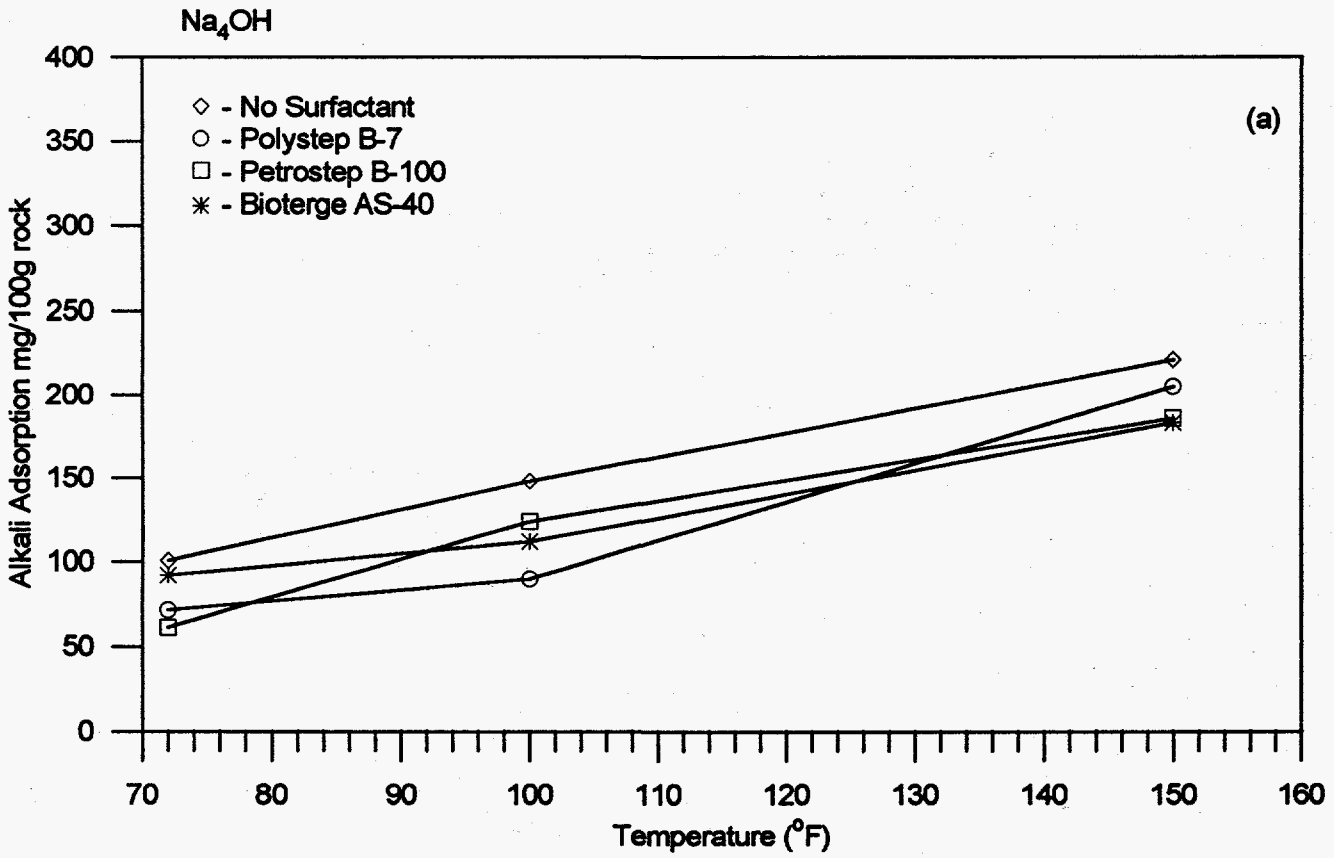


Figure 21

Surfactant Effect on Ammonium Alkali Adsorption onto Crushed Berea at 30 Days versus Temperature



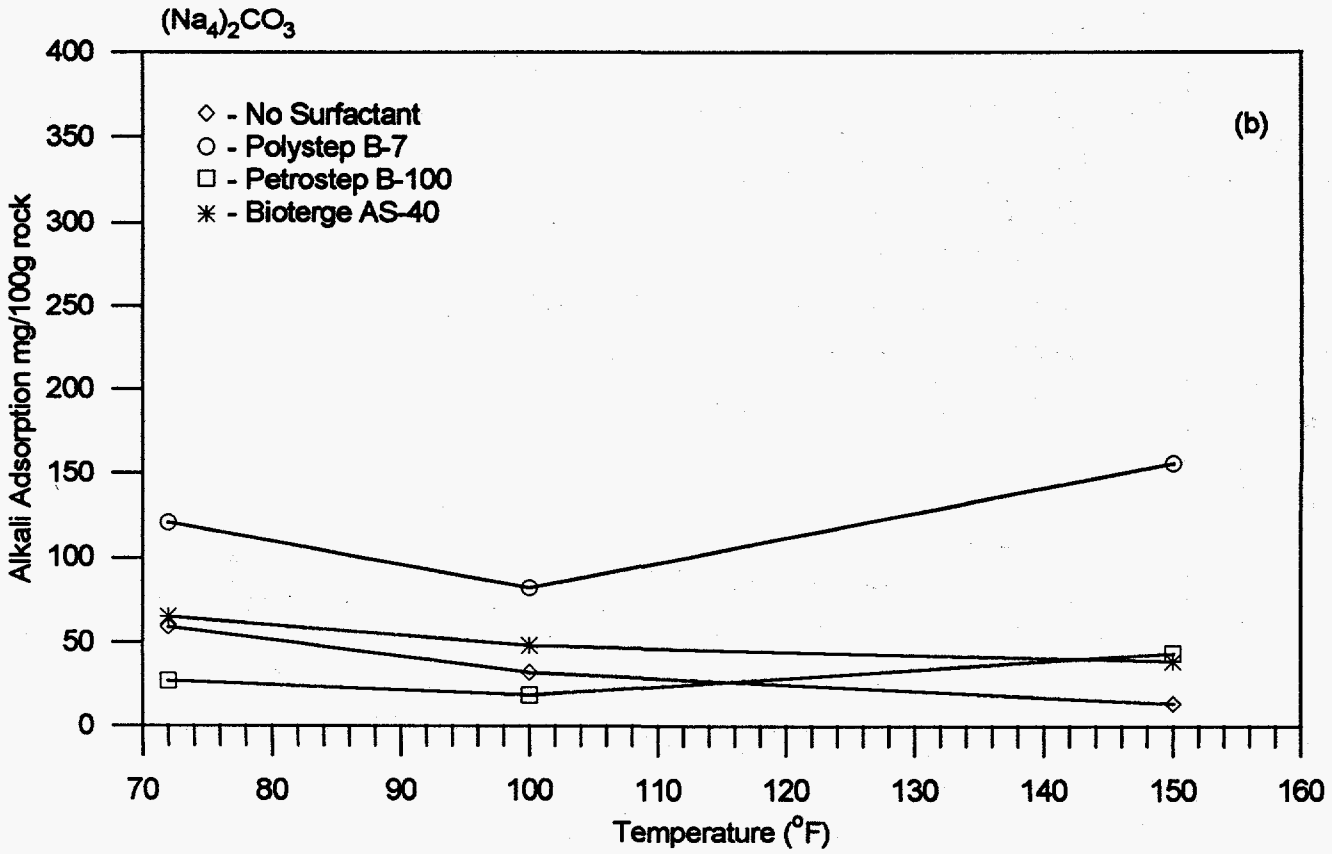
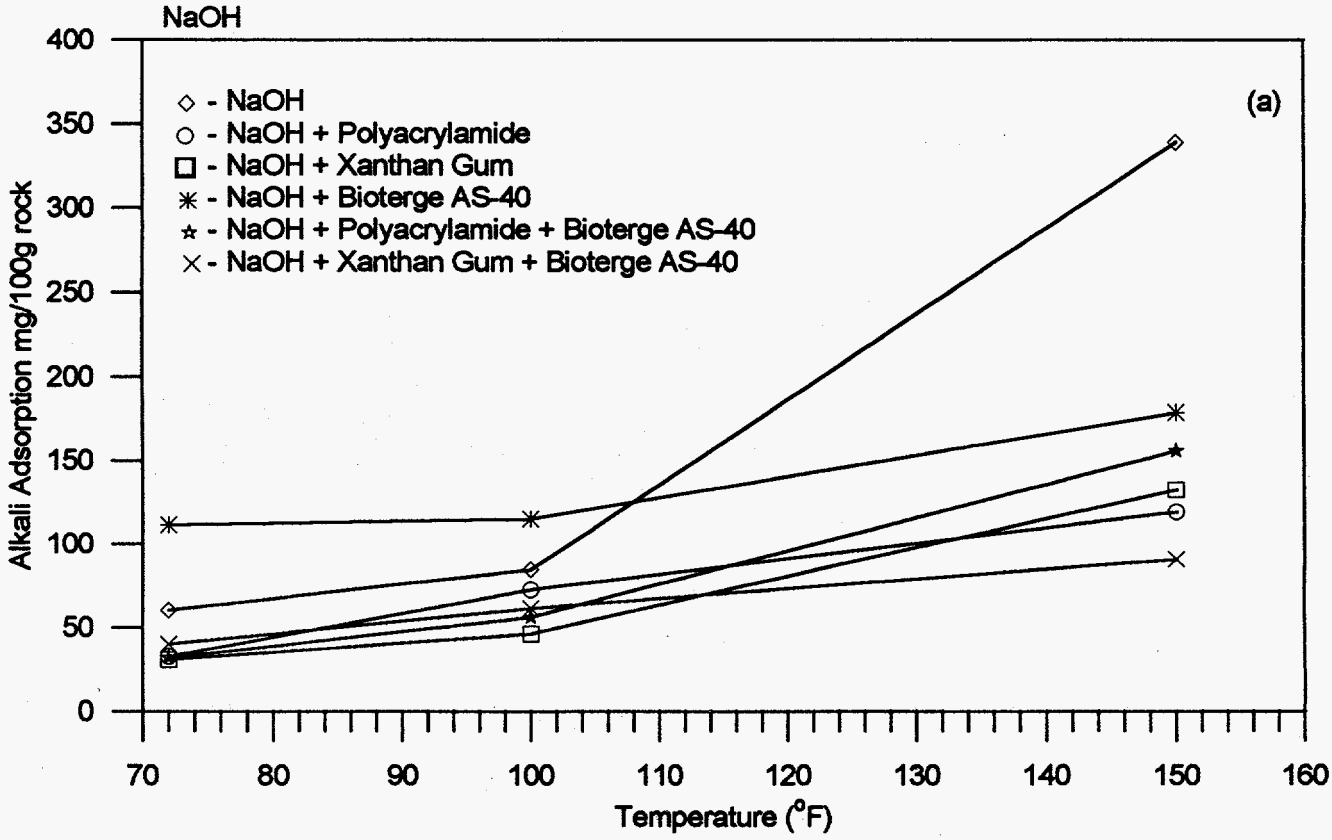


