Measurement and correlation of the interfacial tension for paraffin + CO₂ and (CO₂+N₂) mixture gas at elevated temperatures and pressures

Qiaoyan Shanga, b, Shuqian Xia b, *, GuanWei Cua, Bo Tang a, **, Peisheng Mab

*College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalyzed Probes for Chemical Imaging, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, China
bKey Laboratory for Green Chemical Technology of the State Education Ministry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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A B S T R A C T

Interfacial tension (IFT) is crucial for characterizing the phase and interphase behavior in the enhanced oil recovery (EOR) process. CO₂ and N₂ are commonly used as injection gases in the EOR process. In this work, an experimental apparatus using the pendant drop method was adopted to measure IFTs for the EOR process with different injection gases, temperatures (40.0–120.0 °C) and pressures (0.22–17.32 MPa). The relative Gibbs adsorption isotherm (Γ_i) of a species i on species j were calculated by the experimental IFTs. Theoretically, new correlations were proposed to predict paraffin IFTs for pure CO₂ and mixture gas (CO₂ + N₂) injection. A total of 561 and 268 experimental IFTs were used to derive the correlations for pure CO₂ and mixture gas injection, respectively. The square of correlation coefficient (R²), root mean square error (RMSE) and average absolute relative deviations (AAD) for pure CO₂ were 0.9884, 0.58 and 5.45%, respectively. For the mixture gas injection, the R², RMSE and AARD of the correlation were 0.9851, 0.57 and 4.47%, respectively.

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1. Introduction

The gas injection technique of enhanced oil recovery (EOR) has recently been given increasing attention [1]. Various gases such as natural gas, carbon dioxide (CO₂) and nitrogen (N₂) have been injected into oil reservoirs to increase oil recovery [2]. Among these techniques, CO₂ flooding is known as the most effective method due to its high oil recovery and CO₂ sequestration to reduce greenhouse gas emission [3]. However, in some cases, asphaltene precipitation occurred during CO₂ flooding and caused severe problems such as relative permeability reduction and wettability alteration. To solve the issue of asphaltene precipitation, N₂ was injected into matured oil reservoirs to displace crude oil [4] due to its natural availability and chemical stability at low temperatures [2,5,6].

Generally, the gas injection process included miscible and immiscible displacements. The vanishing interfacial tension (VIT) technique was used to study the miscibility between crude oil and CO₂ systems. (The critical point for CO₂ was t_c = 31 °C and p_c = 7.4 MPa. The ‘interfacial tension’ term, not the ‘surface tension’ term, was used in this study because in that part of the study the CO₂ was under supercritical conditions. The density of supercritical CO₂ varied with pressure to values comparable to a liquid paraffin as studied in Haghbakhsh et al.’s work [7].) The VIT technique is based on the concept that interfacial tension (IFT) between crude oil and injection gas becomes zero when they are miscible [4,5,8–10].

The IFT was a key parameter for characterizing the phase and interphase behavior of the complex fluid systems [11,12]. An accurate IFT value is essential to evaluate the miscible injection process. The content of paraffins was higher than other alkanes in crude oil. Both experimental and theoretical work for the IFT of paraffins and injection gases have been conducted by many researchers. Until now, the most widely used method for measuring IFTs at elevated pressures was the pendant drop method.
[4,6,12–21], Jaeger and Eggers [12] reported on the experimental IFTs of CO₂ + n-pentane/n-heptane systems. The IFTs decreased with pressure and the slope of IFTs versus pressures slightly diminished at elevated pressures for isothermal conditions. Zolghadr et al. [19] measured the IFTs of CO₂ + n-heptane/n-hexadecane with a temperature range of 40–120 °C and pressure range of 0.34–15.51 MPa. Cumicome et al. [18] reported on the experimental isothermal densities and IFTs for three systems (CO₂ + n-dodecane/n-tridecane/n-tetradecane) at 71 °C under elevated pressures. Georgiadis et al. [14] measured IFTs of three systems (CO₂ + n-dodecane/n-tridecane/n-tetradecane) with a temperature range of 25–170 °C and pressures up to the critical points for each isotherm, and concluded that the IFT values showed a small increase with paraffin chain length. Mejía et al. [20] published the experimental IFTs of n-eicosane with a pressure range of 0.1–10.35 MPa at 50 °C. In addition, Tang et al. [21] measured the IFTs of N₂ + n-pentane/n-hexane/n-octane/n-decane with a pressure range 0.1–40 MPa at 40 °C. Garrido et al. [6] presented the experimental IFTs of N₂ + hexane with a temperature range of 30–60 °C and a pressure range 0.1–15.1 MPa. The trend of N₂ + paraffin IFTs with pressure or temperature was similar to CO₂ injection. However, the experimental IFTs of injection gas + paraffin, such as n-heptadecane, n-pentadecane, etc., are still insufficient for detailed design and operation of the EOR process, especially with (CO₂ + N₂) mixture gas injection.

