# ENHANCED OIL RECOVERY TECHNIQUES Syllabus

**Use of surfactants in oil recovery: Chapter 10 (Pages 255-307)**

Introduction- Classification of EOR surfactants- Mechanism of oil displacement by surfactant flooding- Ultra low interfacial tension in relation to oil displacement by surfactant flooding- Factors influencing oil recovery- Surfactant gas flooding for oil recovery- Interfacial phenomena in surfactant gas flooding- Mechanism of surfactant loss in porous media- Present status of the use of surfactants in oil recovery.

# USE OF SURFACTANTS IN OIL RECOVERY

**INTRODUCTION:**

➢ **Surfactant molecules are composed of lipophilic (has sufficient solubility in the solvent) & lipophobic ( is rejected by the solvent) groups.**

➢ **These group structure is known as amphipathic structure.**

➢ **The lipophilic group usually consists of a long hydrocarbon chain.**

➢ **A polymer can also act as a surface active molecule if it has two functional groups, one lipophilic ( solvent loving) and the other lipophobic (solvent hating). Both are shown in fig. 10.1**

➢ **If the surfactant contains a hc chain with less than 12 carbon atoms, it is called water soluble. When hc chain length is greater than 14 carbon atoms, the compounds are called water-insoluble surfactants.**

➢ **The lipophilic group is ionic or highly polar. Surfactants can be classified as anionic, cationic, amphoteric or non-ionic. Anionic surfactants widely used in EOR due to their lower adsorption on the reservoir rocks.**
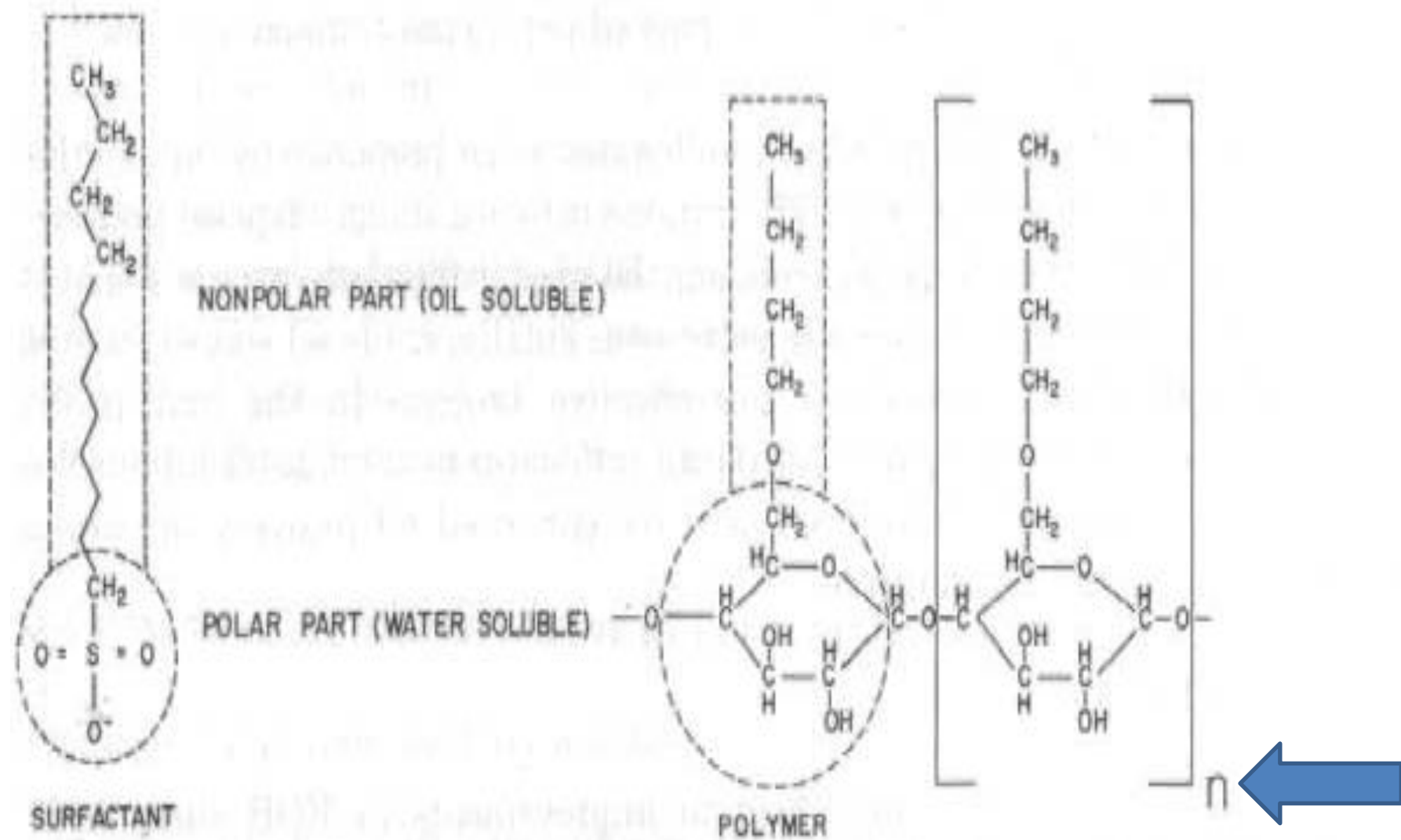
NONPOLAR PART (OIL SOLUBLE)

POLAR PART (WATER SOLUBLE)

SURFACTANT

POLYMER

Fig. 10-1. The structure of surface active molecules. The broken line illustrates the separation of polar and non-polar parts of the molecule.

# CLASSIFICATION OF EOR SURFACTANTS:

## Petroleum sulfonates:

➢ Most of the surfactant formulations for EOR contain petroleum sulfonates, obtained from refinery products.

➢ The pet. sulfonates were prepared by sulfonating gas-oil fractions with sulfuric acid. To avoid sludge disposal problem from this process, crude oil was sulfonated with $SO_3$ to provide cost effective process.

## Synthetic sulfonates:

➢ The synthetic sulfonates may lead to effective improvements in EOR surfactants even though more expensive. They have better resistance to metal ions particularly $Ca^{2+}$ & $Mg^{2+}$.

➢ The first one commercially developed was alkyl benzene sulfonates. The olefin & aromatic feedstocks are the major sources for preparation of alkylates. These were sulfonated with either $SO_3$ or $H_2SO_4$.

➢ The mixed petroleum sulfonate & synthetic sulfonate formulations have resulted in improved oil recovery.

## MECHANISM OF OIL DISPLACEMENT BY SURFACTANT FLOODING:

## Capillary forces and capillary number:

- ➢ The residual oil is in the form of immobile globules distributed through the pores of reservoir rock. The two major forces acting on these immobile globules are capillary & viscous forces.

- ➢ Fig.10.2 shows a correlation between the capillary number and the residual oil saturation in a porous medium. <u>The ratio of viscous forces to capillary forces is called capillary number.</u>

- ➢ $N_c = \mu_w \phi q / \Upsilon_{o/w}$ ………….10.1

  where $N_c$ = capillary no. $\mu_w$ & q are the viscosity and flow rate per unit cross-sectional area of water, $\Upsilon_{o/w}$ is interfacial tension between oil and water, $\phi$ is the porosity of the reservoir.

- ➢ At the end of water flooding the capillary no. is in the range of $10^{-6}$—$10^{-7}$. As it increases, the displacement efficiency also increases.

- ➢ To displace 100% oil it is necessary to increase $N_c$ by 4 orders of magnitude ($10^{-2}$ to $10^{-1}$), shown in fig.10.2

- ➢ For the most efficient displacement of residual oil, the porous media should be water-wet.
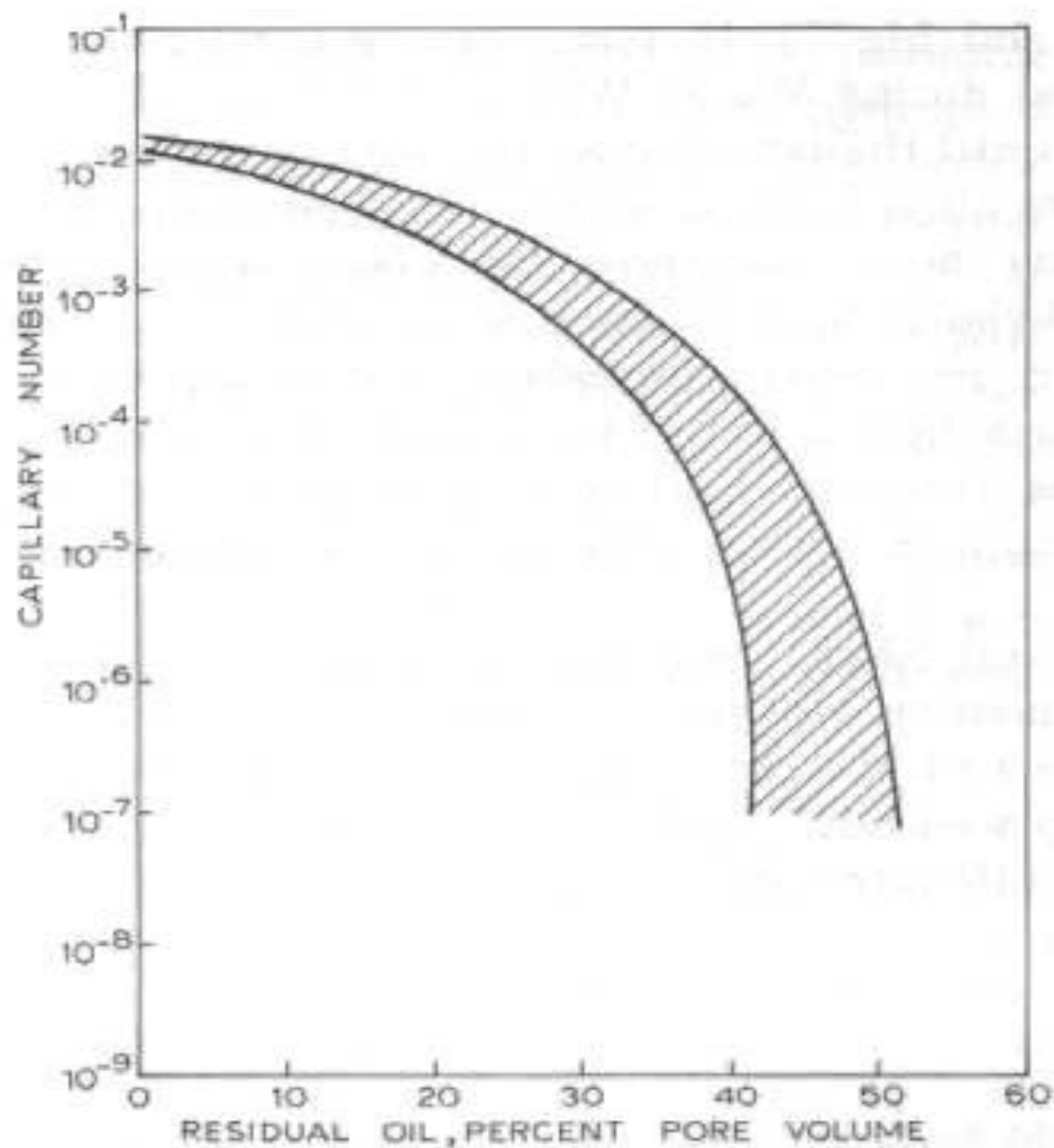
Fig. 10-2. A correlation between capillary number and residual oil saturation.

FOR THE MOVEMENT OF OIL
THROUGH NARROW NECK OF
PORES, A VERY LOW OIL / WATER
INTERFACIAL TENSION IS
DESIRABLE ≃ .001 DYNES/CM

Fig. 10-3. Schematic diagram of the role of interfacial tension in surfactant flooding

**Interfacial phenomena:**

Oil recovery efficiency can be influenced by producing ultra-low interfacial tension between crude oil & brine. **The interfacial tension depends on interfacial charge, interfacial viscosity and wettability.**

**Interfacial tension:**

o **The flow of trapped oil droplets or oil ganglia through the narrow necks of pores is shown in fig.10.3. In the presence of a suitable surfactant, an ultra-low interfacial tension can be achieved at an oil-brine interface.**

o **The main conclusion was the preferred value of R (alkyl chain length) corresponding to a minimum in interfacial tension increases with increasing equivalent weight of the surfactant.**
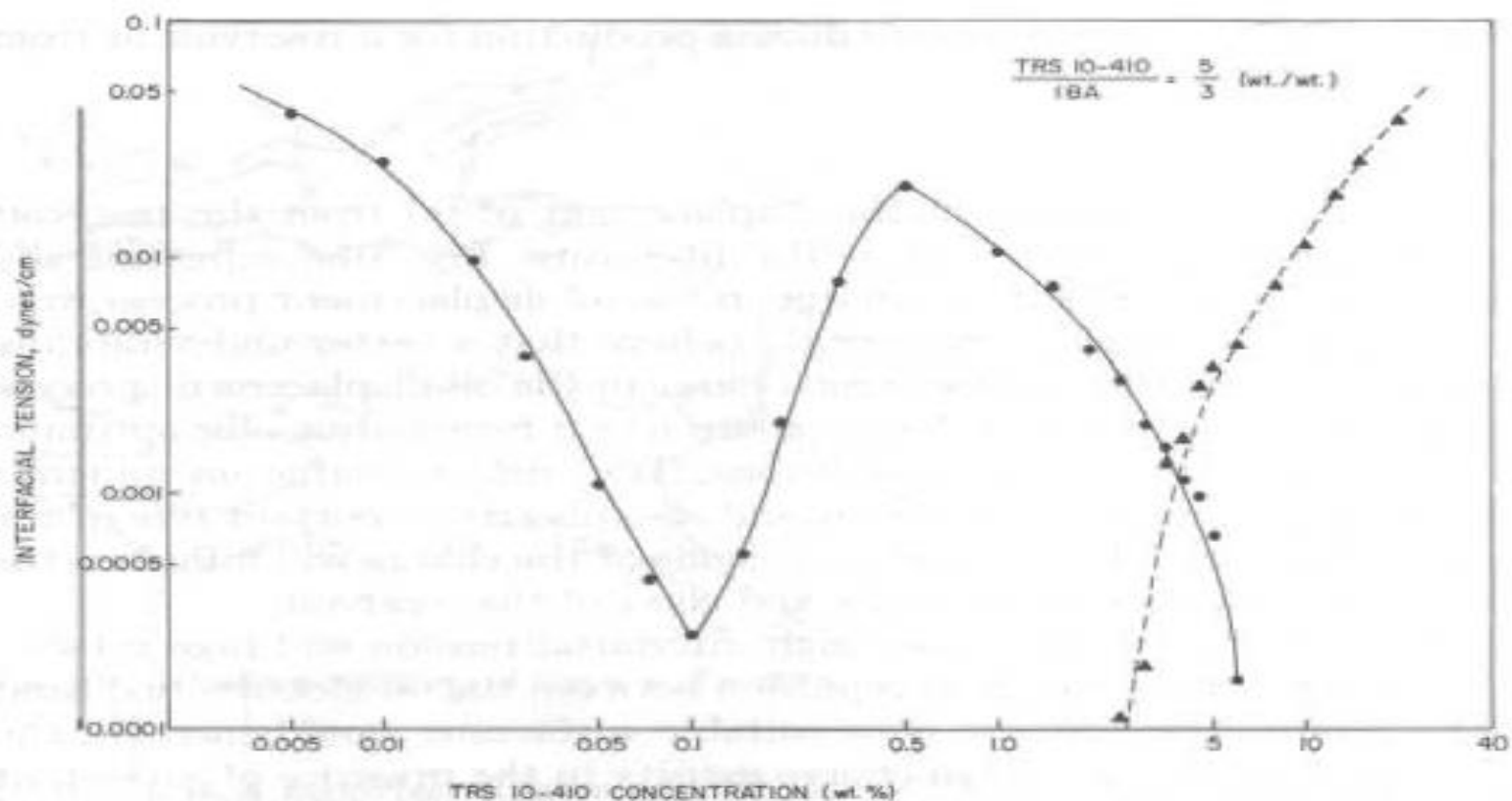
Fig. 10-4. Effect of surfactant concentration on the interfacial tension of TRS 10-410+IBA in 1.5% NaCl with dodecane.

