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**THE USE OF CHEMICAL ADDITIVES WITH STEAM
INJECTION TO INCREASE OIL RECOVERY**

Final Report

By
L. L. Handy

Work Performed Under Contract Nos. AC03-81SF11571
AT03-76ET12076

University of Southern California
Los Angeles, California

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THE USE OF CHEMICAL ADDITIVES WITH
STEAM INJECTION TO INCREASE OIL RECOVERY

Final Report

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ABSTRACT

Surfactants and certain inorganic bases have been evaluated as possible chemical additives to improve performance of steamfloods. Special emphasis was given to chemicals which would reduce the residual oil saturation in regions flooded by hot water below the steam zone. Problems considered were the effect of prolonged exposure to steam temperature on the stability of petroleum sulfonates, the effect of temperature on surfactant adsorption and the effect of temperature on interfacial tensions. Methods were developed for measuring quantitatively the thermal stability of the aryl sulfonate class of surfactant. This class includes the petroleum sulfonates. The best of the surfactants evaluated in this study had marginal stability for use with steamfloods. The surfactants in combination with elevated temperatures do reduce residual oil saturations. Data are presented on the temperature effects on interfacial tensions and on adsorption.

Certain inorganic chemicals which give high pH are effective and inexpensive but hydroxyl ions react with silica in the reservoir. This reaction is accentuated at higher temperatures. Data show that the pH of the injected hot water with caustic decreases with contact time. The experiments did not permit determining if an equilibrium pH would be obtained which would be high enough to be effective in recovering oil. Core floods showed that pH's in excess of 12 would be required to reduce residual oil saturations if sodium hydroxide was the injected chemical. The addition of surfactants with caustic or the use of sodium carbonate may permit recovery of oil at lower pH's.

A reservoir simulator is being developed to predict performance of steamfloods with chemical additives. This has been completed for simple linear floods but is being extended to three dimensions and to more complicated flooding operations. An analytical solution has also been developed to predict the effect of concurrent heat and adsorbed chemical transport on flood performance.

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INTRODUCTION

The major objective of the research to be discussed in this report was to evaluate various chemical additives for steamfloods as to their potential either to increase oil recovery above that obtained from steamflooding alone or to recover the oil at lower steam-oil ratios. The primary emphasis was to find chemicals which would reduce the residual oil saturation in the reservoir volumes which would be flooded by hot water only.

Our concept of the physical processes which would occur in the reservoir changed as we proceeded with the research. Originally we had anticipated that the added chemical would enter the reservoir with the hot water from the steam injection and that the chemical and heat from the water would be transported through the colder reservoir together. The effect of this is to raise the possibility that the chemical would outdistance the temperature bank in the reservoir. In which case the chemical would be operating at reservoir temperature. Any synergistic effect we might have anticipated for the heat and chemical would not be observed. With the very viscous California crudes, however, the only regions in which significant flow of water and oil is likely to occur is the region below the overriding steam. Consequently, most of our current reasoning is based on the assumption that the chemicals will be transported in a near-isothermal region of the reservoir heated by steam condensate.

The chemical additives considered in the research included both organic surfactants and inorganic bases which react with acidic crudes to give low interfacial tensions.

The results of the research will be discussed under the following topical headings.

I. Organic Additives for Steamfloods

- A. Thermal stability of various surfactants which appear economically feasible for use as steam additives.
- B. Precipitation and adsorption of surfactants as functions of temperature.
- C. Effect of temperature on interfacial tension between oil and water with surfactants.
- D. Comparison of oil recoveries resulting from surfactant additives to water at normal reservoir temperatures with those at steam temperatures.

II. Inorganic Additives for Steamfloods

- A. Caustic consumption by reservoir rock as related to temperature.
- B. Effect of temperature and pH on waterflood oil recovery.

III. Predicting Field Performance of Steamflooding with Chemical Additives

- A. Reservoir simulator for predicting field performance of chemical additives with steam.
- B. Analysis of the displacement of viscous oil by the combined injection of hot water and chemical additives.

IV. Conclusions and Recommendations

I. ORGANIC ADDITIVES FOR STEAMFLOODS

Several different chemicals have been proposed for use with steamfloods to enhance the performance of the floods. The use of caustic has been field-tested without success¹. Consideration is being given to the use of foaming agents to reduce the mobility of the steam and improve volumetric sweep efficiency². This portion of our investigations was restricted to evaluating the beneficial effects which might be obtained from adding surfactants with the steam to reduce the residual oil saturation in that region in the reservoir which is swept by hot water. Some evidence suggests that this may not only increase oil recovery from that part of the reservoir but may even improve the volumetric sweep efficiency of the steam itself. Gopalakrishnan has reported related studies from IFP-IMF in Toulous, France³.

The proposed mechanism by which surfactants could improve oil recovery from steamfloods is that the surfactant would travel in the hot water portion of the flood and that as a result of a synergistic effect of temperature and surfactant significantly better results could be obtained with the surfactants than might be obtained at normal reservoir temperature for surfactants in a waterflood. Several subsidiary problems have to be resolved, however, before this process can be recommended for the field. First among these is that a surfactant must be found which can survive the hot water temperatures long enough to complete the recovery process. Second, a surfactant is required which will be effective in reducing the residual oil saturation at elevated temperatures. One of the postulates was that, possibly, higher

temperatures could lead to lower interfacial tensions and greater oil recovery efficiency. Third, if a synergistic effect is to be obtained between temperature and the surfactant, the surfactant must be transported in the hot water zone.

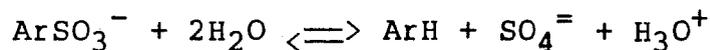
A. Thermal Stability of Various Surfactants

A limited number of studies have been reported in the literature on the stability of surfactants suitable for oilfield operations at temperatures in excess of 100°C. Data have been reported by others for the petroleum sulfonate, TRS 10-80, but no temperatures were stated for those experiments⁴. Our results are for anionic and nonionic surfactants. The anionics include sodium dodecylbenzene sulfonate, an acidic Dowfax sulfonate and several petroleum sulfonates. The petroleum sulfonates include TRS 10-80 manufactured by Witco and Petrostep 465 manufactured by Stepan Chemical Corporation. Dowfax 240 was from Dow Chemical Company. The nonionic was an alkylphenoxypolyethanol manufactured under the trademark of Igepal CO-850 by GAF.

The surfactants were mixed at various concentrations without salt and aged at elevated temperatures in Teflon containers in Parr Acid Digestion bombs. Particular care was taken to eliminate air from the bombs. Long term aging tests were conducted in sealed borosilicate glass vials. In comparing our work with that of others, a major factor is the method used for chemically analyzing for the active surfactant. The most common procedure is the Epton titration, which involves a dye transfer between two phases. We found the end points difficult to detect in this procedure. We used instead UV spectrophotometry. The

bond which ruptures during high temperature aging is the sulfur-aromatic ring bond. Disubstituted aromatic rings have characteristic absorption wavelengths at 220-240 nm and 260-280 nm. When the sulfur-aromatic ring bond ruptures, the absorption at these characteristic wavelengths is decreased. The decrease in the concentration of the active surfactant can be measured quantitatively from the change in the peak heights. Concentrations were determined from a comparison of peak heights with those observed for solutions of known concentration. The alkylphenoxypolyethanols could also be analyzed by UV absorption because these compounds also have a disubstituted aromatic ring. A modification of the Epton titration has been proposed by Mukerjee which is reported to be more quantitative than the original method⁵. We have not tested that procedure.

The decomposition reaction for the petroleum sulfonates is the following:



It would be possible, therefore, to monitor the reaction from a measurement of the pH.

Representative data from our results are given on Figures 1 and 2. The plot of the logarithm of concentration versus time was linear. pH versus time was also observed to be linear. The other anionic surfactants gave similar behavior. These results indicate that the decomposition reaction for the anionics is first order. The decomposition rate for a reaction following first order kinetics is

$$- dC/dt = kC$$

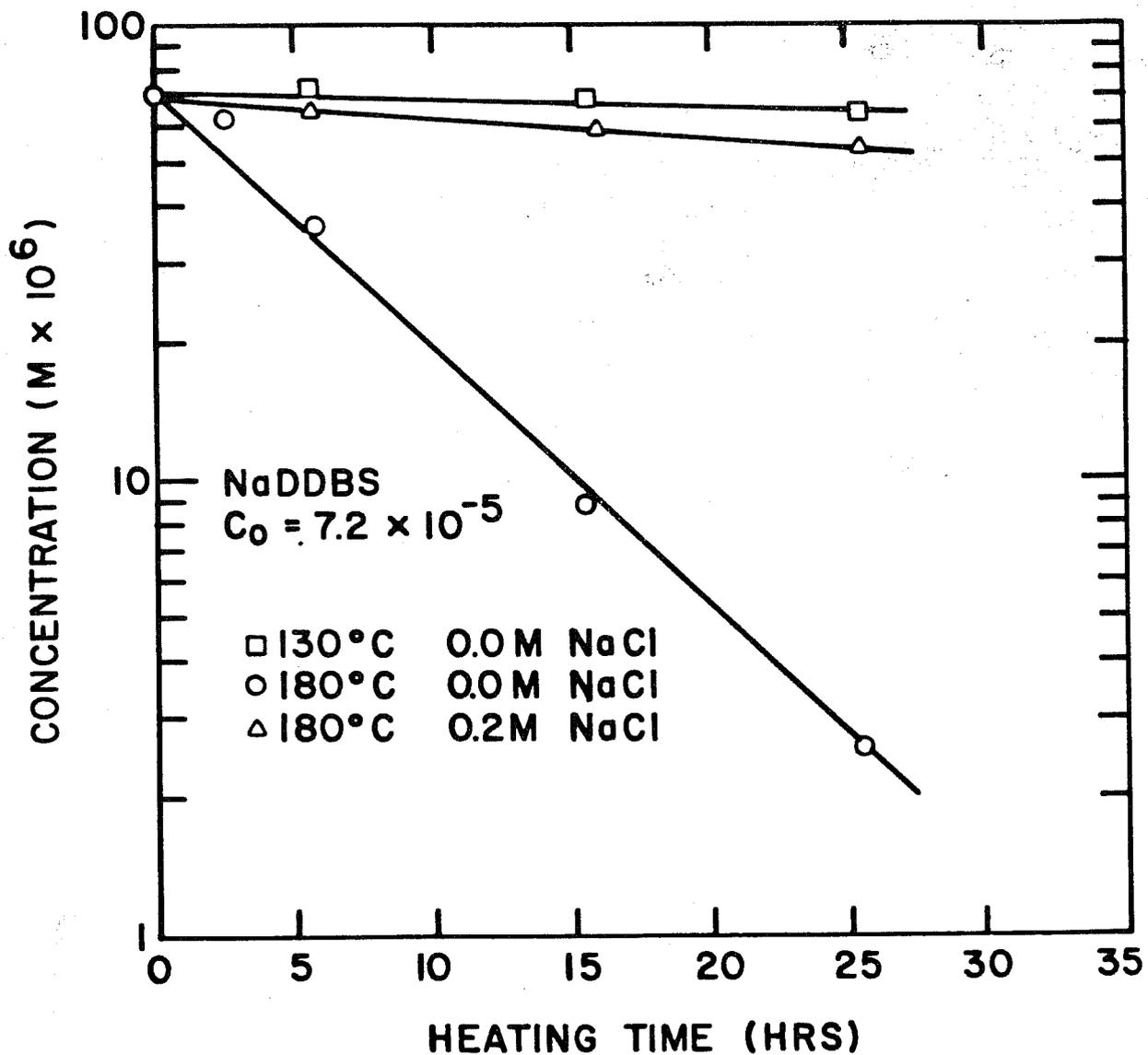


Figure 1. Concentration of NaDDBS as function of heating time at 130°C and 180°C

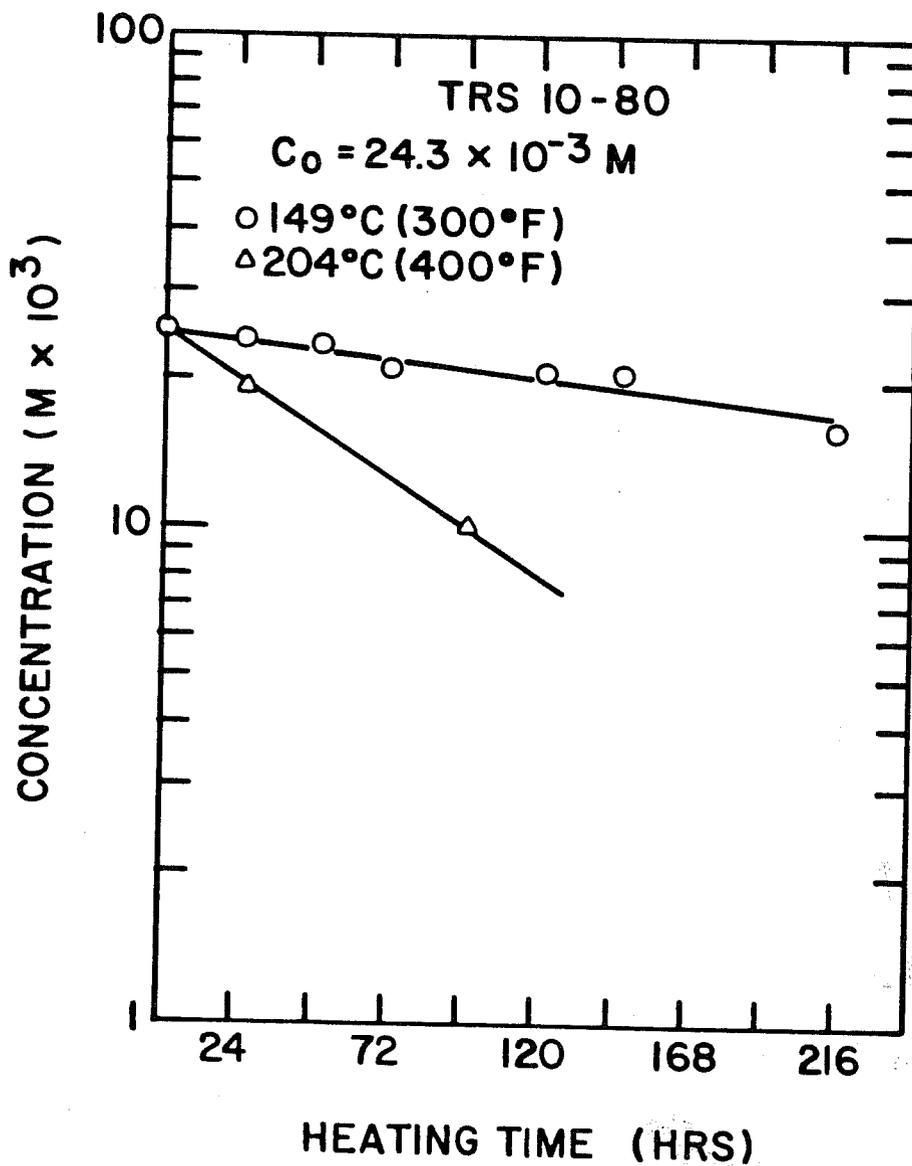


Figure 2. Concentration of TRS 10-80 as function of heating time at 149°C and 204°C

$$C = C_0 e^{-kt} \quad \text{or} \quad \log C = \log C_0 - \frac{kt}{2.303}$$

In these equations C is concentration in moles per liter; C_0 is the initial concentration; t is time in days and k is the rate constant in days⁻¹. The rate constant is determined from the slope of the semilog plot. One can also show that when $C/C_0 = 1/2$, the elapsed time is equal to the half-life of the surfactant.

$$t_{1/2} = \frac{.693}{k}$$

If one has rate constants at several different temperatures, one can determine the activation energy for the reaction. With the activation energy one can determine rate constants and half-lives at other temperatures. This is particularly useful in estimating the stability of surfactants at lower temperatures for which the decomposition rates are low and long times would be required to measure the half-lives. Figure 3 is a plot of the log of the rate constant versus the reciprocal of the absolute temperature for TRS 10-80. This plot is typical of those obtained for the surfactants which were tested. In the equation

$$\log k = \frac{-E_a}{2.303 RT} + B$$

E_a is the activation energy in cal/mole; R is 1.987 cal and T is the absolute temperature in °K. From the slope of the plot one can determine the activation energy.

A summary of decomposition data for several surfactants is given in Table 1. At 180°C Petrostep 465 is the most stable of the surfactants we investigated. Because of its high activation

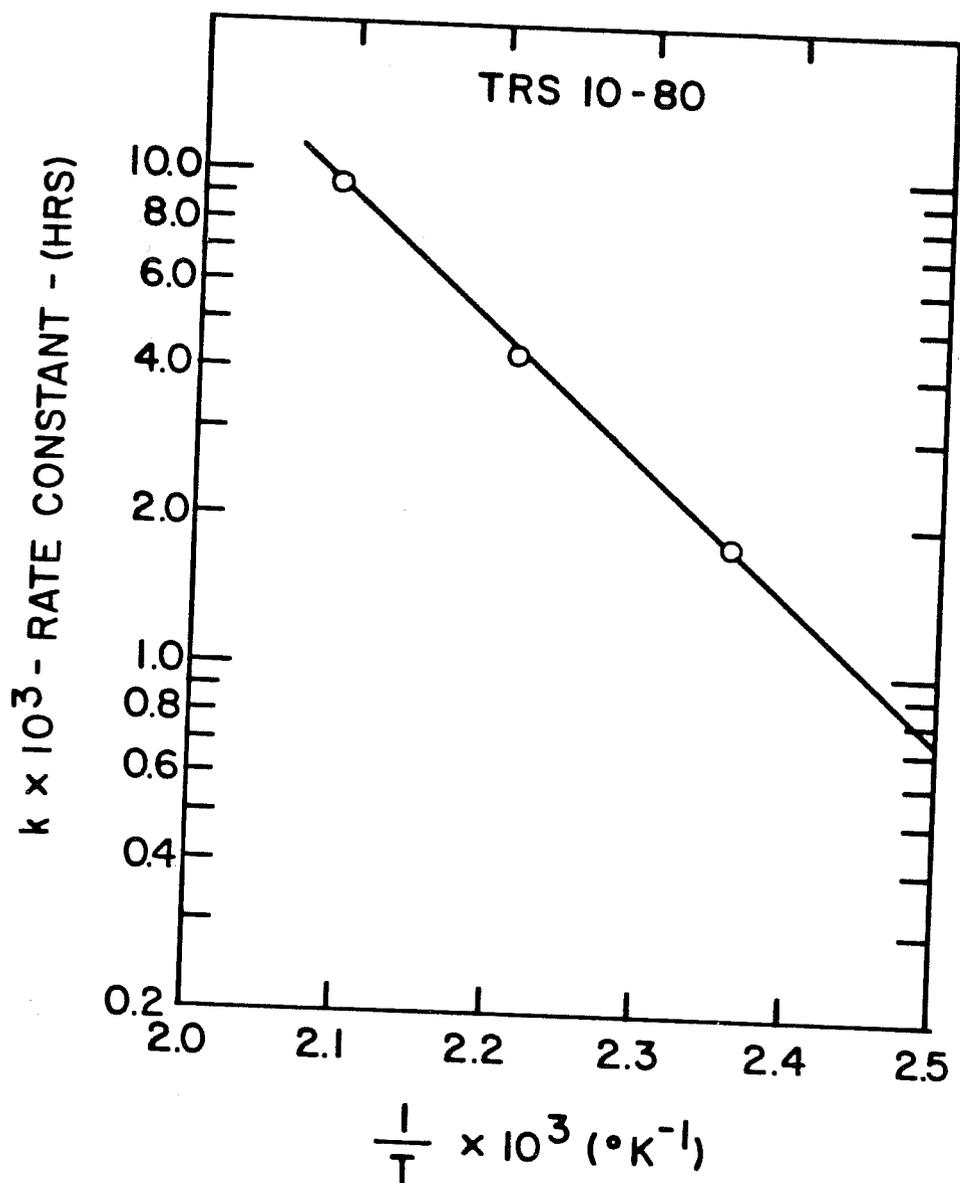


Figure 3. The rate constant (k) as function of $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$) for TRS 10-80

energy relative to the other surfactants, this surfactant would have a half-life of about 16 years at 100°C. None of the surfactants have adequate stability for use at normal steam temperatures. These results would be expected to be representative for aryl sulfonates, but better stabilities have been informally reported for alkyl sulfonates.

TABLE 1
SUMMARY OF DECOMPOSITION DATA FOR SURFACTANTS

Surfactant	Mol. Wt.	Temp. °C	t _{1/2} (days)	E _a (kcal/s)
NaDDBS	348.5	130	6.13	24.0
		180	.22	24.0
		150	13.6	26.0
		180	1.75	26.0
Dowfax 2AO	500	177	5.6 (UV)	NA
			6.9 (pH)	
TRS 10-80	415	149	17.4	12.4
		204.5	3.0	12.4
		180	7.0	12.4
Petrostep 465	465	130	444	25.2
		157	108	25.2
		180	11	25.2
Igepal CO-850	1100	130	.75	8.84
		180	.22	8.84

B. Precipitation and Adsorption of Surfactants as Functions of Temperature

Quantitative data on the effect of temperature on the solubility of petroleum sulfonates have not been reported, but evidence has been cited by several authors that precipitation of the sulfonates occurs at the higher temperatures in natural sandstones^{4,6,7}. This occurs not as a result of a direct temperature effect on the solubility of the surfactants but,

apparently, as a result of an interaction with minerals in the porous media. Reed has measured a significant increase in the solubility of rock minerals at steam temperatures⁸. The petroleum sulfonate ions form precipitates with divalent cations. These precipitates are likely to decrease in solubility with increasing temperature. In general, the presence of salt in the solutions decreases the solubility of the sulfonates.

Ziegler observed turbidity in the produced fluid from a Berea sand pack when sodium dodecylbenzene sulfonate solutions were injected at a concentration of 1400μ mols/liter. However, data in Figure 4 show that surfactant precipitated out of a 0.2 molar salt solution could be redissolved when distilled water was injected and when the temperature was increased. In this experiment the sand pack was flushed with 1374μ mols/liter surfactant in 0.2 M NaCl. Then the pack was flushed with salt solution only, with distilled water and, finally, with distilled water at 180°C . Distilled water redissolved sulfonate precipitated out of brine and an increase in temperature to 180°C did redissolve sulfonate still precipitated at 40°C after the distilled waterflood.

The solubility of nonionic surfactants is not as sensitive to salt concentration as that of the anionic surfactants. On the other hand, the solubility of the alkylphenoxypolyethanols shows a marked sensitivity to temperatures. At very specific temperatures called the cloud points, the ethoxy groups in these compounds lose associated water and the solubility decreases abruptly to form precipitates. The cloud point is a function of

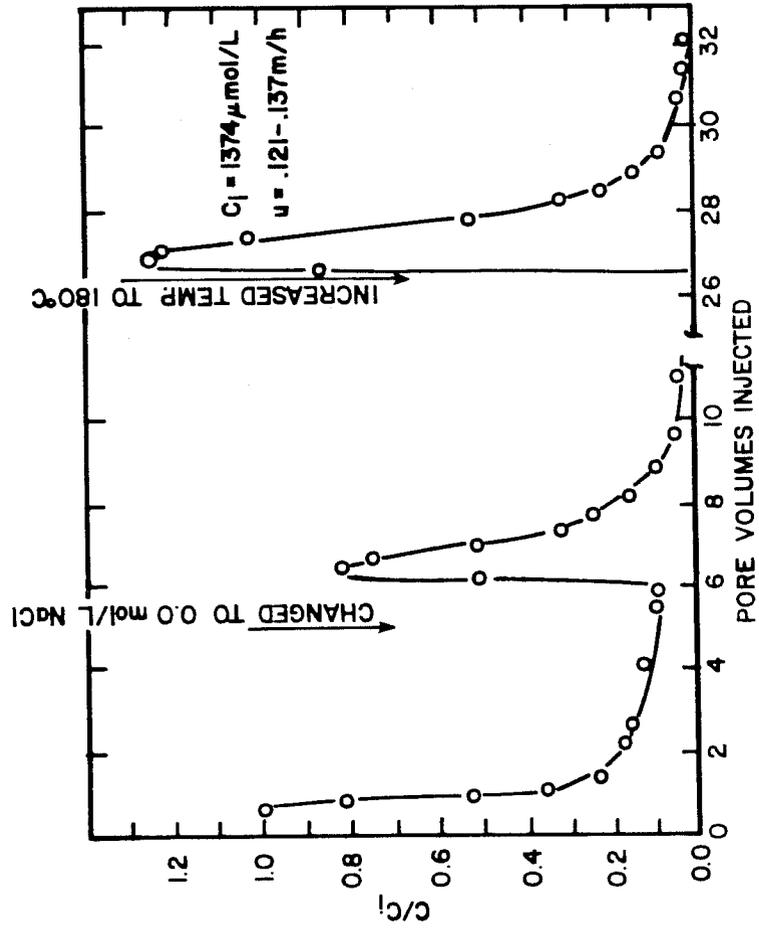


Figure 4. Desorption curve for NaDBS

the molecular weight of the surfactant, the electrolyte composition and the concentration of the surfactant. Cloud points as a function of concentration for Igepal CO-850 are shown in Table 2.

