



Experiment and correlation of the equilibrium interfacial tension for paraffin + CO₂ modified with ethanol



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ABSTRACT

Carbon dioxide enhanced oil recovery (CO₂ 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 CO₂. These problems can be resolved by adding some common solvents as chemical modifiers in CO₂ flooding. In this work, ethanol was chosen as the chemical modifier. The effects of ethanol on the equilibrium interfacial tension (IFT) of paraffin + CO₂ 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 CO₂ 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 CO₂ and pure CO₂ flooding were compared by the IFT average absolute decrease ratio (AADR).

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1. Introduction

The carbon dioxide (CO₂) 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 CO₂ flooding projects have been increasing steadily and CO₂ injection become a popular EOR technology in the near future [2]. However, CO₂ EOR was found some shortcomings such as early gas breakthrough, fingering, asphaltene precipitations [3] because of the low viscosity and density of CO₂. 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 C₁₂ 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 CO₂ 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 CO₂ (SCCO₂) [11–14]. The effects of modifier (including methanol, ethanol and toluene) on the solubility of

SCCO₂ 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 SCCO₂ 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 SCCO₂, 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 SCCO₂ [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 CO₂ EOR process [19,20]. The IFT between crude oil and injection gas was zero during CO₂ miscible flooding [21–24]. The IFTs of crude oil component + CO₂ are crucial in designing EOR process. And the accurate IFT values of paraffin + modified CO₂ play an important role in choosing the modifier and evaluating the effects of modifier on CO₂ EOR process. As mentioned above, some studies have shown that the oil recovery and the solubility of SCCO₂ modified by alcohols. But the equilibrium IFT of paraffin + modified CO₂ 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 CO₂) have been reported in our previous work [25]. In this work, the IFTs of the same five paraffin + the modified CO₂ with ethanol systems were measured at wide range of temperatures, pressures and ethanol mole fractions. The correlation for IFTs of paraffin + modified CO₂ 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 CO₂. The paraffin + modified CO₂ IFTs were compared with the values of paraffin + pure CO₂. 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
<i>n</i> -Nonane	Tianjin Guangfu Technology Development Co., Ltd., China	0.990
<i>n</i> -Undecane	Tianjin Guangfu Technology Development Co., Ltd., China	0.990
<i>n</i> -Tridecane	Tianjin Guangfu Technology Development Co., Ltd., China	0.985
<i>n</i> -Pentadecane	Shanghai Aladdin Industrial Co., Ltd., China	0.990
<i>n</i> -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.

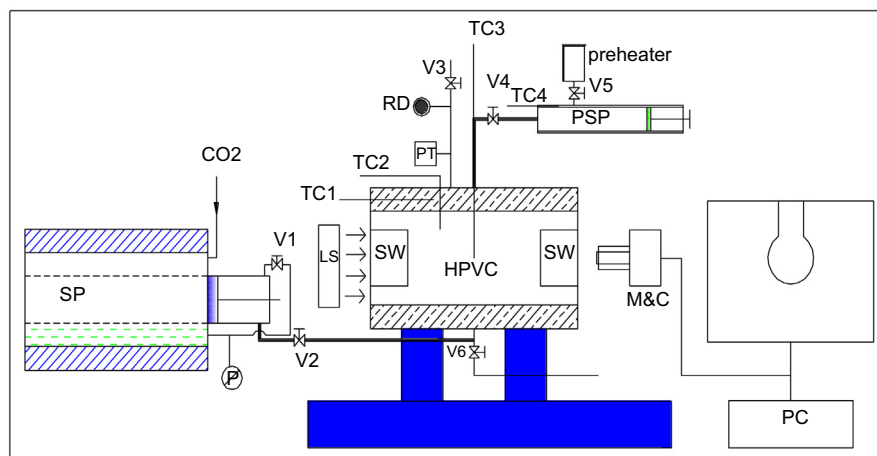
2. Experiment section

2.1. Materials

The purities and suppliers of paraffins, CO₂ 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 CO₂ flow entrance. While CO₂ was injected into the HPVC, ethanol vaporized and interacted with CO₂. The HPVC was heated to the required temperature after CO₂ 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 CO₂ 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; LS, light source;
 PSP, programmable syringe pump; PC, personal computer;
 HPVC, high-pressure view cell; M&C, microscope&camera;
 TC, temperature controller; SW, sapphire window;
 PT, pressure transducer; V, valve;
 RD, rupture disks