Theoretically, numerous studies have been performed to calculate IFT values, such as the parachor method [22,23], the density functional theory (DFT) [14] and the density gradient theory (DGT) [18,20,24]. The prediction ability of parachor method was limited because empirical density correlations were required in this method. Various intermolecular parameters were necessary to calculate IFT by the DFT method. An influence parameter is necessary in the DGT method, which was retrieved from one data point of experimental surface tension of the participating pure substances, and has large effects on the prediction abilities of DGT [24]. For the EOR process, the IFT was influenced by many factors such as the reservoir temperature, pressure, paraffin chain length and injection gas composition. So far, no explicit correlations of IFT values with all the factors for the EOR process were reported in the literature. It is important to obtain accurate and general correlations for calculating IFTs.

An apparatus using the pendent drop method was designed and manufactured in our previous work. It was verified to be reliable and used to determine IFTs of simulated oil-pure/impure CO₂ [25]. The results showed that the IFT of simulated oil-impure CO₂ (a mixture of CO₂ with mole fraction 0.75 and N₂ with mole fraction 0.25) were higher than pure CO₂ injection. To further study the effect of N₂ on the EOR process, the same mixture gas composition of CO₂ and N₂ was used in this work. The IFTs for CO₂/(CO₂ + N₂) mixture gas (1 + paraffin) (2) (including n-nonane, n-undecane, n-tridecane, n-pentadecane and n-heptadecane) systems were measured at a wide range of pressures and temperatures. The relative Gibbs adsorption isotherm (Γₜ) of a species i on species j were calculated by the experimental IFTs. Universal IFT correlations were proposed based on the IFT database, which includes CO₂ and (CO₂ + N₂) mixture gas injection. The correlations relate IFT to reservoir temperature, pressure, paraffin chain length and N₂ mole fraction in injection gas.

2. Experiment

2.1. Materials

The purities and suppliers of five paraffins and two gases used in this study are listed in Table 1. The mixture gas used in this work was a mixture of CO₂ (mole fraction 0.75) and N₂ (mole fraction 0.25). All chemicals were used without any further purification treatment.

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<tr>
<th>Chemical</th>
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<tr>
<td>n-Undecane</td>
<td>Technology Development Co., Ltd., China</td>
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<td>n-Tridecane</td>
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<td>n-Pentadecane</td>
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<tr>
<td>n-Heptadecane</td>
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<tr>
<td>Carbon Dioxide</td>
<td>Tianjin Lufang Industrial gases co., Ltd., China</td>
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<tr>
<td>Nitrogen</td>
<td>Tianjin Lufang Industrial gases co., Ltd., China</td>
<td>0.999</td>
</tr>
</tbody>
</table>

* The purity was mole fraction.

2.2. IFT measurement

The pendent drop method was used to measure the equilibrium IFTs. The schematic diagram of the apparatus and experimental procedure was shown in our previous work [25]. This apparatus includes three major sections: a high-pressure view cell (HPVC), syringe pump (SP) and programmable syringe pump (PSP). The accuracy of the HPVC temperature was ±0.1 °C. The relative uncertainty of the pressure transducer (CYB-20S, Beijing Westzh M&E Technology Ltd., China) was 0.1% with the full scale up to 40 MPa. The densities of the two phases at the equilibrium condition were necessary for the pendent drop method. The densities of pure CO₂ were obtained by the Benedict Webb Rubin Starling equation of state (BWRW EOS) [26]. The BWRW EOS and mixing rules were used to calculate the density of (CO₂ + N₂) mixture gas and shown in the Supporting Information Appendix. Liquid densities were calculated by the National Institute of Standards and Technology [27]. Referring to the literature [14,28], the IFTs were based on bulk phase densities of the pure CO₂, (CO₂ + N₂) mixture gas and paraffin rather than on the actual density of the mixture (paraffins + CO₂ or paraffins + (CO₂ + N₂) mixture gas). The selected plane method were used to obtain the IFT values. The theory and equations can be seen in Andreas et al.’s work [29]. The IFT measurement process was repeated for at least three times to ensure satisfactory repeatability.

The uncertainties of γ were affected by the temperature, pressure, density difference, the experimental reproducibility of γ itself and its standard uncertainties. To quantify these effects in the relative uncertainty (uat) of γ, the following relationship [30] was used:

\[ u^2_{\text{at}}(\gamma) = \left[ \frac{1}{\gamma} \frac{\partial \gamma}{\partial p} \right]_t^2 + \frac{[\partial \Delta p]}{\Delta p}^2 + \left[ \frac{\sigma(\gamma)}{\gamma} \right]^2 \]

where \[ \gamma \] and \[ \Delta p \] correspond to the standard uncertainties in pressure and density, respectively. \[ \sigma(\gamma) \] is the standard deviation of γ which, together with the maximum value of partial derivatives of γ in p, have directly been estimated from experimental data. The average \[ u_t \] was 0.68% for the binary systems in this work, which was calculated from the uncertainties of temperature, pressure, and density difference.

