

# Evaluation of the Foamability Potential of a Novel Biosurfactant Using the Solution to Advective-Diffusive Transport Model in Porous Media With a Linear Adsorption Trend

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Received: April 5, 2018 Accepted: April 26, 2018 Online Published: April 27, 2018

doi:10.5539/ijc.v10n2p56

URL: <https://doi.org/10.5539/ijc.v10n2p56>

## Abstract

While geological sequestration of anthropogenic carbon dioxide is a technically and economically viable option for reducing emissions to the level required to avoid the predicted 2 degrees Celsius increase of atmospheric temperature by the end of this century, efficient sequestration planning is vital for the achievement of this goal.

The petroleum industry has used conventional surfactants in enhance oil recovery projects aimed at prolonging the life span of a field, thereby increasing ultimate reserves. Notable among these is the use of surfactants for injected gas relative mobility control. Therefore, the potential for carbon dioxide mobility control in saline aquifers using surfactant alternating gas injection is huge, given the rich experience that can be tapped from the petroleum industry practice.

Considering the expected surfactant loses in surfactant-enhanced geological sequestration similar to that encountered in the petroleum industry, this paper has used the analytical solution to advective diffusive equation that exists in the literature with a linear adsorption model where, adsorption has been used to predict trends in minimum pressure drop required for foam generation. The greatest utility of this work lies in the fact that the analytical solution is related a linear adsorption model related to a novel surfactant found from biological and hydrocarbon sources of geologic origin. This paper, therefore, extends the work of linear adsorption models for this novel surfactant aimed at exploring improved oil recovery potentials; in addition to exploring its potential for efficient geological carbon storage in saline aquifers.

**Keywords:** surfactant, dispersivity, advective, linear model, adsorption

## 1. Introduction

The exponential trend in energy consumption both at domestic and industrial levels since the industrial revolution has resulted in unprecedented release of anthropogenic carbon dioxide into the atmosphere. Evidence abounds that the pre-industrial level concentration of carbon dioxide 280 ppm (Monroe, 2013) has increased to current a current concentration of 370 moles per liter with a projected increase to a level of 600 moles/L this century (Ziska & Caulfield, 2000). Carbon concentration in the atmosphere is believed to be increasing at a rate of 2-3 ppm/yr meaning the critical value will be reached about 30 years from year 2007. (Global Warming, 2009) The effect of this dramatic increase in carbon dioxide concentration, which is a greenhouse gas is seen in the form of eminent global warming (Solomon *et al.*, 209).

Considering the exponential trend in carbon dioxide emission, the prime goal of geological sequestration is to enhance volumetric sweep efficiency (Verma, 2015), which is defined as the fraction of subsurface pore volume that is occupied by injected carbon dioxide at abandonment. To achieve this goal, higher sweep efficiencies during gas injection must be emphasized. The industry with the greatest experience in subsurface fluid injection is the petroleum industry, which has implemented surfactant enhanced oil recovery schemes since the beginning of the petroleum industry. Quite recently, Vitoonkijvanich *et al.*, (2015), studied surfactant enhanced geological carbon storage using stream tubes. Hirasaki *et al.* (1977) (Hirasaki, Szafranski, Miller, & Wade, 1977) also studied surfactant enhanced remediation of aquifers with dense non-aqueous phase fluids. In all cases, the researchers arrived at the conclusion that surfactant enhanced injection can significantly increase storage efficiency.

In the surfactant enhanced geological storage, surfactants are used to generate foam to improve injected gas relative mobility leading to improved gas injection sweep efficiency. In the water-gas alternating scheme (Zekri *et al.*, 2011), a surfactant solution can be injected to sweep the original brine in the aquifer. This injection can be achieved at higher sweep efficiency due to miscible injection (Aghdam *et al.*, 2013). During the gas injection stage, the presence of surfactant solution in the aquifer will result in foam generation, which increases injected gas dynamic viscosity to improve sweep efficiency. However, in the application of foam enhanced oil recovery, the experience gathered by researchers is that below the critical surfactant concentration no foam will be generated (Vitoonkijvanich *et al.*, 2015). Also, a minimum pressure drop is required to cause foam generation and mobilization in porous media (Frank, *et al.*, 1985). This minimum pressure drop is linked to the interfacial tension between injected gas and surfactant solution.

However, while surfactants have proven to be vital to enhanced oil recovery, one fundamental problem related to their field applications is their adsorption on rock minerals, which constitutes a huge loss to the petroleum industry (Gogoi, 2011). Consequently, immense research efforts to understand the kinetics of adsorption (Gandomkar & Kharrat, 2013) coupled with advanced mathematical modeling of fluid flow in porous media has resulted in the availability of several adsorption models (Kwok *et al.*, 1995) in addition to models of dispersive and advective flow in porous media. The latter models integrate adsorption models to describe the evolution of surfactant concentration in porous media with a fundamental parameter called the retardation (Cameron, 1977).

The petroleum industry is used to using conventional surfactant for tertiary oil recovery projects (Schramm L., 2009). However, recent studies have evaluated the potential of a biosurfactant, Ziziphus Christis, which is also found in oil reservoir for enhanced oil recovery projects (Safian-Boldaji *et al.*, 2013). The motivation for these studies stems from the fact that these surfactants are naturally available and can be extracted for commercial purposes. Considering the availability of the above mentioned valuable mathematical resources, it is my assertion that since the minimum pressure drop is linked to interfacial tension, which in turn is linked to surfactant concentration, the analytical solution to a mathematical model that integrates the appropriate adsorption model can help predict the evolution of the minimum pressure drop required for foam generation in a porous medium. Consequently, the analytical solution to a mathematical model using adsorption kinetic parameters that describe the linear adsorption model where Ziziphus Christis is used for experiments will be an extension of the investigation of this surfactant not only for tertiary oil recovery projects but also for enhanced geological storage of anthropogenic carbon dioxide. This objective will be pursued in this paper.

## 2. Literature Review

### 2.1 Previous Researches in Geological Carbon Storage

Since the beginning of geological storage research activities several researches have been done to understand how efficient a commercial or large-scale project can be embarked upon. Famous among these researches are those related to relative permeability (Chen *et al.*, 2014; Muller, 2011), convective transport of injected carbon dioxide (Sun *et al.*, 2015), wettability changes associated with carbon dioxide injection into saline aquifers (Kim *et al.* 2012; Farokpoor *et al.*, 2013), convective instability (Lindeberg & Wessel-Berg, 1997) and supercritical carbon dioxide interfacial tension variation with salinity, temperature and pressure (Bachu & Bennion, 2002), interfacial Tension between CO<sub>2</sub>, Freshwater, and Brine in the Range of Pressure from (2 to 27) MPa, Temperature from (20 to 125) °C, and Water Salinity from (0 to 334 000) mg·L<sup>-1</sup>, 2009). In addition, researches aimed at understanding carbon dioxide solubility in saline aquifers under supercritical conditions (Pruess & García, 2002), which constitutes solubility trapping (Nghiem, *et al.*, 2009), has also been carried out. It is the view of the present paper that solubility trapping in saline aquifers, which is very essential for bulk carbon immobilization will be most successful following efficient displacement of formation brine and optimization of storage efficiency. To achieve this goal requires learning from the experience of the petroleum industry that has used foam enhanced gas flooding to improve oil recovery during tertiary oil recovery phases.

### 2.2 Physiochemical Processes Associated With Porous Media Fluid Transport With Adsorption

The integrated physiochemical processes of interest in this paper are advective dispersive and adsorption. Advective transport is the flow of a fluid in bulk while dispersion is the spreading of a substance in stream in a direction. The major causes of hydrodynamic dispersion are variation of flow velocity with pores and heterogeneities in the porous medium domain such as higher permeability zones. In this regard, the mechanical dispersion coefficient is defined as the product of Dispersivity, which is a length scale dependent (Peeters & Hofmann, 2015) and velocity. Generally, Dispersivity measures the spreading of a contaminant over a given length of flow and it is governed principally by the hydraulic properties of the porous system in addition to being the sum of molecular and mechanical dispersion. In flow systems with contaminant transport, the presence of dispersion causes the solute front to move faster than the case where advective transport alone was responsible for contaminant transport (Cheremisinoff, 2017). Molecular diffusion occurs due to variation in concentration gradient of species in the direction of flow.

Adsorption is a physiochemical process that is caused by van der Waal interaction (Chen & Al-Saidi, 2012) between a

solid surface and ions or molecules or by electrostatic attraction between an ion or a molecule and a solid surface. The electrostatic origin of adsorption is directly linked to the development of the electric double layer through ionization of surface functional groups at prevailing aqueous solution pH (Frank, *et al.*, 1985). Generally, adsorption of contaminants onto aquifer materials causes an imminent retardation or slowing relative to average interstitial or groundwater flow (Wexler, 1992), which has the potential to reduce water solubility of contaminants; in addition to controlling contaminant volatility (Patil & Chore, 2014) and biodegradability.

