Solid-shelled microspheres loaded with solvent as diluents for extracting blockages by heavy-oil and asphaltene precipitates

Li Hao\textsuperscript{a,b,}, I-Cheng Chen\textsuperscript{b}, Jun Kyun Oh\textsuperscript{b}, Cengiz Yeginc, Nirup Nagabandib, Jyothsna Varsha Talari\textsuperscript{b}, Luhong Zhang\textsuperscript{a}, Mustafa Akbulut\textsuperscript{b,c,d,}\textsuperscript{⁎}, Bin Jiang\textsuperscript{a,}\textsuperscript{⁎}

\textsuperscript{a} School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
\textsuperscript{b} Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, United States
\textsuperscript{c} Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3003, United States
\textsuperscript{d} Texas A&M Energy Institute, Texas A&M University, 9372 TAMU, College Station, TX 77843-3372, United States

A novel type of solid-shelled microspheres was prepared by emulsion templating technique through layer-by-layer self assembly. The regulation controlled by different payloads, surfactants, 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) ratio produced three solid-shelled microspheres with various morphology, sizes, shell thicknesses and brittleness. Such microspheres can be considered as diluent-loaded eggs that can be cracked when forced between narrow rock surfaces or against blocking fluid flow particles. The structural characteristics, size distribution, stability, breakable and release behavior of three payload-in-silica microspheres were investigated by optical microscopy techniques and scanning electron microscopy (SEM) technique, dynamic light scattering (DLS), zeta potential, and ultraviolet-visible (UV-vis) spectroscopy. The results indicated that these three microspheres were relatively uniform in size (1–5 μm) and had a smooth surface with shell thicknesses of 40–120 nm, which also possessed excellent stability. Yet the brittleness of silica shell was obviously different for three solid-shelled microspheres, in detail, the silica shell of toluene microspheres was more brittle and easier to be ruptured than hexane microspheres under external hydrodynamics forces. Sand column tests revealed that the easy-broken toluene-in-silica microspheres prepared from tween-80 template matched the pore throat of reservoir better and achieved higher heavy oil recovery efficiency (94.60%). Such breakable microspheres can provide a selective and targeted diluting approach to extract blockages by heavy-oil and asphaltene precipitates.

1. Introduction

As easy-to-recover hydrocarbons are globally running out, development of approaches for the recovery of hydrocarbons trapped in low and very-low permeability reservoirs is in great demand\cite{1-6}. Typically, crude oil is trapped in the narrow regions between the grains of a sedimentary rock. During recovery, the oil needs to flow through interconnected pores with sizes that vary from the sub-micron to sub-millimeter range\cite{1,7}.

The current efforts to recover such hydrocarbons have faced several critical challenges associated with the low permeable nature of such reservoirs. For instance, the loss of permeability and poor hydraulic conductivity usually lead to serious heterogeneity and low fluid production, and thus influence oil production\cite{8}. Considerable efforts have been made to develop effective treatment techniques for overcoming two challenges: (i) pore blockages by small sandstone rocks and (ii) low mobility of hydrocarbons and displacement fluids in narrow channels due to the attractive intermolecular interactions between rock surfaces and fluids. Besides, heavy crude oils typically have high viscosity values, which poses challenges for their extraction and production due to the low mobility associated with high viscosity. The common methods for improving the mobility of such oils in reservoir settings either rely on increasing the permeability of the reservoir or decreasing the viscosity of heavy oil. The former is typically achieved using etchants such as HCl and HF while the latter can be accomplished by heating or dilution of heavy crude oil\cite{9-11}. Among various treatment methods for heavy hydrocarbon resources, dilution with aromatic and organic solvents such as benzene and toluene has traditionally attracted

\textsuperscript{⁎} Corresponding authors at: Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, United States (M. Akbulut).

E-mail addresses: makbulut@tamu.edu (M. Akbulut), binj@tju.edu.cn (B. Jiang).

https://doi.org/10.1016/j.fuel.2018.07.006
Received 10 December 2017; Received in revised form 30 June 2018; Accepted 2 July 2018
Available online 21 July 2018
0016-2361/ © 2018 Elsevier Ltd. All rights reserved.
much attention because the free energy of mixing of these solvents with heavy crude oil is thermodynamically favorable for these solvents [12–17]. The mixture of shorter chain hydrocarbons such as ethane, propane, and butane, has also been utilized as diluents to ease heavy oil/natural bitumen flow [2]. The main concern with this approach is the high cost of solvents relative to heavy crude oil, the waste of large volume of solvents to the porous media, and the reduction in oil quality with the addition of large amount of solvents. Thus, development of diluents with selective and targeted property is a technologically advantageous concept to improve permeability and flow properties, and then enhance recovery efficiency in heterogeneous reservoirs.

