Molecular dynamics of surfactants at fluid-fluid interface.

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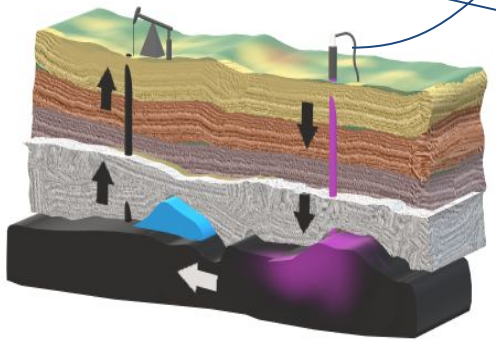
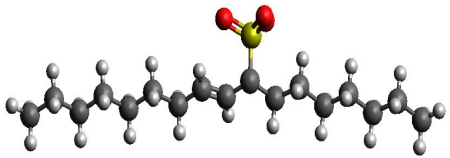
Outline

- **INTRODUCTION AND MOTIVATION**
  - Contextualization
  - Literature review
  - Surfactants
  - Phase diagrams of microemulsion
- **METHODOLOGY**
  - Molecular Dynamics
- **PARTIAL RESULTS**
  - One-Component Oil Interfaces with Surfactants
  - Multi-Component Oil Interfaces with Surfactants
- **NEXT STEP**

Contextualization





Secondary method

Primary method

EOR Method

Enhanced Oil Recovery

Thermal

Chemical

Gas

Surfactants

MD

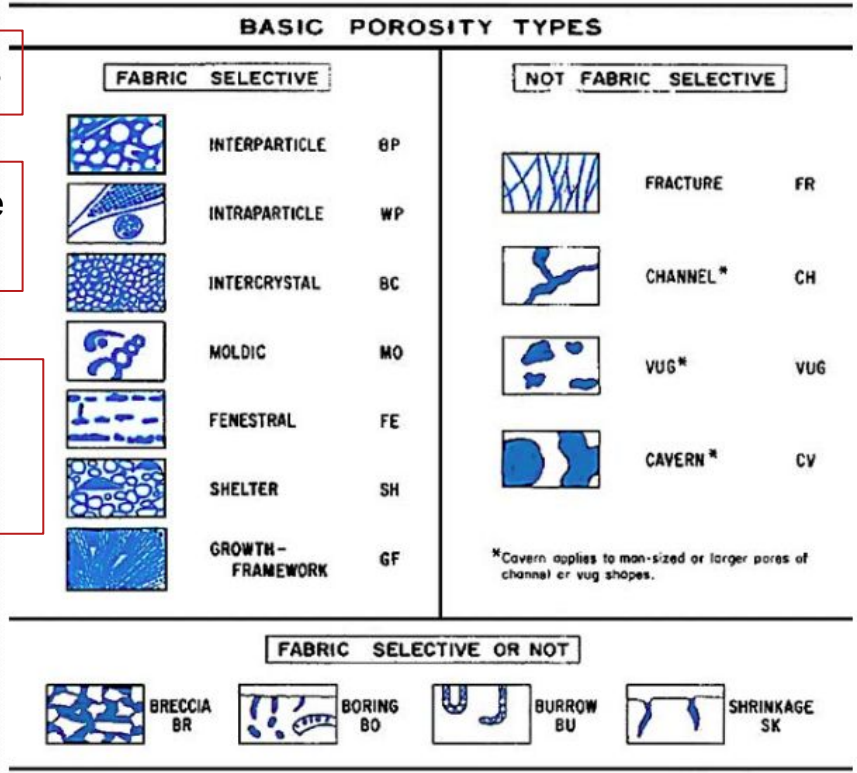
LITERATURE REVIEW(PRE-SALT)

Pre-salt → Section in Santos Basin → Carbonate rocks → calcite, dolomite and quartz. → Diversity of pore geometries in the carbonates