### 2.3 Global Availability of Biosurfactant (*Ziziphus Christis*) and Potential for Enhanced Oil Recovery Projects

In the application of surfactants to enhanced oil recovery in the petroleum industry, economic and environmental constraints must be met due to adsorption, proper interfacial tension reduction and oil recovery efficiency (Spildo *et al.*, 2012). The environmental aspect of the constraint, which emphasises on biodegradability of spent surfactant, has aroused interest in the use of biosurfactant. Consequently, Pordel *et al.*, (2012) investigated the use of extracted surfactant from *zyziphus spina christi* in oil recovery by means of Amott wettability index. In addition, core displacement tests have been performed to determine sweep efficiency of the extracted surfactant from leaves of *zyziphus spina christi* at different concentration (Zendehboudi *et al.*, 2103). Finally, they, Zendehboudi *et al.*, (2013), developed thermodynamic modeling for the adsorption of mentioned surfactant onto carbonate rock surface. In addition to these cited works involving the use of biosurfactant, Rahmati *et al.*, (2015), have also investigated experimentally the effect of Natural Leaf-derived Surfactants on Wettability Alteration and interfacial tension reduction in water-oil system for enhanced oil recovery application

*Ziziphus* species (Rhamnaceae) occur in warm-temperate and sub-tropical regions around the world, and they are commonly used as herbs in folk medicine for the treatment of various diseases, such as digestive disorders, weakness, liver complaints, obesity, urinary problems, diabetes, skin infections, fever, diarrhea, and insomnia (Abdel-Zaher *et al.*, 2005). *Ziziphus Spina-Christi*, for instance, is a wild evergreen tree characterized by spiny branches and small orange fruits that is native to sub-tropical eastern Africa, the Middle East, and the Indian subcontinent, but also widespread in northwestern Africa. In the Middle Eastern regions, leaves of *Z. Spina-Christi* are harvested from the wild or from cultures and sold as herbal medicine. In Iran, the province of Khuzestan is known for the extensive cultivation of *Z. spina-christi*, and leaves are used in Iran as a natural detergent and shampoo due to the saponin content (Bozicevic *et al.*, 2017).

*Ziziphus Christis* also occurs in connection with oil deposits in Iran (Ahmadi & Shadizadeh, 2012)

### 2.3 Relevant Literature Based Models for the Present Work

In the petroleum industry, foam has been used for two primary purposes. They are, its used in connection with gas diversion or mobility control during gas injection for enhanced oil recovery (Gauglitz *et al.*, 2002) and its used for acid diversion in connection with matrix acidization in hydrocarbon well stimulation (Schramm, 1994; Terdre, 2003). In the former case, the generation of foam in oil reservoirs serve to alleviate the huge dynamic viscosity contrast between injected gas and resident oil, which is the principal cause of viscous fingering and viscous instability (Didier, 1992; Moortgat, 2016).

However, while surfactants have proved to be vital inputs in sustaining oil production beyond secondary water flooding schemes, one fundamental problem connected to their field applications is their adsorption on rock minerals, which constitutes a huge loss annual basis (Fabiola, *et al.*, 2007). Consequently, numerous researches designed to understand adsorption trends has led to models of adsorption isotherms, which seek to quantify surfactant adsorption as a function of concentration at a given temperature. In the literature, several adsorption isotherms have emerged, famous among which are the Freundlich model (Freundlich, 1906), Langmuir (Barati *et al.*, 2016), Temkin model (Temkin & Pyzhev, 1940) and the linear model (Ruthven, 1982). Apart from these, there is the general model that gives isotherms of different shapes depending on the values of the parameters of the model (Li *et al.*, 2016). The linear model, which is similar to Henry's law is given as (Ruthven, 1982):

$$\Gamma = K_H C \quad (1)$$

Where:

$\Gamma$  = Amount absorbed in mg/gm of rock

$K_H$  = A constant of the linear isotherm-L/m<sup>2</sup>

$C$  = Concentration of surfactant in the aqueous phase-?

While research has been going on to understand surfactant adsorption, the conditions under which foam generation and mobilization will occur in porous media has also received a great deal of attention. Consequently, there is a consensus

among researchers that there is minimum pressure drop required for foam generation (Gauglitz *et al.*, 2002; Chena *et al.*, 2005; Barati *et al.*, 2016). This minimum pressure drop is linked to the petrophysical properties of the porous medium as (Gauglitz *et al.*, 2002):

$$\Delta P^{\min} = \frac{2\sigma}{L} \sqrt{\frac{\phi}{K}} \quad (2)$$

Where:

$\Delta P^{\min}$  = Minimum pressure drop required for foam generation-Pa

$\sigma$  = Interfacial tension between gas and brine N/m

$K$  = Absolute permeability of porous sample- $m^2$

$\phi$  = Porosity-fraction

In the petroleum and chemical engineering industries, the concentration dependence of surface tension regarding surfactants concentration has been studied (Eastoe & Dalton, 2000). The dependence of surfactant solution surface tension on adsorption is given as (Vizquez *et al.*, 1997):

$$\sigma - \sigma_0 = RT\Gamma^\infty \ln\left(1 - \frac{\Gamma}{\Gamma^\infty}\right) \quad (3)$$

Where:

$\sigma$  = Surface tension of surfactant solution- mN/m

$\sigma_0$  = Initial value of surface tension- mN/m

$R$  = Universal value of surface tension

$T$  = Absolute temperature

$\Gamma$  = Adsorption-mols/ $m^2$

$\Gamma^\infty$  = Equilibrium adsorption-mols/ $m^2$

Under transient conditions, the surface tension is given as:

$$\frac{\sigma - \sigma_e}{\sigma_0 - \sigma_e} = \exp\left(-bt^{\frac{1}{2}}\right) \quad (4)$$

Where:

$\sigma_e$  = Equilibrium value of surface tension-mN/m

$b$  = Concentration dependent constant

$t$  = Time-min

For a two-component system, the relationship between surface tension and excess adsorption at a given temperature and pressure is given as (Gildnyi *et al.*, 1976):

$$\Gamma_{exc} = \frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln(a)} \right)_{TP} \quad (5)$$

Where:

$\Gamma_{exc}$  = Excess adsorption and at the interface over what will prevail assuming the bulk concentration continued to the interface-moles  $m^2$

$R$  = Universal gas constant

$T$  = Absolute temperature-K

$a$  = Activity of surfactant

Equations (1), (3), (4) and (5) provide the opportunity to see a link among adsorption, surface tension and concentration while Eq. (2) links the minimum pressure drop to adsorption through the effect of surfactant adsorption on surface tension. Also, the minimum pressure drop equation is linked to interfacial tension. Therefore, any solution to a mathematical model that integrates adsorption model will provide the opportunity to link surfactant concentration to both the minimum pressure drop required for foam generation and the interfacial tension between carbon dioxide and surfactant solution. What is more, considering dynamic viscosity and surface tension dependence on solution components, Li *et al.*, (2016), used adsorption experiments to determine surface tension and dynamic viscosity dependence of surfactant solution. Thus, considering flow model being a function of space and time, the concentration of surfactant solution versus time and space can be linked to interfacial tension and to the minimum pressure drop for foam generation in a porous medium under surfactant enhanced geological carbon storage. The following section will be devoted to the required mathematical modeling for achieving this objective.

### 3. Mathematical Model

#### 3.1 Shell Mass Balance Approach

The saline aquifer under carbon dioxide injection is schematized in Fig. 1. The aquifer is assumed to have an infinite lateral extent with an infinite radius. It has a geological storage capacity measured by porosity  $\phi$  and an absolute permeability of  $K \text{ m}^2$ . The depth of storage is chosen to be greater than 800 m meters to ensure supercritical conditions of storage (Shariatipour *et al.*, 2012). In this geological storage projects, alternating surfactant solution and carbon dioxide injection would be assumed to be the most optimum strategy for enhancing gas injection sweep efficiency considering the relative mobility control aspect. For mass balance, a differential element of lateral extent,  $\Delta r$ , is considered. This element has a cross section area of  $A_c$ , normal to the flux of injection. In the petroleum engineering literature, linear horizontal flow (Al-Rbeawi & Tiab, 2014) for extensive reservoir have been used for analysis and this paper will endeavor to adopt this type of flow.