Core-shell microspheres are micron-sized objects, encapsulating an active ingredient with an organic or inorganic shell which can control the release of core by changing its porosity, size and thickness [18–22]. Encapsulation is used to protect the core materials from harsh thermal, chemical or mechanical degradation environments [23–25]. SiO₂ is stable under harsh conditions, and hence functions as an ideal shell composite to protect the inner core. Core-shell microspheres possess many promising properties, such as high surface area, thermal and chemical stability, high and adaptable dispersibility, active interfaces, and readily modifiable, which render them with the potential as an easier diluent agent and mobilization for improving permeability and recovering hydrocarbons trapped under challenging conditions [26–32]. Zhao et al. reported poly(octadecyl methacrylate)/3-methacryloxypropyl trimethoxysilane/silica multi-layer core-shell nano-composite with thermostable hydrophobicity and good viscosity break property by surface polymerization, and the resulting material showed marked ability as nano viscosity depressants for crude oil [33]. The use of core-shell microspheres in oil reservoirs during enhanced recovery is not common likely due to the lack of appropriate particle size for low permeability reservoirs and harsh reservoir conditions with high salinity and temperature.

In our previous work [4], we designed a breakable, solid-liquid microemulsion for reservoirs, which can be considered as diluent-loaded eggs. The aim is to confinement-induced release their payload upon encountering solid particles in narrow channels and confining pores blocking hydrocarbon transport recovery. Compared to the traditional bulk diluents distributing throughout heterogeneous reservoirs, diluents-loaded silica-shell microspheres can be targeted and selectively released locally when they are forced into the narrow and confined regions having comparable size with the dimensions of such particles. Therefore, as illustrated in Fig. S1, this approach has potential for reducing the loss of diluents/solvents. For bulk/free diluents, the large volume of solvent not encountering the pore blockages is waste and can harm the quality of oil, whereas for microencapsulated diluents, solvent not reaching the pores is still isolated and can readily be separated and reused. To the best of our knowledge, this is a novel concept about the application of core-shell organic-inorganic microspheres with breakable shells in process of improving relative permeability of heavy oil. Although the proof-of-concept of toluene-in-silica microspheres has been demonstrated in our past work, a systematic investigation of the relationship among various factors, including core materials, surfactants, shell materials, and their concentrations, is still lacking.

Herein, we reported a systematic study on the coating regulation of payload-in-silica microspheres with different sizes and shell thicknesses and brittleness. The roles and correlations of the factors, such as oil phases, surfactants, APTES, TEOS, were analyzed and discussed. This kind of breakable core-shell microspheres provides an alternative candidate for heavy oil recovery in low permeability reservoirs.

2. Material and methods

2.1. Materials

Heavy oil (API of 18.8° and 1.97% S) was obtained from Ecopetrol (Colombia) and used as received. Tetrahydrofuran (THF, ≥ 99%), toluene (≥ 99.5%, ACS grade), tetraethoxysilane (TEOS, ≥ 98%), polyoxyethylene (n = 9) nonylphenylether (Igepal Co-630, average Mn = 617) were purchased from Sigma-Aldrich (St. Louis, MO). Hexane (≥ 98.5%, ACS grade) was supplied by Alfa Aesar (Ward Hill, MA). Tween 80 was purchased from TCI America (Portland, OR). 3-Aminopropyltriethoxysilane (APTES, ≥ 99%) was obtained from Gelest Inc. (Morrisville, PA). All chemicals were used directly without further purification. Quartz sand (pure, 99.8%, 40–100 mesh, Acros Organics, Geel, Belgium) was used for preparing sand columns as model porous media. Unless stated otherwise, all references to water shall be understood to mean Milli-Q water (resistivity of ~ 18.2 MΩ·cm⁻¹).

