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SURFACTANT-ENHANCED ALKALINE FLOODING FOR LIGHT OIL RECOVERY

Quarterly Report for the Period
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OBJECTIVE

The overall objective of this project is to develop a very cost-effective method for formulating a successful surfactant-enhanced alkaline flood by appropriately choosing mixed alkalis which form inexpensive buffers to obtain the desired pH (between 8.5 and 12.0) for ultimate spontaneous emulsification and ultra-low tension. In addition, the novel concept of pH gradient design to optimize flood water conditions will be tested.

SUMMARY OF TECHNICAL PROGRESS

Last quarter[1], we compared the interfacial behavior of two different crude oils, one with a low acid number (Adena) and one with a high acid number (Long Beach). The Adena crude oil has transient interfacial tensions on the order of 0.1 mN/m, and the minimum in interfacial tension occurs at a short time of 100 seconds. The low acid number of Adena oil, does not prevent sufficient interfacial activity. Sufficient interfacial activity occurs at a high pH of 13. A second minimum was found to occur at higher times. This second minimum results from the formation of middle phase.

This quarter we investigated the phase behavior and the regions where in the middle phase occurs. Middle phase was found to go through a maximum with pH, sodium concentration and surfactant concentration. The optimum pH is about 12.0 to 13.5, the optimum sodium concentration is about 0.513 mol/liter, and the optimum surfactant concentration is about 0.2%. The effect of surfactant type was also investigated. Petrostep B-105 was found to give the most middle phase production. A white precipitate was observed in some two-phase samples.

MATERIALS AND EXPERIMENTS

In this study, the crude oil (Adena) used was obtained from SURTEK from Adena field located in Morgan County, Colorado. The oil is a light oil with an API gravity of 41.95, a viscosity of 3.75 cp at 25 °C, and an acid number less than 0.002. The interfacial tension against deionized water is 39 mN/m.

The alkaline solutions are a mixture of sodium hydroxide, sodium bicarbonate, and sodium chloride. All alkalis were obtained from Fisher Scientific Co.

The preformed surfactants Petrostep B-100 (PB100), B-105 (PB105), and B-120 (PB120) were added to the alkaline solution. The surfactant was obtained from Stepan Chemical Company, and the surfactant solutions were made on a 100% basis.

The spinning drop technique was employed to measure transient (non-equilibrated) interfacial tension. The volumetric ratio of water to oil in the spinning drop tensiometer is about 140. The pH was measured using an Orion microprocessor analyzer/901 with a Ross combination electrode designed for low sodium error. All experiments were performed at 25 ^{o}C.

Throughout this study, the solutions were made by diluting an equimolar ratio of sodium bicarbonate/NaOH (referred to as 20/20) with either the same molarity of sodium bicarbonate plus NaCl to keep the total sodium constant or the same molarity of NaOH plus enough NaCl to keep the total sodium constant. By changing the ratio of sodium bicarbonate/NaOH, the pH is changed. Lower pH is obtained by adding the sodium bicarbonate plus NaCl solution to the 20/20 mixture, or a higher pH is obtained by adding the NaOH plus NaCl solution to the 20/20 mixture. It should be noted that 343 mol/m^3 total sodium is about 2.0 wt% sodium bicarbonate/NaOH mixture.

RESULTS AND DISCUSSION

Petrostep B-105

In the first system (0.513 M with 0.1% PB105), a middle phase was observed at a pH of 11.34. The volume of middle phase increased with pH, and was a maximum at pH=12.9. In the 0.2% PB105, the middle phase formation was observed at pHs of 12.9 and above, and was maximum at pHs of 13.13 and 13.24. The largest volume of middle phase in the whole study was observed for pH=13.13, 0.513 M sodium, and 0.2% PB105. When surfactant is increased to 0.5% PB105, only a white precipitate was observed at the interface.

At salinities lower than 0.513 M sodium, a white precipitate is present at the interface. This was observed for the following systems:

- 0.171 M sodium with 0.1, 0.2 and 0.5% PB105
- 0.343 M sodium with 0.1% PB105 (at pH<12.9), 0.2% PB105, and 0.5% PB105.