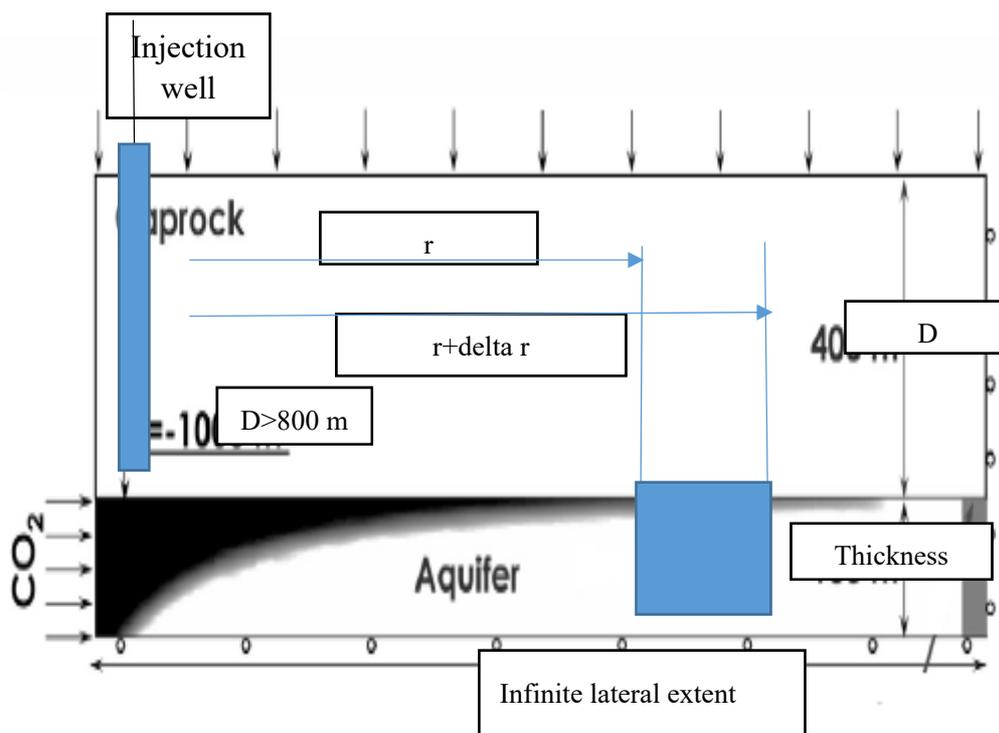


Figure 1. Schematics of Saline aquifer with differential element

The injector is first used to inject surfactant solution to displace formation brine. During the second phase, which is the gas injection phase, carbon dioxide will be injected to facilitate the generation of foam, which will improve the relative mobility of the injected gas. The volume of the differential element is calculated as:

$$V = 2\pi r H \Delta r \tag{6}$$

$A_c$  = Area opened to injection flux

$V$  = Volume of differential element

$\Delta r$  = Lateral extent of differential element

$H$  = Thickness of injection interval

### 3.2 Convective Diffusive Transport Modeling

In this mathematical formulation, a differential volume element of a saline aquifer at a depth typical of carbon sequestration is considered in relationship to the fundamental principle of mass balance. The following are the assumptions:

1. The aquifer is extensive and has a competent cap rock above the injection interval that has enough threshold capillary pressure to sustain the upward migration of injected gas
2. The principal hydraulic processes that control the transport of surfactant in the saline aquifer are advection and dispersion with surfactant adsorption being modeled by the linear adsorption theory
3. Injection of surfactant solution will precede that of gas to facilitate foam generation for gas relative mobility control

Base on the assumptions, the convective and diffusive terms, which constitute the mass flux of injected surfactant solution, are given as (See Figure 1):

$$qC - D\phi \frac{\partial C}{\partial r} \quad (7)$$

$$D_{eff} = D \frac{\phi}{\tau}, \quad q, C, \phi, D, D_{eff}, r, \tau$$

are flow rate, concentration of aqueous solution, porosity of aquifer formation, diffusion coefficient, effective diffusion coefficient radial distance and tortuosity respectively

$D$  = Diffusion in the absence of tortuosity factor- $m^2s^{-1}$

Consequently, the rate of mass entry into the differential volume element at the location,  $r$  is:

$$\left( qC - 2\pi r H D_{eff} \phi \frac{\partial C}{\partial r} \right)_r \quad (8)$$

Where:

The rate at which mass leaves the differential volume element at the exit is:

$$\left( qC - 2\pi r D \phi \frac{\partial C}{\partial r} \right)_{r+\Delta r} \quad (9)$$

$U \frac{\partial C}{\partial r}$  and  $-D_{eff} \frac{\partial C}{\partial r}$  are radial advective and diffusive fluxes respectively

$U$  is the superficial velocity of flow

The rate of mass accumulation in the differential element will be given by:

$$2\pi r H \Delta r \phi \frac{\Delta C}{\Delta t} \quad (10)$$

Where:

$H$  = Thickness of aquifer or injection interval

$H$  = Thickness of aquifer residual formation water saturation behind front-fraction

The application of the statement of mass balance, for diffusive-advective transport leads to the following:

$$\frac{2\pi H \left( rD \frac{\partial C}{\partial r} \right)_r - \pi H \left( rD \phi \frac{\partial C}{\partial r} \right)_{r+\Delta r}}{2\pi r \Delta r H} + \frac{qC|_r - qC|_{r+\Delta r}}{2\pi r H} = \phi \frac{\Delta C}{\Delta t} \quad (11)$$

Hence:

$$\phi \frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) - \frac{U}{r} \frac{\partial C}{\partial r} \quad (12)$$

Where:

$$U = \frac{q}{2\pi r H} \quad (13)$$

### 3.3 Adsorption Modeling

The volume of solid associated with solid in the differential element is given as

$$2\pi r H \Delta r (1 - \phi) \quad (14)$$

The mass of this element is:

$$2\pi r H \Delta r (1 - \phi) \rho_r \quad (15)$$

Where:

$\rho_r$  = Is the mean density of rock

The adsorption is measured as milligram of surfactant per gram of solid phase. Dividing the adsorption by density, therefore, gives surfactant adsorption per unit volume of solid phase. Thus:

$$\frac{S_m}{g_r} = \Gamma \quad (16)$$

$S_m$  = Mass of surfactant adsorbed on rock in the differential volume-milligram

$g_r$  = Weight of rock in the differential element-gram

$\Gamma$  = Weight of surfactant adsorbed per unit volume of rock-milligram per volume of rock

The rate of adsorption of surfactant becomes:

$$RSA = \frac{\partial \Gamma}{\partial t} \quad (17)$$

Where:

$RSA$  = Rate of surfactant adsorption-milligram per volume of rock per unit time

The complete mass balance consisting of transport and adsorption becomes: Solution Assumption.

$$\phi \frac{\partial C}{\partial t} + \frac{\partial \Gamma}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) - \frac{U}{r} \frac{\partial C}{\partial r} \quad (18)$$

### 3.4 Linear Flow Model

1. The aquifer is hydraulically extensive, meaning that the lateral extent is very big compared with the vertical thickness and this causes pressure gradients in the vertical direction to be negligible

2. Vertical flow is negligible
3. Dispersivity in the vertical direction is negligible
4. Geological sequestration of anthropogenic carbon dioxide will be confined to ultra-saline aquifers with hyper salinities

Fig. 2 shows a sketch of the stream lines for flow in the vicinity of a well bore. Based on this model of stream lines, which appear elliptical, a differential element for control volume analysis shows that a constant cross-sectional area of flux can be approximated. This causes the radial advective-dispersive equation to be reasonably approximated by a one dimensional of linear flow as (Chrysikopoulos *et al.*, 1990).

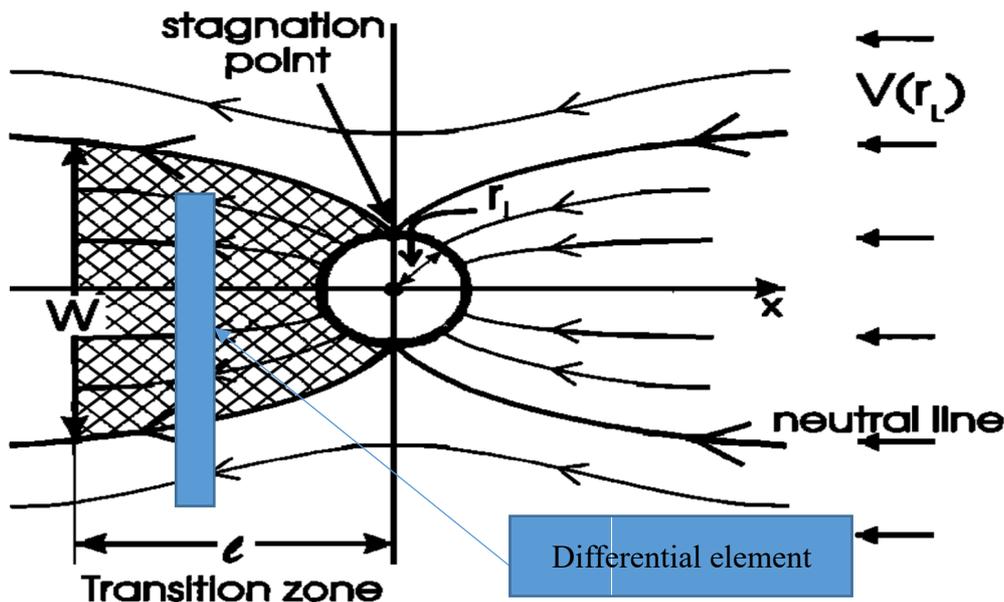


Figure 2. Schematic of linear model (Zlotnik & Logan, 1996)