TABLE 2
SUMMARY OF PHYSICAL AND SORPTION PROPERTIES
FOR IGEPAL CO-850

Molecular Weight = 1,100 CMC = 100 μ mol/L

Cloud Points

C_0 (μ mol/L)	Cloud Point ($^{\circ}$ C)
73	>180
366	113
640	106

Sorption Properties

Tem. ($^{\circ}$ C)	K_{eq} (dm^3/μ mol)	A (μ mol/ m^2)	k_1 (dm^3/μ mol-h)	k_2 ($hours^{-1}$)	H° (kJ)
45	5.78×10^{-2}	0.524	1.2×10^{-2}	0.21	-40.2
70	2.09×10^{-2}	0.705	1.5×10^{-2}	0.72	
95	7.34×10^{-3}	0.831	2.5×10^{-2}	3.41	

If low concentration surfactants are to be used in combination with steamflooding or hot waterflooding in a reservoir, the effect of temperature on adsorption becomes a matter of considerable importance. Surfactant transport could be combined with heat transport through the reservoir. The surfactant concentration shock could either lead or trail the temperature shock. Data will be presented later which shows that interfacial tensions are reduced at higher temperatures. If this is the case, one would prefer to have the surfactant front remain

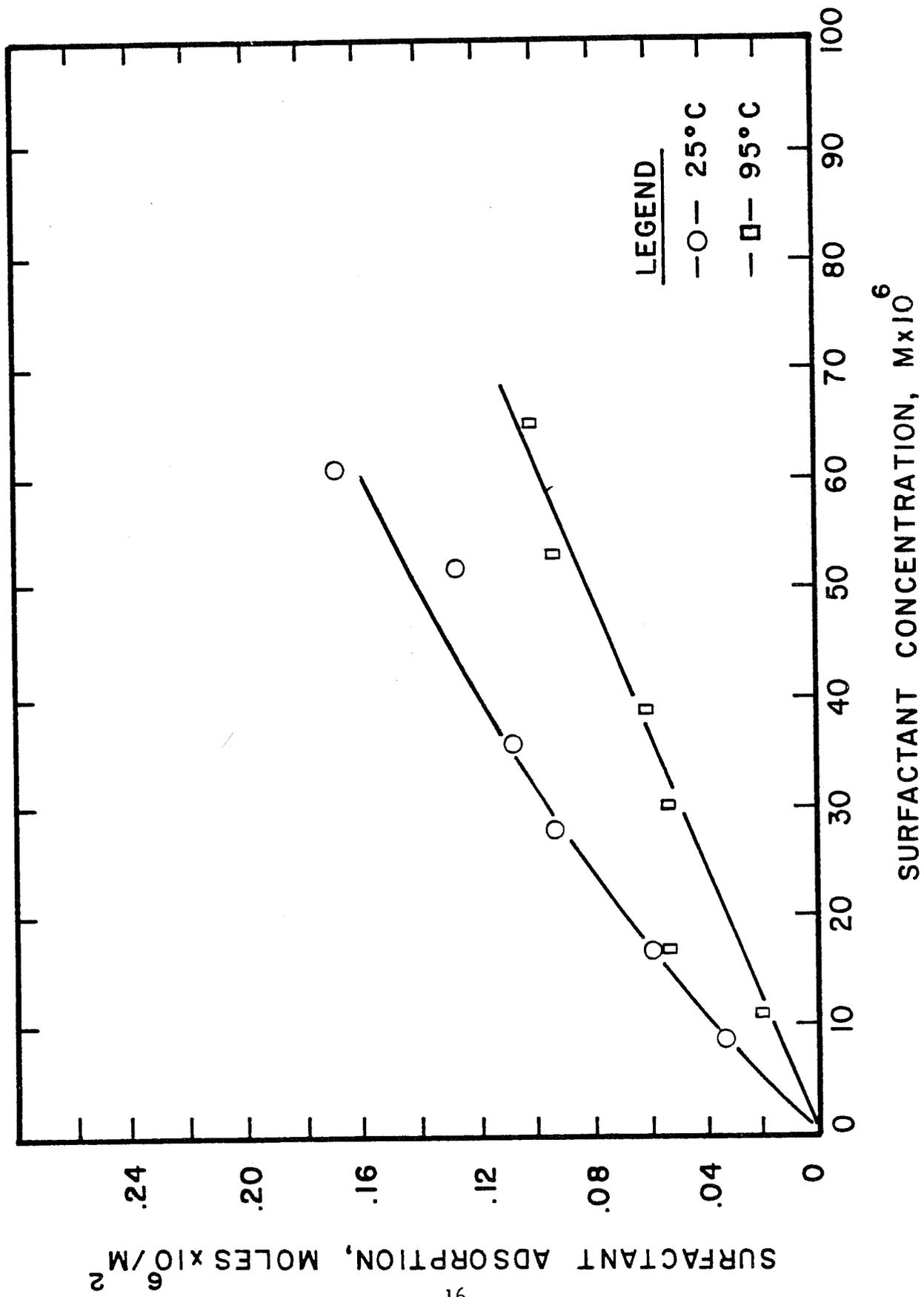
in the heated portion of the reservoir. In steamflooding, however, it is well-established that the steam overrides the oil. The water transporting the surfactant is likely to be moving primarily in a heated region immediately below the steam zone. In that case the surfactant will be moving in a hot portion of the reservoir, under isothermal conditions. Whichever mechanism prevails in the reservoir, adsorption isotherms will be required for the prevailing temperature at which the surfactant is being transported. Consequently, we have made an initial effort to determine adsorption isotherms as a function of temperature for an anionic and a nonionic surfactant.

An abundance of data exists in the literature for adsorption of various surfactants onto different substrates at room temperature. These data were normally obtained by equilibrating the surfactant solutions with the solid surfaces. Measuring adsorption isotherms at steam temperatures is a much more difficult problem.

Ziegler et al. obtained data using a dynamic, chromatographic transport procedure⁶. The porous medium was a disaggregated, fired Berea sandstone, packed in a core holder. The core was saturated with brine or distilled water and placed in an oven to maintain the temperature at the desired value. Surfactant solution was injected, starting at low concentrations. The pore volumes of solution required to move the surfactant through the core were measured. From chromatographic transport theory the quantity of surfactant adsorbed at this concentration could be calculated.

The surfactant concentration in the injected solution was increased stepwise and the volumes required to move each concentration step through the core was measured. The surface area of the sand had been measured by a variation of the BET method. From these data the adsorption isotherm can be calculated. Adsorption isotherms were also measured by the conventional static method at 25°C and 95°C. Dynamic and static adsorption data were obtained for sodium dodecylbenzene sulfonate (NaDDBS) and Igepal CO-850.

As discussed earlier, the NaDDBS has a low solubility in 0.2 molar NaCl and also tended to precipitate at the higher temperatures when in contact with the Berea sandstone. Consequently, only adsorption isotherms obtained by the static method are reported for NaDDBS. These data are shown at 25°C and 95°C for concentrations up to 70 μ mol/L on Figure 5. The results show that adsorption decreases with increasing temperature as one would expect. Data obtained in the absence of salt show less temperature dependence. Because of the precipitation problem, no dynamic data are reported for NaDDBS. The results of desorption experiments are shown in Figure 4, but the slugs of surfactant being produced after reducing the salt concentration or after increasing the temperature had been explained earlier as being more the result of dissolving precipitated surfactant than desorption of adsorbed surfactant. The slug produced after increasing the temperature, however, may have resulted in part from decreased adsorption at elevated temperatures. This would be consistent with the limited static



data showing a decrease in adsorption with temperature.

The experiments with Igepal CO-850 were complicated by the cloud point, which is characteristic of this class of surfactants, and by the instability of this surfactant at high temperatures. Static results are given in Figure 6. Equilibration time for the 95°C curve was limited to three hours. Degradation was a serious problem if significantly longer times were used. The results show a slight temperature dependence. Figure 7 is an example of results obtained by the dynamic method for Igepal CO-850. Surfactant was injected at an initial concentration of 67 $\mu\text{mols/L}$ and at two incremental concentrations higher than the initial. Consistent with a Langmuir-type isotherm, the pore volumes of injected surfactant required to produce the incremental step in concentration decreased with increasing concentration. Dynamic data were obtained at 45°C, 70°C and 95°C. Data were not obtained at higher temperatures because of the limit established by the cloud points. Degradation of Igepal is not a problem in the dynamic procedure because the surfactant is at an elevated temperature only while moving through the core.

The dynamic adsorption isotherms for Igepal are given on Figure 8. At low concentrations adsorption decreases with temperature, but adsorption increases with temperature for concentrations in excess of about 200 $\mu\text{mols/L}$. This effect is also associated with the cloud point. As the ethoxide groups lose their associated water, the surfactant becomes less soluble and would be expected to separate out onto the solid phase more

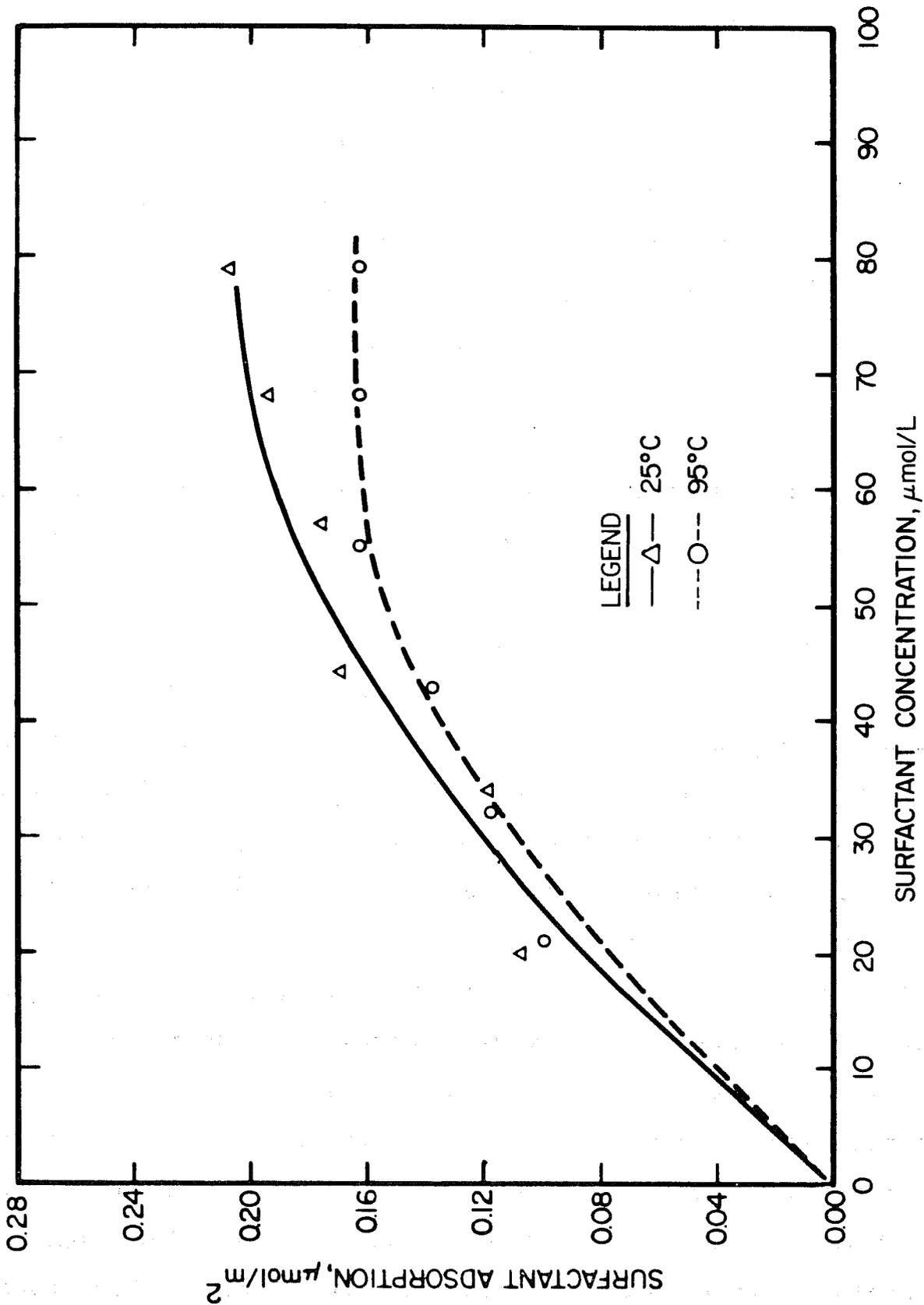


Figure 6. Static adsorption isotherms for Igepal CO-850

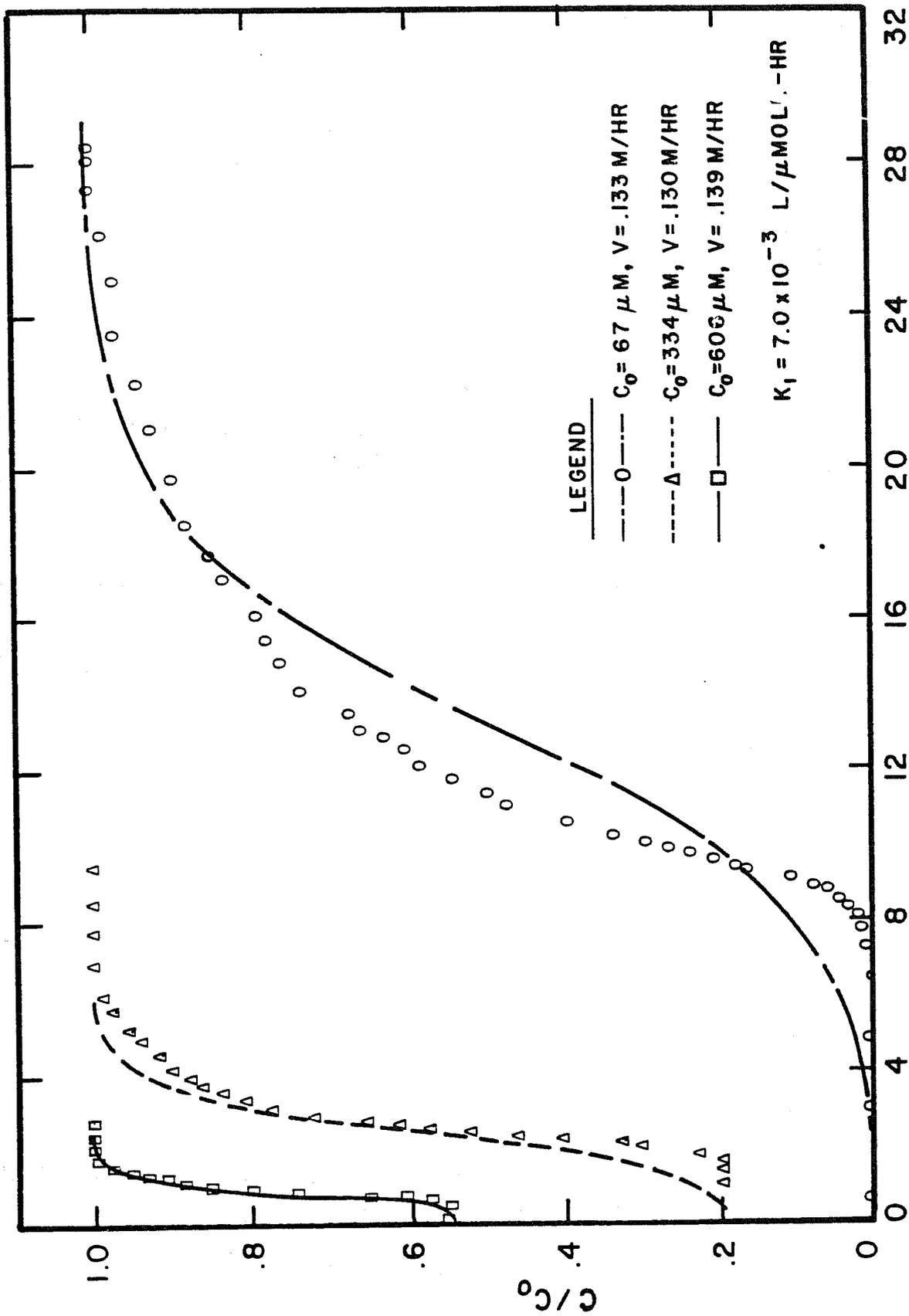


Figure 7. Effluent concentration curves for Igepal CO-850 at $T = 70^\circ\text{C}$. 0.0 M NaCl .

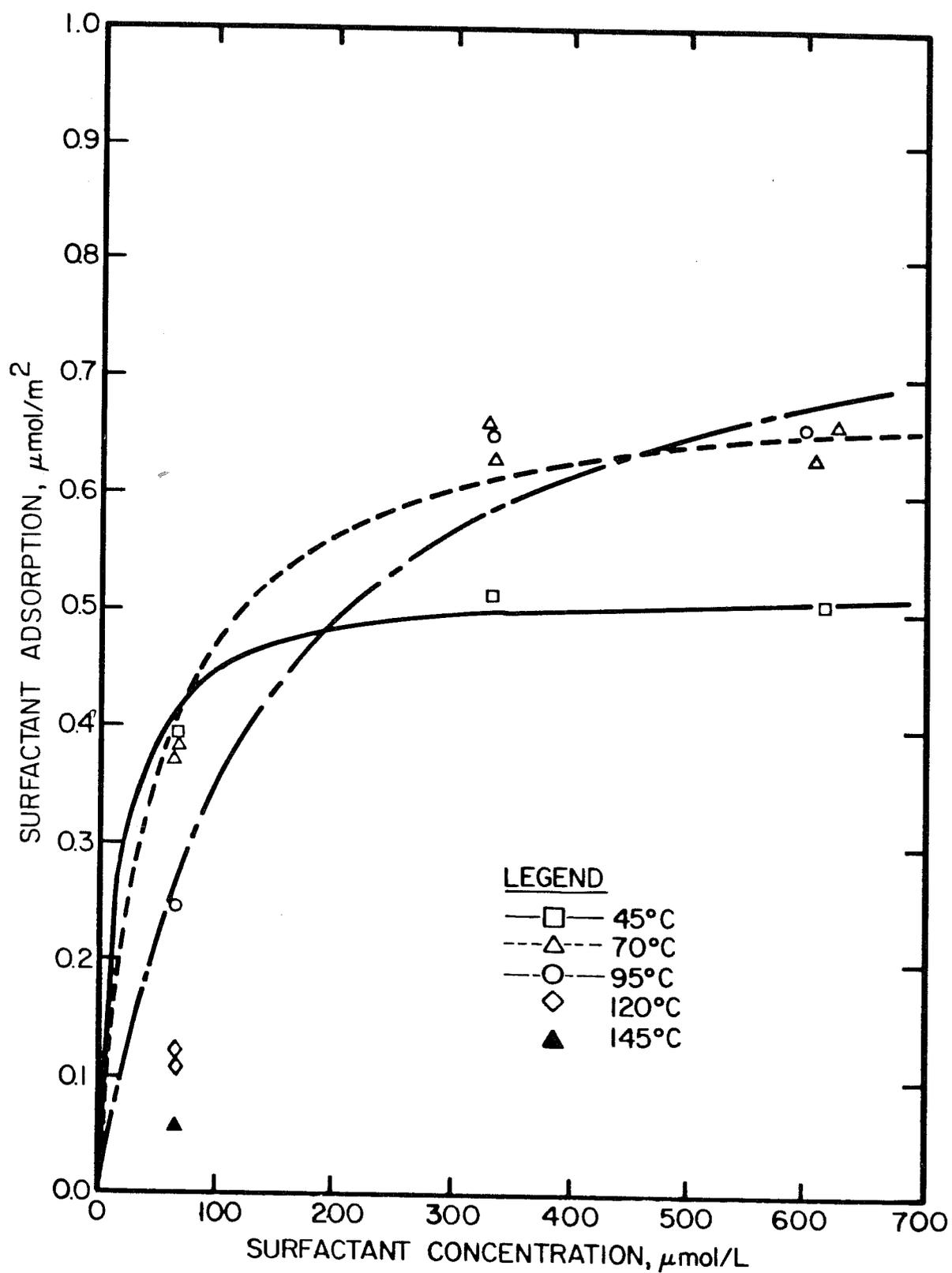


Figure 8. Dynamic adsorption isotherms for Igepal CO-850

readily. The Langmuir constants for Igepal are given in Table 2.

The results of the dynamic method with Igepal indicate that the method is suitable for determining adsorption isotherms at elevated temperatures, but the surfactants, Igepal and NaDDBS, were not suitable for testing the procedure at temperatures in excess of 100°C because of solubility problems.

C. Effect of Temperature on Interfacial Tensions

Few results have been reported giving interfacial tensions of oil-surfactant solutions as functions of temperature^{3,9,10}. These data are required for any process using surfactants in reservoirs but, particularly, for the high temperatures associated with steamflooding. We have used two methods for measuring interfacial tensions as functions of temperature and pressure. These are the pendent drop and the spinning drop methods. The minimum interfacial tension that can be measured on the pendent drop equipment is about 0.1 mN/m and that is with low precision. The spinning drop reportedly gives data below 0.001 mN/m. If time is an important factor in establishing equilibrium between the surfactant solution and the oil, the pendent drop procedure is also less suitable than the spinning drop. In the pendent drop method a drop can be suspended at the most for one-half hour. On the other hand, a drop can be maintained indefinitely in a spinning drop apparatus. Normally, equilibrium times for surfactant solutions and refined oils are small. The problem arises with caustic solutions and crude oils. Some reports have indicated that equilibrium for these systems has not been established even in matter of days. Although the spinning

drop would appear to be the preferred method, we have obtained data by both procedures.

We have modified the spinning drop equipment of Gash and Parrish for use at temperatures to 200°C and pressures to 30 bars¹¹. The design of the spinning drop equipment is such that it is a simple matter to construct an air bath around the capillary tubes which contain the spinning drop. No bearings need to operate at thermostat temperatures. An epoxy was found that was effective in sealing the capillary tubes at the above temperatures and pressures. The epoxy can be easily drilled out of the tubes to permit using them again. Our equipment is easy and inexpensive to build, but it does not have the versatility of that developed at the Technical University of Clausthal¹². Their apparatus operates at higher pressures and temperatures and permits the exchange of fluids in the rotating capillary during the experiments.

An important factor in measuring interfacial tensions by either the pendent drop or the spinning drop method is the density difference between the water and the oil. This becomes particularly critical when measuring interfacial tensions at elevated temperatures. The density of water decreases more rapidly with temperature than that for oil. Consequently, the density difference between water and oil can become quite small at higher temperatures. A small error in estimating these densities can have a significant effect on the calculated interfacial tensions. This problem becomes particularly acute when the oil phase is a crude oil. For some crudes the density

of the oil may, in fact, become greater than that of the water. The spinning drop equipment cannot be used under those circumstances. Density data are readily available for water and can be generated easily for the surfactant and brine solutions. Densities for refined oils and pure hydrocarbons were determined using data from "Petroleum Refinery Engineering"¹³. To correct crude oil densities for temperature, the volume correction factors from ASTM D-206-36, Group 1, were used. Density data for water and three crude oils taken from El-Gassier et al.¹⁴ are shown on Figure 9.

Representative data obtained by the spinning drop method are shown on Figure 10¹⁴. Interfacial tensions were measured between mineral oil No. 9 and TRS 10-80 in various concentrations of salt. The concentration of TRS 10-80 was kept constant at 0.5 g/L. The interfacial tensions showed little dependence on temperature up to 180°C, but they are affected substantially by the salt concentration. The lowest interfacial tensions were observed at salt concentrations of 5.0 g/L. The lower curves on this figure are duplicate runs and show reasonable agreement. Interfacial tensions for TRS 10-80 against a representative crude oil also showed little effect of temperature.

The interfacial tension between the nonionic surfactant, Igepal DM-730 and a 15.9° API California crude oil showed a marked minimum when plotted versus temperature as shown on Figure 11. No salt was present in this example but similar data were obtained with the surfactant in presence of salt. The interfacial tension minima for the nonionics coincided with the

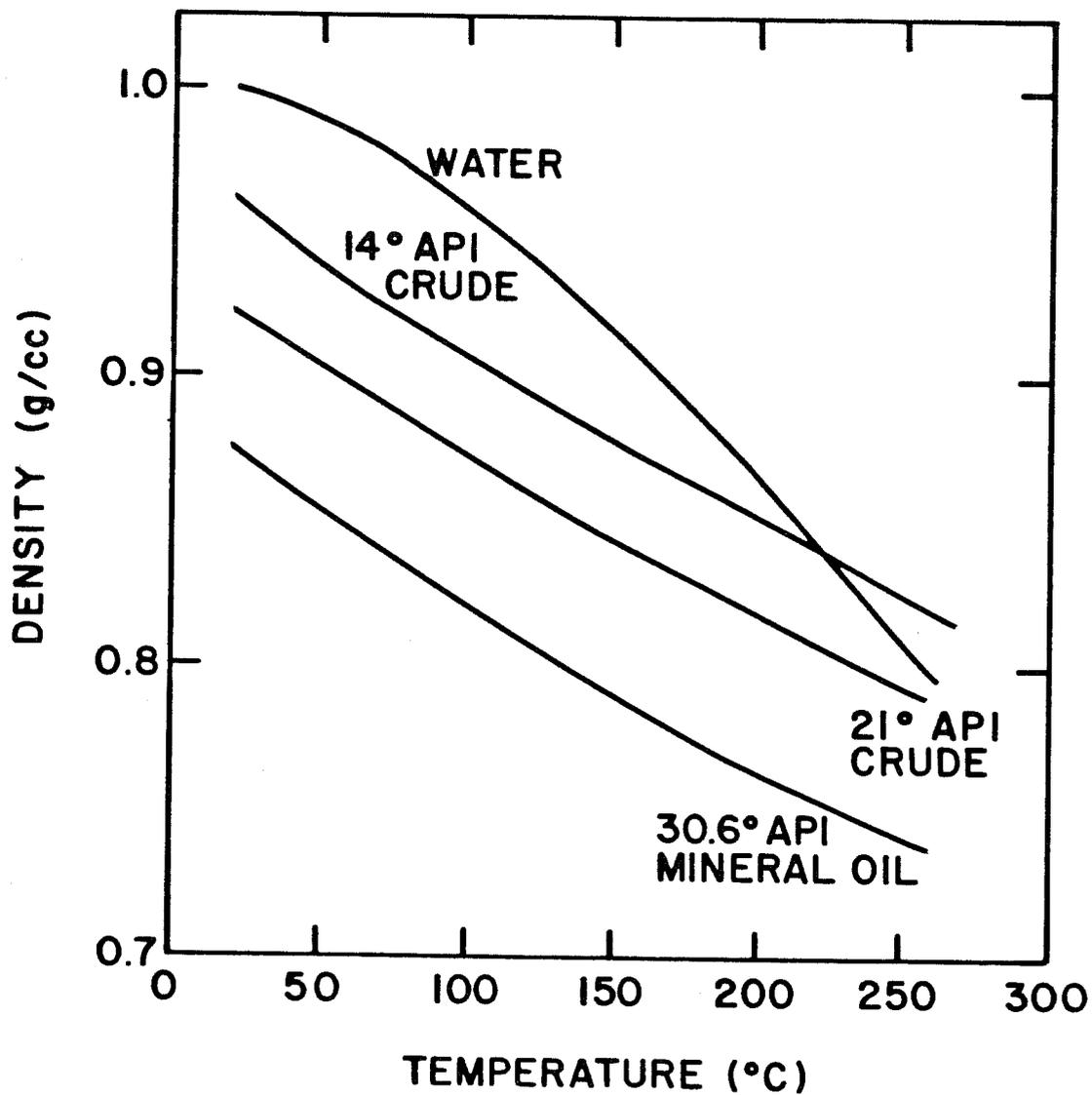


Figure 9. Effect of temperature on density of water and crude oils

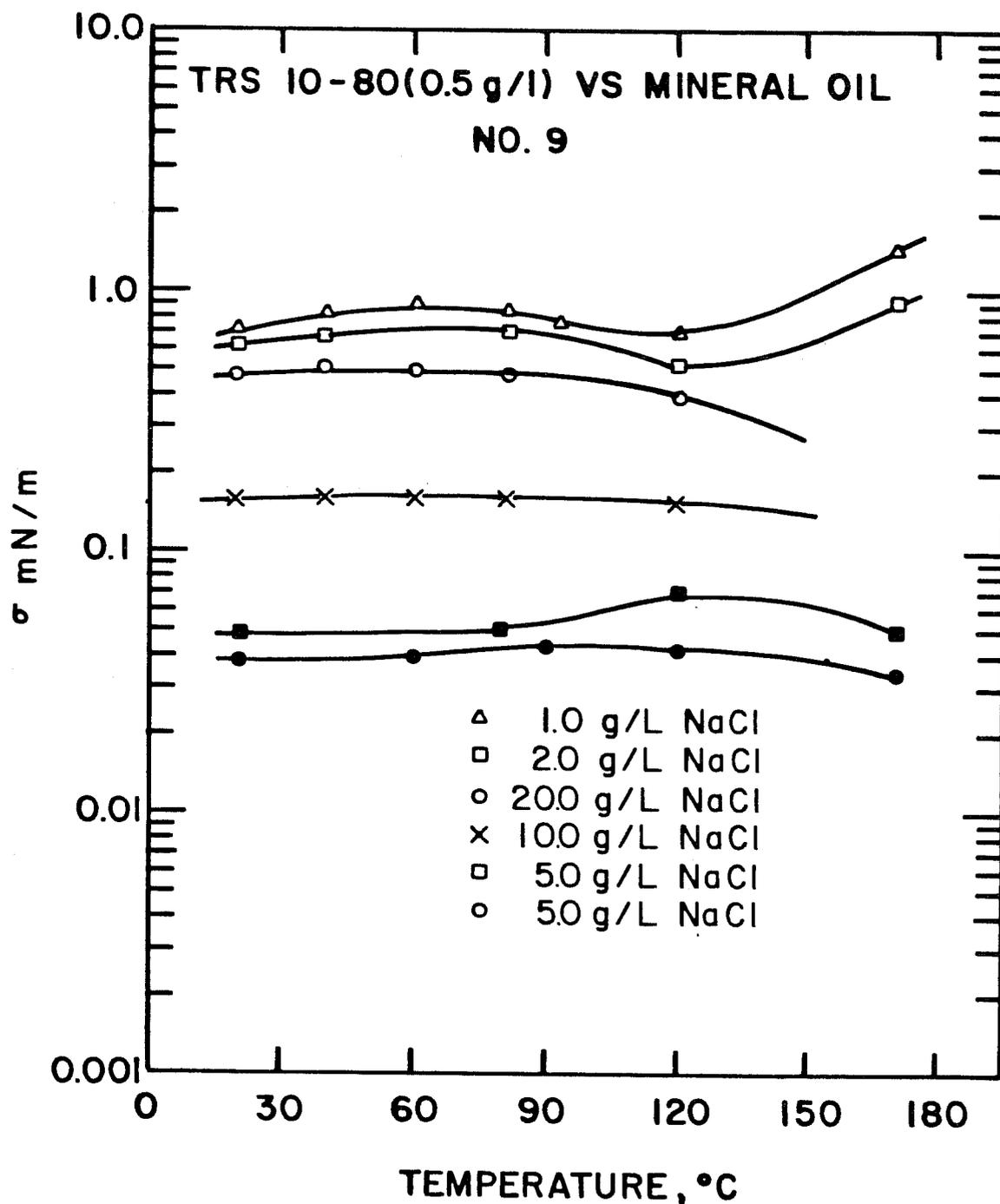


Figure 10. Effect of salt concentration and temperature on interfacial tension of 0.5 g/L TRS 10-80 versus mineral oil No. 9