RESERVOIR

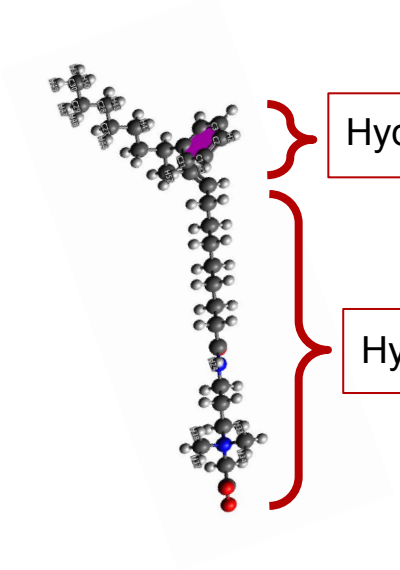
- ➔ Pore geometry:
- ➔ Geological mechanisms:
- ➔ Pressure and Temperature:
- ➔ Acid values (PH)

Direct influence on the fluid/fluid interface.



Vasquez, Guilherme, et al. "Petrogeophysics of the Brazilian pre-salt rocks." *SEG International Exposition and Annual Meeting*. OnePetro, 2019.

Surfactants

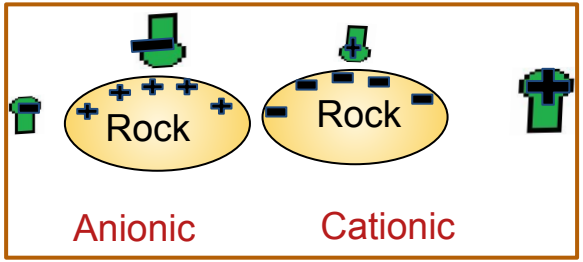


Hydrophilic head

Hydrophobic tails

Surfactant Familie

- Anionic:
- Zwitterionic:
- Cationic:
- Non-ionic:



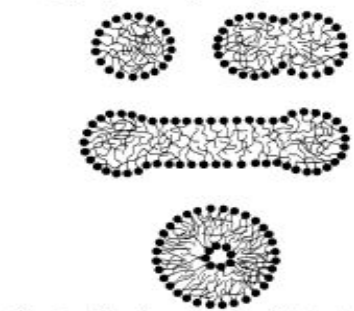
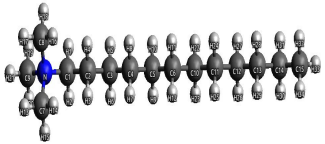


Figure 1. Schematic representation of the structures of surfactant aggregates in dilute aqueous solutions. Shown are aggregates that are spherical, globular, and spherocylindrical micelles and spherical bilayer vesicles.

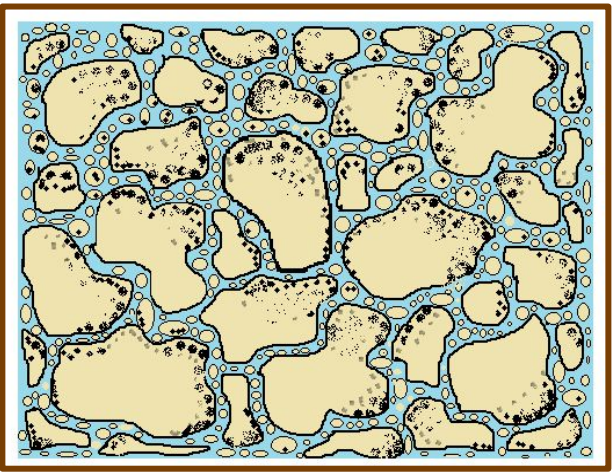
DODECYL TRIMETHYL AMMONIUM BROMIDE (DTAB)

