

EFFECTS OF FERROCENE ON THE SOLUBILIZATION OF
ALKANES IN A MICROEMULSION SYSTEM

ผลกระทบของเฟอโรซีนต่อการละลายอัลเคนในระบบไมโครอิมัลชัน

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Abstract

Ferrocene is a metallic additive that has been used to boost the octane number of gasoline. Even though ferrocene is not an environmental contaminant of high concern, it can be found in soil contaminated with gasoline. Due to its organometallic nature, ferrocene may affect the phase behavior of other alkanes which has been contaminated to the environment and limit their removal using surfactant-enhanced aquifer remediation (SEAR). Therefore, the aim of this work

was to investigate the effects of ferrocene on the solubilization capacity of alkanes in micellar surfactant solutions. The solubilization capacity and column study of alkanes with and without ferrocene were performed in the systems of AMA and AOT at 4% (wt) by mass as suitable surfactant system. The efficiency removals of alkanes and ferrocene (as total Fe) in column study were obtained in range of 74-95% (wt). In this study, different parameters were studied, namely the concentrations of ferrocene, electrolytes, and the types of alkanes.

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บทคัดย่อ

เฟอโรซีนเป็นสารประกอบโลหะอินทรีย์ที่เติมในน้ำมันก๊าซโซลีนเพื่อเพิ่มออกเทน แม้ว่าเฟอโรซีนจะมีใช้สารที่เป็นปัญหาต่อการปนเปื้อนในสิ่งแวดล้อมก็ตาม แต่ด้วยคุณสมบัติของความเป็นสารประกอบโลหะอินทรีย์ อาจทำให้เฟอโรซีนซึ่งผสมอยู่ในน้ำมันก๊าซโซลีนมีผลต่อกระบวนการบำบัดน้ำมันก๊าซโซลีนที่ปนเปื้อนในสิ่งแวดล้อมด้วยวิธีการใช้สารละลายลดแรงตึงผิว ดังนั้นในการศึกษาในครั้งนี้จึงมีวัตถุประสงค์หลักเพื่อประเมินผลกระทบของเฟอโรซีนต่อการละลายของน้ำมันก๊าซโซลีนในสารละลายไมเซลล์ โดยมีการศึกษาถึงประสิทธิภาพการละลายและการศึกษาในคอลัมน์ในระบบของสารลดแรงตึงผิวผสมระหว่าง เอเอ็มเอและเอไอที ที่ความเข้มข้นรวมที่ 4% (โดยน้ำหนัก) ซึ่งเป็นความเข้มข้นที่เหมาะสม พบว่าประสิทธิภาพการกำจัดสารประกอบอัลเคนน้ำมันก๊าซโซลีนและเฟอโรซีน (ในรูปเหล็กรวม) ในการทดลองคอลัมน์อยู่ในช่วง 74-95% ทั้งนี้ในการศึกษานี้ได้มีการประเมินความสามารถในการกำจัดสารประกอบอัลเคนในสถานะต่างๆ ที่แตกต่างกัน อาทิ ความเข้มข้นของเฟอโรซีน ความเข้มข้นของเกลือ และชนิดของสารประกอบอัลเคน

คำสำคัญ: เฟอโรซีน, สารลดแรงตึงผิว, การละลาย, ไมโครอิมัลชัน

Introduction

Ferrocene has been increasingly used as an octane booster for gasoline and diesel despite the fact that it appears to be less effective than lead in raising the research octane number (RON). The growing popularity of ferrocene however is due to it being considered less toxic than tetraethyl lead, which has been banned in

several countries⁽¹⁾. A gasoline or diesel contaminated site can be remediated by flushing the soil with water using a conventional pump-and-treat system⁽²⁾. Due to the limitations of pump-and-treat systems, surfactant solutions traditionally used for oil recovery have been introduced. By using surfactant solutions, enhanced solubilization of organic compounds can be achieved. This mechanism is used in surfactant enhanced aquifer remediation (SEAR) using microemulsions⁽³⁻⁴⁾, which is a technique that has been applied for over the past decade.

Surfactants are surface active molecules that accumulate at interfaces between two different phases (i.e., oil and water) because their structure contains a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail. When placed into a water-oil or water-air system, surfactants accumulate at the interface with their water-like moiety directed to the polar water phase and the oil-like moiety directed to the non-polar oil or less polar air phase. Due to its amphiphilic structure, a surfactant can greatly reduce the interfacial tension between water and oil, even if it is present at a very low concentration⁽³⁾.

Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, gas) by reversible interaction with the micelles of a surfactant in a solvent

to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Solubilization occurs in such a way that contaminant droplets tend to be encased in surfactant micelles.

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10 nm to 100 nm in diameter that are generally obtained upon mixing the ingredients gently. In this respect, they differ markedly from both macro- and mini-emulsions⁽⁵⁾. Microemulsions can transform from one type to another if the hydrophobicity is changed. If the salt concentration is high, the hydrophobic-lipophobic balance (HLB) of an anionic surfactant will decrease. An increase of the salt concentration in an ionic surfactant solution will eventually cause the surfactant to partition into the oil phase⁽⁶⁾. Multiphase microemulsion-containing systems were first described by Winsor. There are three possible types of phases depending on the composition, temperature, and salinity. Two phase systems, called Winsor I and Winsor II, correspond to o/w microemulsions coexisting with excess oil phase and w/o microemulsions with excess water phase respectively. A Winsor III system is formed in equilibrium coexisting with excess oil and water which consist of a middle phase⁽⁷⁾.

Due to a small size of microemulsion and ability to minimize the free energy of a system, a microemulsion is thermodynamically stable and hence can provide very low interfacial tension and high solubilization. These two properties are advantageous for applying SEAR. However, to obtain a suitable microemulsion with a given each alkanes, the natures of the each alkanes and surfactant have to be compatible. Therefore, in this present study a solubilization study was conducted using a solubilized bath experiment for evaluating the solubilization capacity in each alkanes with and without ferrocene. The conditions of the experiment were cover in Winsor type I to type III. The solubilization study was done under Winsor type I, supersolubilization, and Winsor type III microemulsion conditions.

Materials and Methods

Reagents

Ferrocene (98%) was purchased from Sigma-Aldrich Co. (Germany). *N*-alkanes (hexane, C-6, Unilab; octane, C-8, Univar; and decane, C-10) were purchased from Fluka were used as representative of gasoline. Anionic surfactants were used in this research; sodium dihexyl sulfosuccinate (trade name of Aerosol MA or in short AMA with 80% active ingredient) and sodium dioctyl sulfosuccinate (trade name of Aerosol OT or in short AOT) were

purchased from BDH Company (UK). NaCl with 99% purity purchased from Lab-Scan Ltd. (Ireland) was used for the salinity scan conducted in this research. Ottawa sand or silica sand (20-30 mesh) with a low iron content was used as synthetic soil in this study and was purchased from Fisher Scientific Co., Ltd. (UK).

Experimental Procedures

1. Solubilization measurement

The solubilization ability of alkanes with and without ferrocene at a concentration of 100 ppm was investigated by using 4% by mass mixed surfactants (2% AMA: 2% AOT) under Winsor type I, supersolubilization, and Winsor type III conditions. 2 mL of the each alkanes (hexane, octane, and decane) 8 mL aqueous surfactant solution was added into a 50 mL separatory funnel. The funnel was immediately sealed and gently shaken for 1 min. Each sample was performed in duplicate. The vials were allowed to stand for 48 h to obtain equilibrium. 0.1 mL of the aqueous surfactant solution was collected and transferred into a Perkin vial, while 0.5 mL was transferred into vessel for digestion. The alkanes concentration was measured with a GC-HS-FID. Each sample was injected into a GC equipped with a headspace auto sampler (Clarus 500, PerkinElmer Ltd.) at the following conditions: injector temperature was 200 °C,

a column type HP-5 with 30 m x 0.32 mm ID was used with a film thickness of 0.25 µm, an oven temperature of 100- 140 °C was applied, a flame ionization detector at 250 °C was used, and a flow rate of 14 psi utilized. Ferrocene (organometallic compound mixed with alkanes) was determined by atomic absorption spectroscopy (AAS) by acid digestion prior to inject to AAS.

2. Column Experiment

Column experiments were conducted with wet packed silica sand in glass columns (2.5 cm inner diameter) equipped with an adjustable flow adapter purchased from KONTES (Chromatography columns, KONTES CHROMAFLEX TM). The pore volume was evaluated by determining the volume of water replaced in the sand pores packed in the column. The initial volume of water was held in a separate container to be measured first. Then, a small amount of water and sand was gradually added into the column until the desired level of wet sand was reached. After packing the column, the volume of the remained water in the container was continuously measured in order to quantify the volume that is used, which represents the pore volume of the column. The column was then flushed with 20 pore volumes of degassed water containing 0.01 M $\text{Ca}(\text{NO}_3)_2$ at a flow rate of

0.40 mL/min to imitate a groundwater column prior to contamination with alkanes or an alkanes with ferrocene mixture.

