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PREVIEW

2,3-BUTANEDIOL FROM A BACILLUS ISOLATE: A POSSIBLE  
COSURFACTANT FOR MICROBIAL ENHANCED  
OIL RECOVERY SYSTEMS

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OIL RECOVERY SYSTEMS

by

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THESIS

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## ABSTRACT

Eleven oil field bacillus isolates were screened for cosurfactant production capability. Culture CI-20A was shown to produce significant quantities of 2,3-butanediol and was chosen for further study. Biochemical tests showed this bacterium closely resembled Bacillus licheniformis.

CI-20A when grown anaerobically on a sucrose mineral salts medium produced maximum biomass at 40°C and 8% salinity. Butanediol production was greatest at 55°C and 4% salinity. The culture grew well in low concentrations of Pluronic L61 and was not inhibited by the presence of a premium grade crude oil. Product yields improved with the addition of acetoin and the use of smaller inocula.

The relative cosurfactant character of 2,3-butanediol was indexed between ethanol and isopropanol when used to titrate a surfactant system dominated by petroleum sulfonates. Emulsification studies indicated that butanediol had a slight ability to demulsify water in oil emulsions.

2,3-butanediol used as a cosurfactant in a 4% Petrostep 465, 1% Avirol 200/hexadecane system produced middle-phase microemulsions over a salinity range approximating that of an identical system employing isopropanol. CI-20A whole cell culture broth, however,

showed no apparent ability to produce middle phase microemulsions in a similar surfactant/hydrocarbon system.

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## CHAPTER I

### INTRODUCTION

#### Enhanced Oil Recovery

Energy-related agencies today are searching for technology with which to enhance oil recovery. After the primary recovery technique of pumping has proven uneconomical, as much as 60 to 80 percent of the original oil-in-place remains in the reservoir. In an effort to reach such residual oil, Enhanced Oil Recovery (EOR) techniques are employed.

EOR in the form of secondary recovery is termed "water flooding." This method forces water down into the reservoir through injection sites where it "pushes" a portion of the remaining oil towards recovery wells. As a general rule water flooding greatly increases petroleum recovery for several years after its implementation. Yet, eventually such an increase ceases as the flood waters preferentially channel through the strata leaving behind trapped oil ganglia or residual oil tightly bound to the reservoir mineral.

In recent years a wide variety of approaches have been taken in the design of systems to reclaim the oil remaining after the secondary recovery process. An

excellent review of such techniques can be found in an article by Taber (1981). Amongst these so-called tertiary methods, the most economically feasible usually employ chemical additives. Such admixtures aid in the release of the petroleum from the reservoir mineral, thus allowing for mobilization by ensuing water floods.

### Miscible Floods

Miscible floods are tertiary oil recovery techniques which employ solutions that act as though they are miscible with the reservoir hydrocarbons while in turn they can be miscibly displaced by water (Mirkin, 1977). These solutions are aqueous in nature and contain surfactants and cosurfactants. Once injected into oil-bearing strata, a miscible displacement fluid tends to solubilize contacted hydrocarbons resulting in the formation of a microemulsion.

Surfactants. A surfactant is any molecule that is surface active or has a tendency to concentrate at the solution interfaces (Zajic and Seffens, 1982). Such molecules are composed of a polar hydrophilic (water soluble) portion and a non-polar lipophilic (oil soluble) portion. It is the polar moiety that tends to hold the molecular structure in aqueous solution while the non-polar hydrocarbon portion is forced to aggregate with other lipophilic molecules at solution interfaces.



The HLB or Hydrophile-Lipophile Balance of a molecule is an index of the relative size and strength of the hydrophilic and lipophilic groups of the molecule. The original HLB indexing scheme proposed by Griffin (1947) has been modified in recent years and presently ranges from 0 (lipophilic) to 40 (hydrophilic). Its use allows one to grasp an idea of the solubility and phase-partitioning characteristics of a particular surfactant without laborious experimentation.

Chemically, surfactants can be classified as anionic, cationic, amphoteric or neutral. The anionic petroleum sulfonates are the most commonly employed surfactants for oil recovery systems.