2.2. Preparation of surfactant-stabilized emulsions

The oil-in-water emulsions were prepared using toluene or hexane and Milli-Q water in the presence of one of the two non-ionic surfactants (Tween 80 or Igepal Co-630). In a typical run, a stock solution of the surfactant was prepared by dissolving 0.2 mL Tween 80 or Igepal Co-630 in 44.8 mL Milli-Q water (for a concentration of 0.4% w/v surfactant). Then, 5 mL (10% v/v) toluene or hexane as the oil phase was added to the continuous phase and the system was emulsified by vigorous stirring for 2 h. Then, the system was homogenized via ultrasonication in the absence of vigorous stirring for 30 min. These conditions led to a turbid and homogenous suspension, indicating the formation of emulsion droplets. We varied the concentration of Tween 80 or Igepal Co-630 used to prepare the emulsions in the range from 0.2% to 2% v/v. We also changed oil phase concentration from 5% to 10% v/v.

2.3. Encapsulation of emulsion droplets with solid shells

Breakable microspheres were prepared by encapsulation of emulsion droplets in silica-solid shells using APTES and TEOS as comonomer via an emulsion templating technique through layer-by-layer self-assembly. The quaternization of the amine group which produced hydroxide ions made APTES a self-catalyst for the hydrolysis and condensation of silicate without the need of external catalyst [34]. As a typical synthesis, various amounts of APTES, ranging from 0.53 mL to 2.12 mL were added into Milli-Q water, producing final APTES concentrations in the range of 0.034–0.138 M (volume ratio of APTES and TEOS ranging from 1:1 to 4:1). Then, the mixture was vigorously stirred to fully dissolve the reactants. Afterwards, the solution was slowly added into the surfactant-stabilized emulsion while stirring. Sequentially, 0.53 mL TEOS (0.036 M) was added into the freshly prepared emulsion system while stirring and reacted for 24 h at room temperature to obtain toluene-in-silica or hexane-in-silica microspheres dispersion.

2.4. Characterization of solid-shell microspheres

The particle size distribution and zeta potential of solid-shell microspheres in different conditions were measured by use of dynamic light scattering (DLS) and laser Doppler electrophoresis (LDE) methods, respectively via Zetasizer Nano ZS 90 (Malvern Instruments, Ltd., Westborough, MA). The DLS measurements were carried out at a scattering angle of 90° at 25 °C. If the particle size was larger than 3 μm, we utilized optical microscope images to calculate the particle size. The size and shape of different solid-shell microspheres and microscopic visualization were observed by use of an optical microscope (Olympus BX51, Japan). Surface morphology and shell thickness of different kinds of microspheres were characterized by a scanning electron microscope (SEM, JSM-7500F; JEOL, Tokyo, Japan). In SEM measurements, samples were prepared by placing a droplet of microspheres dispersion onto a clean silica wafer, and then evaporating water at ambient temperature. The amount of payload in solid-shell microspheres was quantified using the ultraviolet-visible (UV–Vis) spectroscopy (UV-1800,
Shimadzu, Japan).

2.5. Heavy oil recovery experiments

Heavy oil recovery was evaluated using sand column experiments as described in our previous work [4,35]. Using the gravimetric analysis, the porosity of the sand column was calculated to be 42.05 ± 0.5%, and the corresponding pore volume (PV) was 1.44 ± 0.02 cm³. Afterwards, a pre-defined concentration (10% v/v) of solid-shelled microspheres dispersion in water was injected into the column using a programmable syringe pump (Nexus-6000, Chemyx Inc, Stafford, TX) at a selected flow rate (3.30 mL/min). Pressure gauges were installed at inlet and outlet of the column. Using this setup, the pressure drop was measured to be in the range of 22–40 kPa, corresponding to a pressure gradient in the range of 340–620 kPa/m. Based on these values, we calculated the permeability to be 1.71–3.11 D using Darcy’s Law [36]. According to the Carman-Kozeny equation [37], the corresponding pore throat diameter was calculated to be 35.8 ± 120 μm. The recovered mixture, heavy oil phase, was collected and then dried at 120 °C under vacuum for 24 h to evaporate residual toluene. The percentage of hexane-in-silica microspheres stabilized by Tween 80 (marked as B) can be completely broken with only a few microspheres forming small pores on shell surface. And the thickness of the silica shells was 95.22 ± 4.50 nm for microspheres B. Comparatively, toluene-in-silica microspheres stabilized by Igepal Co-630 (marked as C) have more easily breakable shells and solid-shelled microspheres C with shell thickness of 41.52 ± 4.40 μm can be totally broken, indicating the high brittleness of the thin silica shell, which was probably because of a low condensation degree of TEOS with less amount of APTES. It was also worth noting that most of hexane-in-silica microspheres stabilized by Tween 80 (marked as A) maintained relative good spherical structures, and hexane solid-shelled microspheres A just were cracked to form small holes on shell surfaces, which thickness of silica shell was estimated to be 116.36 ± 4.80 nm.