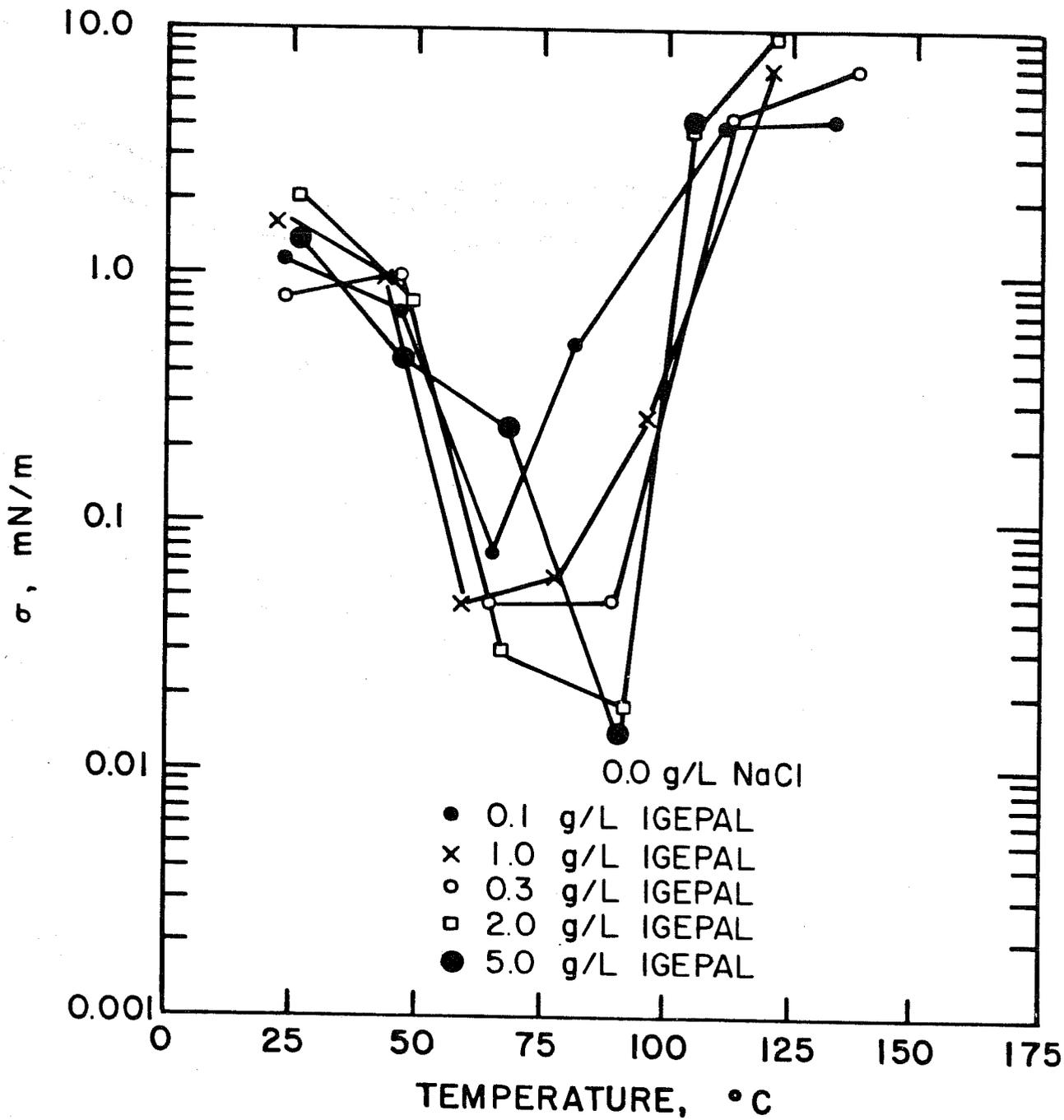


Figure 11. Effect of surfactant concentration and temperature on interfacial tension between TRS 10-80 and crude oil. NaCl = 0.0 g/L

cloud point for the particular surfactant concentration. Since the cloud point indicates a decrease in the surfactant solubility, it is not surprising that the interfacial tension decreases at this temperature. The decrease in transparency of the aqueous phase at the cloud point was a limiting factor in measuring interfacial tensions of nonionics as a function of temperature by either the spinning drop or the pendent drop method.

Additional data have been obtained using a mixture of surfactants against pure hydrocarbons and mineral oils. The equivalent alkane carbon number, EACN, for the surfactant mixtures was calculated as recommended by Jacobson et al.¹⁵. As shown in Figure 12, these mixtures show an abrupt decrease in interfacial tension at temperatures in excess of 120°C. The experiments are being extended to obtain data for several hydrocarbons and, thereby, evaluate the relation between the change in interfacial tensions with temperature and the EACN concept.

D. Comparison of Oil Recoveries Resulting from Surfactant Additives to Water at Normal Reservoir Temperatures with Those at Steam Temperatures

A major objective of this research was to study the possible benefits in additional oil recovery which might be obtained from synergistic effects resulting from combined high temperatures and low interfacial tensions obtained by adding surfactants to the injected steam. Since we were interested, primarily, in the effect of surfactants on oil recovery in that portion of the reservoir which was flooded with hot water, the laboratory

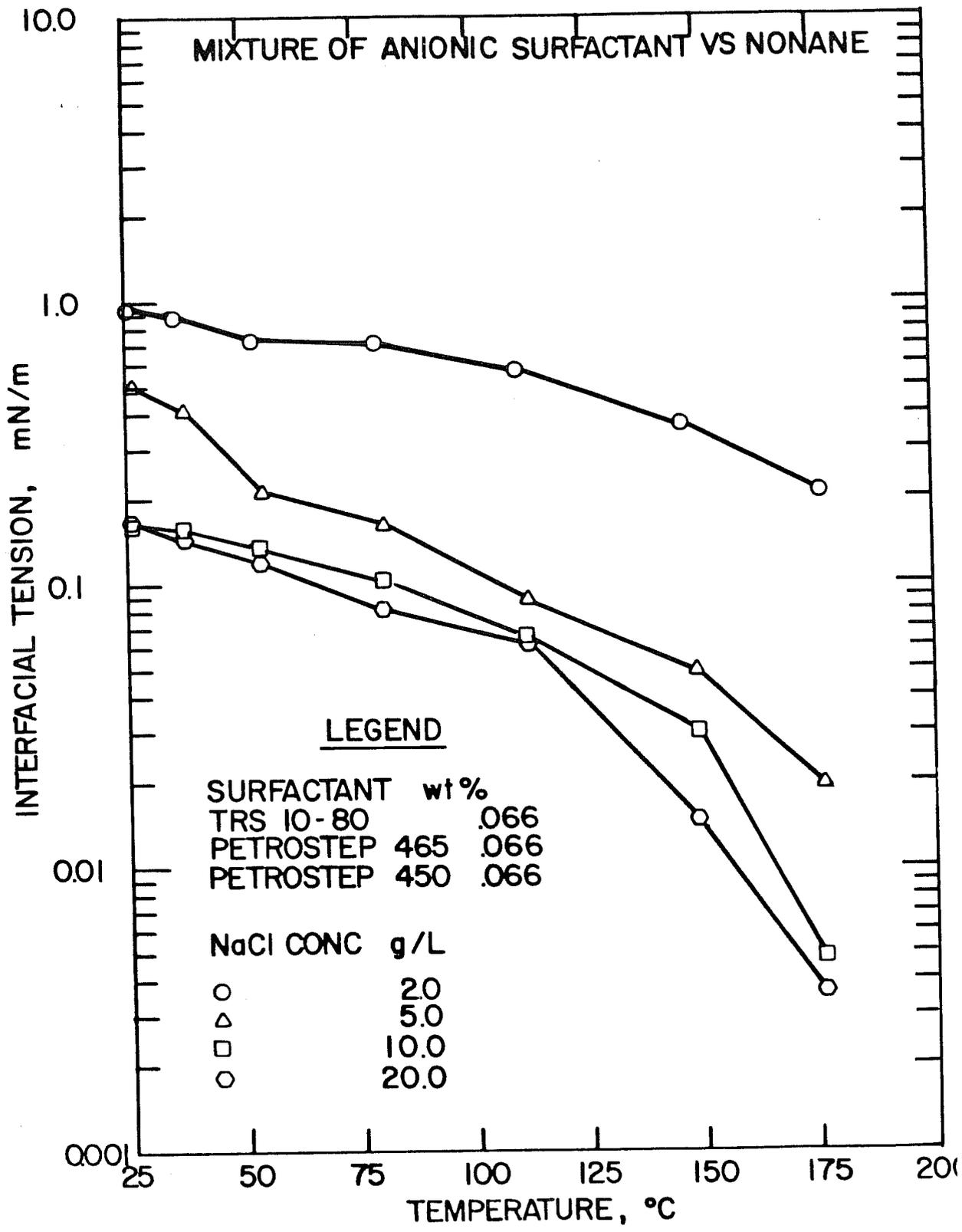


Figure 12. Interfacial tensions as functions of temperature and salt concentration for surfactant mixtures against nona

experiments were waterfloods at various temperatures with and without surfactants added. The experiments and data reported are those of Amabeoku and are discussed in detail in his doctoral thesis¹⁶.

The oils used in these floods were refined oils, blended to give suitable viscosities. Polybutenes manufactured by Chevron Chemical Company were mixed with a No. 9 white oil marketed under the trade name of Kaydol. Several oils were prepared and their viscosities were determined as functions of temperature and plotted on Figure 13. The viscosities ranged from a high of 1443 cp at 25°C to a low of 1.4 cp at 178°C. The porous medium was a fired Berea sandstone with the dimensions of about 5 cm diameter and 30 cm length. The cores were mounted in a Hassler sleeve arrangement in an oven to control temperature. Fluids were injected at constant rate.

The surfactants used in this study were Petronate TRS 10-80 and Petrostep 465. Both are petroleum sulfonates and were purified to 100 percent active component by liquid chromatography. Interfacial tensions between the injected surfactant solutions and the refined oils were measured as functions of temperature using the method described by El-Gassier et al.¹⁴. Results of these measurements for Petrostep 465 at a concentration of 2.5 g/l in a brine containing 10.0 g/l NaCl are shown on Figure 14.

Three floods were performed with TRS 10-80 at temperatures of 25°C, 82.2°C and 177°C. In these floods the surfactant was injected after waterflooding the core to residual oil saturation

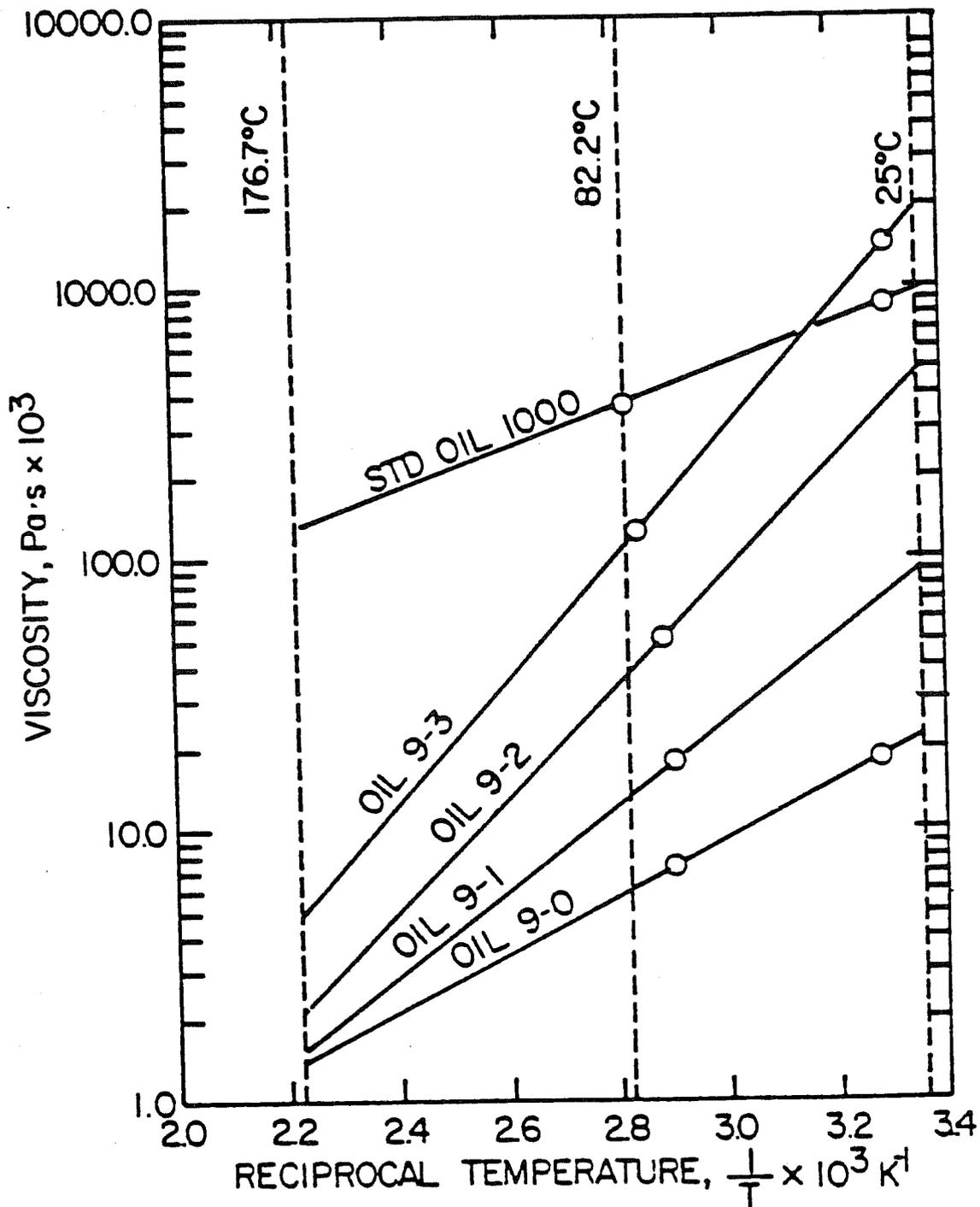


Figure 13. Oil viscosity of Kaydol mixtures as functions of temperature

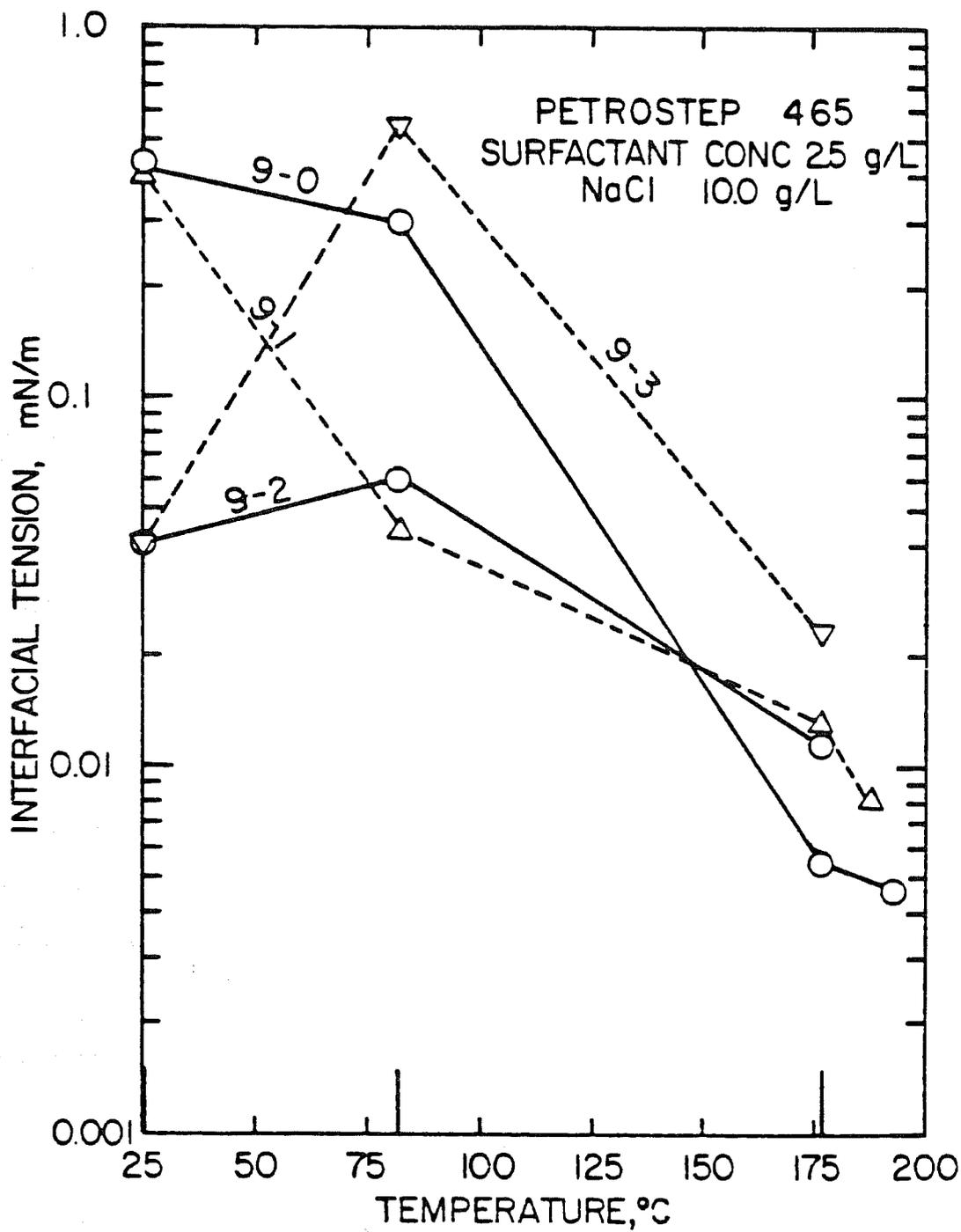


Figure 14. Interfacial tension measurements for surfactant/oil systems

at producing water-oil ratios in excess of 100. The producing water-oil ratios as functions of oil produced in pore volumes are shown on Figure 15. At 25°C the waterflood recovery was 33 percent of the initial oil-in-place. The post surfactant flood recovery was 10.6 percent and represented a 32 percent incremental recovery above that obtained by waterflood. 4.55 pore volumes of surfactant were required to obtain this recovery. Waterflood recovery at 177°C was 77.2 percent pore volumes and that after surfactant flooding was 92.8 percent, an incremental increase of 20 percent. 3.39 pore volumes of surfactant were required in the latter flood. Because our chemical stability tests had indicated that Petrostep 465 was more stable at elevated temperatures than TRS 10-80, we did a more extensive testing of this surfactant. Oil recoveries as functions of fluid injected are shown for three temperatures on Figure 16. Producing water-oil ratios are shown on Figure 17. Excellent oil recoveries were obtained with the Petrostep at the high temperature. However, the oil viscosities ranged only from a high of 22 cp at 25°C to 1.38 cp at 177°C. A more severe test of the combined effect of temperature and interfacial tension reduction was made using an oil with a viscosity of 504 cp at 25°C and 2.15 cp at 177°C. Results are shown on Figure 18. Waterflooding was not possible at 25°C but a comparison can be made at 82.2°C and 177°C. The major factor in these floods was the reduction of the oil viscosity with increasing temperature. Nevertheless, the surfactant did improve oil recovery significantly at 177°C.

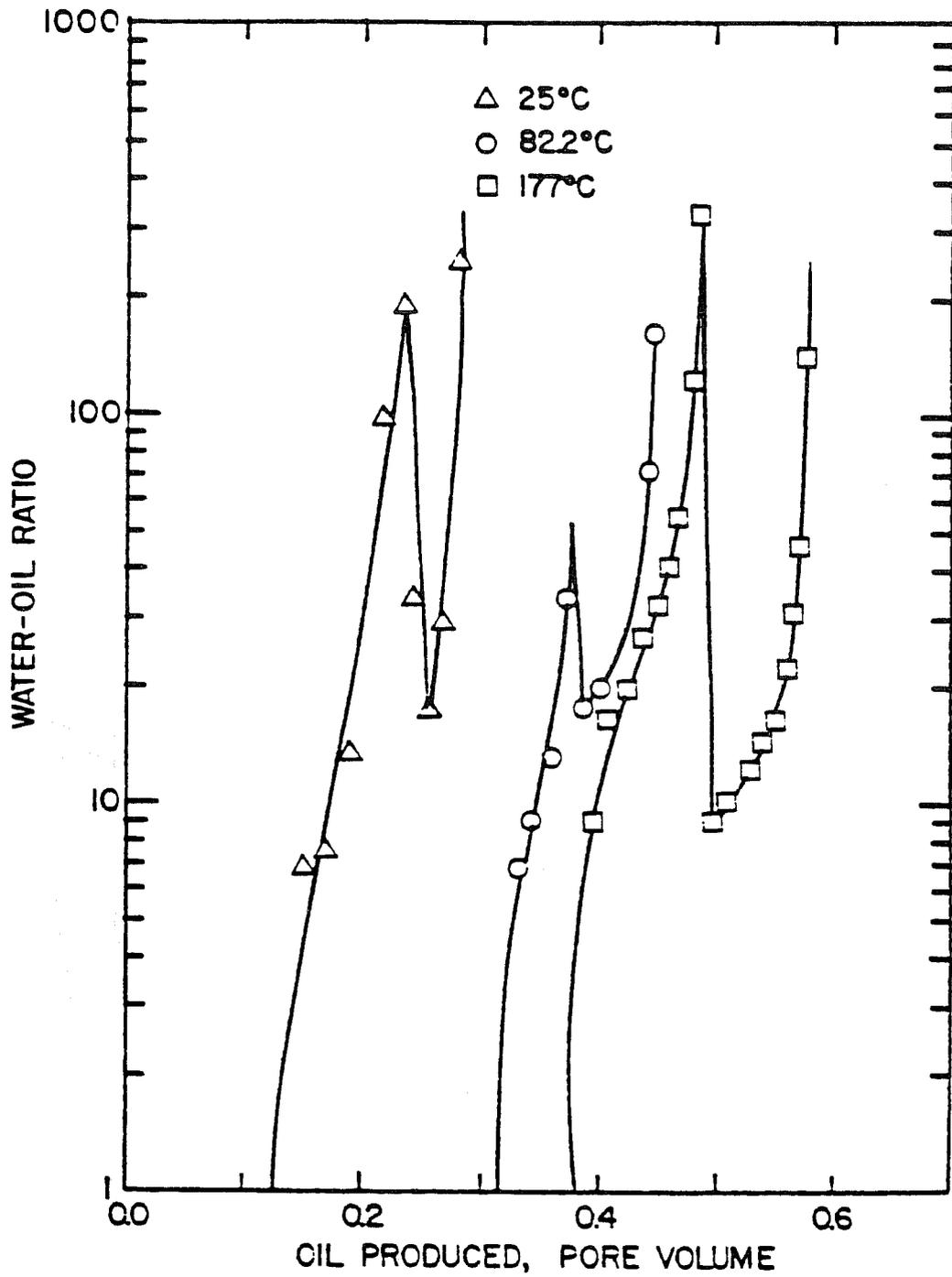


Figure 15. Water-oil ratios for surfactant floods following waterfloods, TRS 10-80

