Lab-scale thermo-physical studies of CO_2 geological storage: Density of CO_2-Brine/decane system

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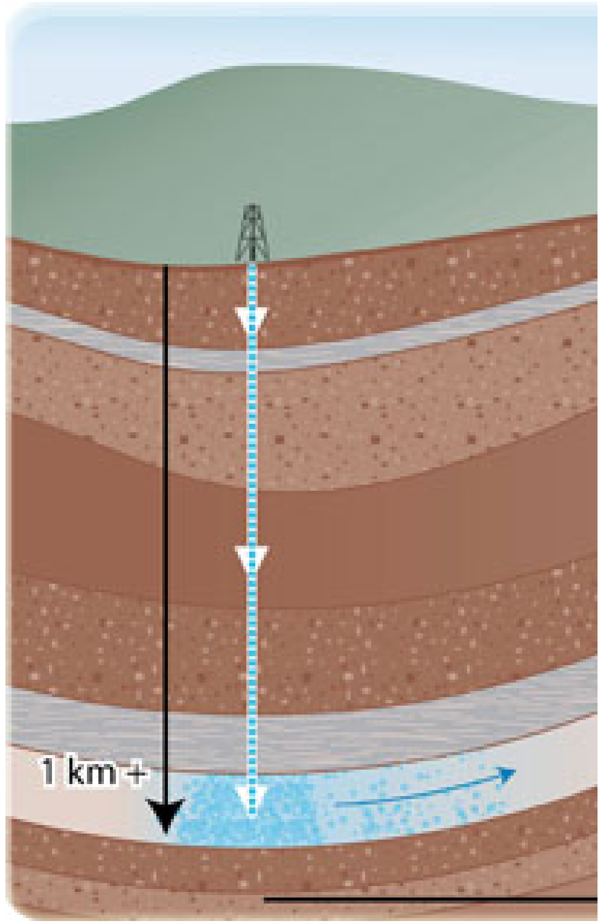
20110713

Outlines

- Background : thermo-physical problems in CO_2 aquifer storage.
- Purpose： what do we want to obtain from this research.
- Density of CO2-brine system.
- Density of CO2-decane system.
- Volume character of CO2-brine/decanne system.
- Conclusions & Discussions.

1.Background

- Density of CO_2-brine system is a key parameter for CO_2 saline aquifer storage
  - Density balance (P-V-T-ρ) affects the storage position and flow direction of CO_2 in saline aquifer.
    - Density decrease, buoyancy is the main drive force-> upward
    - Density increase, gravity is the main drive force -> downward



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2.Purpose

- Provide some thermophysical data or parameters for CO_2 storage project and its numerical simulation:
  - Density of CO_2-brine/decane system at different pressures, temperatures and CO_2 mass fractions.
  - Excess molar volume and apparent molar volume of CO_2-brine/decane system at different pressures, temperatures and CO_2 mass fractions.

