THE CONTINUOUS ANALYSIS OF SURFACTANT CONCENTRATIONS IN COREFLOOD EXPERIMENTS

by

DANNY D. FORREST

DEPARTMENT OF CHEMICAL ENGINEERING

Submitted in Partial Fulfillment of the Requirements of
the University Undergraduate Fellows Program

1979-1980

Charles J. Glover

Chales J. Glover, Faculty Advisor

April 1980

ABSTRACT

One of the major problems in designing an effective tertiary oil recovery process is minimizing the adsorption activity of the surfactant. Information concerning the adsorption behavior of specific surfactants would be very useful, but very little data of this nature is available because the detection methods implemented are either too specific or too time consuming. A noncontinuous detection scheme involving the electrochemical method of polarography has proven to be effective at Texas A & M University, but actual coreflood experiments require a continuous detection scheme. The purpose of this investigation was to develop a continuous detection scheme for the analysis of surfactant concentrations in coreflood experiments.

Calibration curves obtained by implementation of the continuous detection scheme indicated that the surfactant concentration varied linearly with the peak current at the detector. A scheme for the determination of equilibrium adsorption effects in the core sample was developed, but experimental problems prevented the collection of data. A computational outline was developed that allows the adsorption effects in a core sample to be determined from polarographic data alone.

To my parents, Freddie and Shirley Forrest, for giving me their love and support. I love you both dearly.

ACKNOWLEDGEMENTS

I wish to express my heartfelt appreciation to my faculty advisor, Dr. Charles Glover, whose time and advice constituted a tremendous contribution to this research effort.

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

Background and Literature Review

A petroleum reservoir consists of a permeable bed of porous rock containing oil and gas and a bed of overlying rock that prevents movement of the oil and gas. A typical petroleum reservoir contains approximately sixty five percent oil and thirty five percent water at the time of discovery.

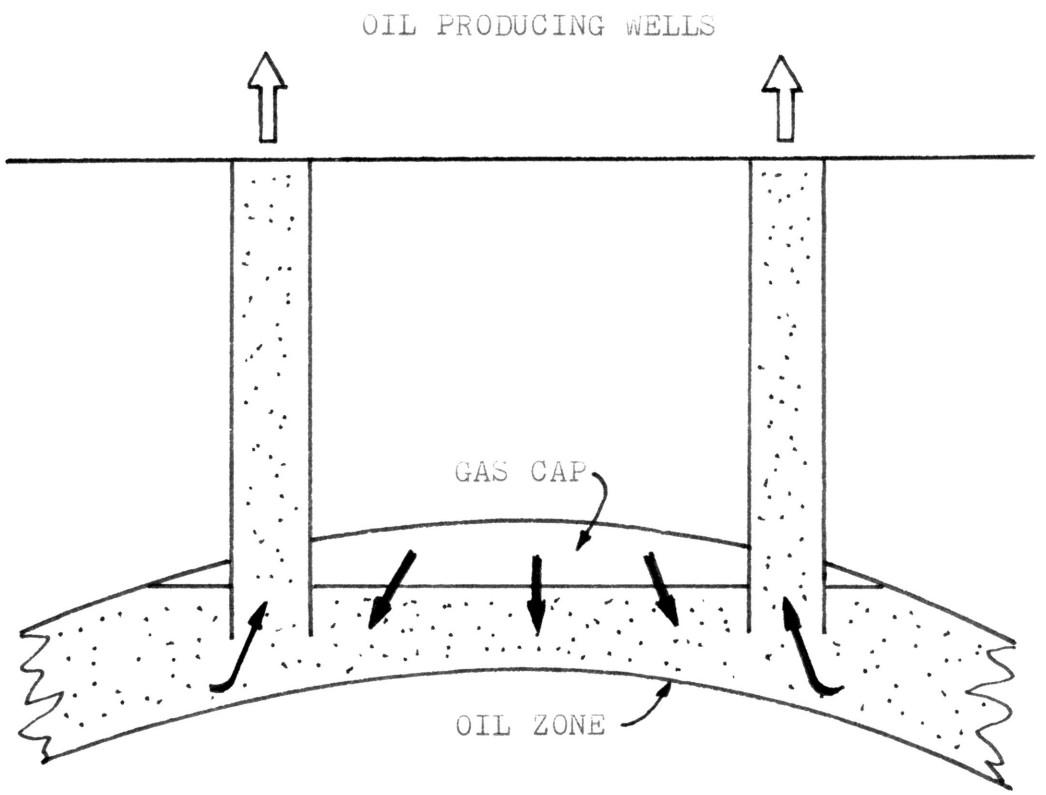
Much attention over the last one hundred years has been directed at the problem of displacement of oil from the porous rock reservoir. Oil recovery processes may be divided into three stages- primary, secondary, and tertiary (or enhanced) recovery.

Primary oil recovery involves the production of oil by means of natural reservoir driving forces. Natural production is typically induced by free gas expansion within the reservoir or by water pressure from outside the reservoir. The energy required for oil displacement by gas expansion comes from one of two sources--the liberation of dissolved gases as reservoir pressure drops during production, and pressure from gas caps trapped in the rock formations above the reservoir (Figure 1). Natural water beds, known as

---

This thesis follows the style and format of the Society of Petroleum Engineering Journal.

Figure 1. Schematic of Gas Cap Drive Reservoir



aquifers, occurring in "...contiguous sand beyond the extremities of the oil zone..." [2] provide the pressure necessary to displace trapped oil droplets by water pressure techniques. Although water is usually considered incompressible, the total compressed volume is large over an entire reservoir. As oil is produced, water moves to displace the oil by expansion of minutely compressed water droplets (Figure 2). Approximately twenty five percent of the oil originally in the reservoir is recoverable by this type of primary technique.

The East Texas field constitutes a special case of primary recovery in that a natural water drive is present to displace trapped oil droplets as an underground water flow is formed (Figure 3). Approximately fifty percent of the oil originally in place in the reservoir is recoverable by this mechanism.

A secondary oil recovery process involves the rejuvenation of nearly depleted reservoirs by the application of external energy to the reservoir.[3] Large injections of gas or water (commonly referred to as waterflooding) act to displace trapped oil droplets. The economic feasibility of this type of technique is very high, and "...every oilfield of significant size and without a natural water drive has been, is being, or will be waterflooded."[4] Despite the success of waterflooding, only about fifty percent of the oil originally in the petroleum reservoir is recoverable by combinations of primary and secondary recovery techniques.

Figure 2. Schematic of Water Drive Reservoir

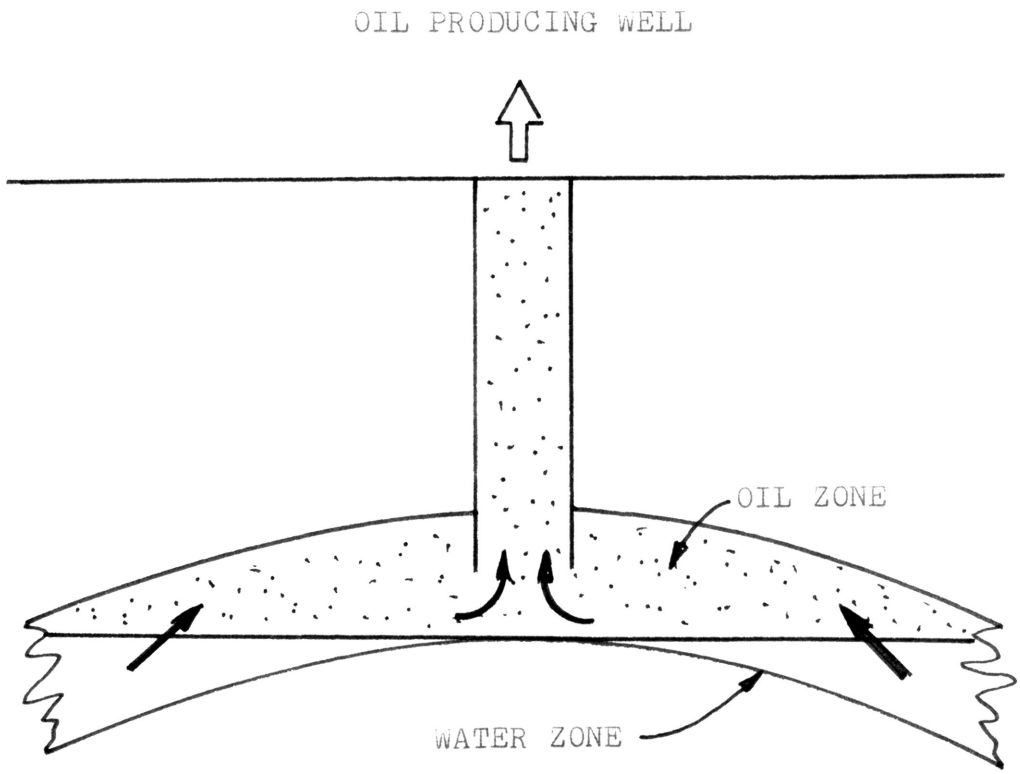
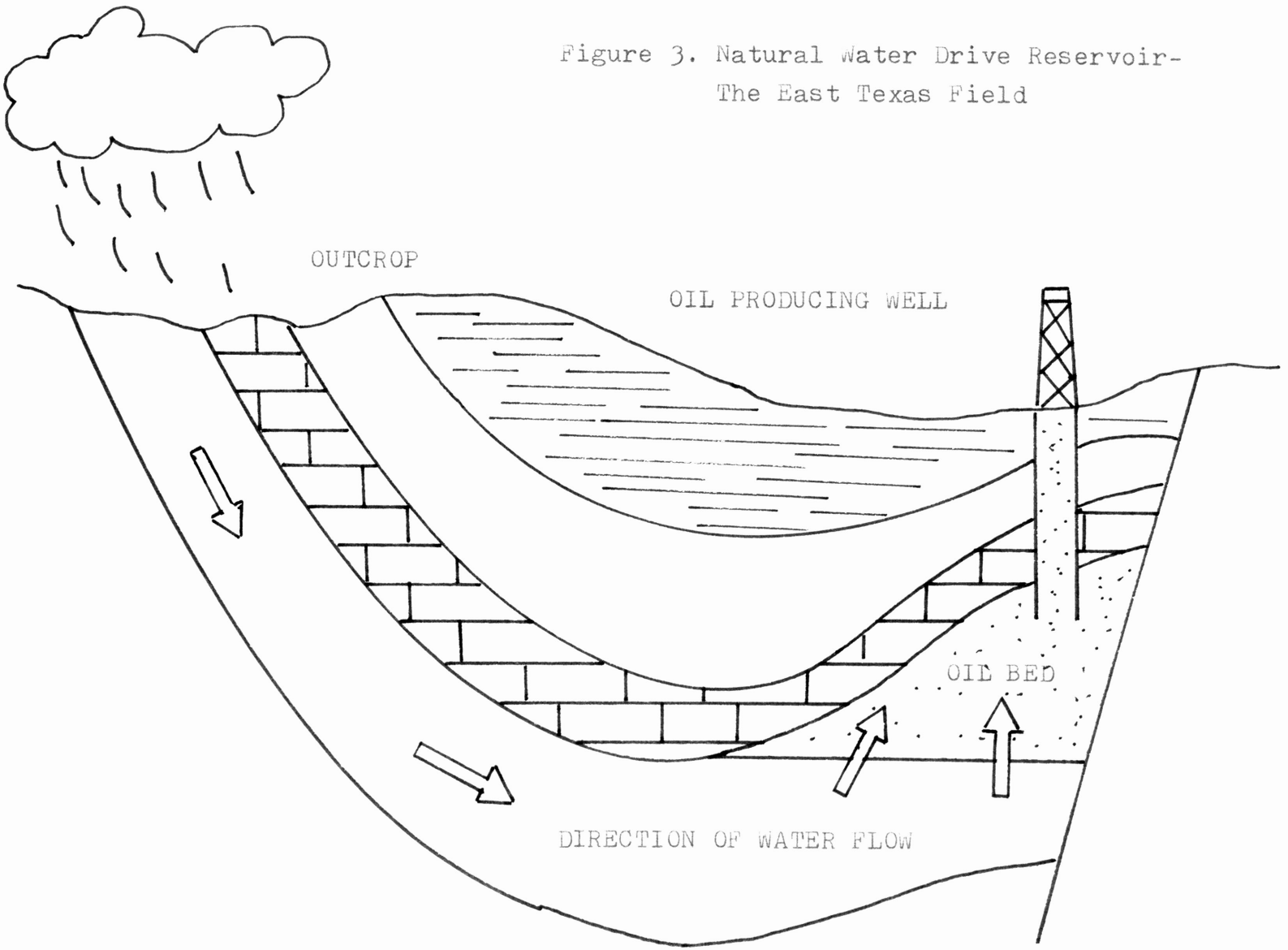


Figure 3. Natural Water Drive Reservoir-
The East Texas Field



Recent changes in the availability and the world market price for oil have renewed interest in methods that will recover a considerable portion of the fifty percent of the original oil remaining in the reservoir.[5] It is estimated that fifty nine billion barrels of crude oil are recoverable from existing fields using enhanced recovery methods.[6] Assuming a base United States consumption of oil of the order of eighteen million barrels per day, this is enough oil to meet United States requirements for oil until the year 1990.[7]

Tertiary oil recovery techniques- including steam flooding[8], hot water flooding[9], carbon dioxide flooding[10], and surfactant flooding[11]- can be used to enhance the recovery prospects of a petroleum reservoir. Each of these methods is best suited for reservoirs having specific characteristics. Surfactant oil recovery techniques are of particular interest in this investigation.

