In apparent viscosity and storage modulus test system considering sulfonic acid type synthesis of Gemini Surfactant

Yanlin Chen, Qingzhe Jiang, Zhaozheng Song*, Ming Ke and Chunpeng Yang
College of Science, China University of Petroleum-Beijing(CUPB), Beijing 102249, CHINA

Abstract
Improvement of recovery after water flooding has become an important issue of oil exploration and development. Existing methods flooding technology is one of the most important oil displacement method. Therefore, the development of low cost, simple synthesis process, the good performance of the surfactant is of great significance. A novel Gemini surfactant type this study amino acid made (Gemini surfactant), use good table Gemini surfactant, temperature tolerance, emulsification and adsorption properties, which by replace a series of Gemini surfactant amino acid type (hereinafter referred to as AHS surfactant) artificial sand filling tube displacement experiments. By displaying the surfactant solution, permeable structure differences sand filling tube 19, found that the oil recovery increased by 24%, or AHS - 14 surfactants can effectively meet the requirements of surfactant flooding, enhanced oil recovery, provided field trials better prepared.

Keywords: sulfonic acid, Gemini surfactant, interfacial tension and oil recovery.

Introduction
After formation of natural energy flow in the formation of crude oil of an oil production and water injection after gas injection of secondary oil recovery, chemical substances, or energy use high-pressure pump group pressure into the formation, formation physical change to improve recovery factor method called "tertiary recovery", its displacement mode contains chemical flooding, polymer flooding and microbial flooding and mixed phase displacement, etc. In order to better improve the residual oil formation in the late development of oil output, "tertiary oil recovery is imminent. Chemical displacement technique is proposed by the method of enhancing oil recovery in the early 20th century, has been widely used each big oilfield (three, four, five). Chemical compound flooding using alkali, surfactant and polymer between the different advantages of each other together in order to achieve better oil displacement effect.

In the 1960 s, China's Xinjiang Kara May oil field to research, Daqing oil field in oil development beginning to conduct the research to enhance oil recovery. Through the study found that asp flooding technology at home and abroad is better than that of a single chemical flooding technology. In recent years, our country basic theory research on complex flooding has made many important achievements. To inorganic alkali and organic or inorganic acid in the crude oil combination can reduce viscosity of crude oil to increase liquidity, using the principle of the asp flooding technology can enhance oil recovery.

Surfactants can greatly reduce the oil-water interfacial tension, on the basis of capillary effect will be better able to make the residual oil formation quickly start to activate the remaining, combined with the oil film or oil wall after the displacement pressure under the action of output as well 2. Polymer after contact with the formation of crude oil can improve the efficiency of oil displacement agent of swept volume and launch more residual oil. To enhance the oil recovery are combined with each other. Through scientific research found that the surfactant flooding to improve oil recovery requirements must keep oil/water interfacial tension to a 10-3 m N/m, because most of the strata in the crude oil composition is different, and surfactant specificity is too strong, the market most petroleum sulfonate, sodium lignosulphonate and alkyl benzene sulfonate to crude oil fell to ultralow oil-water interfacial tension, and most of the surfactant molecules resistance to salt, low temperature resistance. So the prominent surfactant on the capabilities of wide applicability has been focus in the field of composite chemical flooding difficulty

In recent years, the Gemini surfactant (Gemini surfactant) due to its special molecular structure and presents many traditional surfactants that the highly active performance, such as high surface activity, critical micelle low density, good resistance to salt resistant and good compatibility with other oil displacement additives, has become a hot research at home and abroad. 1

Gemini surfactant good table salt resistance of heat-resistant etc., it is introduced into the chemical flooding to enhance crude oil recovery method, in order to solve the single surfactant in the field of tertiary oil recovery within the scope of the existing problems.

The synergistic effect of surfactant mixed system mainly depends on all kinds of surface active agent of the physical and chemical properties. Both Gemini surfactant or the traditional surfactant is after with other surfactants have better table interface performance, the most prominent is after, with non-ionic surfactant to quickly reduce the interfacial tension of table, salt resistance and heat resistance of the surfactant solution is also improved. Rosen, etc. are
studied to reduce the liquid surface tension with C10DADS hybrid system is better than single system containing C10MADS effect.

Collaborative between the surfactant is mainly manifested in two or more than two in the interaction between hydrophilic lipophilic group can show better table interface performance, because Gemini surfactant has two hydrophilic lipophilic group in a fixed way connection between each other.