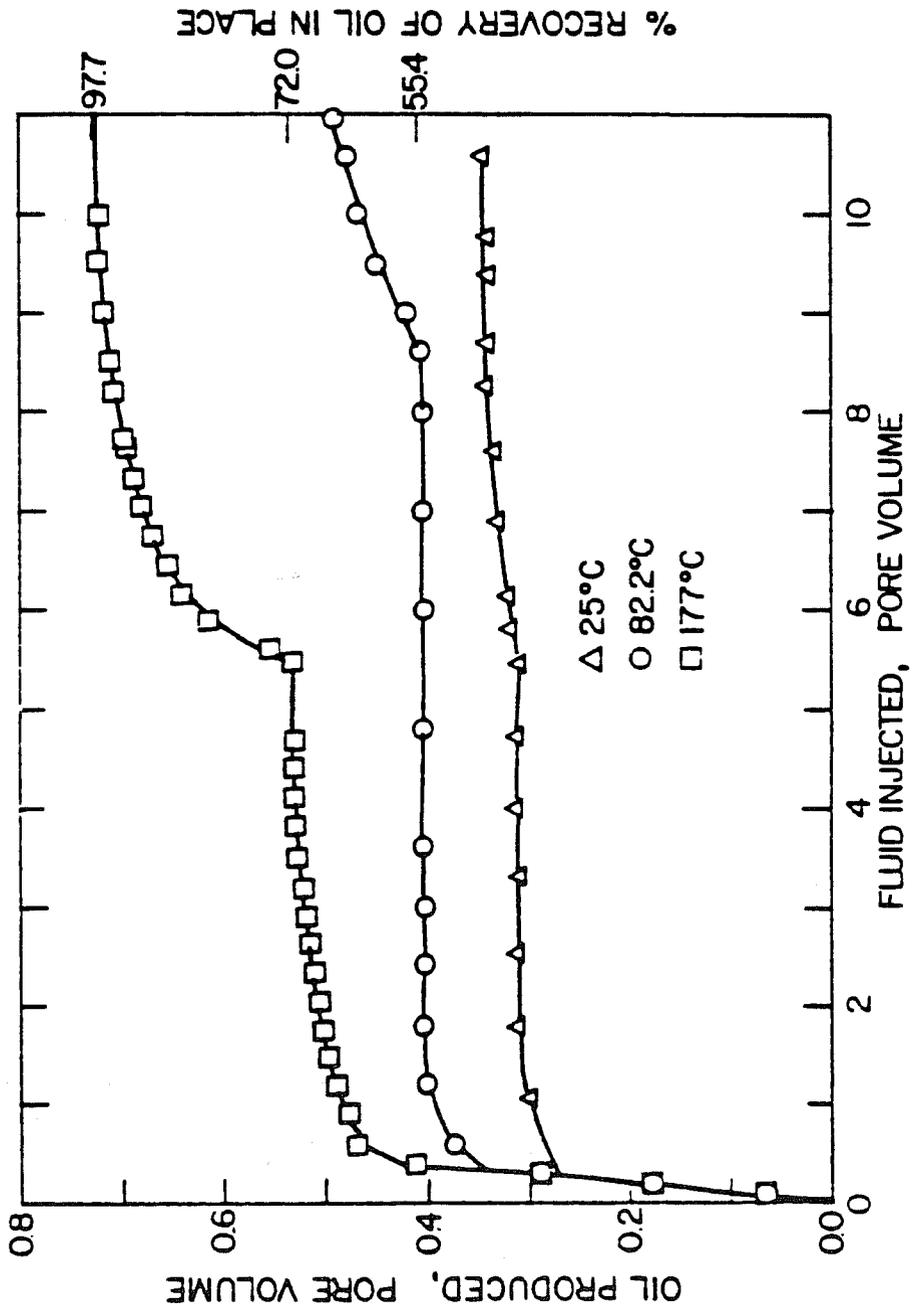


Figure 16. Oil displacement as function of fluid injected for surfactant following waterflood, Petrostep 465

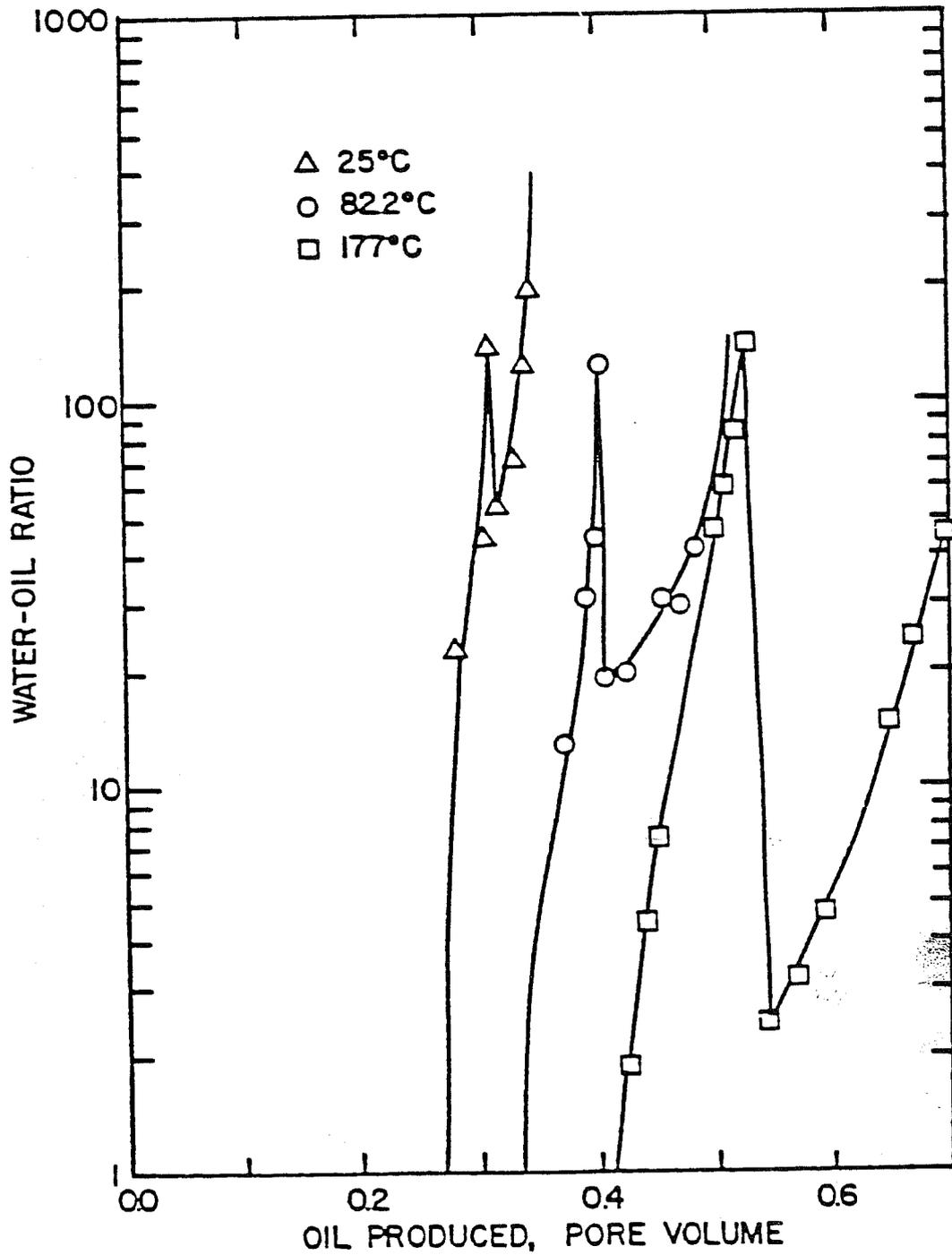


Figure 17. Producing water-oil ratios for surfactant floods Petrostep 465

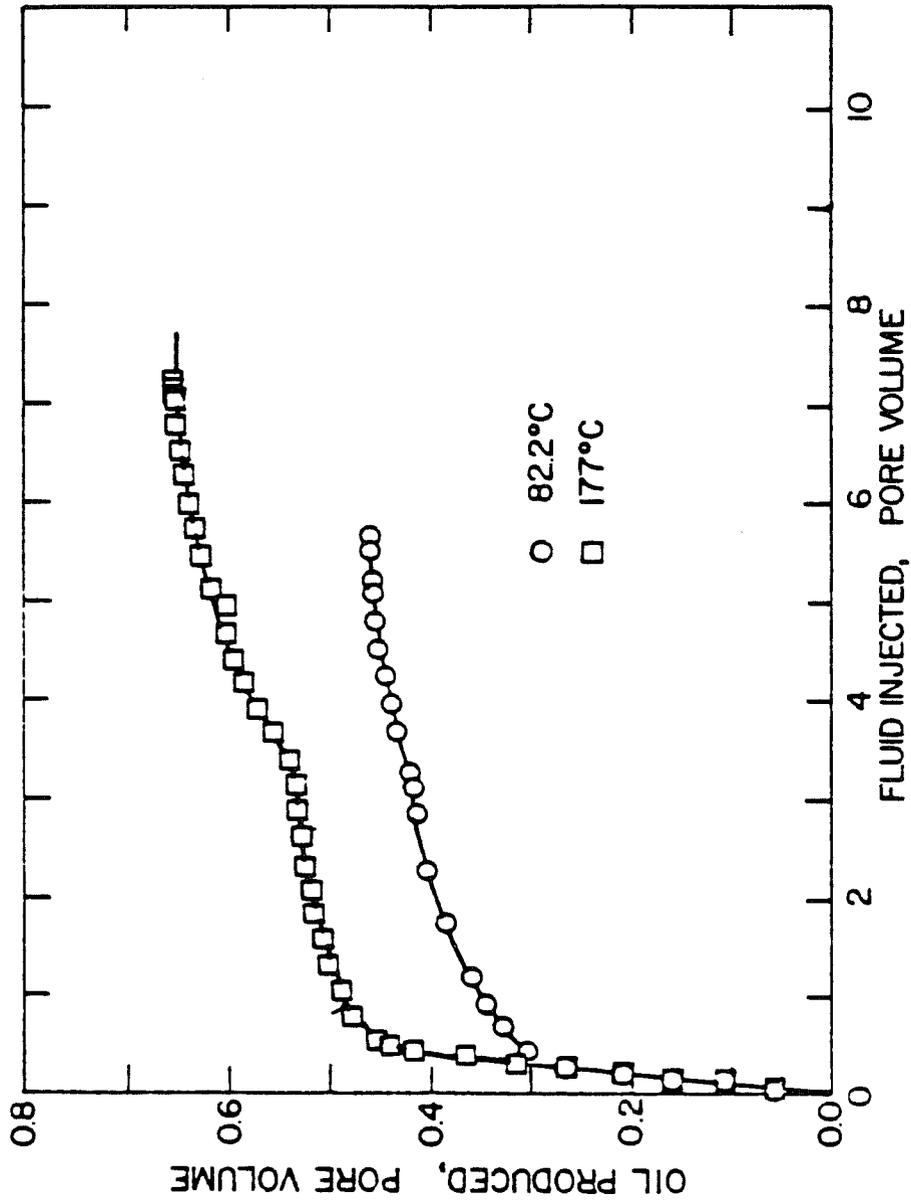


Figure 18. Oil displacement of high viscosity oil using Petrostep 465

Conclusions from these and other related experiments are as follows. Both Petrostep 465 and TRS 10-80 gave additional oil recoveries beyond those obtained by waterflooding at all temperatures. Total oil recoveries of original oil-in-place varied between 44 percent at 25°C and 93 percent at 177°C for Witco TRS 10-80 and between 55 percent and 98 percent for Petrostep 465 over the same temperature range. The combination of interfacial tension reduction by surfactant and oil viscosity reduction at elevated temperatures resulted in significant improvement in oil recovery. Surfactant adsorption in the water-solid interface and, possibly, in the water-oil interface delayed the arrival of the surfactant and increased the water-oil ratios during the period of time over which the additional oil was recovered. However, since the surfactant would be injected during an ongoing steamflood, the most important effects would be the increase in total oil recovery and the decrease in the steam-oil ratio during the flood.

II. INORGANIC ADDITIVES FOR STEAMFLOODS

A number of organic chemicals have been evaluated as possible additives for waterfloods to improve oil recovery. These all result in pH's on the basic side. The mechanisms by which caustic solutions may recover oil from reservoir containing acidic crudes are reviewed by Johnson¹⁷. A principal advantage in using caustic with steamfloods is that many of the heavy oils for which steam is currently being used to increase oil recovery are also acidic crudes and are, therefore, suitable for flooding with high pH solutions. A disadvantage, however, is that the

reservoir rock reacts itself with hydroxyl ions and this reaction will increase with increasing temperature. The major objectives of the research with caustic was to evaluate the effect of pH on oil recovery, especially at temperatures associated with steam injecton. A concurrent objective was to quantify caustic consumption as functions of temperature and rock composition. In particular one must determine if it is possible to propagate through a siliceous reservoir rock at steam temperature a pH high enough to be effective in recovering oil. In this connection the possibility has been proposed that certain high pH solutions may be less reactive than others. In particular, silicate solutions may have already established an equilibrium concentration with the reservoir rock.

A. Caustic Consumption by Reservoir Rock as Related to Temperature

Of primary importance was the question whether a high pH could be propagated through the reservoir. First emphasis was given to investigating this problem. The results of this work are summarized in detail in a thesis by Dehghani¹⁸ and in a paper by Dehghani et al.¹⁹. Both of these have been published since the conclusion of the original work on steamflood additives and include results obtained both as a part of the contract and as a part of more recent contracts. The current status of the work is being reported.

Two effects need to be considered in determining caustic loss. These are ion exchange and chemical reaction. Ion exchange increases the volume of caustic which must be injected

before high pH is produced at the production wells. The pH would eventually arrive at its injection concentration, however, if it were not for chemical reaction in the region of the reservoir containing high pH solution. Prediction of the consumption requires a good knowledge of the reservoir rock and the mechanisms by which the rock reacts with the caustic^{20,21,22,23}. Bunge and Radke²⁴ have attributed the caustic loss to three types of reaction.

1. surface exchange and hydrolysis.
2. congruent and incongruent dissolution.
3. insoluble hydroxide formation by reaction with hardness ions in the reservoir brine and from the rock surface.

The effects of these mechanisms were evaluated in our study by two types of experiments: batch or static experiments and dynamic or flow experiments. In all cases the rock material was either an unfired or fired Berea sandstone. Dynamic experiments were carried out at temperatures up to 180°C, which is at the lower end of the temperature scale for steamfloods. Flow experiments were used to find both the ion exchange isotherms and dissolution rates. For measurement of the amount of ion exchange between the rock and the caustic solution, contact time must be short enough to minimize the effect of dissolution²⁴. Batch experiments cannot be used due to experimental limitations imposed by the elevated temperatures. High flow rate experiments were used to avoid the effect of dissolution on the amount of ion exchange measured. Batch experiments were used to measure the amount of dissolution at longer periods of caustic and rock

contact.

High flow rate experiments with different caustic injection concentrations were conducted at four different temperatures of 80°, 100°, 150°, and 180°C. An effluent hydroxide concentration versus time curve was generated for each experiment. The amount of ion exchange was calculated by integrating this curve. If one assumes an average surface area of 0.93 m²/g for consolidated Berea sandstone, one can plot Figure 19 which shows ion exchange isotherms for tested temperatures. The shape of the curve suggests Langmuir type isotherms. An increase in temperature causes an increase in the amount of ion exchange. The caustic solutions used to generate the data points in Figure 19 were all prepared with distilled water. The core was saturated with 2 percent brine before the start of caustic injection.

The effect of salt concentration on ion exchange was investigated at the higher temperature (180°C) by injecting into the core caustic solutions made with three different brine solutions at concentrations of 5000, 10,000 and 20,000 ppm. The core sample was saturated with brine of the same concentration as was used to prepare the caustic solution. Figure 20 shows the ion exchange isotherms for three salt concentrations at 180°C. The results indicate decreasing ion exchange with increasing salt concentration.

Figure 21 shows a plot of log K_e versus 1/T. The slope of this plot gives the heat of the ion exchange reaction. Since the plot is a straight line the heat of the ion exchange reaction is

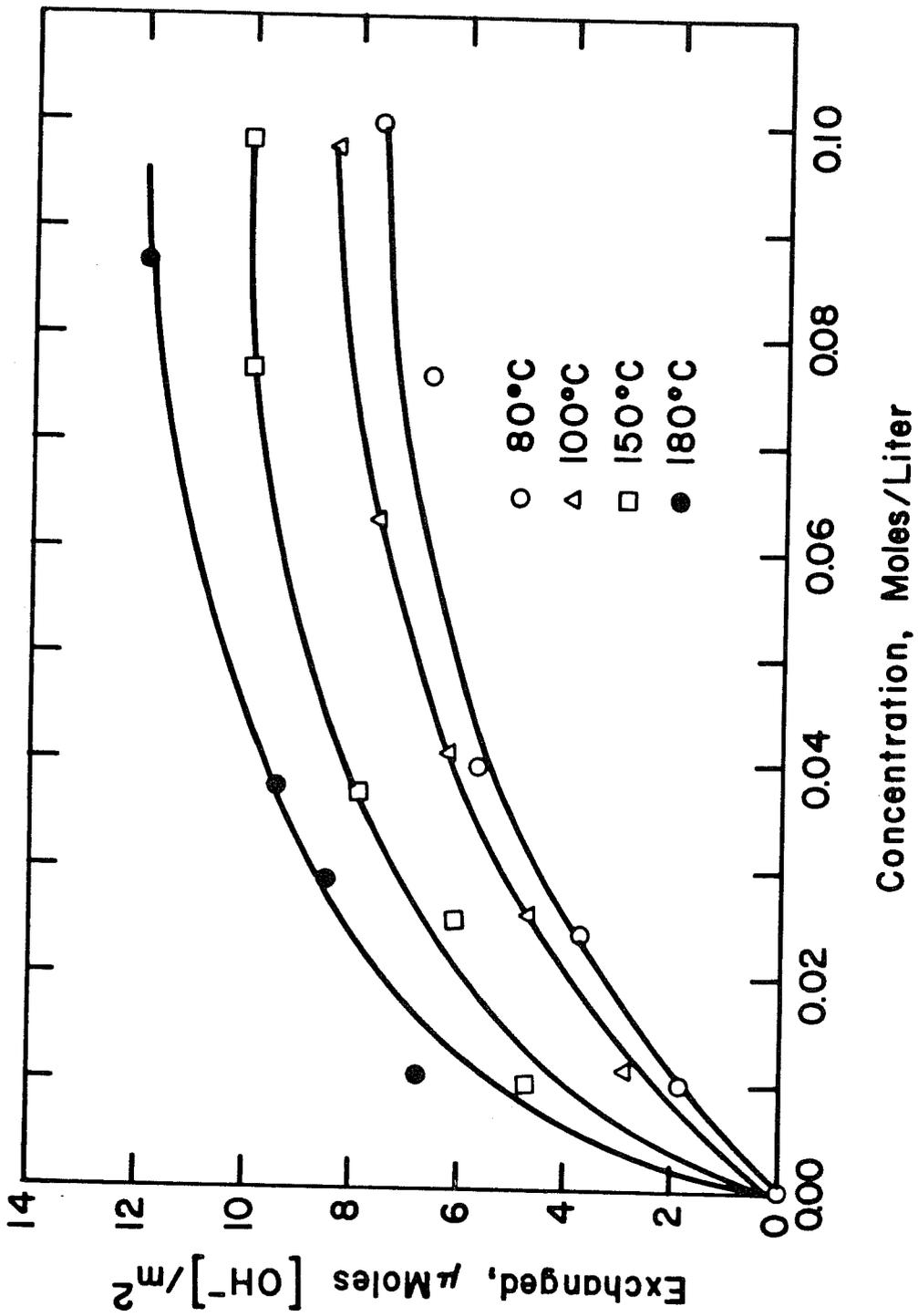
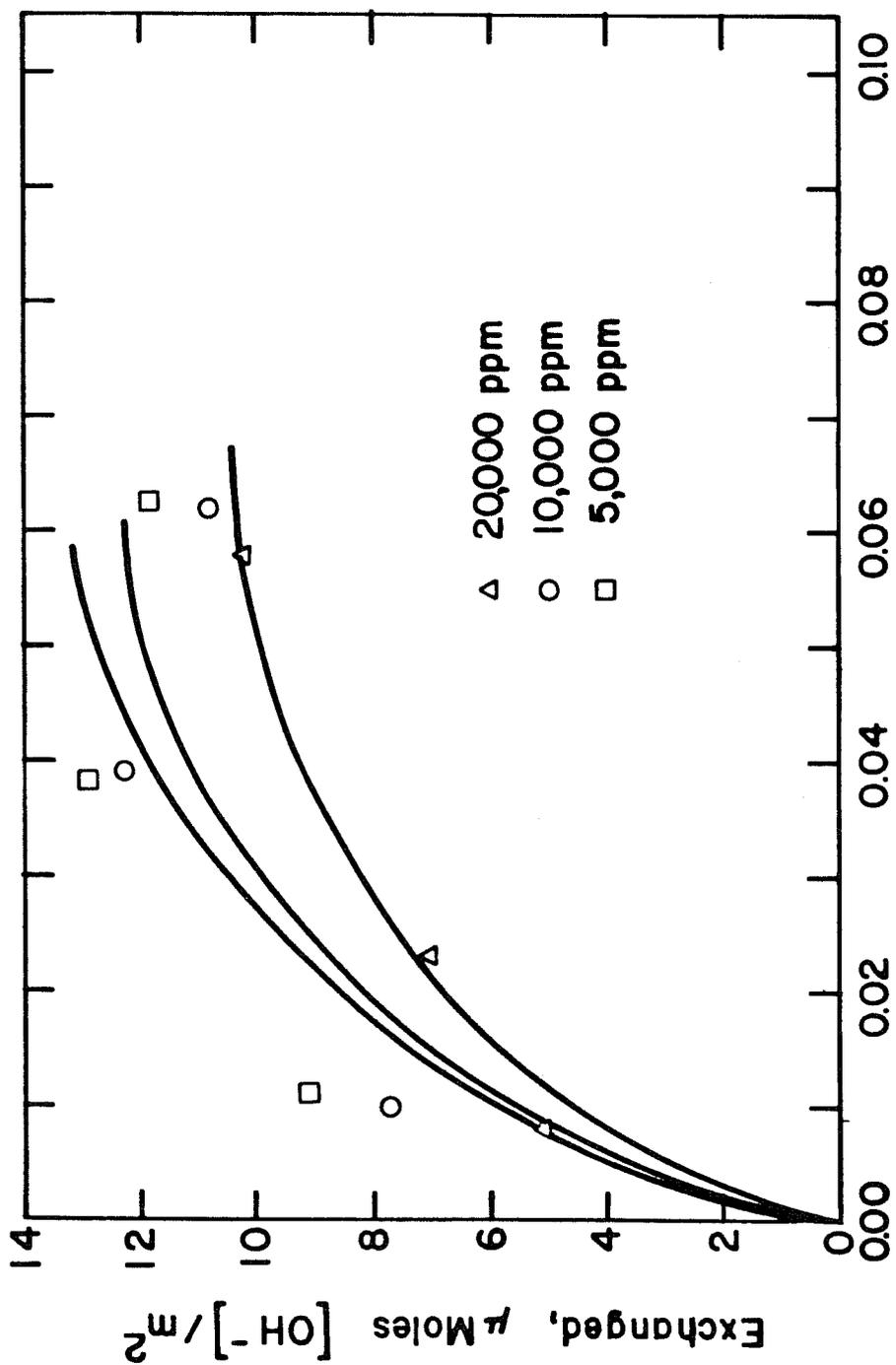


Figure 19. Ion exchange isotherms for caustic and Berea sandstone at different temperatures



Concentration, Moles/Liter

Figure 20. Effect of salt concentration on ion exchange of caustic and Berea sandstone at 180°C

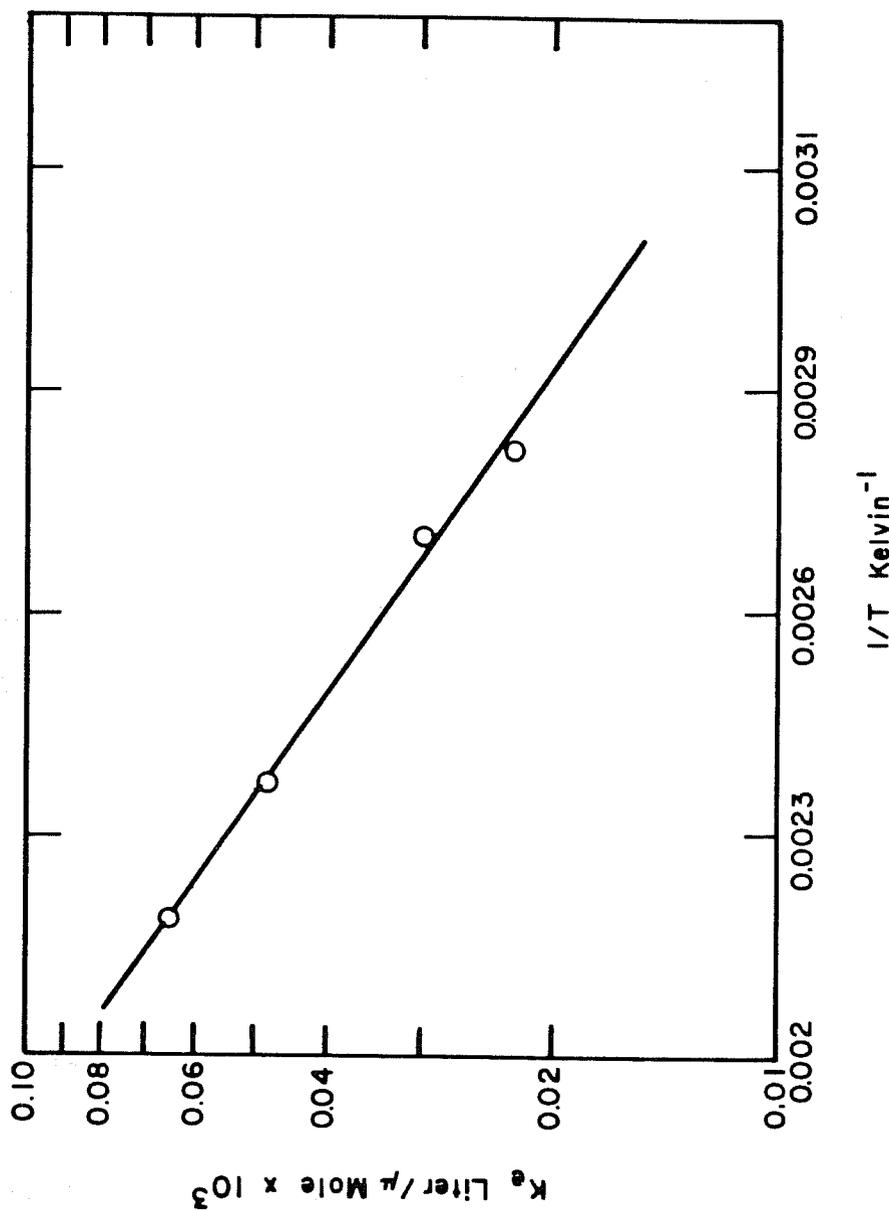


Figure 21. Log of ion exchange equilibrium constant versus $\frac{1}{T}$

constant in the range of temperature tested. Equilibrium constants can be calculated for other temperatures by extrapolation of the straight line plot.

