Drilling Fluids

in most cases = drilling mud, i.e.
an emulsion O/W or W/O
+ a suspension
+ sometimes a foam

Drilling Fluids should ...
- Cool and lubricate the drilling bit
- Take away suspended cuttings
- Counter-pressure & anti-filtration effects

Emulsion structure
- provides “initial” viscosity
- dissolves various kinds of additives ...
  - salts, surfactants, polymers, etc
- suspends particles
- should be stable
- should exhibit a non-newtonian rheology

Drilling Fluids

(O/W or W/O emulsion morphology)

contain:
- water (cools, dissolves and suspends things)
- oil (suspends, lubricates, facilitates drilling)
- clays (viscosity, rheology)
- solid particles to increase density
- surfactants (dispersants, emulsifiers)
- polymers (filtration control, rheology)
- etc...

Physico-chemical Formulation
Phase Behavior versus Formulation
- Attainment of a microemulsion single phase
- Improvement of solubilization
- Additional issues

Available know-how in transforming an emulsified drilling fluid to be removed from unwanted location into a low-viscosity single phase system

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Shear thinning Rheology

- Very fluid at high shear in nozzle

- Plastic fluid

- Better cleaning near wall! Reduces caking!

- Newtonian fluid

Emulsion Models

- Bingham: yield stress, then Newtonian

- Herschel-Bulkley: yield stress, then power law

Shear thinning behavior of emulsions and suspensions

- Orientation, deformation and aggregation issues

- Quiescent state (no motion)

- Flow in direction

- Deflocculation

- Thixotropy

Amphiphilic Polymers (viscosity control)

- Polysacharides, polyacrylamides

- Special polymers

- Hydrophobically modified

- Interactions with surfactants

Cake forming (for filtration control)

- Natural polymer (xanthane, starch, gums)

- Natural modified polymer (CMC, HEC)

- Synthetic copolymers, custom-made polymers, organophilic clays

- Synthetic (part. hydrolyzed polyacrylamide)

- Eventually + complex surfactants

- Cover particles

- Link particles

- Gelify water or oil

Amphiphilic Polymers (for filtration control)

- Colloidal protectors "polymerize" the cake

- (lateral interactions)

- Clay or other solids

- Polymer and/or surfactant
Amphiphilic Polymers  
(for filtration control)

- Gelify the water contained in W/O cake
- PEG

Filtration of drilling fluid results in
- Cake deposit on wall (external filter cake)
- Penetration in porous medium (internal)

Increasing the internal phase ratio in emulsions and suspensions increases viscosity

Consequence

Filtration of drilling fluid results in increasing the internal phase ratio in
- External Filter Cake on wall
- Internal Filter Cake (plug inside porous medium)

Both phenomena reduce the relative permeability for oil production ! = damage

Solution

Concentrated emulsion/suspension must be removed as a low viscosity single phase that can be pumped out

Solids may be dissolved in oil or water

2 phase emulsion should become a single phase = microemulsion

Phase Behavior

Micellar solution or microemulsion

SOW systems
Phase Behavior Diagrams of Surfactant-Oil-Water Systems

Depends on the formulation, i.e. the nature of the species:
- Oil nature, i.e. ACN of alkane
- Water salinity, i.e. wt % NaCl
- Surfactant head group type
- Surfactant tail type and length
- Co-surfactant (e.g. alcohol)
- .......
- Temperature and Pressure

Actually many variables

- variables phase rule # of phases
- Formulation/temperature vs 1 variable (2D)
- Surfactant + oil + water = ternary ✓ 2 independent variables 2D diagram
- Surfactant+alcohol+oil+water = quaternary ✓ 3 independent variables 3D diagram

pseudocomponents required in real cases

SOW 3 D Diagrams >>> 2 D Cuts

We will only deal with: SOW Ternary Diagram

Formulation Scan
phase behavior according to Winsor diagram type WI, WII, WIII

Surfactant Affinity Difference
SAD = µ*W - µ*O
(for instance for ionic systems)

SAD/RT = lnS - K ACN - f(A) + σ - a_T, ∆T ≥ 0

depends on all formulation variables
quantifies the formulation at interface
considerable reduction in number of degrees of freedom
Winsor’s Phase Behavior Types

- W I: SAD < 0, Surfactant prefers water
- W III: SAD = 0, Surfactant prefers a third phase (microemulsion)
- W II: SAD > 0, Surfactant prefers oil

**OPTIMUM FORMULATION**

W III Diagram

- Phase A is a bicontinuous microemulsion
- Phase B is a bicontinuous microemulsion

Bicontinuous Microemulsion

- S1 swollen micelle
- S2 swollen micelle

W III Diagram

Best performance in microemulsion

Zero average curvature Microemulsion

Shwartz surface

All phase diagrams contain a monophasic zone

- If a formulation variable is changed (along a Formulation scan)
  How does solubilization change?

