ADSORPTION OF SURFACTANTS ON CLAY MINERALS

TAHMINEH AMIRIANSHOJA

A thesis submitted in fulfillment of the
requirements for the award of the Master of
Engineering (Petroleum)

Faculty of Petroleum and Renewable Energy Engineering
Universiti Teknologi Malaysia

MARCH 2011

Dedicated to my lovely mother's memory

ACKNOWLEDGEMENT

I would like to thank Universiti Teknologi Malaysia, especially Petroleum Engineering Department, for the permission to conduct my project. With the facilities provided, together with the ready-to-use equipment, I was able to complete my project within the budget.

This project could not have been accomplished without the help of a number of people. Assoc. Prof. Dr. Radzuan Junin, my project supervisor, kept me on the right path with his advice, criticism, feedback and continuous support. His insight was helpful on many occasions. I deeply appreciate the assistance provided by Prof. Dr. Ahmad Kamal Bin Idris. Not forgetting reservoir lab technicians who provided their technical advice and helps in every way they could. Their willingness to work overtime was encouraging.

ABSTRACT

Adsorption of surfactants from aqueous solutions in porous media is very important in enhanced oil recovery (EOR) of oil reservoirs. The loss of surfactants due to adsorption on the reservoir rocks weakens the effectiveness of the surfactant solution injected to decrease the oil–water interfacial tension (IFT). This project investigated the effect of mineralogical composition of adsorbents on adsorption. Experimental results from this study will provide additional insight into the feasibility of surfactant-enhanced flushing. The experiments were divided into two parts. In the first part, the experiments were carried out in a surfactant flooding apparatus and for the second part the experiments were conducted in batches. In dynamic condition, nonionic surfactants were injected into the sand packs in which different amounts of clay minerals (kaolinite and illite) were added. In static condition, adsorbents were mix composition of quartz sand and clay minerals at different percentages exposed to nonionic and anionic surfactants. In both static and dynamic conditions, the amount of surfactant adsorbed was quantified by subtracting the concentration of surfactants after adsorption from the initial one. It was concluded that there is a relationship between adsorption of nonionic surfactants and the amount of clay mineral in the adsorbents since the quantity of surfactant adsorbed by adsorbents raised when the percentage of clay mineral in the adsorbents increased (from 2% to 8% in sand packs and from 5% to 20% in the mixtures). Adsorption power of clay minerals for nonionic surfactants follows the order of montmorillonite >> illite > kaolinite in batch experiments. In sand pack flooding, adsorption power of adsorbents go along the order of illite > kaolinite. Adsorption of the anionic surfactant on all adsorbents was negligible.

ABSTRAK

Jerapan surfaktan daripada larutan berair dalam media berongga adalah sangat penting dalam proses perolehan minyak tertingkat (EOR) bagi reservoir minyak. Ini adalah kerana surfaktan boleh hilang disebabkan ianya terjerap ke dalam batuan reservoir dan dengan demikian mengurangkan keberkesanan buburan kimia yang disuntik bagi tujuan merendahkan tegangan antara permukaan (IFT) minyak-air. Projek yang dijalankan ini adalah bertujuan untuk mengkaji kesan komposisi mineral penjerap ke atas nilai jerapan. Keputusan ujikaji daripada kajian ini akan memberikan maklumat tambahan tentang kebolehgunaannya dalam proses pembilasan surfaktan tertingkat. Ujikaji yang dijalankan dalam kajian ini dibahagi kepada dua bahagian. Pada bahagian pertama, ujikaji telah dijalankan menggunakan radas banjiran surfaktan. Manakala pada bahagian kedua, ujikaji telah dijalankan secara kelompok. Dalam keadaan dinamik, surfaktan bukan-ionik telah disuntik ke dalam padatan pasir yang telah ditambah dengan mineral lempung (kaolinit dan illit) yang kandungannya berbeza-beza dan kemudian dipadatkan dalam pemegang teras. Pada peringkat kedua, penjerap yang terdiri daripada campuran komposisi pasir kuarza dan mineral lempung pada peratusan berbeza didedah kepada surfaktan bukan-ionik dan anionik. Dalam kedua-dua situasi statik dan dinamik, jumlah surfaktan terjerap dikira dengan menolak kepekatan surfaktan selepas jerapan awalan. Disimpulkan bahawa ada hubungan antara jerapan surfaktan bukan-ionik dan jumlah mineral lempung penjerap tatkala kuantiti surfaktan terjerap meningkat apabila peratusan mineral lempung pada penjerap meningkat (daripada 2% hingga 8% dalam padatan pasir dan daripada 5% hingga 20% pada campuran). Kuasa jerapan mineral lempung untuk surfaktan bukan-ionik mengikut turutan montmorilonit >> illit > kaolinit dalam eksperimen kelompok. Dalam ujikaji banjiran padatan pasir, kuasa jerapan penjerap adalah mengikut turutan berikut, illit > kaolinit. Jerapan surfaktan anionik ke atas semua penjerap boleh diabaikan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Oil is the most used nonrenewable source of energy in the world and this has induced the study of new processes for exploration and production of oil reservoirs. Oil and service companies have been investing heavily in increasing the recovery and productivity of old reservoirs, mainly in processes of enhanced oil recovery (EOR).