Figure 22

Temperature Effect on Alkali Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Polymer and Surfactant



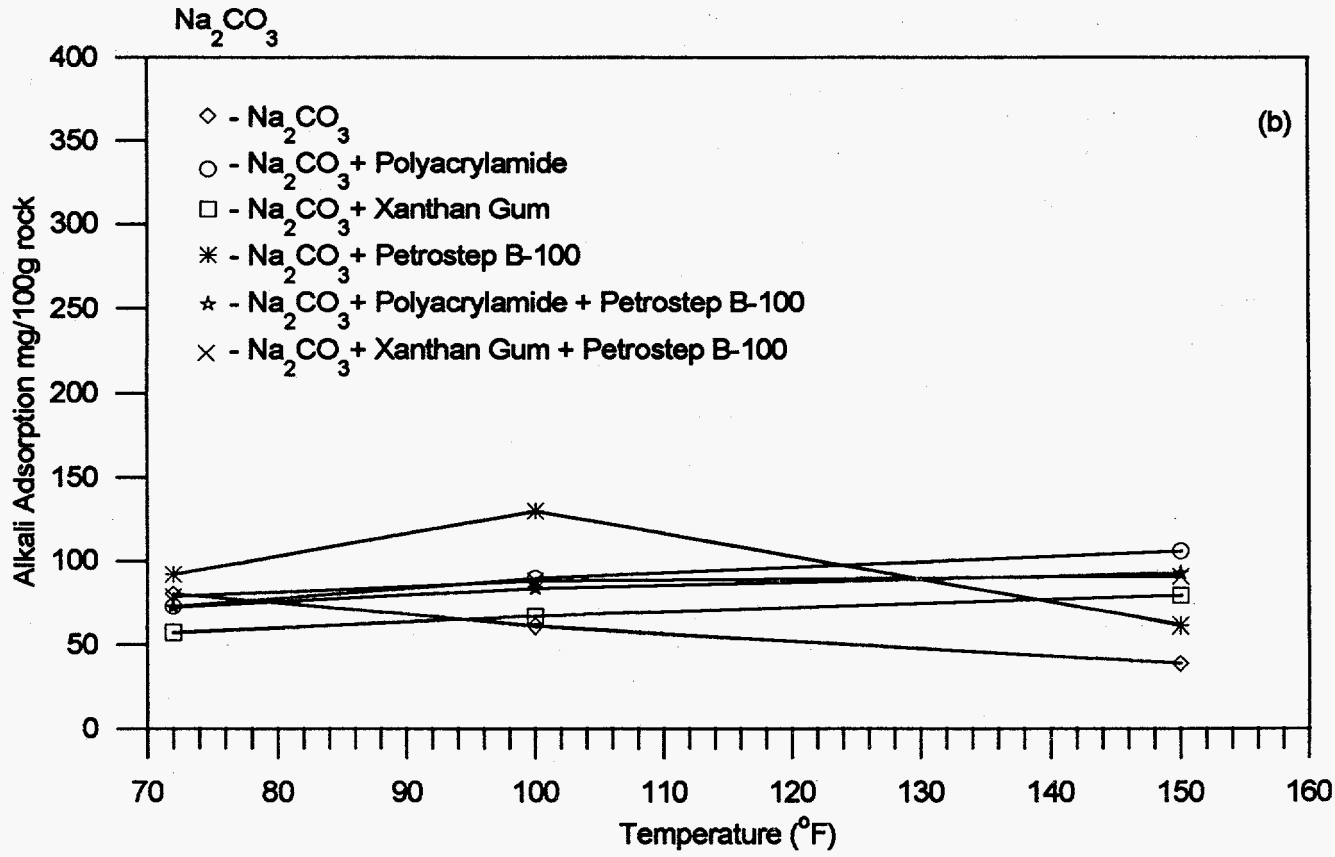
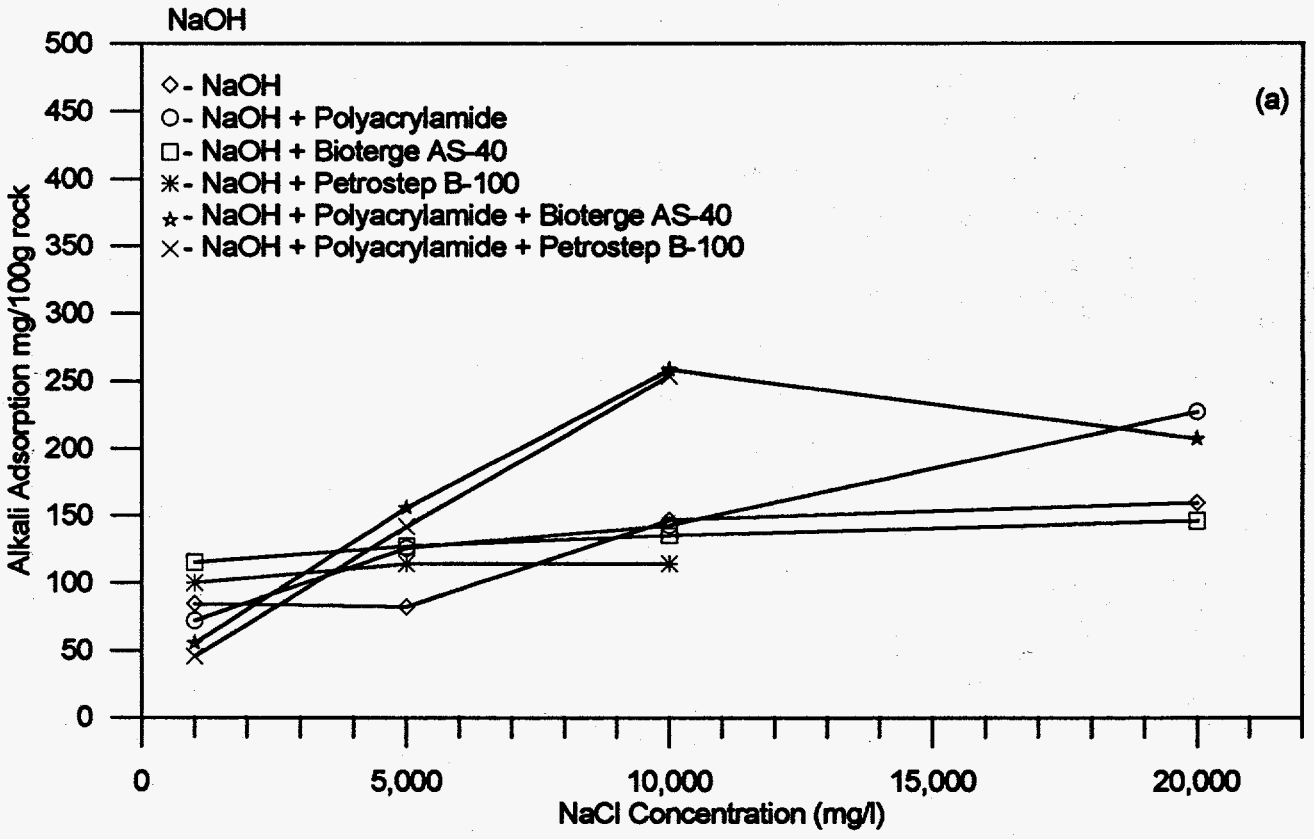