Fig. 1. Schematic diagram of the experimental apparatus.

was shown in our previous work [25,26]. The densities of two phases at the equilibrium temperature and pressure were needed in this method. The ethanol-modified CO₂ densities were obtained by Eq. (1). Liquid densities were calculated by National Institute of Standards and Technology [27]. The same procedure were established for similar systems in literatures [28,29]. The IFT measure process was repeated for at least three times to insure satisfactory repeatability.

A total of 150 IFTs of five systems (*n*-nonane/*n*-undecane/*n*-tridecane/*n*-pentadecane/*n*-heptadecane + CO₂ modified by ethanol) were measured with temperature and pressure range 60–100 °C and 5.06–14.60 MPa, respectively. And the ethanol mole fraction range was from 0.02 to 0.08. The value of ethanol mole fraction at different temperature and pressure were based on the phase equilibrium data of ethanol + CO₂ binary system. They were not larger than the vapor phase composition of ethanol at the phase equilibrium status for ethanol + CO₂ binary system at the same temperature and pressure [30–32] which can ensure the ethanol totally solving in CO₂.

$$\rho_{\text{gas}} = \frac{m_{\text{ethanol}} + \rho_{\text{CO}_2} \cdot \left(V_{\text{cell}} - \frac{m_{\text{ethanol}}}{\rho_{\text{ethanol}}} \right)}{V_{\text{cell}}} \quad (1)$$

$$y_{\text{ethanol}} = \frac{m_{\text{ethanol}}/M_{\text{ethanol}}}{m_{\text{ethanol}}/M_{\text{ethanol}} + \rho_{\text{CO}_2} \cdot \left(V_{\text{cell}} - m_{\text{ethanol}}/\rho_{\text{ethanol}} \right)/M_{\text{CO}_2}} \quad (2)$$

where, ρ is density in g/cm³, y is mole fraction, m is weight in g, V is volume in cm³, M is molecular weight. The ρ_{CO_2} were calculated by BWRS equation of state [33]. The ρ_{ethanol} were obtained in literature [34].

3. Results and discussion

3.1. The effect of temperature, pressure and ethanol fraction on paraffin IFTs

150 IFTs between CO₂ modified with ethanol and paraffins (*n*-heptadecane, *n*-pentadecane, *n*-tridecane, *n*-undecane and *n*-nonane) were obtained at different temperatures and pressures with different ethanol mole fractions. All the experimental IFT data were summarized in Table 2. From Table 2, it can be seen that the IFTs of a paraffin + modified CO₂ system decreased with pressure for isothermal and same y_{ethanol} . Fig. 2 shows the measured equilibrium IFTs for *n*-heptadecane + CO₂ modified with ethanol systems at different conditions. From Fig. 2(a–d), the IFTs of the heptadecane + modified CO₂ system decreased nearly linearly with pressure for isothermal and same y_{ethanol} . The slopes of IFT versus pressures decreased with temperature increasing from Fig. 2(d). This trend was similar to the paraffin + pure CO₂ IFTs as reported in our previous work [25]. The IFTs decreased with the y_{ethanol} increasing as shown in Fig. 2(a–c). So the IFTs between CO₂ and *n*-heptadecane were decreased after CO₂ was modified with ethanol. It is favorable for CO₂ EOR process. The tendency of other paraffin + modified CO₂ systems was almost the same with the *n*-heptadecane + modified CO₂ system as shown in Figs. S1–S4. Besides, the IFTs of different paraffins with the same experimental conditions ($t = 100.0$ °C and $y_{\text{ethanol}} = 0.02$) were shown in Fig. 3. It can be seen that the IFTs increased with the paraffin chain length with the same temperature, pressure and ethanol fraction.