A total of 215 IFTs for CO₂ (1 + paraffin) (2) (including n-nonane, n-undecane, n-tridecane, n-pentadecane and n-heptadecane) systems and 202 IFTs for (CO₂ + N₂) mixture gas (1 + paraffin (2)
systems were measured with the temperature (40.0–120.0 °C) and pressure (0.22–17.32 MPa). All experimental IFT data are shown in Tables S1 and S2.

3. Empirical numerical correlation

3.1. Factors influencing the injection gas + paraffin IFTs

Fig. 1 shows the IFTs as a function of pressure for injection gas (1) + n-heptadecane (2) at different temperatures. For the pure CO2 injection, it can be seen that the experimental IFTs decreased with pressure and approximated the straight lines in the studied ranges. The slope of IFT versus pressure slightly decreased at elevated temperatures. In addition, the IFT decreased with temperature at lower pressures (lower than (4.5–5.5) MPa for CO2 (1) + n-heptadecene (2) systems) and increased with temperature at higher pressures. The IFT exhibits the weakest dependence on temperature at the crossover-pressure. These results indicate that CO2 injection is recommended at lower temperatures above crossover-pressures for maintaining better conditions. The IFTs of CO2 (1) + paraffins (2) as a function of pressure are shown in Fig. 2. The IFTs showed a small increase with paraffin chain length when the temperature and pressure was kept constant. The trend of paraffin IFTs with pressure or temperature was similar to the conclusions in literature [12,14,19]. The N2 in the injection gas caused higher IFTs than pure CO2 injection at pressures higher than approximately 6.5 MPa as shown in Fig. 1. The IFT exhibits the weakest dependence on N2 when the pressure was less than approximately 6.5 MPa. A similar trend with other paraffins is shown in Figs. S1–S4.

3.2. Developing the injection gas + paraffin IFTs models

As mentioned above, the injection gas + paraffin IFTs were strongly related to reservoir temperature, pressure, paraffin chain length and N2 mole fraction in the mixture gas. It is necessary to consider these influenced factors when developing IFT correlations. In this work, the IFTs of paraffin + CO2 system were presented as a function of reservoir temperature, pressure and paraffin chain length. The IFTs of paraffin + (CO2+N2) mixture gas system were correlated with reservoir temperature, pressure, N2 mole fraction and paraffin chain length. Equations (2) and (3) were proposed and utilized to calculate paraffin IFTs for pure CO2 and (CO2+N2) mixture gas injection, respectively.

\[ \gamma = \left( a \cdot t^b + c \cdot t \right) \cdot p \cdot N^d + e \cdot p \cdot N^d + f \cdot t^g + h \cdot N^f \]  
(2)

\[ \gamma = \left( a \cdot t^b + c \cdot t \right) \cdot p \cdot (1 - x_{N_2}) + d \cdot t \cdot N^e + f \cdot p^e + i \cdot p \cdot x_{N_2} + h \cdot N^e \]  
(3)

where \( \gamma \) is IFT in mN/m, \( t \) is reservoir temperature in °C, \( p \) is pressure in MPa, \( N \) is carbon number in paraffin, \( x_{N_2} \) is N2 mole fraction in mixture gas. \( a, b, c, d, e, f, g, h \) and \( i \) are empirical coefficients.

The objective function \( OF \) is expressed as follows:

\[ OF = \min \sum \left( \gamma_{exp} - \gamma_{cal} \right)^2 \]  
(4)

where \( \gamma_{exp} \) and \( \gamma_{cal} \) are the experimental and calculated IFTs, respectively. The empirical coefficients of equations were obtained by the least square method.

The statistical parameters included square of correlation coefficient \((R^2)\), root mean square error \((\text{RMSE})\) and average absolute relative deviations \((\text{AARD})\) were used to evaluate the accuracy of the new models.

\[ \text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} \left( \gamma_{exp} - \gamma_{cal} \right)^2}{n}} \]  
(5)

\[ \text{AARD} = \frac{\sum_{i=1}^{n} \left| \frac{\gamma_{exp} - \gamma_{cal}}{\gamma_{exp}} \right| \times 100}{n} \]  
(6)

For pure CO2 systems, a total of 561 data points including 215 IFTs in this work and 346 IFTs from literature [12,14,18–20] were used to correlate Equation (2). The studied ranges of temperature and pressure were 24.7–169.9 °C and 0.1–19.0 MPa, respectively. For mixture gas systems, 268 data points including 202 IFTs in this work and 66 IFTs from literature [6,21] were adopted to correlate Equation (3). The studied ranges of temperature and pressure were 30.0–120.0 °C and 0.1–40.2 MPa, respectively. The N2 mole fraction was from 0.25 to 1. The correlations was reasonable and adopted in the studied range. The IFT database is given in the Supporting
Information. The database includes the carbon number in paraffin from 5 to 20. The regressed coefficients of Equations (2) and (3) are listed in Table 2.

