Competitive adsorption behaviors of carbon dioxide and n-dodecane mixtures in 13X molecular sieve

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Abstract. The CO_2 cyclic injection has been proven to be effective to enhance tight oil recovery under constant reservoir temperature and down hole pressure conditions. However, the enhance tight oil recovery mechanism was unclear, especially the adsorption of the CO_2 and alkane in the surface. Therefore, it is great important to study the adsorption mechanism of CO_2 and alkane mixtures in tight oil. In this study, a new experimental method and apparatus have been designed to test the change of the mole fraction of CO_2 and $n-C_{12}$ before and after the adsorption equilibrium. Then, the adsorption amount of CO_2 and $n-C_{12}$ was obtained by a mathematical method. Moreover, the adsorption character of CO_2 and $n-C_{12}$ mixtures in 13X molecular sieve and the effect of pressure on the adsorption and amount were studied. The results show that the adsorption of CO_2 and the desorption of $n-C_{12}$ follow the Langmuir adsorption. This study provides a straightforward method to experimentally determine the adsorption properties of the tight oil, which can be used to evaluate enhanced tight oil recovery by CO_2 injection.

1. Introduction

The production of tight oil has increased drastically in North America in the last ten years, due to advanced technologies such as horizontal drilling and multi-staged hydraulic fracturing[1]. However, tight oil is far more costly and difficult to produce than conventional oil because of the low porosity, low permeability [2]. Carbon dioxide tertiary or even secondary oil recovery becomes increasingly important to the production of the tight oil. This is because CO_2 flooding can not only effectively enhance or improve oil recovery but also considerably reduce greenhouse gas emissions. Over the past six decades, there have been extensive laboratory studies, numerical simulations, and field applications of CO_2 flooding in different oil recovery processes for various light and medium oil reservoirs[3]. It has been found from a laboratory study that the ultimate oil recovery factor of a CO_2 secondary flood is over 60% of the original-oil-in-place (OOIP), which is significantly higher than 44%of the OOIP, an average oil recovery factor of a secondary water flood[4]. It has known that the pore size of the tight oil is in a few nanometers to tens of nanometer range and the Specific surface area is larger. So the adsorption of CO_2 in the surface cannot be ignored.

Adsorption from liquid mixtures on solids underlies a number of extremely important processes and plays a significant role in many fields of the natural sciences[5]. The majority of authors studying adsorption at the liquid-solid interface have considered this phenomenon as the molecular exchange process between the bulk and adsorbed (surface) phases at thermodynamic equilibrium[5]. A large density difference was not found in the case of liquid adsorption. The sizes, shapes and possible configurations of solute molecules cover a much broader range than in gas adsorption[6]. The adsorbed phase is formed on a heterogeneous surface of a solid, which is an inert material with a potential energy field above this solid surface. Besides the interaction of adsorbent and each component, and the interaction of benzoic acid and carbon tetrachloride also should be take into account, which has a strong link with the solubility[7].

In this work, the adsorption character of CO_2 and $n-C_{12}$ mixtures in 13X molecular sieve was studied under isothermal and constant external pressure conditions by conducting experimental tests. The motivation for this study was three-fold: First, a new experimental method and set up the apparatus correspondingly was developed. Second, the effect of the external pressure on the adsorption and amounts of CO_2 and $n-C_{12}$ mixtures in tight sandstone was studied.

2. Material and method

2.1. Materials

13X molecular sieve were used as adsorbent which has a larger Specific surface area. The chemical formula of 13X molecular sieve is $Na_2O \cdot Al_2O_3 \cdot 2.45SiO_2 \cdot H_2O$, which is same to clay. For the adsorption measurements, the 13X molecular sieve was ground and sieved to obtain particles with diameter between 75 and 125 μm. The physical and geochemical characteristics of samples, including particle size, skeletal density, porosity, specific surface area, pore volume, pore diameter is listed in Table 1. The density and porosity of the samples were tested by the spontaneous imbibition of H_2O. The specific surface area was obtained by the liquid nitrogen adsorption measurements, which are widely used for determining the surface area of a variety of different solid materials [8].

Table 1. Physical and geochemical characteristics of the samples.

Sample	13X molecular sieve
Particle size (mu)	100-200
Density (g/cm³)	3.043
Porosity (%)	58.0
Specific surface area (m²/g)	632.30
Pore volume (cm³/g)	0.117
Pore diameter (nm)	11.18

[a] BJH adsorption: cumulative volume of pores between 1.7 and 300 nm.

[b] BJH adsorption: average pore diameter.

The CO_2 used in this study were obtained from Tianyuan (Qingdao, China) at purities of 99.999%. The n- dodecane used in this study were obtained from Sinopharm Group (Qingdao, Chian) at purities of 98%. The critical properties[9] of the pure adsorbates are as follows: $T_c(n-C_{12}) = 658.2K$, $P_c(n-C_{12}) = 1.82 \times 10^5$ Pa, $\omega(n-C_{12}) = 0.573$, $T_c(CO_2) = 304.1$ K, $P_c(CO_2) = 73.7 \times 10^5$ Pa, $\omega(n-C_{12}) = 0.225$. The binary interaction parameters of CO_2 and $n-C_{12}$ is 0.1 [10].