Some middle phase formation, although of very small volume, was observed for high pH solutions (above 12.9) with 0.343M sodium and 0.1% PB105.

In general, solutions with salinities ranging from 0.171M to 0.513M exhibited cloudy aqueous phases, indicating some oil-in-water emulsions, and the cloudiness of the aqueous phase increased with pH.

At salinities higher than 0.513 M sodium, the aqueous phase was clear, although of brownish color, some cloudiness appeared with increasing pH, and a precipitate was observed in most cases. The volume of precipitate increased with pH, until it reached a maximum and decreased at higher pHs. For the 0.684 M sodium solutions, the volume of precipitate at the interface was maximum at pH=13.31 with 0.1% PB105, between pH=13.07 and 13.27 for 0.2% PB105, and between pH=12.63 and 13.21 for 0.5% PB105. Therefore, the maximum volume of precipitate occurs at lower pH when the surfactant concentration is increased.

For 1.0 M sodium with 0.1% PB105, only a white precipitate was present at the interface.

Petrostep B-100

Only systems with salinities up to 0.343 M sodium were equilibrated with Adena oil, because the surfactant precipitated in the bulk solution (before contacting with the oil) at higher salinities.

Systems with 0.171 M sodium and 0.1% PB100 exhibited a white precipitate of volume increasing with pH. Middle phase is seen at pHs from 11.07 to 12.8 with 0.2 and 0.5% PB100.

The aqueous phase was opaque, but of a light yellow color. Cloudiness of the aqueous phase was found to decrease with increasing pH, and became translucent at pHs above 12.7, and darkened in color with an increase in surfactant concentration.

Systems with 0.343 M sodium and 0.1% PB100 have a white precipitate at the interface. The volume of this precipitate remains constant with increase in pH.

Petrostep B-120

This surfactant does not exhibit any middle phase formation or precipitate formation. It shows no interfacial activity as seen by visual observation.

Volume of Middle Phase

Table 1 shows the volume of middle phase as a function of sodium and surfactant concentration at a pH of 13.1 for PB105 surfactant. The volume of middle phase goes through a maximum with both sodium concentration and surfactant concentration.

Figure 1 shows a three-dimensional graph of the combined effects of pH and salinity on the phase behavior of the Adena oil for 0.2% PB105. The volume of middle phase is plotted on the vertical axis. Each series of bars in the horizontal direction corresponds to a particular pH. At pH=13.1, one can clearly see that the volume of the middle phase reaches a sharp maximum at 0.513 M Sodium. As the pH is decreased, less middle phase is produced, and that the maximum volume is shifted to lower salinities. At 0.513 M sodium, as the pH is increased from 12.6 to 13.1, the volume of middle phase sharply increases. It should be noted that little or no middle phase is found below pH of 12.6.

Figure 2 shows the transient interfacial tension as a function of pH. There is a direct one-to-one correlation between middle phase formation and interfacial tension. Interfacial tension is ultralow when middle phase is present.

Figure 3 shows a three-dimensional graph showing the combined effects of sodium and surfactant concentration on the volume of middle phase at a pH of 13.1 with PB105. Each type of shading corresponds to a particular salinity. At 0.1% PB105, a maximum occurs in the volume of middle phase at a salinity of 0.513 M sodium. A sharper maximum of middle phase is observed at that salinity when the surfactant concentration is increased to 0.2%. As more surfactant is added, the maximum is shifted to higher salinity and is of lesser extent.

SUMMARY

For a given surfactant concentration, as pH is increased, the maximum volume of middle phase shifts to higher salinities. For a given pH, as surfactant concentration is increased, the maximum volume of middle phase shifts to higher salinities.