Cosurfactants. Cosurfactants can be defined as molecules that aid surfactants in solubilizing hydrocarbons, usually by stabilizing surfactant/hydrocarbon microemulsions. The most common cosurfactants are alcohols three carbons in length or greater.

Research has shown (Kilpatrick et al., 1981) that the microstructure of high concentration surfactant solutions is dramatically altered by the addition of cosurfactants. When in aqueous solution at a concentration referred to as the critical micelle concentration (Shaw et al., 1972), surfactants leave the solution interface in the form of soluble monomers and small spherical micelles. At concentrations much greater than the critical micelle

concentration (CMC) the solution becomes turbid as surfactants begin to pack into larger cylindrical and lamellar micelles (see Fig. 1).

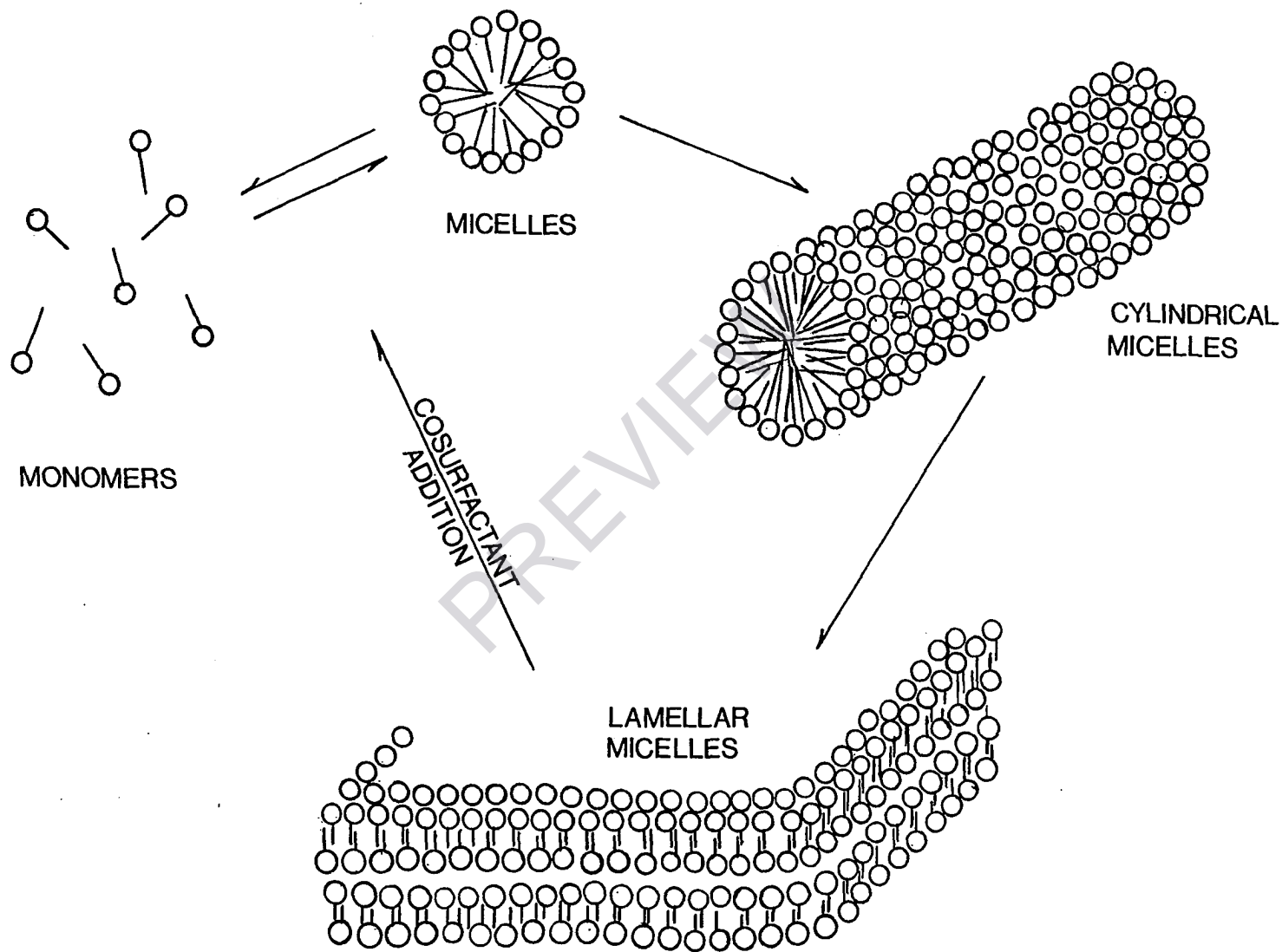
If, however, a cosurfactant is titrated into an opaque lamellar micelle solution, an endpoint is reached where the system becomes transparent. It is believed that prior to the endpoint concentration that the alcohol molecules partition into the lamellar structure with their hydroxylic moieties adjacent to the hydrophilic heads of the surfactant molecules (Kilpatrick et al., 1982). At concentrations above the endpoint the hydrophilic partitioning character of the alcohol induces the lamellar structures to become thermodynamically unfavorable. Thus, the once opaque solution becomes transparent as the alcohols stabilize the surfactant into smaller spherical micelles.