A surface active (surfactant) chemical is usually injected into a porous rock bank to release trapped oil ganglia. The surfactant is a compound composed of petroleum sulfonates, ethyoxylated alcohols, ethers, glycols, or combinations of these components, that is designed to reduce the interfacial tension between trapped oil droplets and rock pores[12]. The surfactant is usually injected into a reservoir in the form of a microemulsion. A microemulsion is a thermodynamically stable solution consisting of highly dispersed particles of oil, water, electrolytes, and amphililic compounds.[13] When

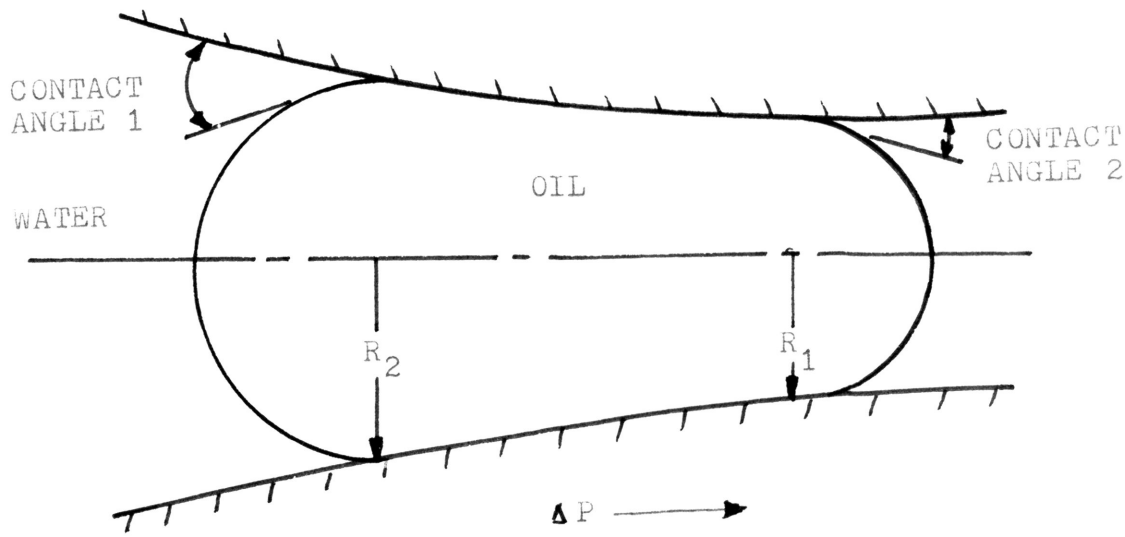
driven through a reservoir, the microemulsion displaces some of the fluids contacted.

A model of an oil droplet trapped by a pore constriction is given in Figure 4. In general, as water flows through adjacent capillaries, a pressure gradient (ΔP) is developed across the trapped ganglia. In order to displace residual oil droplets in a porous rock bank, an additional pressure gradient must be established. The pressure gradient available in the field is on the order of 1-2 psi/ft. Economics generally set this operating limit. The pressure drop required in most recovery methods is two to three orders of magnitude greater than the achievable field limit due to the pore wall geometry, rock wettability effects, and the interfacial tension between the oil droplets and the brine in the reservoir. The ultimate goal in tertiary oil recovery methods is to lower the interfacial tension two to three orders of magnitude below the oil/water interfacial tension.

Typical Surfactant Flooding Process

The action of a surfactant in the surfactant flooding process is directly analogous to the action of a detergent in the removal of oil or grease from clothing. In both cases, the surface active agent acts to lower the interfacial tension between the oil and the water, thus allowing the oil to be displaced. "Surfactant flooding loosens the oil from the fabric of the reservoir rock, and the flooding fluid sweeps

Figure 4. Model of an Oil Droplet
Trapped by a Pore Constriction



it to a producing well."[14]

A typical flooding process occurs in the following manner:

1. Initially, the reservoir usually exists as a continuous water phase with a discontinuous oil phase (Figure 5).
2. A brine preflush may be injected into the reservoir to condition and provide a more nearly optimal environment for the surfactant system.(Figure 6)
3. A slug of micellar fluid is injected to displace the residual oil and formation water.
4. A buffer bank is injected to drive the slug through the reservoir without viscous fingering action (an unstable displacement that results in mixing of the surfactant with other fluids in the bank).
5. A chase water bank is utilized to drive the mobility buffer bank through the reservoir.

A severe limitation in the overall process may be the adsorption of the surfactant onto the reservoir rock. For cases of high adsorption, a considerable excess of surfactant must be injected to maintain the integrity of the slug. The economics in this case become very prohibitive.

Thus, data concerning the adsorption behavior of

Figure 5. Reservoir Conditions Prior to a Surfactant Flood

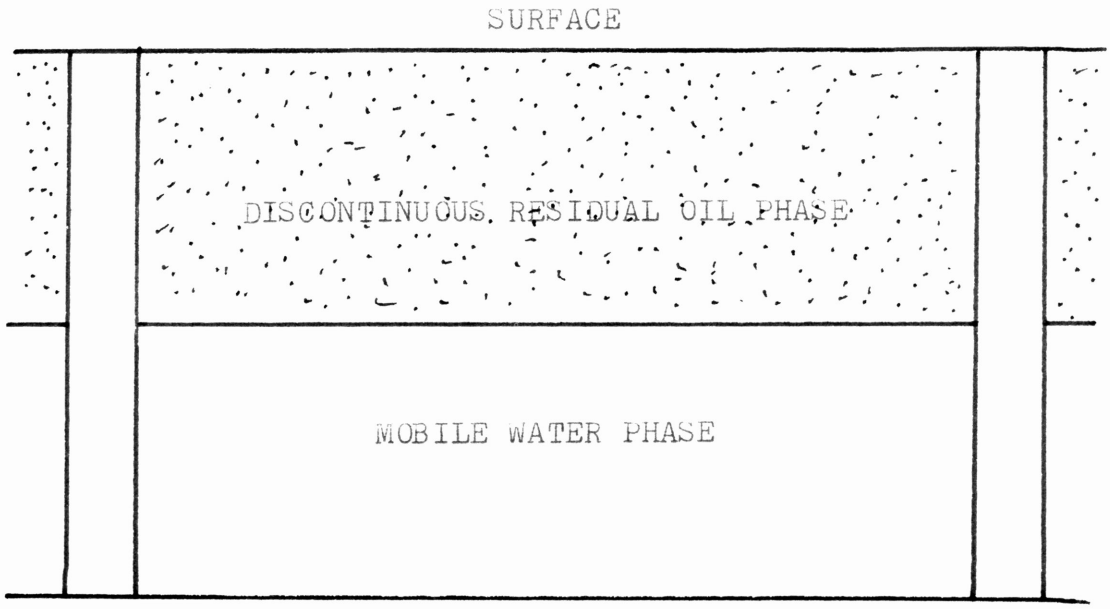
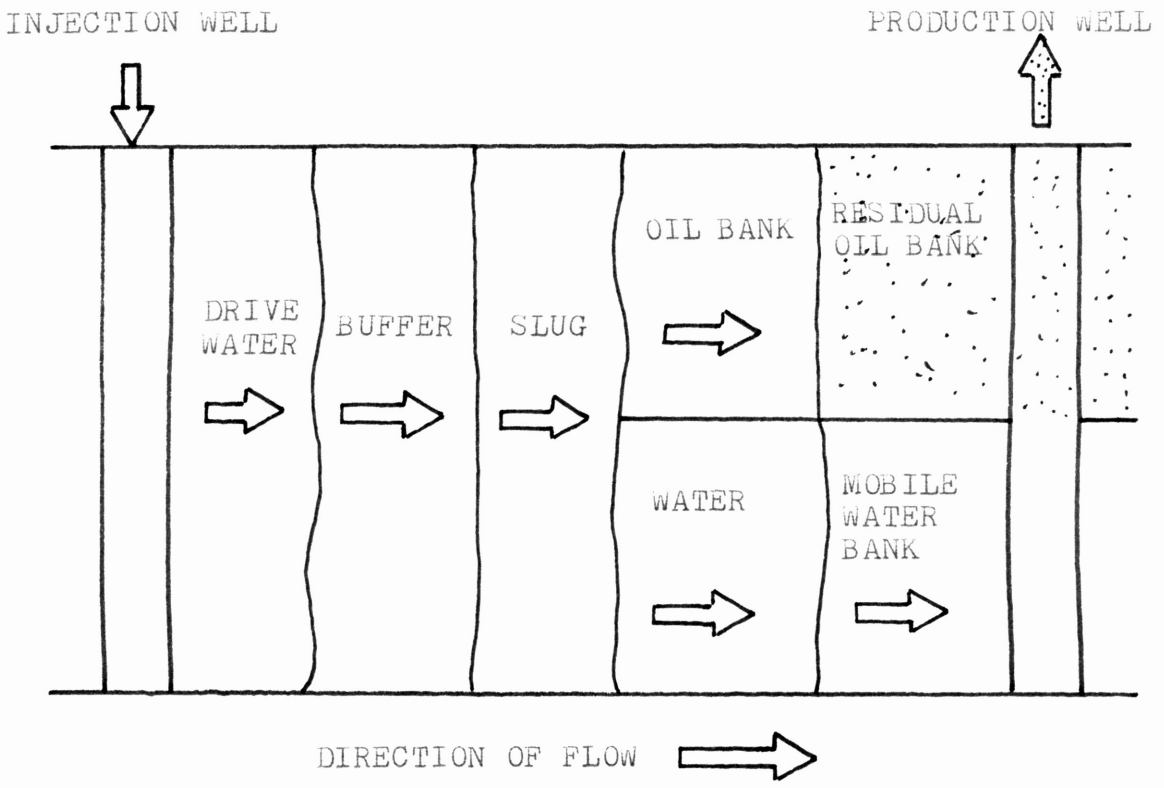


Figure 6. Typical Surfactant Flooding Process



surfactant microemulsion/rock systems would be very useful. Very little research has been conducted in this area.

PROBLEM IDENTIFICATION

The techniques previously implemented in the determination of surfactant adsorption effects in a petroleum reservoir are inadequate in that they are either too time consuming or too specific. Notable examples are ultraviolet spectroscopy for surfactant concentrations in brine solutions[15] and liquid chromatography for the determination of surfactant concentrations in micellar solutions.[16] In essence, there is a lack of a simple method to determine a wide range of surfactant adsorption data for a coreflood system.

It is believed that electrochemical methods are a potential solution to this problem. In particular, work by Hart, et. al.[17] indicates that polarographic detection techniques could be implemented to analyze several classes of nitrated alkyl- and alkane- sulfonates. Determinations of this type have been proven reliable at Texas A & M University.[18] A dropping mercury polarographic detector was implemented with great success. The system offers the ability to make concentration detections over a wide range of surfactant concentrations on a noncontinuous basis. Since most coreflood experiments are run on a continuous basis, a continuous detection scheme is needed to perform the same type of analysis that is supplied by the non-continuous scheme. Therefore, the purpose of this research effort was to develop a workable, continuous polarographic detection scheme to determine the

concentration of surfactants in the effluent stream of a core-flood experiment. The investigation scheme was created for the determination of sodium dodecylbenzenesulfonate (SDBS). This surfactant was chosen because it is generally representative of surfactants used in tertiary oil recovery processes.

A REVIEW OF POLAROGRAPHIC DETECTION

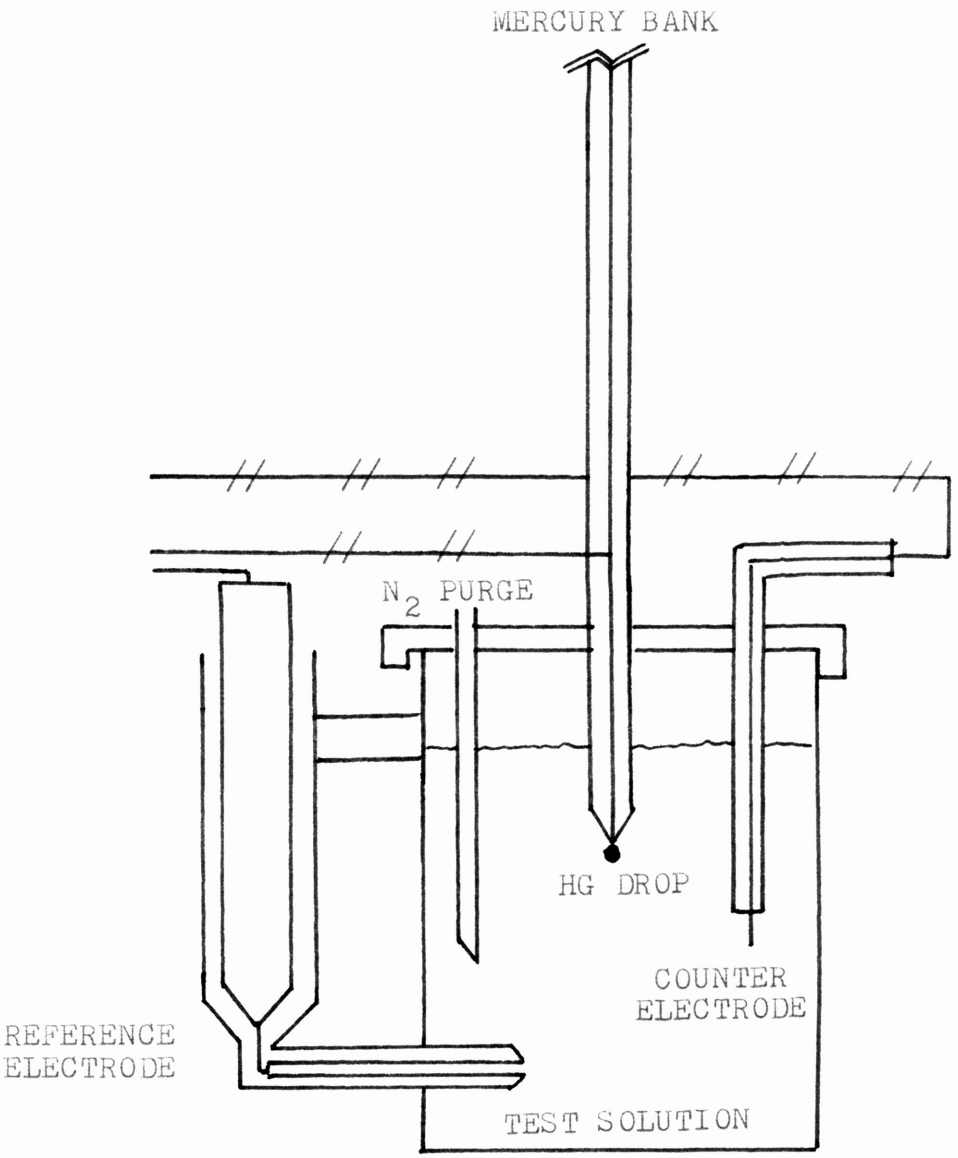
Equipment

Noncontinuous and continuous analysis was carried out in a dropping mercury polarographic detector. The actual detector used was a Princeton Applied Research Corporation Polarographic Analyzer (Model 174A) coupled with a Drop Timer (Model 172A). The reference electrode for the cell was a Fisher # 13-639-50 saturated calomel electrode, and the counterelectrode was a platinum wire. The recorder used was a Houston Instruments 100 x-y Chart Recorder. (See Figure 7)