Two trends are always seen in flow experiments. First, hydroxide ion exchange breakthrough is delayed due to ion exchange and second, the hydroxide ion concentration levels off at a level lower than the injection concentration. The difference between the effluent final hydroxide concentration and the injection concentration is caused by the dissolution reaction.

Flow experiments have been conducted for three injection concentrations. For every injection concentration the effects of temperature, flow rate and presence of clay minerals have been examined. The term "flow rate" throughout this work means volumetric flow rate per unit area.

Figure 22 shows the effect of temperature on the final plateau value in the case of an injection concentration of 0.1 N (pH=13) and a flow rate of 1 ft/day for a fired Berea sandstone core. For a temperature of 150°C, the final pH plateau is 12.65. An increase of the temperature to 180°C caused a shift of the final pH plateau to 12.00. This shows that increase of temperature causes more dissolution. In all the flow experiments, the core was saturated and flooded with 2 percent brine prior to start of caustic injection.

The effect of flow rate has been evaluated by conducting experiments with three rates of 5, 1 and 0.5 ft/day for 180°C and an injection concentration of 0.1 N (pH=13). The results are

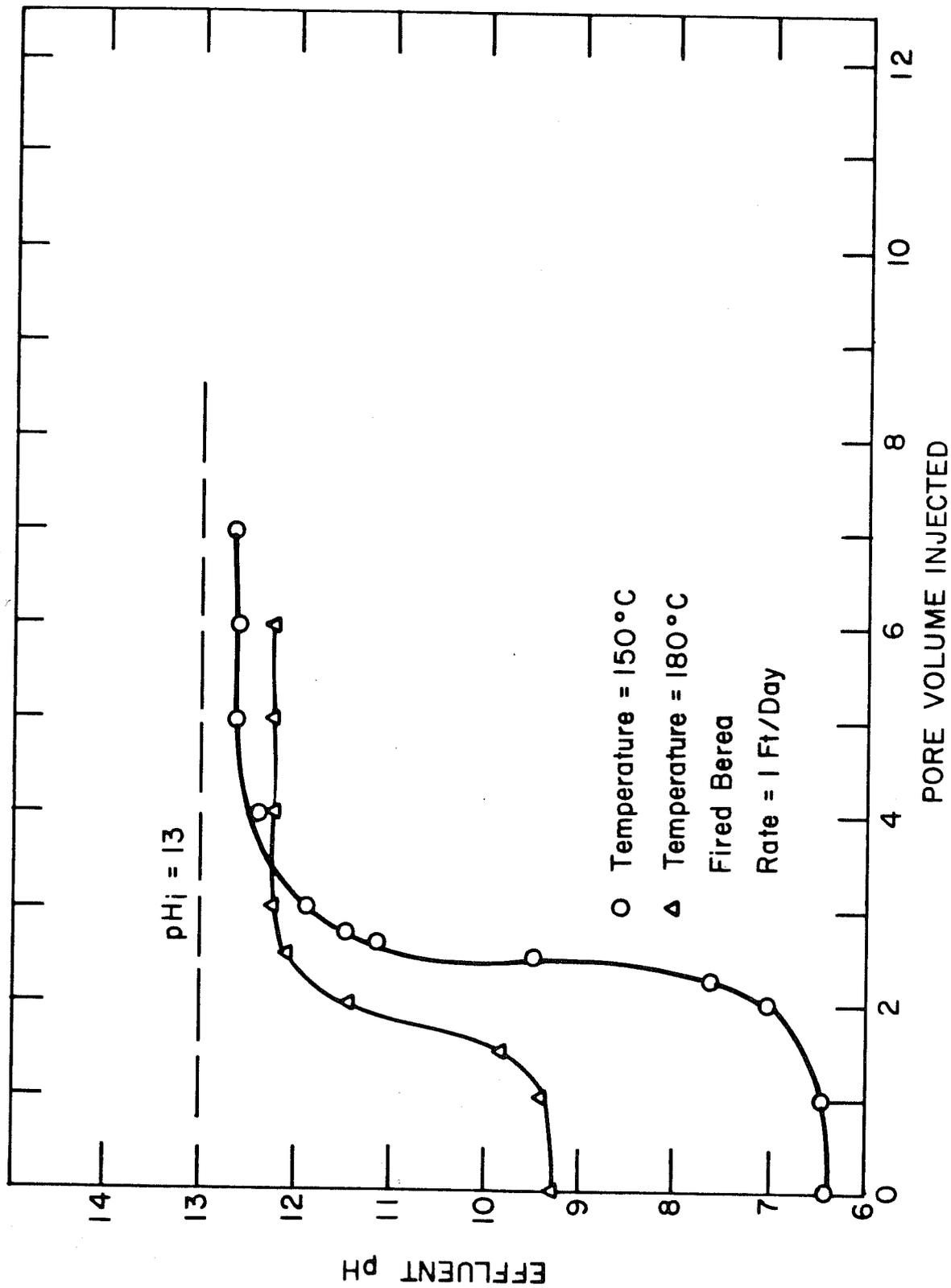


Figure 22. Effluent pH as a function of pore volumes of 0.1 N hydroxide injected in fired Berea at 150° and 180° with a rate of 1 ft/day

shown on Figure 23. A decrease in the rate from 5 to 1 ft/day shifts the plateau from a value of 12.69 down to 12.25 and, finally, at a rate of 0.5 ft/day the final pH plateau is 12.00. The results show that when the rate is decreased, the caustic has more time to dissolve the rock. Similar results on the effect of rate, temperature and injection pH are shown on Figures 24 and 25. All of these results are best summarized in a plot of hydroxide concentration as a function of residence time as shown for 180°C on Figure 26. The effect of temperature for a given injection concentration is shown on Figure 27. Such plots could be used to predict pH at reservoir rates, temperatures and lengths. Both Figures 26 and 27 show a flattening of pH either with decreasing injection pH or decreasing temperature. Batch experiments with fixed amounts of sand and caustic also show a stabilization of the pH suggesting equilibrium may have been obtained as shown on Figure 28. The results are not yet conclusive and further experimental and theoretical work are required to permit a more precise prediction of pH with throughput of caustic at elevated temperatures.

B. Effect of Temperature and pH on Waterflood Oil Recovery

Another significant aspect of the use of inorganic additives with steam was the effect of temperature and pH of the injection water on crude oil recovery. Experiments were performed in which both temperature and pH were varied for the flood water and the effects noted on oil recovery for Berea sandstone cores saturated with brine and an acidic Long Beach crude oil.

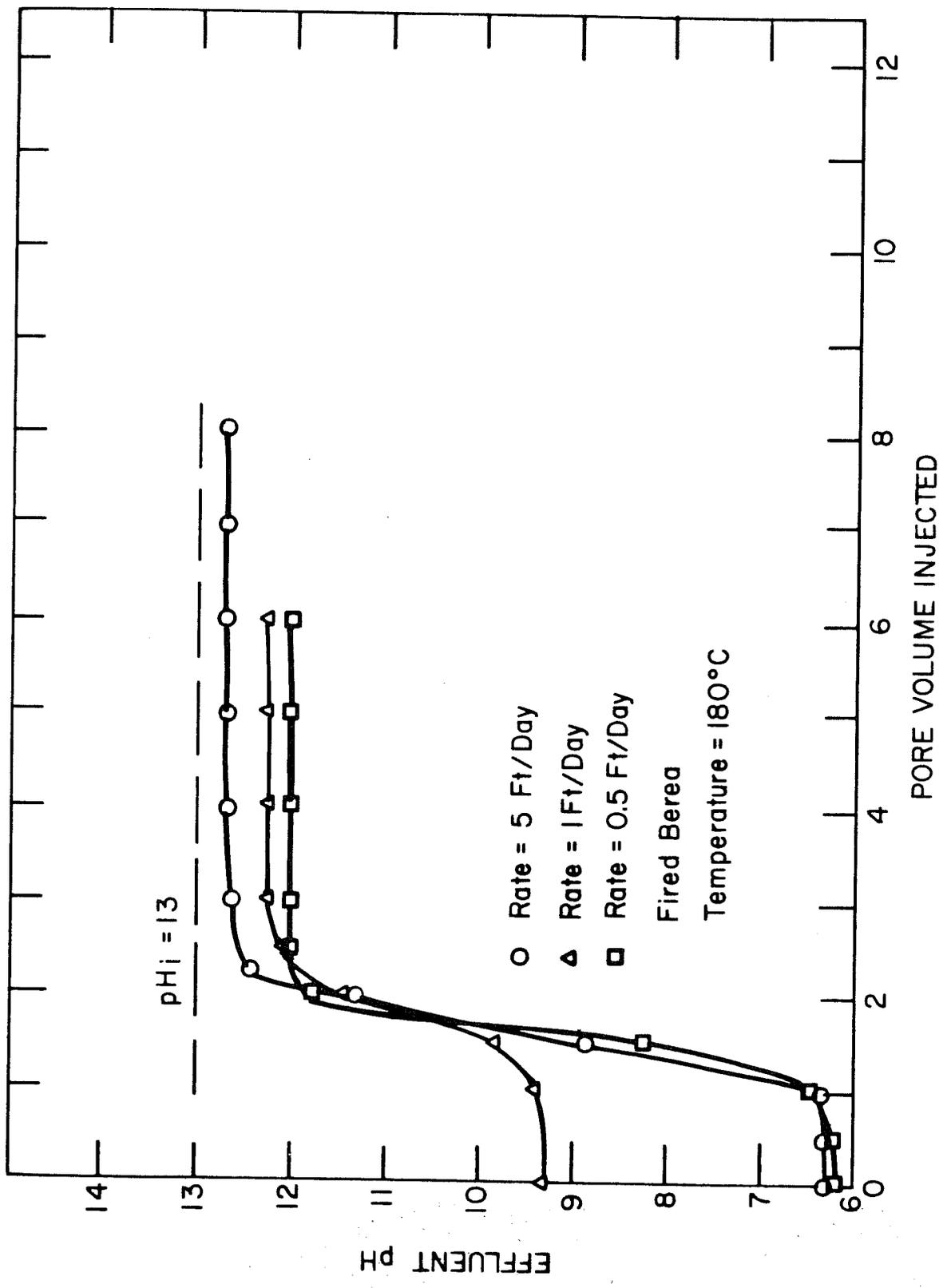
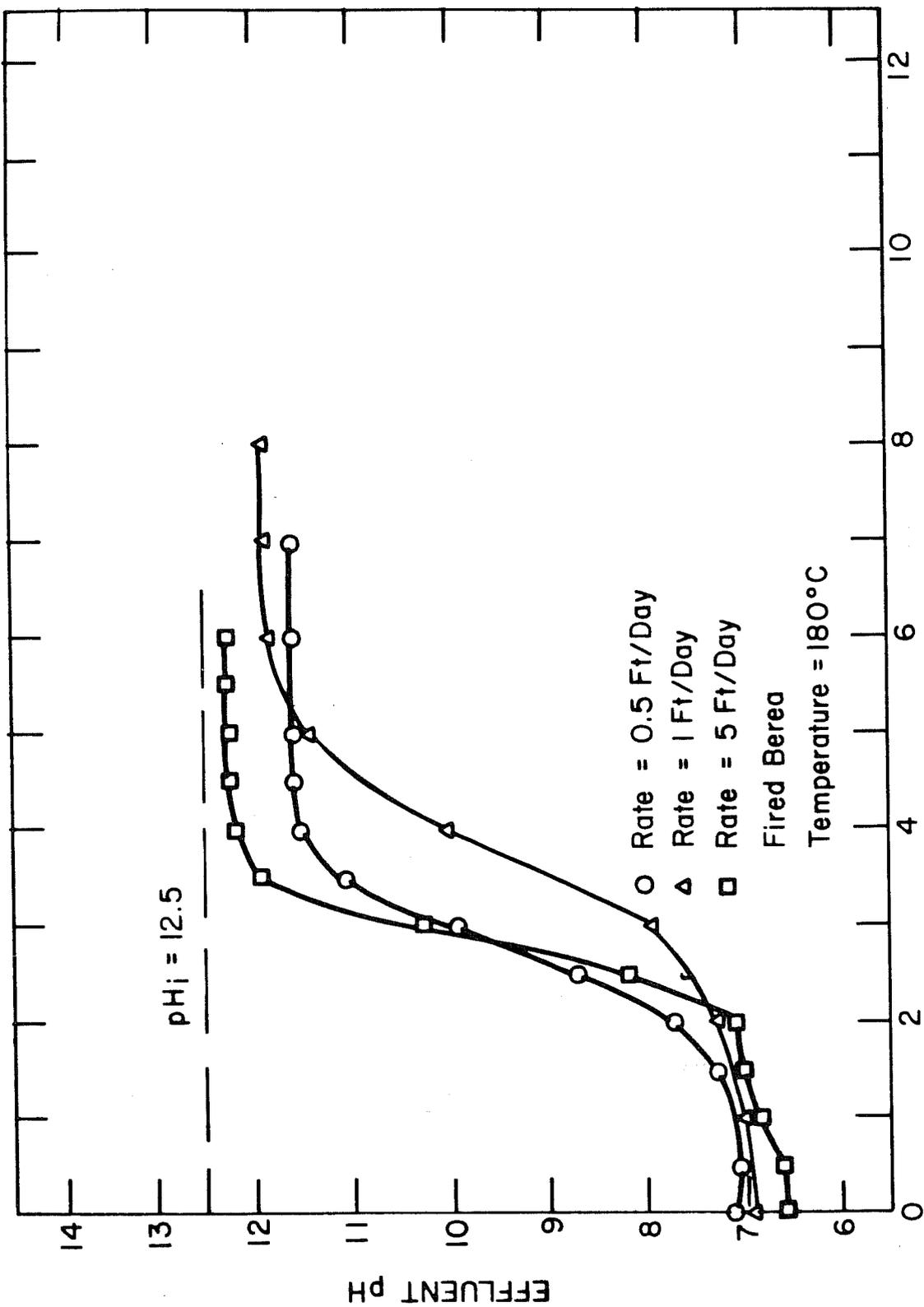


Figure 23. Effluent pH as a function of pore volumes of 0.1 N hydroxide injected in fired Berea sample with three different rates of injection 5, 1, 0.5 ft/day at 180°C



PORE VOLUME INJECTED

Figure 24. Effluent pH as a function of pore volumes of 0.0316 N hydroxide injected in fired Berea sample with three different rates of injection 5, 1, 0.5 ft/day at 180°C

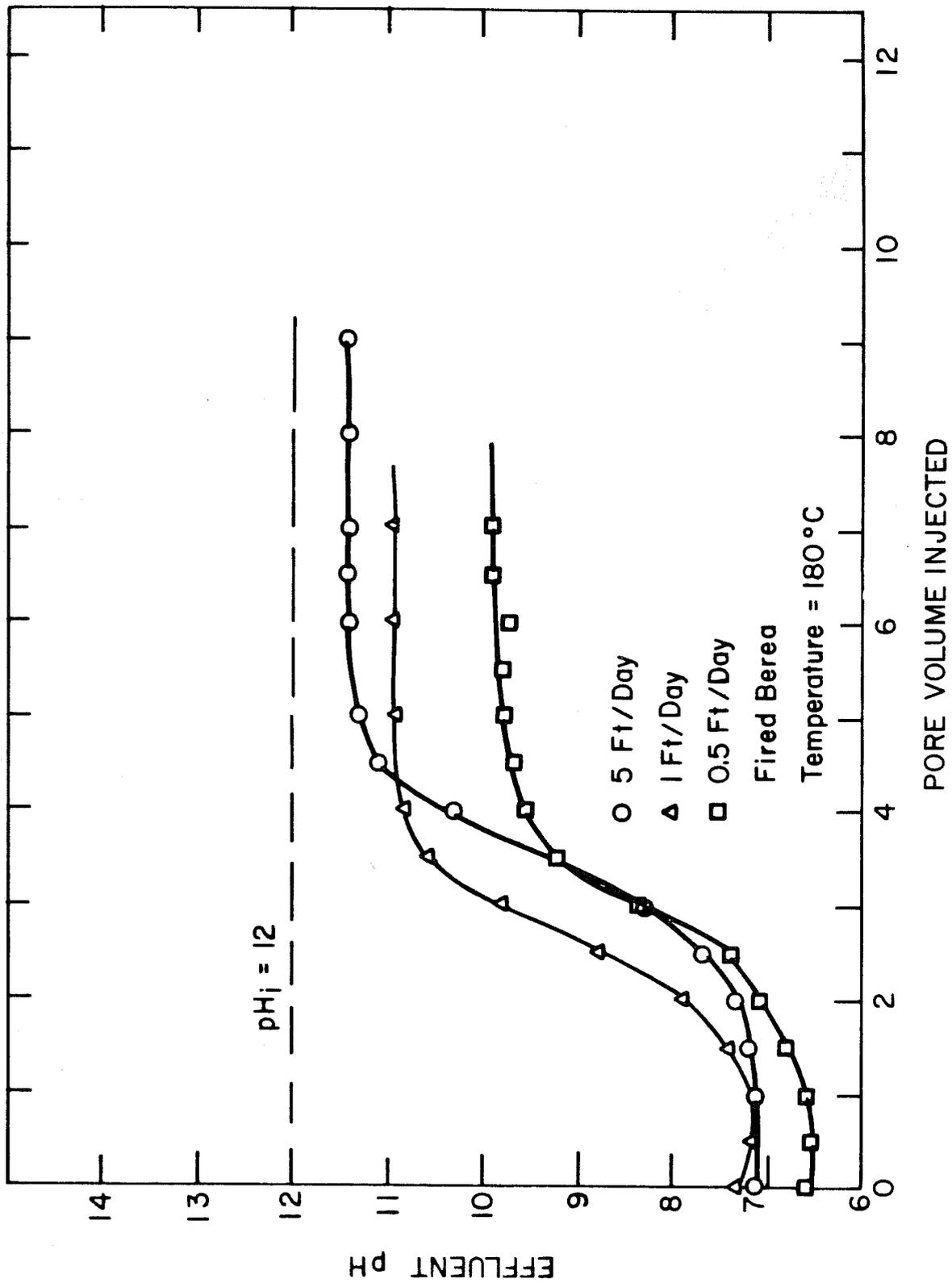


Figure 25. Effluent pH as a function of pore volumes of 0.01 N hydroxide injected in fired Berea sample with three different rates of 5, 1, 0.5 ft/day at 180°C

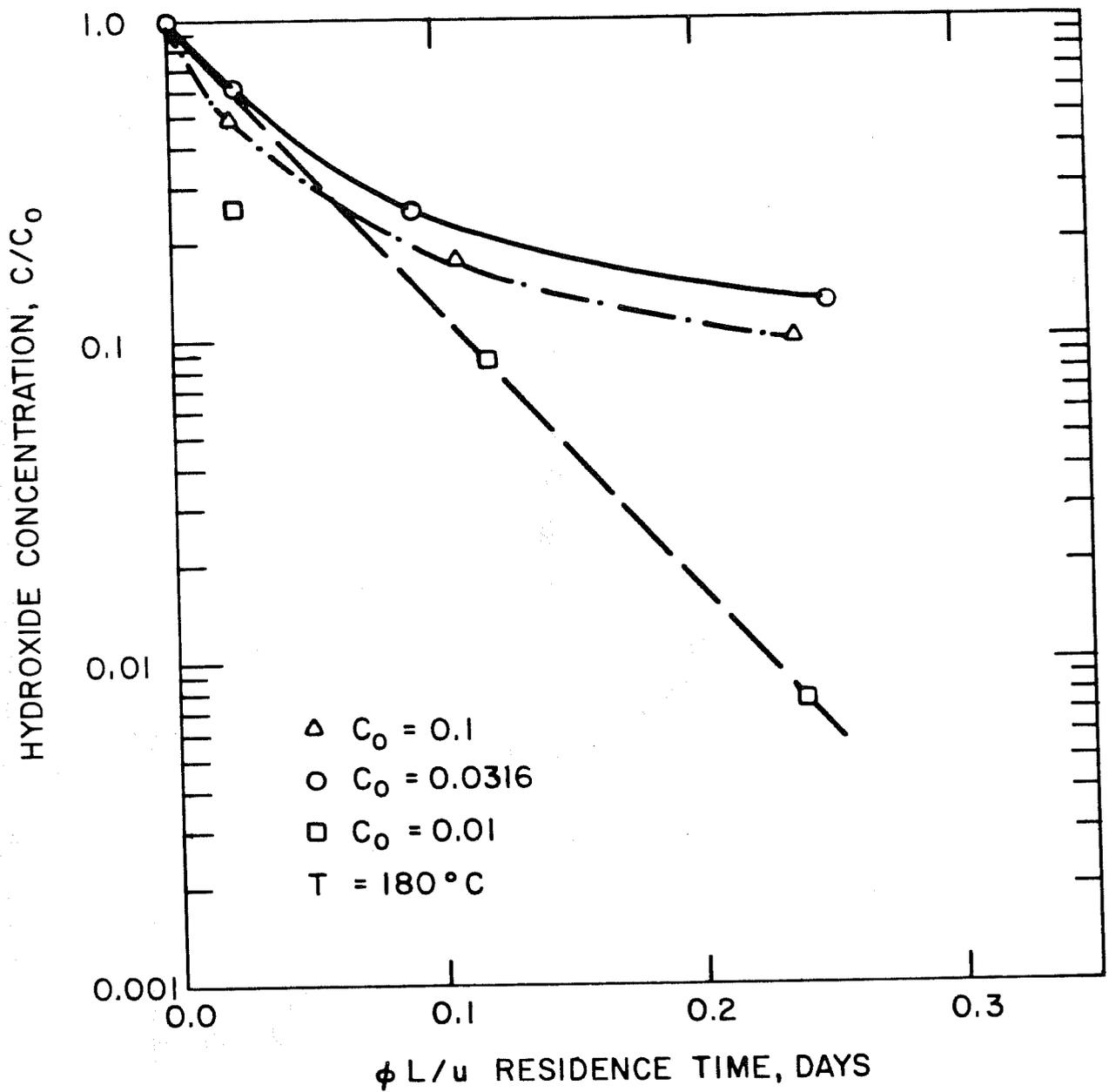
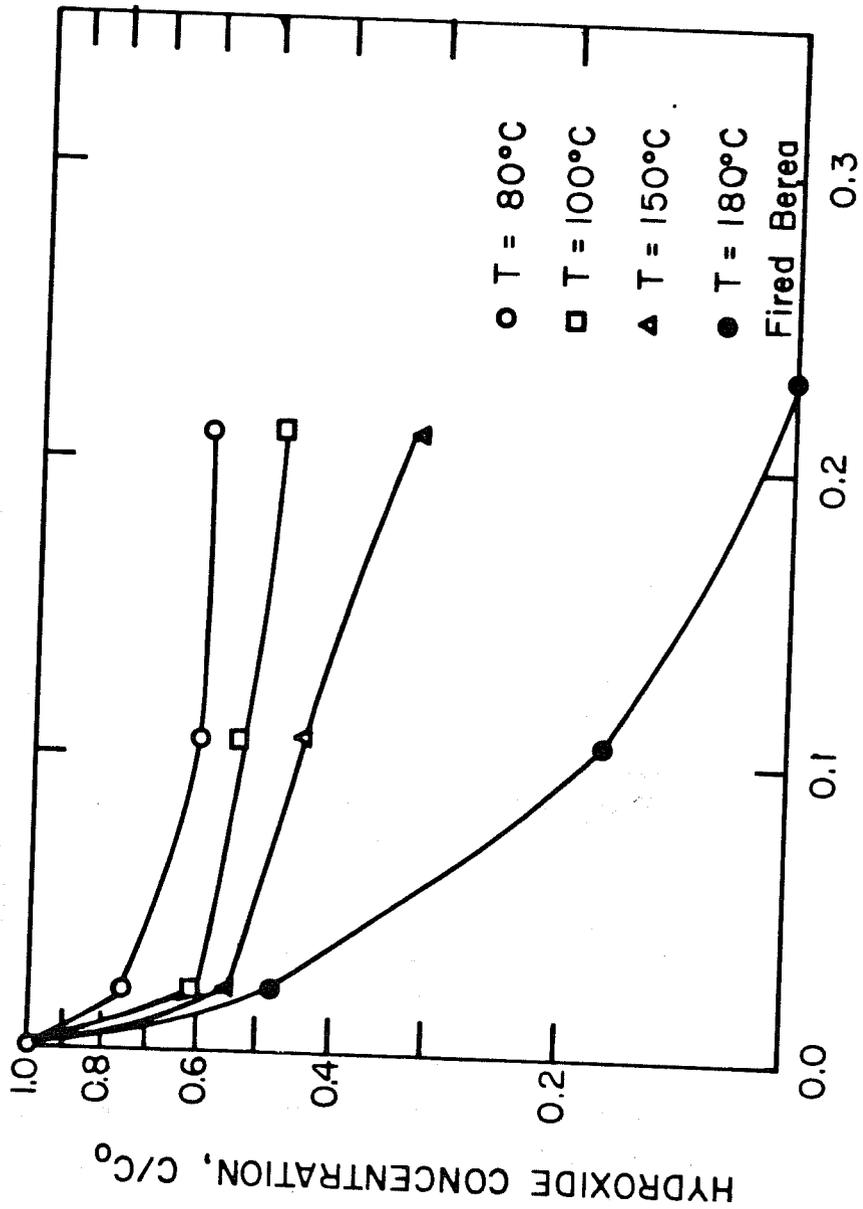


Figure 26. Log of fraction of hydroxide concentration versus residence time for three different initial caustic concentrations: 0.01, 0.0316, and 0.1 N at 180°C for fired Berea samples



$\phi L/u$ RESIDENCE TIME

Figure 27. Log of fraction of hydroxide concentration versus residence time for 0.1 N initial caustic concentration at four temperatures: 80°, 100°, 150° and 180°C for fired Berea samples

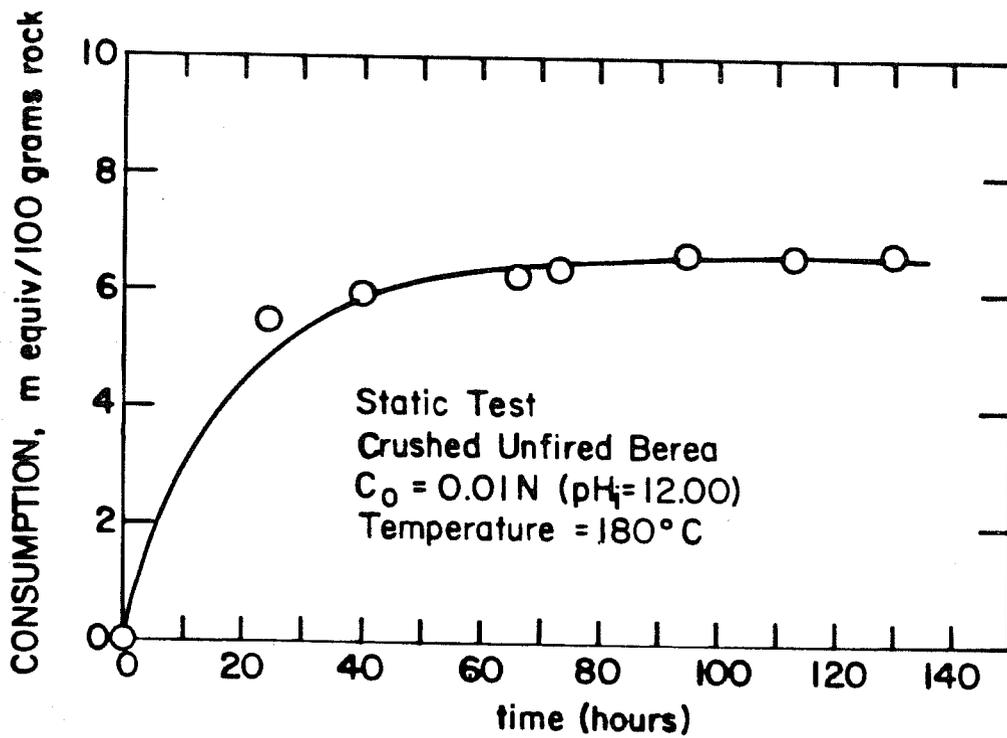


Figure 28. Consumption of hydroxide with contact time for crushed fired Berea sample with initial concentration of 0.01 N and a temperature of 180°C

Effect of Temperature. Four runs in two cores were conducted to evaluate residual oil recovery with caustic after waterfloods. The flood temperatures were 125°C and 150°C at a tertiary flood rate of 5 ft/day for the first two floods. The flood temperatures were 150°C and 180°C at a tertiary rate of 7 ft/day for the third and fourth runs. The injected caustic had pH = 13 and no salt was added. The first two runs recovered 13.1 percent and 22.8 percent of the residual oil, while the next two runs recovered 27.3 percent and 28.6 percent of the residual oil, respectively. No pressure buildup was observed across the cores. Recovery as fraction of oil-in-place and effluent pH are plotted versus total pore volumes injected on Figures 29 through 31 for these runs.