3.2. Mathematical model

From the mentioned above, the IFTs were influenced by many factors. A generalized correlation of IFTs was proposed based on the experimental data. The correlation was a function of reservoir

Table 2

The experimental IFTs (γ_{exp}) between CO₂ modified with ethanol and paraffins (*n*-heptadecane, *n*-pentadecane, *n*-tridecane, *n*-undecane and *n*-nonane) at different temperature (t), pressure (p) and the mole fraction of ethanol (y_{ethanol}).^a

$t/^\circ\text{C}$	p/MPa	y_{ethanol}	$\gamma_{\text{exp.}}/\text{mN/m}$
<i>n</i> -C ₁₇ H ₃₆			
60.0	6.00	0.0199	10.87
60.0	7.03	0.0200	9.00
60.0	7.89	0.0203	7.53
60.0	9.00	0.0201	5.51
60.0	10.00	0.0201	4.06
60.0	10.03	0.0410	2.84
80.0	8.74	0.0194	8.35
80.0	9.49	0.0201	7.43
80.0	10.26	0.0207	6.39
80.0	11.88	0.0203	4.74
80.0	12.61	0.0198	4.02
80.0	10.00	0.0405	5.93
80.0	11.05	0.0400	4.77
80.0	12.00	0.0410	3.64
80.0	12.00	0.0614	3.03
100.0	9.26	0.0225	9.03
100.0	9.46	0.0201	8.69
100.0	10.49	0.0205	7.56
100.0	10.92	0.0195	7.25
100.0	11.46	0.0212	6.81
100.0	12.82	0.0193	5.40
100.0	13.62	0.0206	4.85
100.0	14.60	0.0201	3.99
100.0	10.15	0.0396	7.59
100.0	11.18	0.0411	6.51
100.0	12.60	0.0403	5.14
100.0	12.97	0.0407	4.75
100.0	13.91	0.0411	3.95
100.0	10.06	0.0604	6.95
100.0	11.06	0.0605	5.84
100.0	11.93	0.0616	4.99
100.0	13.02	0.0612	4.22
100.0	14.03	0.0608	3.33
100.0	9.99	0.0820	5.77
100.0	10.98	0.0822	4.80
100.0	12.06	0.0817	4.06
100.0	13.09	0.0819	3.31
100.0	13.90	0.0835	2.63
<i>n</i> -C ₁₅ H ₃₂			
60.0	5.96	0.0202	10.54
60.0	7.00	0.0202	8.45
60.0	8.02	0.0200	6.58
60.0	8.96	0.0203	4.90
60.0	10.06	0.0201	3.16
60.0	9.93	0.0412	2.49
80.0	7.20	0.0226	9.83
80.0	7.93	0.0203	8.77
80.0	8.83	0.0210	7.66
80.0	10.28	0.0207	5.83
80.0	10.96	0.0201	4.91
80.0	11.98	0.0202	3.87
80.0	10.00	0.0406	5.06
80.0	11.02	0.0404	4.01
80.0	11.89	0.0409	3.22
80.0	12.00	0.0613	2.37
100.0	7.43	0.0245	10.20
100.0	8.47	0.0213	9.02
100.0	9.58	0.0218	7.91
100.0	10.41	0.0205	7.06
100.0	11.50	0.0211	5.90
100.0	12.39	0.0205	4.99
100.0	13.51	0.0201	4.01
100.0	9.00	0.0406	7.85
100.0	10.06	0.0400	6.75
100.0	11.20	0.0411	5.56
100.0	12.46	0.0411	4.40
100.0	13.77	0.0409	3.32
100.0	10.04	0.0606	6.02
100.0	11.06	0.0606	5.13
100.0	12.00	0.0613	4.19
100.0	12.99	0.0614	3.32

Table 2 (continued)