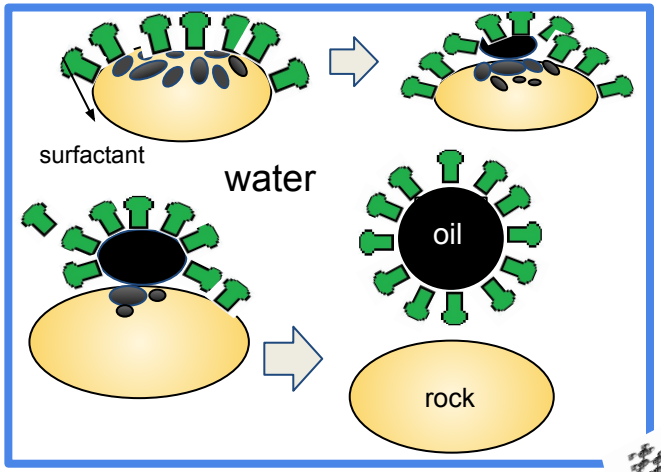


NAGARAJAN, R.; RUCKENSTEIN, E. Theory of surfactant self-assembly: a predictive molecular thermodynamic approach. **Langmuir**, v. 7, n. 12, p. 2934-2969, 1991.

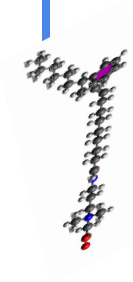
Exploring phase diagrams of microemulsion systems

- **Transition of Winsor:**





Solubilization, Emulsification, and Roll-up



Hydrophilic head

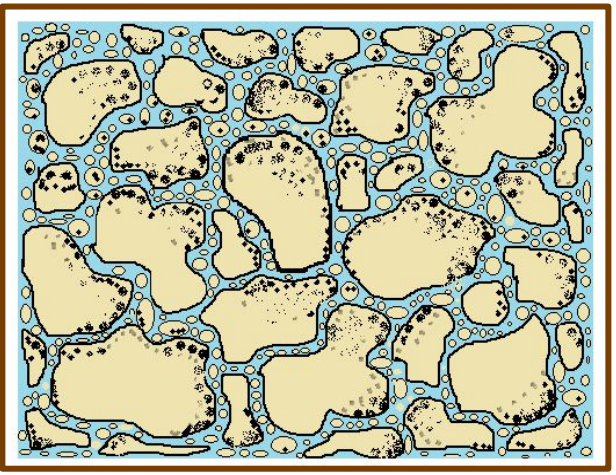
Hydrophobic tails

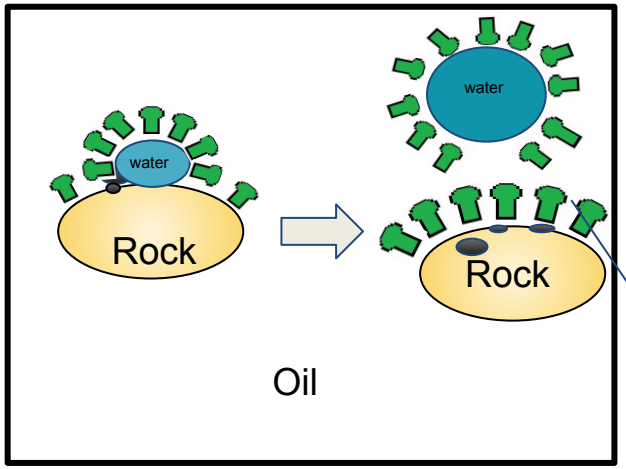
Oil/water microemulsion

positive curvature

Exploring phase diagrams of microemulsion systems

- **Transition of Winsor:**





Water/oil microemulsion

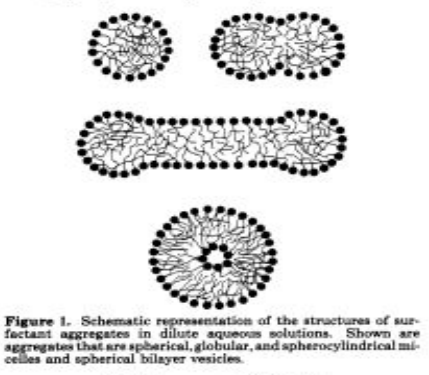
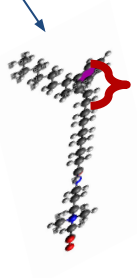


Figure 1. Schematic representation of the structures of surfactant aggregates in dilute aqueous solutions. Shown are aggregates that are spherical, globular, and spherocylindrical micelles and spherical bilayer vesicles.