Figure 23

Increasing Salinity Effect on Alkali Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Surfactant and Polymer



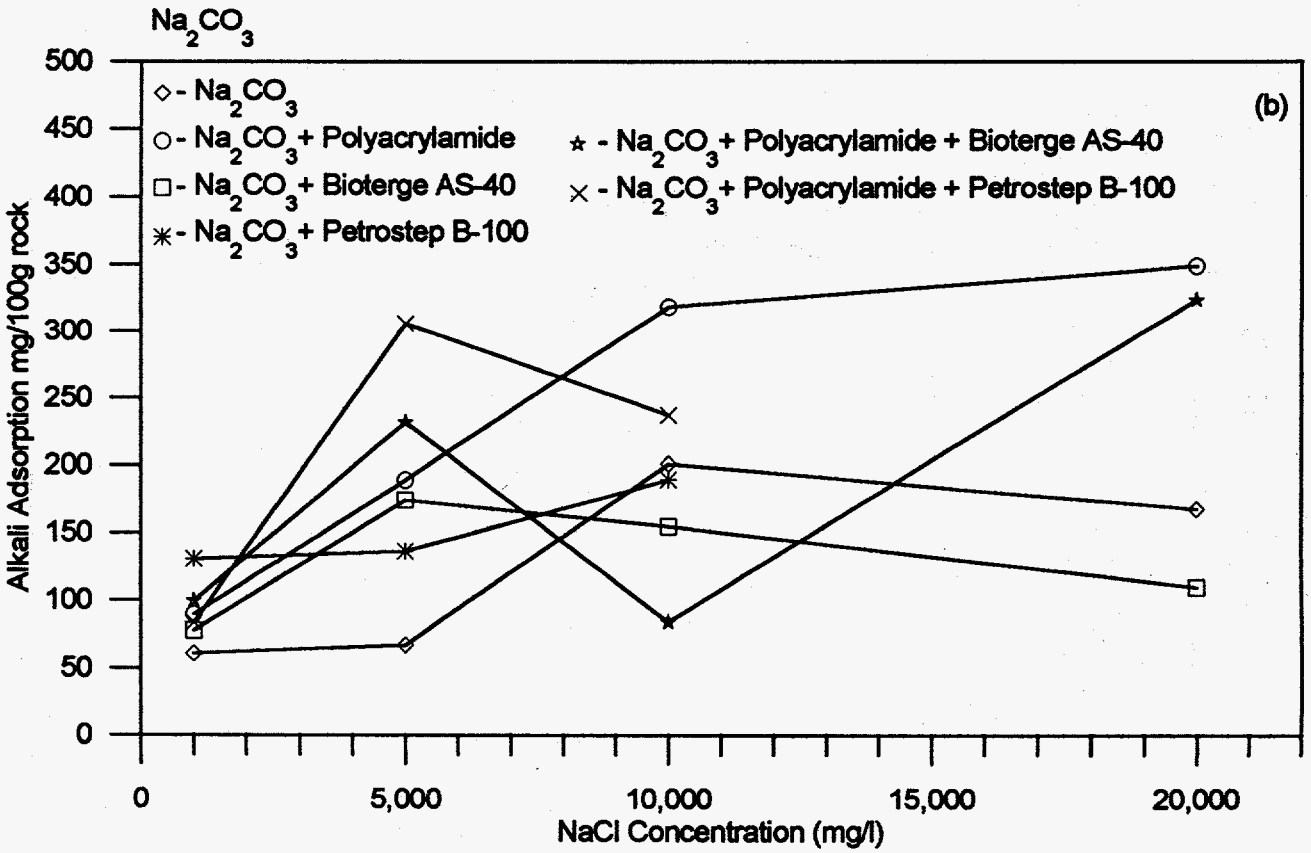
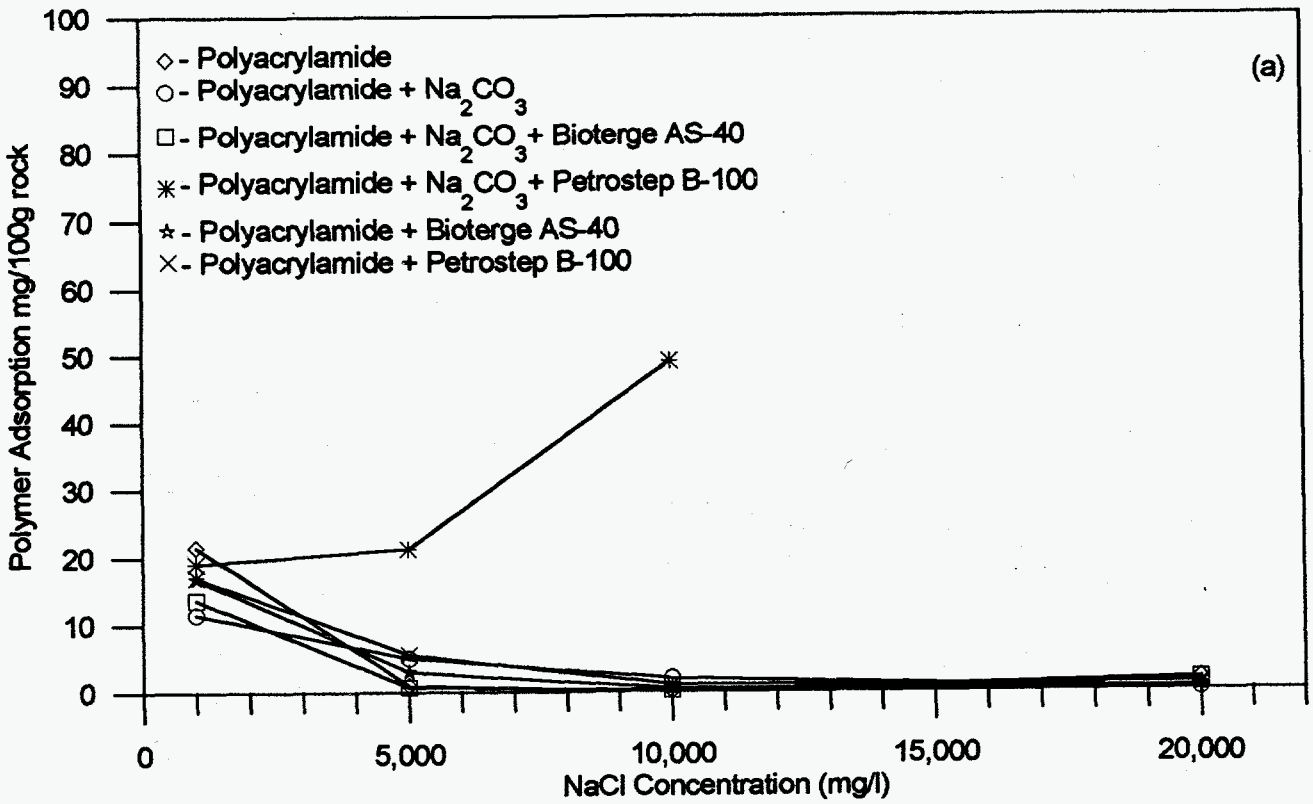


