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Research Progress of the Interfacial Tension in Supercritical CO₂-water / oil System

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Abstract

Carbon dioxide (CO₂) is considered as one of major greenhouse gases, which has a significant contribution to global warming and has attracted more and more attention in recent years. So it’s necessary to develop more efficient technologies to reduce CO₂ emission. Carbon dioxide capture and sequestration (CCS) is one promising option to reduce CO₂. CO₂ flooding technique can enhance the oil recovery and achieve the storage of CO₂ simultaneously. Therefore it is an important technology to support common development in terms of energy and environment. Under the high pressure, the interfacial tension (IFT) can affect fluid flow during the process of CO₂ flooding greatly. Accordingly, there is an important significance to research miscible slug process and improve displacement efficiency. Hence the study of the IFT on supercritical CO₂-water / oil system is indispensable.

In order to understand the characteristic of IFT in-depth, this paper summarizes the IFT of CO₂-water / oil system from the aspect of measuring methods, influencing factors and theoretical models. Currently there are less experimental data of IFT under the high pressures because of measuring difficulties in supercritical CO₂-water / oil system. As one of the most effective measurement methods, the pendant drop method is developed gradually. This paper introduces the fundamental principles of several methods including selected plane method (SP), drop shape analysis (DSA) and axisymmetric drop shape analysis (ADSA). The relationships between pressure, temperature, concentration of CO₂, salinity and IFT are summarized. Generally speaking, the IFT increases with the increasing pressure and salinity, while decreases with the increasing molar fraction of CO₂. The effect of temperature on IFT is controversial in different researches. At the same time, this paper also presents the theoretical models of IFT in supercritical CO₂-water / oil system. The work shows clearly the basic principles and applicable scopes of the statistical thermodynamics theories including density gradient theory (DGT) and density function theory (DFT). Finally, the directions should be strengthened concerning the study of IFT as follows: In terms of experiment, it is necessary to find out a method to measure the practical density difference by tracing system; Besides, a more accurate equation of state (EOS) should be constructed to calculate IFT. Therefore the proper measurement method, accurate injection pressure and concentration of CO₂, rigorous theory and reliable mathematical model can be considered as research directions in future works.

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1. Introduction

Enhanced oil recovery (EOR) by CO₂ flooding is an important technology to support common development in terms of energy and environment, because it not only enhances the oil recovery efficiency up to 8–16% effectively, but also reduces greenhouse gas emission considerably. The major mechanism is proposed during the process of displacement oil by injecting CO₂ that is the mobility improvement, which is mainly attributed to viscosity reduction of the oil phase by gas flooding. The IFT is defined as the free energy per unit surface area of the interface between two phases [1]. Under the high pressure, the adsorption of CO₂ in liquid can easily cause the exchange of interface and the change of phase density. For this reason, in petroleum industry, small variations of IFT have an impact on capillary pressure and permeability, and then the oil flow process through capillary of porous medium are also affected. Especially the process of tertiary recovery, which can not only increase the concentration of organic in the injecting agent, but also reduce IFT greatly in system when the supercritical CO₂ is injected to oil well, thus reduces operating costs and improves recovery. From the above, the IFT of supercritical CO₂-water / oil system is vital parameter to mass and heat transfer during the process of oil refining, coal liquefaction, tertiary recovery etc. The precise and reliable IFT value can be obtained only through the experimental methods. Therefore, it is very critical to choose measurement methods of IFT under the high pressure. And the influencing factors such as temperature, pressure, CO₂ concentration and salinity etc. should be considered before experiment. In addition, theoretical study and reliable models of IFT for CO₂-water / oil system are also the focus during engineering design and industrial application. So this paper introduces measuring methods, influencing factors and theoretical progress of CO₂-water / oil IFT in more detail.

2. IFT measurement method

Many methods have been developed to determine the IFT, and they have the corresponding scope of application and thermodynamics. The IFT value is smaller under the high pressures and elevated temperatures, so it is necessary to choose an appropriate method to measure it. The pendant drop methods including SP, DSA and ADSA are developed gradually.

