MALAYSIAN CRUDE OIL EMULSIONS: 1. PHYSICAL AND CHEMICAL CHARACTERIZATIONS

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ABSTRACT

Emulsion can become very important in all stages in petroleum recovery and processing industry such as drilling, completion, and production of hydrocarbon reservoir. Knowledge of the characteristics of the crude oil and oilfield brine that contributes to the formation of stable emulsion is therefore important. In this study, both chemical and physicochemical properties of different crude oils and oilfield brines from the East Coast of Malaysia were investigated. The crude oils from six different oilfields have been characterized for density, viscosity, surface tension, and interfacial tension. In most cases, the crude oil emulsions are characterized by high amount of saturated hydrocarbon, a varying amount of waxes (8 -15%), and a low content of asphaltene (0 - 14%). It was found that n-paraffin with carbon number between 6 to 20 are generally content in most of crude oil emulsion samples. There is a correlation between the crude oil emulsion viscosity and the waxes content of the crude oil. It was also obtained that the salinity of Malaysian oilfield brines varies between 9.4 to 20.2 and there is correlation between the salinity of oilfield brine and interfacial tension of crude oil emulsion.

Keywords: crude oil emulsion, chemical properties, physicochemical properties, oilfield brine

1. INTRODUCTION

Water-in-crude oil emulsions have long been of great practical interest because of their widespread occurrence in everyday life. Thus, they are of considerable practical significance both in chemical industry and consumer sectors. It can also become very important in all stages in petroleum recovery and processing industry such as drilling, completion, and hydrocarbon productions. With reliable information about crude oil properties and its tendency to form emulsion, therefore, emulsion destabilization equipment, such as coalescence separators, could be reserved for other more useful purpose. The crucial step will hence be to predict emulsion stability by determining the chemical and physicochemical properties of crude oil emulsion samples [1].

Characterization of physical and chemical properties of crude oil emulsion system have to be understood since it is crucial in helping the process engineers to select appropriate solution for the problems encountered. Beside that, detail knowledge of these properties will assist geologist in more accurately predicting where one would expect to find oils and its quality. Chemical characterization is studied by classifying different chemical compound of crude oil. It is classified on the one hand by molecular weight and on the other hand by molecular type [2]. Molecular type is defined as the pattern, which the carbon and hydrogen atoms are attached to each other's. The types of molecules are (a) the simplest molecular type is the series called the straight chain or paraffin such as methane, n-pentane and i-propane; (b) naphthene or cycloparaffin such as cyclopropane and cyclohexane; (c) aromatics, which has a basic structure consisting of a ring of six carbon atoms each with one hydrogen attached on it, such as benzene and toluene; (d) naphthenoaromatics, which is also called complex hydrocarbons, containing aromatics as well as naphthene rings in the same molecule in which the H atoms can be substituted by branched or unbranched alkyl group such as tetralin ($C_{10}H_{12}$) and cyclopentanephenanthrene ($C_{17}H_{14}$) [3,4]. Some of important chemical properties that need to be considered such as chemical composition of crude oil, interfacially active fractions, organic and inorganic content, while physical properties include density, viscosity, surface tension and interfacial tension, water content, salinity, and pour point in order to understand the emulsion formation and stability.

This paper will present some of our preliminary results of characterization study of Malaysian crude oil emulsion and oilfield brine samples.

2. MATERIALS AND METHODS

2.1. Materials

The chemicals used in this study include n-pentane (> 95%, from J.T. Baker), acetone (> 99.5%, from Mallinckrodt), dichloromethane (100%, from Mallinckrodt), methyl alcohol anhydrous (99.9%, from Mallinckrodt), and petroleum ether (40-60°C, from Surechem Product LTD). All chemicals were used as received. The adsorption of crude oil component was performed using silica gel (130-270 mesh, 60 A°, from Aldrich). The six crude oil samples were obtained from the East Coast of Malaysia oilfields (COE1, COE2, COE3, COE4, COE5, and COE6). Some of oilfield brines were also obtained from the same oilfields.