➢ **There are two regions of UL-IFT (ultra low interfacial tension) in TRS 10-410-IBA-dodecane-brine system. In the low surfactant conc. (around 0.1%) region, the system forms two phases, oil-brine in equilibrium with each other, where as high conc. (around 4-8%) region, a middle phase microemulsion is in equilibrium with excess oil and brine, Fig.10.4. The formation of a L-IFT requires an optimum electrolyte conc. and salinity, and the value of alkyl chain length (R) corresponding to minimum IFT is the same for alkylbenzene sulfonates and alkylsulfonates.**

**Fig. 10.5 delineates the effect of salt conc., oil chain length and surfactant conc. on the IFT of pure and impure alkylbenzene  sulfonates. It is evident that the ultra-low IFT occurs at a specific surfactant**
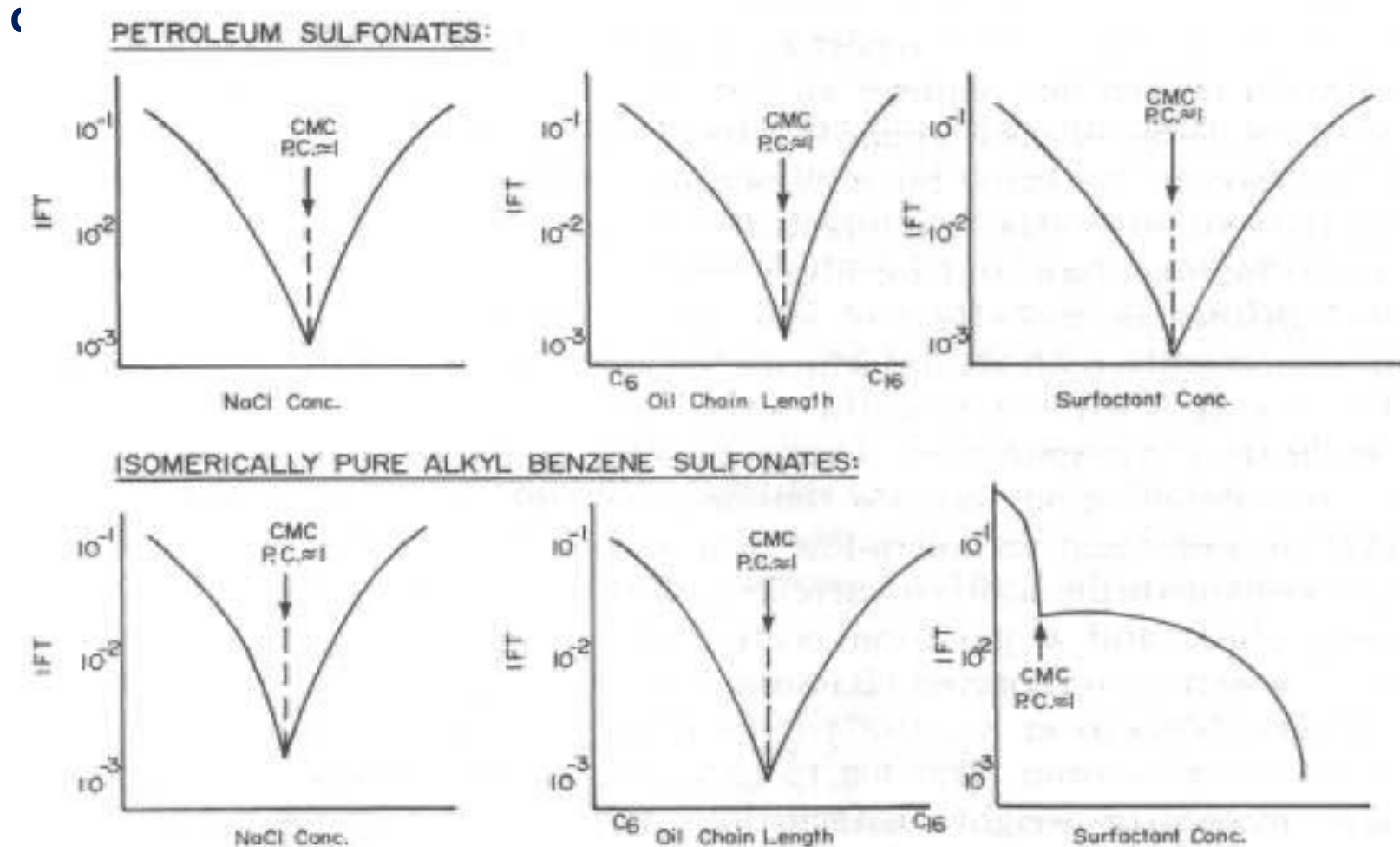


Fig. 10-5. Schematic diagram of the effect of salt concentration, oil chain length, and surfactant concentration on the interfacial tension of pure and impure alkyl benzene sulfonates.

**Interfacial Charge:** Fig.10.6 summarizes the relevance of surface charge in the oil displacement process from the reservoir channels. A better understanding of the magnitude and nature of interfacial charge in the oil -displacement process can contribute significantly to the design of surfactant formulations for optimum performance under given reservoir conditions.

- A low surface charge density causes high IFT & high IFV as well as low electrical repulsion between the oil globules and sand particles Fig.10.6

- The addition of a suitable surfactant would increase IF charge density.

- This high charge density in the presence of surfactant would result in a decrease in IFT & IFV, and would also result in an increase in electrical repulsion between oil globules & sand particles.

- This facilitates the movement of oil ganglia through the pore channels if the oil does not adhere to the sand particles fig.10.6.
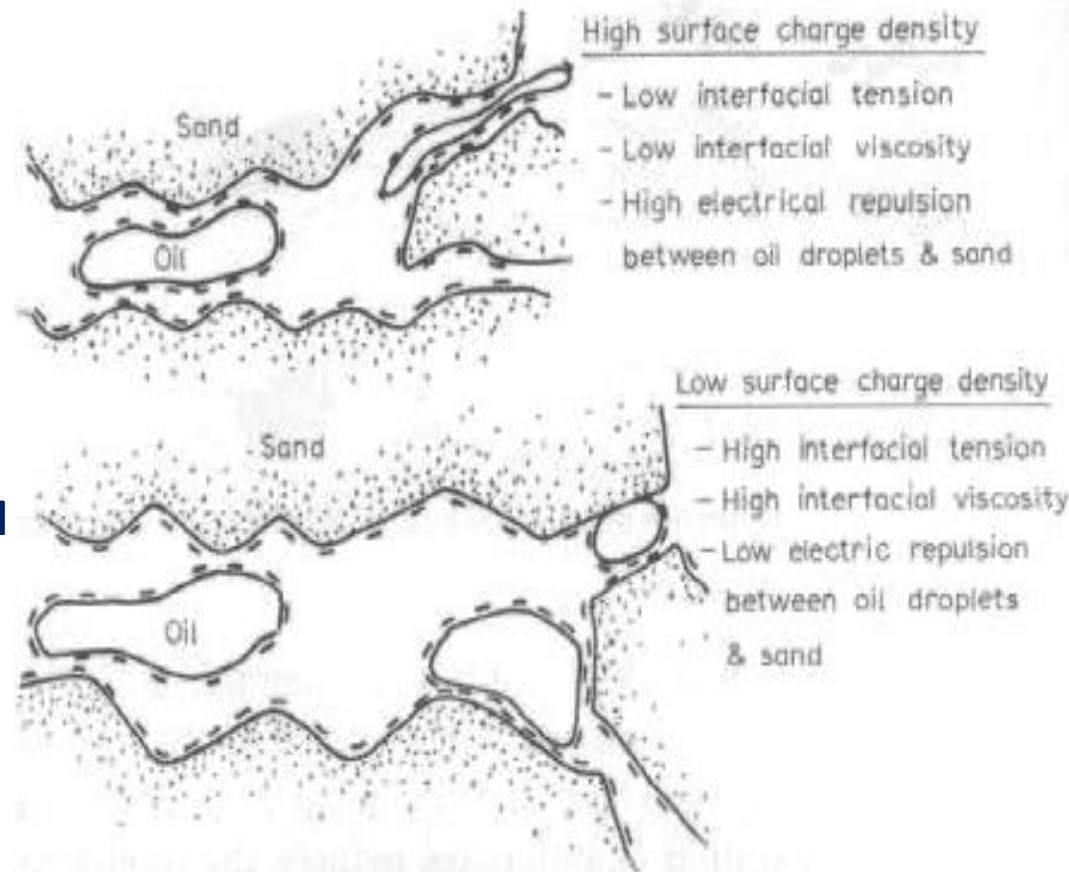


High surface charge density
- Low interfacial tension
- Low interfacial viscosity
- High electrical repulsion between oil droplets & sand

Low surface charge density
- High interfacial tension
- High interfacial viscosity
- Low electric repulsion between oil droplets & sand

Fig. 10-6. Schematic diagram of the role of surface charge in the oil displac

**Interfacial Viscosity:**

- **The efficient oil recovery, the displaced oil ganglia must coalesce and form an oil bank (fig.10.7). A very low IFV is required for the coalescence of the oil ganglia to form an oil bank.**

- **Fig.10.8 shows the movement during surfactant injection of an oil bank which coalesces with more oil ganglia resulting in further displacement of residual oil towards the producers.**

- **The high IFV in crude oil-brine systems containing a mixture of natural surfactants in the oil phase can be attributed to the presence of polar asphaltenes & resins.**

- **Further increase in conc. of sulfonates reduces IFV, because more natural surfactants are displaced from the interface.**
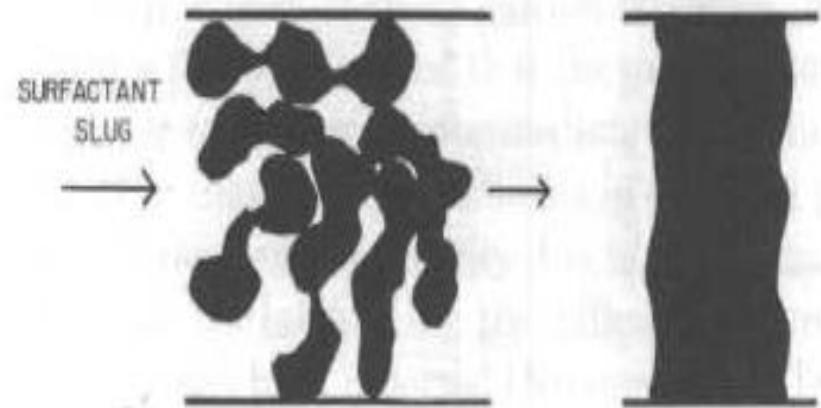


DISPLACED OIL GANGLIA MUST COALESCE TO FORM A CONTINUOUS OIL BANK FOR THIS A VERY LOW INTERFACIAL VISCOSITY IS DESIRABLE

Fig. 10-7. Schematic diagram of the role of interfacial viscosity
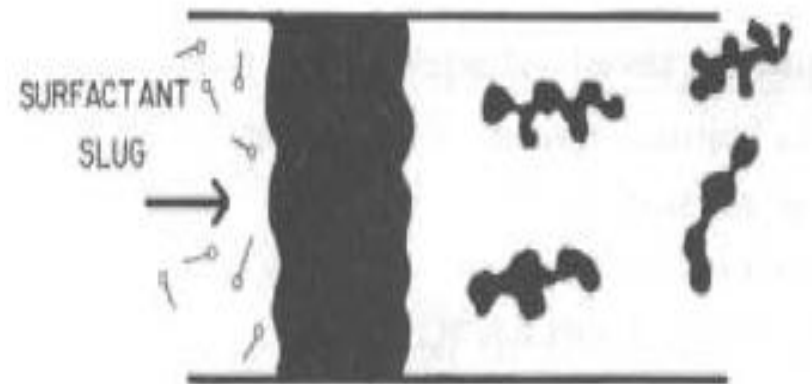


COALESCENCE OF OIL GANGLIA WITH OIL BANK CAUSES FURTHER DISPLACEMENT OF OIL

Fig. 10-8. Schematic diagram of the role of coalescence of oil

Fig 10-9 summarizes the results of coalescence time as a function of sodium chloride concentration in aqueous surfactant solution. The coalescence time decreases with increasing sodium chloride concentration and reaches a minimum at 1.5% NaCl concentration. At 1.5% NaCl concentration, the coalescence time is about 25 times lower compared to that in the absence of NaCl. The coalescence time is inversely related to the interfacial shear viscosity (Fig. 10-9). The highest coalescence rate, therefore, would result the maximum increase in the droplet diameter and would promote oil bank formation.
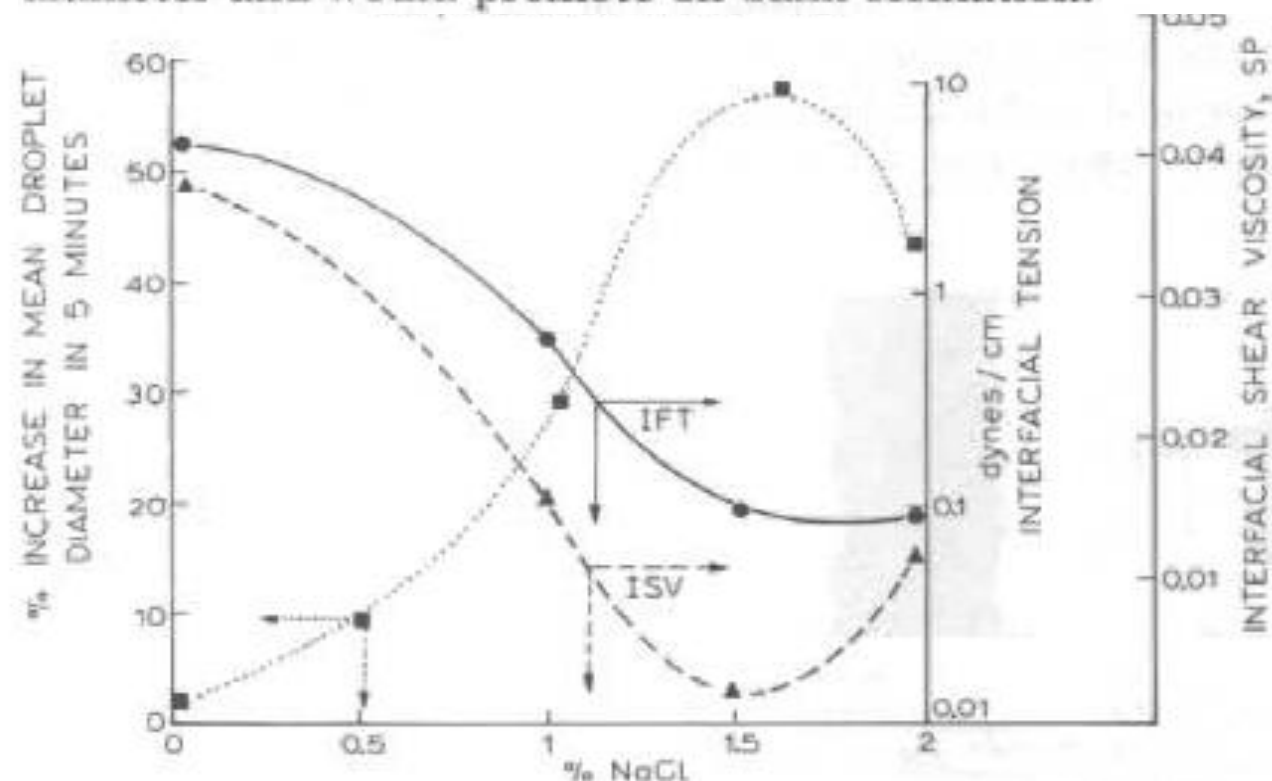


Fig. 10-9. Interdroplet coalescence and interfacial properties for varying brine concentrations. (After

**Wettability:** # The wettability of rock surfaces can be changed by adding a simple salt, acid or base to the flood water. NAOH can effectively change rock surfaces from oil-wet to water-wet.

# Fig.10.10 illustrates the role of the wettability of the solid surface on oil ganglia. The oil-wettable surfaces lead to poor oil displacement whereas the water-wettable surfaces lead to efficient oil displacement.