4% by mass mixed surfactants (2% AMA: 2% AOT) was flushed into the column individually in an upward mode at a flow rate of 0.4 mL/min. A fraction collector (Model Frac 920, Amersham Bioscience) was used to collect the elution from the column every 0.25 pore volumes. Then, the removed alkanes and ferrocene were determined by GC-HS-FID as described earlier. The characteristics of the effluent were observed to determine the total Fe solubilization and the free phase oil as oil mobilization. The alkanes removal efficiency from soil was calculated based on the amount of ferrocene solubilized and mobilized in the flushing solution.

Result and Discussion

Solubilization study

After equilibrium of solution was reached, the supernatant solution was

analyzed for alkanes and total Fe. From Figure 1, the results show the same trend for all cases (alkanes concentration in the systems of with and without ferrocene) with increasing salinity of the systems, the solubilization of the alkanes increases. However, only hexane solubilization that found to be decreased when ferrocene is added to the system while an increasing of octane and decane solubilization occurs in the system of mixing with ferrocene. In each supersolubilization condition of alkanes (at NaCl 1.2% by mass, hexane; 1.6% by mass, octane; 2% by mass, decane), the highest solubilization of octane was found for both the systems with and without ferrocene while hexane with ferrocene was found lowest. For the Winsor type III condition (1.4, 1.9, and 2.3% by mass of NaCl for hexane, octane, and decane, respectively.), hexane was found to solubilized highest while the lowest solubilization was decane. Among the 3 alkanes, the shorter alkane carbon number (ACN), implying lower hydrophobicity.

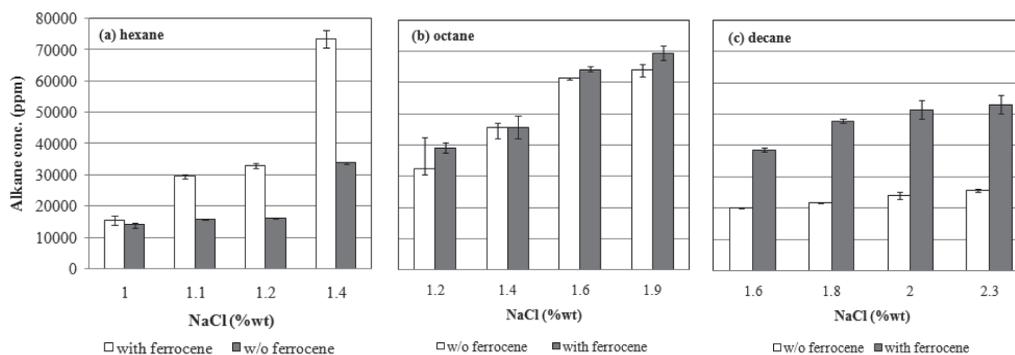


Figure 1 Solubilization of alkanes in the systems without and with ferrocene at 100 ppm at various salinities

It can probably be expected that the system of 2% by mass of AMA and 2% by mass of AOT is more suitable to form middle phase with hexane rather than a more hydrophobic oil like decane. This is confirmed by the result that once ferrocene was added, Equivalent Alkane Carbon Number (EACN) of mixed decane and ferrocene was reduced, hence the solubilization of decane was decreased. It is interesting to point out here that for the case of octane, having an ACN closest to those of ferrocene (8 and 8.386 for octane and ferrocene, respectively), the solubilization shows slight increase.

Another important finding was that the solubilization of total Fe (Fe) corresponded to the solubilization of alkanes that an increase in electrolyte concentration and changed type of microemulsion (see Figure 2). It was also shown that ferrocene can be solubilized in micellar systems. In addition, the same trend of solubilization of alkanes and ferrocene (as Fe) was found in all cases. This may indirectly indicate that ferrocene is miscible well the three alkanes and ratio of solubilization of solubilized mixture oil still similar to the initial ratio. From this result, it can be expected that the flushing surfactant solution for remediation contaminated alkanes will remove contaminated ferrocene at the same time.