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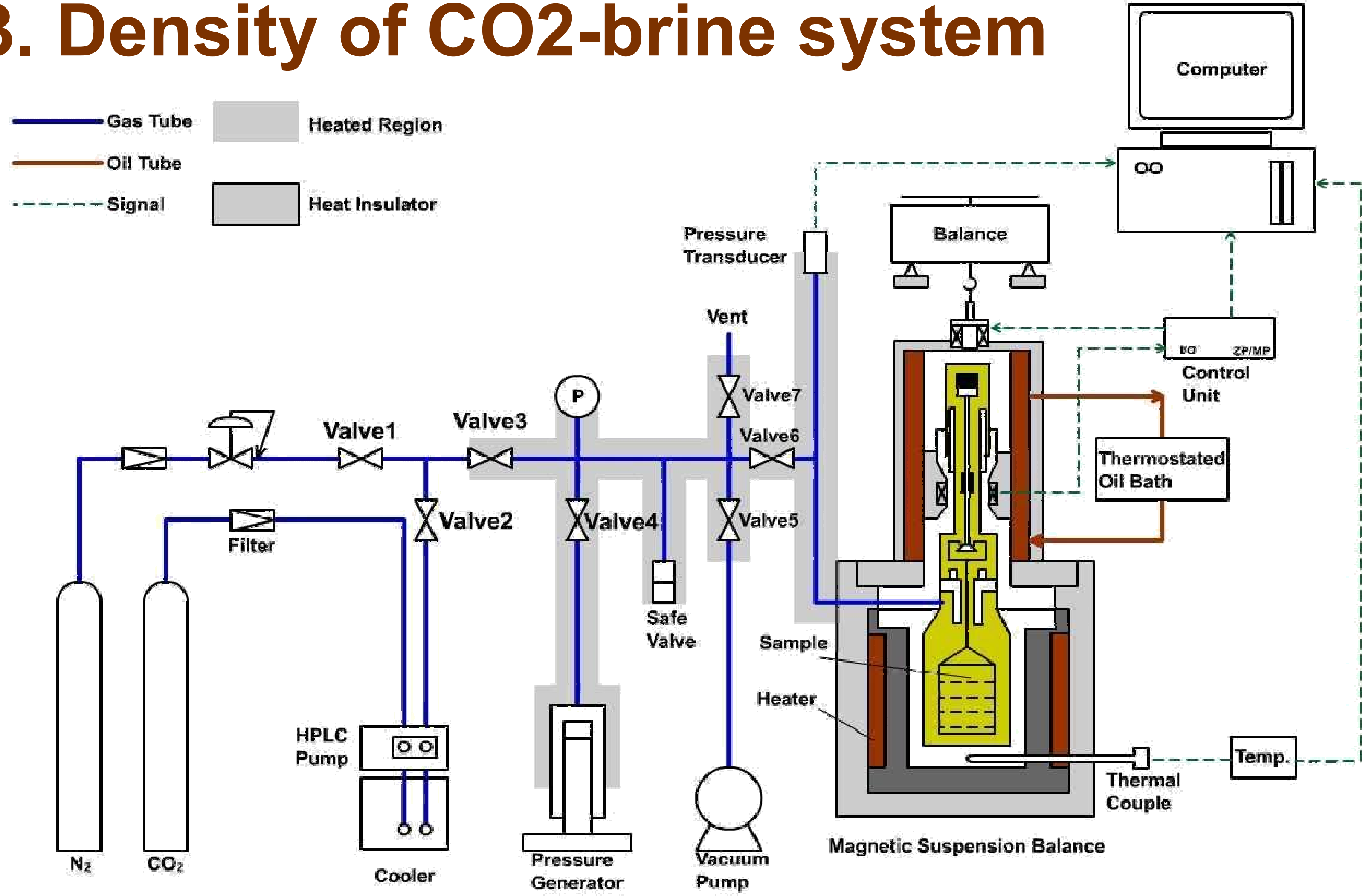