# The proper choice of surfactant can selectively alter the rock wettability.

# The oil recovery at water breakthrough in water-wet systems is much higher than in oil-wet systems.

# The mobilization of trapped oil is most difficult for rocks having intermediate wettability.

# Under given reservoir conditions a lower apparent viscosity is required for mobility control in water-wet systems.

# The use of additives to alter the rock wettability is a promising approach for enhanced oil recovery
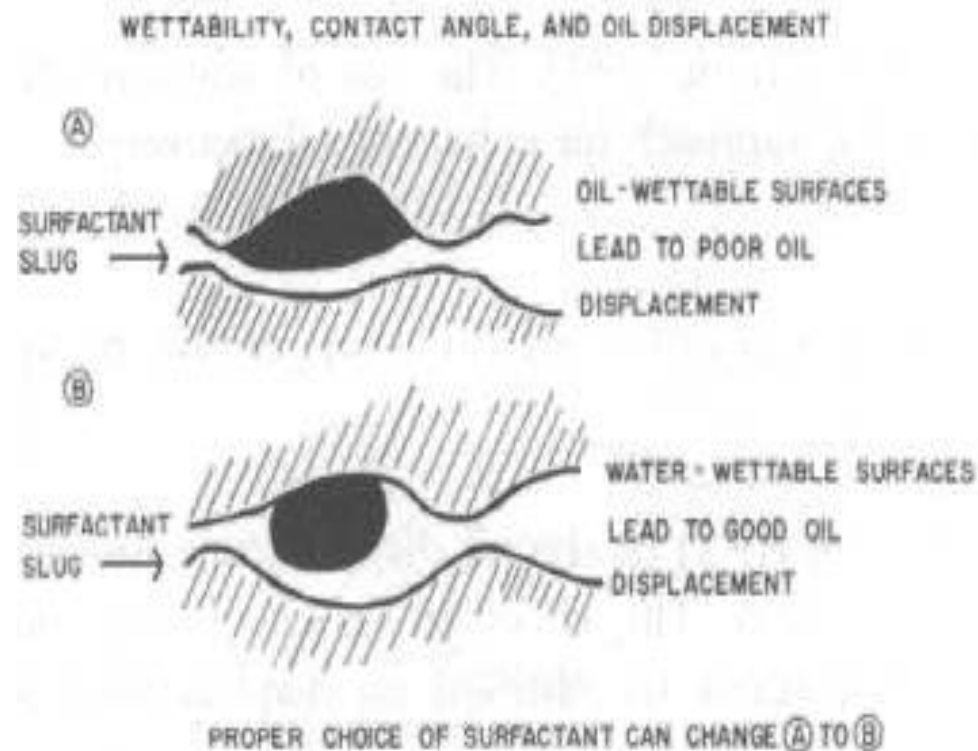
WETTABILITY, CONTACT ANGLE, AND OIL DISPLACEMENT

Ⓐ
SURFACTANT SLUG →
OIL-WETTABLE SURFACES LEAD TO POOR OIL DISPLACEMENT

Ⓑ
SURFACTANT SLUG →
WATER-WETTABLE SURFACES LEAD TO GOOD OIL DISPLACEMENT

PROPER CHOICE OF SURFACTANT CAN CHANGE Ⓐ TO Ⓑ

Fig. 10-10. Schematic diagram of the role of wettability and

## ULTRA-LOW IFT IN RELATION TO OIL DISPLACEMENT SURFACTANT FLOODING:

### Effect of salt concentration on IFT :

➤ The IFT is strongly dependent on the solid of the aqueous phase and at a critical salt conc. the IFT approaches its minimum value.

➤ By changing the salinity of the aq phase, the relative solubilities of the surfactant in the oil and water can be varied significantly.

➤ By replacing paraffinic crude with naphthenic crude, the region of minimum IFT would move down and to the right as indicated by the arrow in fig.10.11.

➤ A specific surfactant conc. and salinity is required for the formation of ULIFT. As the salt conc. is varied in the aq phase, the partition coefficient of the surfactant between oil and water is altered, which seems to be responsible for achieving ULIFT.

➤ In order to delineate the effect of salt on IFT and partition coefficient a molecular mechanism (Fig.10.12) has been proposed.

➤ The surfactant conc. in the oil phase increases with increasing salt conc. in aq phase. At low salt conc., most of the surfactant stays in aq phase. At high salt conc. the surfactant dissolves into oil phase. At intermediate conc. the surfactant conc. (highest) is the same in both oil & water (optimal salinity).

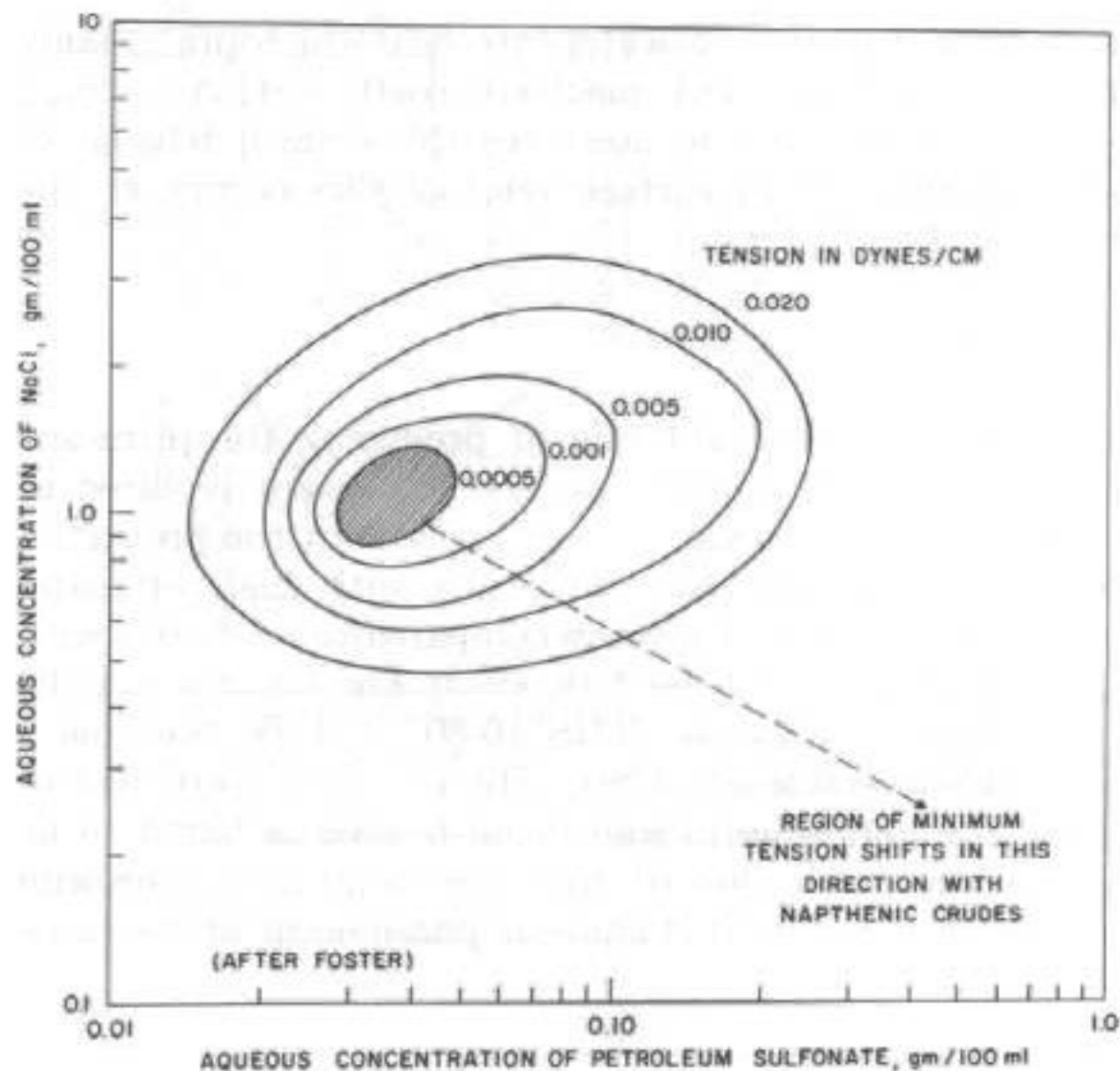➤ The partition coefficient at optimal salinity was also found to be unity.

Fig. 10-11. Interfacial tension contour map for petroleum sulfonate–NaCl–water system against intermediate paraffinic crude. (After Wilson, 1977, p. 5, fig. 2; courtesy of the Academic Press, New
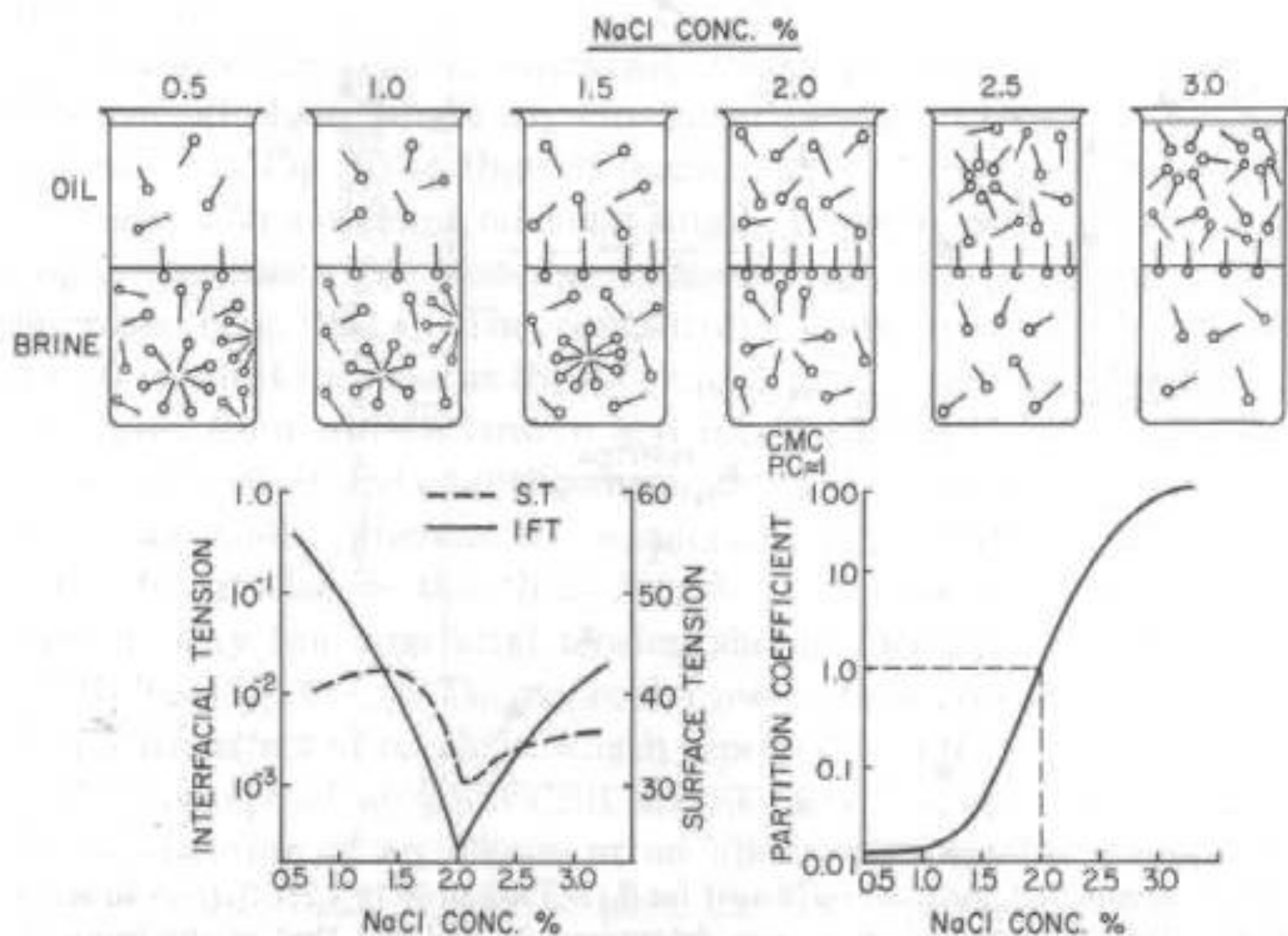
Fig. 10-12. The molecular mechanism for the effect of salt concentration on interfacial tension and surface tension.

**Effect of oil chain length on IFT:**

- The nature of the oil plays an important role in producing ultra-low IFT.

- The conc.s of both salt & surfactant required to produce a minimum in IFT vary significantly with the properties and chain length of oil.

- It was shown that crude oils with high aromatic $H_2$ content produced lower IFT compared to crude oils with lower aromatic $H_2$ content.

- Fig.10.13 shows IFT for a petroleum sulfonate (TRS 10-80) in 1.5% NaCl as function of oil chain length. The partition coefficient of surfactant corresponding to minimum in IFT is found to be unity (fig.10.13).

- Fig.10.14 illustrates the proposed molecular mechanism for the effect of oil chain length on IFT. The partitioning of the surfactant in the oil phase decreases with increasing oil chain length.

- The conc. of surfactant in the brine phase must increase as the oil chain length is changed from $C_6$ to $C_{16}$. It was confirmed from ST & IFT measurements that the conc.s of surfactant in aq phase equilibrated with $C_6$ to $C_8$ oils below the CMC, whereas the surfactant conc. in the aq phase would be smaller as the chain length of the dissolved oil is increased.

- The molecular mechanism proposed in Fig.10.14 explains clearly the effect of oil chain length reported by previous investigators.
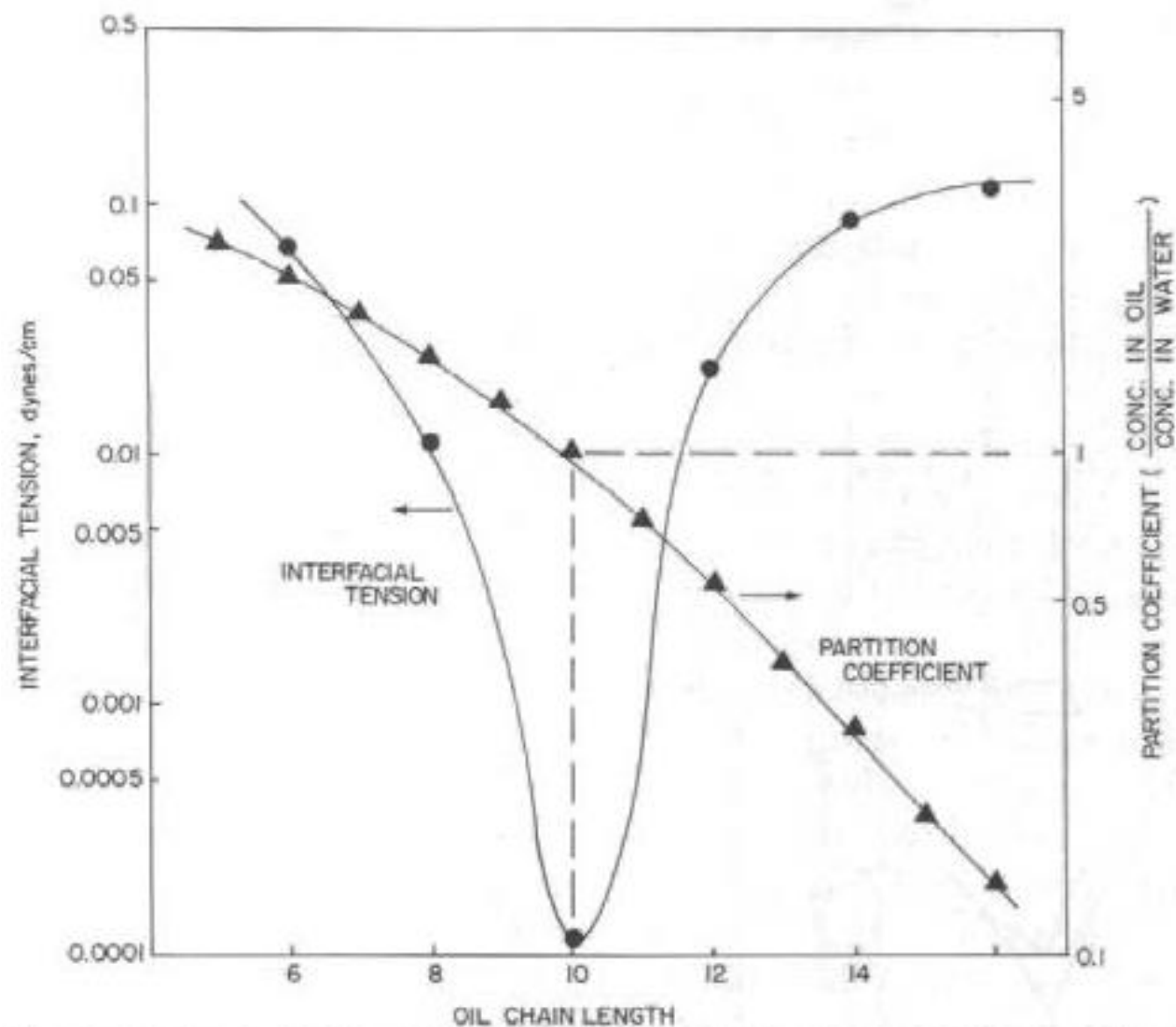
Fig. 10-13. Interfacial tension and partition coefficient for 0.1% TRS 10-80 in 1.5% NaCl with oil of various chain length. The concentration in oil was determined by UV and that in the brine by methylene blue absorption measurements.