In light of the flow schematics of Figure 2, a one-dimensional advective-diffusive transport with adsorption component has been mathematically described elsewhere (Lapidus & Amundson, 1952): The equivalent form of their equation can be written as:

$$\phi \frac{\partial C}{\partial t} + \frac{\partial \Gamma}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} \tag{19}$$

A linear isotherm under isotropic exchange conditions may be generally classified as either a reversible or irreversible reaction. The simplest form is the linear isotherm which represents an irreversible system trend described by the following model: (Ogata, 1964)

$$\frac{\partial \Gamma}{\partial t} = KC \tag{20}$$

Where:

$C$  = Liquid phase concentration equal to the concentration of surfactant-mass per unit volume

$\Gamma$  = Solid phase adsorption-mass per unit volume of solid

$K$  = A constant of the linear isotherm- $s^{-1}$

$$\phi \frac{\partial C}{\partial t} + KC = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} \tag{21}$$

Hence:

$$\frac{\partial C}{\partial t} + \frac{K}{\phi} C = \frac{D}{\phi} \frac{\partial^2 C}{\partial x^2} - \frac{U}{\phi} \frac{\partial C}{\partial x} \quad (22)$$

This is a second order linear partial differential equation.

#### 4. Analytical Solution

##### 4.1 Solution with Diffusion and Advective Transport

Equation (21) is a second order linear partial differential equation in light of the invoked linear adsorption model. The following are the boundary conditions for solution of the concentration evolution of surfactant in the saline aquifer:

$$\begin{aligned} C(0,t) &= C_0 \\ C(r,0) &= 0 \end{aligned} \quad (23)$$

$$C(\infty,t) = 0$$

The Laplace transform of Eq. (21) gives:

$$\frac{\phi}{D} \frac{\partial C}{\partial t} + \frac{K}{D} C = \frac{\partial^2 C}{\partial x^2} - \frac{U}{D} \frac{\partial C}{\partial x} \quad (24a)$$

$$\frac{d^2 C(s)}{dx^2} - \frac{U}{\phi} \frac{dC(s)}{dx} - \xi_s C(s) - \psi C(s) = 0 \quad (24b)$$

$$\frac{d^2 C(s)}{dx^2} - \lambda \frac{dC(s)}{dx} - (\xi_s + \psi) C(s) = 0 \quad (24c)$$

Where:

$s$  = Laplace transform variable

$$\lambda = \frac{U}{D}$$

$$\xi = \frac{\phi}{D}$$

$$\psi = \frac{K}{D}$$

The solution to this equation was given by Ogata and Banks (1961) as:

$$C(x,t) = J \frac{2}{\sqrt{\pi}} \exp(-\mu t) * \exp(\mu t) \frac{\sqrt{\pi}}{2} \left( \frac{1}{2} \right) \left[ \begin{aligned} & \exp \left\{ \frac{U}{2D} x [1 - (1 + \omega)^{1/2}] \right\} \operatorname{erfc} \left\{ \frac{x - Ut(1 + \omega)^{1/2}}{2\sqrt{Dt}} \right\} \\ & + \exp \left\{ \frac{Ux}{2D} [1 + (1 + \omega)^{1/2}] \right\} \operatorname{erfc} \left\{ \frac{x + Ut(1 + \omega)^{1/2}}{2\sqrt{Dt}} \right\} \end{aligned} \right] \quad (48a)$$

Substitution of J, after simplification of the quantity before the square bracket gives the final solution as:

$$\frac{C(x,t)}{C_o} = \left(\frac{1}{2}\right) \left[ \exp\left\{\frac{U}{2D}x[1-(1+\omega)^{1/2}]\right\} \operatorname{erfc}\left\{\frac{x-Ut(1+\omega)^{1/2}}{2\sqrt{Dt}}\right\} + \exp\left\{\frac{Ux}{2D}[1+(1+\omega)^{1/2}]\right\} \operatorname{erfc}\left\{\frac{x-Ut(1+\omega)^{1/2}}{2\sqrt{Dt}}\right\} \right] \quad (25)$$

Where:

$$\omega = \frac{4\phi KD}{U^2} \quad (26)$$

#### 4.2 Steady Solution

For steady state conditions, Eq. (24a) becomes:

$$\frac{D}{\phi} \frac{\partial^2 C}{\partial x^2} - \frac{U}{\phi} \frac{\partial C}{\partial x} - \frac{K}{\phi} C = 0 \quad (27)$$

Thus:

$$\omega \frac{d^2 C}{dx^2} - \Omega \frac{dC}{dx} - \delta C = 0 \quad (28)$$

$$\omega = \frac{D}{\phi}$$

$$\Omega = \frac{U}{\phi} \quad (29)$$

$$\delta = \frac{K}{\phi}$$

Using the characteristic equation involving the variable m, the solution is given as:

$$C(x) = A \exp\left(\frac{\Omega}{2\omega}x + \frac{x}{2}\sqrt{\frac{\Omega^2}{\omega^2} + 4\frac{\delta}{\omega}}\right) + B \exp\left(\frac{\Omega}{2\omega}x - \frac{x}{2}\sqrt{\frac{\Omega^2}{\omega^2} + 4\frac{\delta}{\omega}}\right) \quad (30)$$

Using a similar argument regarding the boundary condition Eq. (23c), the solution is given as:

$$C(x) = B \exp\left(\frac{\Omega}{2\omega}x - \frac{x}{2}\sqrt{\frac{\Omega^2}{\omega^2} + 4\frac{\delta}{\omega}}\right) \quad (31)$$

Hence:

$$C(x) = C_o \exp\left(\frac{\Omega}{2\omega}x - \frac{x}{2}\sqrt{\frac{\Omega^2}{\omega^2} + 4\frac{\delta}{\omega}}\right) \quad (32)$$

#### 4.3 Effect of Linear Adsorption Model on Minimum Pressure Drop Required for Foam Generation

Putting Eq. (2), Eq. (3), Eq. (5) and Eq. (25), it becomes easy to see the explicit dependence of the surface tension of surfactant solution on surfactant concentration and hence the dependence of the minimum pressure drop expressed by Eq. (2), on space and time in the aquifer domain during the surfactant solution injection phase.

### 5. Application of Analytical and Numerical solutions to Practical Field Problems

#### 5.1 Core Characteristics

The application of the analytical solution to a practical field problem depends on the availability of data regarding injection rate, surfactant diffusivity in brine, the linear adsorption constant and the petrophysical properties of the porous system, namely porosity and permeability. In this regard, Memon *et al.*, (2017), studied a new natural surfactant found in oil deposits in Iran. The following data can be extracted from their published work:

Table 1. Core and surfactant (Memon, Elraies, & Al-Mossawy, 2017)

Parameter	Value
Coe length -cm	7.66
Core diameter-cm	3.81
Injection rate of surfactant solution- $\text{cm}^3 \text{min}^{-1}$	0.24
Number of pore volumes of surfactant solution- $\text{cm}^3$	0.3
Permeability- mD	165
Porosity-fraction	0.19
Area of core- $\text{cm}^2$	11.34
Interfacial tension between injection water and 0.6% of AOS +0.6% LMDO surfactant formulation	1.24

#### 5.2 Parameters of the Linear Model

Mohsen *et al.*, (2013) also studied Zyziphus Spina Christi obtained from a biological source by hydro distillation of wild leaves. They conducted a static adsorption test based on an outcrop of sandstone samples. Appendix 3 shows their fitted graph to the linear model. Based on this appendix a maximum adsorption of 24 mg/gm of rock was obtained with a linear adsorption coefficient of  $0.199 \text{ Lm}^{-2}$  with regression coefficient of 0.978, which is quite satisfactory. Hence, to link surfactant concentration to interfacial tension and minimum pressure drop required for foam generation, the data of Memon *et al.*, (2017) and the linear adsorption model of Mohsen *et al.* (2013) with a maximum adsorption of 24 mg/gm will be integrated for computational purposes. In this regard, data on core dimensions and petrophysical properties will be taken from the former while data on adsorption characteristics will be taken from the latter. The motivation for this decision stems from the fact that petrographic examination of the core samples used by Mohsen *et al.*, (2013) shows abundance of quartz and dolomite minerals, which are similar to those of cores used by Memon *et al.*, (2017). A surfactant concentration of an initial surfactant concentration of 0.5 M, will be assumed for computation.