2.2. Methods

2.2.1. Physical characterization

The physicochemical characterization involves the determination of density, viscosity, surface tension and interfacial tension, salinity, pour point, and pH. The densities were determined using pycnometer at 25.5 ± 0.5 °C, and using double distillated water as reference material. Viscosity measurement was performed at several temperatures using computerized Brookfield Viscometer apparatus and the water bath was used to maintain the temperatures. Surface and interfacial tension were measured at 25.5 ± 0.5 °C by using Kruss Digital Tensiometer K10ST (Ring Method). Salinity and conductivity of oilfield brines were measured by using Conductometer. Pour point measurement was performed according to Standard Test Method (ASTM Designation D97-93). The pH of oilfield brine was determined by using Horiba pH-meter Series F-21.

2.2.2. Chemical characterizations

The chemical characterization involves the determination of the aromatic, polar and saturated hydrocarbons, waxes, asphaltenes, and resin components existed in the samples. The separation of interfacially active components was carried out according to the procedure described by Ese et al. [5]. The asphaltenes were precipitated by diluting the crude oil with n-pentane (1:5, v/v) at room temperature. The suspended solid was separated by centrifugating the solution at 3000 rpm for 12 minutes. The precipitated was filtered from the mixture and then dried at the room temperature for 1 hour. Resin fraction was then obtained by adsorbing it on solid silica particles. The resin was then desorpted from silica particles by dissolving it in 7% (v/v) methanol in dichloromethane followed by evaporation. Waxes components were precipitated in acetone at –20 °C and separated by filtering using Whatman filter paper (110 mnϕ) [6]. Qualitative analysis of crude oil emulsion samples was carried out using High Temperature Gas Chromatography (HTGC) and Lastroscan.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties

Table 1 presents some physicochemical properties of the crude oil emulsion samples measured at 25.5 ± 0.5 °C. The density varies from 0.79 to 0.87 gr/cm^3, viscosity at 30 °C varies between 3.6 to 8.76 cP and at 50 °C varies from 2.94 to 6.48 cP. Surface tensions are all in the narrow range between 25.3 to 29.6 mN/m, while interfacial tension, using oilfield brine of COE1 are between 27 to 35 mN/m. Pour point varies from –6 to 27 °C and pH varies in narrow range between 6.1 to 7.09.

Table 1. Physicochemical properties at 25.5 ± 0.5 °C

Physical properties	Types of Crude Oil/Oilfield Brines					
Crude Oil	COE1	COE2	COE3	COE4	COE5	COE6
Density (g/cm3)	0.8131	0.812	0.8648	0.7816	0.7947	0.8222
Viscosity (cP), 30 °C	4.56	6.48	8.76	3.48	3.6	5.4
, 50 °C	3.00	3.60	6.48	2.94	2.94	4.32
Surface tension (mN/m)	27.2	25.6	29.6	25.3	25.7	26.4
Interfacial tension (mN/m)	27.7*	35.7*	32.8*	29.6*	33.8*	34.7*
pH				26.4	26.9	
Pour point, °C	3	27	-6	15	6	27
Oilfield Brines	COE1			COE4	COE5	
pH	8.33			7.95	7.95	
Conductivity (MHOS)	15,900			25,300	32,700	
Salinity	9.4			15.2	20.2	

*: Using COE1 oilfield brine

In general, the densities of Malaysian crude oil samples have similar densities to some crude oils of Norwegian Continental Shelf, which vary between 0.79 to 0.89 g/cm^3. Correlation of salinity and interfacial tension shows that COE1, COE4, and COE5 have high oilfield brine salinity and lower interfacial tension. It also appears that the viscosity increases with increasing the surface tension. This could be explained that concentrated polymer film at interface may show elastic or viscous properties, and hence make it difficult to break the corresponding emulsion, either because insufficient energies involved in collisions between droplets, or the kinetics of breaking is slow compared to the times involved in the collisions [7,8]. It correlates with the viscoelastic properties of the monolayers formed by the surface acti ve fractions.

3.2. Chemical properties

Table 2 presents some fundamental chemical properties of the crude oils. It shows that most of the crude oil samples have asphaltene content lower than 1%. A similar result was also reported by Johansen et al. [1] for Norwegian's crude oils.