Theory

The polarographic detection method operates on the principle that a mercury drop is continuously generated that serves to complete an electrical circuit with the counter-electrode. Since the current in the electrical system depends on the potential input as well as the concentration of the solution in the detection cell, the theory behind differential pulse polarography suggests that the surfactant concentration in the cell may be determined from plots of measured current as a function of potential input. Polarographic peaks are generated with height proportional to the concentration of the surfactant solution analyzed.

Figure 7. Schematic of the Dropping Mercury Electrode Equipment



EXPERIMENTAL

General Procedure for the Indirect Determination of SDBS

The solutions analyzed were prepared in a manner similar to that proposed by Becker in " The Electrochemical Analysis of SDBS in Solutions Containing Oilfield Impurities"[19];

1. Thirty milliliters of an acid solution consisting of a 50-50 mixture (by volume) of 70 percent nitric acid and 98 percent sulfuric acid was pipetted into a flask.
2. The surfactant solution to be analyzed was pipetted into the flask in a two milliliter aliquot.
3. The resultant mixture was mixed well and allowed to stand for one hour.
4. The reacted solution was diluted with 32 milliliters of distilled water and mixed well.
5. The test solution was prepared by pipetting a known aliquot of the above solution (0.1-1.2 ml) into 40 milliliters of supporting electrolyte. The supporting electrolyte used was a pH 12.0 buffer solution consisting of 0.5M sodium phosphate dibasic and 0.5M sodium hydroxide.
6. The test solution was added to the polarographic

cell which had been purged with nitrogen for twenty minutes prior to detection. The nitrogen was scrubbed by passage through two towers containing an aqueous solution of vanadium (III) chloride over amalgamated zinc.

The polarographic conditions were as follows:

- Mode: Differential Pulse Polarography
- Modulation Amplitude: 25 mv peak to peak
- Scan Rate: 5 mv/sec
- Potential Range Scanned: 0.0 v to -0.75 v
- Drop Time: 0.5 sec
- Current Range Scanned: 0 to 2 μA full scale
- Temperature: Room Temperature (20-23°C)

Required Reaction Conditions

At this point, several important reaction conditions described in the work by Becker[20] should be cited:

- The volumetric ratio between the acid mixture and the SDBS solution required for complete nitration of the surfactant was found to be 15:1. Acid/surfactant ratios of less than this ratio gave some slight variation in the polarographic results obtained.
- A one hour reaction time for the nitration process was found to be adequate for complete conversion.
- The pH of the test solution in the polaro-

graphic cell was required to remain constant with a value of 12.0. It was found that well defined polarographic peaks were obtained at this pH. Also, a minimum acid/buffer ratio of 1.2:40 was specified.

Results and Discussion

The current at -0.68 volts vs. SCE was determined with solutions of known SDBS concentrations in the polarographic cell. Prior investigations indicated that a polarographic peak was generated at -0.68 volts for SDBS solutions.[21] The set of polarographic peaks generated is given in Figure 8. It is evident that an increase in the surfactant concentration in the polarograhic cell was accompanied by an increase in polarographic peak height. A calibration curve was generated giving surfactant concentration in the detection cell as a function of peak height (detected current).(See Figure 9). As in the cases reported in the literature, the surfactant concentration was found to vary linearly with the height of the polarographic peaks generated over the range of concentrations examined. The major sources of experimental error encountered were pipetting errors, errors in preparing the standard solutions, and the surface active properties of the nitrated SDBS molecule.

Figure 8. Noncontinuous Polarographic Scans

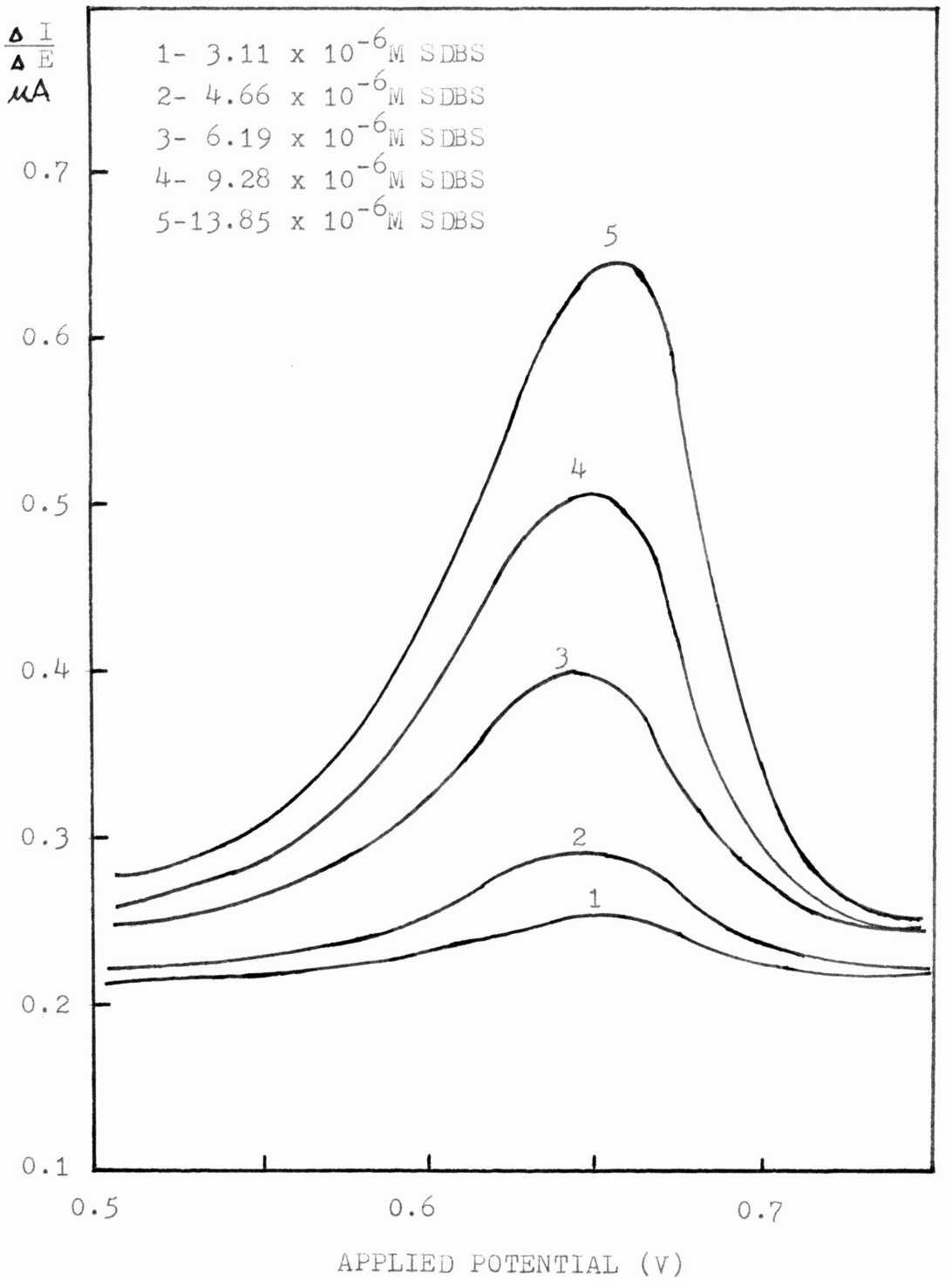
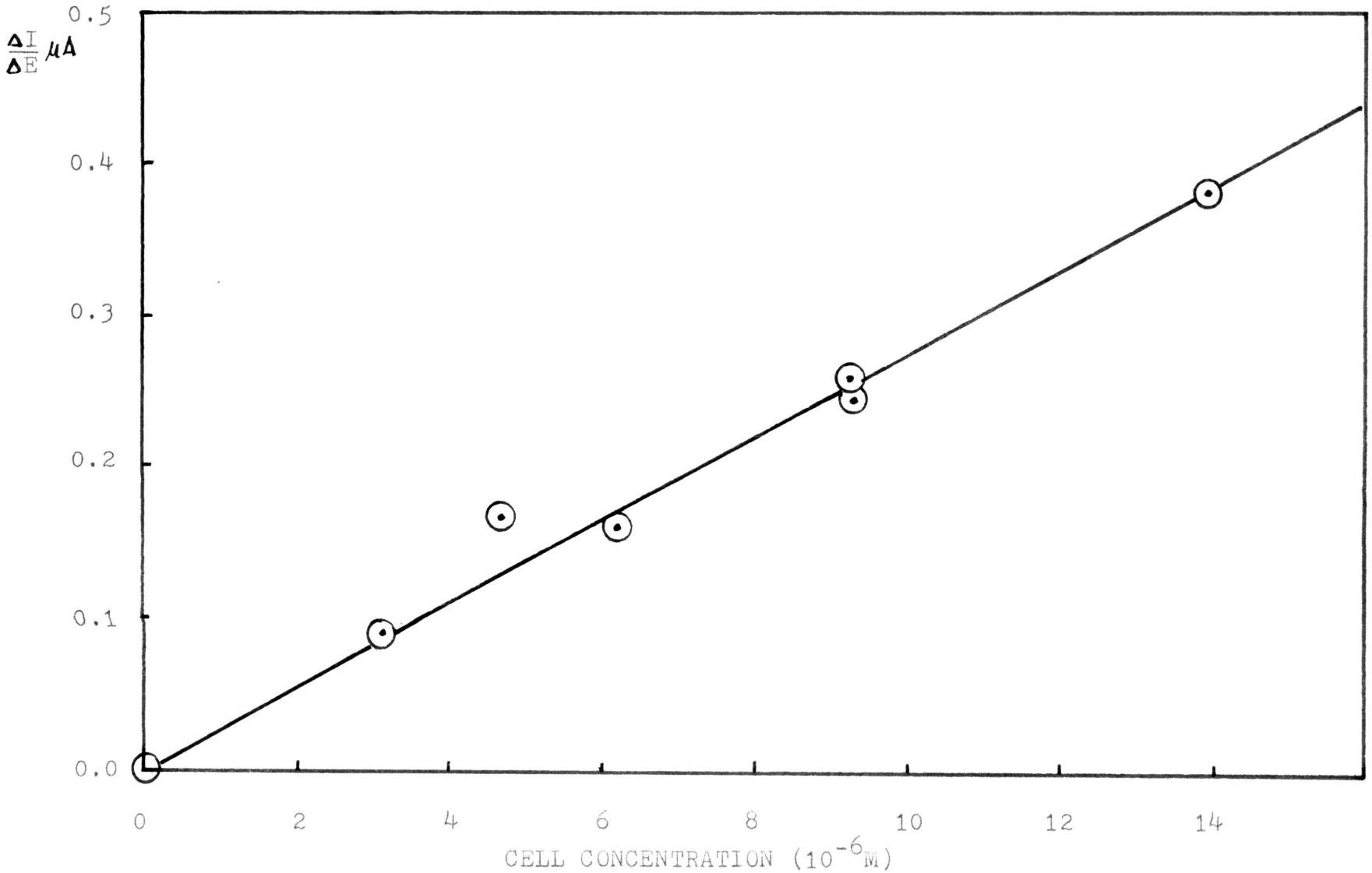