#### 5.3 Computation of Relevant Parameters

The final solution to the model equation (48b) contains parameters that deserve to be computed for theoretical testing. They are the following:

$U$  = The superficial velocity of fluid in porous media- $\text{ms}^{-1}$

$D$  = Dispersivity- $\text{m}^2\text{s}^{-1}$

#### 5.4 Choice of Dispersion Coefficient

Unfortunately, none of the literature sources from which the above data were taken has information about dispersivity. However, in the literature, two theoretical developments have appeared for predicting dispersion coefficient of porous media (Ramirez *et al.*, 1980). By modeling the rock as a bundle of parallel capillary tube, Taylor found the dispersion coefficient to be proportional to pore velocity to the second power (Taylor, 1953). Also, by modeling the rock as a series of connected mixing chambers of uniform size, Aris and Amundson (Aris & Amundson, 1957) found the dispersing coefficient to be proportional to pore velocity.

Ramirez, *et al.*, (1980), performed a single-phase tracer tests with Berea sandstone core samples with permeability 810 md and porosity 22%. They concluded from their experimental results that for flow rates in the range of  $10^{-3}$ - $10^{-1}$  cc per second, mechanical mixing effects are dominant and diffusive, or tortuosity effects are negligible. Appendix 1 shows their experimental results presented as dispersivity versus flow rate. The flow rate given in Table 1 corresponds to  $3.33 \times 10^{-3}$  cc per second. From Table 2, the porosity of 0.19 is quite closer to 22%. Based on Appendix 1, the dispersion coefficient in light of the given flow rate is  $4 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ . To test the suitability of Appendix 1 for the selection of dispersivity, a dispersion coefficient based on the conclusion of Aris and Amundson (1957) will be computed in the

following manner:

Step 1: Calculate the mean pore radius using Leveret approach Zhou *et al.*, (2012)

Step 2: Calculate the interstitial velocity as the ratio of superficial velocity to porosity

Step 3: Multiply interstitial velocity by mean pore radius to get mean dispersivity

In this regard, the constant of proportionality is assumed to be equal to the mean pore radius. The computed value of dispersivity is  $1.0 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ . This value is quite close to that predicted by Appendix 1

Table 2. Computations based on Literature data (Memon *et al.*, (2017))

rea-m <sup>2</sup>	
Bulk volume-m <sup>3</sup>	$8.7289 \times 10^{-5}$
Pore volume-m <sup>3</sup>	$1.658 \times 10^{-5}$
Number of pore volumes-	0.3
Number of pore volume injected	0.3
Flow rate-m <sup>3</sup> s <sup>-1</sup>	$4.0 \times 10^{-9}$
Total volume injected-m <sup>3</sup>	$4.975 \times 10^{-6}$
Time of injection-s	1243.84

### 5.5 Derivation of the Reaction Rate Constant

From the Linear Model of Memon *et al.*, (2017) the following can be written:

$$\Gamma = K * C \quad (33)$$

The linear model used in the derivation of Eq. (21) is:

$$\frac{d\Gamma}{dt} = KC \quad (34)$$

Where:

$\Gamma$  = Adsorption-moles per volume of rock

$K = \text{s}^{-1}$

$C$  = Concentration-moles per liter

This means dividing the right-hand side Eq. (33), which is in milligrams per gram of rock by the molecular weight of saponin, we get the number of moles of surfactant adsorbed. If this figure is further multiplied by the density of rock, we get the number of moles of surfactant adsorbed per unit volume of rock. This is the same as Eq. 20 and has concentration unit. If the result is divided by the time of surfactant injection, we get an equation that expresses that expresses rate of change of mass and or concentration. To carry out this calculation, the density of calcite was taken to be  $1271 \text{ kgm}^{-3}$ . The molecular weight of saponin was taken from the work of (Bozicevic *et al.*, 2017). The value is 943.54 g per mole with the following formula:



The result gives the Following Equation:

$$\Gamma = \frac{0.199 * 2710 * 10^{-3}}{1244} = 4.595 * 10^{-7} * C \quad (35)$$

Equation (55) gives the adsorption rate constant equal to  $4.595 \times 10^{-7} \text{ s}^{-1}$ , considering the linear adsorption model used for the derivation of the advective diffusive equation.

### 5.6 Computation of Other Hydraulic Parameters

Hydraulic parameters required for computations using Eq. (25) are the dispersivity, porosity, permeability and superficial velocity and the respective rations of parameters. Porosity and permeability are found in Tab.1. Dispersivity has already been determined using Appendix 1. Calculated parameters are found in appendix 2 (calculated parameters)

### 5.7 Derivation of Surface Tension versus Distance and Calculation of Minimum Pressure Drop Required for Foam Generation

To calculate the minimum pressure drop required for foam generation as given by Eq. (2), the effect of surfactant concentration on water or aqueous solution surface tension must be addressed. The solution to the problem requires calculation of the surface tension of surfactant solution as a function of surfactant concentration considering adsorption changes with distance.

Assuming an initial surfactant concentration of 0.5 M, the rigorous approach of Yu *et al.*, (2000) was employed to calculate the initial surface tension of surfactant solution. The value is  $0.052 \text{ mNm}^{-1}$ . Equation (55) was then used to calculate adsorption based on the linear model. Calculated adsorption in milligram per grams of rock was then used to calculate surface tension versus corresponding surfactant concentration. The equilibrium or maximum adsorption parameter of Ziziphus Christis found in Eq. (3) was taken from the experimental plots of Mohsen *et al.*, (2013) (See Appendix 3). Once surface tension of aqueous solution as a function of concentration and distance is known, calculation of the minimum pressure drop required for foam generation versus distance and time was achieved using Eq. (2).

### 5.8 Results and Discussion

In the literature, more complex adsorption models, notably the bilinear model have been used to predict adsorption in porous media (Gupta & Greenkorn, 1973). This paper adopts a rather simplified approach by invoking the linear model, since industrial experiences show that surfactants are generally employed at low concentrations for tertiary oil recovery projects (Rosen *et al.*, 1995). The basis for the application of the linear adsorption model parameters to the solution of the model differential equation under dynamic conditions in this paper is instant adsorption equilibrium. What is more, the dynamic adsorption capacity assumes that only that part of a bed that is called the Equilibrium Zone (EZ) is saturated while the part called the mass transfer zone is under saturated (GROUP, 2010) and this distinction applies mostly to gas adsorption. In the case of surfactant adsorption, the adsorbing phase is non-gaseous. On this note, the parameters of the static model must be similar to that of a dynamic adsorption experiment. In the application of the analytical solution, data from literature sources were chosen objectively and systematically. For instance, justifying the choice of the linear model, it is appropriate to mention the scholarly work of (Ogata, 1961) where the linear model related to adsorption was central to the technical work. What is more, the parameters of the linear model used in this paper were derived using samples of the geologic material. Generally, the degree of adsorption is determined from bench scale experiments consisting typically of mixing contaminant samples with aquifer or rock materials, and measuring adsorption thereof, based on standard procedures (Cheremisinoff, 2017). The literature-based chosen linear model for the present work, therefore, has a scientific validity. I assumed an initial concentration of surfactant solution to be 0.5 M.

Fig.3 shows transient state plots of surfactant concentration versus time for different times of injection of surfactant solution into the core sample. The plots reveal a general decrease of concentration with distance for all times of injection as well as a general increase of concentration with distance as time of injection progresses. During the transient state, the breakthrough time occurs after 4146.44 seconds.