$t/^\circ\text{C}$	p/MPa	y_{ethanol}	$\gamma_{\text{exp}}/\text{mN/m}$
100.0	14.03	0.0608	2.52
100.0	8.99	0.0814	6.56
100.0	9.97	0.0820	5.63
100.0	10.97	0.0822	4.68
100.0	11.80	0.0827	3.83
100.0	13.00	0.0826	2.80
100.0	13.97	0.0833	1.90
<i>n-C₁₃H₂₈</i>			
60.0	6.02	0.0202	9.71
60.0	7.08	0.0200	7.97
60.0	8.03	0.0201	5.82
60.0	8.97	0.0202	4.15
60.0	10.00	0.0202	2.30
60.0	9.93	0.0412	1.70
80.0	7.63	0.0211	8.45
80.0	8.76	0.0214	6.90
80.0	10.17	0.0209	4.94
80.0	11.09	0.0200	3.77
80.0	11.86	0.0204	2.89
80.0	10.05	0.0402	4.30
80.0	10.99	0.0406	3.35
80.0	11.90	0.0408	2.16
100.0	7.95	0.0225	8.77
100.0	9.42	0.0224	7.03
100.0	11.32	0.0214	5.02
100.0	12.52	0.0204	3.75
100.0	13.64	0.0206	2.95
100.0	9.10	0.0401	6.72
100.0	10.10	0.0405	5.73
100.0	11.26	0.0408	4.51
100.0	12.46	0.0412	3.47
100.0	13.77	0.0409	2.26
100.0	9.00	0.0610	6.30
100.0	10.00	0.0610	5.17
100.0	11.06	0.0608	4.30
100.0	11.99	0.0615	3.25
100.0	12.98	0.0616	2.39
100.0	9.96	0.0823	4.59
100.0	11.04	0.0817	3.69
100.0	12.04	0.0821	2.53
<i>n-C₁₁H₂₄</i>			
60.0	5.06	0.0201	10.95
60.0	6.13	0.0196	8.52
60.0	7.09	0.0199	6.45
60.0	7.99	0.0202	4.86
60.0	9.03	0.0199	2.99
80.0	6.61	0.0203	8.58
80.0	7.31	0.0223	7.62
80.0	8.01	0.0202	6.71
80.0	8.80	0.0212	5.70
80.0	9.57	0.0201	4.52
80.0	10.34	0.0204	3.54
80.0	10.03	0.0404	3.23
100.0	7.57	0.0240	7.75
100.0	8.42	0.0216	6.86
100.0	9.56	0.0220	5.63
100.0	10.54	0.0206	4.55
100.0	11.58	0.0208	3.58
100.0	7.95	0.0407	7.04
100.0	9.09	0.0398	5.65
100.0	10.01	0.0404	4.62
100.0	11.20	0.0411	3.40
100.0	8.09	0.0599	6.30
100.0	9.12	0.0601	5.11
100.0	9.93	0.0615	4.25
100.0	10.93	0.0615	3.24
100.0	10.02	0.0817	3.83
100.0	10.99	0.0821	2.93
<i>n-C₉H₂₀</i>			
60.0	6.04	0.0201	7.24
60.0	7.01	0.0202	5.39
60.0	7.97	0.0201	3.56
80.0	7.45	0.0217	5.94
80.0	8.79	0.0211	4.12

Table 2 (continued)

$t/^\circ\text{C}$	p/MPa	y_{ethanol}	$\gamma_{\text{exp}}/\text{mN/m}$
80.0	9.52	0.0201	3.12
100.0	7.55	0.0241	6.28
100.0	8.54	0.0202	5.13
100.0	9.52	0.0219	4.09
100.0	10.50	0.0206	3.07
100.0	7.50	0.0607	5.59
100.0	8.47	0.0609	4.40
100.0	9.52	0.0609	3.18
100.0	10.61	0.0603	2.37

^a Standard uncertainties u are $u(t) = 0.1$ °C, $u(p) = 0.02$ MPa, $u(y) = 0.002$ and the relative uncertainty $u_r(\gamma) = 0.82\%$. The calculation process of relative uncertainty was shown in our previous work [25].

temperature, pressure, paraffin chain length and ethanol mole fraction in CO₂. It was shown in Eq. (3) and used to calculate paraffin IFTs for ethanol modified CO₂ systems.

$$\gamma = (a \cdot t^b + c \cdot T) \cdot p + (d \cdot t + h) \cdot N^e + f \cdot p^g + i \cdot y_{\text{ethanol}} \quad (3)$$

where, γ is IFT in mN/m, t is reservoir temperature in °C, p is pressure in MPa, N is carbon number in paraffin, y_{ethanol} is ethanol mole fraction. a , b , c , d , e , f , g , h and i are empirical coefficients.