4. Results and discussion

4.1. The relative Gibbs adsorption isotherm

The experimental IFTs can be used to predict the relative Gibbs adsorption isotherm ($\Gamma_{ij}$) of a species $i$ on species $j$, which was used to explain the adsorption of CO$_2$ in paraffin. According to Masterton et al.’s [31] and Cumicchio et al.’s [18] work, for a gas–liquid system with changing pressure, the $\Gamma_{ij}$ equation was shown by the following expression:

$$\Gamma_{ij} = -\frac{\rho_i}{M_i} \left(\frac{\partial \gamma}{\partial p}\right)_t$$  \hspace{1cm} (7)

where the slope ($\partial \gamma/\partial p$)$_t$ is obtained from experimental values of $\gamma$ ~ $p$. $\rho_i$ and $M_i$ are the density and molecular weight of the injection gas, respectively, $\rho_1$ was obtained by the BWRS EOS in the work.

The adsorption of injection gases (1) in paraffin (2) was approximately quantified by the relative Gibbs adsorption isotherm ($\Gamma_{12}$). The $\Gamma_{12}$ was calculated by Equation (7), and the detailed results were shown in Supporting Information. The comparisons of $\Gamma_{12}$ for pure CO$_2$/mixture gas (1) + n-heptadecane (2) as a function of pressure ($p$) at different temperatures are shown in Fig. 3. $\Gamma_{12}$ increased with pressure and decreased with temperature for pure CO$_2$ injection. For the mixture gas, the $\Gamma_{12}$ was lower than the values of pure CO$_2$ at the same pressure and temperature. The similar trend of other systems are shown in Figs. S5–S8. As mentioned above, we can see that the trends of $\Gamma_{12}$ with changing temperature and pressure were opposite the trends of the IFTs.

4.2. The empirical numerical correlation

To test the reliability of the new correlations, the IFTs calculated by the new correlations were compared with the experimental IFTs. The detailed calculated results are presented in the Supporting Information.

The overall calculation results of the correlations for pure CO$_2$ and mixture gas are shown in Tables 3 and 4, respectively. For pure CO$_2$ systems, the overall $R^2$, RMSE and AARD were 0.9884, 0.58 and 5.45%, respectively, as listed in Table 3. Fig. 4 shows the comparison between the experimental IFTs and the calculated values from Equation (2). It can be seen that the majority of points are located in the vicinity of the bisection in Fig. 4. For the mixture gas systems, Table 4 lists the detailed calculation results of Equation (3), including $R^2$ of 0.9851, RMSE of 0.57 and AARD of 4.47%. The scatter plot of the experimental IFTs versus the calculated IFTs from Equation (3) is shown in Fig. 5. Fig. 5 and Table 4 demonstrate that Equation (3) can calculate the mixture gas + paraffin IFTs precisely.

In other words, it is reliable for calculating IFTs of paraffin + CO$_2$/CO$_2$ + N$_2$ mixture gas using the new correlations.

To further examine and validate the accuracy of the new correlations, the methods of Leave One Out Cross Validation (LOOCV) and external validation were used to investigate the applicability of the new correlations.

4.2.1. Leave One Out Cross Validation (LOOCV)

LOOCV is the method that leaves out a set of samples for each test, while the other samples form a training set. If there are $k$ samples, $k$ times training and $k$ times testing are required. The samples are used adequately in LOOCV. The prediction abilities of Equations (2) and (3) were tested by LOOCV and are listed in Tables 3 and 4. For pure CO$_2$ systems, the $R^2$ (0.9883) and RMSE (0.57) for LOOCV were almost the same as in Equation (2). The AARD (5.10%) for LOOCV is slightly less than that (5.45%) of Equation (2). For mixture gas systems, the $R^2$ (0.9859), RMSE (0.55) and AARD (4.46%) for LOOCV were nearly the same as in Equation (3). From the above, the new models are feasible for predicting IFTs of paraffin + CO$_2$/CO$_2$ + N$_2$ mixture gas.

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Fig. 3. The comparisons of relative Gibbs adsorption isotherm for pure CO$_2$/mixture gas (1) + n-heptadecane (2), $\Gamma_{12}$, as a function of pressure ($p$) at different temperatures.
The comparisons between the experimental IFTs and predicted values by Equation (2) for paraffin + CO₂ systems.

The comparisons between the experimental IFTs and predicted values by Equation (3) for paraffin + mixture gas systems.