**Fig.10.14 illustrates the proposed molecular mechanism for the effect of oil chain length on IFT. The partitioning of the surfactant in the oil phase decreases with increasing oil chain length.**
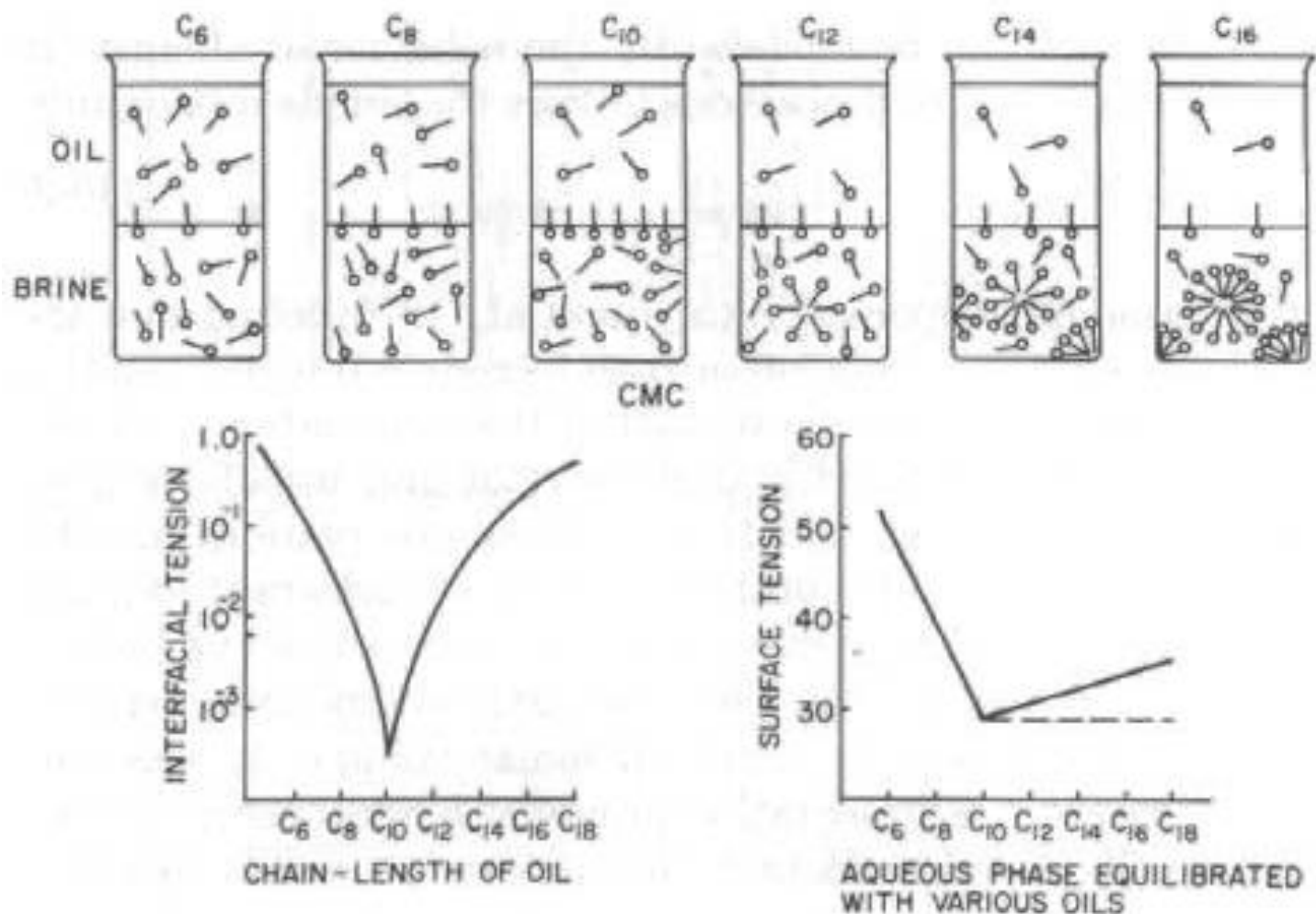


Fig. 10-14. The molecular mechanism for the effect of chain length of oil on interfacial and surface tensions.

**Effect of surfactant concentration on IFT:**

- The IFT decreases with increasing surfactant conc., and at a critical conc. IFT approaches its minimum value. Beyond this, the IFT increases with an increase in surfactant conc.

- The aq phase is predominantly responsible for the ultra-low IFT.

- From surfactant partition measurements, it was shown the no. of surfactant monomers in oil and brine phase increases with increasing conc. of surfactant.

- The molecular mechanism for the effect of surfactant conc. on IFT minimum was proposed for the TRS 10-80-n-octane brine system (fig.10.15).

- The molecular mechanisms for the effects of salt conc. (fig.10.12), oil chain length (fig.10.14), and surfactant conc. (fig.10.15) explain all results of U-L IFT.

- This unified understanding of the molecular mechanisms for producing ultra – low IFT could be utilized in designing surfactant formulations for EOR under particular reservoir conditions.
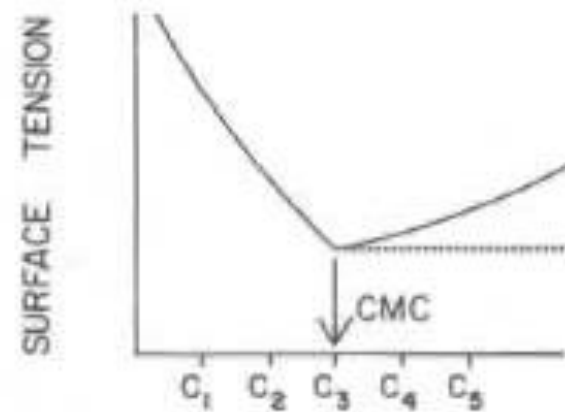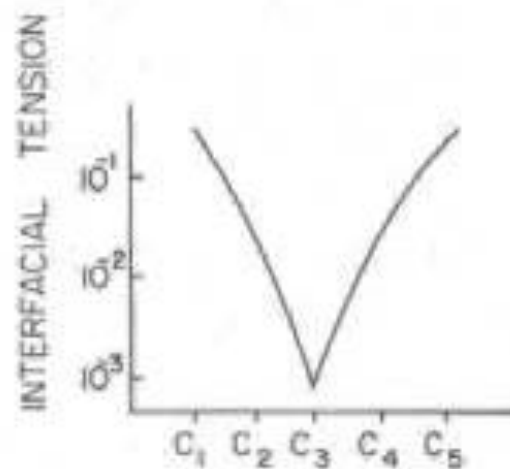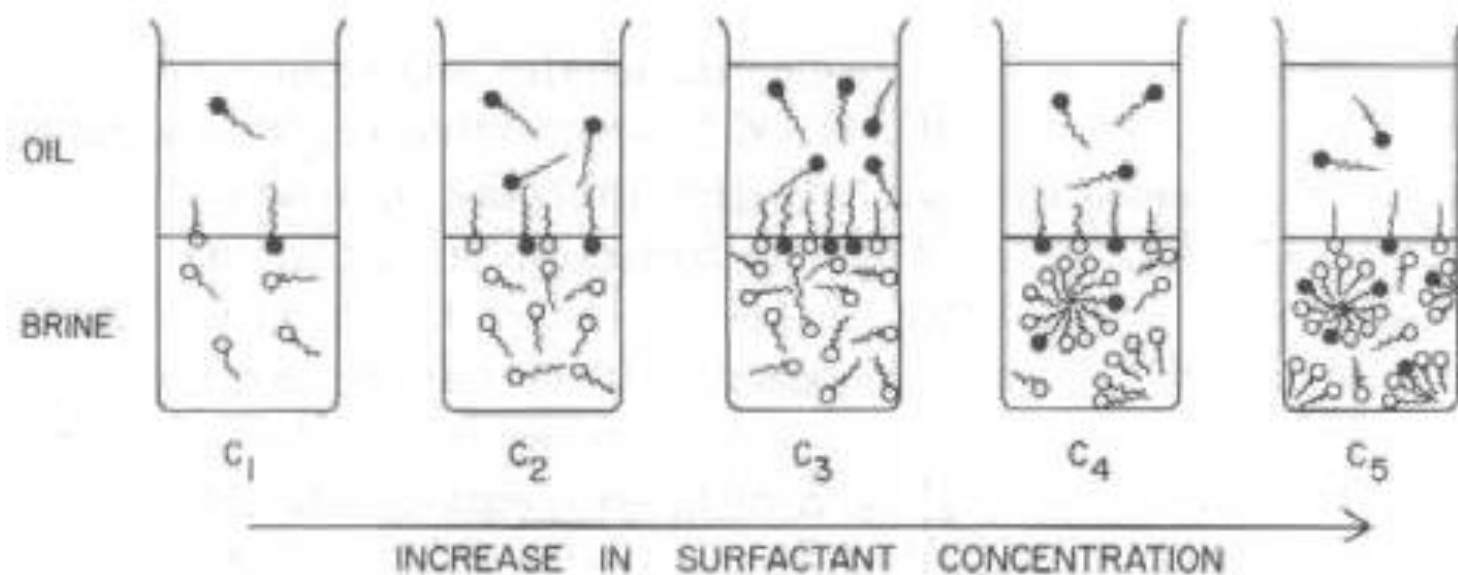
Fig. 10-15. The proposed molecular mechanism for the effect of surfactant concentration interfacial and surface tensions.

**Effect of interfacial charge on IFT:**

- The IFC influences IFT. For several systems, a minimum in IFT and a maximum in electrophoretic mobility (EM), which is an indirect measure of IFC density, has a definite correlation with the IFT for oil-surfactant systems.

- Fig.10.16 shows the electrophoretic mobility and IFT as a function of surfactant conc. For the TRS 10-80-n-octane-brine system.

- This system exhibits a minimum in IFT at 0.05% TRS 10-80 conc., whereas the electrophoretic mobility exhibits a striking maximum.

- A particular conc. of NaOH, the IFT between crude oil and caustic solution exhibits a minimum. In order to understand the mechanisms of U-L IFT in crude oil-caustic systems, electrophoretic measurements were also carried out for these systems.

- Fig.10.17 represents the IFT & EM of a crude oil at several conc.s of NaOH. It is evident that the region of minimum IFT coincides with that of the max. EM.

- The natural surfactants containing carboxylic groups present in the oil react with NaOH & determine the magnitude of the charge at oil-caustic interface.

- These results suggest that the higher IFC density is responsible for the minimum in IFT in crude oil-caustic systems.
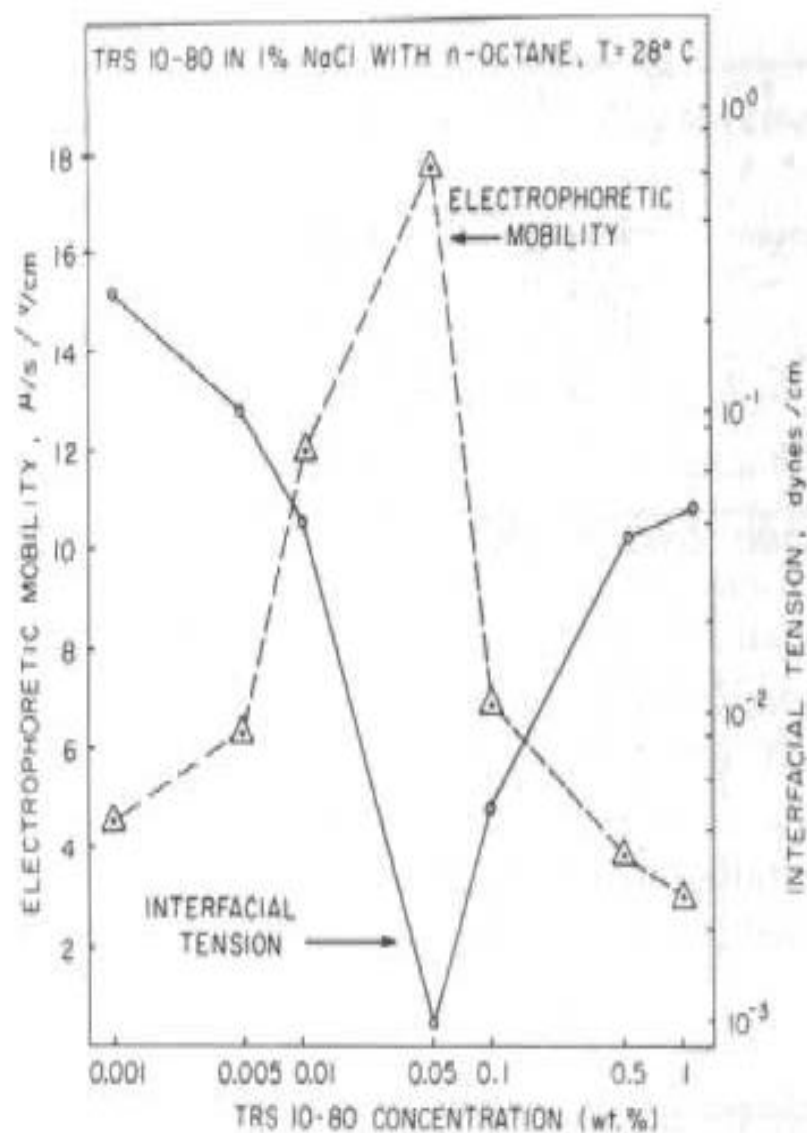
Fig. 10-16. A correlation between interfacial tension and ele electrophoretic mobility for TRS 10-80–n octane–brine system.
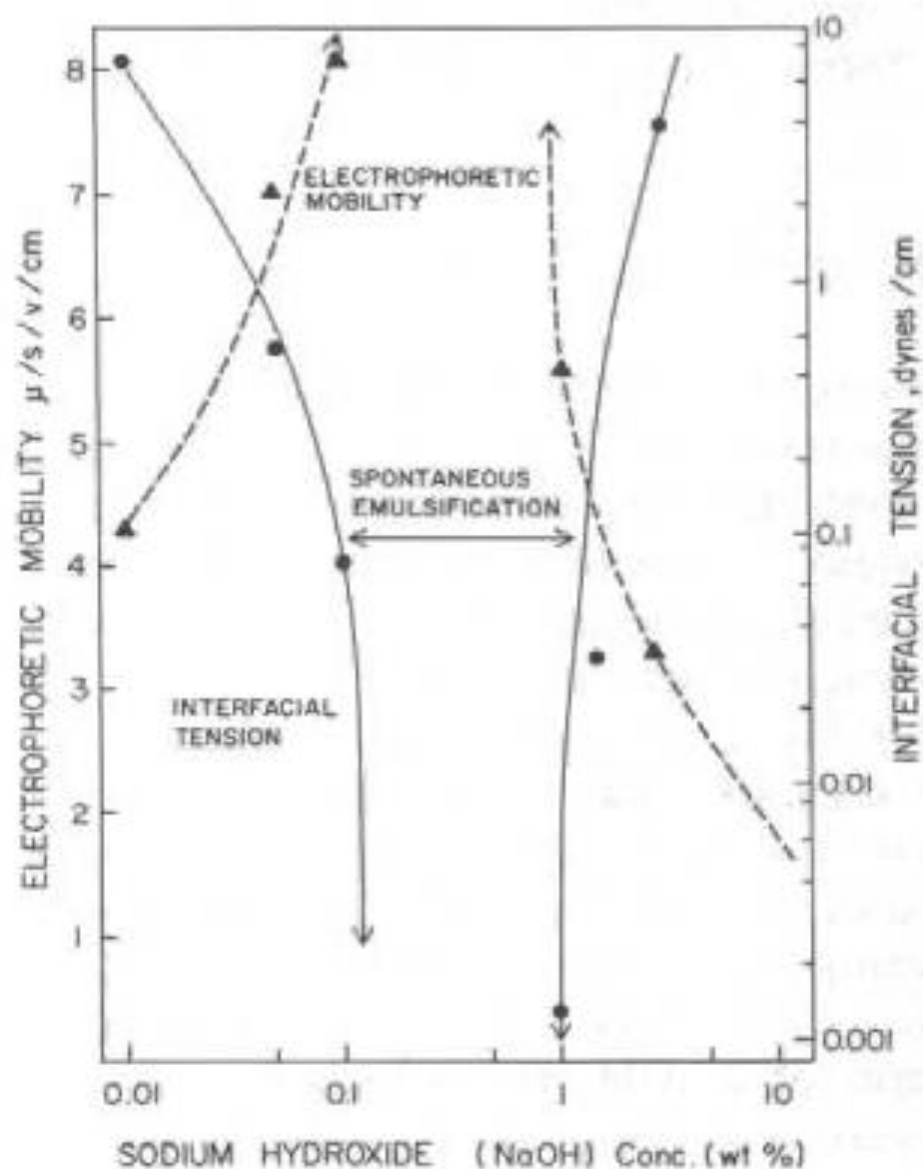
Fig. 10-17. A correlation between interfacial tension and electrophoretic mobility for crude oil–NaOH