For the selected plane method (SP), the plane size after the pendent drop image is measured, and the IFT can be worked out through the modified Bashforth-Adams equation [2] to determine correction factor of drop shape [3,4]. This method was proposed at the end of the 19th century, the measurement precision was less than 2~3% at the experimental conditions [5]. But this method has been displaced gradually by drop shape analysis (DSA) and axisymmetric drop shape analysis (ADSA). In the DSA method, the coordinate of the whole droplet profile could be determined by using computer digital techniques, and then coordinated point values are fitted to Bashforth-Adams equation to acquire capillary constant which is key to calculate IFT [2]. Generally, the accuracy of measurement is about 0.1% [6].

With the rapid development of the technology of digital image processing, an accurate interfacial profile of the pendant drop can be obtained by the ADSA method. The drop profile which is a best fit for numerical calculation is found through solving the Laplace equation, and then a equation is construct to calculate the IFT by using the equality between the equation of axisymmetric interface and ordinary
differential equation of arc length [5,7]. The accuracy of ADSA method is better than DSA, and the ADSA method has become the focus because of the simple operation and wide measurement range (0.01 to several hundred mN/m).

The difference between the densities of gas and liquid phase could be measured by the pendant drop analysis method. The accuracy of IFT value can be improved further if the mixed phase density replaces the density of pure substance. What’s more, the factors including build-up time of droplet, temperature and pressure etc. are also critical to measure the IFT accurately.

3. The influence factors of IFT

It is a huge and complicated system when CO₂ is sequestrated in geological conditions especially depleted oil reservoirs. In order to predict the capacity of CO₂ flooding crude oil and the security of sequestration, it is necessary to study the IFT change with pressure, temperature and CO₂ concentration in the supercritical CO₂-water / oil system. At the same time, it’s meaningful to the guide the design and site selection of CO₂ geological sequestration. In recent years, the researches of IFT in different systems are listed in table 1.

Table1. Interfacial tension measurements in CO₂-water / oil system in literatures

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>Temperature (℃)</th>
<th>Pressure(MPa)</th>
<th>System</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wesch [8]</td>
<td>PD-SP</td>
<td>25-60</td>
<td>0-30.0</td>
<td>CO₂-water</td>
<td>1997</td>
</tr>
<tr>
<td>Changyu Sun [9]</td>
<td>PD-SP</td>
<td>66</td>
<td>15.0-33.4</td>
<td>CO₂-crude oil + water</td>
<td>2005</td>
</tr>
<tr>
<td>Akutsu [10]</td>
<td>PD-SP</td>
<td>20-60</td>
<td>7.5-16.5</td>
<td>CO₂-water + surfactant</td>
<td>2007</td>
</tr>
<tr>
<td>Georgiadis [12]</td>
<td>PD-DSA</td>
<td>25-101</td>
<td>1.0-60.0</td>
<td>CO₂-water</td>
<td>2010</td>
</tr>
<tr>
<td>Bikkina [13]</td>
<td>PD-DSA</td>
<td>20-60</td>
<td>1.5-20.8</td>
<td>CO₂-water</td>
<td>2011</td>
</tr>
<tr>
<td>Chalbaud [14]</td>
<td>PD-ADSA</td>
<td>27,71,100</td>
<td>4.5-25.5</td>
<td>CO₂-seawater</td>
<td>2009</td>
</tr>
</tbody>
</table>

3.1. Pressure
The influence of pressure on the IFT has been investigated by many researchers. Generally, it is found that the IFT decreases with increasing pressure for both CO₂-reservoir brine and CO₂-crude oil systems, this is attributed to the adsorption of CO₂ molecules and the higher CO₂ solubility at elevated pressures [15].