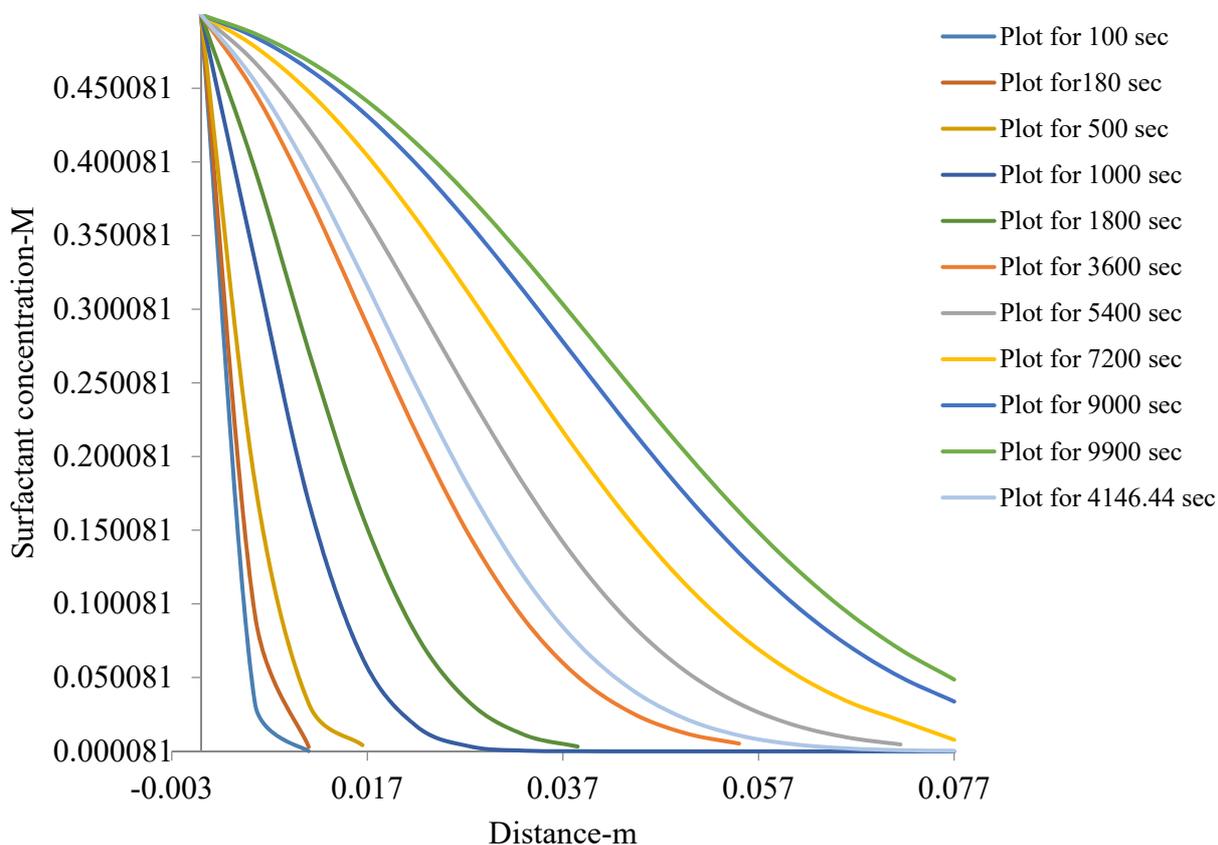


Figure 3. A plot of surfactant concentration versus distance along core

Fig. 4 shows a plot of surfactant concentration versus distance obtained from the solution of the differential equation for steady state conditions (Eq.54). The time steady occurs after 120 days of continuous injection.

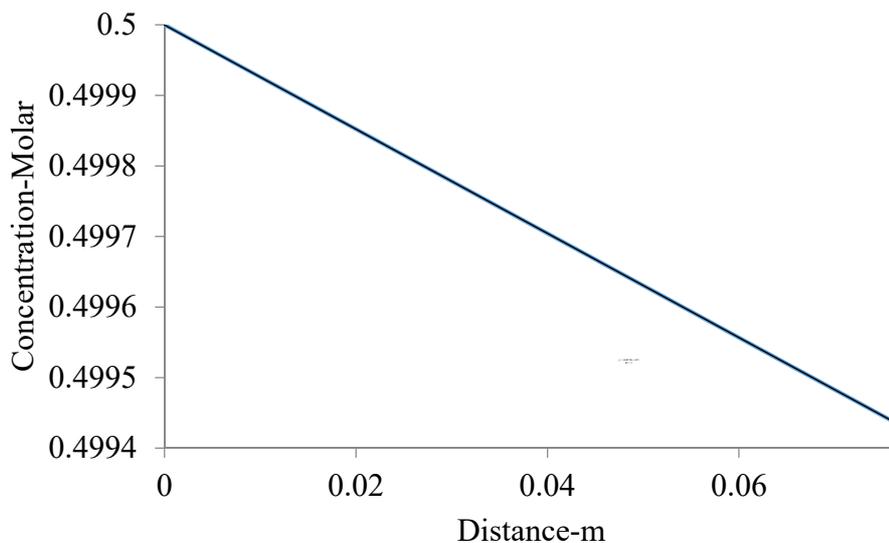


Figure 4. A plot of surfactant concentration versus distanced for steady state

Generally, the surface tension of brine will decrease with increasing surfactant concentration until the critical micelle concentration is reached (Anna *et al.*, 2012). This means as adsorption of surfactant occurs, the surface tension of aqueous solution will increase with distance from the point of injection. Within the frame work of intermolecular forces effect on interfacial tension (Oss *et al.*, 1988), an increase in surfactant surface tension with distance means an overall

increase in the interfacial tension between injected gas and resident aqueous solution of surfactant brine, following the initial stage of surfactant injection into the aquifer, porous system to displace resident formation brine. With a decrease in mean pore radius due to adsorption coating of pore walls (Renshaw *et al.*, 1997) and increase in interfacial tension with distance from the point of injection, the minimum pressure drop required for foam generation will increase with distance at all times of injection, including the steady state conditions. In all cases, a minimum value of the minimum pressure drop will be encountered at the point of injection while the maximum value will occur at the aquifer boundaries and this trend is clearly shown by Fig. 5, which shows a plot of surface tension versus distance at all times of injection.

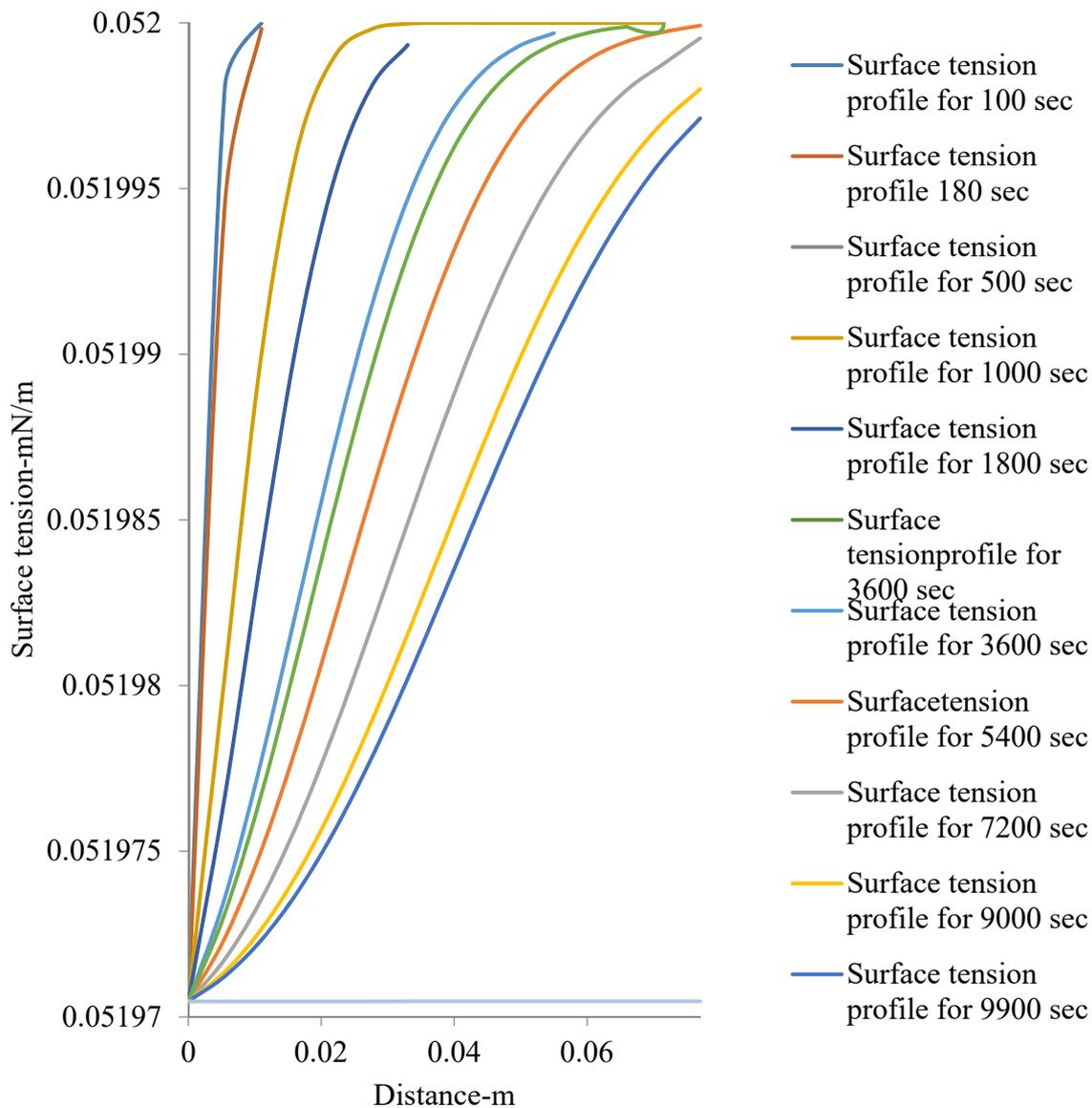


Figure 5. A plot of surface tension versus distance for different times of injection

Considering Eq. (2), the minimum pressure drop required for foam generation in a porous system is a function of rock and fluid properties, namely, interfacial tension between injected gas and surfactant solution in the aquifer, the length of the porous system, porosity and permeability. The square root of the ratio of porosity to permeability is the reciprocal of mean sediment pore radius in accordance with Leverets dimensionless capillary pressure function (Zhou *et al.*, 2012). Thus, as adsorption of surfactant occurs, there will be a decrease in mean pore radius with a corresponding increase in pressure drop. Fig.6, which shows a plot of minimum pressure drop required for foam generation for different times of injection reveals the pressure increase trend.