So when the distribution of the surfactant system contains Gemini surfactant has a better effect of compound. For example, in the process of oil displacement sulfonic acid type Gemini surfactant and non-ionic surfactant compound with after the salt tolerance of temperature resistance than choose single compound with the sulfonate surfactant system good oil displacement effect on conversion.

**Material and Methods**

Strategy of crude oil is an important energy resource, how to increase oil recovery factor is an important research work. Surfactant flooding and binary and ternary composite containing surfactant flooding is the main technologic adopt a "three". The selection of surfactant has important significance. Reportedly Gemini surfactant than single surfactant has a better oil displacement effect, although the synthesis of Gemini surfactants cost is higher, but in industrial applications has better physical and chemical performance than ordinary surfactants. High table (world) surface activity in the smaller concentrations that can be achieve ultra-low interfacial tension values between the oil and water can better improve the oil recovery. Solubility is good, can be adapted to different salinity formation reservoir can improve water flooding effect of needs. Its adsorption on the surface of the rock is low less loss of surfactant adsorption improve the surfactant flooding economic benefits. Surfactant low critical micelle density surfactants effect is good, in the same amount of oil dissolve the need when the Gemini surfactant less than conventional surfactants, you can better use the micro emulsion flooding technology. Good compatibility with other oil displacement additives can further improve the existing common surfactant application range effectively reduce the cost of Gemini surfactant oil displacement. Gemini surfactant is relatively stable at high temperatures, be helpful for its application in high temperature.

The molecular structure of the conventional surfactant is composed of two parts, the hydrophilic and hydrophobic structure, which is an asymmetric "hydrophilic and lipophilic" knot Fig. 1A). And Gemini surfactant molecular structure is different from the conventional surfactants, its molecular structure is constituted by at least two hydrophilic groups and two hydrophobic chains, in the hydrophobic chain end or hydrophilic chain closer to the end, by the connection on the basis of chemical bonds in the form of connection. Fig.1 B).

Such as carboxylic acid type anionic Gemini surfactant has stronger than SDS salt resistance and resistance to calcium soap dispersion, allowed more of Gemini surfactants used in high salinity oil reservoir, expanding the scope of the tertiary reservoir application?

**Nanomaterials:** Gemini surfactant as template agent and the preparation of nanometer materials reported more resistant adhesive. At the same time because of Gemini surfactants with the essence of the amphiphilic properties, can be well used in the synthesis process of nanomaterials.

Especially in the field of Nano research material production and forming process of the research of Gemini surfactants. For example, within the scope of the different concentration, the molecular structure of the liquid crystal phase internal phase from a side trip to layer gradually transition phase. The synthesis process of different appearance molecules copied to other material with special morphology of nanoparticles can be prepared. Esme to aqueous solution of C12-2 - C12, cl - 2 (2%), the formation of the rod cation micelle for flexible template synthesis of gold nanoparticles, its dosage is far less than that required for achieve the same effect the dosage of the conventional surfactant acetyl trim ethyl ammonium chloride (30%). Xiao-dong Zhou and so on synthesis of the imidazole quaternary ammonium salt type of Gemini surfactants synthesis of the products can be used as decorative materials agent. After study is Gemini surfactant changed the material of the decoration and molecular configuration, well suitable for the synthesis of nanomaterials field.

**Other aspects:** Gemini surfactant with its unique molecular configuration, performance with high table activity, in the transitional phase has a special arrangement, relatively stable molecular film, features such as low CMC values, greatly saves costs, is more advantageous to promote the Gemini surfactants in the field of comprehensive use. Application prospect is very broad to become the most potential of surfactant on the market.

**Common technology:** This study with alkyl fatty amine (including carbon number 12, 14, 16, 18) respectively, 3 - chloral - 2 - hydroxyl propyl sulfonic acid sodium, dichloride tri ethylene glycol as the main raw material, a new type of amino sulfonic acid sulfonic acid was synthesized, Gemini surfactant and its surface activity, oil/water interfacial activity, temperature tolerance, adsorption, emulsification, intensive research.
At the same time, for the first time the amino sulfonic acid type Gemini surfactant was applied to chemical compound with oil displacement system and the binary flooding system, found that the amino sulfonic acid type between Gemini surfactant and surfactant and polymer had good compatibility. Further study of amino sulfonate Gemini surfactant and reduce oil-water interfacial tension between crude oil Mechanism, and improve the universality of Gemini surfactants used.