## FACTORS INFLUENCING OIL RECOVERY:

➢ **The oil displacement efficiency (DE) depends upon several variables like optimal salinity, mobility control, microstructures of surfactant formulations and interactions between surfactant and polymer.**

## Optimal salinity (OS):

- **The relative solubilities of petroleum sulfonates in oil and water phases are strongly dependent on the salinity of the aq phase.**

- **In a certain salinity range, the systems consisting of surfactant, cosurfactant, oil and brine form three phases; lower, middle & upper phase microemulsion**

- **The salinity at which an equal volume of oil & water is solubilized in middle-phase microemulsion is termed optimal salinity.**

- **If one considers only the IFT , the oil DE should be max. at the optimal salinity.**

- **The oil recovery efficiency is a max. at OS for 0.5 PV slug of 5% TRS+ (Fig.10.18).**

- **A correlation between oil DE & capillary no. is illustrated in fig.10.19. At OS (1.5% NaCl), the max. amount of oil 72% was recovered.**

- **It was observed that at OS the DE of crude oil & pure alkaline mixture in sand packs was a maximum. Fig.10.19 shows the surfactant conc. in the effluent is a function of the no. of pore volumes of fluid injected. The surfactant breakthrough was earliest when the injected surfactant slug contained brine of higher than OS.**
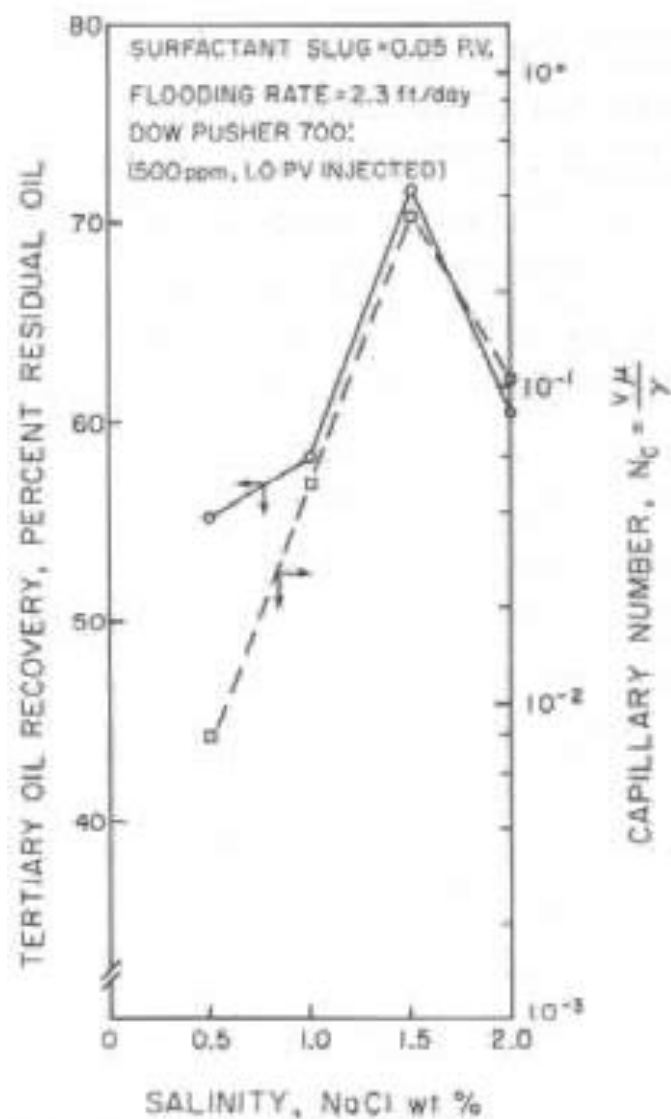
Fig. 10-18. Effect of salinity on the tertiary recovery and capillary number.
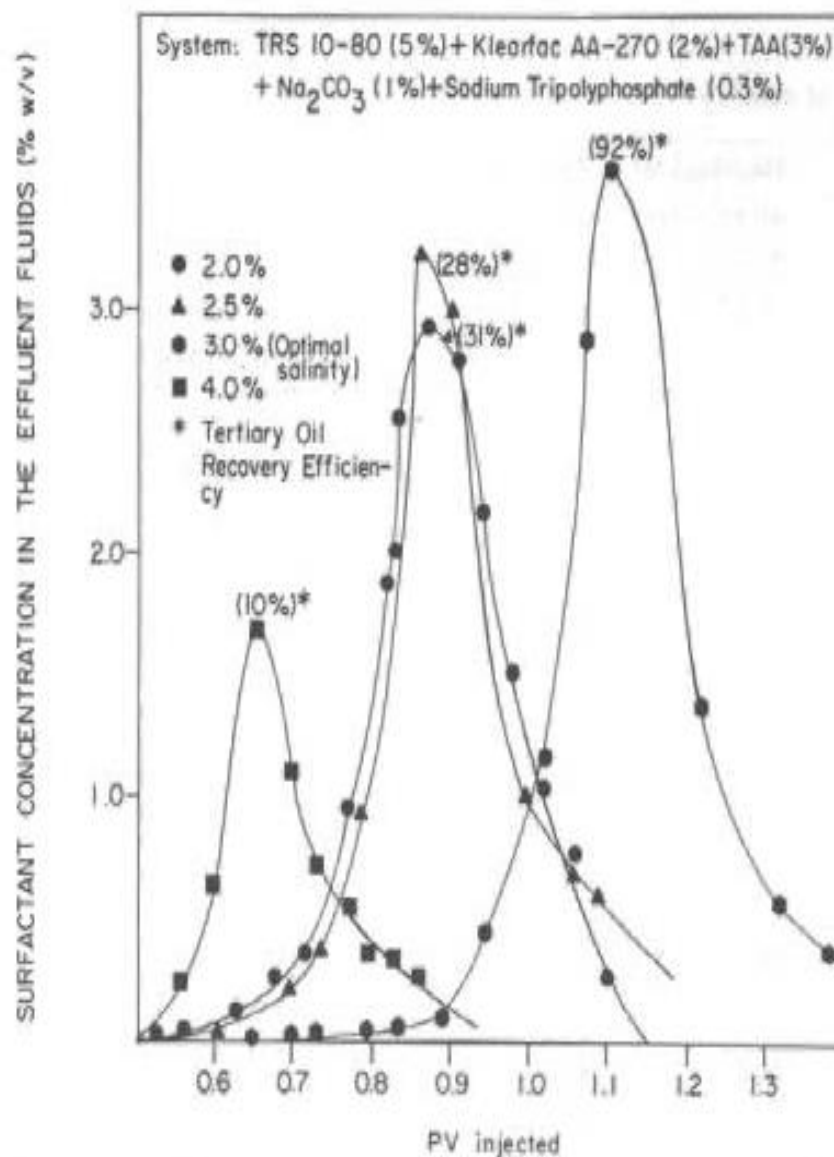
Fig. 10-19. Effect of salinity on surfactant concentration in the effluent fluids.

**Mobility control:**

- For an efficient oil displacement by surfactant flooding, the mobility controlling polymer should be less mobile than surfactant slug and oil bank.

- Loss of mobility control in the fluid sequence causes fingering, so DE reduces.

- In designing a surfactant formulation, it is an important consideration.

- Mobility control was achieved through a reduction in both the $\mu$ and K.

- The effectiveness of the polymer solutions as mobility control agents depends on the polymer conc., shear degradation, adsorption, gel formation, pseudodilatant flow, salt conc. and temperature.

**Surfactant-polymer interaction (SPI):**

- SPI can lead to a considerable reduction in efficiency of oil recovery process.

- The SPI not only occur in the surfactant-polymer mixing zone, but also throughout the entire surfactant slug due to invasion of micellar slug by polymer molecules, which move more rapidly than the carrier water.

- The surfactant-polymer mixing takes place due to both dispersion effects as well as excluded volume effects during the flow of polymer molecules.

- The mixing and invasion of the surfactant slug by polymer molecules forms two phases of different viscosities. The entrapment of the high viscosity phase can effectively remove some components & reduces the efficiency of the process.

## The effect of several variables on SPI and oil displacement efficiency.

(1) Surfactant–polymer interactions are minimized when salinity of the mobility buffer bank (polymer) is lower than the salinity of the surfactant slug.

(2) Increasing temperature facilitates surfactant–polymer interactions.

(3) Polymer invasion of the micellar bank (surfactant slug) and surfactant–polymer interactions can be eliminated if the polymer is insoluble in the micellar fluid.

(4) Surfactant–polymer interactions can also be eliminated by addition of surfactant solubilizers (e.g., cosurfactants or cosolvents) in the surfactant slug or polymer.

(5) The salinity shock design for the polymer solution employs two slugs of polymer solution in which the first polymer slug is at the optimal salinity. This provides ultra-low IFT and maintains mobility control, whereas the second polymer slug at a much lower salinity is capable of reducing the surfactant loss. Oil recovery in Berea cores was as high as 86% even in the presence of 3% $NaCl + 1\%$ $CaCl_2$ in connate water.

(6) If the salinity of the polymer solution was at the optimal salinity of the preceding surfactant formulation, oil recovery in porous media was favorable over a wide range of connate water salinities for both aqueous and oleic surfactant formulations. Oil recovery drastically decreased when the salinity of the polymer solution was shifted from the optimal salinity, even when the connate water was at the optimal salinity. These results indicate that the processes occurring at the surfactant–polymer mixing zone dominate the oil displacement efficiency.

**Microstructures of surfactant formulations:**

The surfactant formulations used for EOR can be in the form of several structures: micellar solutions, microemulsions, liquid crystalline dispersions.
The formation of these microstructures depends upon the composition of surfactant formulation. Oil DE may be influenced by these structures.
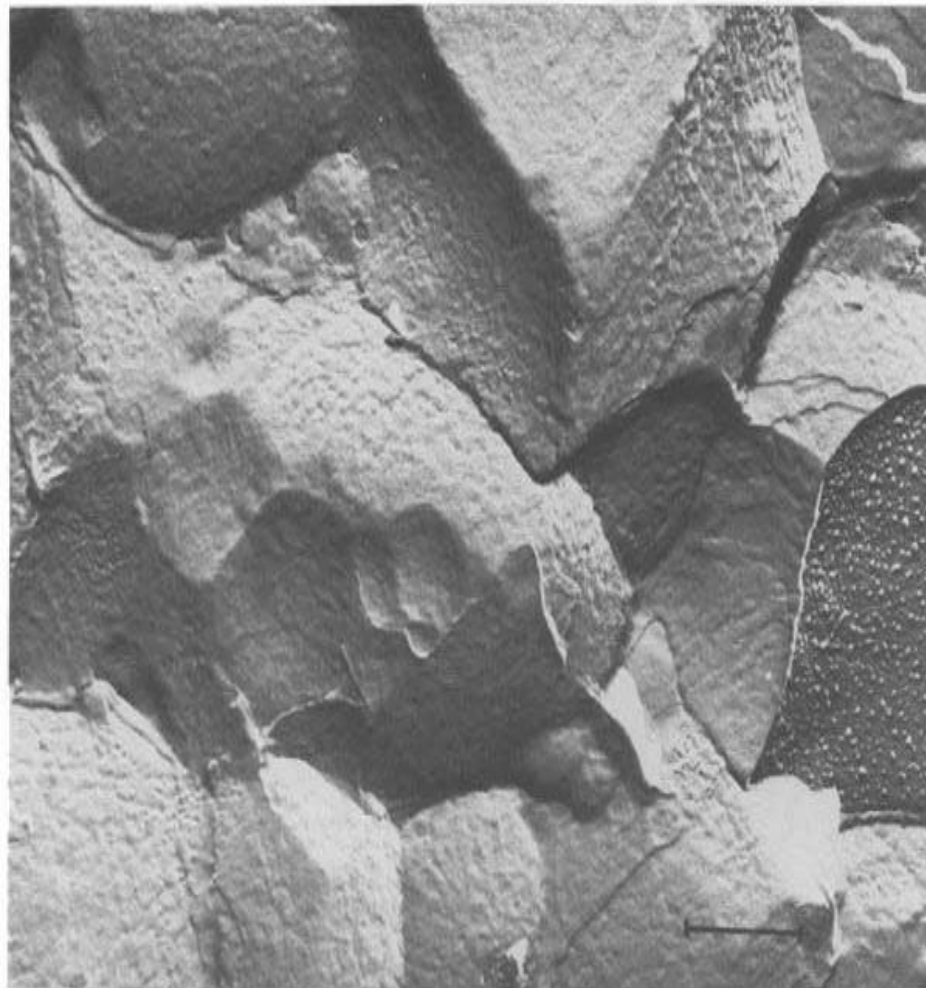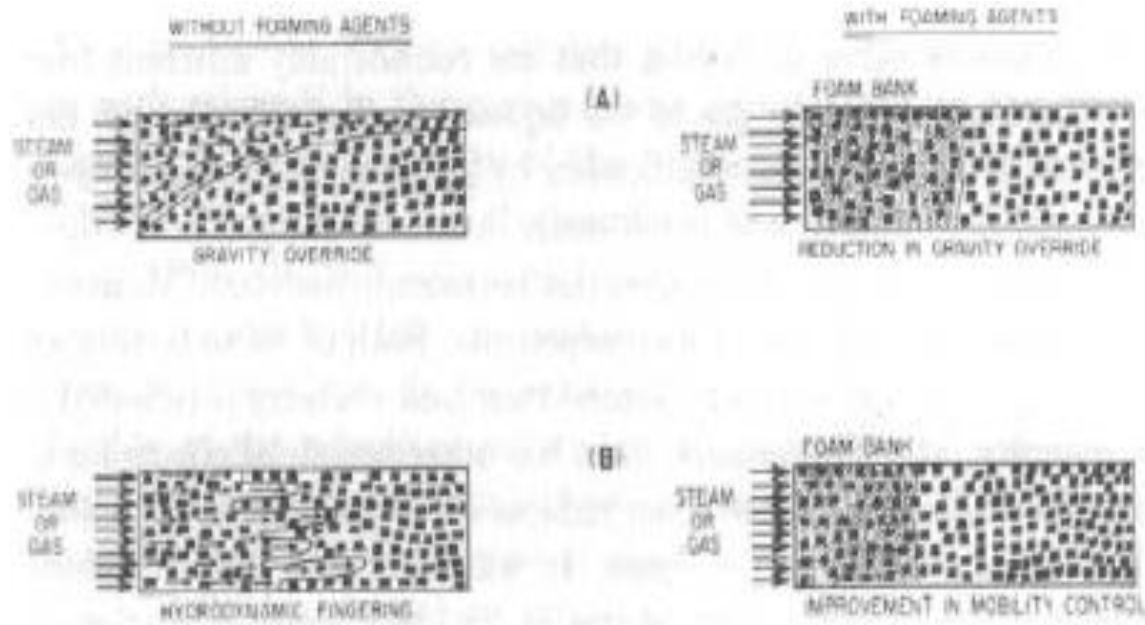


Fig. 10-25. Electron-micrograph of 5% TRS 10-410+3% isobutanol in 2% NaCl. 60,000×, bar = 0.5

Fig. 10-24. Electron-micrograph of 5% TRS 10-410+3% isobutanol in 2% NaCl. 36,000×, bar = 1 μm.