REFERENCE

1. Wasan, D.T., Progress Report submitted to DOE for the period July 1-September 30, 1993.

Table 1. Volume of Middle Phase at pH=13.1

Sample	Salinity M [Na]	PB105, wt%	Volume middle phase, ml	Volume middle phase, % tot. vol.
12	0.343	0.1	0.85	5
16b	0.513	0.1	1.7	8.5
92	0.684	0.1	0.2	1
109	1.0	0.1	0.3	1.5
28	0.343	0.2	0.3	1.5
33	0.513	0.2	2.7	13.5
98	0.684	0.2	0.3	1.5
45	0.343	0.5	0	0
50	0.513	0.5	0.2	1
104	0.684	0.5	1	5

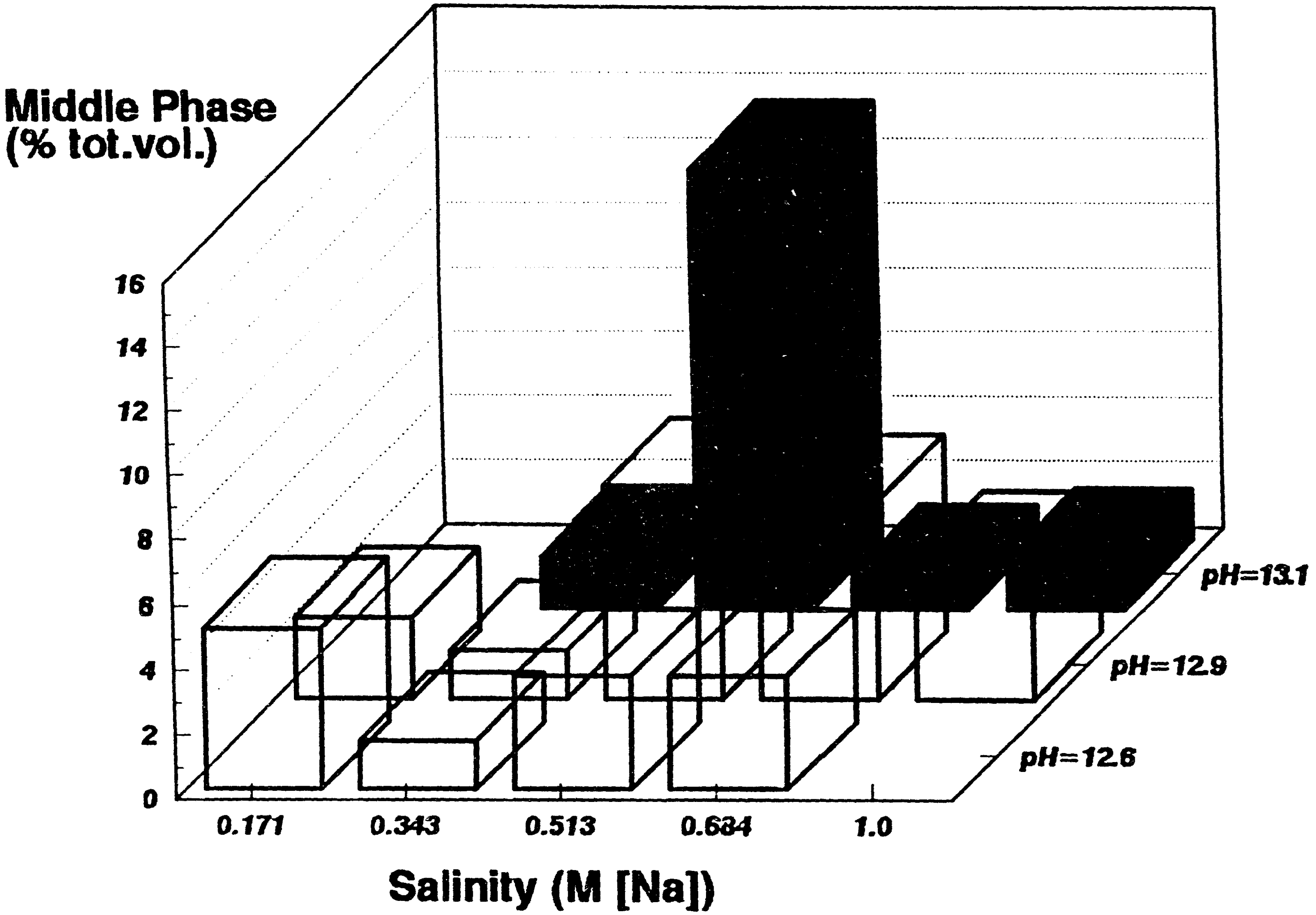

Figure 1. Volume of Middle Phase at 0.2% PB105

