

ADSORPTION OF SURFACTANTS ON CLAY MINERALS

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Dedicated to my lovely mother's memory

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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 kebolegunaannya 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

CHAPTER	TITLE	PAGE
	TITLE PAGE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF FIGURES	xi
	LIST OF TABLES	xiv
	LIST OF APPENDICES	xvi
1	INTRODUCTION	1
	1.1 Background of Research	1
	1.2 Statement of Problem	2
	1.3 Research Objectives	3
	1.4 Scope of Study	4
2	LITERATURE REVIEW	5
	2.1 Introduction to Enhanced Oil Recovery	5
	2.1.1 Miscible Displacement Processes	6
	2.1.2 Thermal Process	7

2.1.3	Chemical Process	8
2.1.3.1	Surfactant Flooding	8
2.1.3.2	Mechanisms of Oil Displacement by Surfactant Flooding	9
2.2	Petroleum Reservoir Rock	11
2.2.1	Sandstone Reservoir Rock	12
2.2.2	Pore Space	13
2.2.3	Classification	15
2.3	Clay Mineral	19
2.3.1	Clay Mineral Properties	20
2.3.2	Structures and Mineralogy of Clay Minerals	21
2.3.3	Surface and Interface Chemistry of Clay Minerals	21
2.3.3.1	Surface Atoms	22
2.3.3.2	Surface Structures and Properties	22
2.3.3.2.1	The Neutral Siloxane Surface	23
2.3.3.2.2	Constant Charge Sites	23
2.3.3.2.3	The Hydroxyl Surface	24
2.3.4	Clay-Water Interactions	24
2.3.5	Types of Clays	24
2.3.5.1	The Kaolinite Group	25
2.3.5.2	The Montmorillonite Group	25
2.3.5.3	The Illite (or The Clay-mica) Group	26
2.3.5.4	The Chlorite Group	27
2.4	Surfactant Fundamentals	28
2.4.1	Surfactant Structure	28
2.4.2	Classification of Surfactant	28
2.4.3	Surfactant behavior in solution	29
2.5	Adsorption of Surfactant in Porous Media	30

2.5.1	Effect of Organic Matter (OM) and Clay Content of Soil on Adsorption	32
2.6	Summary	36
3	METHODOLOGY	37
3.1	Introduction	37
3.2	Sand Pack Flood Test	37
3.2.1	Sand pack Flood Apparatus	38
3.2.2	Sand Pack Model	38
	3.2.2.1 Base Sand Pack	40
	3.2.2.2 Model Packing	40
	3.2.2.3 Mix Composition	40
3.2.3	Procedure of Sand Pack Flood Test	41
3.2.4	Surfactant Used	42
	3.2.4.1 Triton X-100	42
	3.2.4.2 TX N-75	42
3.2.5	Determination of Porosity and Permeability	43
	3.2.5.1 Porosity Determination	43
	3.2.5.2 Measurement of Permeability	43
3.2.6	Measurement of Surfactant Concentration by UV Spectrophotometer	44
3.3	Adsorption Study by Surface Tension Technique	45
3.3.1	Adsorbents	45
3.3.2	Surfactants	47
	3.3.2.1 Sodium Dodecylsulphate	47
	3.3.2.2 Preparation of Testing Fluids	47
3.3.3	Determination of Samples Mineralogical Composition by X-ray Diffraction Measurements	48
3.3.4	Surface Tension Measurement	49
3.3.5	CMC by Surface Tension Measurement	50

4	RESULTS AND DISCUSSION	
4.1	Introduction	51
4.2	XRD Results of Samples	51
4.3	Adsorption Study in Dynamic Condition	52
4.3.1	Adsorption of Tx-100	52
4.3.2	Adsorption of TX N-75	57
4.4	Adsorption Study by Surface and Tension Techniques	61
4.4.1	Adsorption of Nonionic Surfactants	61
4.4.1.1	Adsorption of TX-100	62
4.4.1.2	Adsorption of TX N-75	66
4.4.2	Adsorption of Anionic Surfactant (SDS)	69
5	CONCLUSIONS AND RECOMMENDATIONS	72
5.1	Research Conclusions	72
5.2	Recommendations for the Future Work	73
	REFERENCES	74
	Appendices A-B	80-90