Effect of Salt. The effect of salt concentration at constant temperature and pH are evaluated in the fifth and sixth experiments. Temperature was set at 180°C and pH at 13. The salt content of the caustic solution was varied from zero to 20,000 ppm. In the case of 20,000 ppm salt, 32.3 percent of the residual was recovered. In the case of 10,000 ppm salt, 26 percent of the residual was recovered. No pressure buildup across the core was observed. Recovery as fraction of oil-in-place and effluent pH are plotted versus total pore volumes injected for the first of these experiments on Figure 32.

Effect of Tertiary Flood Rate. The effects of tertiary flood rate were evaluated at 180°C. Tertiary flood rate was 2 ft/day as compared to 7 ft/day for the early runs. No additional oil was recovered with a caustic solution at pH of 13 (no salt)

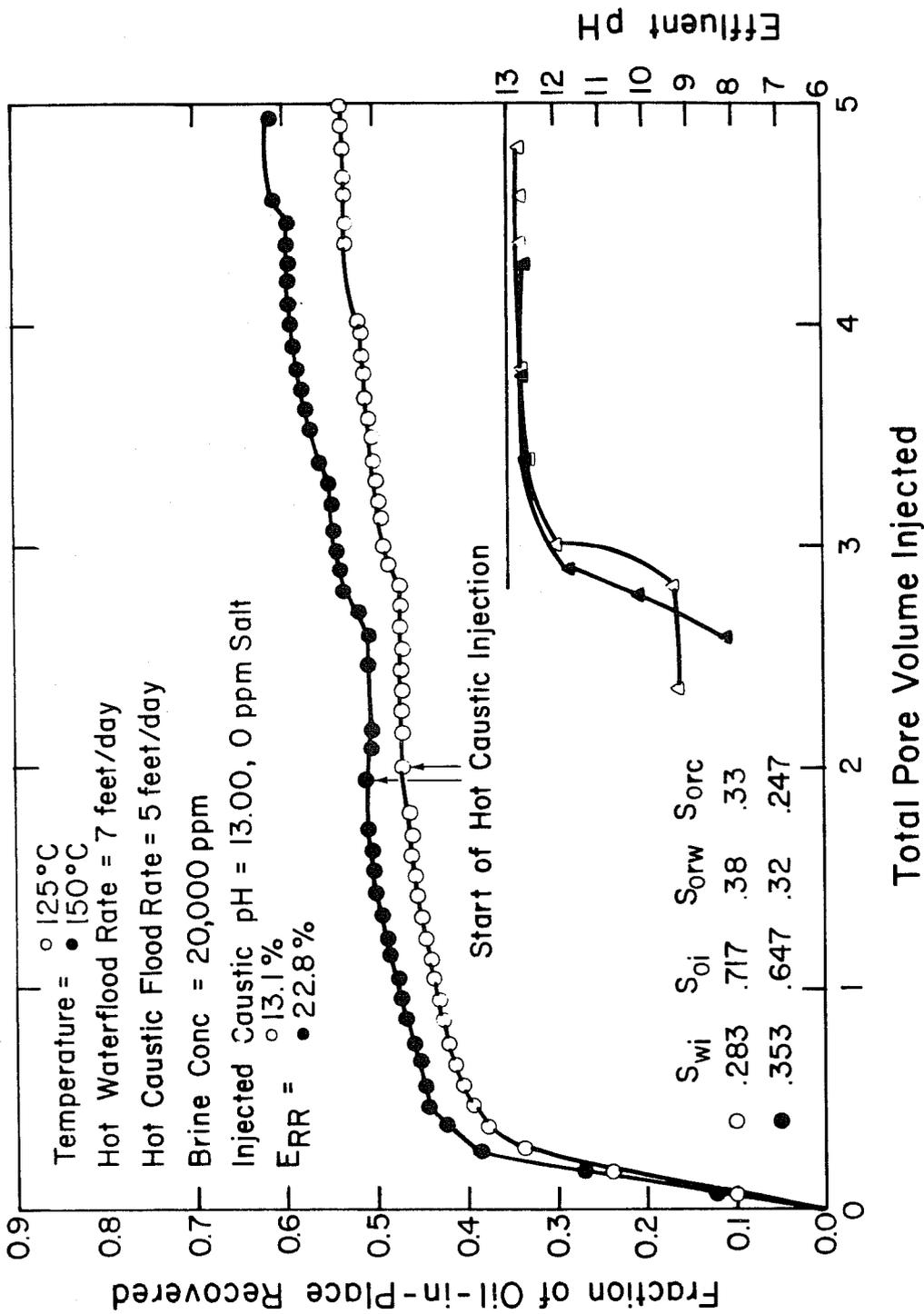


Figure 29. Comparison between recovery performance and caustic consumption at 125°C and 150°C for a tertiary flood rate of 5 ft/D

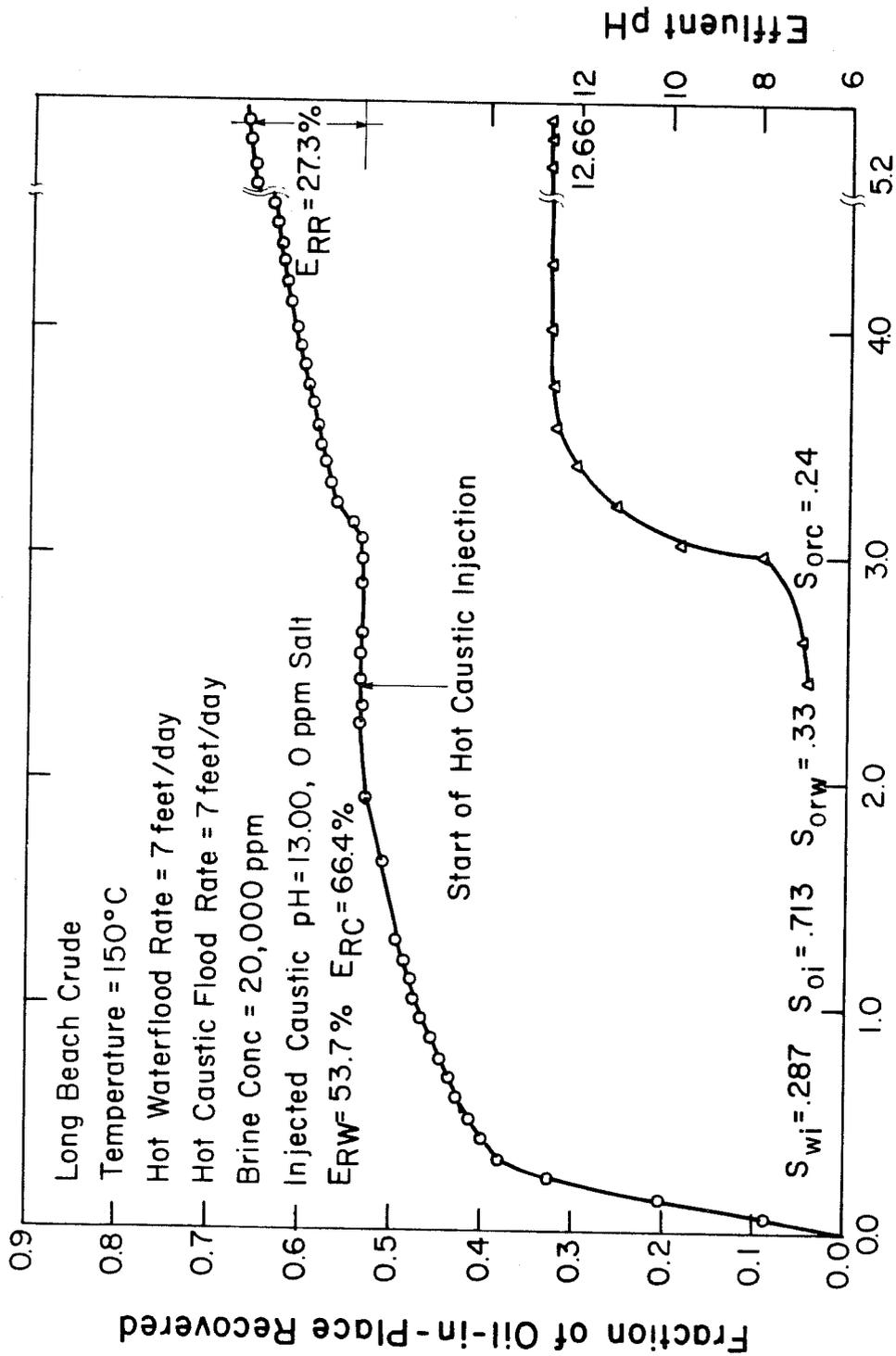


Figure 30. Recovery performance and caustic consumption

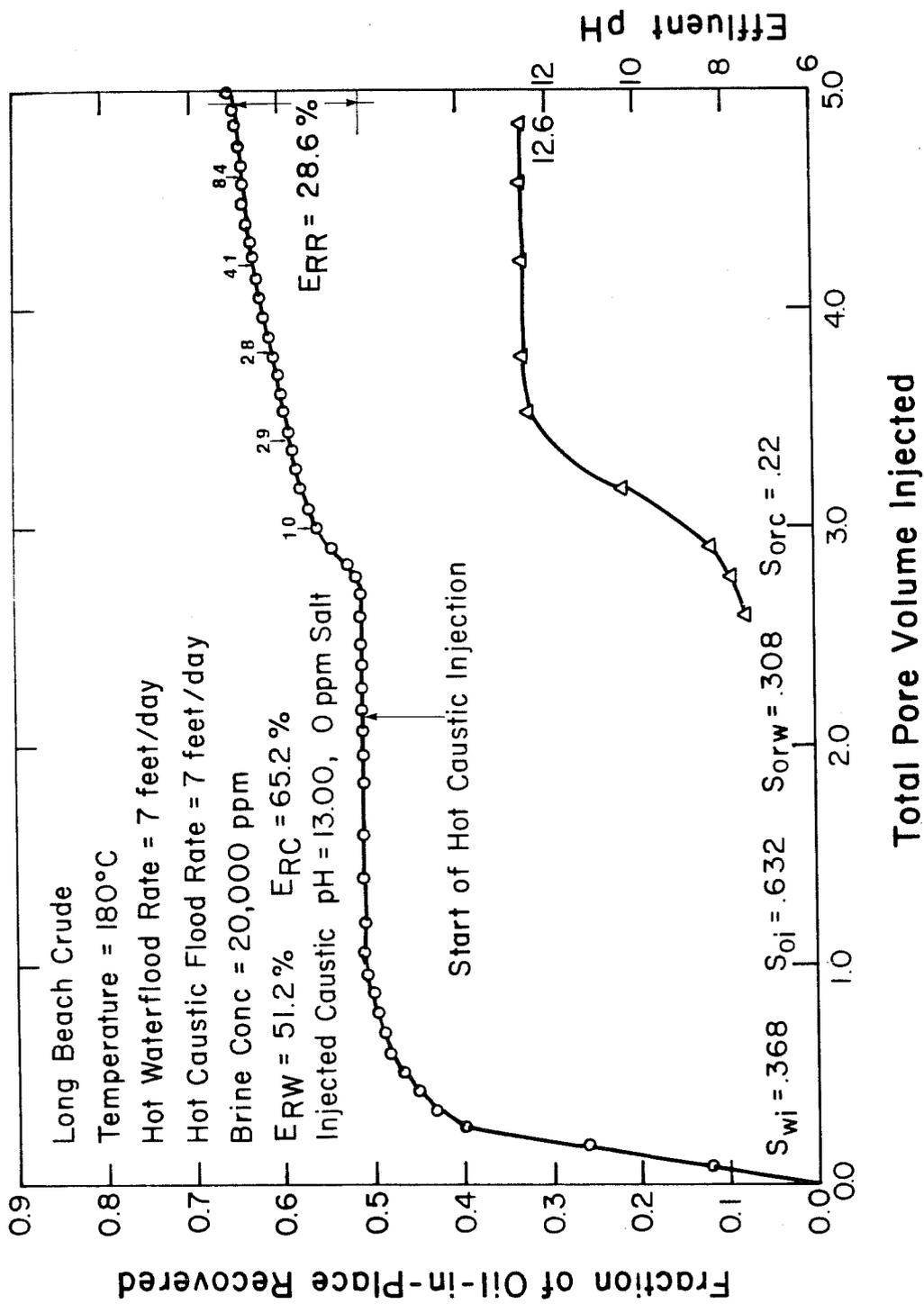


Figure 31. Recovery performance and caustic consumption at 180°C for a tertiary flood rate of 7 ft/D

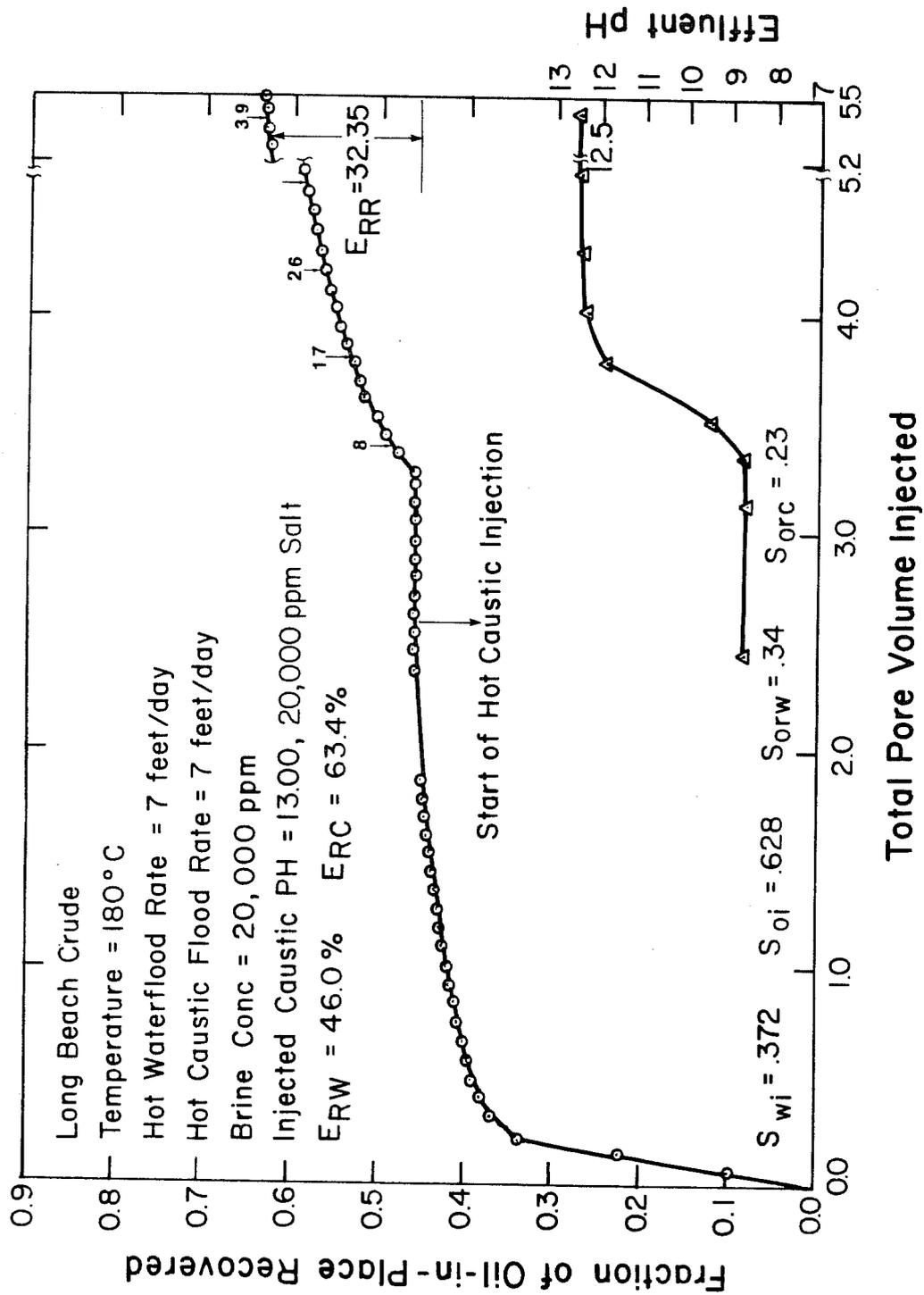


Figure 32. Effect of salt on tertiary recovery of acidic oil

injected at a rate of 2 ft/day. But the pressure drop started building up across the core as more caustic was injected. On the other hand, a run which contained 20,000 ppm salt in the caustic solution with a pH of 13 recovered about 18.5 percent of the residual oil. A small pressure buildup was observed but it decreased as oil started being produced. Recovery as fraction of oil-in-place and effluent pH are plotted versus total pore volumes injected on Figure 33.

Effect of Injection pH. The effect of pH was evaluated at pH = 12 and salt concentration of 10,000 ppm. The first run was at 180°C and the second run at 150°C. At this low pH no additional oil recovery was obtained for a tertiary flood at a rate of 7 ft/day. Effluent pH after four pore volumes of caustic injection was 9.0 for the higher temperature.

Effect of Oil Saturation. The effect of initial oil saturation was evaluated at rates of 7 and 2 ft/day. These two displacement runs were performed on separate cores with no prior waterflooding. Injected solution had a pH of 13 with 10,000 ppm salt. Flood rates were 7 ft/day and 2 ft/day. The ultimate recoveries were comparable to those obtained for the tertiary floods. Recovery as a fraction of oil-in-place versus total pore volumes injected for these runs is shown on Figure 34.

Effect of Surfactant. Finally, the effect of adding a surfactant to the caustic was evaluated and results are reported for four floods. Temperature was set at 180°C. The four displacement experiments were performed on four different cores. One run was conducted in the absence of oil to study surfactant

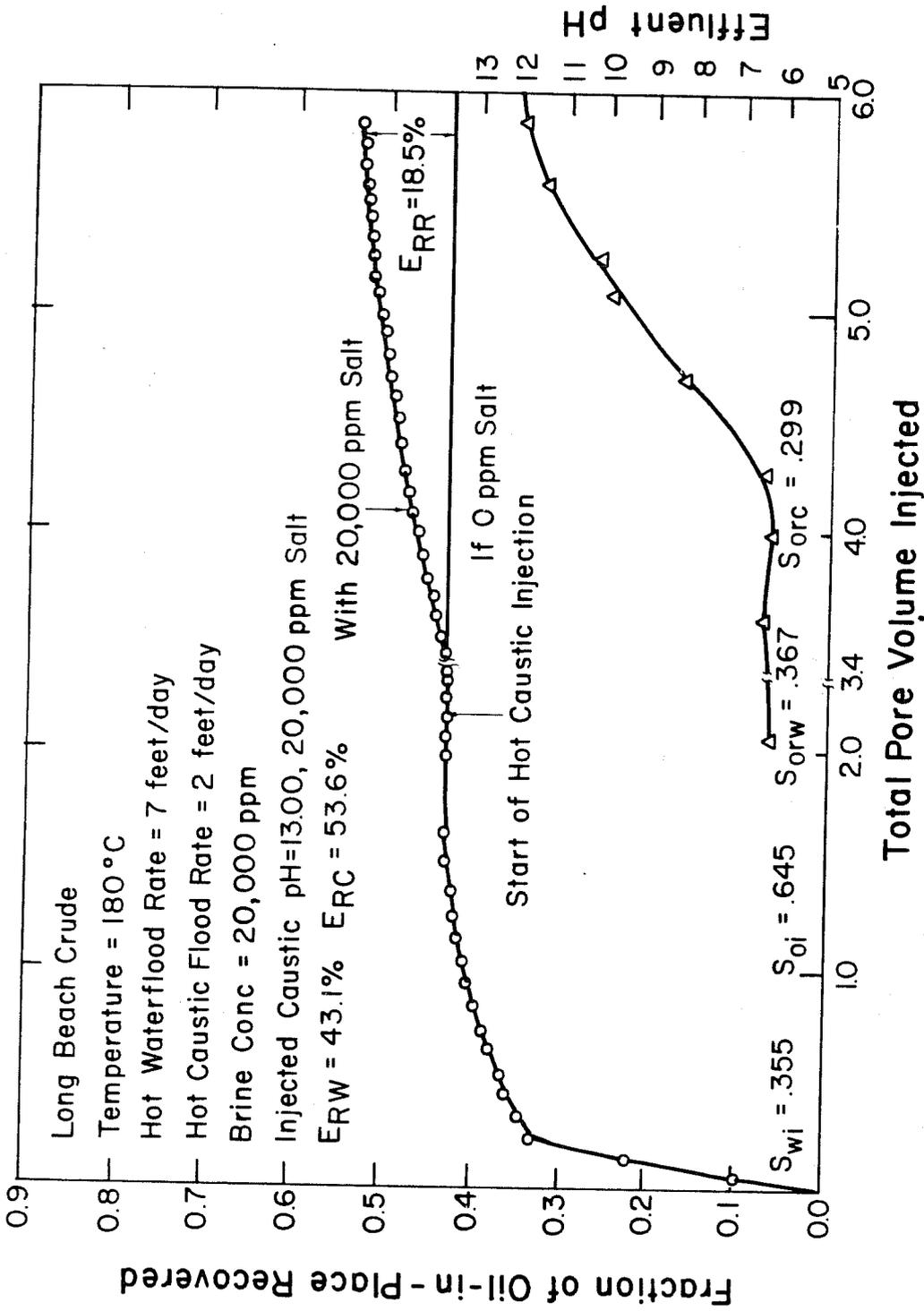


Figure 33. Effect of flood rate on tertiary recovery of acidic oil

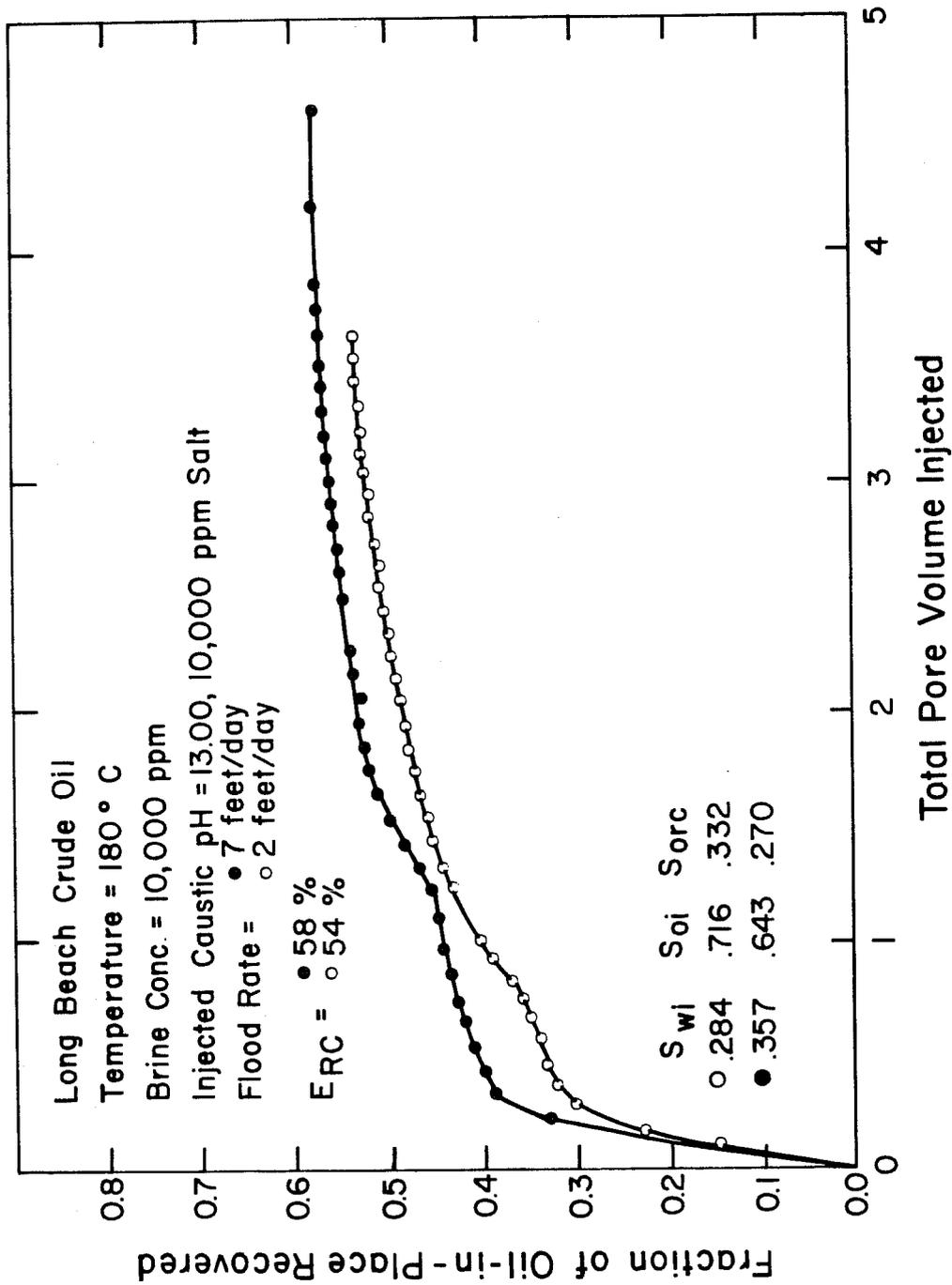


Figure 34. Effect of oil saturation on recovery efficiency

adsorption. The other three runs were performed on cores saturated with crude oil.

