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Experiment and correlation of the equilibrium interfacial tension for paraffin + CO_2 modified with ethanol

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ABSTRACT

Carbon dioxide enhanced oil recovery (CO_2 EOR) process is widely used in petroleum industry in recent years. But it has some shortcomings, such as early gas breakthrough, fingering, asphaltene precipitations, because of the low viscosity and density of CO_2. These problems can be resolved by adding some common solvents as chemical modifiers in CO_2 flooding. In this work, ethanol was chosen as the chemical modifier. The effects of ethanol on the equilibrium interfacial tension (IFT) of paraffin + CO_2 systems were investigated with different ethanol contents, temperature range 60–100 °C and pressure range 5.06–14.60 MPa, respectively. New correlation for predicting the IFTs of paraffin + modified CO_2 systems were proposed based on 150 experimental IFT values. The square of correlation coefficient (R^2), root mean square error (*RMSE*) and average absolute relative deviations (*AARD*) were 0.9948, 0.15 and 2.49%, respectively. The paraffin IFTs for modified CO_2 and pure CO_2 flooding were compared by the IFT average absolute decrease ratio (*AADR*).

1. Introduction

The carbon dioxide (CO_2) flooding for enhanced oil recovery (EOR) has obtained much attention in the petroleum industry due to its high displacement efficiency and relatively low cost [1]. Recently, the CO_2 flooding projects have been increasing steadily and CO_2 injection become a popular EOR technology in the near future [2]. However, CO_2 EOR was found some shortcomings such as early gas breakthrough, fingering, asphaltene precipitations [3] because of the low viscosity and density of CO_2. Furthermore, the minimum miscibility pressure (MMP) may not be reached as a result of reservoir complexity and multiplicity. Consequently, the crude oil components heavier than C_{12} still remain in the reservoir as reported in Hwang et al. work [4].

Numerous researchers studied the way to increase the density and viscosity of CO_2 or reduce asphaltene precipitations by adding surfactants [5], alcohols [6–8], chemicals [9,10] or their combination [4] in order to enhance oil recovery. Among these substances, the alcohols were widely evaluated for extracting various substances by supercritical CO_2 ($SCCO_2$) [11–14]. The effects of modifier (including methanol, ethanol and toluene) on the solubility of $SCCO_2$ extraction were investigated by Kohler et al. [14], and the results of these modifiers were similar except that toluene indicated a major defect because of its high boiling point. Rudyk et al. [6] studied the bitumen extraction from crude oil by $SCCO_2$ modified with ethanol and isopropanol, the liquid recovery of bitumen with ethanol higher than that with isopropanol. Rudyk et al. [15] also investigated the effects of modifiers including methanol, ethanol, propanol and acetone on crude oil recovery by $SCCO_2$, and the average total oil recovery increased in the following order: acetone, propanol, methanol, ethanol. Furthermore, many studies reported that ethanol produced a higher extraction and solubility of the solutes in $SCCO_2$ [16–18] because it is a prominent hydrogen bonding acceptor.

The equilibrium interfacial tension (IFT) is a key parameter for characterizing the phase and interphase behaviour of the complex fluid systems in CO_2 EOR process [19,20]. The IFT between crude oil and injection gas was zero during CO_2 miscible flooding [21–24]. The IFTs of crude oil component + CO_2 are crucial in designing EOR process. And the accurate IFT values of paraffin + modified CO_2 play an important role in choosing the modifier and evaluating the effects of modifier on CO_2 EOR process. As mentioned above, some studies have shown that the oil recovery and the solubility of $SCCO_2$ modified by alcohols. But the equilibrium IFT of paraffin + modified CO_2 systems were not reported in the literatures.

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The IFTs of five systems (*n*-nonane/*n*-undecane/*n*-tridecane/*n*-pentadecane/*n*-heptadecane + pure CO_2) have been reported in our previous work [25]. In this work, the IFTs of the same five paraffin + the modified CO_2 with ethanol systems were measured at wide range of temperatures, pressures and ethanol mole fractions. The correlation for IFTs of paraffin + modified CO_2 systems was proposed based on the experimental IFTs. The IFTs were related to the function of reservoir temperature, pressure, carbon number in paraffin and the mole fraction of ethanol in CO_2. The paraffin + modified CO_2 IFTs were compared with the values of paraffin + pure CO_2. The effects of ethanol on the equilibrium IFTs were evaluated and the IFT average absolute decrease ratio (*AADR*) was discussed.