Figure 9. Calibration Curve for Noncontinuous Detection Case



THE CONTINUOUS ANALYSIS SCHEME

Introduction

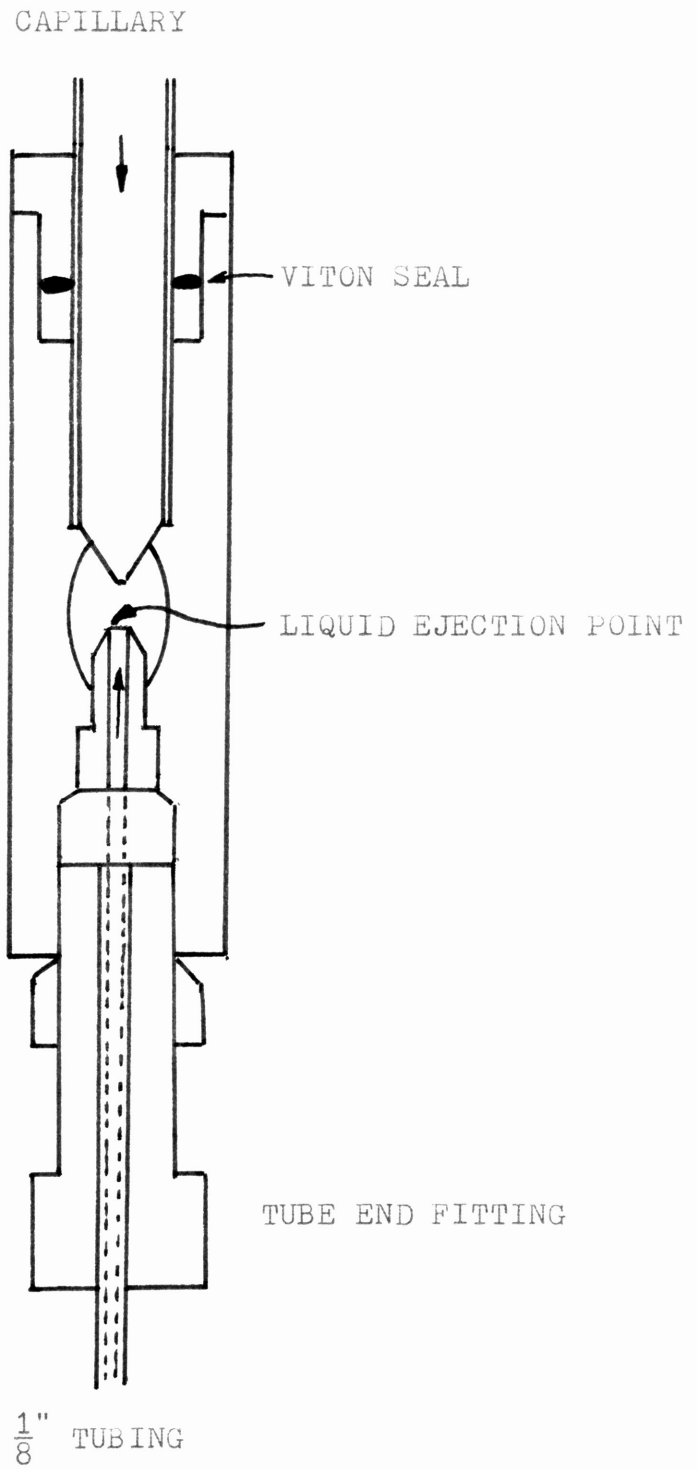
The experimental results obtained for the noncontinuous polarographic detection scheme seem to indicate that a continuous flow analysis scheme for the determination of surfactant concentrations in a coreflood experiment could be developed. Since most coreflood experiments are carried out on a continuous basis, a scheme of this type would be very useful. Polarographic measurements could be made on a continuous basis, and results could be drawn by comparison of measured peak currents to calibration plots.

Development of Calibration Curves

Polarographic measurements were performed on a continuous basis by implementation of the Princeton Applied Research Corporation Polarographic Analyzer (Model 174A) in conjunction with an LC Adapter Assembly (see Figure 10). In general, as the test solution is pumped into the detection cell, a delivery tip directs the solution toward a mercury drop hanging from a capillary directly above the delivery tip. The electrode reaction current is recorded on a strip-chart recorder as in the noncontinuous flow case.

Continuous polarographic detection was performed on test solutions of constant surfactant concentration for the construction of calibration curves. The test solutions were prepared in the same manner as the test solutions for the

Figure 10. Continuous Flow Adapter



noncontinuous detection scheme. The results of the polarographic voltage scans are given in Figure 11. It should be noted that an increase in the concentration of the surfactant stream resulted in an increase in the current peak height detected. A calibration curve giving SDBS solution concentration as a function of peak height for the continuous flow cell is given in Figure 12. The correlation presented is a linear least squares fit of the experimental data. As in the case of noncontinuous detection, the concentration of the surfactant solution was found to vary linearly with the peak current detected over the range of surfactant concentrations studied.

Finally, experimental tests were run to determine the effects of mercury drop time and voltage scan rate on the detector response generated. The compiled results indicated that the fastest drop rate (0.5 sec) gave the least drifting of the response baseline. Also, comparison of the voltage scan rates indicated that scan rates of 2 millivolts per second and 5 millivolts per second gave essentially the same recorded peak currents (Figure 13). Therefore, a scan rate of 5 millivolts per second was implemented in the continuous detection scheme to minimize the time span required for experimental runs. A summary of the complete polarographic detector settings is as follows:

Figure 11. Continuous Polarographic Scans

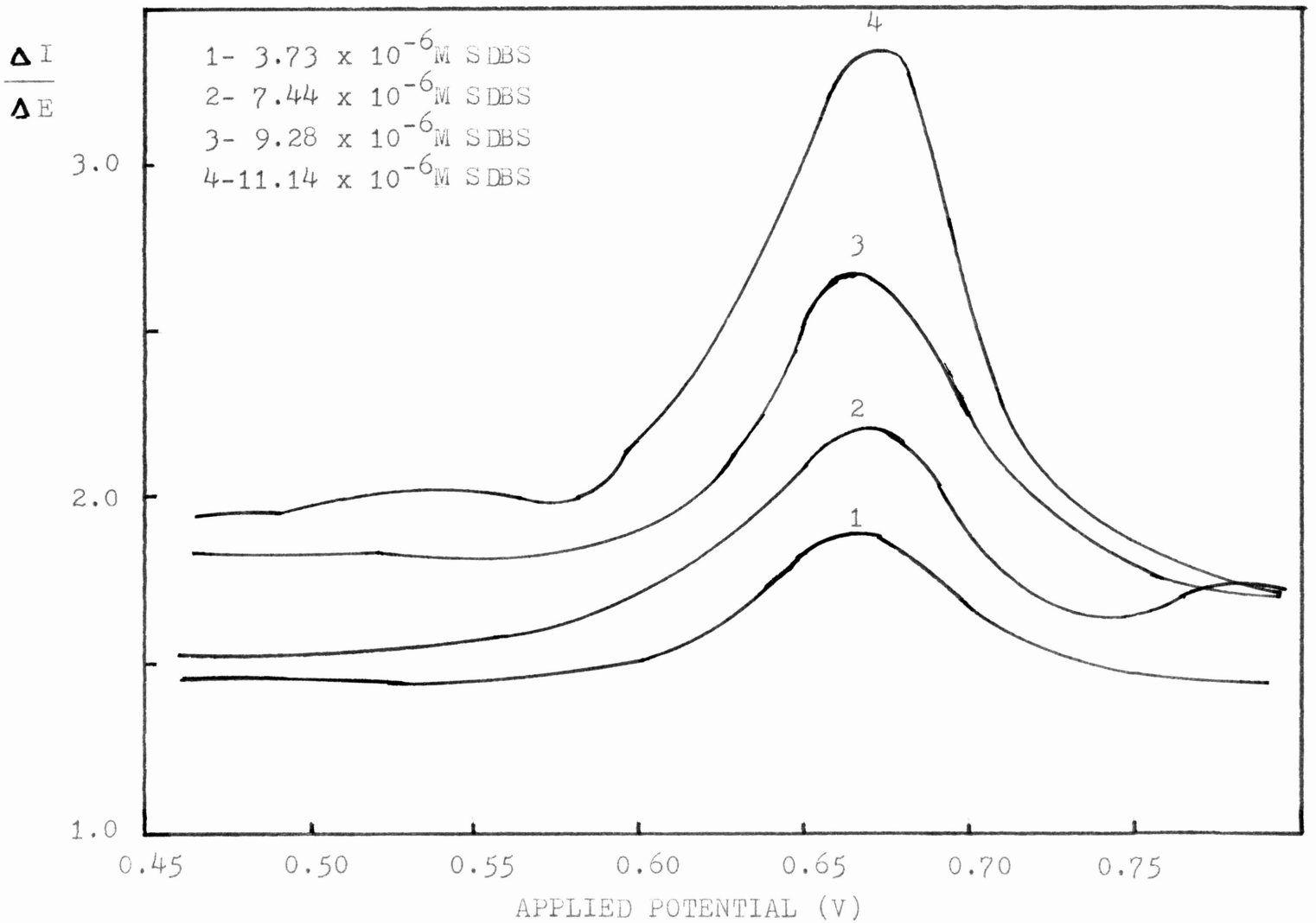


Figure 12. Calibration Curve for Continuous Detection Case

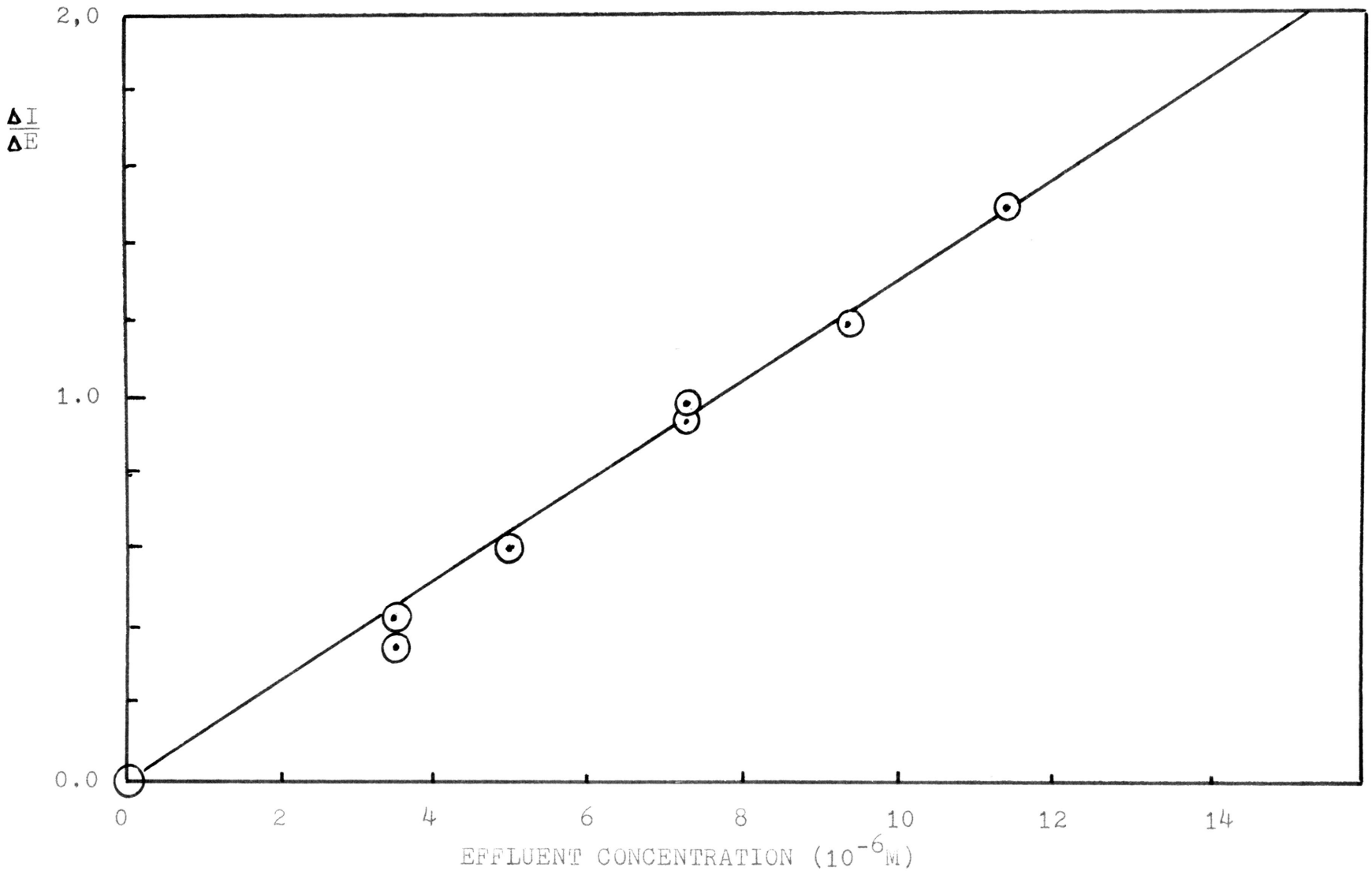
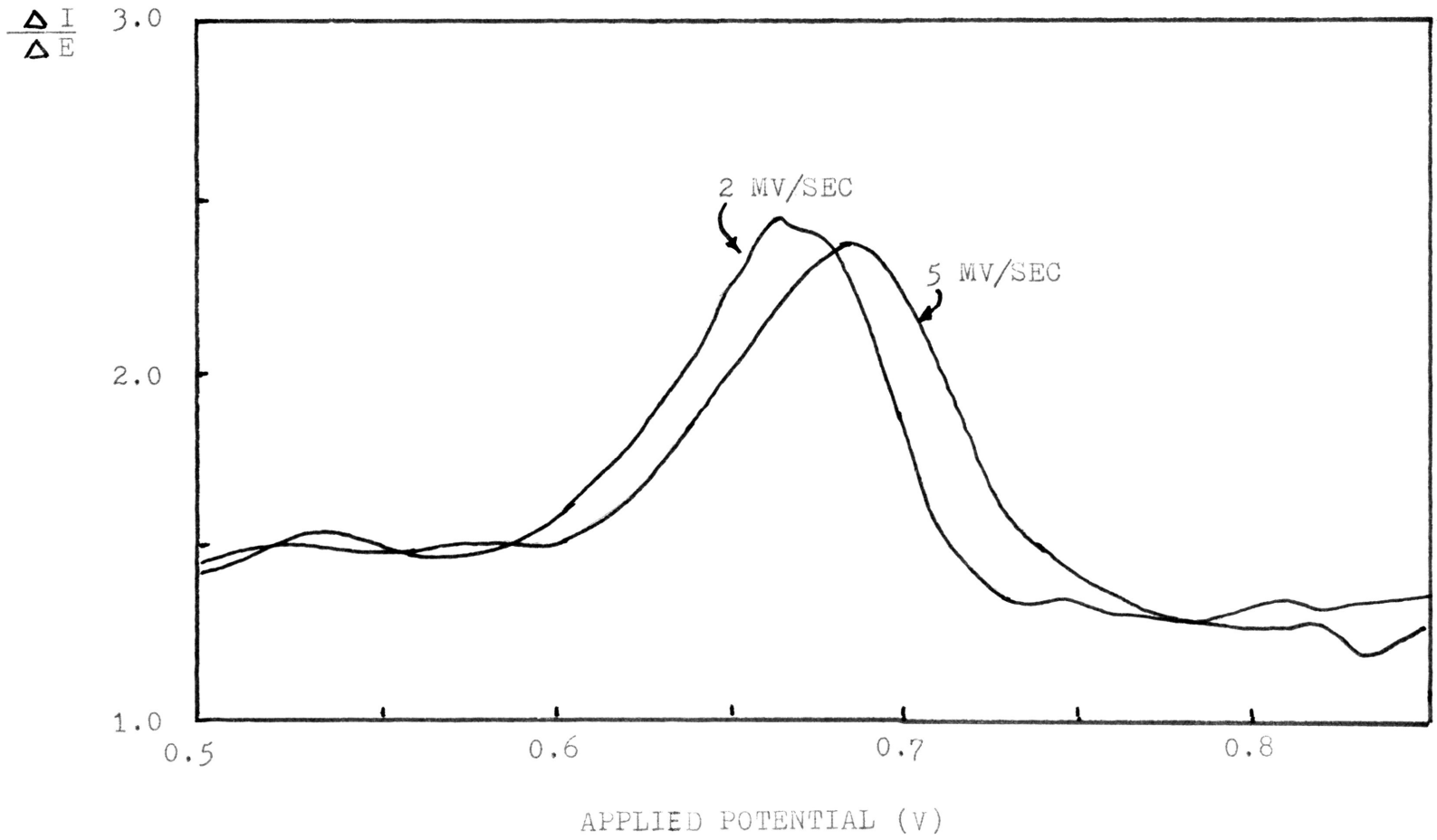