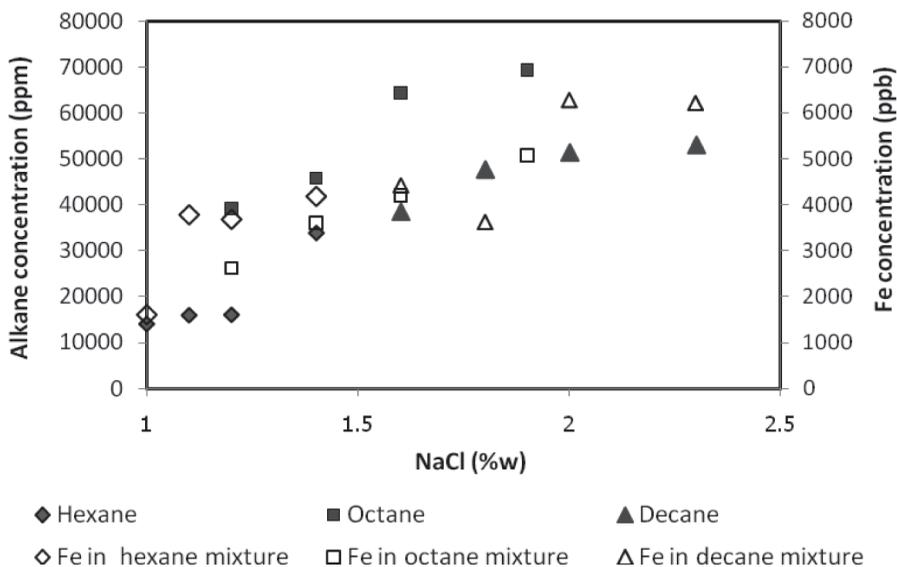


Figure 2 Solubilization of alkanes and ferrocene (as Fe) in the systems of without and with ferrocene at 100 ppm at various salinities.

Column study

The column study was conducted to imitate the actual subsurface remediation. The selected surfactant system (2AMA: 2AOT at 4% by mass) from solubilization study at the supersolubilization formula (1.6 and 2.0% NaCl for octane and decane, respectively) were used in the column experiments with decane and octane with and without ferrocene.

1. Removal alkanes

The result shows that by flushing surfactant solution, alkanes can be removed in the range of 85 to 92%. As a consequence, the surfactant flushing approach can be

considered to be a procedure for remediation of contaminant material containing alkanes mixed with ferrocene.

As expected, the surfactant solution initially mobilized a portion of the trapped alkanes which migrated vertically downward through the column. The maximum solubilization of alkanes occurred after this mobilization. The effectiveness of oil removal by surfactant solution is primarily attributable to a high ability of the solution to dramatically lower the interfacial tension between alkane (for both systems with and without ferrocene) and water, creating oil-surfactant-water micelles, and producing oil-in-water microemulsions⁽⁴⁾.

The system with 2% by mass of NaCl as supersolubilization condition of decane for both systems of with and without ferrocene were found to be slightly different than the mobilization of the decane without ferrocene (see Figure 3), the mobilized oil came out in the first pore volume (PV) while those of the system of decane with ferrocene the mobilized oil came out from the column after second PV of flushing and slightly lower than the system without ferrocene. These differences can be explained in part by the proximity of their EACN. On the other hand, the solubilization and mobilization of octane with ferrocene by the surfactant solution at 1.6% (w) of NaCl (supersolubilization condition) was found higher than that of the with octane only. However, both octane and decane from the column experiment were agreed with the results of the solubilization study. Moreover, for the column of octane with and without ferrocene flushing with the

surfactant at 2% by mass of NaCl (all formulation forming Winsor type III microemulsion) showed that almost oil removal, higher than 95% of the total was from mobilization (Table 1). It is not surprising because middle phase provides very low interfacial tension, hence the oil mobilization would spontaneously occur before the oil would be solubilized in micelles. As a consequence, several studies suggest that middle phase microemulsion be avoided because of vertical migration (high mobilization)⁽⁹⁾. However, in this present study, since the mixture oils, octane and decane with ferrocene, with a low proportion of ferrocene (100 ppm), the oils may still be regarded as LNAPL, vertical migration may not be a crucial concern. From results of this study confirm the previous works that the supersolubilization condition as Winsor type I was increasing the solubilization and reducing mobilization in the same time⁽¹⁰⁾.