Considering only conventional processes, it is assumed that just about 30% of the original oil in place is recoverable (Curbelo *et al.*, 2007). The use of more advanced methods appeared when the reserves based on conventional methods start to decline. Therefore, the target for EOR processes corresponds to 70% of the original oil in place, which will remain in the reservoirs after conventional production.

The enhanced recovery methods are processes that seek an additional recovery of the reservoirs, which have not been exploited in a fully efficient manner. As a consequence, they retain a large amount of hydrocarbons after their natural energy is depleted. These methods have been developed with the objective of allowing for a larger production than that provided just by the natural energy of the reservoir and consist basically of the flooding of fluids aiming to move the oil out of the pores of the rock. Thus, the injected or displacing fluid should push the oil, known as displaced fluid, out of the rock and, at the same time, should occupy the space left.

Among the methods used in the advanced recovery of petroleum are the chemical methods, which comprise surfactant flooding. Surfactant flooding may be used with the purpose of reducing the interfacial tensions between oil and water, increasing the displacement efficiency (Schramm, 2000)

Surfactant flooding is considered as a method of additional recovery of oil from partially depleted reservoirs. Surfactants displace trapped oil in a porous media by lowering the interfacial tension, altering the rock wettability, and improving mobility. Such parameters are considered as microscopic aspects of displacement. The mechanism of action of the surfactant in a porous medium, partially filled with oil and brine, is still not very well understood. In water wet systems, for example, the oil in place, after water flooding, consists mainly of isolated oil drops within the pores. In order to mobilize the residual oil trapped by capillary forces in oil reservoirs, many enhanced oil recovery methods rely on reducing the oil–water interfacial tension (IFT) to extremely low values, often to 10^{-2}dyne/cm or less (Curbelo *et al.*, 2007). Therefore, it is important to keep low interfacial tensions for large periods of time.

1.2 Statement of the Problem

The complexity of the surfactant system in porous media increases with the effects of other parameters, such as: heterogeneity of the rock, interaction of the surfactants with reservoir fluids, coalescence of the oil drops and surfactant adsorption (Curbelo *et al.*, 2007). The surfactant flooding process, however, faces problems due to loss of high cost surfactant in the form of adsorption and retention in the porous media.

The loss of surfactant from the main chemical slurry during surfactant flooding is a main determinant in process performance and economy. It has been shown that the nature of the adsorption isotherm depends to a large extent on the type of surfactant used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in solution and, also, of cosurfactants and alcohols. The adsorption of surfactants can be influenced by the charge on the rock surface and fluid interfaces (Liu *et al*., 2004).

Recently, few authors such as Zhu *et al*. (2003), Rodriguez-Cruz *et al*. (2005) and Sanchez-Martin *et al*. (2008) have attempted to study the influence of the mineralogical composition of the clay fraction on adsorption of the surfactant.

Despite recent efforts, the quantity of surfactant adsorption cannot be predicted based on sorbent attributes. Therefore investigation on adsorption of surfactant to rocks that varied in lithological characteristics (mineralogy, grain size, texture, and other physical properties of rock) is subsequently necessary precondition for assessing the effectiveness of proposed enhanced oil recovery (EOR).