Hydrophilic head

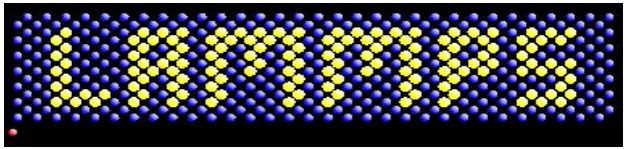
Hydrophobic tails

negative curvature

Methodology

Molecular Dynamics

- Surfactants Dodecyl box



- CGenFF CHARMM General Force Field and SPCE.

INTERFACES

- Surfactant/Water
- Surfactant/Brine
- Surfactant-Brine/Heptane
- Surfactant-Brine/Toluene
- Surfactant-Brine/Heptol

$$U = \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi [1 + \cos(n\phi - \delta)] + \sum_{\text{impropers}} k_\omega (\omega - \omega_0)^2 + \sum_{\text{Urey-Bradley}} k_u (u - u_0)^2 + \sum_{\text{nonbonded}} \epsilon \left[\left(\frac{R_{\min_{ij}}}{r_{ij}} \right)^{12} - \left(\frac{R_{\min_{ij}}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{\epsilon r_{ij}}$$

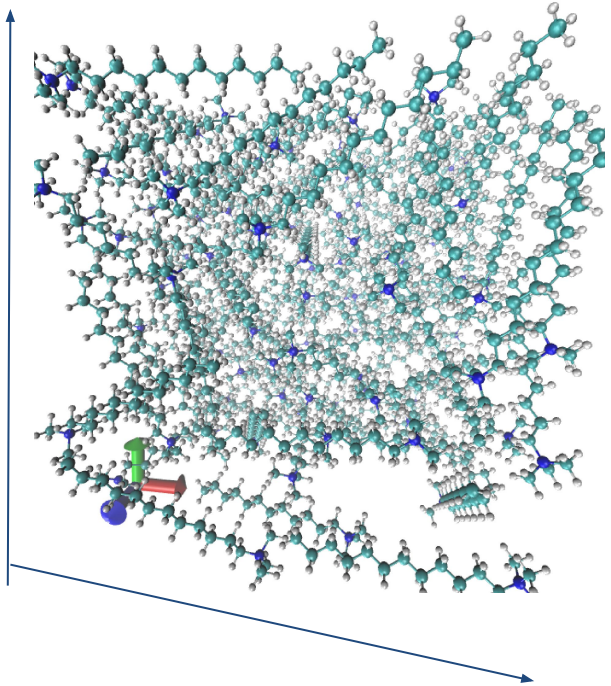
$$\mathrm{F}_i = -\nabla U(\mathrm{r}) = -\sum_{j \neq i}^{N} \frac{\partial u(r_{ij})}{\partial r_{ij}} \hat{\mathrm{r}}_{ij}$$

Partial Results

Computational Details

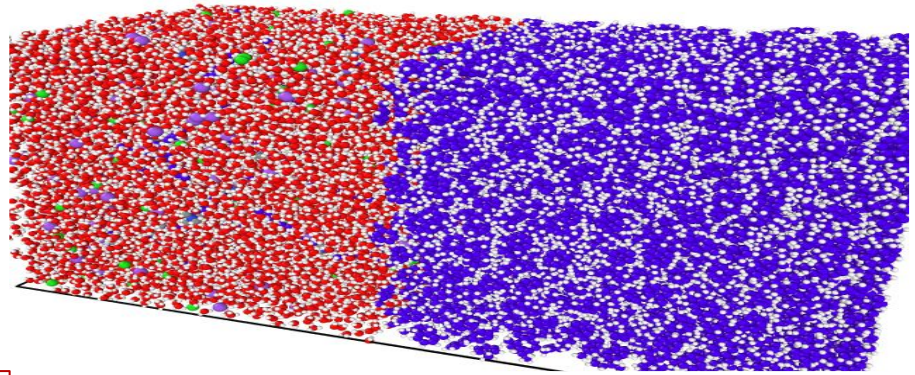
- Thermostat: Nosé-Hoover
- LJ cutoff : 8,5Å e 10,0Å
- Integrator: 0.5 fs time step
- PPPM 10,0Å
- Ensemble: NVT, NPT
- T = 300K and P = 1atm
- 100 molecules of the DTAB (N=1, H=34 E C=15)
- Tolerance 2.0