# SURFACTANT-GAS (FOAM) FLOODING FOR OIL RECOVERY:



- Steam and gases ($CO_2$ & $N_2$) can be injected into the reservoir for heavy oil and light oil recovery respectively in EOR systems.

- The lighter gas phase tends to flow on top and ride over the liquid phases in the reservoir because of density differences between gas and liquid phases.

- This preferential movement of gas through the upper part of the reservoir is called gravity override (Fig10.27A). At reservoir conditions, the viscosity of the injected gases is often 10-100 times lower than the oil viscosity.

- At these unfavorable viscosity (Mobility) ratios, gases have the great potential to channel (finger) through the oil (Fig.10.27B).
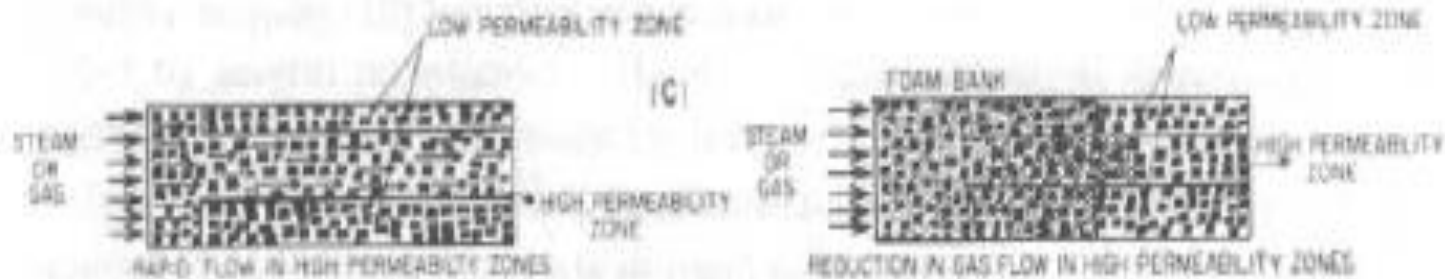
Fig. 10-27. Possible effects of foam on transport of steam or gas in porous media.

- If the reservoir consists of rocks with variable permeability, steam or gases have the inherent tendency to flow preferentially through the more permeable zones compared with low-permeability zones (Fig.10.27C).

- Because of channeling and gravity override, the heat distribution is not uniform during steam flooding. During gas-steam flooding, early break through of the gas phase at the production wells is common.

- To minimize these uneconomical problems in gas-steam flooding processes for efficient oil recovery, the possible mechanisms is to have steam and/or gas present as the phase of a foam.
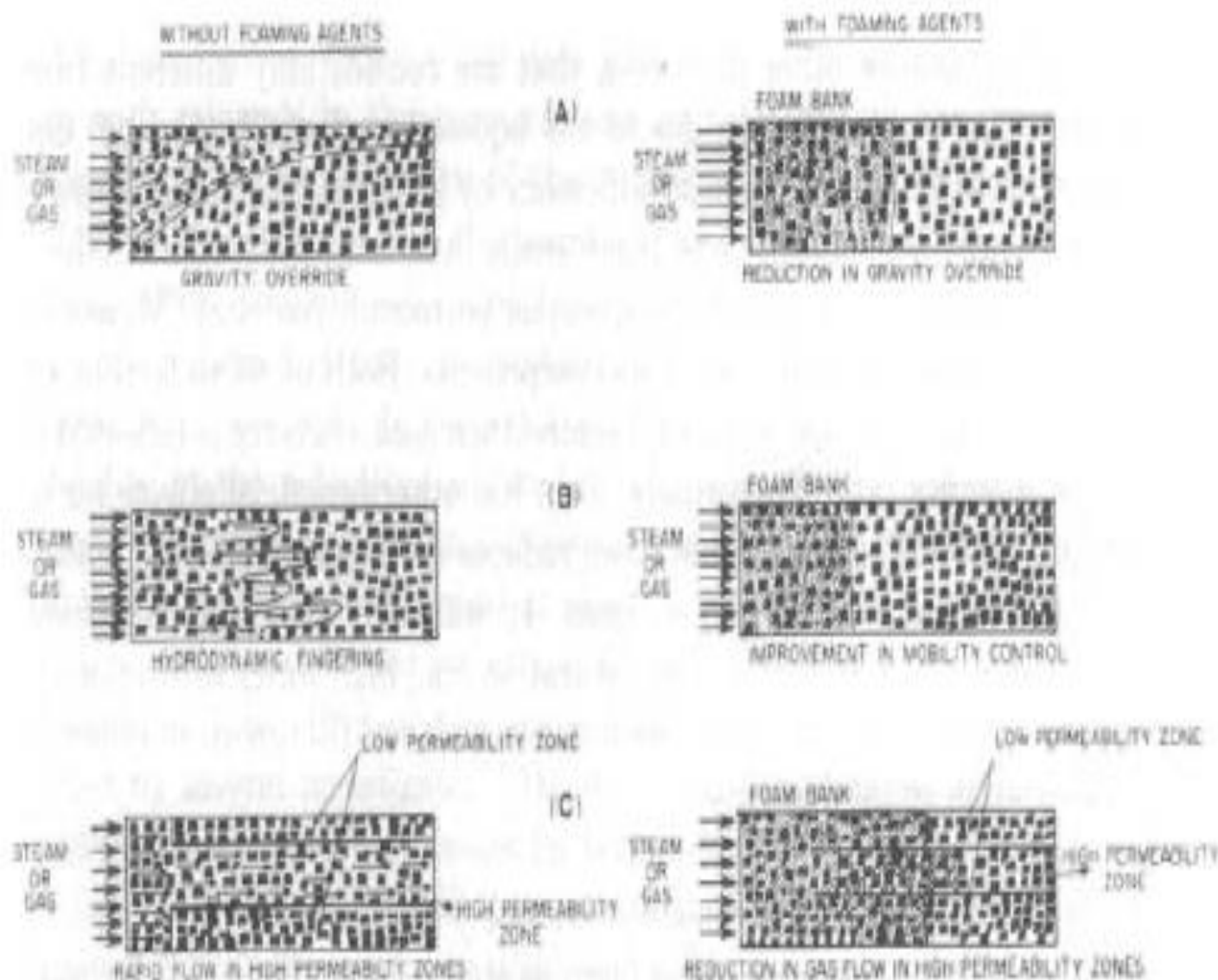
Fig. 10-27. Possible effects of foam on transport of steam or gas in porous media.

## Role of surfactants in gasflooding processes:

- Surfactants with foaming ability can be used to reduce the mobility of the gas phase, the channeling & gravity override can be decreased. By injecting a water soluble solvent followed by steam or gas, it has been observed that foam increases trapped gas saturation in porous media, so oil saturation decreases.

- Foam has a high potential for reducing gas mobility ( 80-95% gas). Foam is a relatively low-density material which can easily overcome gravitational effects. Foam viscosity is greater than that of its components. Both of these factors are favorable for efficient oil displacement.

- The surface activity of foam reduces oil-water IFT and facilitates wetting of oil-wet surfaces. Foam generation capacity is high at low oil saturation ( high water saturation) of the reservoir.

## Surfactant-steam flooding for heavy oil recovery:

- It was observed that some surfactants lose their ability to function after several days at $100^0C$, whereas others are still fully effective for a period of 1 week.

- The ability of surfactants to generate foam increases with increasing temp.

- At a minimum steamflood temp ($177^0C$), the half-lives for the most stable surfactants evaluated were about 11 days. The effect of surfactant conc. & salt on the stability of TRS 10-80 has been investigated at various temps.

**Surfactant-CO$_2$ flooding for light oil recovery:**

➢ At elevated pr CO$_2$ flooding can recover additional oil. In addition, super-critical CO$_2$ develops multicontact miscibility with various crude oils, resulting in a very efficient oil displacement in porous media.

➢ CO$_2$ is costly compared with water. Several methods have been tried, to minimize the amount of CO$_2$ required for optimum oil recovery.

➢ First, a CO$_2$ slug was injected rather than continuous injection of CO$_2$ . This slug was followed by water. In the second method, CO$_2$ slugs were injected while the producing wells were shut in to avoid severe fingering & pr sinks. In the third method, alternate slugs of CO$_2$ & water were injected.

➢ The main objective was to reduce CO$_2$ channeling by reducing its mobility.

➢ The primary requirement for CO$_2$ mobility control is a surfactant with proper chemical stability, adsorption characteristics, and foaming or emulsifying capability. An anionic surfactant was recommended for the improvement of the CO$_2$ process.

➢ For water flooded reservoirs, it is highly desirable to maintain the greatest mobility reductions in oil-free reservoir zones. It appears, this process has a high potential to achieve selective mobility reduction of CO$_2$.

A comparison of the results of steam flooding alone and steam-surfactant (foam) flooding shows that the latter has the potential to recover 25% more bitumen from oil sand than steamflooding alone.

o **Steam foams are more effective than air foams in displacing oils.**

o **Fig.10.28 shows the effect of oil viscosity on residual oil saturation after air & steam foam flooding**

o **Compared to steam foam flooding, the effectiveness of air foams in recovering additional oil decreases with increasing oil viscosity.**

o **The higher oil recovery by steam foam flooding is presumably due to reduction in the oil viscosity and higher foaminess of the surfactants during steam injection compared with air injection.**
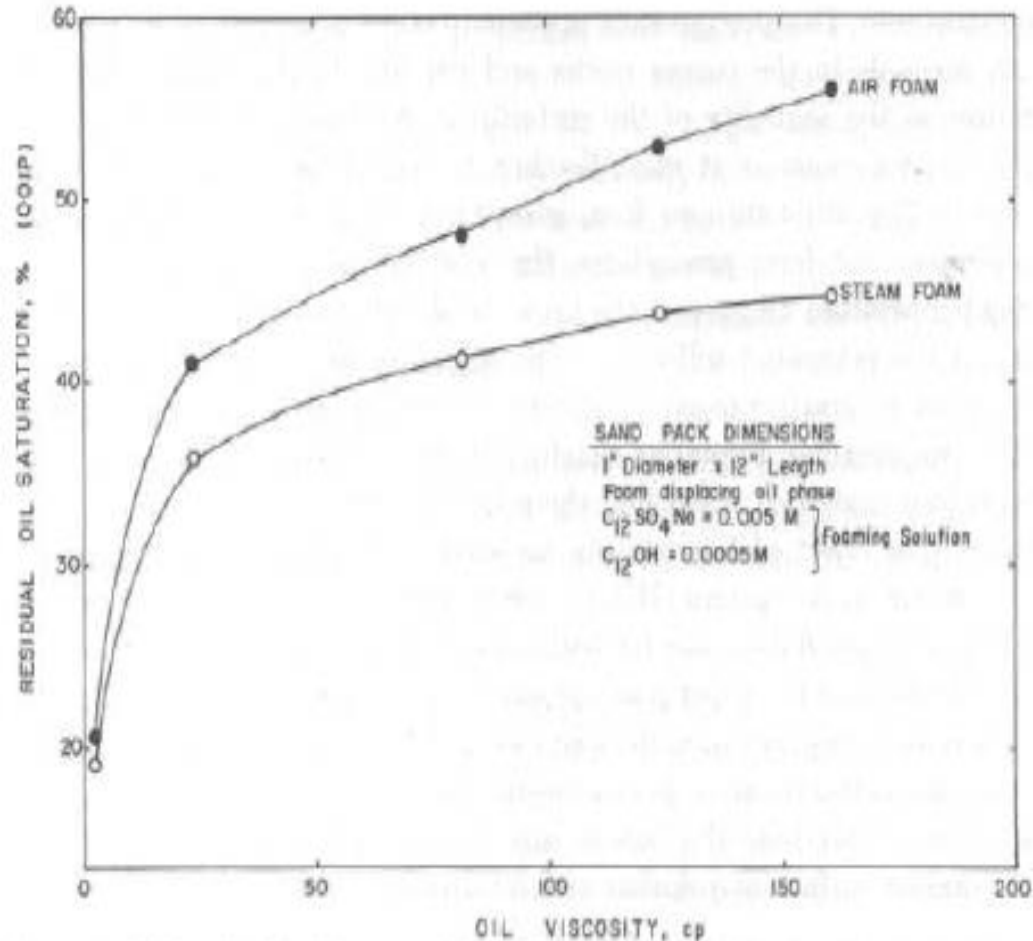


Fig. 10-28. Effect of oil viscosity on residual oil saturation after air and steam foamflooding.
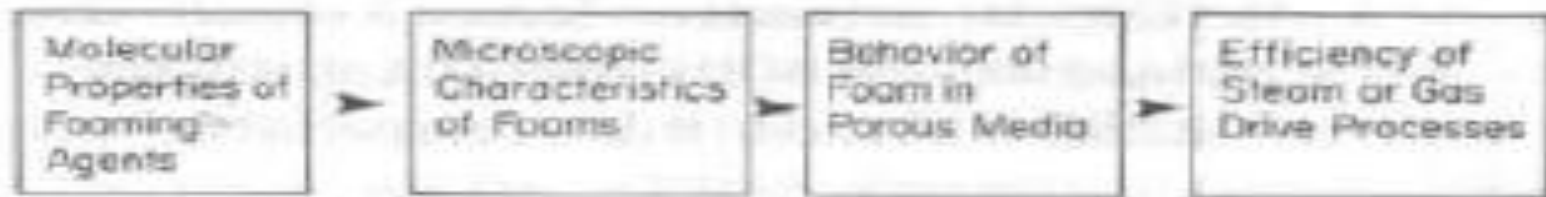
Fig. 10-29. A correlation of molecular properties of surfactants with the efficiency of steam-gas-drive processes.

**INTERFACIAL PHENOMENA IN SURFACTANT-GAS (FOAM) FLOODING:**

- Fig.10.29 shows the interrelationship of molecular properties of surfactants with EOR efficiency of steam or gas-driven processes. The molecular properties of foaming agents can influence the microscopic characteristics of foam which in turn can influence its flow behavior in porous media and recovery efficiency.

**Surface properties of surfactant solutions: Surface tension (ST):**

- Low ST foaming solutions tend to produce stable foams at lower concentrations. ST determines the surface activity which in turn can influence the properties of foams. In order to correlate the ST with flow behavior of foam through porous media, STs of various surfactants have been measured.

- A decrease in ST was observed with increasing temp. A similar trend in the variation of ST with temp was observed in the presence of NaCl.

- The effect of surfactant conc. on the ST of commercial solutions was determined.

## Surface viscosity (SV):

- The SV can influence the stability of foams. A high SV reduces the rate of thinning of liquid films resulting in high foam stability.

- For mixed surfactant systems, a max. in SV was observed when both components of the mixed surfactants had the same chain length.

- It was observed that the SV increases with increasing surfactant conc. & these results were also correlated with other surface properties of surfactant solutions, microscopic characteristics of foams & flow behavior of foam in porous media.