Figure 13. Comparison of Voltage Scan Rates



- Mode: Differential Pulse Polarography
- Modulation Amplitude: 25 mv peak to peak
- Scan Rate: 5 mv per second
- Potential Range Scanned; 0 to -0.75 volts
- Drop Time: 0.5 sec
- Current Range Scanned: 0 to 5 μA full scale
- Temperature: Room Temperature(20-23 ^{o}C)

Application of the Continuous Detection Scheme to Coreflood Experiments

The principles of polarographic detection may be applied to an actual coreflood experiment (see Figure 14). The core sample implemented was a rectangular Berea sandstone core of dimensions 15"x1"x1". The core was cast in a polyester-based epoxy resin prior to the actual coreflooding process to prevent loss of the test solution to the environment. Plexiglass fittings were designed for the ends of the core sample to the specifications outlined in Figure 14A. The packed column required for mixing the acid solution and the surfactant test solution was designed with the following fabrication criteria:

- A glass column (12 mm outside diameter, 41 inches long) filled with 0.3 mm glass beads was implemented to minimize adsorption effects in the mixing process.
- A void volume of 0.3 was assumed for the initial column design specifications.

Figure 14. Continuous Detection Scheme for the Determination of Surfactant Concentrations

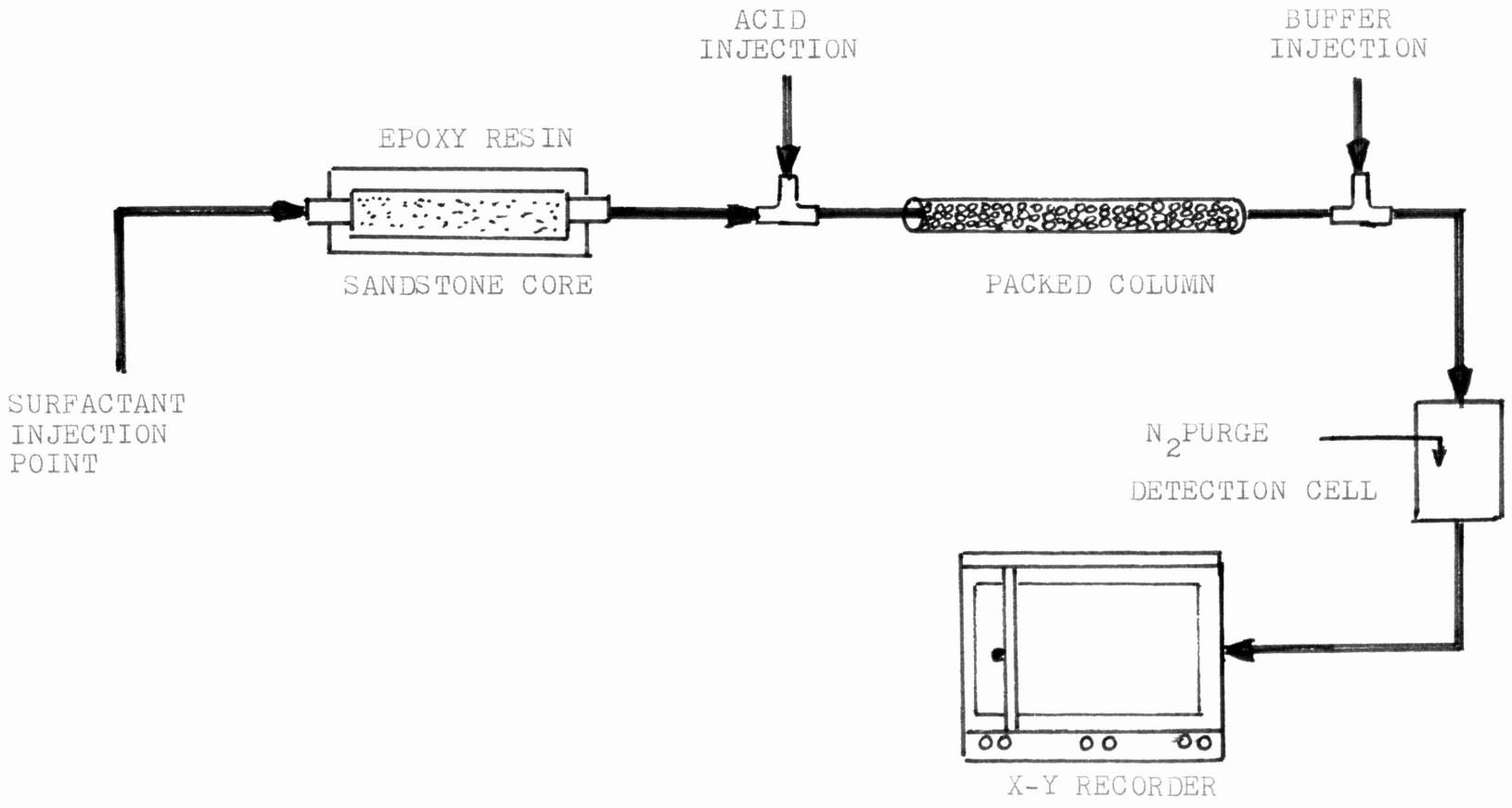
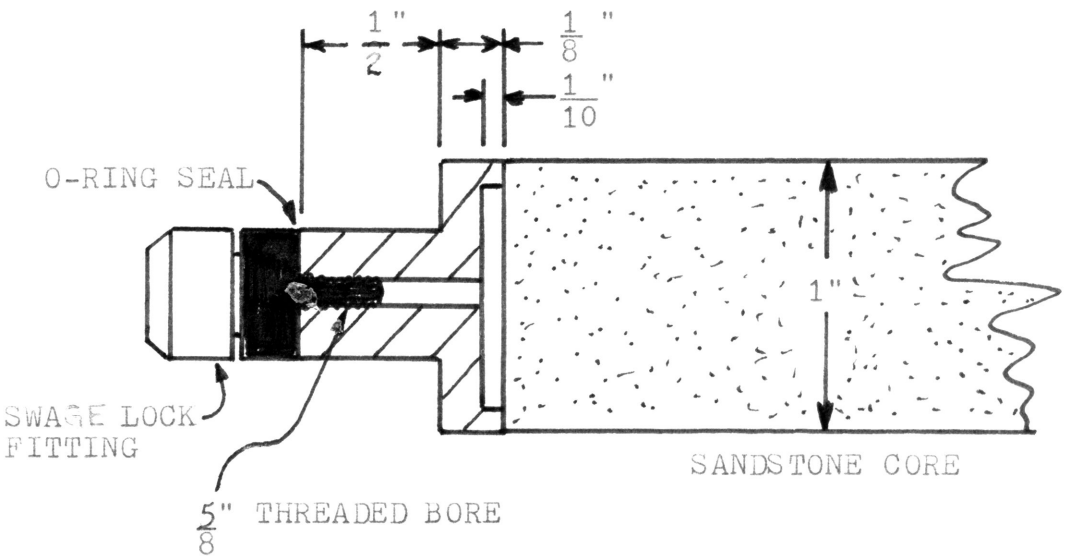


Figure 15. Core Fitting Specifications



- A minimum dead time of one hour was specified for the column so that ample time was available for nitration of the SDBS test solution.

The core sample effluent stream is mixed with the acid mixture on a continuous basis at a ratio (by volume) of 15:1. The effluent from the packed column is mixed with the buffer solution (pH 12.0) at a mixing tee at a ratio (by volume) of 40:1. The analysis is carried out in a continuous flow detection cell, and the peak current at a constant voltage (-0.68 volts vs. SCE) is recorded as a function of experimental run time. The detector response is then implemented to determine the adsorption effects in the core sample.

Experimental Results

The detection scheme outlined in Figure 14 was assembled for operation, but several experimental difficulties hindered the gathering of useable data. For example, the acid to buffer flow ratio (given as 1:40 in previous investigations) was reduced to approximately 1:16 (by volume) in the experimental runs to reduce the overall run time appreciably. This reduction proved to be a mistake, in that the intensified acidity in the detection cell resulted in a reaction with the dropping mercury that blocked flow in the mercury capillary. It is recommended that a buffer flush line be coupled with the detection cell in

future studies to allow maintenance of a constant pH in the detection cell. Secondly, the mixing process involving the acid solution and the surfactant test solution (containing a minute quantity of sodium chloride) resulted in the evolution of hydrogen chloride gas in the packed column. The accumulation of gas caused a decrease in the volume occupied by the liquid in the column, thus reducing the reaction contact time available. In further studies, a vent system should be supplied at the column entrance to allow the trapped gas a route to escape to the atmosphere.

DETERMINATION OF ADSORPTION EFFECTS

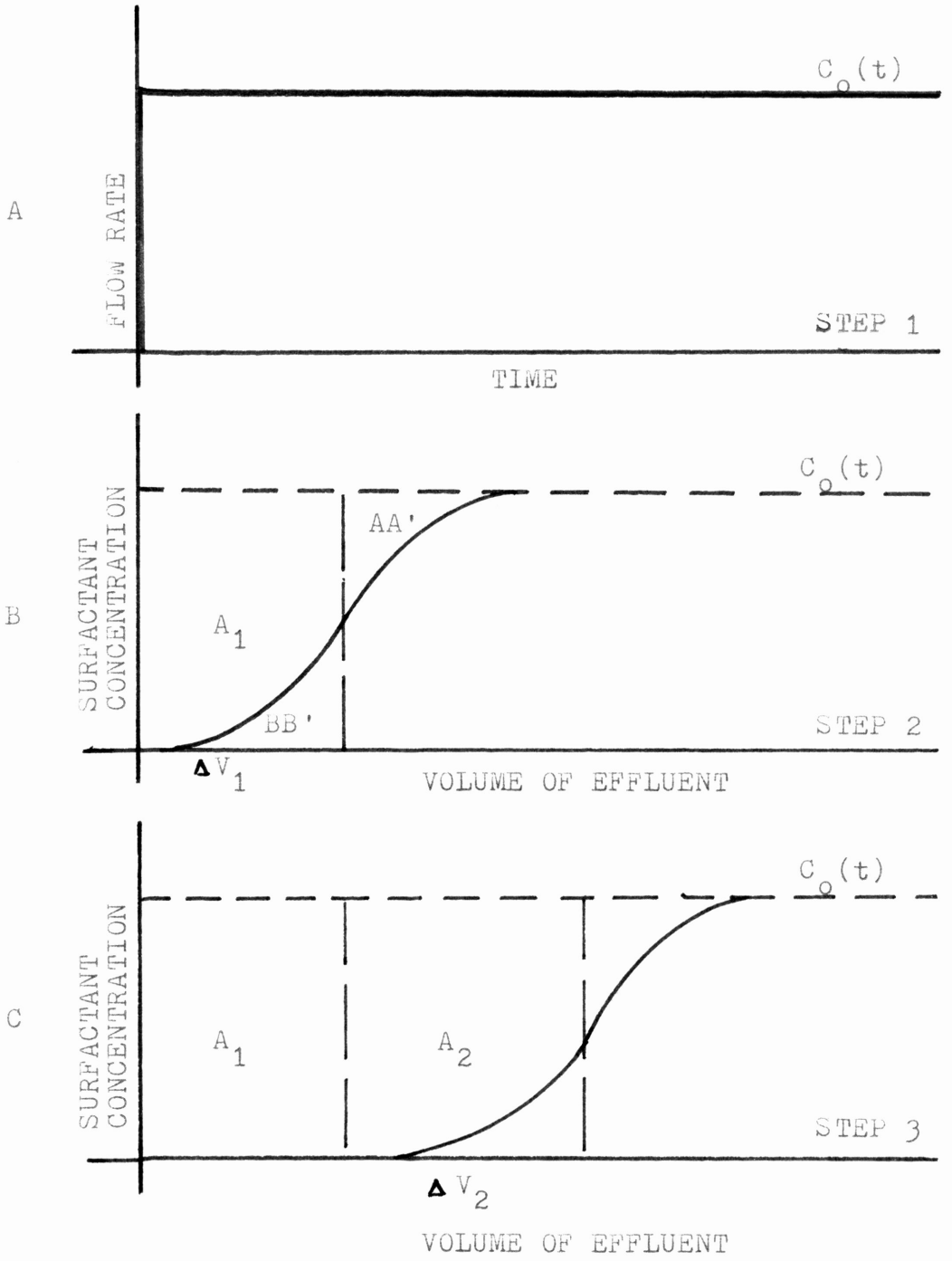
Introduction

Despite the failure of the coreflood test runs, a procedure was developed for the determination of surfactant adsorption effects in a coreflood experiment from the principles of adsorption theory and continuous flow polarography.