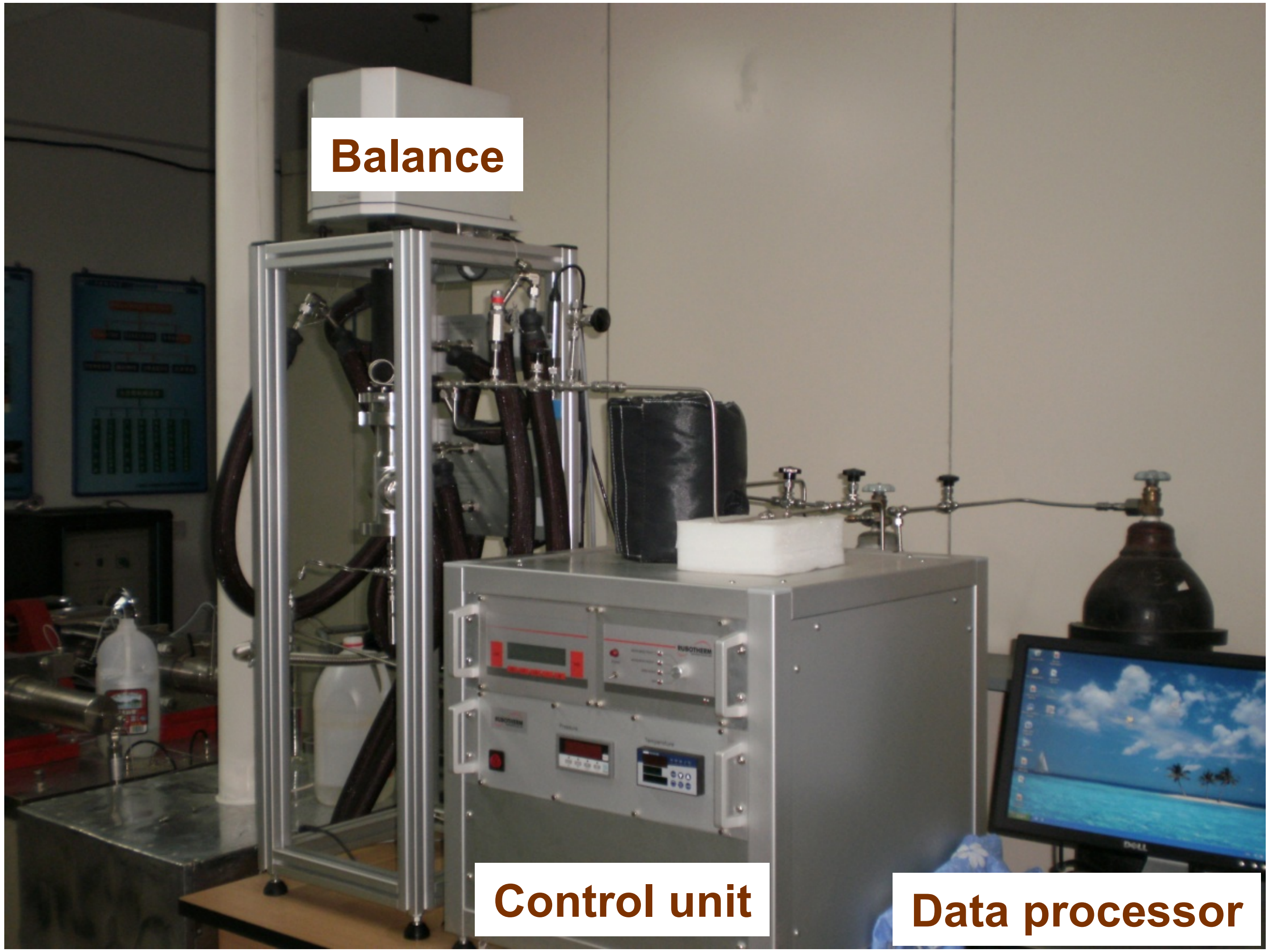
3. Density of CO2-brine system