2.2. Adsorption test

An experiment method for determining the adsorption amount in high pressure and high temperature was proposed for the first time based on the immersion method in this study, a scheme of which is shown in Fig. 1. The core of this scheme is comprised of PVT cell, pressurization device, feeding device and oil-gas separator. The PVT cell was the heart of the set-up, which is the place of the binary

mixtures adsorption by the samples. It has an inner diameter of 3.0 cm and a volume of about 50 cm³; it was designed and built for operation up to 25 MPa and 200 °C, and it had a plunger for pressurization. In addition, a booster pump was used to modifying the position of the plunger to maintain a system pressure. The pressure transducers (Honeywell, USA) used to record the pressures of the PVT cell and the booster pump has a resolution of $0 - 6.9 \times 10^{-4}$ MPa and an accuracy of $\pm0.065\%$. The feeding device included a CO_2 storage cylinder, an n- C_{12} storage cylinders and a balance, which has a resolution of 0 - 2200.00 g and an accuracy of 0.01 g. The composition of the binary mixtures was obtained by the variation of the storage cylinders' mass. The oil-gas separator was consisted of a short pipeline (0.685 ml), a container (10 ml) which filled with absorbent cotton and a gas-flowmeter. The temperature of the set-up was kept constant in a stove with a temperature resolution of $\pm0.1℃$.
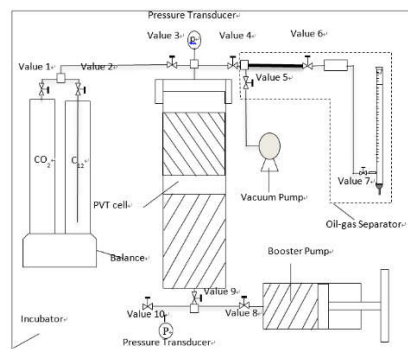

Fig. 1 Schematic diagram of apparatus for the adsorption of mixtures in pore media

The total volume of the system (V_t), the total amount of CO_2 and n- C_{12} in the system (N_0), the initial mole fraction of component i (x_i) and the mole fraction of component i in the bulk phase at thermodynamic equilibrium (x_i^l) can be obtained by the above measurement procedure.

2.3. Calculation of the adsorption amount

The adsorption amount of component i (N_i^s) of binary mixtures can be calculated directly follows from its defining equation (1):

$$N_i^s = N_i - Vc_i^l \tag{1}$$

where N_i^s is the adsorption amount of component i, mol; N_i is the total amount of component i in the system, mol; c_i^l is its concentration in the bulk phase after adsorption equilibrium, mol/ml; V is the volume of free phase, ml. However, the V is changed with the adsorption amount, which is difficult to test, because the volume of the kerogen will change with the adsorption of the mixtures. So a mathematical method was used to calculated the N_i^s. Same to the equation [2], the total amount of adsorbed and dissolved phase N^s, which was the sum of the adsorption amount of CO_2 and n-C_{12}, was shown as

$$N^s = N_0 - Vc^l \tag{2}$$

Where N^s is the total amount of adsorbed and dissolved phase, mol; c^l is the concentration of bulk phase, mol/ml. Then, V was eliminated from equation (1) and (2). In this manner, the equation (3) was obtained.

$$(N_0 - N^s)\frac{c_i^l}{c^l} = N_i - N_i^s \tag{3}$$

Taking into account that c_i^l/c^l can be replaced by the mole fraction of component i in the bulk phase (x_i^l), the following equation was obtained:

$$N_i^s - N^s x_i^l = N_i - N_o x_i^l \tag{4}$$

Because N_i can be represented as N_0*x_i, the equation (5) was obtained.

$$N_i^s - N^s x_i^l = N_0 \Delta x_i^l \tag{5}$$

where Δx_i^l was the difference between x_i and x_i^l. The right-hand side does not depend on anything other than experimentally measurable quantities. The adsorption amount per unit mass was shown as:

$$n_i^s - n^s x_i^l = \frac{N_0 \Delta x_i^l}{m} \tag{6}$$

where n_i^s was the adsorption amount per unit mass of composition i, mol/g. n^s was the adsorption amount per unit mass of the adsorbed and dissolved phase, mole/g. m was the mass of sample, g. It was seen from the equation(6) that $N_0 \Delta x_i^l/m$ had a linear relationship with x_i^l. Schay and Nagy consider that this is most probably due to n_i^s and n_j^s remaining constant over that section of the isotherm, i.e. that for a considerable range of x, the composition of the adsorbed and dissolved phase remains constant. So the n^s can be determined by the slope of linear section of the relationship of $N_0 \Delta x_i^l/m$ and x_i^l[11, 12]. The n^s was assumed constant within range of all mole fraction. So, n_i^s can be obtained by the equation (7).