Figure 24

Increasing Salinity Effect on Polymer Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Alkali and Surfactant



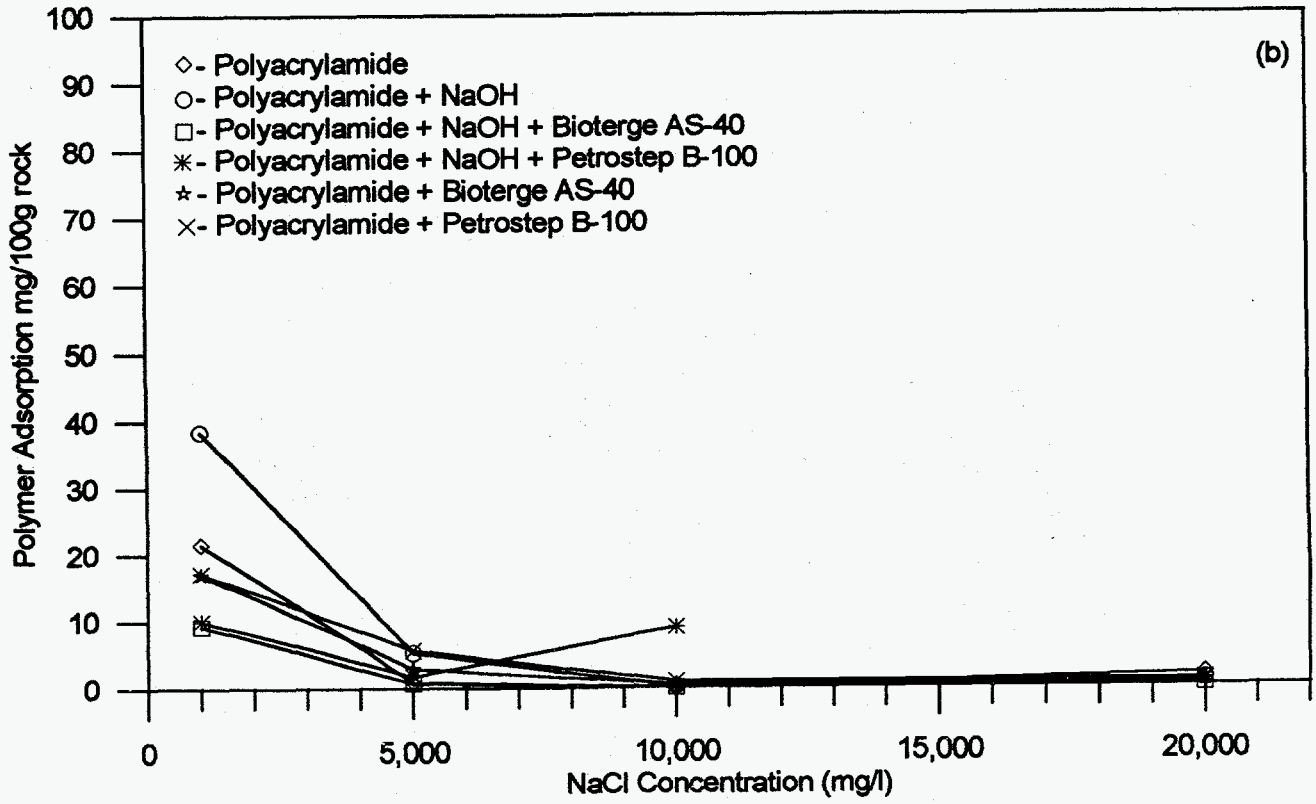
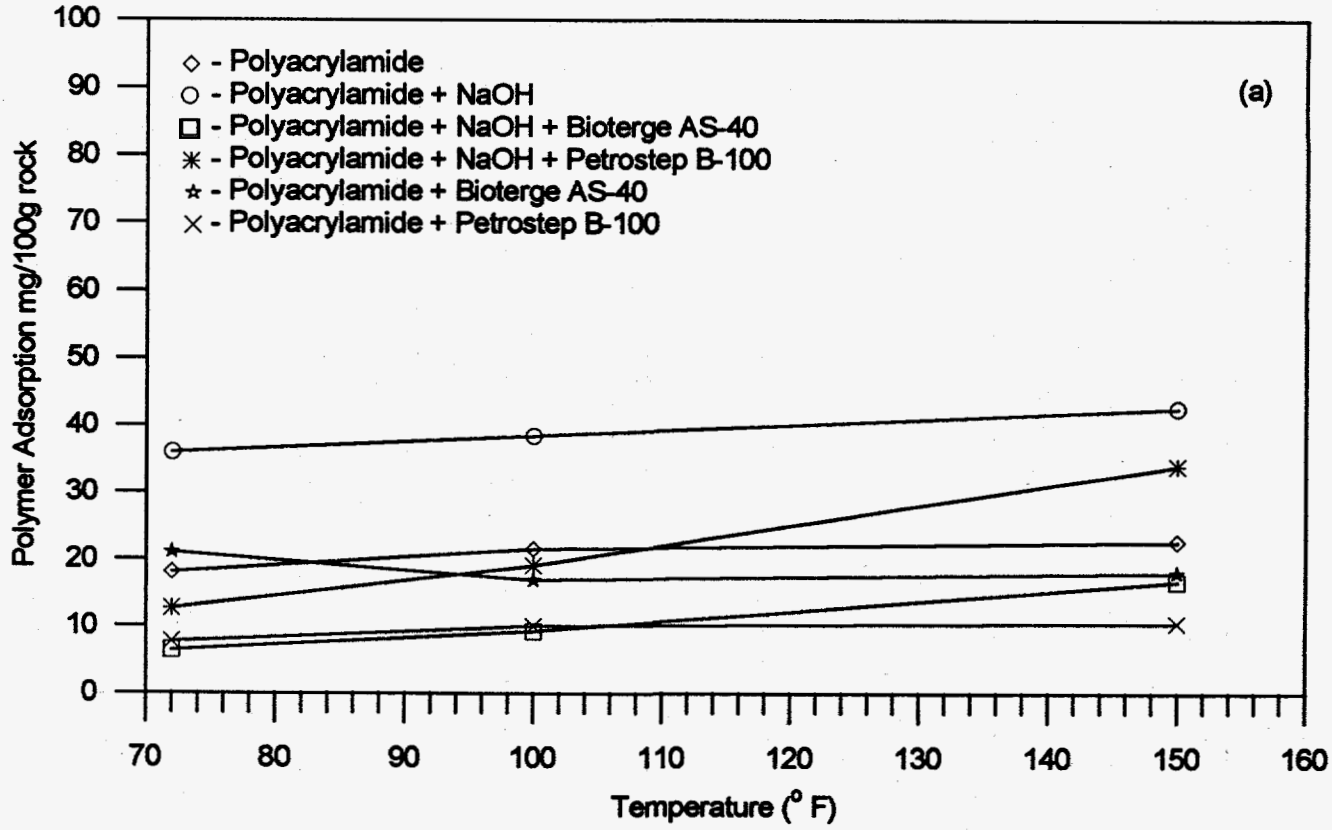