Schematic diagram of MSB



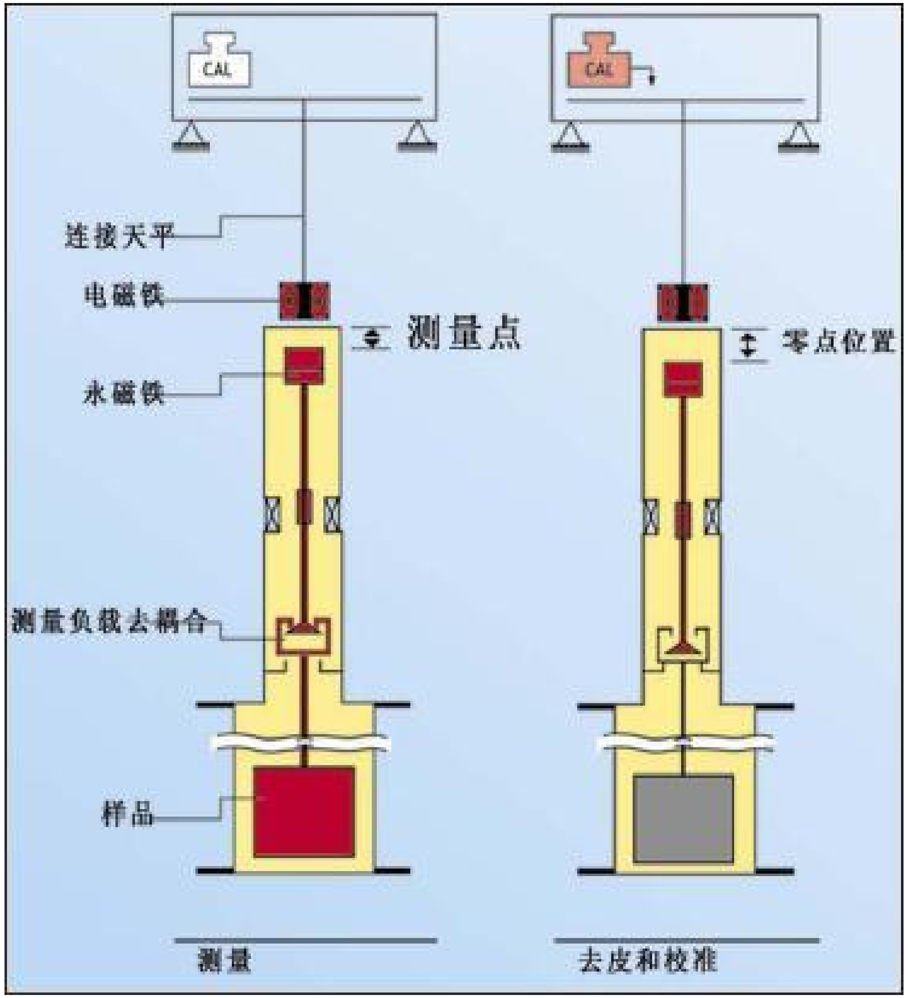
Photograph of MSB system

3.1 The principle of density measurement with MSB

- **Archimedes Principle :**

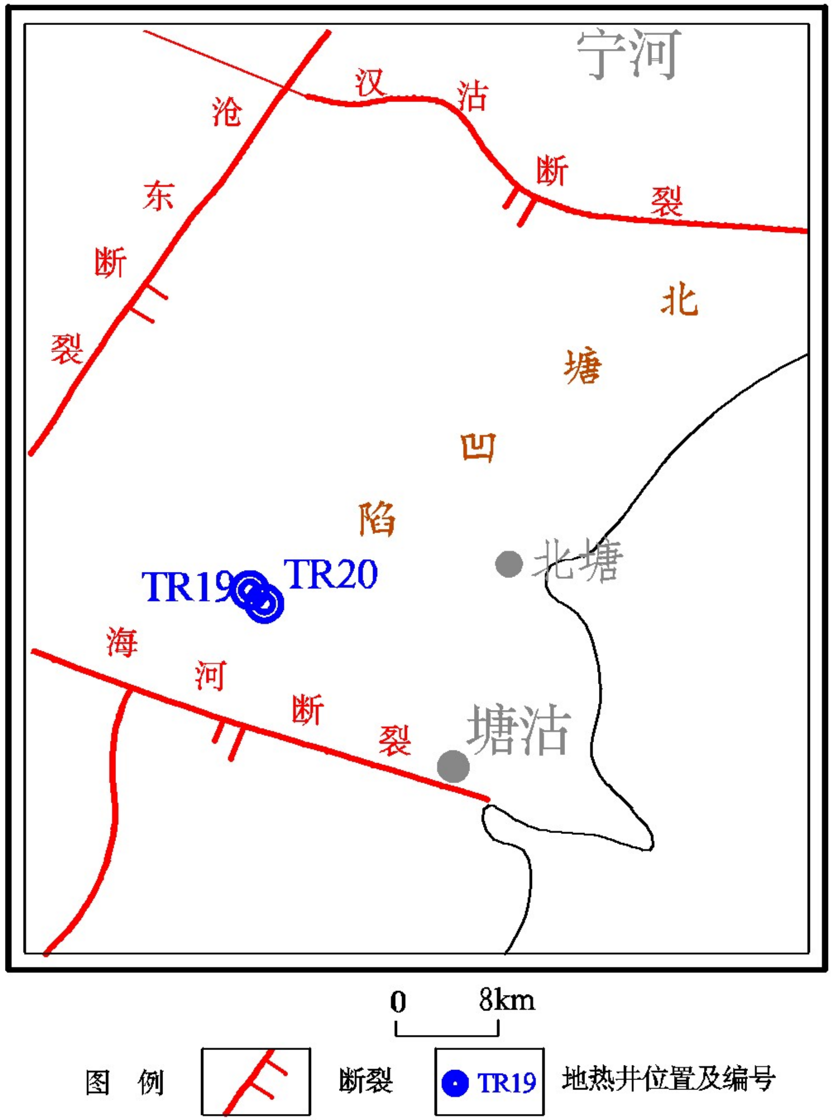
$$\rho = \frac{m - W}{V_s}$$

m – the mass of sinker under vacuum
W – the apparent mass of sinker in the measurement condition
$\boldsymbol{V_s}$ – the corrected volume of sinker in the measurement condition



3.2 Tianjin Formation

- **Participate in a CO2 storage demonstration project in Tianjin city, located in the northeast of North China Plain.**
- **The Tianjin Formation is a 23-69m thick massive sandstone formation located at a depth of 1480-1653m.**



The composition analysis of Tianjin Formation

ion	concentration/mg•L^{-1}
Ca^{2+}	1.790
Na^{+}	460.550
Mg^{2+}	3.427
K^{+}	16.000
Fe^{2+}	0.245
Cl^{-}	449.686
SO_4^{2-}	201.041
HCO_3^{-}	120