Ultimately, the concentration profile of the core effluent stream will be implemented to evaluate coreflood adsorption effects. This profile is not directly measureable because nitration of the surfactant test solution and dilution with pH 12.0 buffer are required prior to detection. At any rate, if the concentration profile of the core effluent stream is known as a function of experimental run time (or effluent volume), it is possible to obtain the equilibrium adsorption of the core sample as well as the rate of adsorption. In general, adsorption effects are determined by the additional time required for the surfactant stream to flow through the core sample as compared to the case if there were no adsorption effects in the core sample.

Adsorption theory may be implemented to determine the changes response functions will undergo when subjected to the effects of equilibrium adsorption. For the case of no adsorption in the core sample, the system response to a step-change in the flow rate of the surfactant test solution (refer to the continuous detection scheme outlined in Figure 14) is given in Figure 15:

Figure 15. System Response for the Case of No Adsorption



STEP 1: A step change in the flow rate of the surfactant stream entering the core sample is introduced.

STEP 2: The response function representing the concentration of the surfactant effluent stream as a function of volume of effluent leaving the core sample is given in Figure 15-B. A front line may be estimated by evaluating the point on the response curve where the area above the curve (indicated by AA') is equivalent to the area below the response curve (indicated by BB'). For the case of no adsorption in the core sample, this response front will coincide with an effluent volume equivalent to the pore volume of the core sample (i.e., the area indicated by A_1, where $A_1 = C_o \Delta V_1$, is the void volume of the core sample. This value is available experimentally.)

STEP 3: The response function obtained by polarographic detection of the packed column effluent stream (see Figure 14) is given in Figure 15-C. A front line may be estimated by the method outlined in STEP 2 of this discussion. The resultant

area (indicated by A_2, where $A_2=C_o\Delta V_2$) represents the void volume of the packed column. This value may also be determined experimentally.

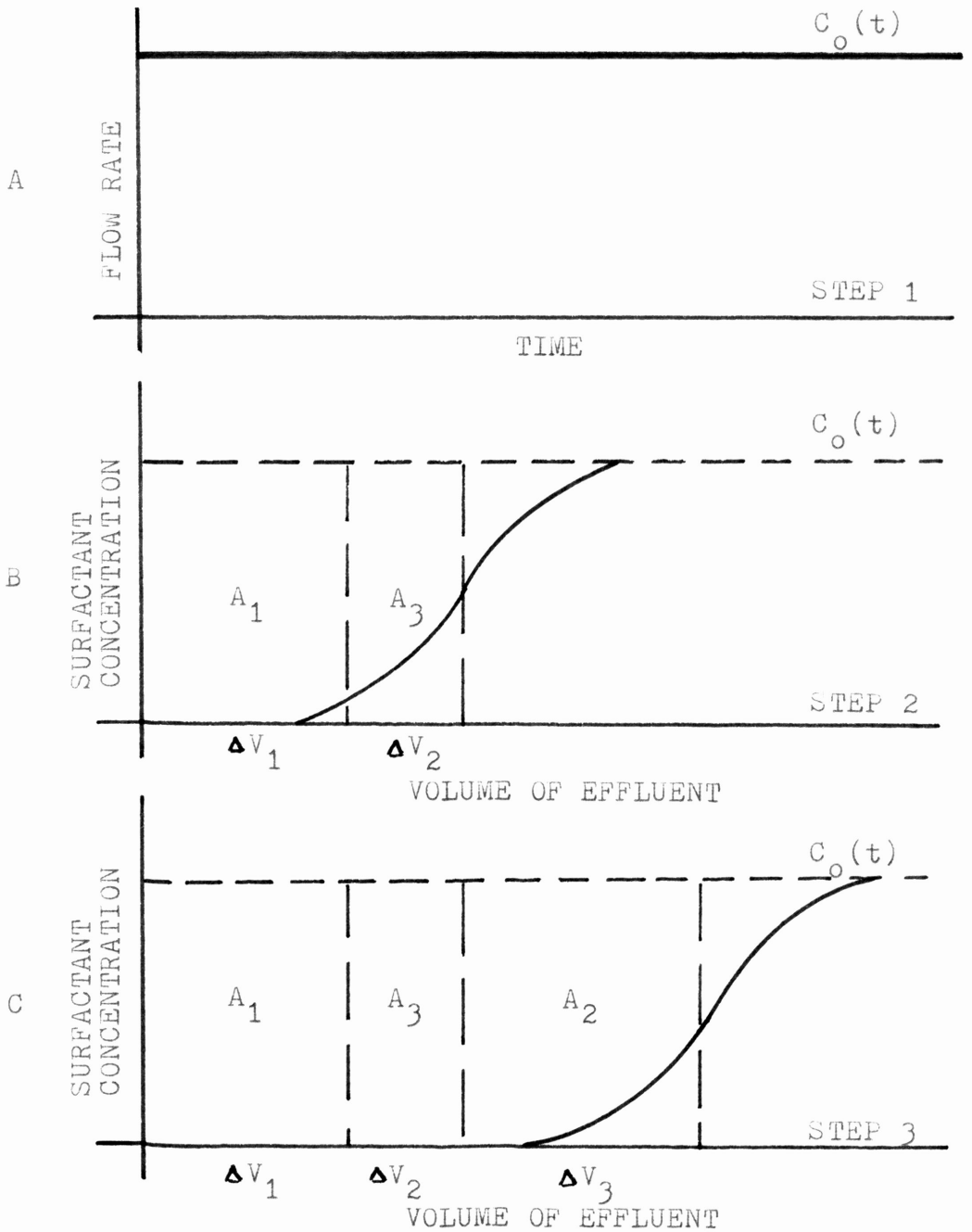
For the case involving adsorption in the core sample, the system response to a step-change in the flow rate of the surfactant test solution is given in Figure 16:

STEP 1: A step change in the flow rate of the surfactant stream entering the core sample is introduced.

STEP 2: The response function representing the concentration of the surfactant effluent stream as a function of the volume of effluent leaving the core sample will be delayed by the pore volume of the core sample(ΔV_1 of Figure 16-B)- as in the case of no adsorption, and by the degree of adsorption in the core sample (ΔV_2 of Figure 16-B). The difference in the response front detected in this case and the response front defined by the void volume of the core sample (see Figure 15-B) specifies the equilibrium adsorption in the core sample (A_3 of Figure 16-B where $A_3=C_0\Delta V_2$.)

STEP 3: The response function obtained by

Figure 16. System Response for the Case With Adsorption



polarographic detection of the packed column effluent stream is given in Figure 16-C. The response function is delayed by the pore volume of the packed column alone if the assumption is made that no adsorption occurs in the column. (The glass column was fabricated with this assumption as a design criteria.)

Experimental Determination of Adsorption Effects

The system response to a step-change in surfactant flow rate entering the system outlined in Figure 14 can be determined by the process of continuous polarographic detection previously discussed. If the final response function is known, the response front may be determined. The void volume of the packed column may be subtracted from the final response front line to yield the response front line of the core effluent stream response function. Since the void volume of the core sample may be determined experimentally, the difference between the calculated core effluent response front and the response front for the case of no adsorption is the equilibrium adsorption in the core sample.

The Convolution Integral

An important concept in the analytical schemes required to obtain the core effluent response function is the convolution integral. In general, if the impulse response function for a system modelled by a number of tanks in series

is known, the response ($C(t_i)$) of the system to any arbitrary input function may be calculated at discrete time intervals by the relation:

$$C(t_i) = \int_0^{t_i} X(t)\ Y(t-\eta)\ d\eta \qquad \text{(I)}$$

where: t_i = the time the response is to be calculated for

$X(t)$ = the value of the impulse response function of a system modelled by "n" tanks in series evaluated at time t

$Y(t-\eta)$ = the value of the input function evaluated at time $t-\eta$

η = an arbitrary time interval

In practice, the convolution integral is evaluated numerically by implementation of the relation:

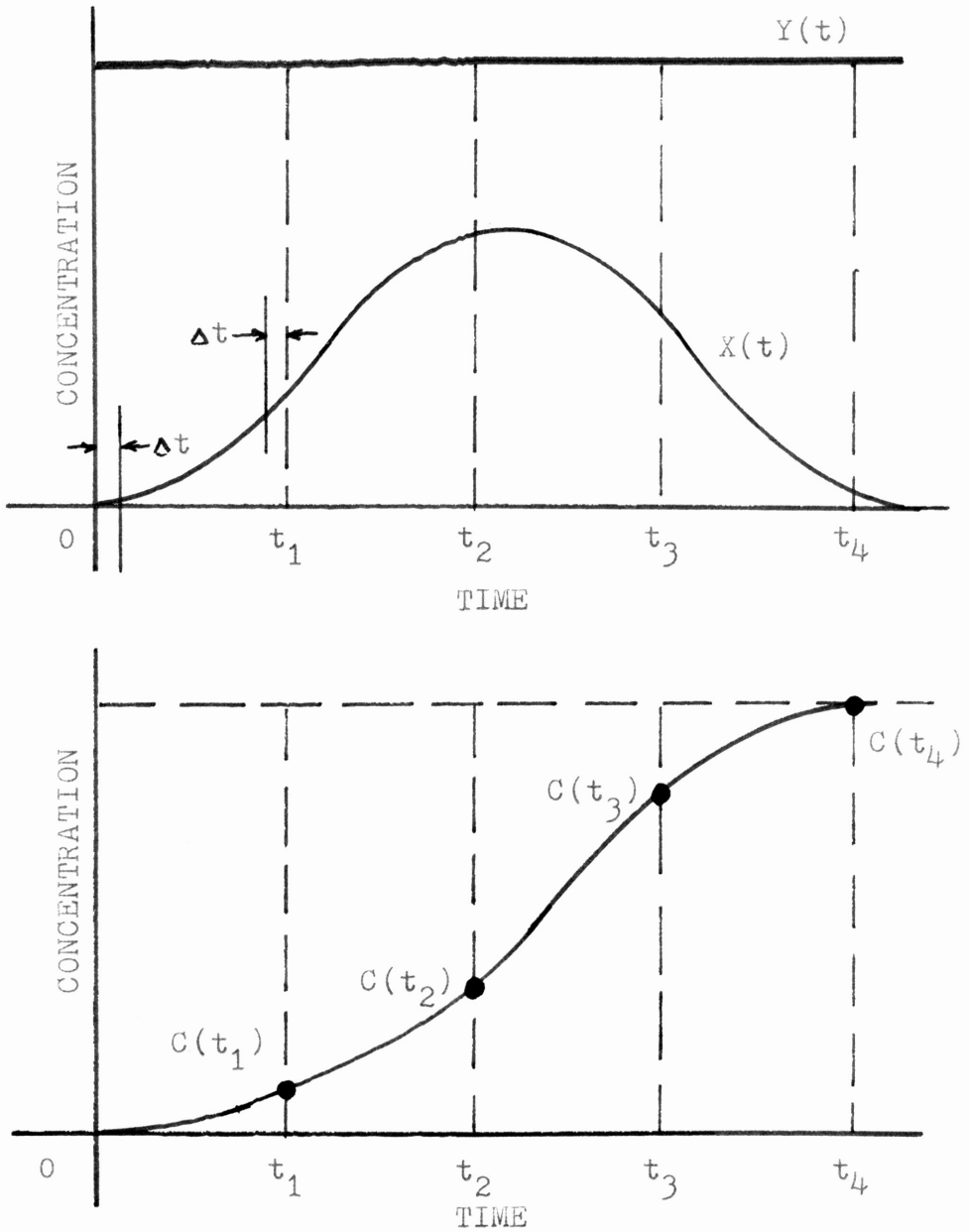
$$C(t_i) = Y(t_i-0)X(0)\Delta t + Y(t_i-\Delta t)X(\Delta t)\Delta t + Y(t_i-2\Delta t)X(2\Delta t)\Delta t + \ldots + Y(0)X(n\Delta t)\Delta t \qquad \text{(II)}$$

where: Δt = the time increment implemented in the numerical integration

n = the number of time increments implemented in the numerical integration between t=0 and $t=t_i$ (see Figure 17).