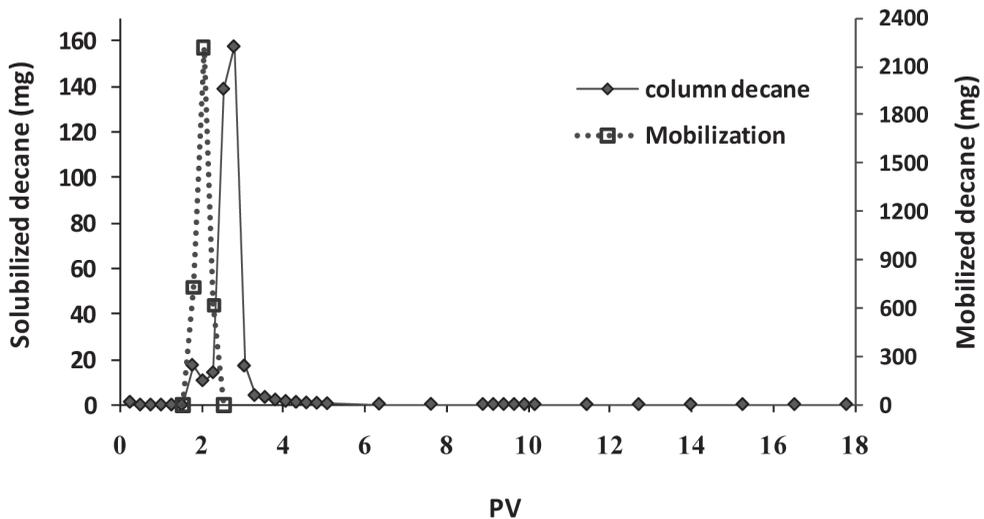


Figure 3 Mass of solubilized and mobilized decane removed with the surfactant solution of 2AMA:2AOT (4% w) with 2% by mass NaCl % (w) from the decane contaminated column

Table 1 Column flushing test alkanes results in 2AMA:2AOT (4% by mass) surfactant system

Parameter	alkanes					
	octane	octane+	octane	octane+	decane	decane+
	@ NaCl	ferrocene	@ NaCl	ferrocene	@ NaCl	ferrocene
	1.6% by mass	@ NaCl 1.6% by mass	2% by mass	@ NaCl 2% by mass	2% by mass	@ NaCl 2% by mass
Pore volume	32.77	32.98	29.01	30.21	31.46	31.52
Residual saturation (%)	16.54	15.79	15.84	15.83	19.64	22.12
Removal efficiency (%)						
- solubilization	7.9	8.4	0.01	0.02	9.07	9
- mobilization	78.38	82.63	84.76	87.15	83.73	76.56
Total removal (%)	86.28	91.04	84.77	87.17	92.8	85.56
Mass balance (%)	86.28	91.67	84.77	87.36	92.92	90.5

2. Removal of ferrocene

In the same column experiments described in section 1 removal alkane, ferrocene removal by the surfactant solution was evaluated by analysis of total Fe to indicate the ferrocene removal as shown in Table 2. It should be noted here that in this study, mobilized oil is assumed to have same proportion of ferrocene as the initial (100 ppm of ferrocene), thus the different efficiency of alkanes and ferrocene removal was based on solubilization phenomena of the two compounds. From Figures 4a to 4c, the results show obviously that for the system of octane with ferrocene either flushing of the surfactant solution

containing 1.6 or 2.0 %NaCl, ferrocene solubilized along with octane in the first 1 to 3 PVs while in the case of decane, ferrocene was found to be solubilized less than decane and used surfactant up to almost 20 PVs to complete performance. As compared the solubilization between alkanes (octane and decane) and ferrocene (as total Fe), the same trend was for all cases that the system of octane with ferrocene flushing by the surfactant solution with 2% NaCl yield the lowest solubilization for both octane and ferrocene. The observation corresponds to the results found in the slubilization study.

Table 2 Column flushing test total Fe results in 2AMA:2AOT (4% by mass) surfactant system

Parameter	Total Fe		
	octane+ ferrocene	octane+ ferrocene	decane+ ferrocene
	@ NaCl 1.6% by mass	@ NaCl 2% by mass	@ NaCl 2% by mass
Pore volume	32.98	30.21	31.52
Initial total Fe(ppb)	519.72	477.12	666.263
Residual saturation (%)	0.0006395	0.0005378	0.0007847
Removal efficiency (%)			
- solubilization	8.05	0.47	8.23
- mobilization	85.27	85.59	68.972
Total removal (%)	93.32	86.07	77.2
Mass balance (%)	101.3759	107.5883	97.49