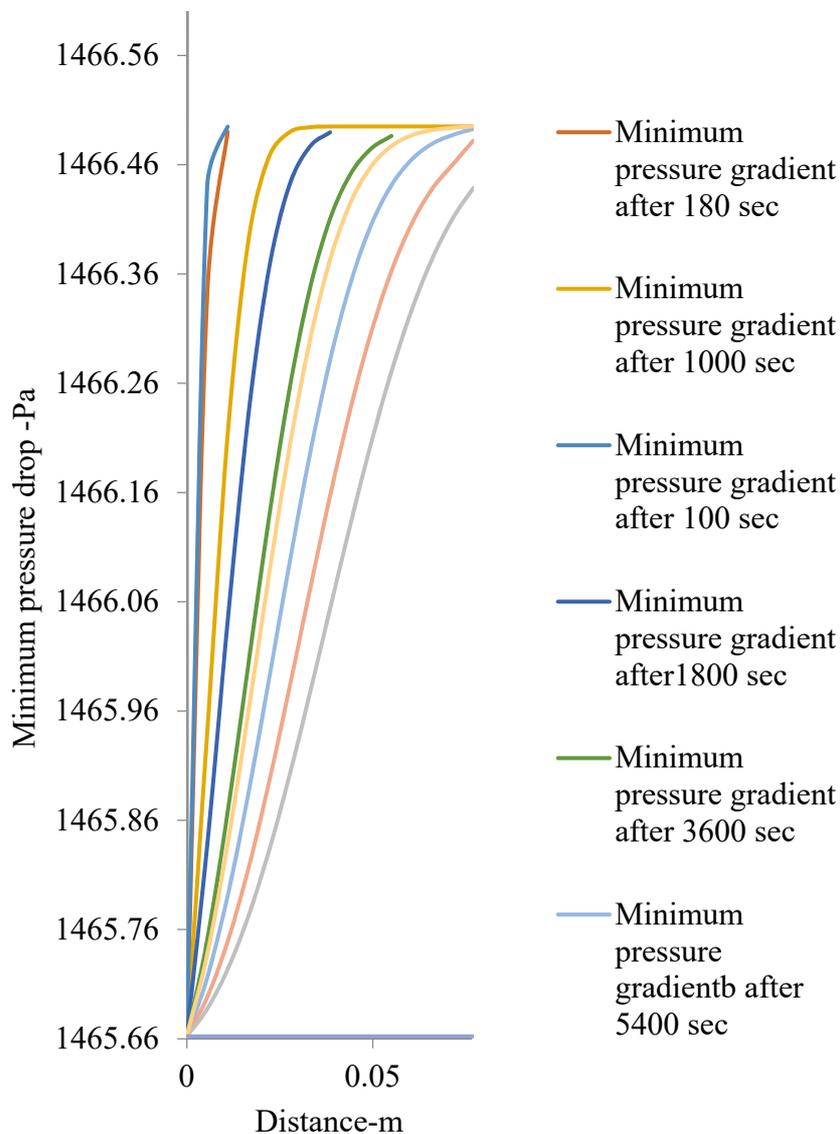


Figure 6. A plot of minimum pressure drop versus distance for different times of injection

Figure 6 shows a plot of surface tension of injected surfactant solution versus concentration at steady state conditions of surfactant injection. The plot shows a linear relationship. In the literature, a plot of surface tension versus the logarithm of surfactant concentration is known to give a linear relationship (Lin *et al.* 1999). Therefore, the trend shown by Fig.7, where the horizontal axis is linear contradicts theory.

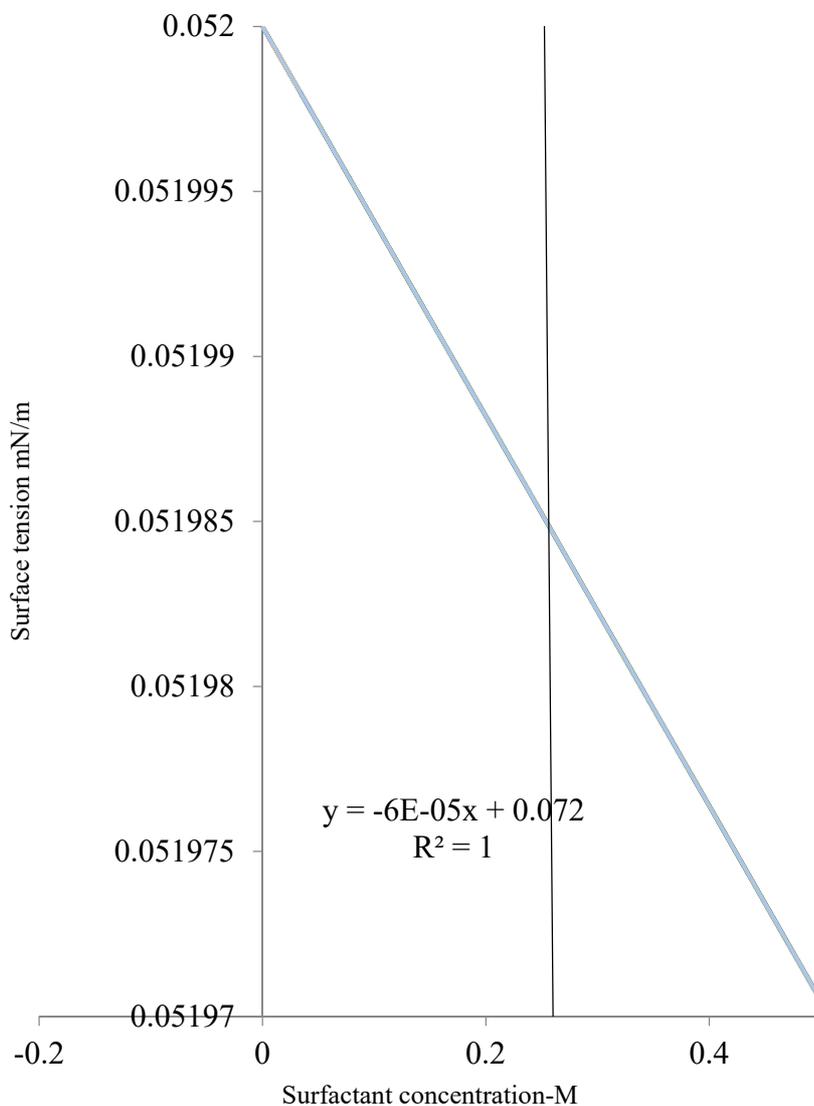


Figure 7. A plot of surface tension versus surfactant concentration at steady state conditions

However, considering Eq. (3), where surface tension is linked to adsorption, the trend given by Fig.7 can be approximated in accordance with the following mathematical argument:

Equation 3 gives the following:

$$\sigma - \sigma_0 = RT\Gamma^\infty \ln\left(1 - \frac{\Gamma}{\Gamma^\infty}\right)$$

The linear adsorption model gives the following equation:

$$\Gamma = KC$$

Where all parameters have their usual meanings:

Substitution of the second equation into the first equation for adsorption gives the following equation:

$$\sigma - \sigma_0 = RT\Gamma^\infty \ln\left(1 - \frac{KC}{\Gamma^\infty}\right) = RT\Gamma^\infty \ln(1 + \delta C) \tag{36}$$

Where:

$$\delta = \frac{K}{\Gamma^\infty} \quad (37)$$

In the first place, Eq. (36) shows that at maximum adsorption, the following can be written:

$$\begin{aligned} \sigma - \sigma_0 &= RT\Gamma^\infty \ln\left(1 - \frac{KC}{\Gamma^\infty}\right) = RT\Gamma^\infty \ln(1-1) = \ln(0) = 0 \\ &\Rightarrow \sigma = \sigma_0 \end{aligned} \quad (39)$$

This is to be expected because at maximum adsorption, there is no more adsorption as injection continues so the concentration of surfactant solution at every point in the porous medium must be equal to the initial concentration.