In the run without oil the solution was caustic (pH = 13) with 10,000 ppm salt. 500 ppm Petrostep 465 was added to the solution and was injected into the core at 7 ft/day. Effluents were analyzed for pH and surfactant concentration. pH values were determined by a pH meter and surfactant concentrations were measured by UV spectrophotometer. The effluent pH and surfactant concentration as C/C_0 are plotted versus total pore volumes injected on Figure 35. The surfactant and hydroxyl ion are seen to be produced with about the same fluid throughput.

Two floods were performed with an injection concentration of 500 ppm Petrostep 465 and 10,000 ppm salt. The tertiary flood rate was 7 ft/day. In the first of these the pH was 12. 7.2 percent of the residual oil was recovered. In the second the pH was 13. The oil recovery was 40 percent of the residual oil. Recovery as fraction of oil-in-place for the two runs and effluent pH for the high pH run are plotted versus total pore volumes injected on Figure 36.

In the final run, surfactant concentration was increased to 1500 ppm in a caustic solution of pH = 13 with 10,000 ppm salt. All other factors remained constant. 48 percent of the residual oil after waterflood was recovered. Recovery as fraction of oil-in-place, effluent pH and surfactant concentration as C/C_0 are plotted versus total pore volumes injected on Figure 37.

In summary the caustic and surfactant floods to date have shown:

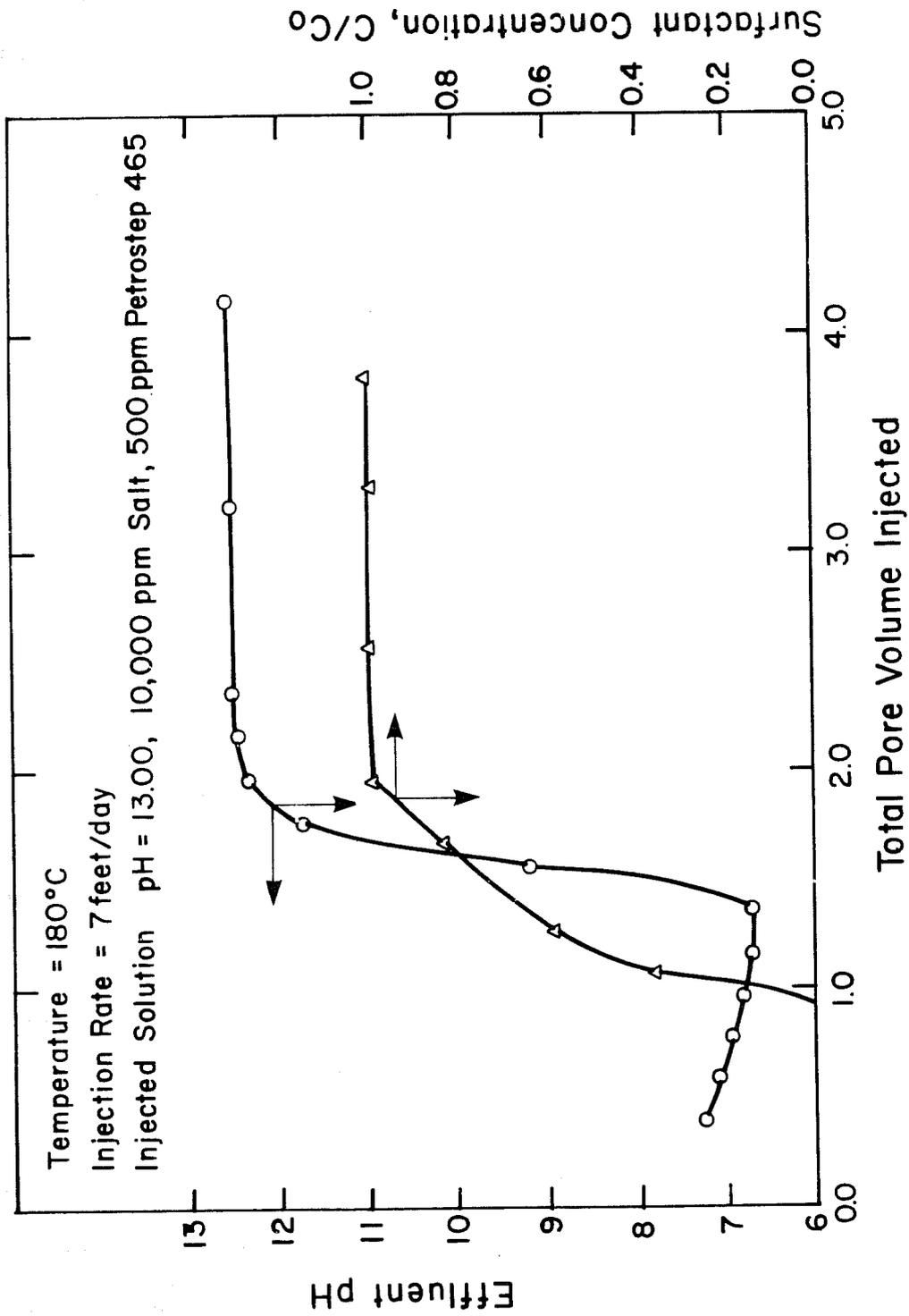


Figure 35. Caustic consumption and surfactant adsorption in absence of crude oil

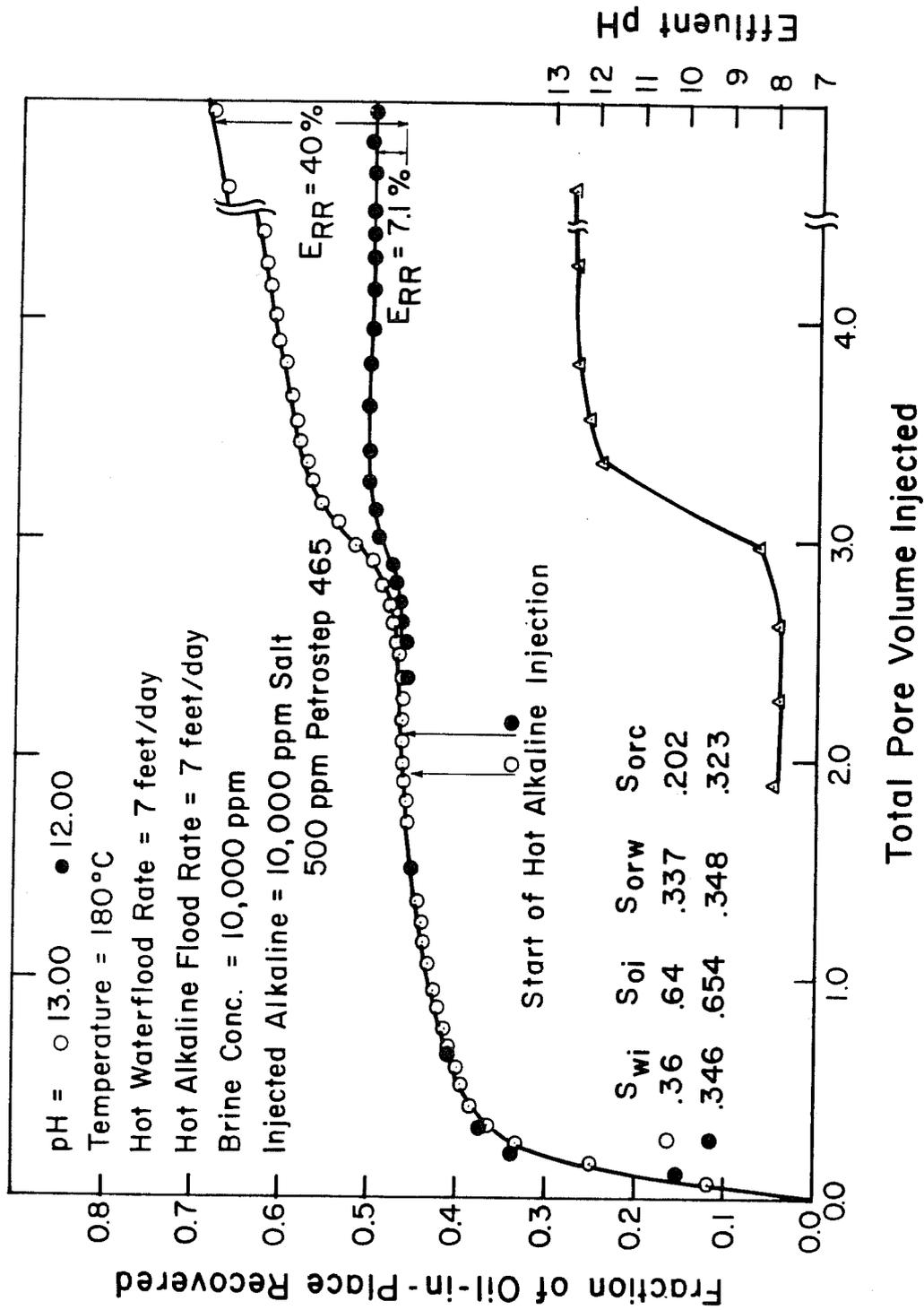


Figure 36. Comparison between recovery performance curves for pH 12 and 13 at same salt and surfactant concentration

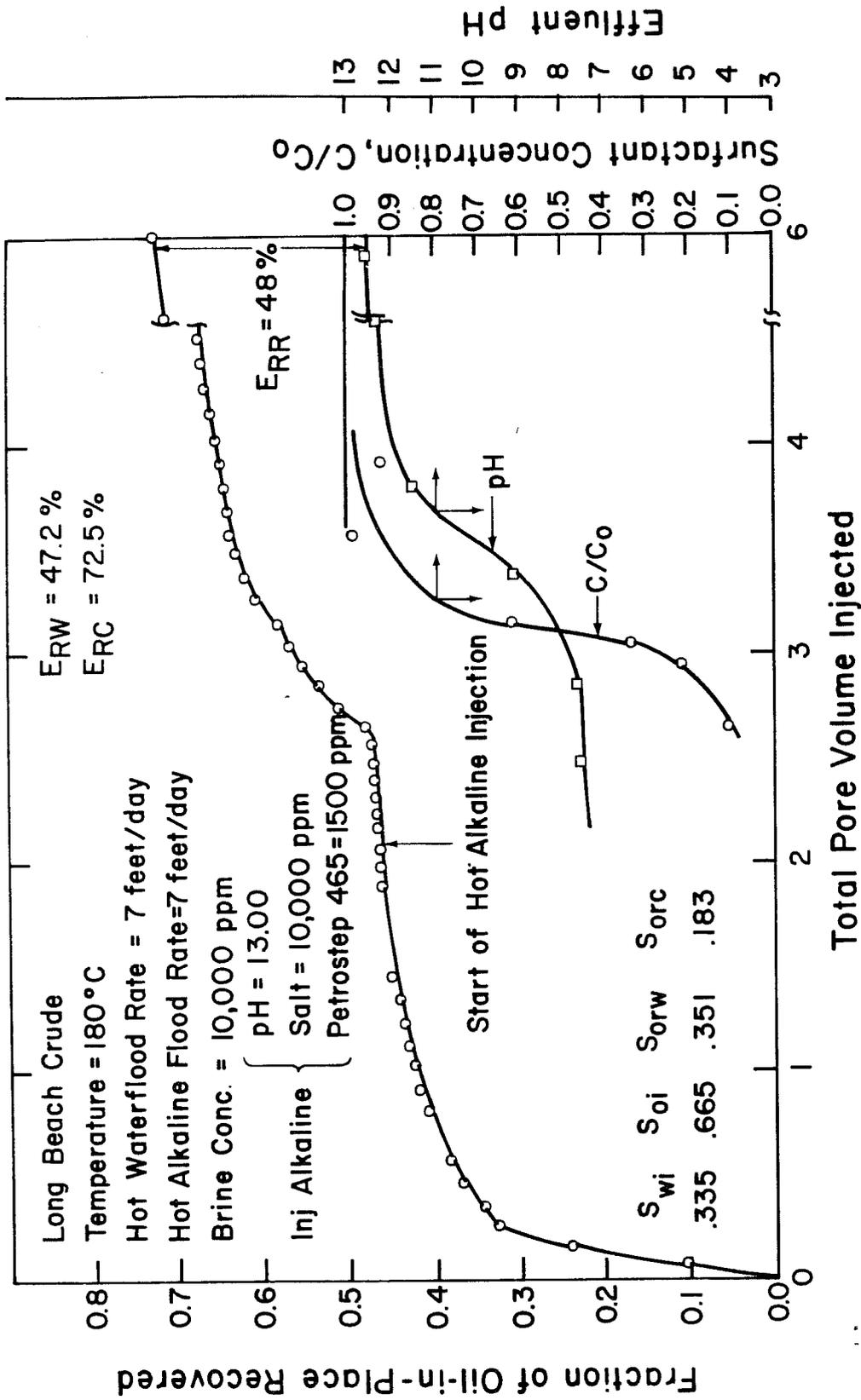


Figure 37. Recovery performance, caustic consumption and surfactant adsorption for combined surfactant and caustic solution

1. For caustic floods at elevated temperatures, tertiary recovery of acidic crude oil:
 - a. Increases with increasing temperature. This has been attributed to decreasing IFT with increasing temperature and to better emulsion mobility as a result of decreasing fluid viscosities.
 - b. Increases with increasing flood rate because of a higher capillary number and/or shear rate.
 - c. Increases if salt is added to the injected caustic. Salt decreases the IFT and, possibly, increases the rate of emulsion coalescence.
 - d. Increases when surfactant is added to the injected caustic as a result of a lower IFT but many factors not yet studied may affect observations.
 - e. Increases with increasing pH, again as a result of lower IFT
2. Caustic consumption in the presence of oil increases with temperature and decreases with rate for core floods in a given length core.
3. Surfactant adsorption is relatively small for the surfactant used in the floods. The produced concentrations approached the injection concentrations after about 1.5 pore volumes of injection. This can be attributed to the high pH and temperature.
4. No significant oil bank was formed ahead of the injected chemicals either caustic or surfactant. The additional

oil recovery was produced along with the chemicals.

5. Surfactant increases the effectiveness of the caustic.

At pH 12 oil was recovered with surfactant but not without surfactant.

III. PREDICTING FIELD PERFORMANCE OF STEAMFLOODING WITH CHEMICAL ADDITIVES

A. Reservoir Simulator for Predicting Field Performance of Chemical Additives with Steam

After making various exploratory calculations using simpler displacement prediction techniques, it was decided to develop a general purpose steamflood simulator incorporating chemical additives. Although it was recognized that such a development is a major undertaking, we concluded that the flexible and powerful analytical capability which would be gained thereby warranted the effort required.

To this end we first formulated the governing set of equations describing the model of the process we elected to consider. This model consisted of 14 variables:

1-6 Pressure and saturation of oil, gas and water phases,

7-8 Mole fraction of oil component 1 and 2 in the oil phase,

9-11 Mole fraction of oil component 1 and 2 and water in the vapor phase, and

12-13 Composition of chemical additive in the water phase and on the rock surface.

14 Temperature

The 14 equations relating these variables are:

1-4 Mass balances for component 1 and 2, water and

- chemical additive,
- 5 Energy balance,
- 6-7 Capillary pressure curves for oil/gas and oil/water interfaces,
- 8 Phase saturation sum to unity,
- 9 Mole fractions of component 1 and 2 in oil phase sum to unity,
- 10 Mole fractions of component 1 and 2 and water in the vapor phase sum to unity,
- 11-12 Equilibrium ratio of mole fractions in the liquid and vapor phase for component 1 and 2,
- 13 Partial pressure of water vapor equals vapor pressure of water, and
- 14 Equilibrium between concentrations of chemical additive on rock surface and in the water phase.

In the solution process equations 1-5 and 10 are solved simultaneously for oil pressure, oil and water saturation, temperature, concentration of component 1 in the oil phase and concentration of the chemical additive in the water phase. Given the values of these 6 variables, the values of the remaining variables are computed directly from the remaining equations.

Equations 1-5 are nonlinear partial differential equations. To solve these simultaneously they must be converted to finite difference equations; since the latter are also nonlinear their simultaneous solution along with Equation 10 requires a trial-and-error (iteration) process. When computer program for carrying out this solution process have been imbedded in a system

of computer routines for inputting data and manipulating it in required ways, for storing values of solution variables as they are calculated through simulated time, and for printing various output reports, a thermal/chemical simulator has been created. Once created, of course, the simulator can be used to predict recovery with various thermal/chemical injection schemes and to derive via a series of such predictions an improved understanding of the behavior of such processes under various conditions.

In addition to the conventional assumptions made to describe three phase fluid flow in a porous media subjected to thermal gradients the following assumptions relative to mass transfer between phases are imposed:

- a) One of the oil components is involatile; the coexisting compositions of the other at every point in the oil and gas phases within the porous media are in thermodynamic equilibrium.
- b) The composition of both oil phase components in the water phase is zero.
- c) The chemical additive is insoluble in the oil phase; the coexisting equilibrium concentrations in the water and on the rock satisfy a Langmuir-type equation at each point within the porous media.
- d) The interfacial tension between the oil and water phases is a nonlinear function of the concentration of the chemical in the water phase.
- e) Reductions in oil/water interfacial tension result in lowered residual oil and water saturations and in an

improvement in the relative permeability of both oil and water. At each point in the porous media these reductions are characterized by the capillary number, which measures the ratio of viscous to capillary forces.

After formulating the equations and writing the computer routines required to carry out thermal/chemical simulations, it became apparent that to render the simulator operational would require much more time than is reasonable for a doctoral dissertation. Therefore, the goal was changed to complete an isothermal model to simulate the effect of a chemical additive in a waterflood.

This goal was achieved as reported elsewhere^{25,26}. The isothermal chemical simulator considers 6 variables:

- 1-4 Pressure and saturation of oil and water phases, and
- 5-6 Composition of chemical additive in the water phase and on the rock surface.

The 6 equations relating these variables are:

- 1-2 Mass balances for oil, water and chemical,
- 4 Capillary pressure curve for oil/water interface,
- 5 Phase saturations sum to unity, and
- 6 Equilibrium between concentrations of chemical additives on the rock surface and in the water phase.

In the isothermal chemical simulator Equations 1-3 are solved simultaneously for oil pressure, water saturation and composition of chemical in the water phase. To this end these nonlinear partial differential equations are converted to a set of simultaneous nonlinear algebraic equations giving the values of

P_o , S_w and C at the end of a time step in terms of the known values at the beginning of a time step. Solutions are obtained via an iteration process. Given the values of P_o , S_w and C at the end of the time step, the corresponding values of the other variables are computed directly from the remaining equations.

After debugging (which was a time consuming and tedious process) the isothermal chemical simulator was used to predict recovery in a vertical cross section resulting from the injection of various size slugs containing different concentrations of chemical additive. As is shown in Figure 38 from References 25 and 26 for the chemical system considered, interfacial tension passed through a minimum as surfactant concentration increased. In all cases simulated oil was assumed to be initially at residual saturation for a non-chemical waterflood, so that any oil recovered results from a reduction in residual oil saturation by the chemical additive. This reduction is depicted as a function of capillary number on Figure 39 from Reference 27. Other figures in Reference 26 present recovery curves for the various situations simulated.

From these results we concluded that gravitational forces and oil viscosity can have a significant impact on recovery in a chemical flood. For a system such as we considered which has a critical middle concentration (minimum of λ vs. C) injection concentration and slug size greatly affect predicted recovery.

A second major accomplishment whose effectiveness was demonstrated by the isothermal simulator was the development of a new finite differencing scheme for concentration of chemical

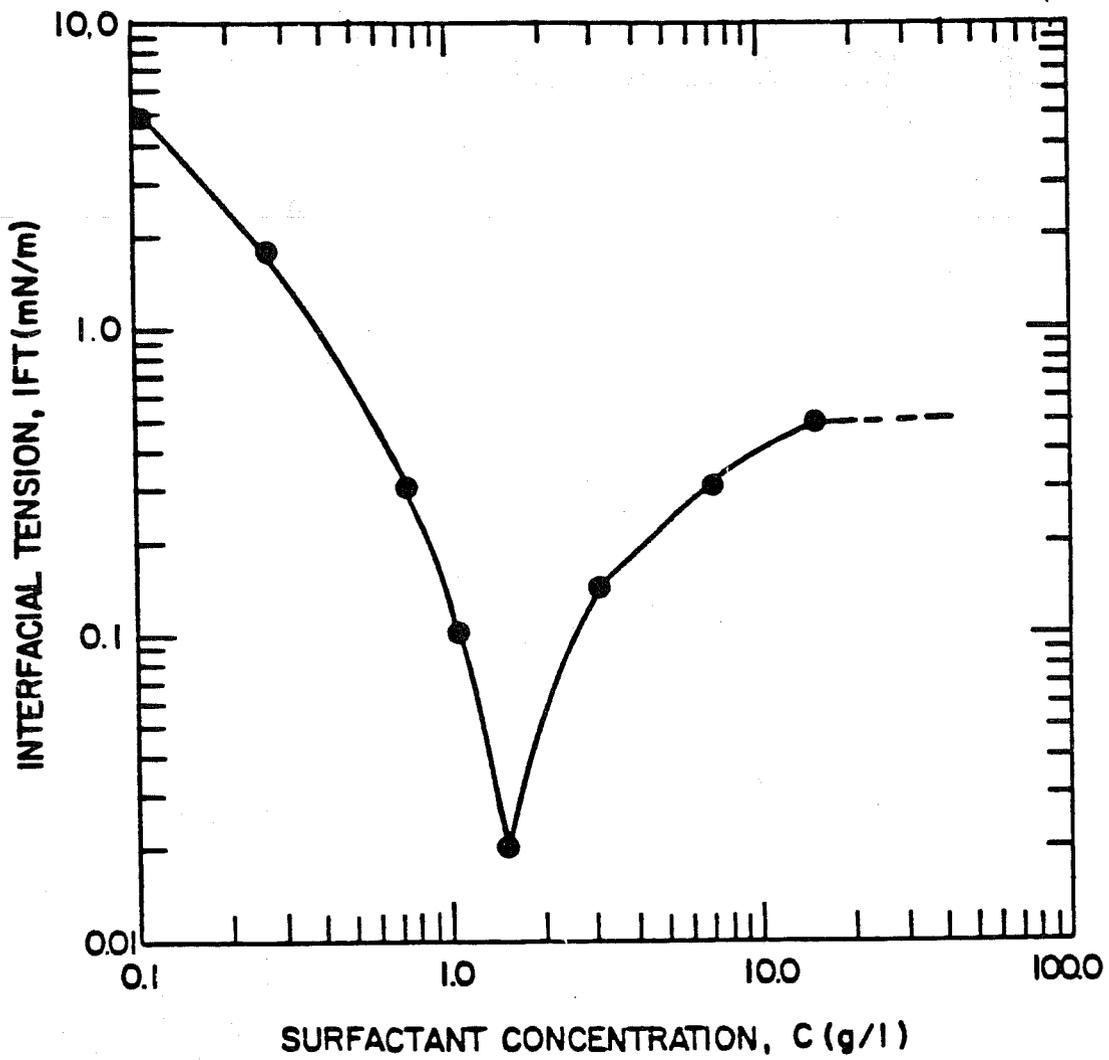


Figure 38. Typical interfacial tension as function of surfactant concentration

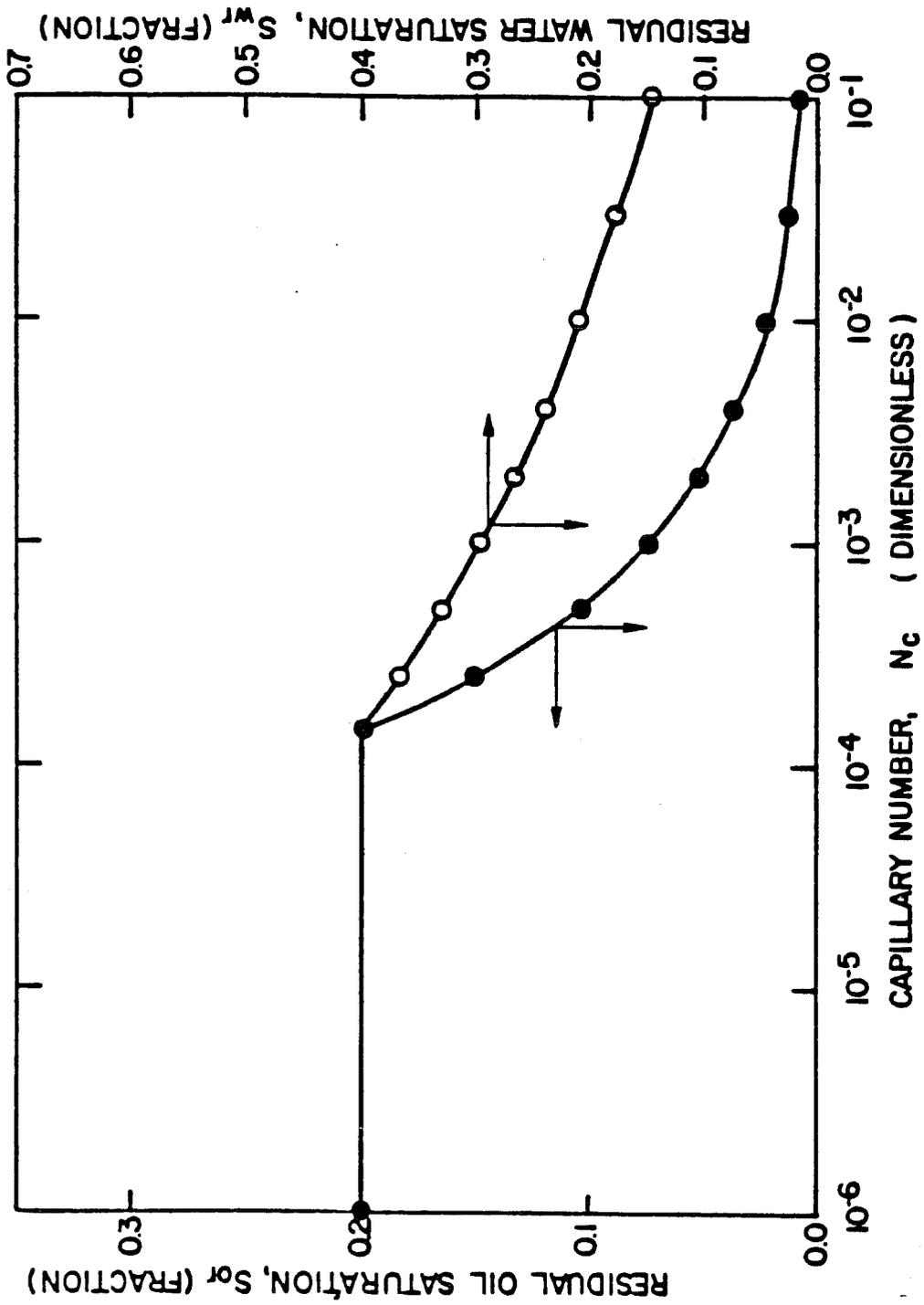


Figure 39. Typical oil and water residual saturations as function of capillary number

additive in the water phase, C. This technique eliminates almost entirely the numerical dispersion of the moving concentration profile. In the absence of absorption this new method reproduces nearly exactly in a finite difference model the concentration profile computed theoretically for a moving concentration slug. This technique which can be readily adapted to any quantity being transported by convection, overcomes one of the most serious problems which has troubled and slowed the development of accurate simulators of complex oil recovery processes for 25 years.