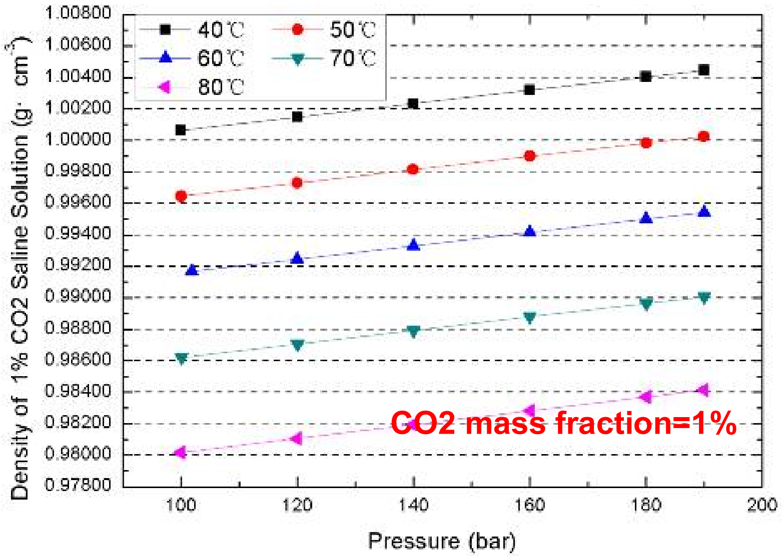
pH of the fluid：8.44 at 17.4℃

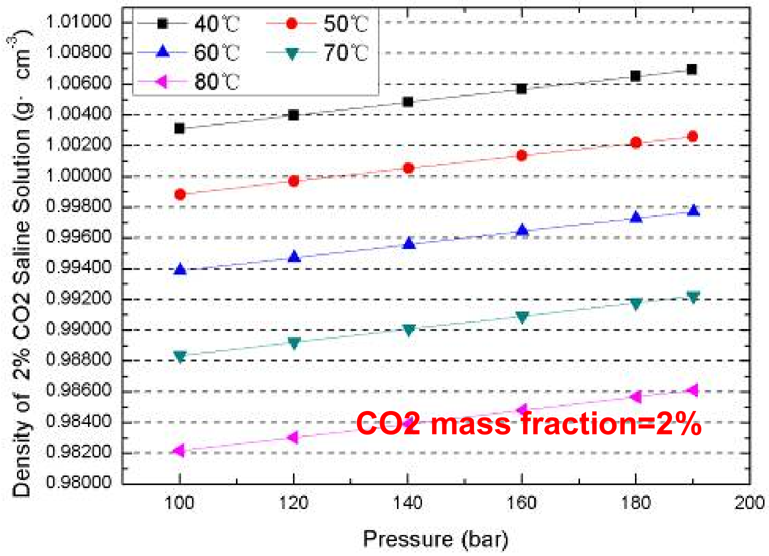
Hydrochemical type：HCO_3·Cl-Na type

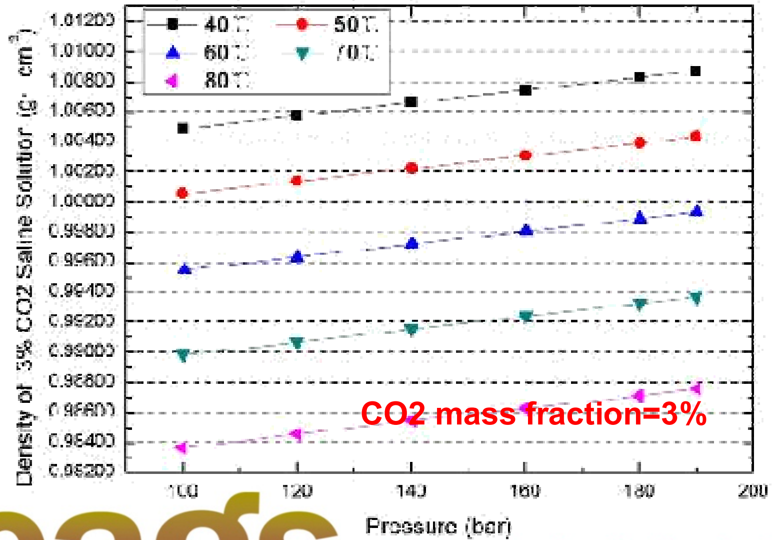