In order to obtain the system response to an arbitrary input function, the convolution process must be performed at discrete time intervals along the time axis (t_1, t_2, t_3, etc.). A computer program for the numerical convolution

Figure 17. The Principle of Convolution



of a step-increase function is given in the Appendix, along with a table of the calculated response function values. The value of the step response function may also be calculated analytically by the relation:

$$C(t) = \left[1 - \exp(-nt/\tau) - (nt/\tau)\exp(-nt/\tau) - \cdots - \frac{(nt/\tau)^{n-1}}{(n-1)!}\exp(-nt/\tau)\right] * H \qquad \text{(III)}$$

where: n= the number of tanks modeled in series

τ = the system time constant

H= the magnitude of the step change employed.

The analytical values for the response function are also given in Table 1 of the Appendix to verify the validity of the convolution calculations performed by the computer. It should be noted that any function (discrete or continuous) could be implemented as the input function to the program.

Characterization of the Packed Column

One of the requirements of the convolution integral is that the impulse response function of a system modelled by "n" tanks in series be defined at each time, t. In general, the impulse response function is given by the relation:

$$Y(t) = \left[\frac{(nt/\tau)\ \exp(-t/\tau)}{(n-1)!\ \ t}\right]^{n} \qquad \text{(IV)}$$

where: n= the number of tanks modelled in series

τ= the system time constant.

Therefore, if the parameters n and τ are known, the impulse response function for the system is known. In the coreflood experimental scheme outlined in Figure 14, the

packed column may be modelled quite accurately by "n" tanks in series. Once the column has been characterized, the convolution integral may be implemented on a trial and error basis to determine the core effluent stream response function simply by knowing the response function at the polarographic detector. The core effluent response curve may then be used to obtain the core adsorption information needed for effective core flood design.

The packed column parameters (n and τ) may be determined experimentally by utilization of the scheme depicted in Figure 18. In general, a step change in the surfactant flow rate is administered to the packed column. The volume ratios suggested for the acid, surfactant, and buffer solutions are equivalent in this scheme. The effluent stream concentration (peak current) is monitored as a function of time by the polarographic detector at a constant potential. The computational scheme given in Figure 19 may then be employed to obtain accurate values for the column parameters, n and τ.

Obtaining the Core Effluent Response Function

Once the response data for the packed column has been reproduced by convolution and the exact values of n and τ are known, the impulse response function for the column (modelled by "n" tanks in series) can be determined. In order to obtain the variation of the surfactant concentration with time at the core (and ultimately the adsorption effects

Figure 18. Apparatus Schematic for Obtaining Packed Column Parameters

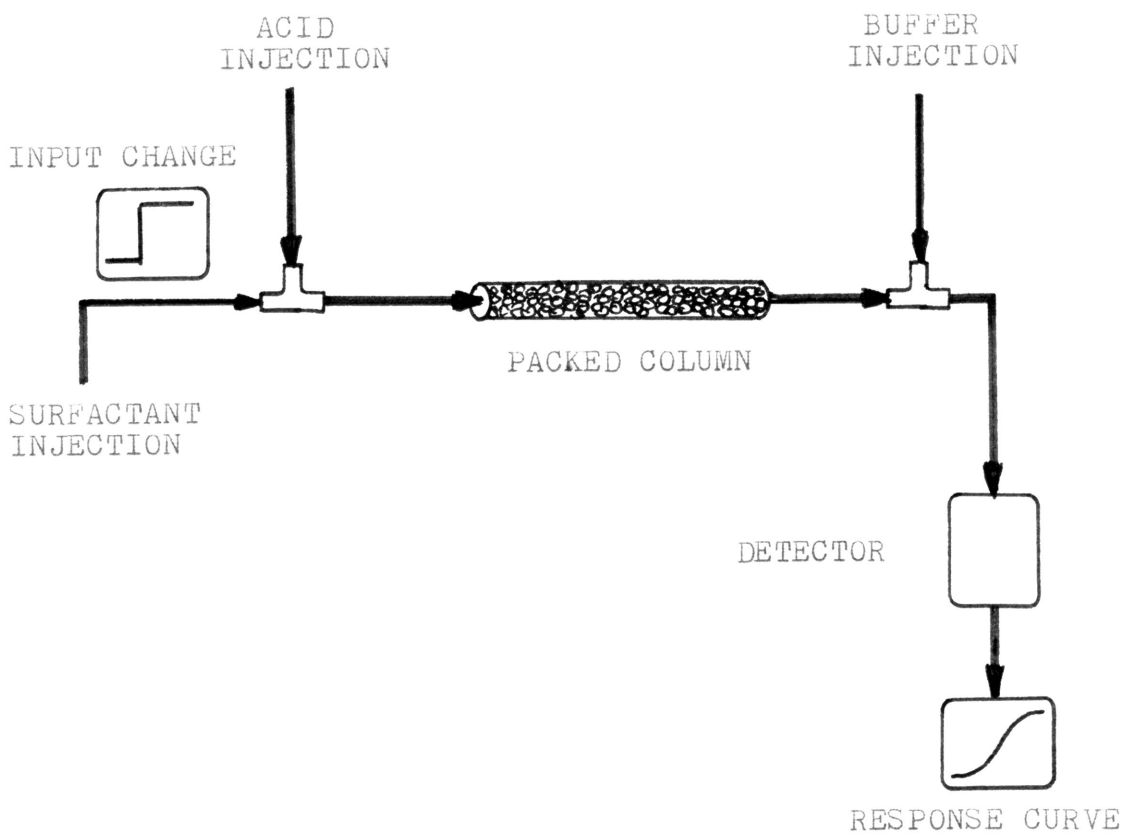
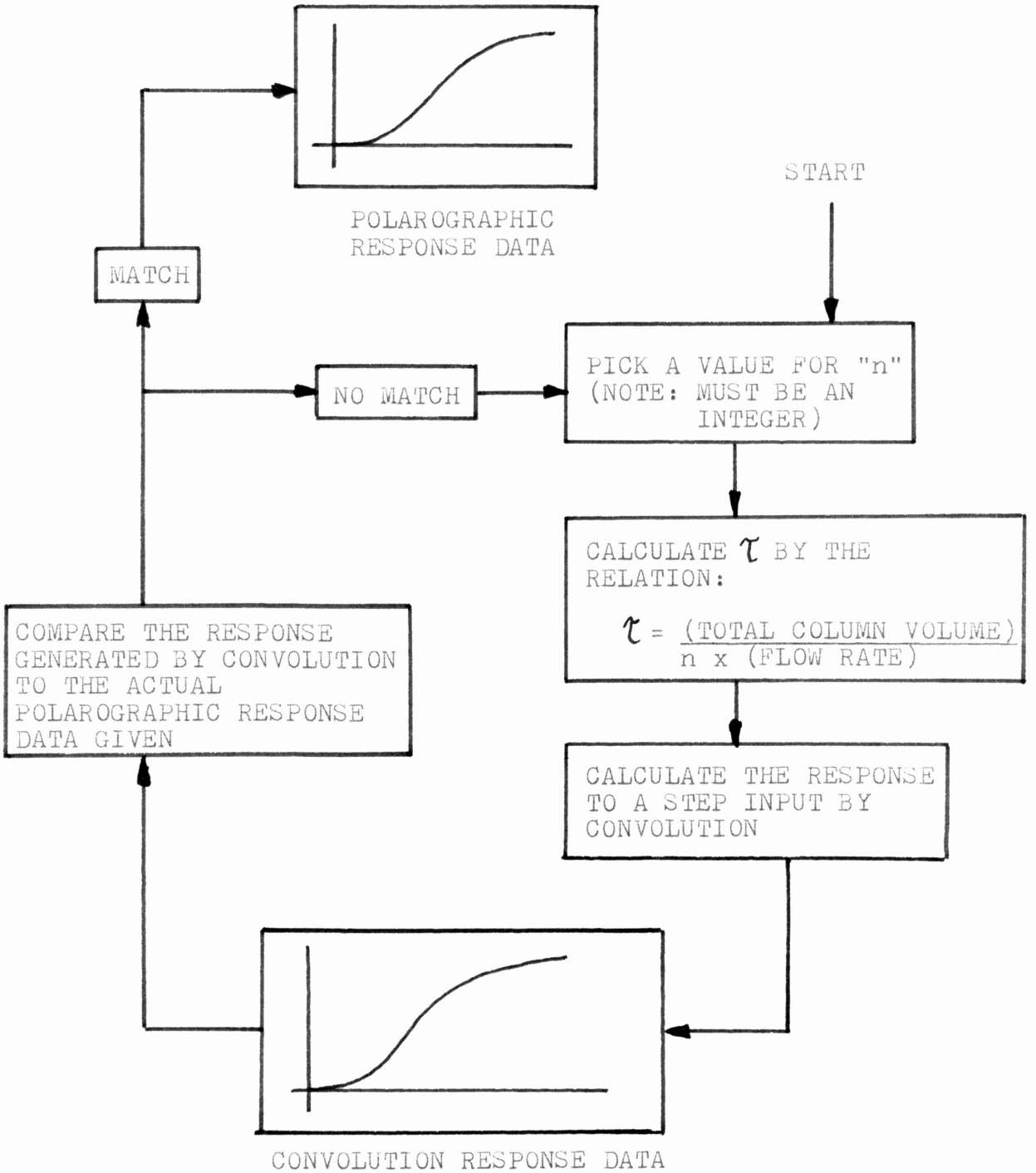


Figure 19. Computational Scheme for Obtaining Column Parameters



in the core sample), a model for the core sample response function must be chosen. Initially, for the sake of simplicity and obtaining a response estimate, a second order linear response model should be chosen of the form:

$$Y(t) = 1.0 - A \exp(-t/\tau_1) - B \exp(-t/\tau_2) \qquad (V)$$

where: τ_1, τ_2 = system time constants

A, B = constants

A second order linear response function is generally characterized by two parameters- τ_1 and τ_2. Therefore, the core effluent response may be determined in the following manner:

STEP 1: The experimental apparatus of Figure 14 is assembled.

STEP 2: A change in the surfactant flow rate (i.e., step, impulse, log-normal, normal, etc.) is administered to the core sample.(Only the step change case will be considered in the remainder of this discussion. It should be noted that the principles involved are applicable to any arbitrary input function).

STEP 3: Continuous polarography is used to obtain the surfactant concentration as a function of experimental run time for the overall scheme.

STEP 4: The computational scheme outlined in Figure 20 may be employed to obtain the required response function.

Once the polarographic response data has been reproduced by convolution, the adsorption effects in the core sample may be evaluated by implementation of the principles previously presented. An outline of the graphical scheme is given in Figure 21.

Figure 20. Computational Scheme for Obtaining the Response of the Core Effluent Stream