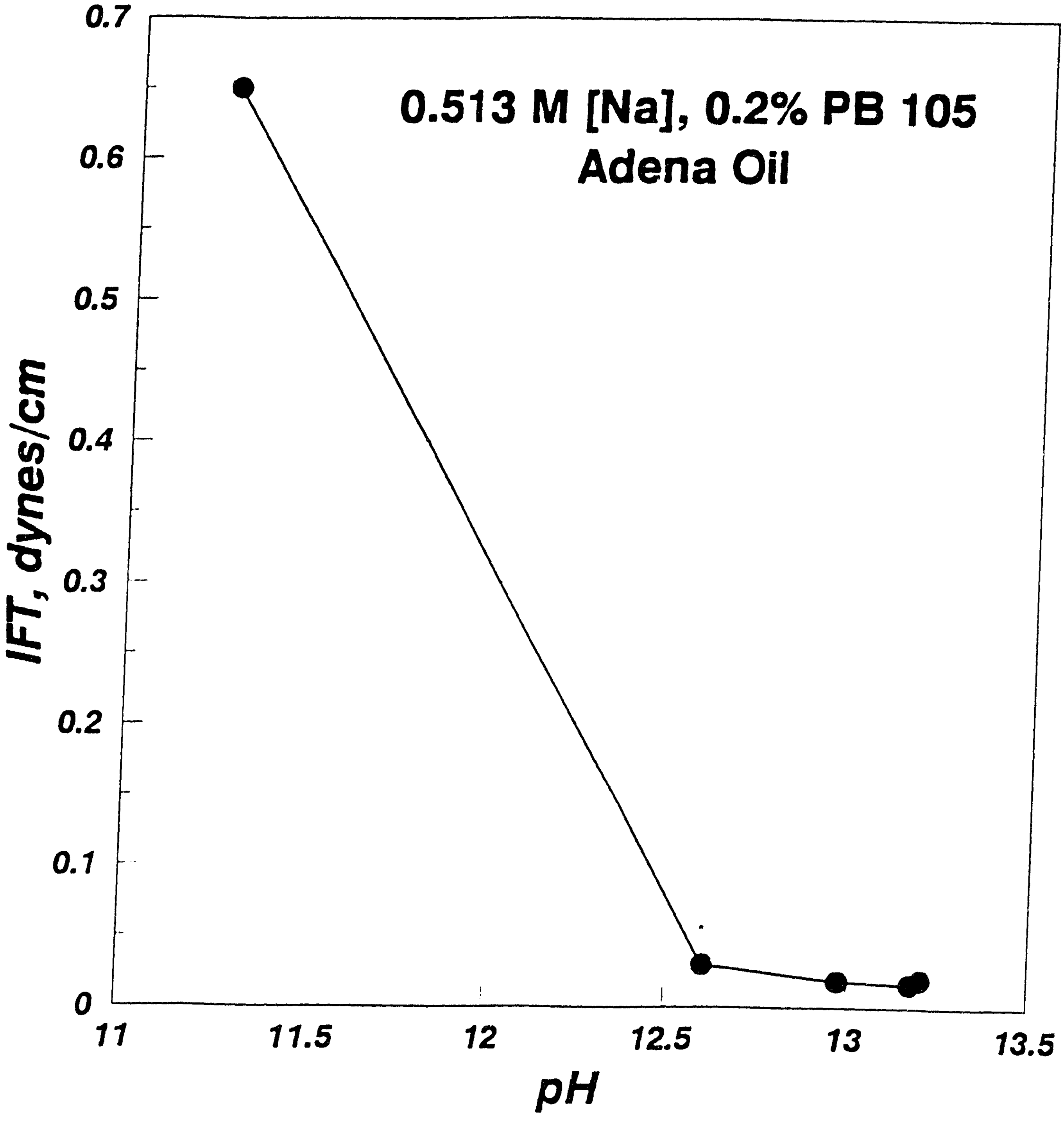

Figure 2. Transient Interfacial Tension as a Function of pH

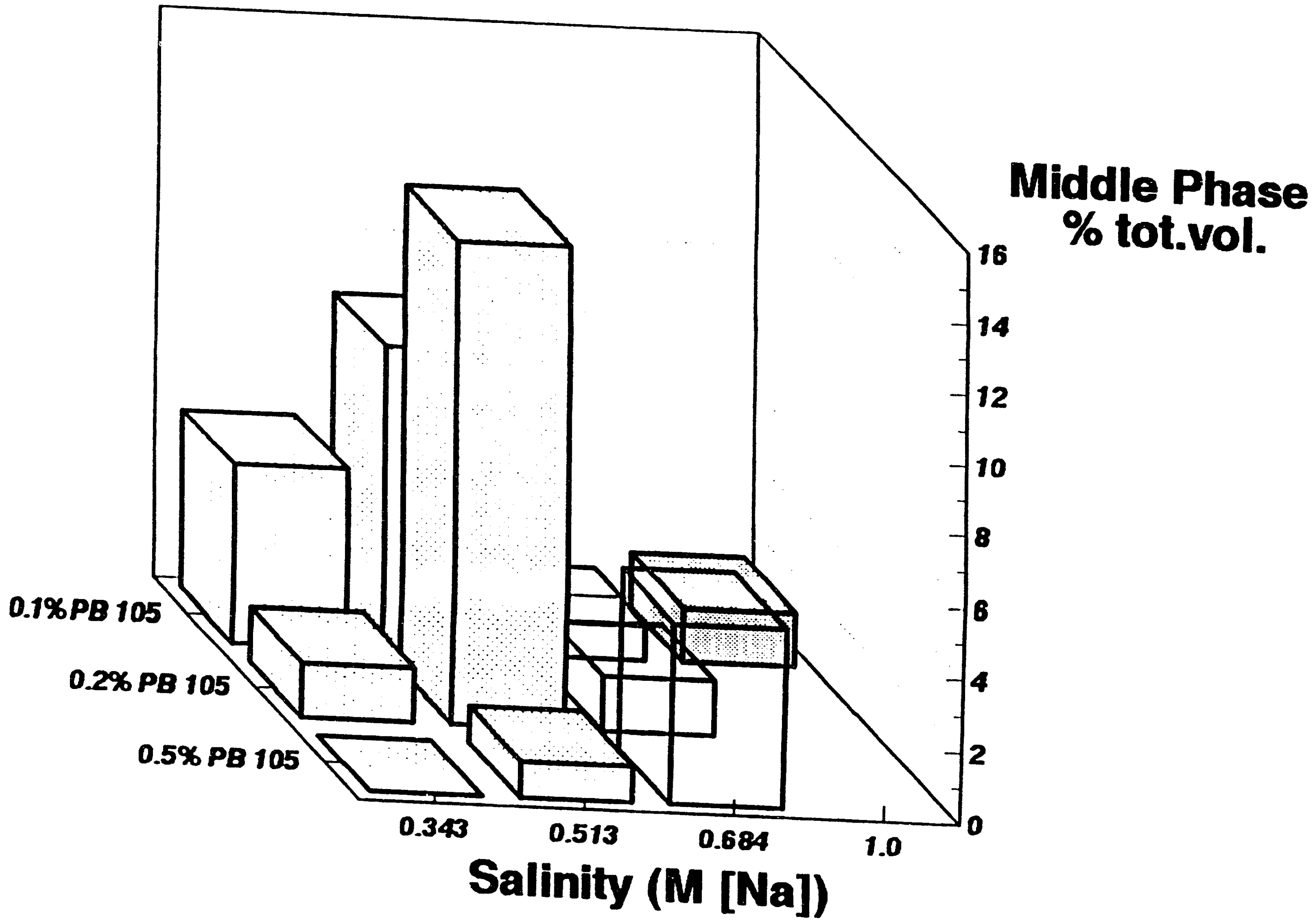

Figure 3. Volume of Middle Phase at pH=13.1

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