$$n_i^s = \frac{N_0 \Delta x_i^l}{m} + n^s x_i^l \tag{7}$$

3. Results and discussion

The adsorption test of CO_2 and $n-C_{12}$ mixtures was done at 20 MPa (60 ℃) in the different pressure. First, it should be noted that the CO_2 in the liquid phase was unsaturated state during the test. On the one hand, if the CO_2 in the liquid phase was saturated state, the system has triple phase (adsorption phase, liquid phase and gas phase), which was complex. On the other hand, the mole fracture of CO_2 in liquid phase did not change in the same pressure and temperature (the max mole fracture of CO_2 was 0.50 and 0.80 in 6 and 12 MPa, respectively), when the CO_2 was saturated in the liquid phase. Therefore, it was not necessary to study the adsorption of CO_2 and $n- C_{12}$ in the saturated state.

Fig. 2 shows the $N_0 \Delta x_{CO_2}^l/m$ for the CO_2 and $n- C_{12}$ mixtures as a function of the $x_{CO_2}^l$ in 13X molecular sieve. It was clearly shown that the $N_0 \Delta x_{C_{12}}^l/m$ had a linear relationship with $x_{C_{12}}^l$, when $x_{CO_2}^l$ was larger than 0.25. According to the study of Schay and Nagy, the composition of the adsorbed and dissolved phase remains constant (7). So the n^s can be determined by the slope of linear section of the relationship of $N_0 \Delta x_{C_{12}}^l/m$ and $x_{C_{12}}^l$ according to the equation (6). The n^s of 6MPa, 12MPa and 20MPa were 0.0085, 0.0092 and 0.0095 mmol/g, respectively, which were negative value of the slope of the linear section. The adsorption amount of CO_2 ($n_{CO_2}^s$) and $n-C_{12}$ ($n_{C_{12}}^s$) in the shale can be obtained by equation (7).
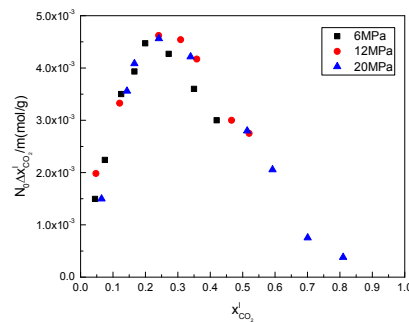
Fig. 2 The relationship of N0Δxl C12/m and xl C12 in different pressure

Fig. 3 shows the adsorption amount of CO_2 and n-C_{12} as a function of the $x_{CO_2}^l$ in 20 MPa for different pressure. It was obvious that the $n_{CO_2}^s$ increased with the $x_{CO_2}^l$ ($x_{CO_2}^l<0.30$) and then remained constant ($x_{CO_2}^l>0.30$) as shown in Fig.3 (a). At the same time, the n-C_{12} desorbed from the surface and then remained constant ($x_{CO_2}^l>0.30$) as shown in Fig.3 (b). Because the CO_2 reached adsorption saturation in the 13X molecular sieve. Therefore, the $n_{CO_2}^s$ remained constant ($x_{CO_2}^l>0.25$) for the 13X molecular sieve. The results show that the adsorption amount of CO_2 in the 13X molecular sieve increased with the pressure, because the total adsorption amount increased from 0.0085 mol/ml to 0.0095 mol/ml when the pressure increased from 6 MPa to 20 MPa.
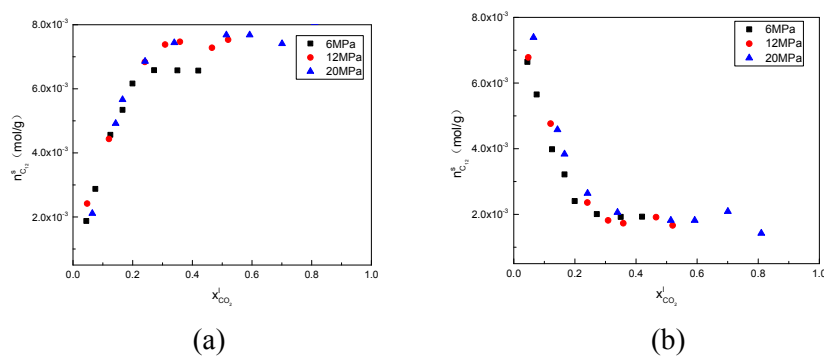

(a)   (b)

Fig. 3 The adsorption amount per mass as a function of the xl CO2 in 20 MPa: (a) CO2, (b) n-C12.

4. Conclusion

A new experimental method is designed and applied to measure the adsorption of n- dodecane and CO_2 mixtures in 13X molecular sieve. The main idea of the method is measuring the mole fraction of CO_2 in the free phase at thermodynamic equilibrium by changing the initial mole fraction of CO_2 and keeping the external pressure of the shale particles constant. Experiment results showed that, the adsorption of CO_2 and the desorption of n-C_{12} follow the Langmuir adsorption.

Acknowledgments

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