The objective function OF is expressed as Eq. (4):

$$OF = \min \sum (\gamma_{\text{exp.}} - \gamma_{\text{cal.}})^2 \quad (4)$$

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

The square of correlation coefficient (R^2), root mean square error ($RMSE$) and average absolute relative deviations ($AARD$) were used to evaluate the accuracy of new models.

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (\gamma_{\text{exp.}} - \gamma_{\text{cal.}})^2}{n}} \quad (5)$$

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

A total of 150 paraffin + modified CO₂ IFTs were used to correlate the Eq. (3). The IFT database were presented in the Table 2. The regressed coefficients of Eq. (3) were listed in Table 3. The calculation results of Eq. (3) were shown in Table 4. The detailed calculated results were shown in the Supporting information. The overall R^2 , $RMSE$ and $AARD$ were 0.9948, 0.15 and 2.49%, respectively. From Table 4, the new correlation can accurately calculate the IFTs of paraffin + modified CO₂ systems.

3.2.1. 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 ability of Eq. (3) was tested by LOOCV. The R^2 (0.9948), $RMSE$ (0.15) and $AARD$ (2.41%) for LOOCV are approximate to the values of Eq. (3) as shown in Table 4. The new correlation is feasible to calculate IFTs of paraffin + modified CO₂.

3.2.2. External validation

In this method, the database is randomly divided into training set (115) and testing set (35). The correlation was regressed by training set with the same parameters in Eq. (3). The IFTs of testing set were predicted by this correlation. The statistical parameters of training and testing set were listed in Table 4. The R^2 , $RMSE$ and