Figure 25

Temperature Effect on Polymer Adsorption onto Crushed Berea at 30 Days Co-Dissolved with Alkali and Surfactant



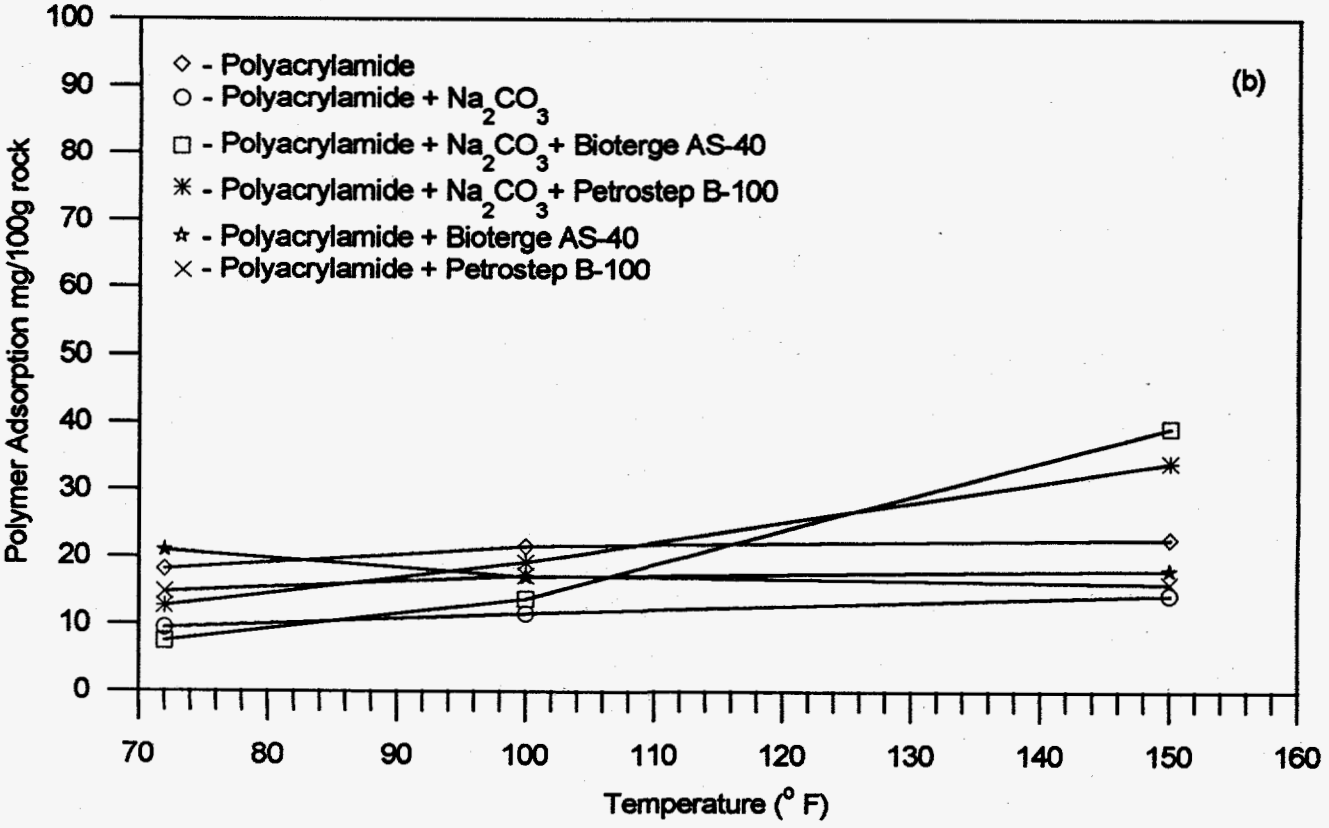


Figure 26

Comparison of Water and Alkaline-Surfactant
Relative Permeability Curves

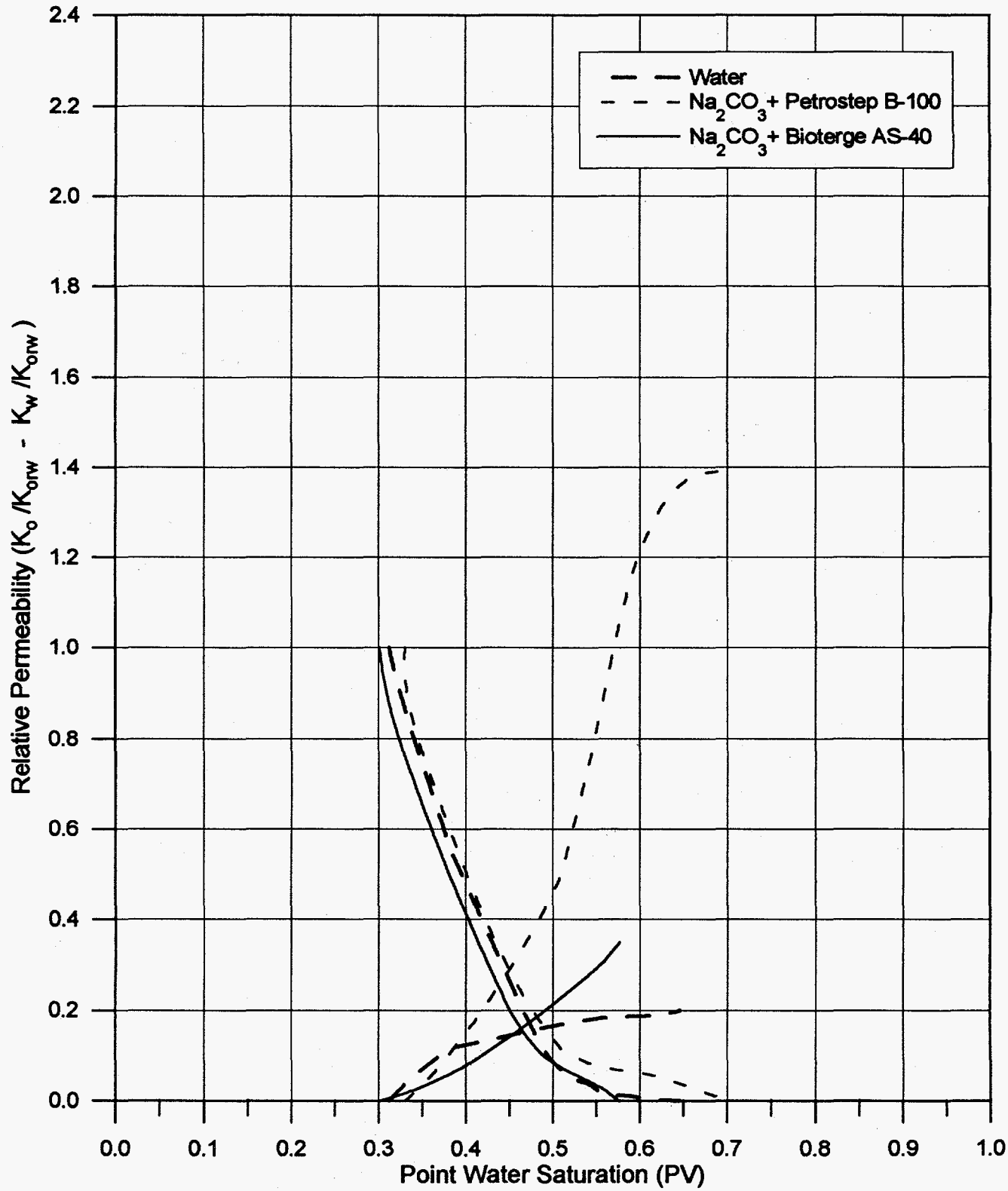


Figure 27

Comparison of Alkaline-Surfactant and Alkaline-Surfactant-Polymer Relative Permeability Curves