➔ 50 ps NVT
➔ 1 ns NVT
➔ 1 ns NPT
➔ 1 ns NPT

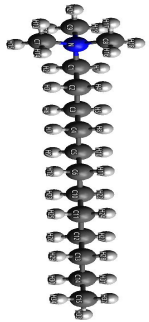


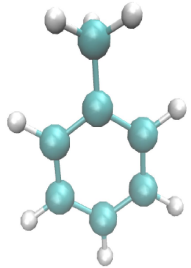
One-Component Oil Interfaces with Surfactants

- **70 x 140 x 70 Å**
- **5 τ % NaCl**
- **Toluene/Surfactant-Brine**
  → number 2.901 / 17.118



- ➔ 50 ps NVT
- ➔ 2 ns NPT
- ➔ 2 ns NVT structural property and dynamics
- ➔ 2 ns NPT to calculed IFT



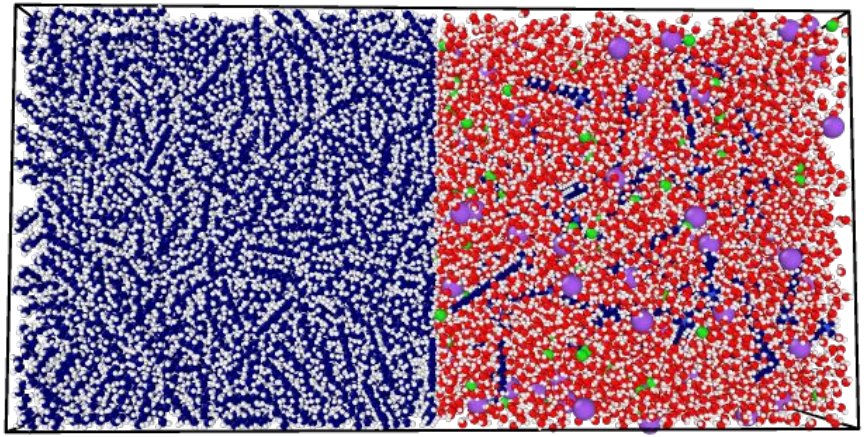


DTAB

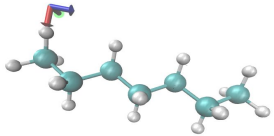
ρ = 0,8623 g/cm³

One-Component Oil Interfaces with Surfactants

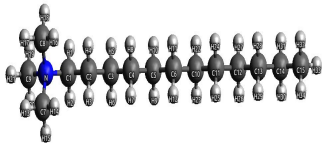
- **70 x 140 x 70 Å**
- **5 τ % NaCl**
- **Heptane/Surfactant-Brine**
  → number 2.089 / 11.468



- ➔ 50 ps NVT
- ➔ 2 ns NPT
- ➔ 2 ns NVT structural property and dynamics
- ➔ 2 ns NPT to calculed IFT