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	Correlation of residual oil saturation with capillary number at trapping and mobilization.	10
2.2	Examples of sandstone reservoir rocks	13
2.3	Framework of reservoir sand with interstitial clay and cement	14
2.4	Three general types of dispersed clay in sandstone reservoir and their effect on capillary pressure	16
2.5	Three general types of dispersed clay in sandstone reservoir and their effect on permeability	17
2.6	Classification of sandstones by composition	18
2.7	Tetrahedral sheet	21
2.8	Octahedral sheet	21
2.9	Structure of kaolinite layer	25
2.10	Structure of montmorillonite	26
2.11	Structure of illite	27

2.12	Typical surfactant molecular structures	29
2.13	Abstraction isotherms of SDS and SDBS onto Sepiolite	35
3.1	Sand pack flood apparatus	39
3.2	UV-spectrophotometer model 6305	44
3.3	KrussTensiometer	50
4.1	TX -100 concentrations as a function of the pore volume of fluid produced of sand pack with kaolinite amount of 2% (a), 5% (b) and 8% (c)	53
4.2	TX -100 concentrations as a function of the pore volume of Fluid produced of sandpack with illite amount of 2% (a), 5% (b) and 8% (c)	54
4.3	Surfactant loss as a function of clay content	55
4.4	TX N-75 concentration as a function of the pore volume of fluid produced of sand pack with illite amount of 2% (a), 5% (b) and 8% (c)	58
4.5	TX N-75 concentration as a function of the pore volume of fluid produced of sand pack with kaolinite amount of 2% (a), 5% (b) and 8% (c)	59
4.6	Surfactant loss as a function of clay content	59
4.7	Surface tension of TX-100 before and after equilibration with quartz sand-illite mixture	64

4.8	Surface tension of TX-100 before and after equilibration with quartz sand-kaolinite mixture	64
4.9	Surface tension of TX-100 before and after equilibration with quartz sand-montmorillonite mixture	64
4.10	Surface tension of TX N-75 before and after equilibrationwith quartz sand-illite mixture	66
4.11	Surface tension of TX N-75 before and after equilibrationwith quartz sand-kaolinite mixture	66
4.12	Surface tension of TX N-75 before and after equilibrationwith quartz sand-montmorillonite mixture	67
4.13	Surface tension of SDS before and after equilibrationwith quartz sand-illite mixture	70
4.14	Surface tension of SDS before and after equilibration with quartz sand-kaolinite mixture	70
4.15	Surface tension of SDS before and after equilibrationwith quartz sand-montmorillonite mixture	70

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	XRD results of quarry sandstone	19
3.1	Properties of sand pack (porous media)	40
3.2	Properties of sand-clay packs	41
3.3	Variables for materials involved in batch experiments	46
4.1	XRD results of quartz sand and clay minerals samples	52
4.2	TX-100 surfactant loss in the samples	56
4.3	TX N-75 loss in the samples	60
4.4	Surface tension data for TX-100 before and after equilibration with kaolinite	65
4.5	Surface tension data for TX-100 before and after equilibration with illite	65
4.6	Surface tension data for TX-100 before and after equilibration with montmorillonite	65

4.7	Surface tension data for TX N-75 before and after equilibration with montmorillonite	68
4.8	Surface tension data for TX N-75 before and after equilibration with illite	68
4.9	Surface tension data for TX N-75 before and after equilibration with kaolinite	68
4.10	Surface tension data for SDS before and after equilibration with illite	71
4.11	Surface tension data for SDS before and after equilibration with montmorillonite	71
4.12	Surface tension data for SDS before and after equilibration with kaolinite	71

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	X-Ray Diffraction Results	80
B	Surfactant Concentrations of Pore Volume Produced of Sand Pack with Various Amounts of Clay Minerals	88

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.

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