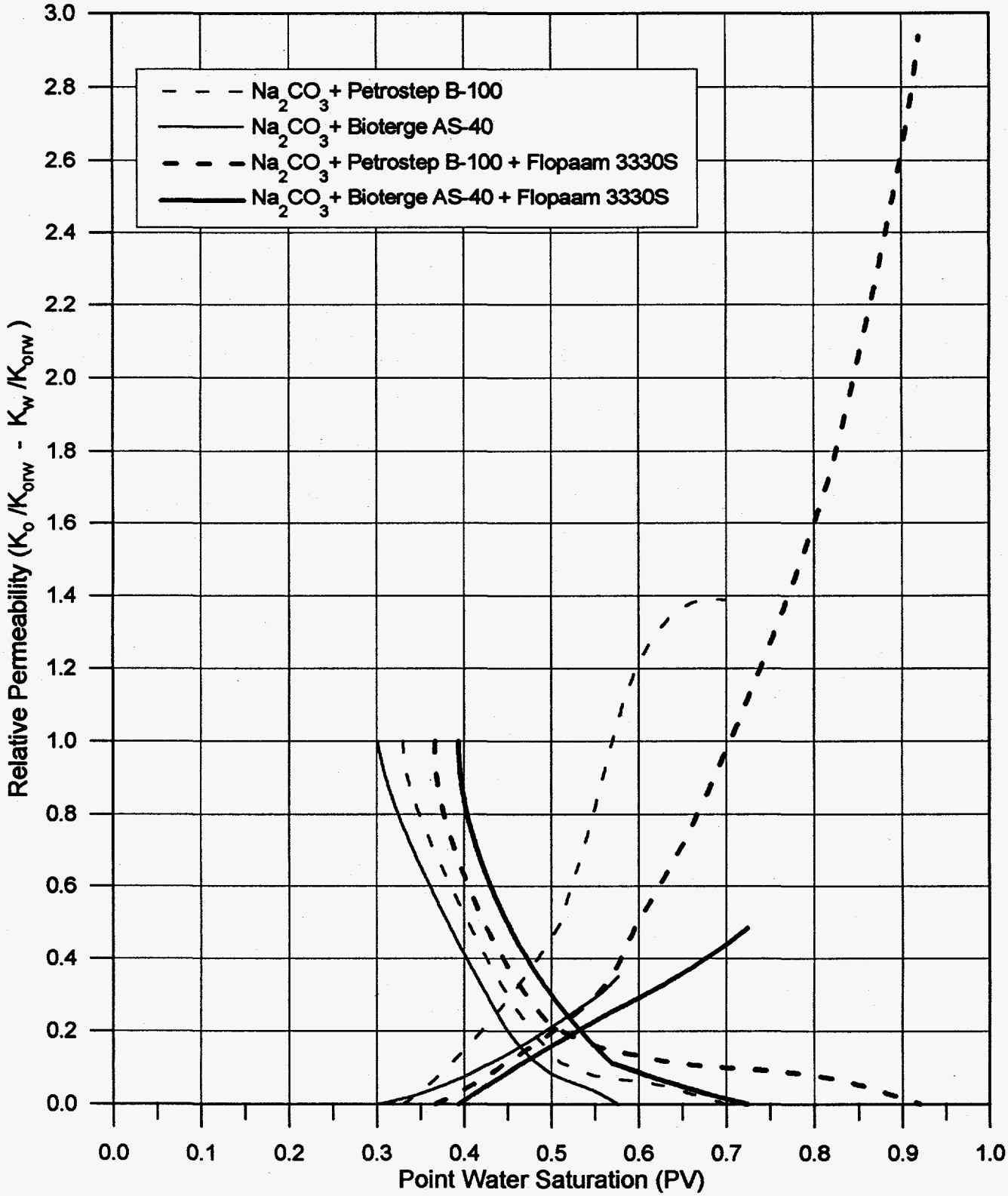


Figure 28

Polymer Concentration Effect on Alkaline-Surfactant-Polymer Relative Permeability Curves

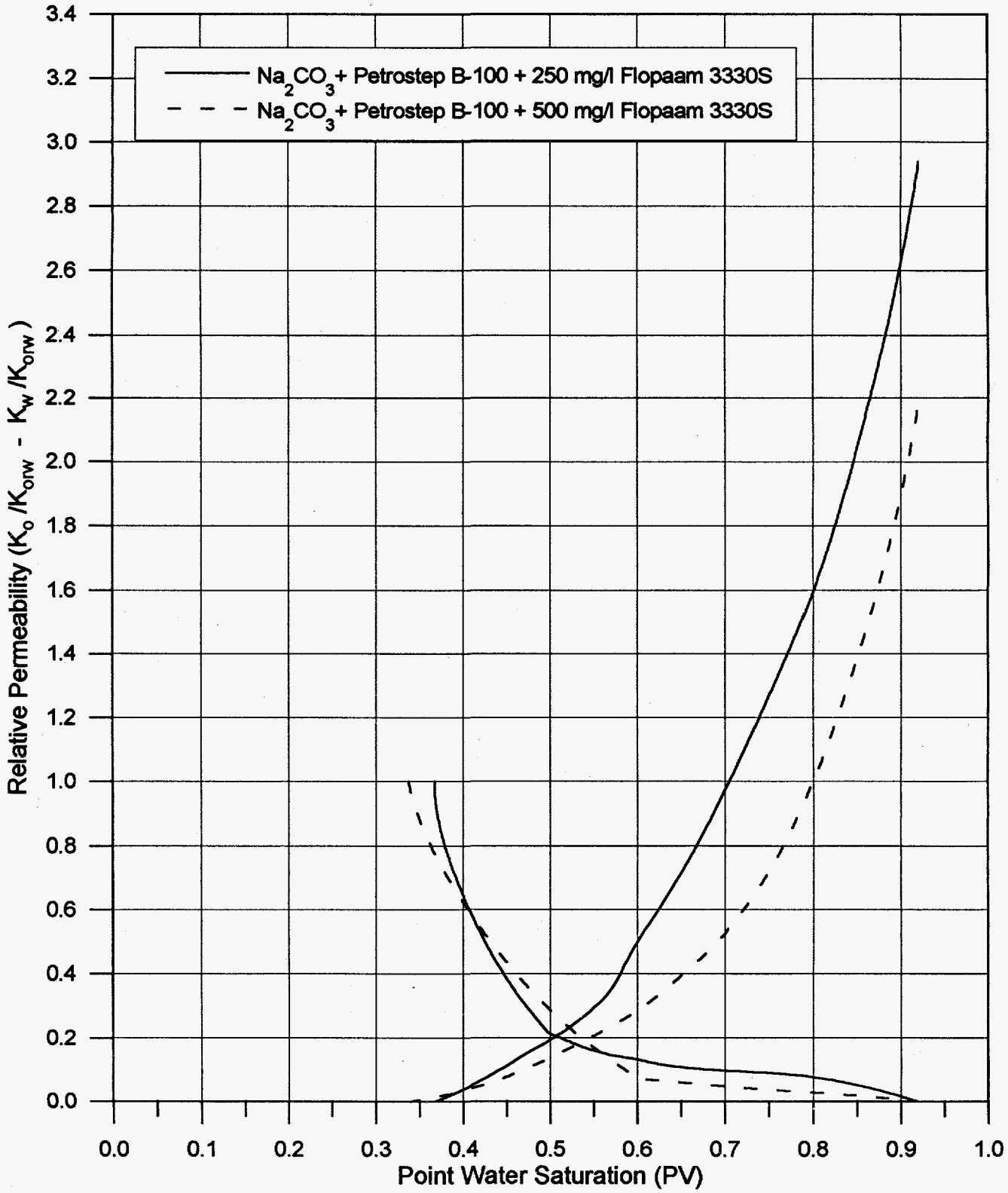


Figure 29

Rock Type Effect on Water and Alkaline-Surfactant-Polymer Relative Permeability Curves