ρ = 0,6795 g/cm³

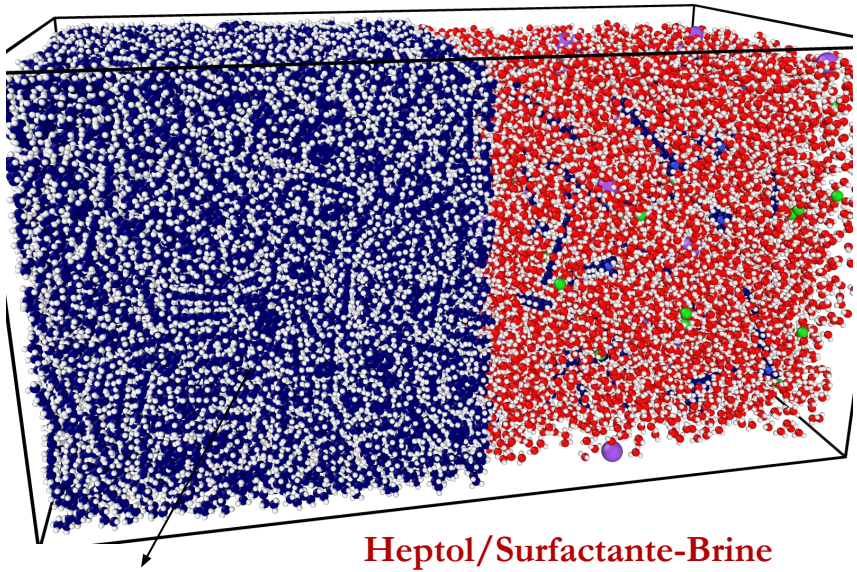


Heptane/Surfactante-Brine

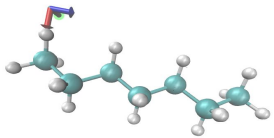
Multi-Component Oil Interfaces with Surfactants

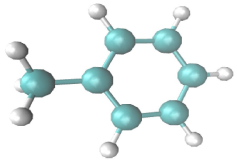
- 50 ps NVT
- 2 ns NPT
- 2 ns NVT structural property and dynamics
- 2 ns NPT to calculed IFT

- HEPTOL: 50% Heptane and 50% Toluene



Heptol/Surfactante-Brine



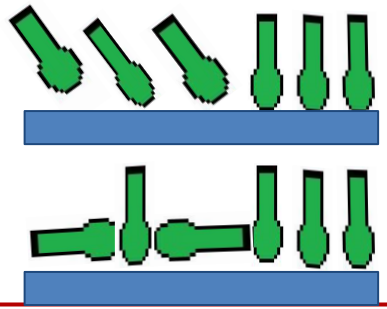


ρ = 0,6795 g/cm³

ρ = 0,8623 g/cm³

Next step

- Calculate the Tilt and Rotation Angle of Chain Molecules. (Surfactant Bilayers: Temperature-dependent tilt)
- Interfaces between multi-component oil and brine/surfactant.
- Oil model 8 and 36 components.
- CMC



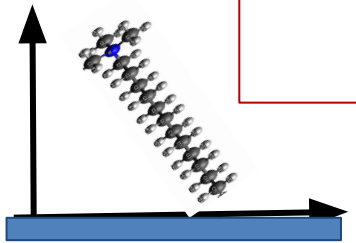


Tabela 6.3.1 – Valores de IFT das interfaces entre os modelos de cloretos e cada tipo de óleo, incluindo a água do mar. O erro padrão é de 0,2 mN/m

Salmoura	τ%	Médio	Leve	HepTol	Tolueno	Heptano
$CaCl_2$	1,0	49,7	50,2	45,3	41,4	51,7
	3,5	51,3	49,6	46,8	42,1	52,6
	5,0	51,5	51,2	45,5	42,7	51,2
$MgCl_2$	1,0	50,1	49,5	44,4	40,7	51,8
	3,5	51,0	49,3	45,1	41,2	51,5
	5,0	52,7	48,7	47,1	43,8	52,4
NaCl	1,0	49,3	49,9	44,3	41,9	51,8
	3,5	50,3	50,3	45,3	42,2	51,3
	5,0	50,3	50,7	45,9	41,6	51,5
KCl	1,0	50,5	48,6	43,4	40,9	51,5
	3,5	50,4	48,4	44,2	42,7	52,3
	5,0	50,2	48,9	45,6	41,1	51,5
Água do Mar	3,5	50,8	49,9	45,6	42,4	51,7

Components Oil models

Tabela 4.0.1 – Composição das moléculas para o modelo de óleo proposto neste trabalho.