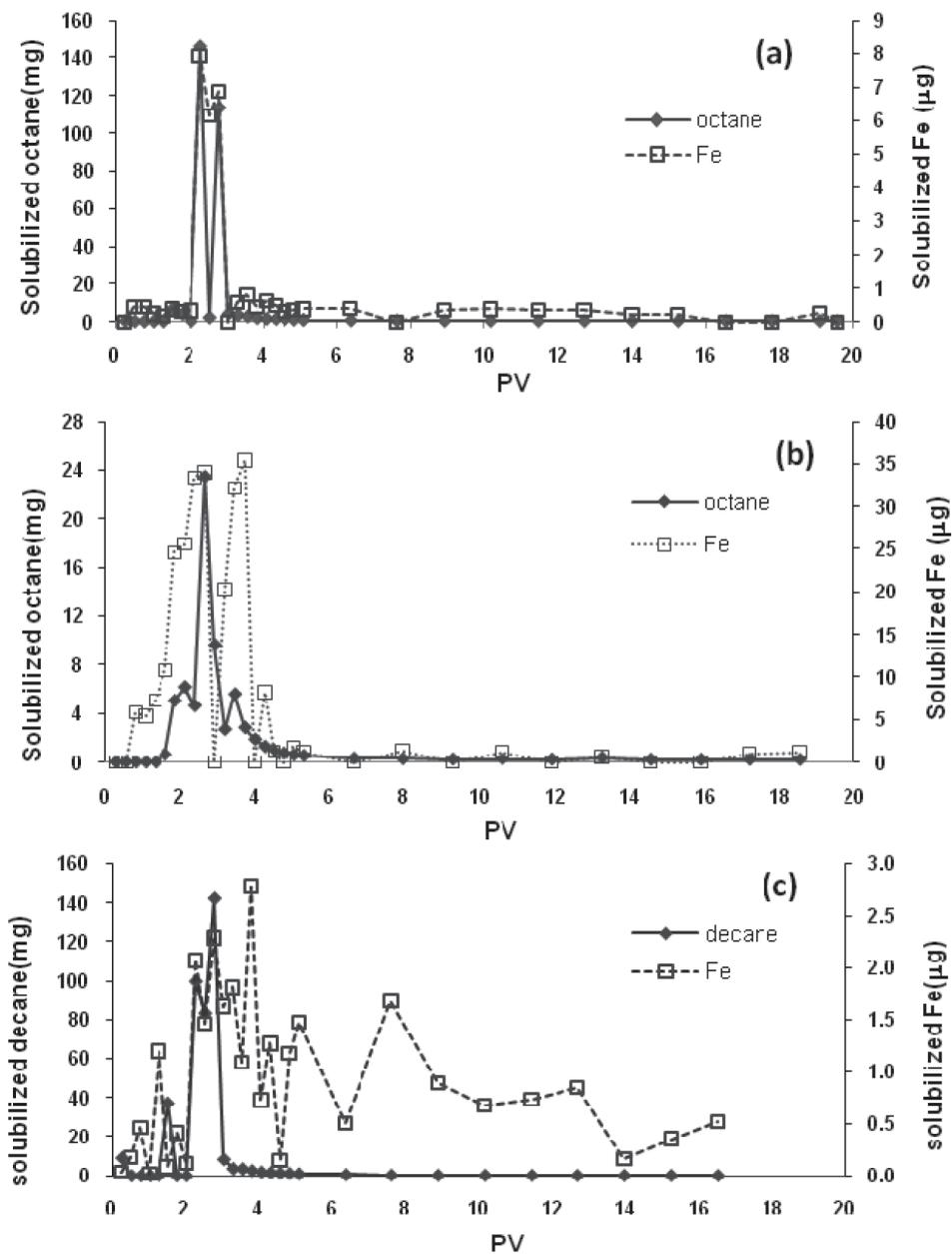


Figure 4 Plots between mass of alkanes with ferrocene and total Fe solubilization, mobilization and pore volume in 2AMA:2AOT at 4%wt surfactant system of (a) octane at 1.6%wt NaCl; (b) octane at 2.0%wt NaCl; and (c) decane with 2%wt NaCl

Conclusion

For solubilization of alkanes in the same surfactant solution, hexane and decane show opposite result with octane, insignificant different were found for the system with or without ferrocene. Moreover, another finding on solubilization is that ferrocene (as total Fe) solubilization found to be the same trend as alkanes. In addition, both solubilization and column study indicate that ferrocene can be removed by the technique of surfactant flushing for alkanes removal. As consequent, ferrocene may not be major concern as contaminants as compared to other organometallic compounds.

The surfactant solubilization capacity of alkanes with and without ferrocene occurred differently in solubilization, and column studies. It was shown that ferrocene affect alkanes on solubilization by microemulsion technique.

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