Such an obtainable endpoint when titrating with an alcohol is regarded as evidence for cosurfactant character. Where this endpoint occurs (in terms of concentration) can be used as an index of the cosurfactant character of an alcohol relative to other alcohols titrated into the same surfactant system.

Microemulsions. Microemulsions have been described as thermodynamically stable, microstructured fluid phases of variable composition that incorporate substantial amounts of oil, water, surfactants and cosurfactants (Bennet et al., 1981). Oftentimes the microstructure of these solutions is

Figure 1. Diagram of microstructure formation upon increasing surfactant concentration and titrating with a cosurfactant.

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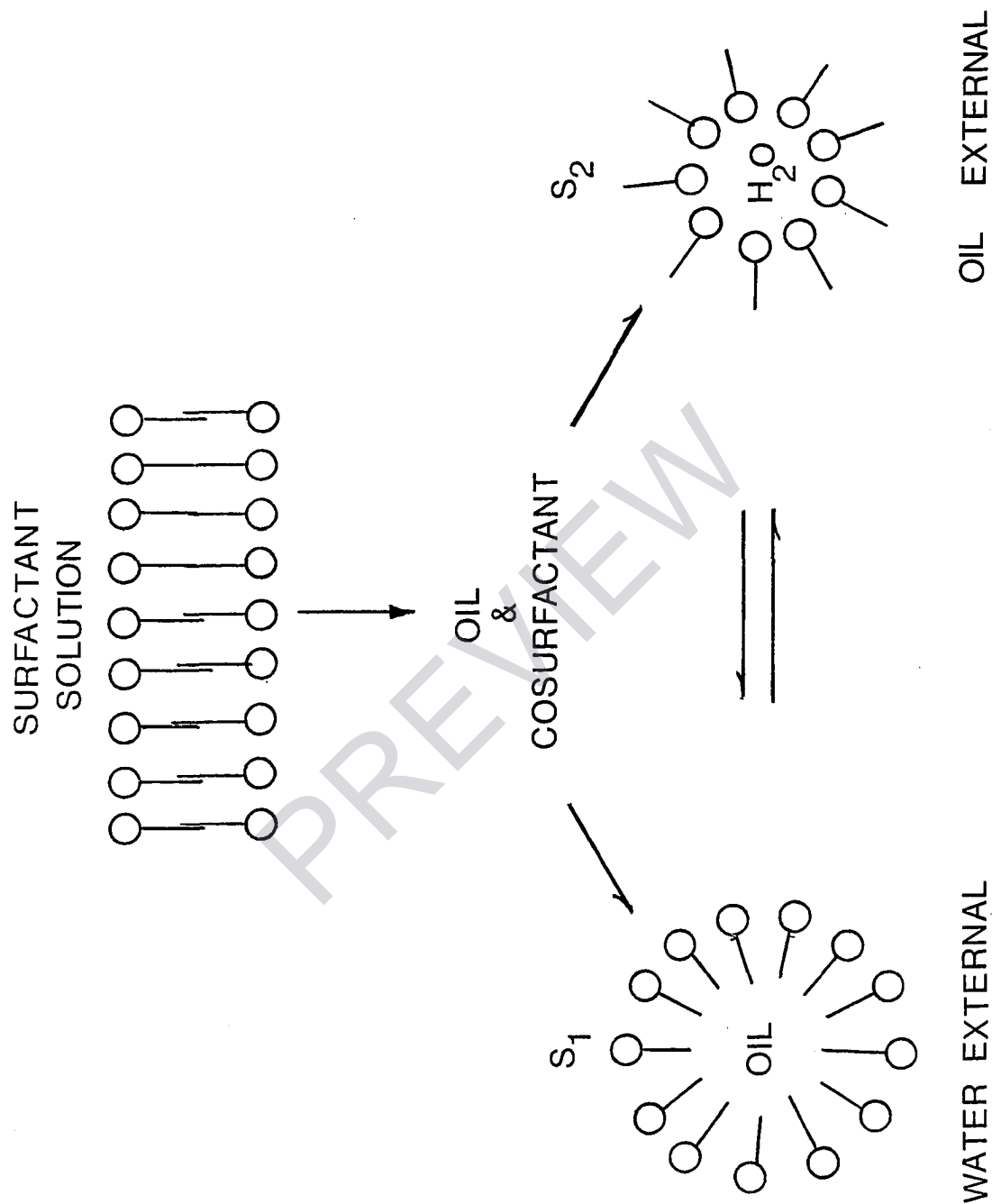
likened to a swollen, simple micellar system. This is, however, somewhat misleading in that the structures present in a microemulsion are of an order of magnitude larger than simple micelles, 100 Å and 10 Å in diameter, respectively.