This research is mainly focused on the experimental study of adsorption quantity of single surfactant on adsorbents with different mineralogical composition in static and dynamic conditions. Experimental results from this study will provide additional insight into the feasibility of surfactant-enhanced flushing for reservoir rock (sandstone) system and supply valuable information for development of the effective and safe surfactant-enhanced oil recovery technologies.

1.3 Research Objectives

The objectives of this study are to:

1. Evaluate the adsorption of nonionic and anionic surfactants on a variety of adsorbents which are different in mineralogical characteristics,

2. Investigate the relationship between adsorption of surfactants and mineralogical characteristics of the sorbents.

1.4 Scope of Study

The scopes of this study are:

1. The research involves laboratory testing which were conducted using measuring devices to determine the quantity of surfactant adsorption and characterize mineralogical samples,
2. In this study, experiments were divided in two parts. In the first part, experiments were conducted in surfactant flooding apparatus. Two different nonionic surfactants were used in concentration of 30% above their CMC,
3. In surfactant flooding, absorbents were mixed compositions of quartz sand and clay minerals (kaolinite and illite). These minerals were compacted in different amounts to prepare sand packs with various porosities (33%, 36% and 38%). Clay and quartz content of samples were between 0-8% and 92-100% respectively,
4. In the second part, batch experiments were conducted. The variables for materials involved were primary surfactant concentration ranged from 0.005wt% to 1wt%, type of surfactant (nonionic and anionic), and mineralogical characteristics of samples,
5. In batch experiments, samples were prepared by mixing quartz and clay minerals such as kaolinite, montmorillonite and illite. Clay and quartz content of samples were between 0-20% and 80-100% respectively.

REFERENCES

Atun, G., Tunçay, M., Hisarli, G., Talman, R.Y., Hoşgörmez, H. (2009). Adsorption Equilibrium Between Dye and Surfactant in Single and Binary Systems onto Geological Materials. *App Clay Sci*. 45, 254–261.

Baviere, M. (1991). *Basic Concepts in Enhanced Oil Recovery Processes.* London: Elsevier Science Publishers LTD.

Bradley, H.B., Gipson, F.W., Odeh, A.S., Sizer, P.S., Mortada, M., Raymer, L.L. and Smith, G.L. (1987). *Petroleum Engineering Handbook*. U.S.A: Society of Petroleum Engineers.

Breen, C., Clegg, F., Herron, M.M., Hild, G.P., Hillier, S., Hughes, T.L., Jones, T.G.J., Matteson, A., Yarwood, J. (2008). Bulk mineralogical Characterisation of Oilfield Reservoir Rocks and Sandstones Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy and Partial Least Squares analysis. *J Petrol Sci and Eng*. 60, 1–17.

Brownawell, B.J., Chen, H., Zhang, W. and Westall, J.C. (1997). Sorption of Nonionic Surfactants on Sediment Materials. *Environ*. *Sci Thecnol*. 31, 1734-1741.

Cano, M.L. and Dorn, P.B. (1996). Sorption of Two Model Alcohol Ethoxylate Surfactants to Sediments. *Chemosphere*. 33(6), 981-994.

Curbelo, F.D.S., Santanna, V.C., Eduardo, L., Barros Neto, E.L., Dutra Jr., T.V., Castro Dantas, T.N., Dantas Neto, A. A. and Garnica, A.A.C. (2007). Adsorption of Nonionic Surfactants in Sandstones. *Colloids and Surfaces A: Physicochem. Eng*. 293(1), 1–4.

Donaldson, E.C., Chilingarian, G.V., and Teh, F.Y. (1985). *Enhanced Oil Recovery, I: Fundamentals and Analyses*. Amsterdam: Elsevier Science Publishers B.V.

Donaldson, E.C., Chilingarian, G.V., and Teh, F.Y. (1989). *Enhanced Oil Recovery, II: Processes and Operations*. Amsterdam: Elsevier Science Publishers B.V.

Foster,W.R. (1973). A Low-Tension Water-Flooding Process. *J. Petroleum Technology*. 25(2), 205 – 210.