3. Results and discussion

3.1. Structural characterization

In this paper, we developed three solid-shelled microspheres using various payloads, surfactants, and APTES/TEOS ratio. The experimental conditions used for preparing these solid-shelled microspheres are listed in Table 1. We found that the morphology, size, shell thickness and brittleness of solid-shelled microspheres depended strongly on such these parameters.

Fig. 1 displayed morphology of hexane-in-silica and toluene-in-silica microspheres prepared from different conditions. From optical microscope images in Fig. 1(a), (d), (g), it can be seen that all of these three solid-shelled microspheres were relatively uniform with smooth surfaces and particle size was estimated to be 4.80 ± 0.21 μm, 1.72 ± 0.20 μm, and 0.96 ± 0.12 μm, respectively. While the corresponding emulsion droplet sizes without silica layer were obtained to be 1.10 ± 0.04 μm, 0.83 ± 0.09 μm, and 0.60 ± 0.18 μm from DLS measurements, respectively. It also indicated that both Tween 80 and Igepal Co-630 can act as a stabilizer to preserve a smooth surface for solid-shelled microspheres. Different surfactants produced various particle sizes because of interfacial tension differences.

As observed from SEM images in Fig. 1(b, c), (e, f), (h, i), three solid-shelled microspheres possessed breakable silica shell structures under ultra-vacuum system in SEM and then hexane or toluene encapsulated in microspheres was released from the broken shell. However, the breakable shell surface morphology was obviously different among such three microspheres. Most of toluene-in-silica microspheres stabilized by Tween 80 (marked as B) can be completely broken with only a few microspheres forming small pores on shell surface. And the thickness of the silica shells was 95.22 ± 4.50 nm for microspheres B. Comparatively, toluene-in-silica microspheres stabilized by Igepal Co-630 (marked as C) have more easily breakable shells and solid-shelled microspheres C with shell thickness of 41.52 ± 4.40 μm can be totally broken, indicating the high brittleness of the thin silica shell, which was probably because of a low condensation degree of TEOS with less amount of APTES. It was also worth noting that most of hexane-in-silica microspheres stabilized by Tween 80 (marked as A) maintained relative good spherical structures, and hexane solid-shelled microspheres A just were cracked to form small holes on shell surfaces, which thickness of silica shell was estimated to be 116.36 ± 4.80 nm.

3.2. Colloidal stability of solid-shelled microspheres system

Three solid-shelled microspheres formed by silica layer were very stable against aggregation for an indefinite period of time. Such microspheres suspensions that had been kept for 30 days or more showed no significant changes in particle size based on optical microscope and DLS measurements. The surfactants and surface amine groups of APTES provided stabilizing effect to the microspheres through steric and charge repulsion and increased in the interfacial elasticity resulting in enhanced colloidal stability [39,40].

In order to clarify the colloidal stability, zeta potential of hexane-in-water and toluene-in-water emulsion stabilized with Tween 80 or Igepal Co-630 without silica shells was measured and the obtained values for emulsions related to microspheres A, B, C were 15.00 ± 4.81 mV, −28.60 ± 6.29 mV, and −34.73 ± 3.19 mV, which indicated that all emulsions possess good colloidal stability and can be applied for solid-shell microsphere formation as emulsion templates. Subsequently, zeta potential of three microsphere suspensions with silica shell prepared using different parameters was investigated. The loading of APTES and TEOS on the hexane-emulsion or toluene-emulsion droplets surface decreased magnitude of zeta potential to 2.70 ± 0.62 mV, −7.42 ± 0.86 mV, and −8.04 ± 1.14 mV for solid-shelled microspheres A, B, C by overcoming the repulsive effects of the electrical double layers to allow the finely sized oil droplets to form larger droplets through coalescence, which presumably owing to the protonation of amino groups in APTES resulting in a condensation reaction with TEOS. This reduction was presumably owe to the hydrolysis of APTES and protonation of amino groups which led to NH₄⁺ ions form and adsorb on the surface of hexane-in-water or toluene-in-water emulsion. Afterwards, hydrolysis of TEOS and condensation reaction of APTES and TEOS continued to decrease surface charge density.