The generally accepted description of microemulsion structure is that as proposed by Windsor (1954). This model suggests that when an aqueous surfactant system in the lamellar micelle state contacts a hydrocarbon there forms either a water external ( $S_1$ ) microemulsion or an oil external microemulsion ( $S_2$ ) (see Fig. 2). Whether the equilibrium of the system is shifted toward the formation of an  $S_1$  or an  $S_2$  state is dependent upon such factors as the overall oil/water ratio of the system and the concentration of the electrolytes present.

Research has shown that increasing the salinity of microemulsion systems will induce the inversion of an  $S_1$  state to an  $S_2$  state (Healy and Reed, 1976). At an intermediate salinity within this range a separate middle phase often appears that is in equilibrium with both the upper oil and lower aqueous phases already present within the system. It is proposed that the addition of the salt decreases the interdroplet repulsion resulting from the surfactant's polar moieties and hence produces a close-packed state for the oil in water microemulsion which separates out to form a middle phase (Shaw et al., 1977).

Figure 2. A schematic diagram of microemulsion structure as proposed by Windsor.

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For a given surfactant-cosurfactant/hydrocarbon system the average of the salt concentrations over which a middle phase is formed is referred to as the optimal salinity. At this particular salinity the interfacial-free energy between the middle and upper phase is at a minimum as is the interfacial-free energy between the middle and lower phase. As a result, the middle phase contains an equivalent amount of both hydrocarbon and water (Salegar et al., 1979a). The ability to attain optimal salinity is considered very desirable in the design of a miscible flood system. This is due to the fact that the physical state of a system at optimal salinity has a very high degree of oil solubilization (oil/water 1:1) and minimum interfacial-free energies which aid in releasing oil from mineral in aqueous-dominated systems.

The role of cosurfactants in the formation of microemulsions is poorly understood. The general conceptualization is that the cosurfactants crosslink between surfactant molecules to stabilize the  $S_1$ - and  $S_2$ -type microstructures. Research on the roles of cosurfactants in microemulsions has shown that different alcohols tend to shift the optimal salinity of a given surfactant/hydrocarbon system. The use of longer chain more hydrophobic alcohols has been shown (Salager et al., 1979b) to decrease the optimal salinity relative to microemulsions containing lower weight hydrophilic alcohols.