Fytianos, K., Voudrias, E. and Mouratidou, T.H. (1998a). The Sorption-Desorption Behavior of Linear Alkylbenzene Sulfonate in Marine Sediments. *Chemosphere*. 36(9), 2067-2074.

Gogarty, W.B. (1976). Status of Surfactant or Micellar Methods. *JPT*. 28(1), 93 – 102.

Green, D.W. and Willhite, G.P. (1998). *Enhanced Oil Recovery*. Richardson, Texas: Society of Petroleum Engineers.

Haigh, S.D. (1996). A Review of the Interaction of Surfactants with Organic Contaminants in Soil. *Sci Total Environt*. 185, 161-170.

Harwell, J.H., Schechter, R.S. and Wade, W.H. (1985). Surfactant Chromatographic Movement: An Experimental Study. *AIChEJ*. 31, 415-427.

Hill, H.J., Reisberg, J. and Stegemeier, G.L. (1972). Aqueous Surfactant Systems for Oil Recovery. paper SPE 3798 presented at the *1972 Improved Oil Recovery Symposium of the Society of Petroleum Engineers of AIME.* April 16-19. Tulsa, Oklahoma, USA.

Hower, W.F. (1969). Adsorption of Surfactants on Montmorillonite. *Clay Clay Miner*. 18, 97-105.

Joshi, T., Mata, J. and Bahadur, P. (2005). Micellization and Interaction of Anionic and Nonionic Mixed Surfactant Systems in Water. *Colloids Surf. A.* 260, 209-215.

Krumbein, W.C. and Monk G.H. (1942). *Permeability as a Function of the Size Parameters of unconsolidated Sand.* USA: American Institute Mining and Metallurgy Engineering, Technology Publication.

Levitz, P., Van Damme, H. and Keravis, D. (1984). Fluorescence Decay Study of the Adsorption of Non-ionic Surfactants at the Solid-Liquid Interface. 1. Structure of the Adsorbed Layer on a Hydrophilic Solid. *Phys. Chem.* 88, 2228-2235.

Liu, Q., Dong, M., Zhou, W., Ayub, M., Zhang, Y.P., Huang, S. (2004). Improved Oil Recovery by Adsorption-Desorption in Chemical Flooding. J *Petrol Sci and Eng*. 43(1-2), 75-86.

Liu, Z., Edwards, D.A. and Luthy, R.G. (1992). Sorption of Non-ionic Surfactants onto Soil. *Water Res.* 26, 1337-1345.

Muherei, A.M. (2009). *Adsorption of Surfactants to Shale and Sandstone and Its Effect on Oily Drill Cuttings Decontamination.* Doctor Philosophy, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia.

Morrow, N.R. (1991). *Interfacial Phenomena in Petroleum Recovery*. New York, USA: Marcel Dekker, Inc.

Murray, Haydn. (2007). *Applied Clay mineralogy: Occurrences, Processing, and Application of Kaolins, Bentonites, Palygorskite-sepiolite, and Common Clays.* Amsterdam: Elsevier.

O zdemir, O., C¸ Inar, M., Sabah, E., Arslan, F., C¸ elik, M. (2007). Adsorption of Anionic Surfactants onto Sepiolite. *J Hazard Mater*. 147, 625–632.

Paria, S. (2008). Surfactant-Enhanced Remediation of Organic Contaminated Soil and Water. *Adv Colloid and Interface Sci*. 138, 24–58.

Paterson, I.F., Chowdhry, B.Z., Carey, P.J. and Leharne, S.A. (1999). Examination of the Adsorption of Ethylene oxide-Propylene Oxide Triblock Copolymers to Soil. *J Contam Hydrol*. 40(1), 37-51.

Peters, E.J. (2008). *Petrophysic*. Unpublished note, The University of Texas at Austin.

Podoll, R.T., Irwin, K.C and Bredlinger, S. (1987). Sorption of Water-Soluable Oligomers on Sediments. *Environ Sci Technol*. 30(4), 1328-1335.

Puig, J.E., Scriven, L.E., Davis, H.T., and Miller,W.G. (1982). *Fluid Microstructures and Enhanced Oil Recovery.* In Wason, D. and Payatakes, A. (Ed.) *Interfacial Phenomena In Enhanced Oil Recovery*. New York, USA: American Institute of Chemical Engineers.