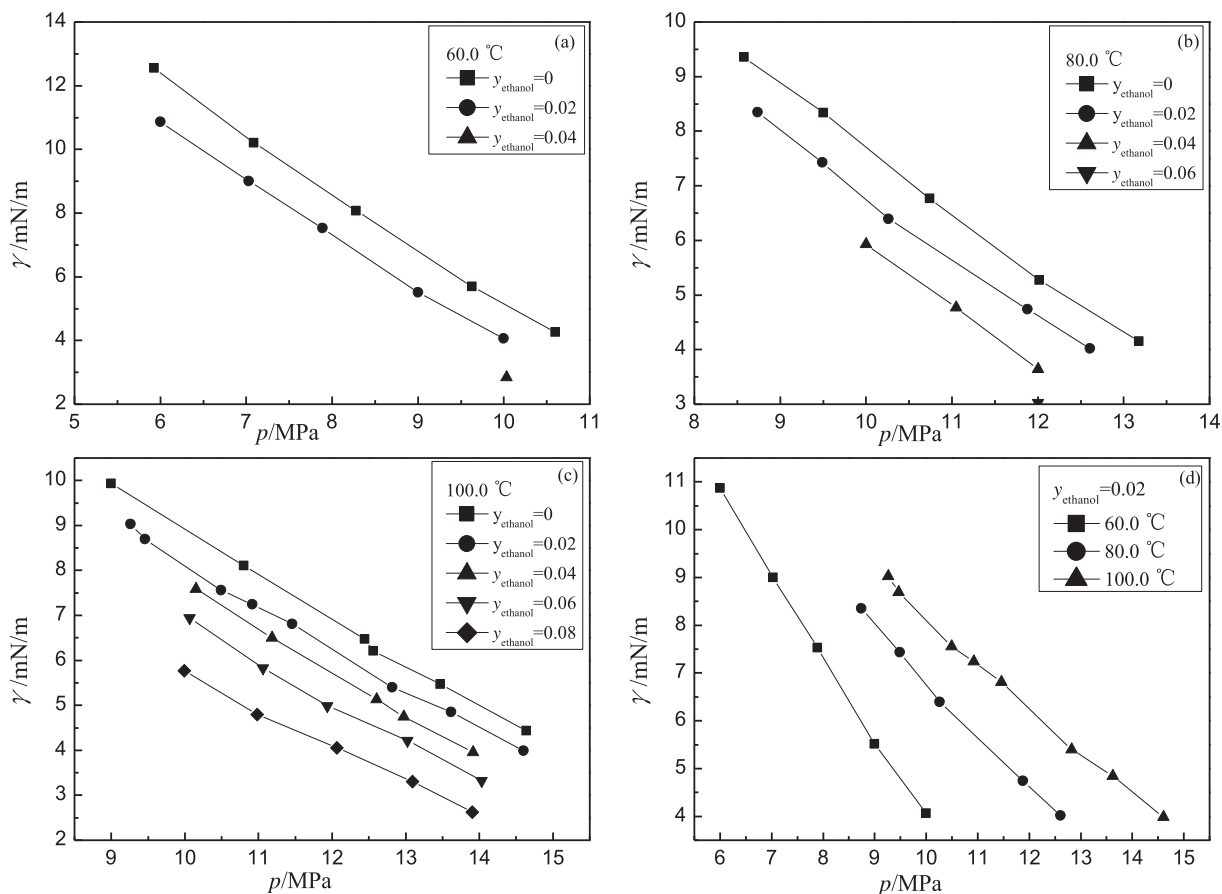


Fig. 2. The IFTs of n -heptadecane + CO₂ modified with ethanol versus pressure for different temperatures and y_{ethanol} . (The data for $y_{\text{ethanol}} = 0$ were taken from our previous work [25].)

AARD in training set are almost the same with those of all data points. Table 4 verified that the model can estimate paraffin IFTs well for the modified CO₂ systems.

3.3. The IFT reduction ratio analysis

The IFT average absolute decrease ratio (AADR) was defined by the Eq. (7). $\gamma_{\text{mod.cal.}}$ and $\gamma_{\text{CO}_2\text{cal.}}$ were calculated at the same

temperature and pressure by Eq. (3) in this work and Eq. (8) in our previous work [25], respectively.

$$AADR = \frac{\sum_{i=1}^n \frac{|\gamma_{\text{mod.cal.}} - \gamma_{\text{CO}_2\text{cal.}}|}{\gamma_{\text{CO}_2\text{cal.}}} \times 100\%}{n} \quad (7)$$

Table 3

The values and standard errors of coefficients of Eq. (3).

Coefficient	Value	Standard errors
a	-166.8209	41.8882
b	-1.2201	0.0711
c	0.0017	0.0003
d	-0.1582	0.0271
e	-0.4794	0.0830
f	43.4303	2.0912
g	-0.2345	0.0322
h	-31.7713	1.6249
i	-29.6159	0.7031

Table 4

The results of Eq. (3) prediction ability test by LOOCV and external validation methods.

Status	Data points	R^2	RMSE	AARD%
Model	150	0.9948	0.15	2.49
LOOCV	150	0.9948	0.15	2.41
Training	115	0.9949	0.15	2.42
Testing	35	0.9952	0.16	2.60

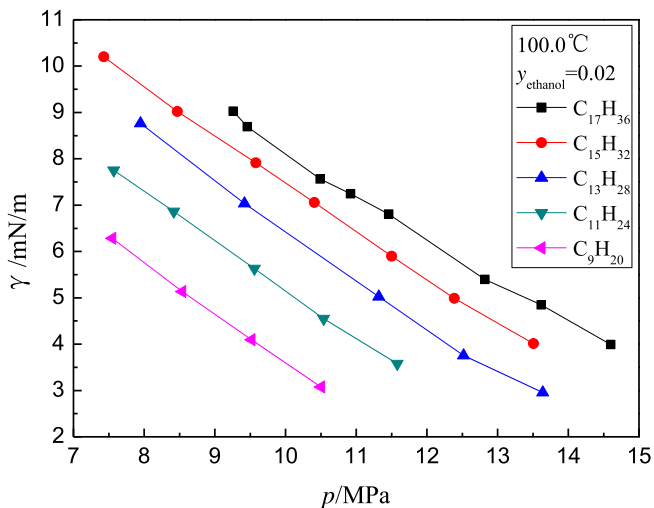


Fig. 3. The IFTs of different paraffins with the same experimental conditions ($t = 100.0$ °C and $y_{\text{ethanol}} = 0.02$).