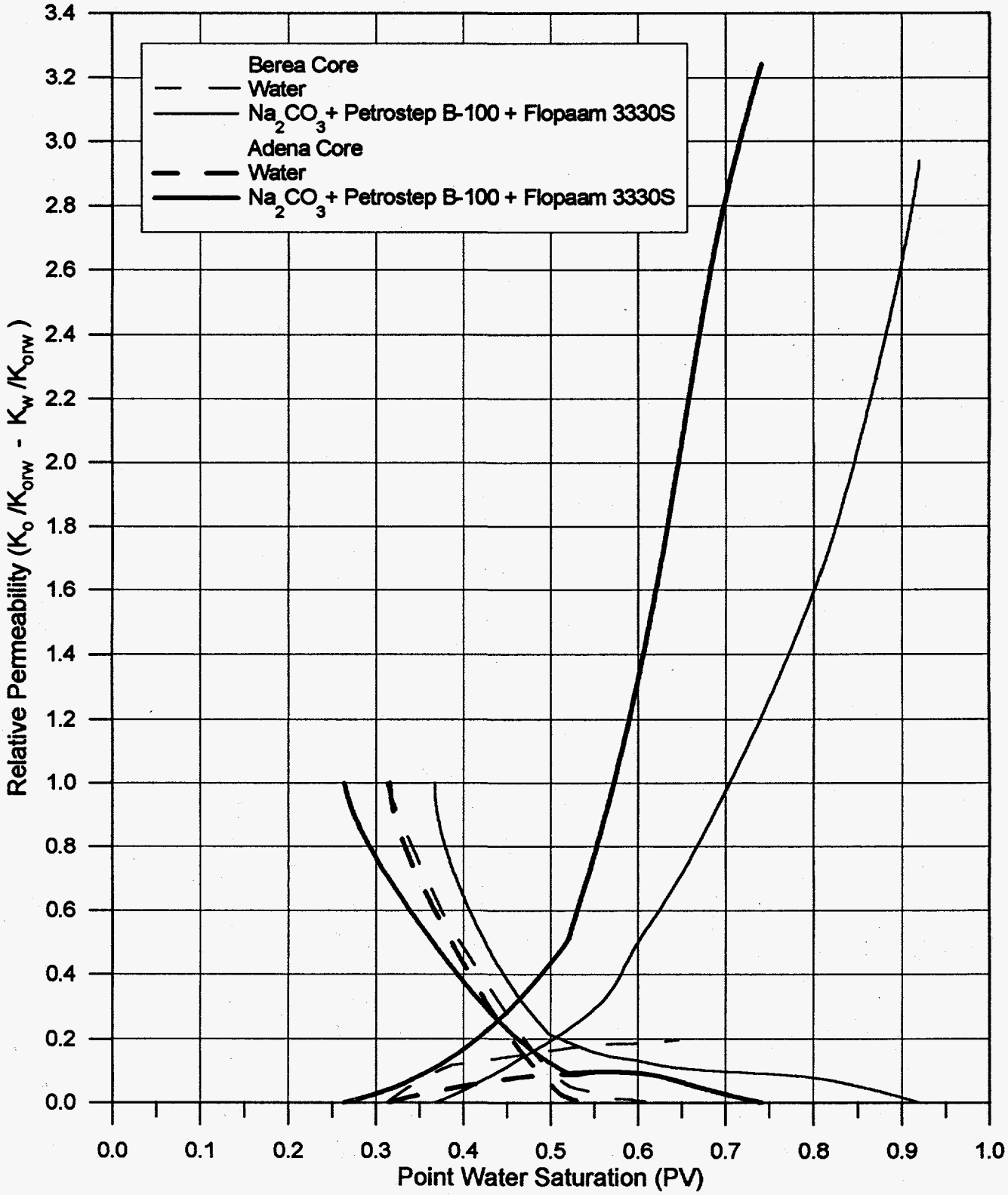
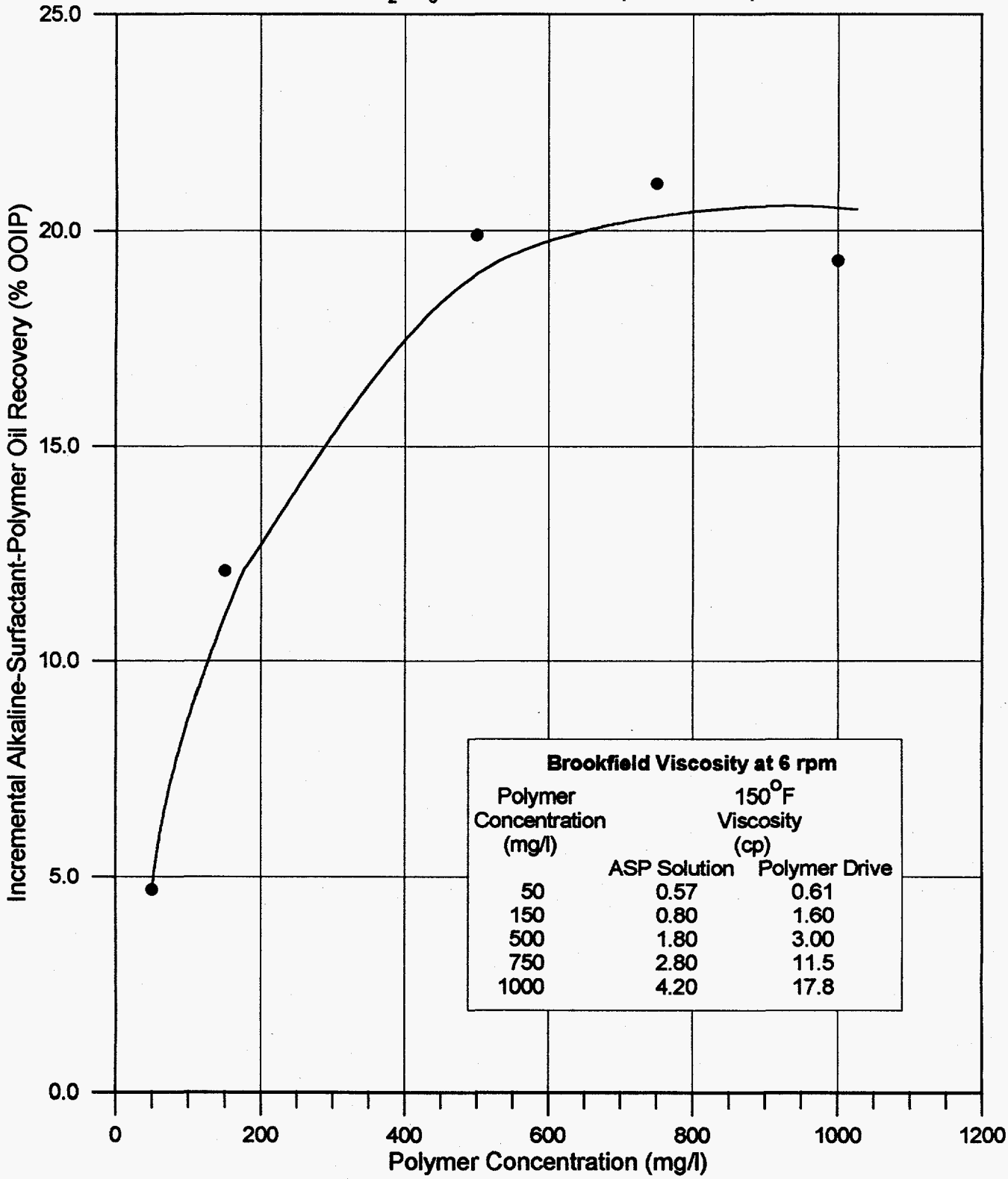


Figure 30

Polymer Concentration Effect on Radial Coreflood Oil Recovery by Alkaline-Surfactant-Polymer Solutions

ASP Solution = 1.0 wt% Na_2CO_3 + 0.2 wt% Petrostep B-100 + Flopaam 3330S



Brookfield Viscosity at 6 rpm

Polymer Concentration (mg/l)	150°F Viscosity (cp) ASP Solution	150°F Viscosity (cp) Polymer Drive
50	0.57	0.61
150	0.80	1.60
500	1.80	3.00
750	2.80	11.5
1000	4.20	17.8