## Foaminess of surfactants:

- Among other properties of surfactant formulations for foam flooding processes, the foaminess of a surfactant solution is more important than foam stability.

- The presence of an in-situ foam bank between the displacing gas phase and displaced liquid improved both breakthrough time and ultimate recovery.

- The foam producing capacity of the surfactant solution increases with increasing surfactant conc. and temp. The foaminess of the surfactant solutions as a function of temp can be correlated by the following equation.

- $F = F_{20} \, e^{A(T-20)}$ ………….10.3 where A is a constant ($1.6 \times 10^{-3}$), F is the foaminess of surfactant solution at temp T ($^0$C) and $F_{20}$ is the foaminess at $20^0$C.

# Foam stability:

- Surfactants play an important role in the foam stability & formation of foams. Foam stability was determined by measuring half-life of foams. Half-life is the time required to reduce foam volume to half of its initial value. It is observed that the ethoxylated sulfonates are the most effective surfactants.

- Foam stability (e.g., half-life) decreased with increasing temp. Among all surface properties of the surfactant solutions measured, the effect of temp on foam stability was most pronounced.

# Microscopic characteristics of foams: Average bubble size:

- The bubble size can influence the efficiency of the foamflooding process.

- Fig.10.30 shows photo micrographs of various foams containing sodium dodecyl sulfate and dodecanol.

- Mixed surfactants of equal chain length ($C_{12}H_{25}SO_4$ Na + $C_{12}H_{25}OH$) produced smaller foam bubbles as compared to mixed surfactants of dissimilar chain length ($C_{12}H_{25}SO_4$ Na + $C_nH_{2n+1}OH$, where n = 8,10,14 &16).

- The molecular packing at the interface is strongly influenced by the chain length compatibility of the mixed surfactants due to the occurrence of thermal disturbances (e.g., oscillational, rotational, vibrational motions).

- The smaller bubbles displaced more fluid as compared to the large size foams.
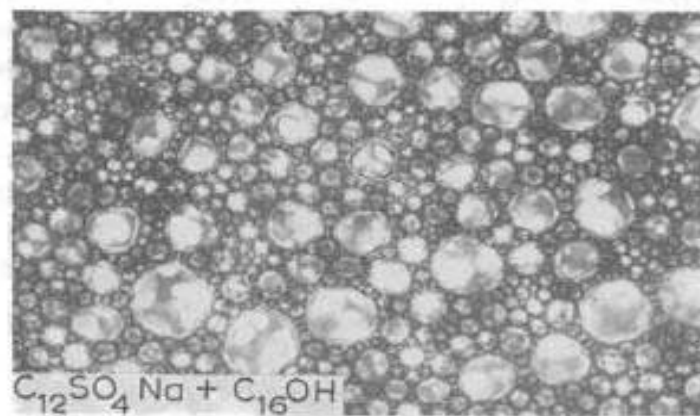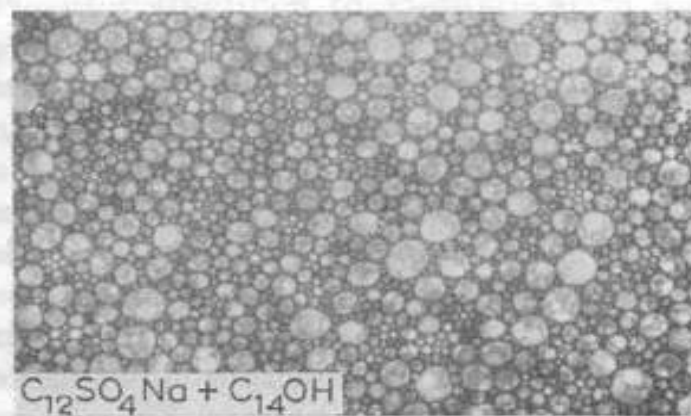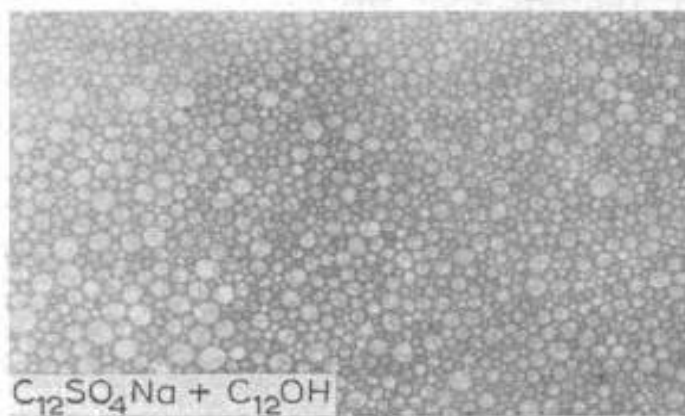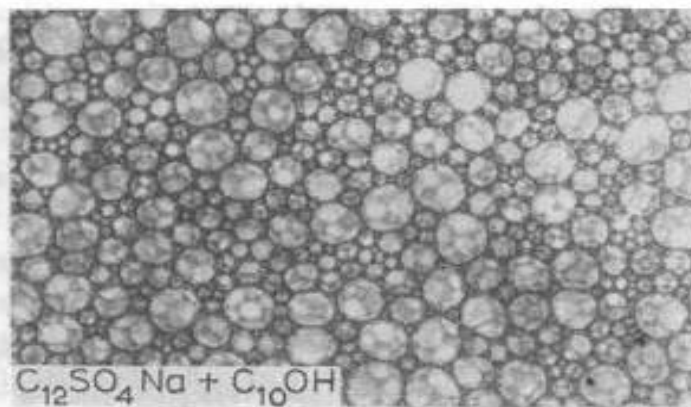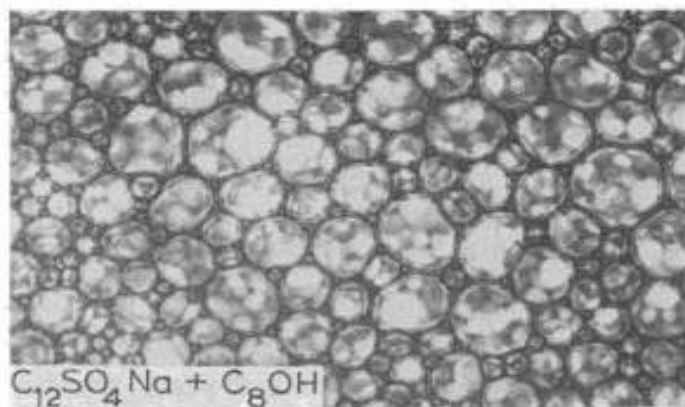
Fig. 10-30. Photomicrographs of foams containing $C_{12}H_{25}SO_4Na$ (0.005 M) and various alkyl alcohols (0.0005 M) at 15 minutes after the foams were produced.

# Effect of temperature on bubble size:

- The temp of most petroleum reservoirs is higher than the surface temp.

- Fig.10.31 illustrates the photomicrographs of foams containing sodium dodecyl sulphate & dodecanol at various temps. The surfactants can produce initially smaller size bubbles at higher temps compared with lower temps. At a particular temp, the bubble size increases slightly in the presence of brine.

- The variation in bubble size as a function of time at various temps is shown in fig.10.32. The bubble size increases with elapsed time due to coalescence. It increases rapidly with time at higher temps.

- It is evident that the surfactant solutions produced smaller bubbles

initially at higher temperatures. In Fig. 10-32, the curves intersect each other at a particular elapsed time which indicates that, at a specific time, the surfactant solutions produce the same size foam at various temperatures. To calculate the size of foam bubbles, a quantitative correlation among bubble size, temperature and time has been established (Sharma et al., 1984):

$$r = (aT + b)t + (cT + d) \tag{10-4}$$

where $r$ is the radius of foam bubbles, $T$ is the temperature, $t$ is the elapsed time, and $a$, $b$, $c$ and $d$ are the constants. The values of these constants for the system studied are: $a = 2.96 \times 10^{-4}$ cm/min °C; $b = -5.70 \times 10^{-4}$ cm/min; $c = -1.82 \times 10^{-4}$ cm/°C; and $d = 3.14 \times 10^{-2}$ cm.
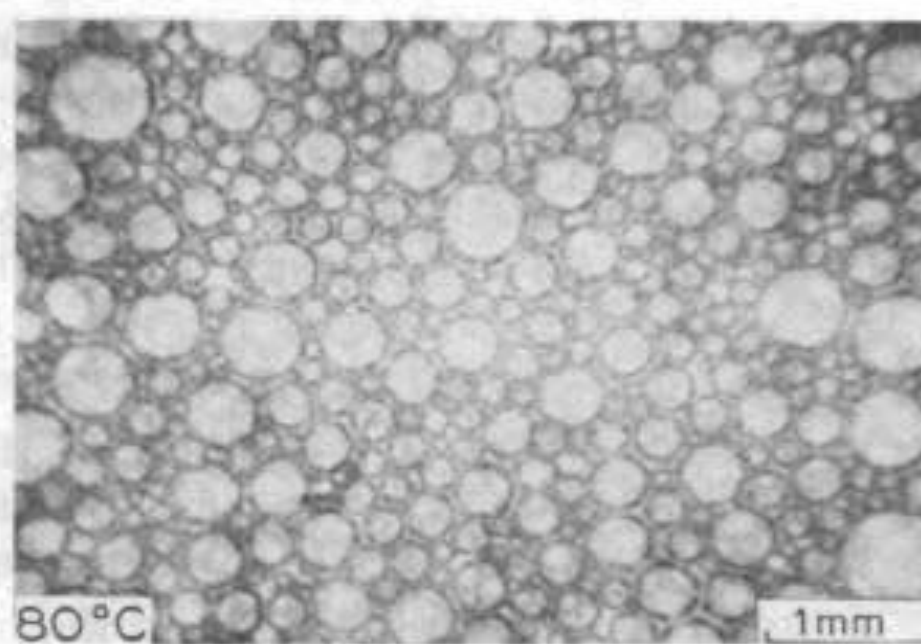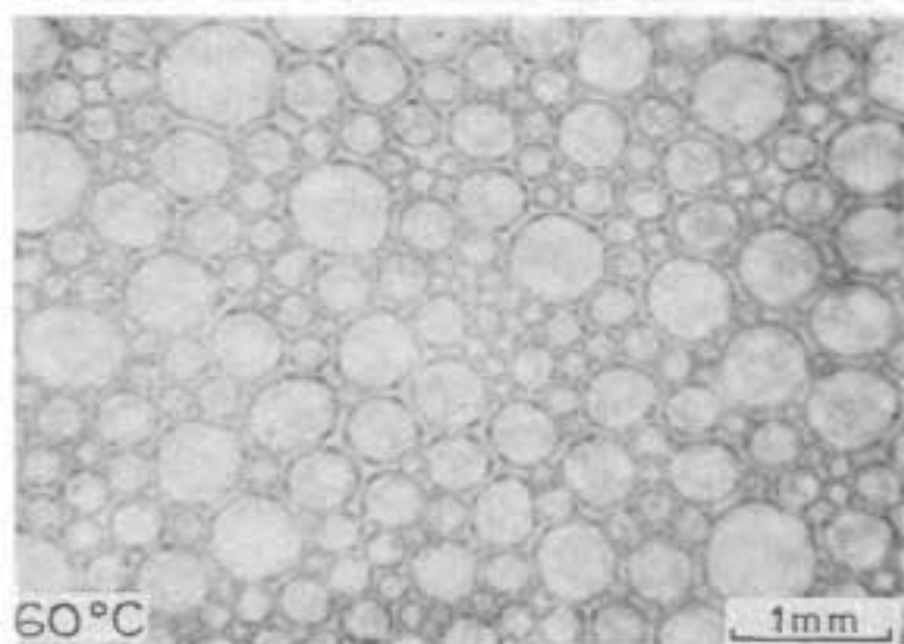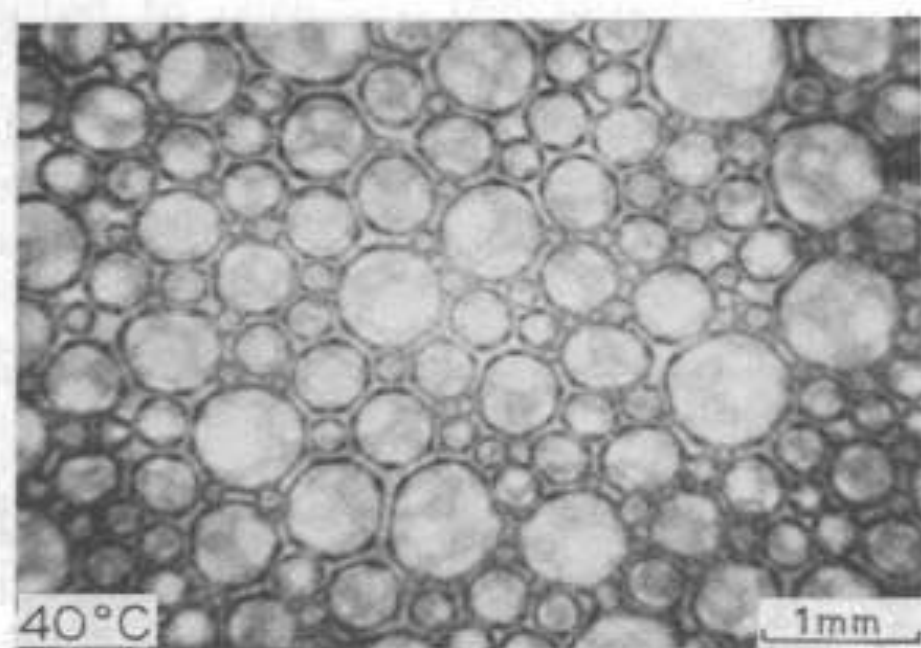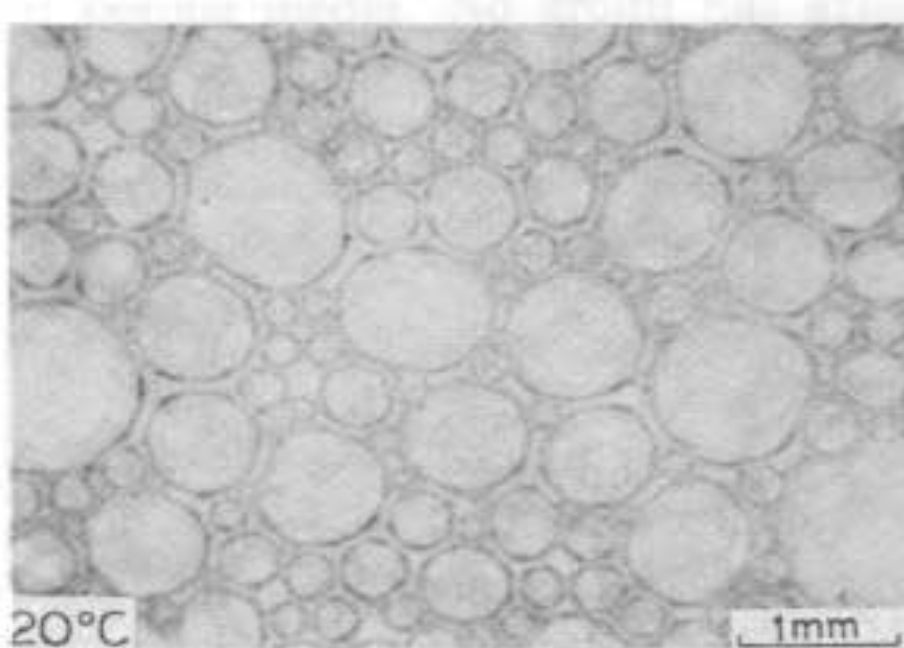
Fig. 10-31. Photomicrographs of foams containing $C_{12}H_{25}SO_4Na$ (0.005 M) and $C_{12}H_{25}OH$ (0.0005 M) at various temperatures.
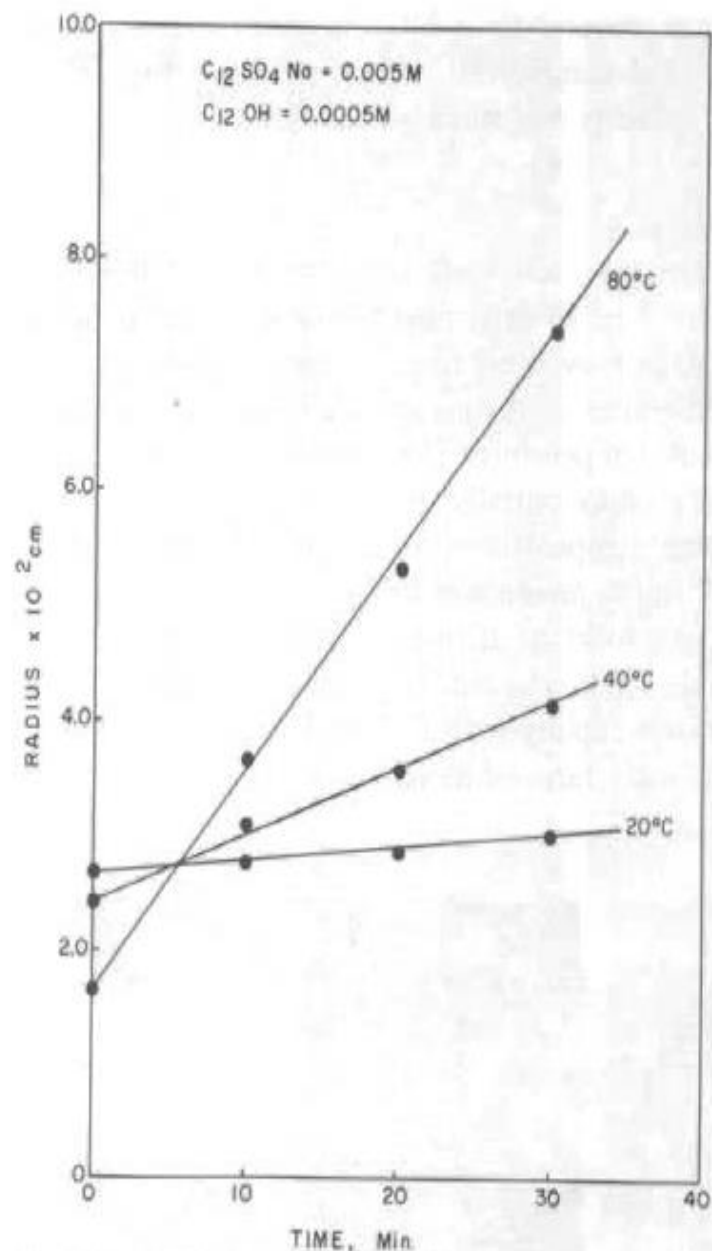
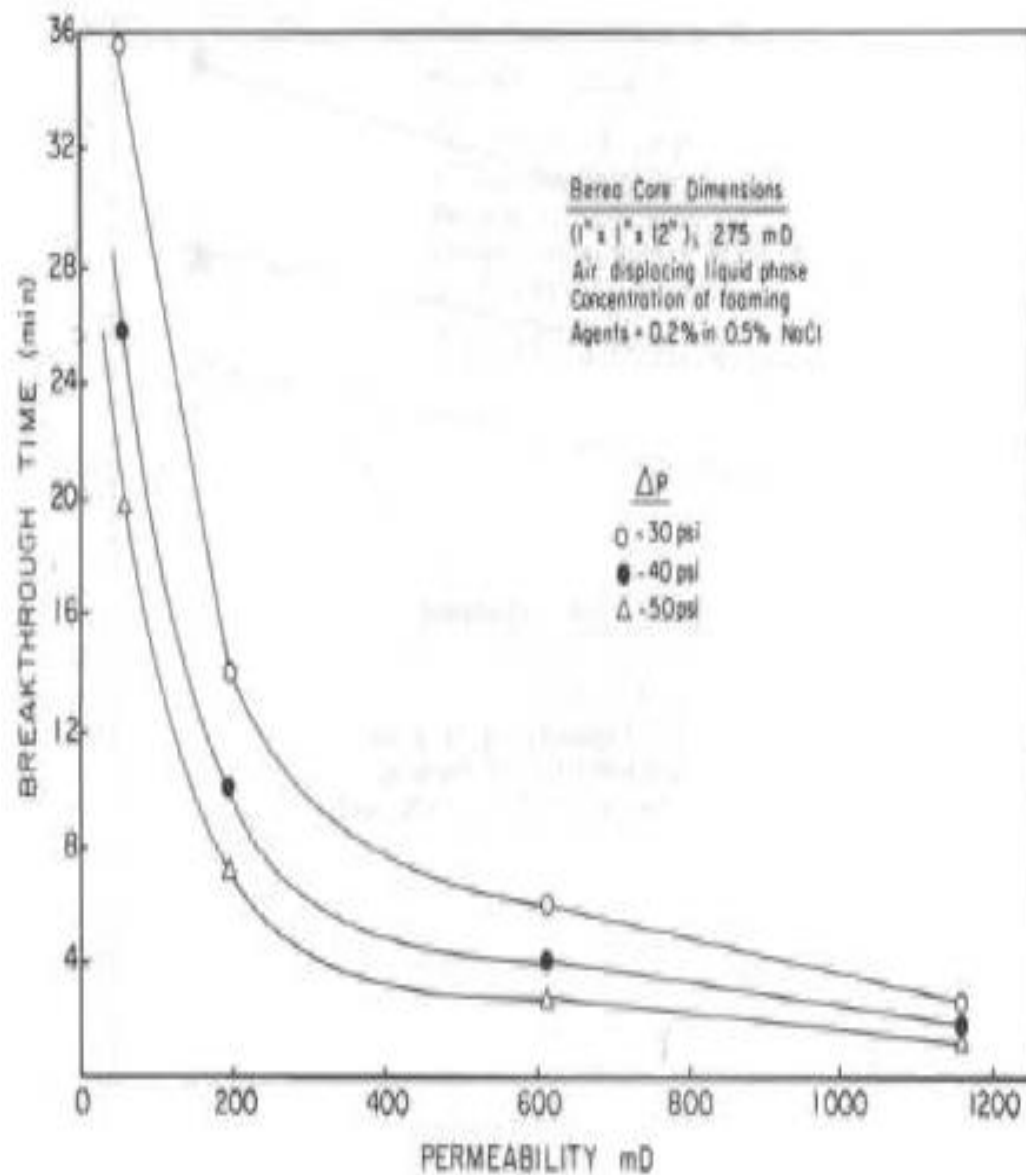Fig. 10-32. Bubble size in foams as a function of time at differe