**Gemini surfactant and the formation of core:** Water or oil wet rock and the change of the contact Angle between the Gemini surfactant, the researcher on the mechanism of the reverse wetting. The composition, structure and reservoir in different blocks the formation by surfactant between compound with to reduce the specificity of the surfactant, develop low-cost surfactant formula suitable for all kinds of mineral deposits. The high cost of Gemini surfactants, optimize the synthesis conditions, can work out the preparation process of the marketization, improve the production rate, cost estimation of various composite flooding experiment, through the new well design and reconstruction of old well further produce more stable.

Surfactant for err is given priority to with sulfonate surfactant, mostly because it has good heat resistance salt resistance. In order to achieve good emulsification and solubility, can choose contain oxygen ethyl or oxygen propyl block of non-ionic surfactant. Therefore this study with alkyl fatty amine (including carbon number 12, 14, 16, 18) respectively, 3 - chloral - 2 - hydroxyl propyl sulfonic acid sodium and chloride tri ethylene glycol as raw material, through two-step nucleophilic substitution reaction, synthetic containing hydroxyl, ethyl sulfate type of Gemini surfactant.

**The synthesis of Gemini surfactant:** From Figure 4 shows, in the infrared absorption spectrum of 2920, 2850 strong absorption peak for CH3-, -CH2-asymmetric C-H stretching vibration absorption peak, 3440 wide absorption peak for the hydroxyl hydrogen bond association after stretching vibration absorption peak, 1663 for fatty amine bending vibration peak, 1465 for methyl and methylene stretching vibration absorption peak, 1366 for methyl symmetric bending vibration absorption peak. 1189cm, 1100cm is the hydroxyl on the C-O stretching vibration absorption peak; 1060 for the sulfonic acid group of the symmetric stretching vibration peak by the map shows that the product is a single chain amino sulfonic acid surfactant. Therefore, based on the infrared absorption spectrum can be seen within the molecule containing the target hydroxyl groups of amino sulfonic acid and acetic ether oxygen radicals groups. Gemini surfactants with amino sulfonic acid.
Fig. 4: FTIR spectra of amino sulfonate Gemini surfactant

Were taken in a certain amount of synthetic product AHS-12, AHS-14, AHS-16, AHS-18 surface active agent placed in the beaker, add an appropriate amount of distilled water for stirring the configured to different concentrations of surfactant solution. The surface tension of the solution was measured at different concentrations of AHS surfactants. Experimental temperature: room temperature 25°C. The mole concentration of Gemini surfactant is the horizontal coordinate, and the surface tension value is the vertical coordinate, and the result is shown in Figure 5.

Fig. 5: The surface tension of Gemini surfactant

This paper by twelve amine type synthetic amino sulfate Gemini surfactant (AHS) as an example, shows a series of amino sulfonic acid type of Gemini surfactants synthesis method. By 14 amine and method of synthesis of Gemini surfactants are basically the same. Three flasks containing the reflux condenser pipe fixed on an electric blender, respectively to three flasks with twelve amine 37.1 g, tetra butyl ammonium bromide 0.1 g, 100 ml isopropyl alcohol, control the reaction temperature is 50°C, 30 min.

After 41.3 g of 3 - chloral - 2 – hydroxyl propyl sulfonic acid sodium and 100 ml of distilled water immiscible chase at 30 d/min speed drop to join the system, and finished up to 85°C, the continuous reaction 7.5 h, product into a reddish transparent liquid, to remove product rotating distillation solvent after cooling, get sticky and thick, coarse product ethyl alcohol recrystallization, in the suction filter to get white powder, continuous recrystallization with anhydrous ethanol three times. It will get the white powder of vacuum drying to get the middle.

Body product N - dodecyl - amino ethyl sulfonic acid sodium, the product yield was 82.4%.

Will three flasks containing the reflux condenser pipe fixed on the electric mixer, respectively to three flask adding intermediates N - dodecyl - amino ethyl sulfonic acid sodium, anhydrous sodium carbonate and N, N - dimethyl form amide 200 ml, reaction temperature is 100°C, 30 min after stirring, slowly add dichloride tri ethylene glycol 11.25 g, and continuous reaction after 12 h. The reaction liquid cooling after the suction filter, rotate the filtrate distillation to remove the solvent. The coarse product ethyl alcohol recrystallization in the suction filter to get white powder, repeat the above operation with anhydrous ethanol three times recrystallization. Will get the white powder of vacuum drying to get final product sulfuric acid type of Gemini surfactants, the yield was 78.6%.

Gemini surfactant indoor sand filling tube displacement experiment: In Chang Qing oil field geology and reservoir distribution, according to the permeability and the size of the poor design, sand filling tube displacement test validation AHS - 14 Yu Chang Qing surfactant can apply non homogeneous formation of oil field. Sand filling tube displacement experiment is surfactant evaluation method to improve recovery factor is the most clear.