Classe	Porcentagem (%)	Componentes
C_3	0,61	Propano
NC_4	0,32	Butano
IC_4	1,07	Isopropano
NC_5	0,82	Pentano
IC_5	1,46	Isobutano
C_6	3,17	Hexano, ciclohexano
C_7	5,78	Heptano, benzeno, cicloheptano, tolueno
C_8	7,45	Octano, ciclooctano, o-xileno, m-xileno, p-xileno
C_9	6,59	Nonano, 1,2,3-Trimetilbenzeno, 1,2,4-trimetilbenzeno, 1,3,5-trimetilbenzeno
C_{10}	6,03	Decano, naftaleno
C_{11}	4,94	Undecano
C_{12}	4,43	Dodecano
C_{13}	4,51	Tridecano
C_{14}	3,80	Tetradecano, antraceno, fenantreno
C_{15}	3,74	Pentadecano
C_{16}	2,86	Hexadecano, pireno
C_{17}	2,50	Heptadecano
C_{18}	2,67	Octadecano
C_{19}	2,38	Nonadecano
C_{20+}	34,88	Eicosano, benzopireno

Componente	Número de moléculas	$\rho_{calculado}$	ρ_{expt} [131]	Erro (%)
Hexano	2343	0,6436	0,6549	1,7
Heptano	2105	0,6704	0,6795	1,3
Octano	1885	0,6912	0,6984	1,0
Nonano	1718	0,7075	0,7142	0,9
Decano	1582	0,7226	0,7300	1,0
Undecano	1460	0,7328	0,7402	1,0
Dodecano	1357	0,7421	0,7495	1,0
Benzeno	3450	0,8513	0,8738	2,6
Tolueno	2902	0,8505	0,8623	1,4

CELASCHI,YURE M. **Modelagem de fenômenos interfaciais combinando simulações moleculares e aprendizado de máquina com aplicações em processos de recuperação de petróleo**. 2019. 174. Tese (Doutorado em Nanociências e Materiais Avançados) - Universidade Federal do ABC, São Paulo, 2019.

Gibbs free energy model

$$G_f = N_w \mu_w^o + N_{sA} \mu_{1A}^o + N_{sB} \mu_{1B}^o + \sum_{g=2}^{\infty} N_g g \Delta\mu_g^0$$

$$g\Delta\mu_g^o = \mu_g^o - g_A \mu_{1A}^o - g_B \mu_{1B}^o .$$

$$G_m = kT\left[N_w \ln X_w + N_{1A} \ln X_{1A} + N_{1B} \ln X_{1B} + \sum_{g=2}^{\infty} N_g \ln X_g \right]$$

$$G' = G - N_w \mu_w^o - N_{sA} \mu_{1A}^o - N_{sB} \mu_{1B}^o$$

$$= \sum_{g=2}^{\infty} N_g g \Delta\mu_g^0 + kT\left[N_w \ln X_w + N_{1A} \ln X_{1A} + N_{1B} \ln X_{1B} + \sum_{g=2}^{\infty} N_g \ln X_g \right]$$

$$\frac{G'}{kT} = \sum_{g=2}^{\infty} N_g g \frac{\Delta\mu_g^0}{kT} + N_w \ln X_w + N_{1A} \ln X_{1A} + N_{1B} \ln X_{1B} + \sum_{g=2}^{\infty} N_g \ln X_g$$

NAGARAJAN, R.; RUCKENSTEIN, E. Theory of surfactant self-assembly: a predictive molecular thermodynamic approach. **Langmuir**, v. 7, n. 12, p. 2934-2969, 1991.

Free energy of formation of the aggregate-water core interface.

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_{\text{int}} = \frac{\sigma_{agg}}{kT}\left(a - \alpha_{gA}a_{oA} - \alpha_{gB}a_{oB}\right)$$

Aggregate-water core interfacial tension.

$$\sigma_{tail} = 35{,}0 - 325M^{-2/3} - 0{,}098(T - 298)$$

$$\sigma_w = 72{,}0 - 0{,}16(T - 298)$$

$$\sigma_{agg} = \sigma_{tail} + \sigma_w - 2\sqrt{\sigma_{tail}\sigma_w}$$

Hydrocarbon surface tension

NAGARAJAN, R.; RUCKENSTEIN, E. Theory of surfactant self-assembly: a predictive molecular thermodynamic approach. **Langmuir**, v. 7, n. 12, p. 2934-2969, 1991.

Acknowledgments

Cluster
Josephson

IFUSP
Instituto de Física da USP

equinor

sampa

CNPq
Conselho Nacional de Desenvolvimento
Científico e Tecnológico

Thank you for your attention