A further improvement in numerical techniques was the development of a new method for fitting functions to tables of data. The fitted functions are smooth and continuous and have continuous first derivatives everywhere linear programming is used to fit these spline-like functions to tables of data.

Based upon what was learned in the isothermal effort, a completely revised system of finite difference equations for the thermal/chemical simulator was developed. The new transport differencing scheme which worked so well for chemical concentration was applied to all transported variables. Given the revisions it was decided that only minor portions of the previous FORTRAN programs could be used with this new formulation. Thus, coding of an entirely new set of FORTRAN routines was initiated.

Conclusions and Recommendations. Results to date have given greater understanding of the behavior of the chemical flood process and have demonstrated the efficiency of the new

techniques developed to effect this complex simulation. The development of the thermal/chemical simulator needs to be carried to completion. Following this an extensive series of parameter and process studies should be conducted and the thermal/chemical simulator thoroughly documented to allow widespread distribution of the program to other researchers.

B. Analysis of the Displacement of Viscous Oil by the Combined Injection of Hot Water and Chemical Additives

The primary objective in the chemical assisted thermal recovery processes described above is the achievement of a notable improvement in the recovery performance over the unassisted cases, obtained by the combined action of temperature and interfacial tension effects. The main function of chemical additives in isothermal enhanced recovery processes is to alter the mobility characteristics of the flowing phases by reducing the interfacial tension between aqueous and oleic phases, thus decreasing residual oil saturations and increasing the relative permeability of oil to flow²⁸. This effect, if acting in a synergistic way with the increased oil mobility achieved at high temperatures, is expected to considerably enhance the microscopic recovery efficiency of standard thermal recovery processes.

Clearly, the viability of such combined injection schemes rests on the hypothesis that the injected chemical additive has its synergistic effect on the heated region of the reservoir, and particularly on the hot liquid region preceding advancing condensation fronts (e.g., in steam injection). Therefore, it is of critical importance for the successful implementation of an assisted process to determine the region of residence of the

injected additives, with the ultimate objective of designing optimal injection schemes that maximize displacement efficiency. In an attempt to address this complex subject, we elected to study the simpler case of an adiabatic hot waterflood assisted by the simultaneous injection of a chemical additive. Such a study, besides its own importance for combined hot water and chemical injection processes, will enable us to gain considerable insight on the rates of propagation of chemical and temperature fronts in the liquid zone preceding steam fronts in the combined steam injection process.

We consider the combined injection of hot water and chemical additive in one-dimensional reservoir geometries. For simplicity the study was restricted to high injection rates such that effects of dispersion, heat conduction, capillarity, and lateral heat losses are negligible. The chemical was allowed to partition in the aqueous phase and to be adsorbed on the rock surface following equilibrium adsorption. The effects of temperature on fluid viscosities and adsorption isotherms, and of interfacial tension on residual oil saturation and relative permeabilities were incorporated in a standard fashion^{6,29}. The ensuing mathematical formulation of the process was cast into a system of hyperbolic, partial-differential equations, the solution of which was obtained analytically by method of generalized simple waves³⁰ (coherence)³¹. Temperature, concentration, saturation profiles and recovery efficiencies were derived for both continuous and chemical slug injection.

The results of the mathematical analysis for the case of

continuous injection reveal that, as anticipated, adsorption plays a major role in determining the region of residence of the chemical. Specifically, it was found by an exact analysis, that there exists a critical value of the chemical additive concentration, η_{cr} , such that when the injection concentration η_i exceeds this value, $\eta_i > \eta_{cr}$, the chemical travels ahead of the temperature front, while when the injection concentration is lower than the critical value, $\eta_i < \eta_{cr}$, the chemical resides entirely in the heated region of the reservoir. An approximate estimate of η_{cr} valid in a substantially large range of typical parameter values, when temperature effects on adsorption are negligible, is provided by the expression (Figure 40)

$$\eta_{cr} \sim \frac{0.7}{g_1} \quad (1)$$

where g_1 is the adsorption parameter in the Langmuir isotherm

$$g = \frac{\eta}{g_1\eta + g_2} \quad (2)$$

Equation (1) further implies that at the critical concentration the adsorption isotherm has reached its plateau value. This result is a consequence of the large difference between the volumetric heat capacities of rock and oil, and the assumed large slope of the adsorption isotherm at the origin. Similar expressions hold for adsorption isotherms other than Langmuir type.

The reduction in the residual oil saturation attained at the critical value was evaluated by employing the simple representation⁵

$g_1 \eta_{cr} \sim 0.7 \Rightarrow \eta_{cr} \sim 0.99g$ plateau

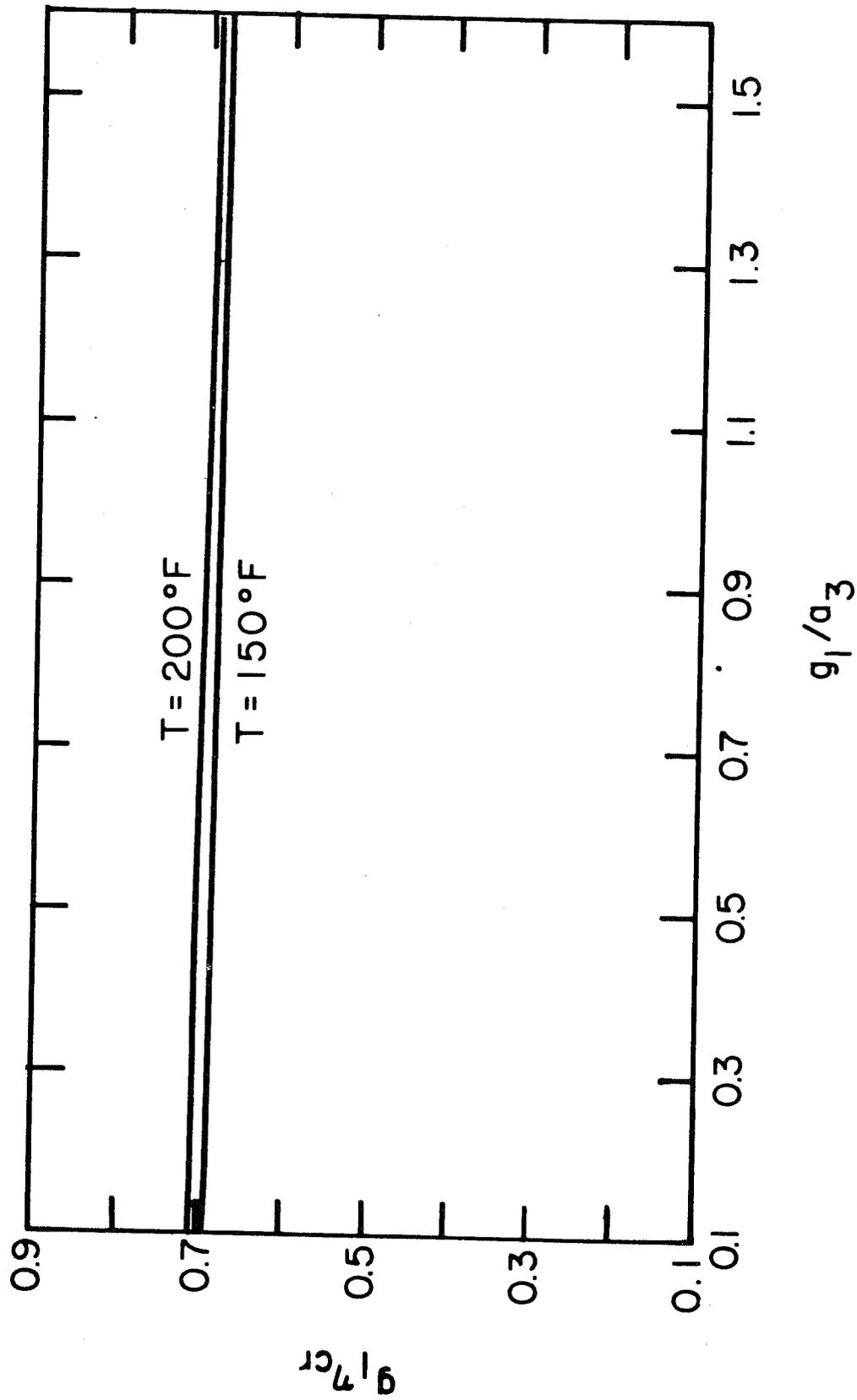


Figure 40. Critical concentration for various values of g_1/a_3 and temperature

$$S_{or} = a_1 + a_2 \exp[-a_3 \eta] \quad (3)$$

and normalizing concentration by the rate of residual saturation reduction

$$C = \eta a_3 \quad (4)$$

Equation (1) then becomes

$$C_{cr} \sim \frac{0.7}{g_1/a_3} \quad (5)$$

which shows that for low values of the ratio g_1/a_3 (high adsorption plateau values and/or high rates of reduction of the residual oil saturation) the residual saturation at the critical concentration has reached its irreducible value a_1 , while for high values of the ratio g_1/a_3 the reduction in the residual saturation at the critical value is minimal. Thus, it is apparent that, although beneficial for a simultaneous reduction of residual saturation and oil viscosity, designing a continuous injection process such that the chemical resides in the heated region may not prove effective, in some cases, for the mobilization of a significant amount of trapped oil (Figure 41).

The above conclusions, valid for continuous injection, do not furnish an accurate test of the validity of the hypothesis that optimal performance is obtained when the chemical resides in the heated region of the reservoir. A proper assessment of this claim is only provided from the simulation of the recovery performance during slug injection. Using the analytical method described above, the recovery performance of the assisted hot waterflood in a tertiary recovery process was calculated. By properly maximizing the recovery performance, an optimum slug

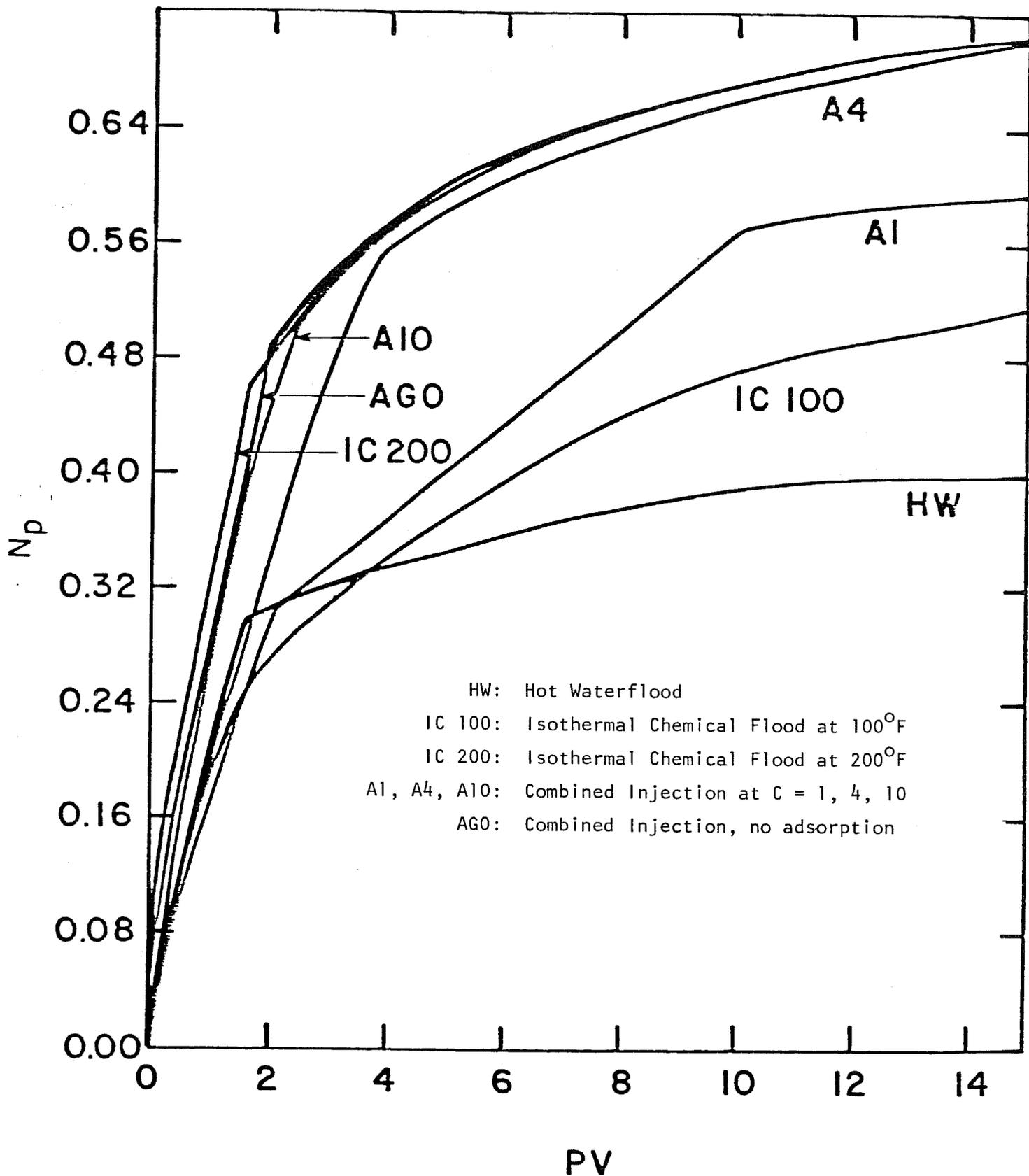


Figure 41. Recovery curves for continuous injection, secondary flooding
 (20° API $g_1/a_3 = 0.1$) $C_{cr} = 7$

size $t^{OP}(\eta_i)$ was determined as a function of the injection concentration. The corresponding maximum recovery performance index

$$I(\eta_i) = \max_{t_p} \frac{N_p}{\eta_i t_p} = \frac{N_p^{OP}}{\eta_i t_p^{OP}(\eta_i)} \quad (6)$$

was then evaluated at different values of the injection concentration η_i . Figures 42, 43 show plots of I versus C for different values of API density and the ratio g_1/a_3 . It is observed that in the range examined the curve exhibits a sharp maximum at concentration values which are always less than or equal to the critical values (Equation 5). For example, for an oil of density 20° API, the maximum occurs near $C=1$, while for an oil of density 30° API, the maximum value occurs at a concentration which appears to be proportionally related to the critical concentration. In both cases, the performance index I and the sharpness of the curve increase with an increase in g_1 (decrease in the adsorption plateau), as expected. Thus, the recovery performance appears to be more sensitive to the injection concentration as the adsorption level decreases.

These results lend support to the hypothesis that optimum recovery performances are obtained when the injected chemical slug resides entirely in the heated region of the reservoir. For fixed values of the parameter ratio g_1/a_3 , the injection concentration and chemical slug size that maximize tertiary recovery performance can be estimated from the above analysis.

In summary, it was shown that in the combined hot water, chemical additive injection process, a critical value η_{cr} exists, such that when the injected concentration lies above this

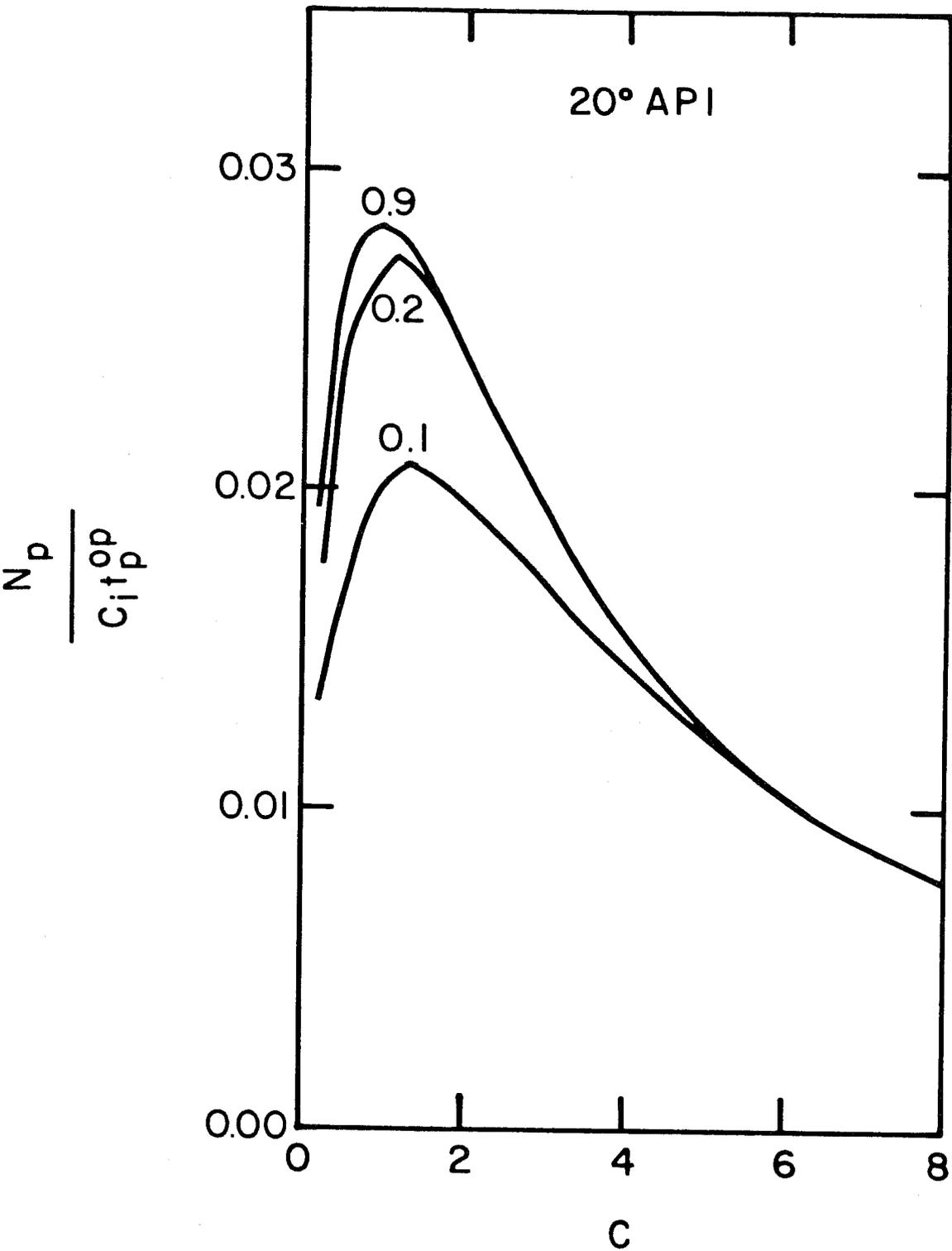


Figure 42. Recovery performance index for various values of g_1/a_3 (20° API)

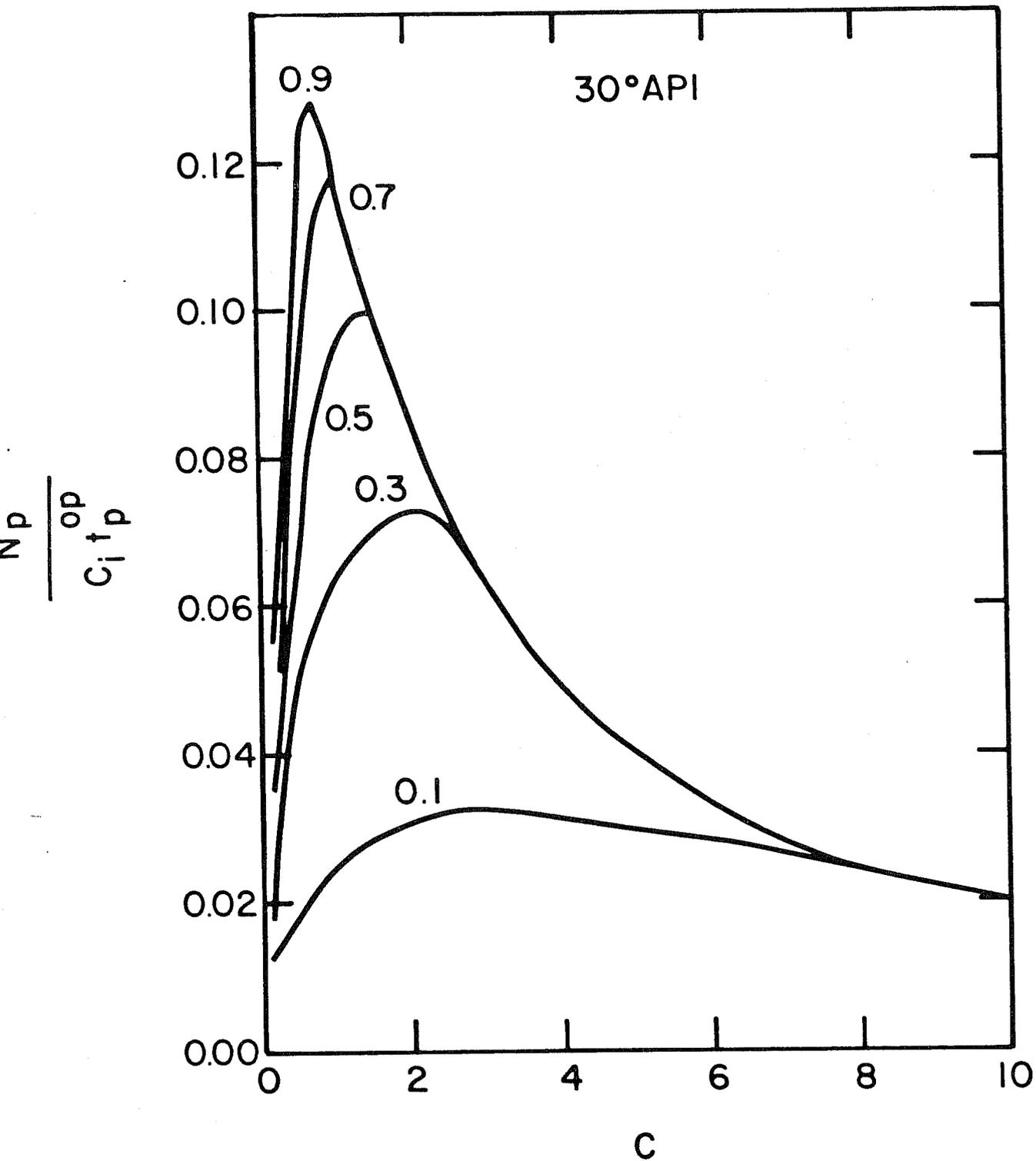


Figure 43. Recovery performance index for various values of g_1/a_3 (30° API)

value the chemical travels ahead of temperature fronts. A significant portion of the injected chemical slug resides in the unheated region of the reservoir in this case. By contrast, when the injected concentration lies below η_{cr} , the chemical resides entirely in the heated region, resulting in more efficient displacement. An analysis of the recovery efficiency for typical conditions indicates that the assisted injection is a viable enhanced recovery process. In particular, it is shown that the recovery performance in a tertiary recovery process is maximized when the injected concentration lies below the critical value. Further studies on the assisted hot water injection with chemical partitioning in the oleic phase, as well as on the assisted steam injection process are currently under investigation.

CONCLUSIONS AND RECOMMENDATIONS

The thermal stability of a number of petroleum sulfonates has been evaluated. The general conclusion from the data obtained is that those surfactants which contain an aromatic sulfonate bond (this includes petroleum sulfonates) will have marginal thermal stability for the long time these surfactants would be at elevated temperatures during a steamflood. Reduction of interfacial tension along with reduced oil viscosities at steam temperatures does result in decreased residual oil saturation. Another class of cationic surfactants, the alkyl sulfonates, is reported to have much better thermal stability than the aryl sulfonates. The alkyl sulfonates are being used as foaming agents and also appear to have potential for reducing residual oil saturations. These surfactants were not evaluated in this report but further study of this type of surfactants is warranted.

The low cost of sodium hydroxide makes this chemical attractive as a steamflood additive but the question about the extent of its loss in reactions with reservoir silica is yet to be resolved. If the caustic maintains its high pH, core floods indicate that it can be very effective in reducing residual oil saturation. Possibly appropriate silicate solutions can be injected which are at equilibrium with the reservoir rock and will, therefore, maintain their pH. The use of silicates at high temperatures needs further investigation. A theoretical study should be made using known equilibrium constants for the caustic-silicate systems to predict the fate of injected caustic in a

sandstone reservoir and to determine the pH level one is likely to be able to maintain at steam temperatures. The effect of temperature on the interaction of caustic and reservoir clay materials has yet to be evaluated.

Substantial progress has been made in the development of the thermal/chemical simulator but much remains to be done. Of particular interest, beyond what is already proposed, is the application of the simulator in predicting performance of a foaming agent when added to steam to improve mobility ratios and sweep efficiencies. The solution to this problem will involve much of the data developed in this report but will require an extension of the studies on adsorption and chemical stability. Further work is required on the mechanisms by which foaming agents reduce steam mobility and on procedures for incorporating this knowledge as developed into the simulator.

The results to date suggest that chemical additives have a good possibility of being beneficial in steamflooding but a number of problems remain which require further investigation. These include an evaluation of a much wider selection of surfactants and development of screening methods to make these evaluations systematically. Much yet needs to be done in improving volumetric sweep efficiency for steamfloods and in understanding the physical processes by which this may be done. The use of inorganic additives still has a strong appeal but again a more diversified investigation is required to select suitable chemicals which will hold up in the reservoir and have the desired effects in reducing residual oil saturations.

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APPENDIX

LIST OF PUBLICATIONS

The following lists give publications resulting from the contracts. These include only those presented or published through December 1983.

Published Papers

1. Ziegler, V.M. and Handy, L.L.: "Effect of Temperature on Surfactant Adsorption in Porous Media," SPEJ (April 1981) 218-226.
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