Table 5

The values of coefficients of Eq. (8).

Coefficient	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>
Value	−15.8	−0.305	−0.00490	0.177	3.68	−18.0	0.179	37.3

Table 6The AADR% of alkanes at different temperature and y_{ethanol} .

<i>n</i> -Alkane	<i>t</i> /°C	y_{ethanol}			
		0.02	0.04	0.06	0.08
<i>n</i> -C ₁₇ H ₃₆	60.0	18.73	37.38		
	80.0	12.72	23.25	36.96	
	100.0	8.28	16.65	26.11	36.04
<i>n</i> -C ₁₅ H ₃₂	60.0	16.80	38.17		
	80.0	10.02	22.08	39.28	
	100.0	6.11	14.67	25.96	36.16
<i>n</i> -C ₁₃ H ₂₈	60.0	15.05	42.84		
	80.0	7.06	21.95		
	100.0	5.12	12.91	25.20	36.43
<i>n</i> -C ₁₁ H ₂₄	60.0	9.03			
	80.0	3.84	19.76		
	100.0	1.24	11.42	22.07	39.20
<i>n</i> -C ₉ H ₂₀	60.0	6.45			
	80.0	2.69			
	100.0	1.44		24.91	

where, $\gamma_{\text{mod.cal}}$ and $\gamma_{\text{CO}_2\text{cal}}$ are paraffin IFTs for modified CO₂ and pure CO₂ injection, respectively.

$$\gamma = (a \cdot t^b + c \cdot t) \cdot p \cdot N^d + e \cdot p \cdot N^d + f \cdot t^g + h \cdot N^d \quad (8)$$

where, γ , t , p and N is same to Eq. (3). a , b , c , d , e , f , g and h are empirical coefficients. The values of empirical coefficients in Eq. (8) was shown in table 5.

The calculated AADR was given in table 6. From Table 6, the AADR increased with the ethanol mole fraction while reduced as the temperature increase. Therefore, more ethanol and lower temperature are favorable for CO₂ enhanced oil recovery.

4. Conclusions

IFT experiments have been conducted for five paraffin + CO₂ modified with ethanol systems. The range of experimental temperatures, pressures and ethanol mole fraction range were 60–100 °C, 5.06–14.60 MPa and 0.02–0.08, respectively. A total of 150 paraffin + modified CO₂ IFTs were obtained. The IFTs of paraffin + modified CO₂ systems were affected by the temperature, pressure, paraffin chain length and ethanol mole fraction. The IFTs decreased with pressure and y_{ethanol} for isothermal. And the slopes of IFT versus pressure decreased with temperature. A correlation of the IFTs for modified CO₂ injection was proposed, which presented the IFTs as the function of reservoir temperature, pressure, paraffin chain length and ethanol mole fraction in CO₂. The R^2 , RMSE and AARD of the correlation were 0.9948, 0.15 and 2.49%, respectively. The R^2 , RMSE and AARD for LOOCV and external validation were almost the same with the values of all data points. The results devote that the new model can precisely estimate paraffin IFTs for modified CO₂ with ethanol. The paraffin + modified CO₂ IFTs were compared with the values of paraffin + pure CO₂. The IFTs between CO₂ and paraffins were decreased after CO₂ was modified with ethanol. It is favorable for CO₂ EOR process. The IFT average absolute decrease ratio (AADR) was introduced and calculated. The values of AADR increased with the ethanol mole fractions and decreased as the temperature increasing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2017.08.031>.

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