Fig. 10-33. Effect of the permeability of porous media on breakthrough time

**Effect of pressure on bubble size:**

- It is known that with increasing pr the conc. of surfactants at an interface increases and ST decreases. **The bubble size of flowing foam in a capillary tube decreases with increasing pr.** The smaller size foams are more effective in displacing fluid and in reducing gas mobility in porous media.

**Flow through porous media behavior of foams: Fluid displacement efficiency:**

- The presence of foam in a porous medium considerably increases the fluid recovery both in sand packs & Berea cores. The volume of fluid collected at gas breakthrough at a producing site is termed as fluid displacement efficiency. The fluid displacement efficiency increased with temp ($20-40^0C$).

**Breakthrough time (BT):** The BT is defined as the time required by gas to travel from injection site to production site. As the saturation increases, the fluid saturation decreases. The BT decreased sharply up to a pr drop of 4 psi. Beyond this pr a gradual decrease in BT was observed in sand packs. The BT increased with increasing temp. The decrease in BT was observed with increasing permeability (50-200mD) of the sandstones (Fig.10.33)

**Gas mobility:** Fig 10.34 illustrates the effect of the K of porous media on relative air mobility at different pr drops. As the temp and pr drop increases, the effective air mobility in porous media decreases (Fig.10.35). A sharp decrease in effective air mobility was observed up to $40^0C$, and beyond this temp a gradual decreases in effective air mobility was observed.
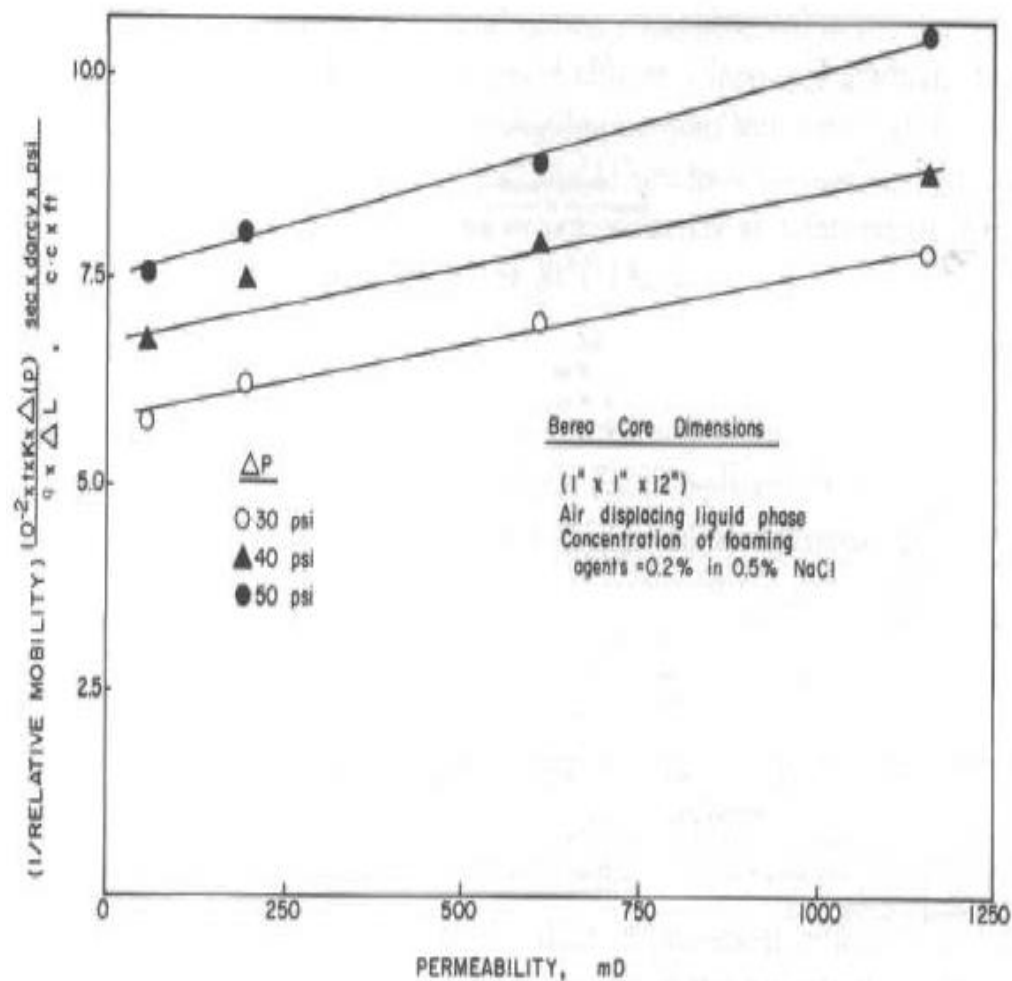
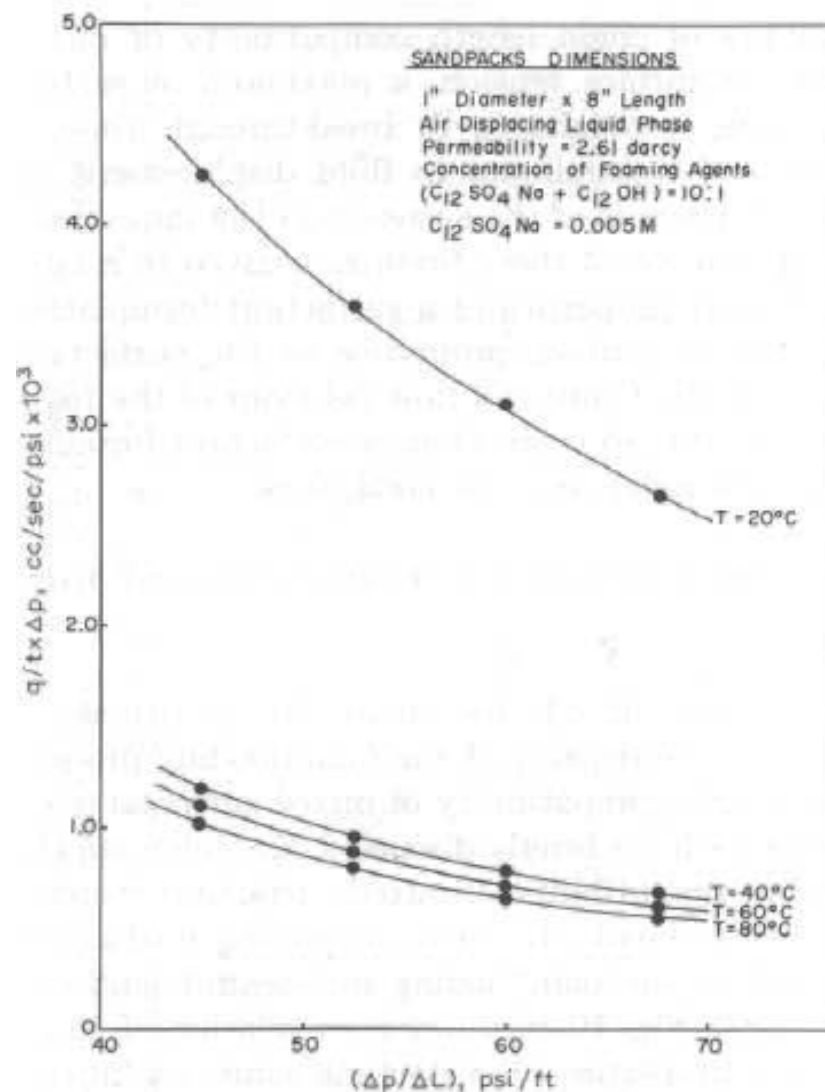Fig. 10-34. Effect of the permeability of porous media on relative air mobility at different pressure drops ($\Delta p$).



Fig. 10-35. Effect of pressure gradient ($\Delta p/\Delta L$) on effective air mobility at different temperatures

## MECHANISM OF SURFACTANT LOSS IN POROUS MEDIA:

➤ Success or failure of various oil recovery process which use surfactant injection depends on the degree of retention of surfactants during the course of flooding. The following is a brief description several mechanisms responsible for loss of surfactants in porous media.

### Surfactant adsorption:

• In the surfactant flooding process, as the surfactant slug comes into contact with the reservoir rock and brine, there would be a loss of surfactant due to adsorption at solid-liquid interface. Only part of the total surfactant injected in the reservoir, is available for oil displacement.

### Surfactant precipitation:

• During surfactant flooding, the surfactant slug may contact both the connate water & injected water. The presence of divalent cations in connate water may result in precipitation of the surfactant. Their presence may also alter the oil-surfactant solution IFT due to the difference in ionic content between the injected water and connate water.

### Surfactant degradation:

• Thermal stability of surfactants at reservoir temps is required for efficient oil displacement. Thermal degradation of a sulfonate in aq media can be explained by equilibrium hydrolytic reactions. The surfactants were found to be effective even after heating at $200^0C$ for 24 hrs.

**Surfactant- polymer mixing:**

- The loss of surfactants is the major which determines the optimum volume of the expensive micellar fluid required to displace residual oil. Several micellar fluids are not compatible with the polymer from the mobility buffer bank. This surfactant loss reduces oil DE & increases chemical requirements.

**Surfactant partitioning in residual oil phase:**

- The mechanisms of producing ultra-low IFT between brine & oil phase is the equal partitioning of surfactant with the brine & oil phase. If the IFT is sufficiently high, oil phase trapping occurs in porous media, which also causes surfactant loss due to its partitioning in oil.

**PRESENT STATUS OF THE USE OF SURFACTANTS IN OIL RECOVERY:**

- These EOR flooding processes have developed slowly so far because of associated high risks, high costs, complicated technology. In US, active projects involving surfactant injection had been started from 1977 onwards and increased to many fold.

- At present, all of these processes are complicated and are not well understood.

- The state of the art in the use of surfactants in light & heavy oil recovery is at the research stage so far. New developments & improvements are required for theses processes to become economically feasible.