Bourrel M., Schechter R. S., Microemulsions and Related Systems, Marcel Dekker, New York 1988
The “height” of polyphasic zone (amount of surfactant+alcohol) S+A at fixed oil/water composition (e.g. 50/50) is monitored. The lowest “height” = maximum solubilization at optimum formulation.

Normal Case (Winsor type phase behavior)

The aspect of these diagrams changes with formulation:
- surfactant type,
- alcohol/surfactant mixture
- salinity
- temperature
- etc...

Effect of salinity on the pseudoternary diagram: toluene (T), active mixture AM (Butanol/SDS), Water (W).

Effect of active mixture composition on pseudoternary: toluene (T), 1.5% NaCl brine (W), active mixture (Butanol/SDS).

Beware

4 components = 3 D Diagrams

3 D Quaternary diagrams and pseudoternary 2 D cuts

With 4 components, Winsor's diagram pattern becomes approximate

Pseudoternary Cut Representation

S/A = 70/30

W/O

S/A = 65/35

W/O

S/A = 55/45

W/O

S/A = 50/50

W/O

S/A = 80/20

W/O

S/A = 75/25

W/O

R. E. Antón, Tesis MS UDO-ULA, 1981

With 4 components, Winsor's diagram pattern is sometimes completely wrong
(when a change in composition induces a change in formulation)

With 4 components, the path to reach the best monophasic system may be estimated by the arrow from the added formula to drilling fluid

Here the added formula contains the same WOR, but a hydrophilic surfactant mixture S2 that combines with the drilling fluid lipophilic surfactant S1

With 4 components, the path to reach the best monophasic system may be estimated by the arrow from the added formula to drilling fluid

Here a second injection after b1 or b2, from the easy to move 3 f system in (+)

by adding a third surfactant formula S3.

Here the S1-S2 + additives performance has been enhanced to get a region with less S2

system best change

With 4 components, Winsor's premise to improve the solubilization in microemulsion (1954)

(a) Best solubilization when R = AcylAcyl = 1
(b) Increase the surfactant head and tail sizes to increase interactions with both oil and water (at R=1)
(c) Limit when tail is too long > precipitation
(d) May go further with branching

(a)

(b)

(c)

Microemulsion single phase

W/O emulsion drilling fluid

W/O ratio constant

Injected formula

O/W ratio constant

S1

S1

S2

S2

S3

S3

O/W ratio constant

W/O ratio constant

(a)

(b)

(c)
Three more recent tendencies to improve the solubilization: inter-/intra-molecular mixtures

a) Inter-molecular mixture of hydrophilic+lipophilic surfactants
b) Addition of Lipophilic Linker (LL) and Hydrophilic Linker (HL)
c) Intra-molecular mixture in an extended surfactant

Some other features have to be taken into account:
- How to dissolve particles?
- How to adjust wettability?
- How to handle the process?
- How about using a $3\psi$ behavior?
- How about having a nanoemulsion? etc...

How to dissolve solid particles?
- Some particles like CaCO$_3$ may be dissolved in acid pH.
- Many surfactants are not sensitive to weak or strong acid, particularly salts of strong acids (sulfonates) or glucosides. However some are sensitive, like sulfates (that hydrolyse)
- Other substances precipitated as Ca$^{2+}$ or Mg$^{2+}$ salts may be dissolved in water by a chelating agents like EDTA, NTA etc
- In practice not all the particle have to be dissolved... If a substantial part is dissolved the decrease of the internal phase ratio lowers the viscosity and the rest may be dragged away.

How to adjust wettability?
- Wettability depends on the surface state of a solid (particles and porous medium), particularly the surfactants adsorption.
- Particle wettability alters the "Pickering" emulsion stabilization, and could produce very stable suspensions.
- Wettability is (partially) related to the formulation, and thus the use of SAD equation could help!

But wettability exhibits hysteresis Thus depends on the process

Typical Phase Behavior Study

Remediation Process of Formation Damage

Soaking with microemulsion "a la carte" formulated Microemulsions
See more details and references in the review to be published in *Energy & Fuel*.