3.3. Toluene loading behavior

UV spectroscopy was utilized to prove the presence of toluene in solid-shell microspheres B and C, and to quantify and compare the toluene amount in them. To this end, the absorption at a wavelength of 261 nm, which is a characteristic peak for toluene, was selected in the experimental parameters for preparing different solid-shell microspheres.

In order to compare the breakability or forced release behavior of three solid-shelled microspheres, we tried the forced injection approach into

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Payload</th>
<th>Payload concentration (%)</th>
<th>Surfactant</th>
<th>Surfactant concentration (%)</th>
<th>APTES/TEOS ratio (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>hexane</td>
<td>10</td>
<td>Tween 80</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>B</td>
<td>toluene</td>
<td>10</td>
<td>Tween 80</td>
<td>0.4</td>
<td>4.0</td>
</tr>
<tr>
<td>C</td>
<td>toluene</td>
<td>10</td>
<td>Igepal Co-630</td>
<td>0.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>
a sand column as breaking stimuli, which was relevant and applicable to the reservoir conditions. The changes in the mean particle size were used as criteria of release. Fig. 3 displayed the particle size distribution after treating under forced injection for three solid-shelled microspheres. As observed in aspect of particle size changes, forcing solid-shelled microsphere suspensions into a porous media was an effective approach to rupture their silica shell resulting in the leakage of toluene or hexane from the solid-shelled microspheres. Among them, toluene-in-silica microspheres C was most easily broken with fragile silica shell evidenced from no microparticle detecting after forced injection process. While after the microsphere suspensions A and B passed through the column, it displayed two different peaks in particle size distribution, indicating the releasing of organic solvents but the partially breakage of solid-shell microspheres.

The aforementioned comparison among three solid-shelled microspheres demonstrated that solvents, surfactants, and APTES/TEOS ratio gave a significant effect on particle size, silica shell thickness, even brittleness and fragility of final products. Thus, it is necessary to investigate the roles and correlations of these factors.

3.5. Effect of payload

Fig. 4 presented optical microscope images for hexane-in-water emulsion and hexane-in-silica shell microspheres with different amounts of payload. For hexane emulsion prepared from 0.4% Tween 80, the average droplet size was $1.02 \pm 0.16 \mu m$, then the value was dramatically increased up to $3.10 \pm 0.12 \mu m$ after the silica shell grew with 0.095 M APTES and 0.036 M TEOS coating on 5% hexane emulsion. And with the increase of hexane concentration, the average droplet size increased to $4.80 \pm 0.21 \mu m$ for 10% hexane-in-silica microsphere. In our previous work using toluene as payload, the average particle size was $2.31 \pm 0.09 \mu m$ and $2.67 \pm 0.18 \mu m$ for 5% and 10% toluene-in-silica shell microsphere, respectively [4]. The results revealed that larger concentration of hexane or toluene supplied more reaction sites for the monomer and thus led to more active condensation and formation of larger particles. It also indicated that oil phase type and content in emulsion determined the size of solid-shelled microspheres.

3.6. Effect of surfactant

The system with larger concentration of surfactants produced smaller droplet-sized solid-shelled microspheres, as displayed in Fig. 5.
In detail, it can be observed that a significant reduction in the average particle size as the concentration of Tween 80 was increased from 0.2% to 0.4% for solid-shelled microspheres, and then when continuing to increase the surfactant amount, the particle size decreased slightly. For microspheres prepared from Igepal Co-630-stabilized emulsion, the particle size decreased from 0.2% to 0.6% Igepal Co-630, and then the decrease trend became slow. In the synthesis procedure, growing solid-shelled microspheres were stabilized against aggregation by surfactant molecules. The larger amount of surfactants led to less free aqueous space, resulting in the formation of fewer monomers in each micelle, and thus, a reduction in particle size [41]. Moreover, the particle size of Igepal Co-630-stabilized solid-shelled microsphere was obviously smaller than that of Tween 80-stabilized microsphere. This was mainly related to the hydrophilic-lipophilic balance (HLB) value of surfactant which influenced the droplets through a reduction in interfacial tension of the oil/water interface. Igepal Co-630 has a lower HLB which gives a lower activation energy for homogeneous nucleation and leads to more nuclei and smaller droplets.