Oil-water relative permeability are essential to describe reservoir data, the parameter has a significance of reservoir recoverable oil/gas, at the same time, it can be dynamically simulated formation reservoir in the lab, evaluating permeability and oil recovery, the relationship between service for field test. This parameter is often in the laboratory with columnar core water permeability measurement. The determination of oil and water relative permeability is divided into steady state method and unsteady method. The unsteady method experimental time is shorter, in conformity with the reservoir water flood recovery history and has been widely adopted. Unsteady method is divided into constant speed and constant pressure method, most oil fields adopt transient test this parameter. The experimental study of the unsteady method of constant speed Jones its basic theory is to ignore capillary force of Darcy's law and a series of continuity equation.

\[
\frac{KA}{\theta L} = \frac{Q}{P} \quad (1)
\]

\[
K = \frac{Q\theta L}{PA} \quad (2)
\]
In the process of experiment, the test of two different core permeability demands extremely reasonable, consistent with the actual formation permeability. By testing the permeability of low permeability cores for 29 md, high permeability core permeability is 550 md, poor of 19, poor is bigger. According to reports in the literature and the related data this data in accordance with the requirements of different permeability, consistent with the actual formation of Chang Qing oil field exploitation.

**Results**

Container to add a certain amount of simulated oil center, run the test software and according to the steps to open the advection pump, to 3.00 mL/min flow pressure, saturated one by one, make different permeability core fully saturated, record data, when flow is constant, the moisture content of 99% to stop putting pressure on, shut down the advection pump, to decrease to 0.001, the disconnect device, container record center residual volume, residual oil in the effluent volume and relevant data such as dead volume, the volume calculation of saturated oil.

![Fig. 6: The test of saturated oil](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The test of saturated oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different permeability sand filling tube (ml)</td>
<td>29</td>
</tr>
<tr>
<td>Saturated volume (ml)</td>
<td>32</td>
</tr>
</tbody>
</table>

The table 2 shows that oil recovery in low permeability sand filling tube for 10 ml, it may be that the displacing fluid percolation from high permeability reservoir, so high permeability reservoir are oil is greatly 34 ml to permeability reservoir. Water drive recovery factor 45%, the figure 3 shows that after water flooding, core inside still have a lot of residual oil, due to the interfacial tension between oil and water too big residual oil droplets will start, so there are still a lot of in the more pore residual oil.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The recovery of water flooding oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different permeability</td>
<td>Low permeability</td>
</tr>
<tr>
<td>Oil recovery (ml)</td>
<td>10</td>
</tr>
</tbody>
</table>

The concentration of 0.3% AHS - 14 surfactant solution container to join I to center, connection method is the same as water drive device, run the test software and according to the steps to open the advection pump, to 3.00 mL/min flow pressure, record data, the observed phenomenon, core section as shown in table 3.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>The recovery of the surfactant flooding oil</th>
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<tbody>
<tr>
<td>Different permeability</td>
<td>Low permeability</td>
</tr>
<tr>
<td>Oil recovery (ml)</td>
<td>8</td>
</tr>
</tbody>
</table>

The table 3 shows that oil recovery in low permeability sand filling tube is 8 ml, oil recovery in high permeability sand filling tube is 17 ml. Surfactant flooding total recovery is 24%, the figure 4-3 shows that after surfactant flooding, core internal residual oil is less, show that AHS - 14 surfactant after contact with the sand filling tube of crude oil, can quickly activate residual oil by capillary effect, using its own emulsification oil-water out together. So the surfactant has a better effect on displacement on the reservoir.

Aimed at the characteristics of reservoir in Chang Qing oil field and the present situation of oil displacement, the design is poor for 19 parallel double pipe sand filling experiment, the results of water flooding recovery efficiency is 45%, the surfactant flooding recovery efficiency is 24%. Show that AHS - 14 surfactant flooding has a good effect, can better use the surfactant flooding technology.