Table 2. Chemical properties of 6 crude oil emulsion samples from the East Coast of Malaysia

Types of crude oil	Chemical analysis (% w/w)								
	Asphalthene	Resin	Oil free interracially active fraction and waxes		Wax	Water content	Saturated Hydrocar-bon	Aromatic Hydrocar-bon	Polar
			Non -volatile	Volatile					
COE1	1.35	35.32	33.24	15.35	11.81	2.93	70.62	17.43	11.95
COE2	0.55	36.43	43.38	1.69	13.41	4.54	81.59	15.46	2.95
COE3	0.13	32.01	44.96	4.62	15.37	2.91	45.63	45.95	8.42
COE4	0.08	20.94	55.51	13.95	9.13	0.39	80.47	16.18	3.35
COE5	0.06	29.81	51.78	9.26	8.68	0.41	77.51	18.14	4.35
COE6	0.37	21.5	24.97	22.03	13.42	17.71	75.42	20.74	3.84

Tables 1 and 2 show a clear correlation between high wax content and high viscosity. For instance, the COE3 has the highest wax content and viscosity. This tendency was also reported by Sjoblom et al. [1,9]. Beside that, most of interfacial tension values are higher than surface tensions, which are contrary to the results reported by Johansen et al [1], which most of interfacial tensions are lower than surface tension except for two cases, which interfacial tension significantly exceeds the surface tension. This might be due to high amount of wax content. The crude oils having wax content more than 10%, will have interfacial tension higher than surface tension [1]. For instance, the COE1, COE2, COE3, and COE4 have wax content more than 10%. Wax content also affects on pour point, which the crude oil samples with higher wax content will have higher pour point. The COE3 has high wax content but have low pour point. This might be due to its have low suspended solid compared to the other crude oil samples since suspended solid also affects on pour point.

Figure 1 (a-f) presents HTGC results for crude oil emulsion samples. In general, all samples have high paraffin content having carbon number between 6 to 20. This means that the paraffin is the most abundant hydrocarbon of most of the crude oil samples. Paraffin wax and similar components that can be obtained from crude oil samples consist of compound higher than $C_{23}H_{48}$ and are predominantly straight-chain alkanes with some branched compounds. Based on some studies, most crude oils contain of 39% n-paraffin, 32% isoparaffin, 27% naphthenes, and 1% aromatic [3]. As