Using series expansion, the right-hand side of Eq. (36) can be expanded as:

$$\begin{aligned} \sigma - \sigma_0 &= RT\Gamma^\infty \ln\left(1 - \frac{KC}{\Gamma^\infty}\right) = RT\Gamma^\infty \ln(1 + \delta C) = -\delta C - 0.5\delta^2 C^2 - 0.333\delta^3 C^3 \\ &\quad - 0.25C^4 - 0.2\delta^5 \dots \end{aligned} \quad (40)$$

Considering the linear model, which assumes lower concentrations, powers of concentration above 2 may be neglected to give the following equation after solving for surface tension:

$$\sigma = -\delta C + \sigma_0 \quad (41)$$

Based on Eq. (40), the linear plot of surface tension versus surfactant concentration at steady state conditions as shown by Fig. 7 is to be expected with a negative gradient and initial surface tension as predicted in this equation.

Generally, Fig. 3, Fig. 5 and Fig. 6 show gradual changes in gradients with time. Ziziphus Christis is a new biosurfactant, also found in association with petroleum deposits. Being a surfactant of biological origin in addition to its presence in petroleum deposits, the potential for its use in tertiary oil recovery projects like conventional ones has been explored in the literature. Consequently, adsorption experiments, where crushed rock samples have been contacted with solutions of Ziziphus Christis have been performed in the literature. Accordingly, adsorption of this surfactant has been found to obey a linear model. In this paper, I have used the linear model of adsorption to derive a mass balance in the form of linear partial differential equation of second order. I have solved the equation based on physically realistic boundary conditions. Based on the solution, I have used a linear adsorption data from literature to determine numerical constants of the solution to the differential equation. Assuming an initial surfactant concentration 0.5 Molar, I have calculated concentration versus distance for adsorption onto a calcite core sample of specified porosity, permeability and length. Superficial velocity was determined based on injection rate found in the literature. Dispersivity was deduced from Appendix 1.

### 5.9 Conclusion

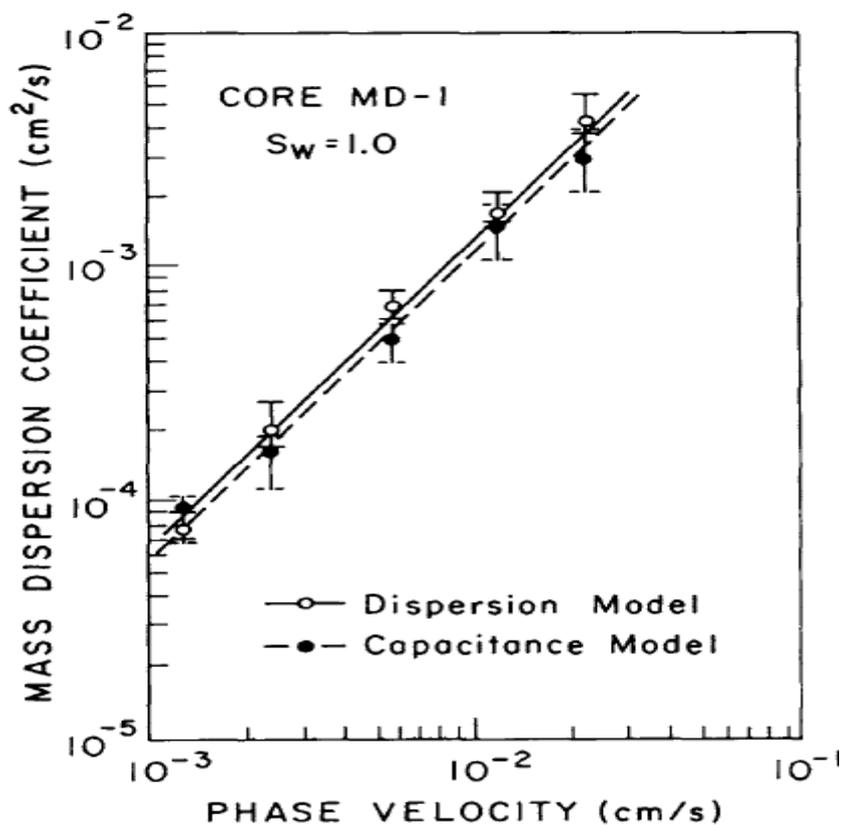
While several studies have appeared regarding the adsorption of Ziziphus Christis on reservoir rock samples, the present study is the first to present analytical calculation solution to advective-dispersive transport of Ziziphus Christis in a porous medium with a linear adsorption model. The following sums up the conclusion of this study:

1. The dynamic adsorption behavior of Ziziphus Christis shows a gradual decrease in gradient with time of injection, which is indicative of a gradual increase of surfactant concentration in brine with time in the porous medium.
2. This trend in adsorption, considering advective-dispersive transport in porous media with a linear adsorption model has been reported elsewhere (Ogata, 1961)
3. In terms of the minimum pressure required for foam generation in porous medium, the minimum pressure drop will increase with distance at all times of injection and become time independent during the steady state period.

4. Considering the appreciably low surfactant concentration used in this study, the biosurfactant can be said to have a foamability potential similar to traditional surfactants found in the petroleum industry
5. Given that the analytical solution to the model differential equation uses parameters of the linear adsorption model reported from literature in connection with adsorption experiments using *Ziziphua Christis*, the present work based on dynamic adsorption is an extension of the investigation of this surfactant not only for enhanced oil recovery but also for surfactant enhanced geological storage projects.

### Appendices

Appendix 1: Dispersion coefficient versus phase velocity (Ramirez, Shuler, & Friedman, 1980),



## Appendix 2: Calculated Parameters Based on Literature Data

$$U = 3.51 * 10^{-6} \text{ ms}^{-1}$$

$$D = 4 * 10^{-8} \text{ m}^2 \text{ s}^{-1}$$

$$\frac{U}{D} = 87.75 \text{ m}^{-2} ?$$

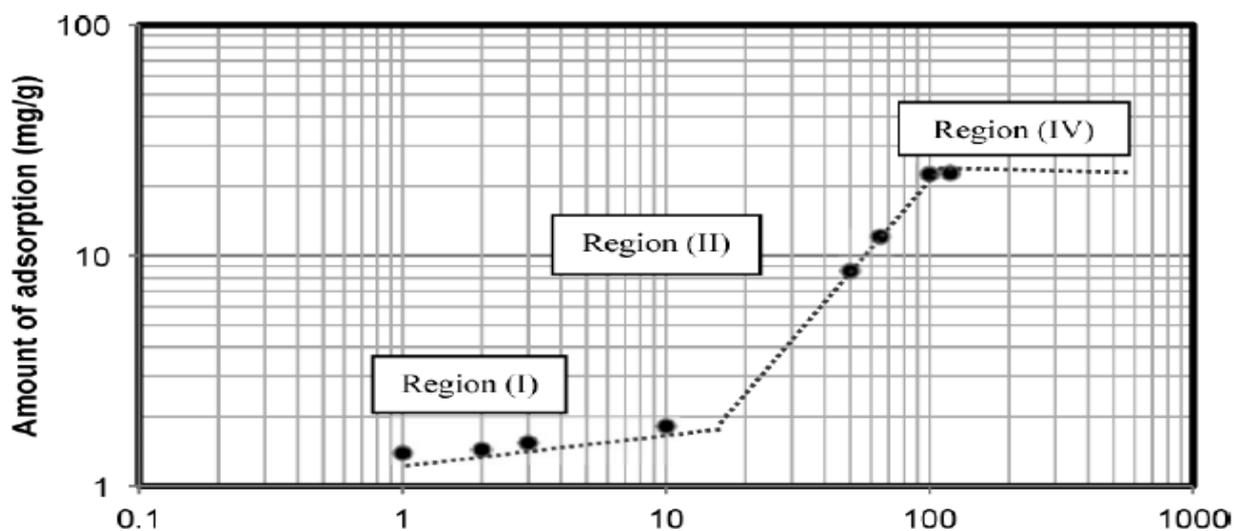
$$\frac{U^2}{D^2} = 7700 \text{ m}^{-2}$$

$$K = 5.251 * 10^{-8} \text{ s}^{-1}$$

$$\frac{\delta}{\omega} = \frac{K}{D} = 1.131 \text{ m}^2$$

$$\frac{\Omega}{\omega} = \frac{U}{D} = 87.75 \text{ m}^{-1}$$

$$\mu, \omega ? = 6.82 * 10^{-5}$$

Appendix 3: Adsorption with maximum value (Mohsen *et al.*, 2013)

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