Alkyl chain length of Gemini changing wettability of solid surface

In order to study the cationic Gemini surfactant structure on the solid surface wettability regularity and mechanism of the influence of me. The choice of different hydrophobic alkyl chain length of cationic Gemini surfactants for the oil wet and wet solid table. The change of the surface is wettability.
Table 4

Gemini surfactant change wettability on the surface of the results

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
<th>Oil wet surface</th>
<th>Water wet surface</th>
<th>Oil wet surface</th>
<th>Water wet surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS-12</td>
<td>0</td>
<td>118</td>
<td>65</td>
<td>37</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>24</td>
<td>37</td>
<td>60</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>22</td>
<td>32</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>GS-14</td>
<td>0</td>
<td>116</td>
<td>79</td>
<td>32</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>20</td>
<td>65</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>22</td>
<td>74</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>GS-16</td>
<td>0</td>
<td>110</td>
<td>74</td>
<td>32</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>22</td>
<td>74</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>22</td>
<td>74</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 7: Gemini surfactant change wettability on the surface of the results

Three kinds of Gemini surfactant hydrophobic alkyl chain length (carbon) respectively for 12, 14 and 16, because of the surfactant molecules in oil surface adsorption, all can change oil wet surface into water wet surface, contact Angle respectively by two 1180 e! 116 "and 110 reduced to e / 2 110. 370 and 400; similarly, surfactant molecules in the water Adsorption on the surface of the wet surface water change for weak water wet surface, contact Angle respectively by e = 240! 200 and 180 to e = 760! 64 and 47 "/" in the process, three kinds of Gemini surfactants on the solid surface wettability change direction is consistent, But change the magnitude of the difference, embodied in: with the increase of hydrophobic alkyl chain length, the wettability of solid surface Sex change the size of the lower "analysis think this is because the length of the hydrophobic group is different, lead to their changing solid table Surface wettability showed differences".

Conclusion

In order to improve oil recovery, there is now many ways, in this study, in order to better enhance the recovery on the existing basis, we study the sulfonic Gemini surfactants. By synthetic amino acid series Gemini surface performance test Gemini surfactants. Basis determined by the Tour de France series AHS surfactant surface tension method, different concentrations, surface tension of various surfactant critical micelle concentration of the surfactant under on the AHS surface active agent concentrations the increase in the oil / water interfacial tension value represents the tendency of decrease of the first increase. We need to finally get the active agent, and the use of research to get active agent can greatly increase oil recovery.

Through this study, we found that an amino acid-type surfactants (AHS) and the Gemini surfactant and table series AHS surfactant interfacial surface tension measuring torque, synthetic surfactant series in AHS. AHS found –14 surface the critical micelle levels of the active agent is at least 0.68 L tendency - 1; AHS - 14 surfactant having a good time-temperature resistance, heat temperature can reach 80 °C, which can be adapted to the hot water flooding technology and is suitable for high temperatures formation; AHS good emulsifying properties of surfactants, water in oil emulsion phase stable salinity stratification 50,000 mg L solution /. So it has good compatibility between the surfactant and polymer or surfactant additives. Although this study active agent achieved good results, but because of the active agent complex production process, demanding conditions, so we need further research in order to have an easier way to get more efficient active agent.

Three kinds of Gemini surfactant hydrophobic alkyl chain length (carbon) respectively for 12, 14 and 16, because of the surfactant molecules in oil surface adsorption, all can change oil wet surface into water wet surface, contact Angle respectively by two 1180 e! 116 "and 110 reduced to e / 2 110. 370 and 400; similarly, surfactant molecules in the water Adsorption on the surface of the wet surface water change for weak water wet surface, contact Angle respectively by e = 240! 200 and 180 to e = 760! 64 and 47 "/" in the process, three kinds of Gemini surfactants on the solid surface wettability change direction is consistent, But change the magnitude of the difference, embodied in: with the increase of hydrophobic alkyl chain length, the wettability of solid surface Sex change the size of the lower "analysis think this is because the length of the hydrophobic group is different, lead to their changing solid table Surface wettability showed differences".

Cationic Gemini surfactants in reducing oil dynamic interfacial tension on ice with different dynamic interfacial tension Character, at the same time, the different characteristics of the dynamic interfacial tension and oil recovery has a close correlation between” Properties of cationic surfactants on the surface of the solid adsorption on solid surface plays a main role, adsorption If by cation exchange, on the other hand, cationic surfactant structure and system environment also affects the Yang Ion Gemini surfactant adsorption on solid surface saturated” In terms of impact on solid surface wettability, cationic Gemini surfactants oil-wet surface can be eventually change.

For hydrophilic even strong hydrophilic surface; For water wet solid surface, cationic Gemini surfactants hydrophilic surface can be eventually Change as the weak hydrophilic surface, and not in the reverse wetting” Gemini surfactant (interface) in the table on the arrangement of than single
head (ordinary) surfactant close together, leading to a Gemini surfactant in surface can reduce system, and shows the change of solid surface properties, etc. Than ordinary surfactants has more prominent performance”.

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