Figure 31

Cumulative Oil Recovery of an Alkaline-Surfactant-Polymer Solution with and without a Prior Waterflood

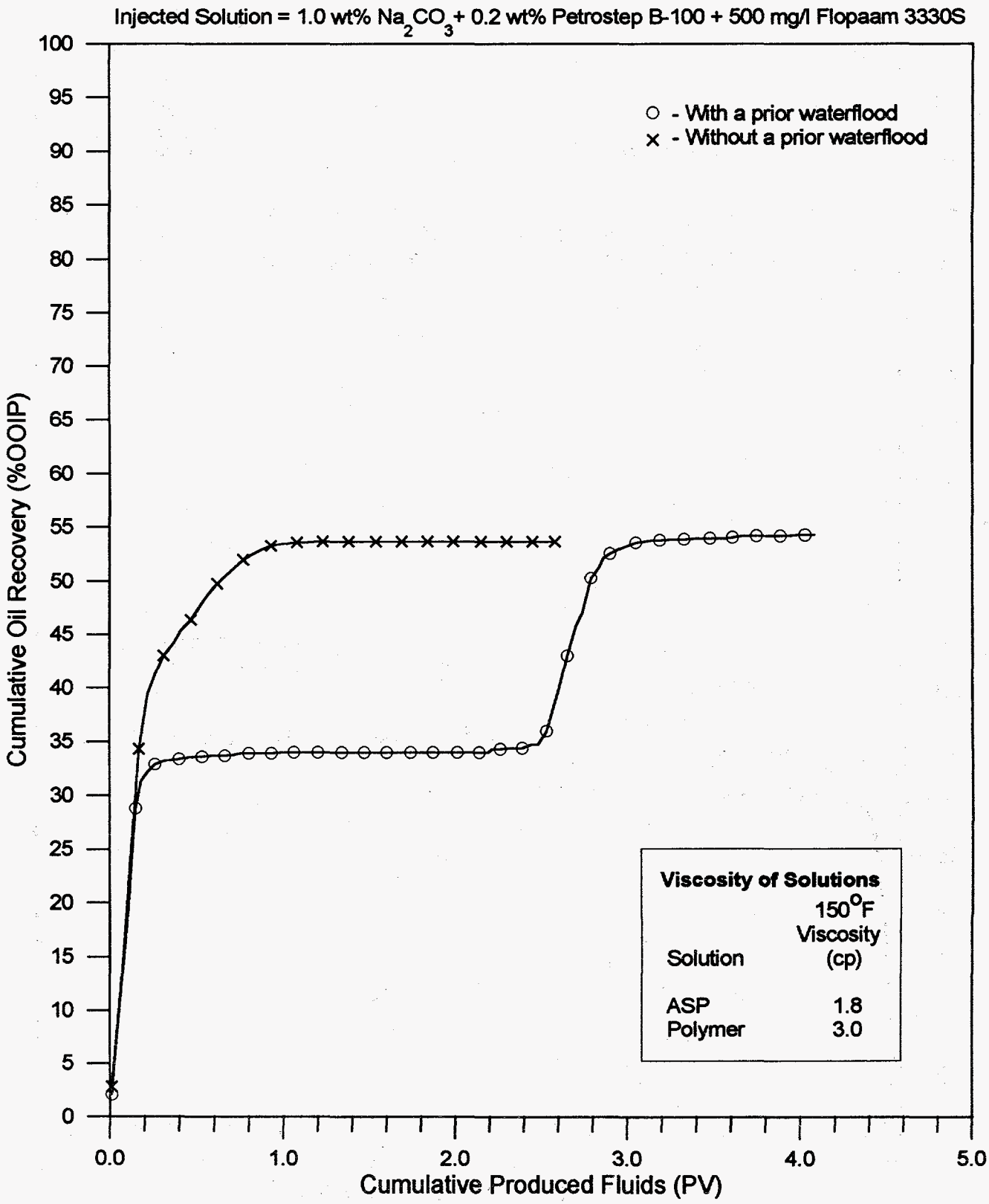
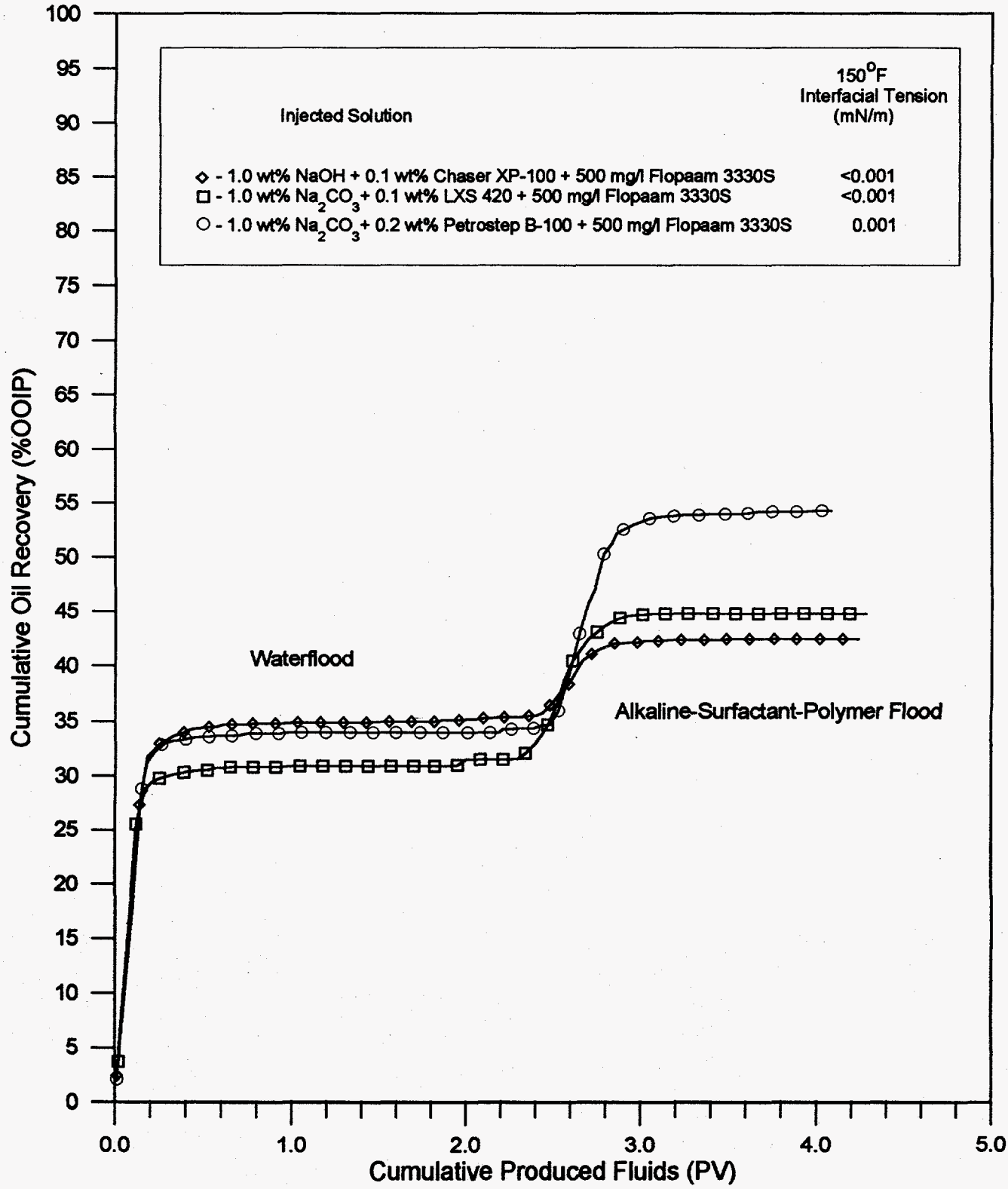


Figure 32

Cumulative Oil Recovery versus Cumulative Produced Fluids of Different Chemical Solutions with Ultra Low Interfacial Tension Values



☆U.S. GOVERNMENT PRINTING OFFICE: 1995 - 660-029/20012