3.7. Effect of APTES/TEOS

The concentration of APTES also plays a role in determining particle size. As shown in Fig. 6, solid-shelled microsphere used Igepal Co-630 as surfactant increased in size from 0.53 ± 0.07 μm to

![Image](image-url)
1.72 ± 0.11 μm with increase in self-catalyst APTES concentration. It can be explained that higher concentration of APTES increased the pH of the solution, which raised the rates of hydrolysis and condensation. The APTES molecules seemed to be mainly incorporated on the surface of the emulsion droplets and the particle size was enlarged. Besides, APTES provided more comonomer to the system and the increase in the amount of monomer resulted in the increase of particle size. However, with an increase in APTES content, the TEOS content should appropriately decrease to avoid the homogeneous nucleation of monomers [42]. The good match between APTES and TEOS content is essential to avoid the formation of core-free silica particles.

3.8. Heavy oil recovery behavior

In order to evaluate the effectiveness of solid-shelled microspheres with different parameters for enhanced hydrocarbon recovery in low permeability reservoirs, a series of heavy oil flooding tests were conducted in a sand column. The comparison of three solid-shell microspheres (A, B, C) prepared from different parameters on heavy oil recovery efficiency were presented in Fig. 7. As observed, at low injection volumes, solid-shelled microsphere C was the most effective means to recover heavy oil trapped in the porous media with recovery efficiency of...
54.27 ± 4.06% using 13.9 PV dispersion. At higher injection volumes, solid-shelled microsphere B acquired a higher percent recovery with heavy oil recovery efficiency up to 94.60 ± 3.41% using 34.7 PV dispersion, exceeding the efficiency of microsphere C at the same injection volume (73.69 ± 9.13%). Solid-shelled microsphere B had a low adsorption capacity and was easily washed-out and displaced more heavy oil in porous media. As stated above, solid-shelled microsphere C had more fragile and thin silica shell and was easier to break and release its payload under external force resulting in higher recovery efficiency initially. However, subsequently, it easily led to the particles aggregation because of larger surface-to-volume ratio resulting from its small particle size, and therefore it possessed high surface energies, which may limit fluid flow in the channels and slow down the recovery rate. Unfortunately, the heavy oil recovery efficiency of solid-shelled microsphere A (hexane-loaded microspheres) was not much satisfactory which may because its silica shell thickness was a little thick and not so brittle to be broken upon encountering solid particles in narrow channels and pores blocking heavy oil transport recovery. The relative magnitude of particle size and pore throat of reservoir is shown to influence the efficiency of heavy oil recovery using diluent loaded microencapsulates [37]. The current heuristics is that the initial particle size of microcarrier is smaller than the one tenth of diameter of pore throat to ensure the effective transport of carriers in pore channels [43]. The low efficiency of microspheres A in mobilizing heavy oil can partly be ascribed to the mismatch between microsphere size and pore throat diameter of the column, which can prevent the transport of microspheres into the lower section of the column. Comprehensively, toluene-loaded microspheres B stabilized with Tween 80 possessed more excellent ability to recover heavy oil trapped in porous media.

4. Conclusions

In summary, a series of breakable solid-shelled microspheres with different preparation parameters was developed and investigated as diluents applied in narrow channels and pores blocking hydrocarbon transport recovery. The roles and correlations for systematically synthesizing silica-shelled microspheres with controllable surface morphologies, particle sizes, and silica shell thickness were introduced, which can be regulated by tuning preparation factors such as payload type and concentration, surfactant type and amount, and APTES/TEOS ratio. Hexane-in-silica shell microsphere had large particle size and thick silica shell and was not brittle to be broken, while toluene-in-silica shell microsphere stabilized with Igepal Co-630 exhibited totally different property with small particle size and very fragile and brittle silica shell. The core–shell structure of microspheres formed by hexane or toluene wrapped with an inert and breakable silica layer provided ease of protection and releasing payload. The present study also showed the heavy oil recovery efficiency results obtained from sand column tests using three different solid-shelled microsphere dispersions. Among them, toluene-in-silica solid-shelled microsphere using Tween 80 as a surfactant provided excellent heavy oil recovery efficiency up to 94.60%. The realization of breakable solid-shelled microspheres will be beneficial to enhanced hydrocarbon recovery and improving permeability of reservoirs.

Declarations of interest
The authors declare no competing financial interest.

Acknowledgement
The authors gratefully appreciate the financial support from the China Scholarship Council (CSC).

Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.fuel.2018.07.006.

References