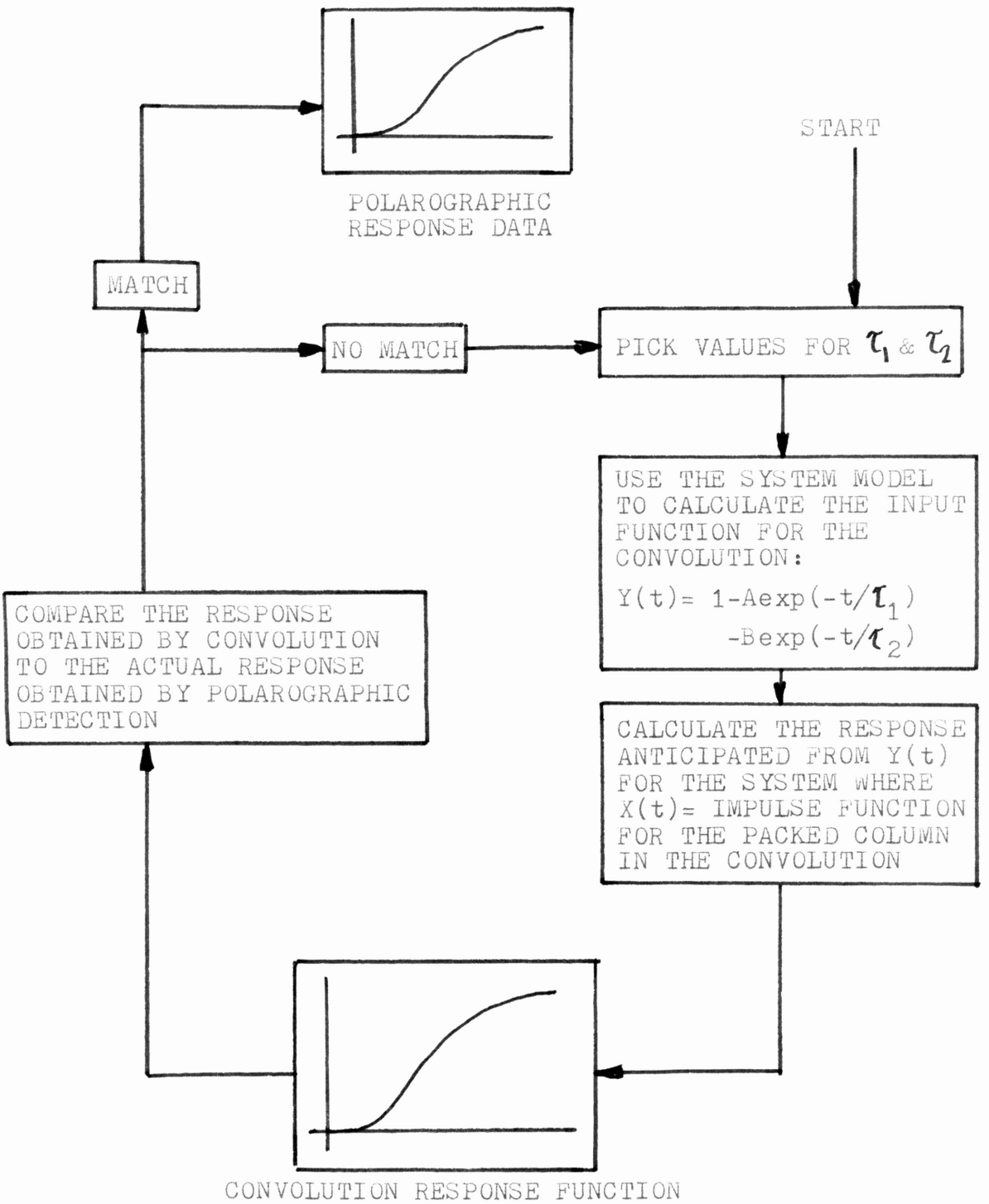
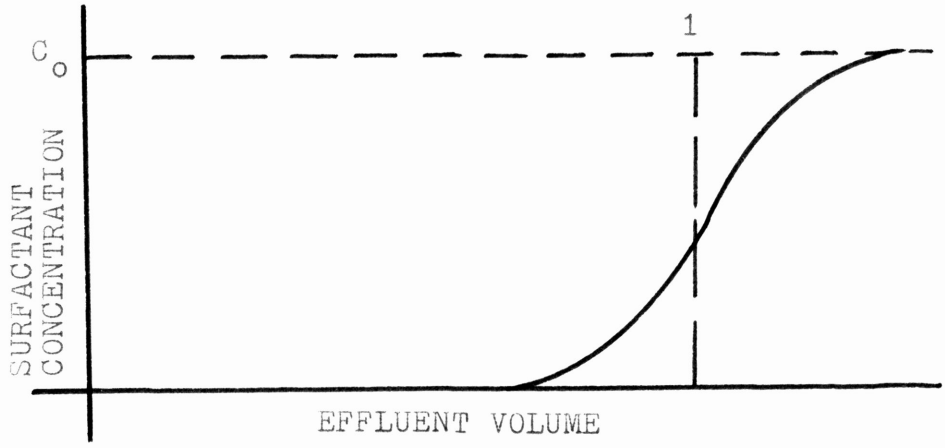
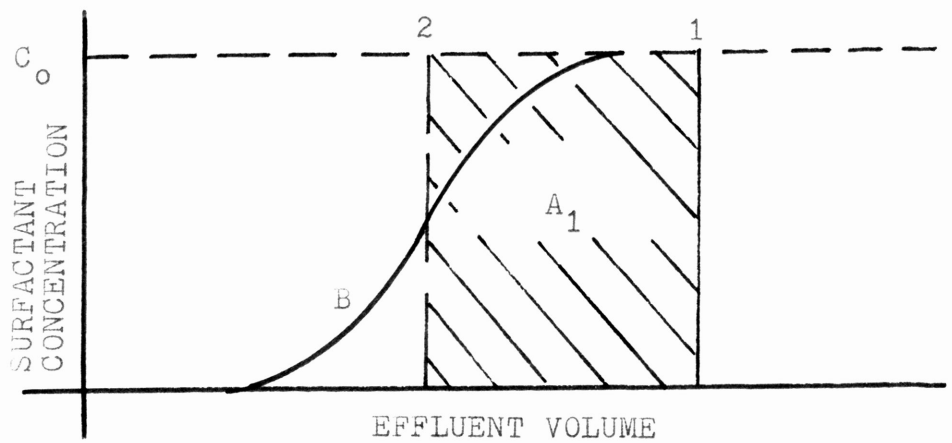


Figure 21 A. Evaluation of Adsorption Effects in the Core Sample



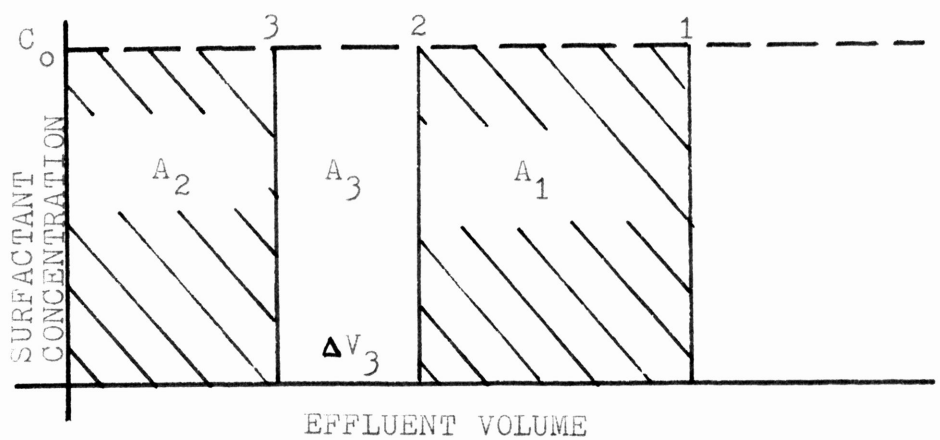
1. The response data obtained by polarographic analysis (in the form of surfactant concentration vs. time) is converted to the form of surfactant concentration vs. effluent volume by multiplying the time axis by the column effluent flow rate.
2. A front line is estimated by previously described methods.

Figure 21 B. Evaluation of Adsorption Effects in the Core Sample



1. The void volume of the packed column (A_1) which has been characterized by the parameters n and τ is subtracted graphically from the polarographic response front (1)
2. The resultant response front (2) is the response front of the response curve calculated by the computational scheme outlined in Figure 19.(B= the calculated response)

Figure 21 C. Evaluation of the Adsorption Effects in the Core Sample



1. The difference between the response front calculated by convolution (2) and the response front given by the void volume of the core sample (3) is the equilibrium adsorption in the core sample. A_2 and front line, 3, are specified experimentally. The numerical value for the equilibrium adsorption is given by the relation:

$$A_3(\text{adsorption}) = C_o \times \Delta V_3$$

SUMMARY

Recent changes in the availability and the world market price for oil have renewed interest in methods that will recover a considerable portion of the oil remaining in reservoirs after primary and secondary recovery techniques have been employed. A method that seems promising is surfactant flooding, but one of the major problems in designing an effective flooding process is minimizing the adsorption activity in the reservoir. To date, very little data concerning the adsorption behavior of surfactants is available, primarily because the detection methods developed are either too time consuming or too specific. An electrochemical method known as polarography has proven to be effective on a noncontinuous detection basis, but actual coreflood experiments require a continuous detection scheme. The purpose of this investigation was to develop a scheme of this type.

The polarographic results obtained indicated that the surfactant concentration of the test solutions analyzed varied linearly with the peak current at the detector for the continuous flow case as well as the noncontinuous flow case. A continuous detection scheme for the determination of adsorption effects in the core sample was developed, but several problems arose that prevented the collection of experimental data.

Despite this circumstance, the principles of continuous polarographic detection and system response were used to create a computational scheme that would allow the equilibrium adsorption of surfactant in the core sample to be determined from the system detector response alone, assuming no surfactant adsorption occurs in the packed column. The scheme developed is a general one that is applicable to all types of functional inputs at the core sample.

LITERATURE CITED

1. Clark, Norman J.: Elements of Petroleum Reservoirs, Storm Printing Corporation, Dallas (1960),P.67.

2. Ibid.,p. 68.

3. Becker, Michael: "The Electrochemical Analysis of Sodium Dodecylbenzenesulfonate in Solutions Containing Oilfield Impurities",Texas A&M University(1979),p. 2.

4. Interstate Oil Compact Commission, "Secondary and Tertiary Oil Recovery Processes", Oklahoma City OK.,September,1974.

5. Johansen, Robert T.: "Overview of Selected Oil Recovery Processes", Journal of Rheology, 23(1979),p. 169.

6. Ibid.

7. Ibid.,p.170.

8. Johansen, R., p. 173.

9. Ibid.

10. Ibid., p. 177.

11. Ibid., Pp. 171-2.

12. Reed, Ronald and Robert Healy: "Some Physiochemical Aspects of Microemulsion Flooding: A Review," Exxon Production Research Corporation, Houston, p. 8.

13. Ibid.

14. Johansen, R., p. 172.

15. Trogus, F. J., et. al.,Soc. Pet. Engr. Jour., 18(1977) Pp. 353-7.

16. Suffridge, F. and D. L. Taggart, SPE Paper #6596, International Symposium on Oilfield and Geothermal Chemistry, June 27-8, 1977.

17. Reed,R., Pp. 9-11.

18. Becker, M.,Pp. 15-19.

19. Ibid., Pp. 13-16.

20. Ibid., p. 14.

21. Ibid., p. 35.

APPENDIX

COMPUTER PROGRAM TO PERFORM CONVOLUTION

```
C*************************************************************
C     THIS PROGRAM IS DESIGNED TO NUMERICALLY GENERATE THE
C     RESPONSE OF A SYSTEM MODELLED BY "N" TANKS IN SERIES
C     TO VARIOUS INPUT FUNCTIONS BY USE OF THE CONVOLUTION
C     INTEGRAL
C*************************************************************
C     N      =THE NUMBER OF TANKS IN SERIES TO BE MODELLED
C     TAU    =THE SYSTEM TIME CONSTSNT
C     T      =THE TIME INTERVAL AT WHICH RESPONSE VALUES
C             ARE CALCULATED
C     DELTAT=THE INCREMENT OF TIME OVER WHICH THE CONVOLUTION
C             IS PERFORMED
C     M1     =THE NUMBER OF DELTAT'S PER TIME INTERVAL T
C     M2     =THE NUMBER OF T'S TO BE EVALUATED FOR THE FUNCTION
C     F      =FUNCTION INPUT
C     CONVOL=THE FUNCTION APPROXIMATING THE RESPONSE OF A
C             SYSTEM TO A GIVEN INPUT
C*************************************************************
      REAL TAU,H,CONVOL(100),RESPON(100)
      READ,N,TAU
      READ,T,M1,M2
      DELTAT=T/M1
      TIME=0.0
      DO 1 IN=1,M2
      TIME=TIME+T
      T1=0.0
      T2=TIME
      READ,H
C*************************************************************
C     INITIALIZE THE CONVOLUTION FUNCTION FROM THE ENDPOINTS
C*************************************************************
```

```
      CONVOL(IN)=F(N,T2,TAU,H)*G(N,T1,TAU)*DELTAT
      M3=IN*M1
      DO 1000 JI=1,M3
      FT=TIME-DELTAT*JI
      GT=T1+JI*DELTAT
C*************************************************************
C     COMPUTE THE VALUE OF THE CONVOLUTION FUNCTION AT T(IN)
C*************************************************************
      CONVOL(IN)=CONVOL(IN)+F(N,FT,TAU,H)*G(N,GT,TAU)*DELTAT
1000  CONTINUE
1     CONTINUE
C*************************************************************
C     CALCULATE THE ACTUAL RESPONSE OF THE SYSTEM TO A STEP
C     INPUT AT DISCRETE TIME INTERVALS FOR COMPARISON
C*************************************************************
      DO 300 J=1,M2
300   RESPON(J)=0.0
      TIME=0.0
      DO 20 J=1,M2
      TIME=TIME+T
      DO 30 I=1,N
30    RESPON(J)=RESPON(J)-(((N*TIME/TAU)**(I-1))*
     *EXP(-N*TIME/TAU)/(FACT(I-1)))*H
20    CONTINUE
C*************************************************************
C     PRINT THE COMPUTED VALUES
C*************************************************************
      DO 400 I=1,M2
      TIME=I*T
      PRINT 4,TIME,CONVOL(I),RESPON(I)
4     FORMAT('0',10X,E14.7,20X,E14.7,20X,E14.7)
400   CONTINUE
      STOP
      END
```

```
C*************************************************************
      FUNCTION F(N,TIME,TAU,HEIGHT)
      REAL HEIGHT
      F=HEIGHT
      RETURN
      END
C*************************************************************
      FUNCTION G(N,TIME,TAU)
      G=0.0
      IF(TIME.EQ.0.0)GO TO 20
      I=N
      G=(((I*TIME/TAU)*(EXP(-TIME/TAU)))**I)/(FACT(I-1)*TIME)
     *+G
20    CONTINUE
      RETURN
      END
C*************************************************************
      REAL FUNCTION FACT(IX)
      FACT=1.0
      IF(IX.LE.1)RETURN
      DO 10 II=1,IX
      FACT=FACT*II
10    CONTINUE
      RETURN
      END
C*************************************************************
```

Table 1. Summary of Convolution Data

SECONDS	ACTUAL RESPONSE VALUE	RESPONSE VALUE 100 STEPS/ INT	RESPONSE VALUE 1000 STEPS/INT
6.00	0.300774 E-05	0.116561 E-05	0.307510 E-05
12.00	0.468264 E-03	0.474578 E-03	0.468259 E-03
18.00	0.110276 E-01	0.111602 E-01	0.110277 E-01
24.00	0.813280 E-01	0.919843 E-01	0.813280 E-01
30.00	0.318289 E 00	0.320091 E 00	0.318290 E 00
36.00	0.839244 E 00	0.842672 E 00	0.839244 E 00
42.00	0.169505 E 01	0.170005 E 01	0.169507 E 01
48.00	0.283376 E 01	0.283985 E 01	0.283376 E 01
54.00	0.412592 E 01	0.413234 E 01	0.412593 E 01
60.00	0.542070 E 01	0.542674 E 01	0.542070 E 01