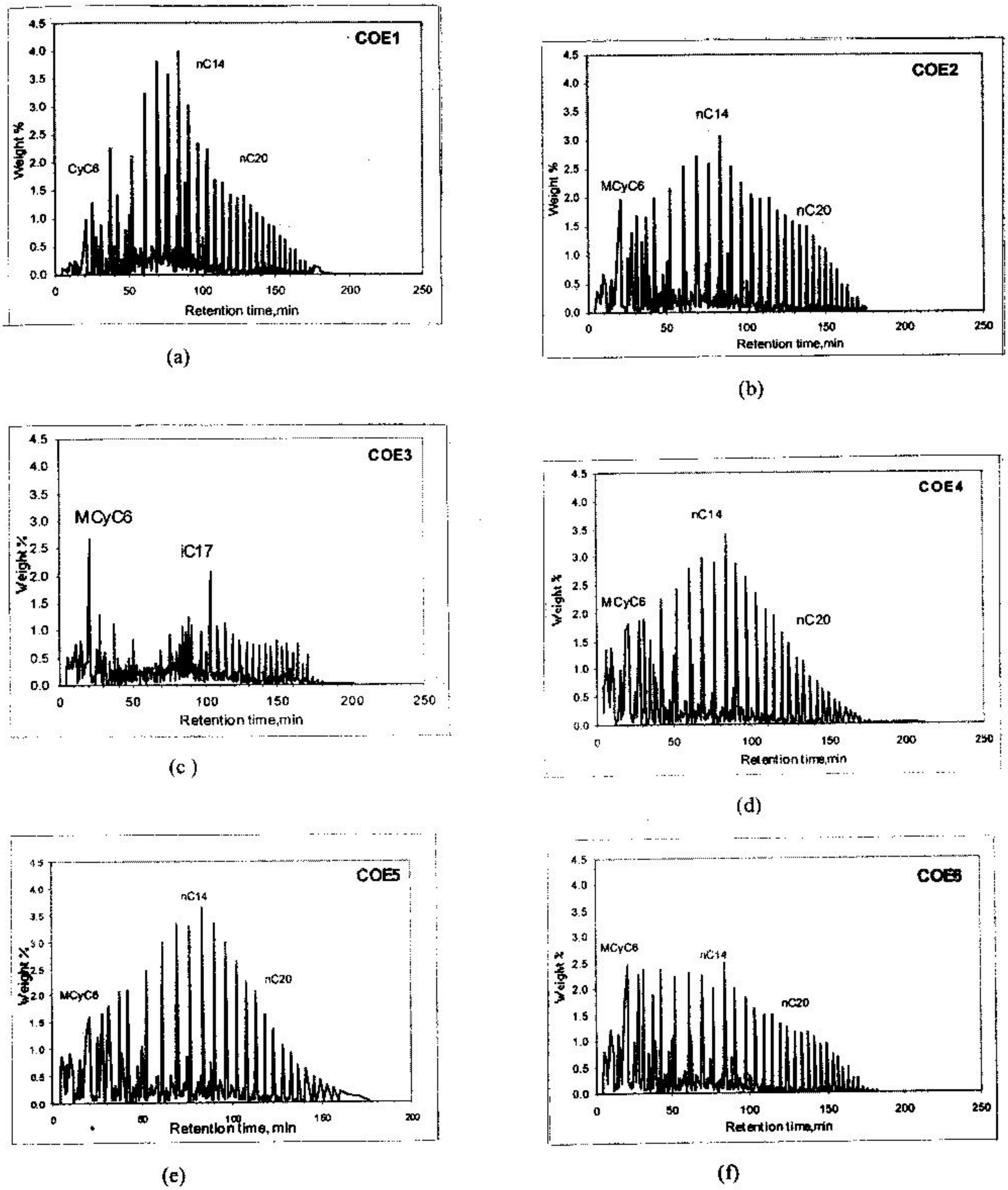

Figure 1 (a-f). Chromatograms of the High Temperature Gas Chromatography (HTGC) for 6 crude oil emulsion samples.

shown in Table 2, the saturated hydrocarbon, which is mostly n- paraffin, existed in high percentage for all samples understudy.

The COE3 contains saturated hydrocarbon and aromatics similar to other samples but it also contains high cyclohexane (C_yC_6) (Fig. 1c). The most common naphthene in crude oil is 5-6 membered rings, which contains up to 50% naphthene. This information is useful in assessment of maturation level of crude oil. The tetra and penta cycloalkanes find abundant in young and immature crude oils [3].

3.3. Emulsion formation and stability

The COE4 and COE5 have similar physicochemical and chemical properties, which mean that both crude oils could have similar stability. Based on Table 2, the COE1 has the lowest Interfacial tension (IFT), indicates that the crude oil sample has highest stability compared to the other samples. According to Sjoblom et al. [10], showed that lower IFT will form more stable emulsion. It could be caused by high asphaltene contents, the interfacial active fraction that exists in the crude oil samples. It was found out that asphaltene particles appear to be regularly stacked in lamellar structure, then resemble the structure of the lamellar liquid crystalline mesophase at water-oil interface, which occurs in surfactant system and enhance significantly the emulsion stability [1].

The stability can also be seen from resin/asphaltene ratio. Schorling [11] showed that high resin/asphaltene ratio decrease the emulsion stability because resin is predominantly effective as a dispersant of asphaltene. The COE1, COE2, and COE3 could have high stability since they have low resin/asphaltene ratio. These crude oils also have high water content and suspended solid, which could enhance the emulsion stability. The suspended solid that existed as solid inorganic particles will accumulate at the oil-water interface and rise to a protecting layer with mechanical stability and flexibility sufficient to stabilize water crude oil emulsion [9].

4. CONCLUSION

From crude oil emulsion samples investigated, it shows that increasing salinity of oilfield brine could decrease the interfacial tension of the crude oil. There is a correlation between wax content and viscosity, which higher wax content results higher crude oil viscosity. Most of the samples contain high n-paraffin with carbon number between 6 to 20 and high saturated hydrocarbon (45 – 82%). The physicochemical and chemical properties of the COE4 and COE5 are quite similar, which could be meaning that the stability of both crude oil emulsions is quite the same. Asphaltene, waxes, water, or suspended solid content can affect on stability of crude oil emulsion.

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