For CO₂-water system, the quasi-static pendant drop method was utilized to measure IFT at temperatures ranging from 278 to 335 K and pressures from 0.1 to 20.0 MPa, the IFT showed a pronounced dependence on pressure and temperature [16]. In addition, the change of IFT relates to critical pressure (Pc). In the conditions of pressure, temperature and water salinity, the analysis results of Bachu and Bennion [11] revealed that at constant temperature and salinity, the IFT steeply decreased with increasing pressure in the range P < Pc, and it trended to a constant value after falling slowly at higher pressures; What’s more, the change of IFT with pressure is relative to phase state. The experimental IFT values were generated by Bikkina et al. [13] in the conditions of 1.5–20.8 MPa and 298–333K. It was observed that the IFT decreased with pressure at both subcritical and supercritical temperatures when the CO₂-rich phase was gas. But the IFT was not relevant to pressure and temperature when the CO₂-rich phase was liquid or supercritical fluid. Similarly, for CO₂-oil system, the IFT decreases with increasing pressure. In recent years, the experimental measurement of IFT is conducted between CO₂ and oil covering a wide range of pressure. Under various pressure and temperature conditions, the results of Wang and Zhang [17,18] showed that the IFT linearly decreased with increasing pressure in CO₂-crude oil system. Furthermore, for the crude oil + reservoir brine system and the CO₂ + crude oil + reservoir brine system, the IFT remain almost constant at different pressures, but the IFT of the latter is slightly lower at higher pressure because more CO₂ dissolves in the brine and oil phases [15]. SO CO₂ injection can be successfully used to enhance oil recovery by decreasing the IFT of reservoir fluid and water, reservoir fluid and CO₂.

3.2. Temperature

There are two reasons for the effect of temperature on the liquid IFT: On the one hand, intermolecular interactions forces of liquid become weaken with increasing temperature, which leads to the molecules energy loss from inner to surface of liquid. On the other hand, the bulk densities beside the interface are affected by temperature change [19]. Some scholars consider that the IFT decreases with temperature going up. For CO₂-water system, the experimental data was reported by Chiquet et al. [7] at 308–383 K. The results showed that the IFT values swing from 30 to 23 mN/m. And for CO₂ + crude oil system, the results of LuoYu Xiang et al. [20] revealed that the IFT coefficient between crude oil and gas phase decreased with increasing temperature. The contrary conclusion was gained by others under the different experiment conditions. Daoyong Yang et al. [5] measured the IFT between reservoir brine and CO₂ at 27, 58°C and pressure up to 30 MPa. The results demonstrated that the IFT increased as temperature increase because of the lower CO₂ solubility at higher temperature. Yet Bachu et al. [13] proposed that the dependence of IFT on temperature was related to CO₂ phase. The IFT increased with rising temperature at T<Tc (critical temperature), and increased again after the values decreased obviously around the critical point. Finally, the IFT values trended to a constant at T>Tc and high temperatures. On the aspect of theory, when temperature goes up, the increase of IFT has been proved by Xiaosen Li et al. [21]. The DGT and PC-SAFT were combined to predict the IFT in CO₂-water system. In the experimental temperature range, the IFT decreased at low pressure while increased at high pressure with rising temperature. The effect of temperature on IFT is so complex that it should be taken into account in the future.

3.3. Component concentration
The IFT can be affected by CO₂ concentration. The influence of CO₂ molar composition \(x_{CO2}\) on IFT was studied by Changyu Sun et al. \[9, 22\] as CO₂ was injected to crude oil + reservoir water under stratum conditions. The experimental data showed that the IFT value decreased when \(x_{CO2}\) changed from 0 to 65 mol\%. And when \(x_{CO2}\) was 65 mol\%, CO₂ and crude oil were completely miscible each other, in other words, 65 mol\% was the best injection ratio of CO₂. Certainly, the salinity can also cause the change of the IFT. The experiments of IFT were conducted by Chalbaud et al. and Bachu et al. \[11, 14\] when salinity covered the range from 5 to 150 g/L and from 0 to 334 g/L. The results showed that the IFT increased with increasing water salinity at constant pressure and temperature, which was consistent with the molecular dynamics simulation. But, the influence of salt on IFT is so little as to be unnoticeable when 20 g/L NaCl is added to CO₂-water system \[7\]. What’s more, Lingling Zhao et al. \[23\] also indicated that the interactions between water molecules and between CO₂ molecules (“self” interactions) contribute positively to the IFT, while the interactions between water and CO₂ molecules (“cross” interactions) contribute negatively to the IFT.

4. Theoretical study on IFT

Interfacial phenomena of complex mixtures play a crucial role in a number of industrial processes, but the experimental measurement in situ is difficult and expensive. So the development of reliable and predictive IFT modeling tools is a pressing requirement. In the past decades, the thermodynamic methods including Gibbs and statistics have been proposed to calculate IFT. Usually, the traditional Gibbs thermodynamic method is simple in terms of mathematical form and calculation, but the physical interpretation of parameter in model is ambiguous, and extrapolating ability is not very good. Whereas the statistical thermodynamic is used to study the actual IFT by the density distribution and interaction among molecules on interface layer. Consequently, as molecular thermodynamic theory, DGT and DFT have become powerful tools to research interfacial property.