Table 1
Purities and suppliers of chemicals and gas used in this study.

Chemical	Supplier	Purity
n-Nonane	Tianjin Guangfu Technology Development Co., Ltd., China	0.990
n-Undecane	Tianjin Guangfu Technology Development Co., Ltd., China	0.990
n-Tridecane	Tianjin Guangfu Technology Development Co., Ltd., China	0.985
n-Pentadecane	Shanghai Aladdin Industrial Co., Ltd., China	0.990
n-Heptadecane	Tianjin Heowns Biochemical Technology Co., Ltd., China	0.990
Ethanol	Tianjin Guangfu Technology Development Co., Ltd., China	0.998
Carbon dioxide	Tianjin Liufang Industrial gases co., Ltd., China	0.999

The purity was mole fraction, and all chemicals were used without any further purification treatment.

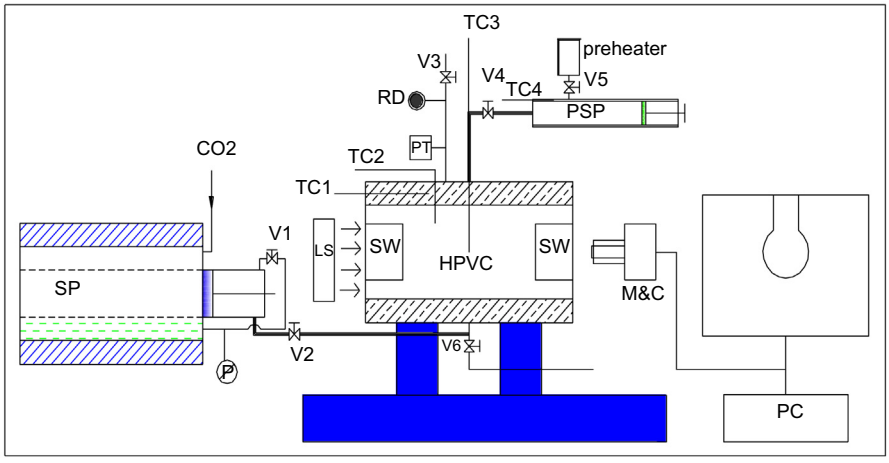
2. Experiment section

2.1. Materials

The purities and suppliers of paraffins, CO_2 and ethanol used in this study were listed in Table 1. All the chemicals were used without any further purification treatment.

2.2. IFT measurement

The IFT was measured by pendent drop method. The IFT measurement apparatus was designed and built by our research group, which was shown in Fig. 1. This apparatus involves three major components: high pressure view cell (HPVC), syringe pump (SP) and programmable syringe pump (PSP). The known weight of ethanol were put on a cotton ball and set at the glass plate, then the glass plate was put into the HPVC at the CO_2 flow entrance. While CO_2 was injected into the HPVC, ethanol vaporized and interacted with CO_2. The HPVC was heated to the required temperature after CO_2 injected into cell, and the pressure of HPVC increased with temperature. The liquid was injected into cell to produce pendent drop at the tip of the syringe needle after pressure and temperature were stable. The pendent drop was saturated with the CO_2 modified by ethanol. Because the speed of drop formation was very slowly, and the syringe needle was long enough for the drop was saturated by gas atmosphere. Moreover, the valve between PSP and syringe needle was check valve. It can prevent the liquid from returning to the pump. The dynamic pendant drop images were obtained by camera and automatically stored in the computer. The accuracy of the HPVC temperature was ±0.1 °C. The relative uncertainty of pressure transducer was 0.1% with the full scale up to 40 MPa. A detailed description and experimental procedure



SP, syringe pump;
PSP, programmable syringe pump;
HPVC, high-pressure view cell;
TC, temperature controller;
PT, pressure transducer;
RD, rupture disks
LS, light source;
PC, personal computer;
M&C, microscope&camera;
SW, sapphire window;
V, valve;

Fig. 1. Schematic diagram of the experimental apparatus.