Rao, D.N., Ayirala, S.C., Abe, A.A., and Xu, W. (2006). Impact of Low-Cost Dilute Surfactants on Wettability and Relative Permeability. *2006 Symposium on Improved Oil Recovery,* April 22 – 26.Tulsa, Oklahoma, USA.

Rodríguez-Cruz, M.S., Sanchez-Martin, M.J., Sanchez-Camazano, M. (2005). A Comparative Study of Adsorption of an Anionic and a Non-ionic Surfactant by Soils Based on Physicochemical and Mineralogical Properties of Soils. *Chemosphere*. 61(1), 56-64.

Rosen, M.J. (2004). *Surfactant and Interfacial Phenomena*. New York: John Wiley and Sons.

Sánchez-Martín, M.J., Dorado, M.C., Del Hoyo, C. and Rodriguez-Cruz, M.S. (2008). Influence of Clay Mineral Structure and Surfactant Nature on the Adsorption Capacity of Surfactants by Clays. *J Hazard Mater.* 150, 115-123.

Schramm, L.L. (2000). *Surfactants: Fundamentals and Applications in the Petroleum Industry*, United Kingdom.

Shen, Y.H. (2000). Sorption of Non-Ionic Surfactants to Soil: The Role of Soil Mineral Composition. *Chemosphere.* 41(5), 711-716.

Singh, V.S and Pandey,B.R. (1982). Role of Adsorption in Improved Oil Recovery by Surfactant Flooding. *J Sc Ind Res.* 41, 54-57.

Slider, H.C. (1983). *Worldwide Practical Petroleum Reservoir Engineering Methods.* Tulsa, Oklahoma: PennWell Publishing Company.

Somasundaran, P. and Huang, L. (2000). Adsorption Aggregation of Surfactants and their Mixtures at Solid-Liquid Interfaces. Adv. *Colloid Interface Sci*. 88, 179-208.

Spinier, E.A., Zornes, D.R., Tobola, D.P., Moradi-Araghi, A. (2000). Enhancement of Oil Recovery Using a Low Concentration of Surfactant to Improve Spontaneous and Forced Imbibition in Chalk. paper SPE 59290 presented at the *2000 SPE/DOE Improved Oil Recovery Symposium.* April 3-5. Tulsa, Oklahoma, USA.

Van Poollen, H.K. (1980). *Fundamentals of Enhanced Oil Recovery. Tulsa*. Oklahoma: Pennwell Corp.

Wade, W.H., Morgan, J.C., Schechter, R.S., Jacobson, J.K., and Salager, J.L. (1978). Interfacial Tension and Phase Behavior of Surfactant Systems. paper SPE 6844 presented at the *1978 SPE-AIME 52nd Annual Fall Technical Conference an Exhibition.* October 9 – 12. Tulsa, Oklahoma, USA.

Willhite, G.P. (1986). *Waterflooding.* Richardson, Texas: Society of Petroleum Engineers.

Zhang, R. and P. Somasundaran (2006). Advances in Adsorption of Surfactants and Their Mixtures at Solid/Solution Interfaces. *Adv Colloid Interface Sci.* (123-126), 213-229.

Zhao, B., Zhu, L., Li., W. and Chen, B. (2005). Solubilization and Biodegradation of Phenanthrene in Mixed Anionic-Nonionic Surfactant Solutions. *Chemosphere*. 58, 33-40.

Zhou, W. and Zhu, L. (2004). Solubilization of Pyrene by Anionic-Nonionic Mixed Surfactants. *J Hazard Mater*. B109, 213-220.

Zhu, L. and Feng, S. (2003). Synergistic Solubilization of Polycyclic Aromatic Hydrocarbons by Mixed Anionic-Nonionic Surfactants. *Chemosphere*. 53, 459-467.

Zhu, L., Yang, K., Lou, B. and Yuan, B. (2003). A Multi-Component Statistic Analysis for the Influence of Sediment/Soil Composition on the Sorption of a Nonionic Surfactant (Triton X-100) onto Natural Sediments/Soils. *Water Res*. 37(19), 4792-4800.