4.1. Density Gradient Theory (DGT)

In previous works, some empirical approaches are widely used to calculate IFT, they can describe accurately the procedure but have not the predictability. The DGT has become a standard tool to represent the interfacial systems so far. The method is based on the van der Waals theory for inhomogeneous fluids \[24\]. The Helmholtz free-energy density is expanded as a Taylor series through two terms. The first term in the expansion is evaluated at each local density using an EOS for the bulk fluid. And the density profile is truncated after the second square-gradient term. The main limitation of the DGT methodology is the introduction of influence parameter in the square-gradient term of the expansion. Usually, the influence parameter is fitted from the experimental IFT data of pure fluids, and then transferred to mixtures \[25\]. For CO₂-water / hydrocarbons systems, the DGT approach has been widely used to describe the planar interface properties qualitatively by combining SAFT. In recent years, the PC-SAFT or SAFT-VR Mie EOS combine with DGT is employed to investigate IFT for CO₂-water system \[21, 26\]. For CO₂-n-alkanes system, Müller and Mejía \[27\] predicted the interfacial properties of subcritical CO₂-decane, and calculated the IFT by SGT (square gradient theory)-SAFT-EOS. The PCP (perturbed-chain polar)-SAFT-EOS instead of the PC-SAFT-EOS was used to predict the IFT in polar CO₂ and non-polar n-alkanes system, the theoretical results was consistent with the experimental data \[28\]. The DGT and the crossover soft-SAFT were applied to predict the IFT of CO₂-butanes mixtures by Vilaseca and Vega \[29\].

4.2. Density Functional Theory (DFT)
The DFT is considered as one of the most successful theoretical treatments on the study of interfacial phenomena. Compared with DGT, the DFT offers an entirely predictive approach with no adjustable parameters. The basic thought of DFT is to construct a free-energy functional of inhomogeneous system, and then the IFT can be calculated. Generally speaking, two parts are included in the free-energy functional on the basis of different range interactions: the ideal and short-range interactions are incorporated in a reference term, yet the long-range interactions are included in a perturbative term. The reference term can be treated with different approximations such as a local density approximation (LDA), weighed density approximation (WDA) and fundamental measure theory (FMT) etc. The interactions between the molecules in fluid were taken into account in the perturbative term of DFT [25].

The progress and application of DFT can be found in CO2-water / oil mixtures as follow. At first, the DFT approach was coupled with the ubiquitous van der Waals EOS to estimate the IFT of light gases, alkanes, and gas-alkanes binary mixtures [30-32]. More recently, a free-energy functional LDA combined with SAFT-EOS was presented by Kahl and Winkelmann [33], it had a specific contribution due to capillary-wave roughened the surface. For inhomogeneous fluid phases, Gross [34] proposed a free-energy functional based on PCP-SAFT-EOS with LDA. Finally, the DFT approach incorporated with the SAFT-VR was used to represent the interfacial properties of CO2-water / n-alkanes mixtures [35, 36].

Both DGT and DFT approaches require equation of state to evaluate the bulk properties of the heterogeneous phases. The free-energy functional of DGT approach is obtained by a given equation of state and the values of influence parameter. But the treatment functional of DFT depends on the approximations which are employed, e.g., LDA or WDA, mean-field or non-mean-field, etc. as well as the reference equation of state used for the bulk fluid [25]. Hence, the key question is the selection of the appropriate functional for describing accurately the inhomogeneous system.

5. Summary and Prospect

The progress has been made greatly on the study of IFT for CO2-water / oil system, but it should be improved further at high pressure as follow:

1) The calculation of IFT is related to phase density difference which is the function of pressure, temperature and CO2 concentration and so on in different system, so it is necessary to find out a kind of precision instrument for tracking actual phase density difference online.

2) It is also crucial to construct an equation of state which is suitable to supercritical CO2-water / oil system for calculating IFT accurately.

3) In addition, the influence of the same molecular and intermolecular interactions on IFT needs to be investigated further.

Acknowledgements

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