Fluid temperature：40-80℃

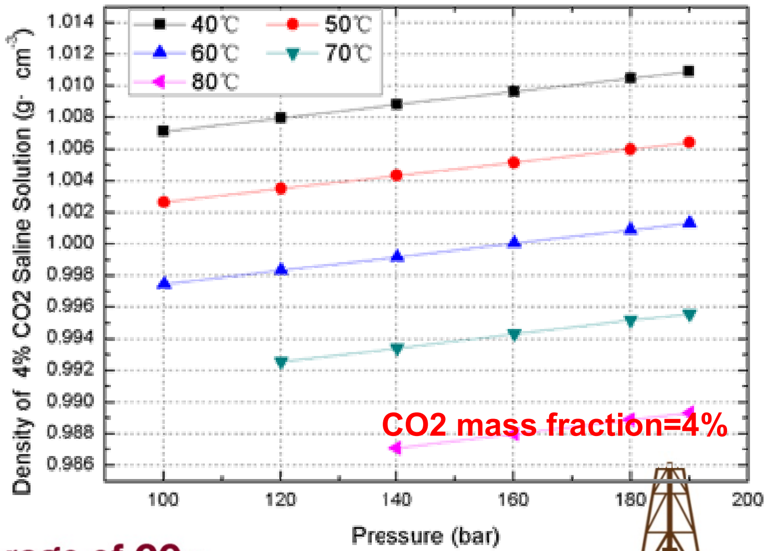
Reservoir depth：1486-1653m

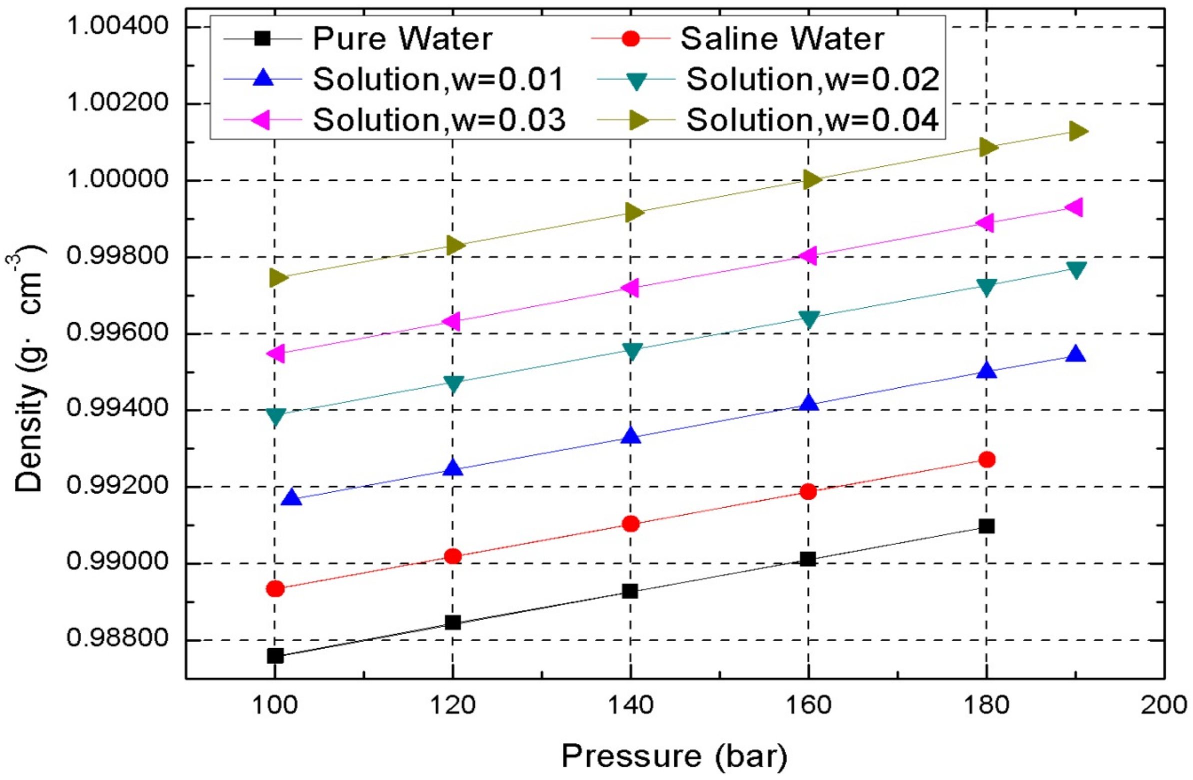
3.3 CO2-brine density change with pressure ＆temperature









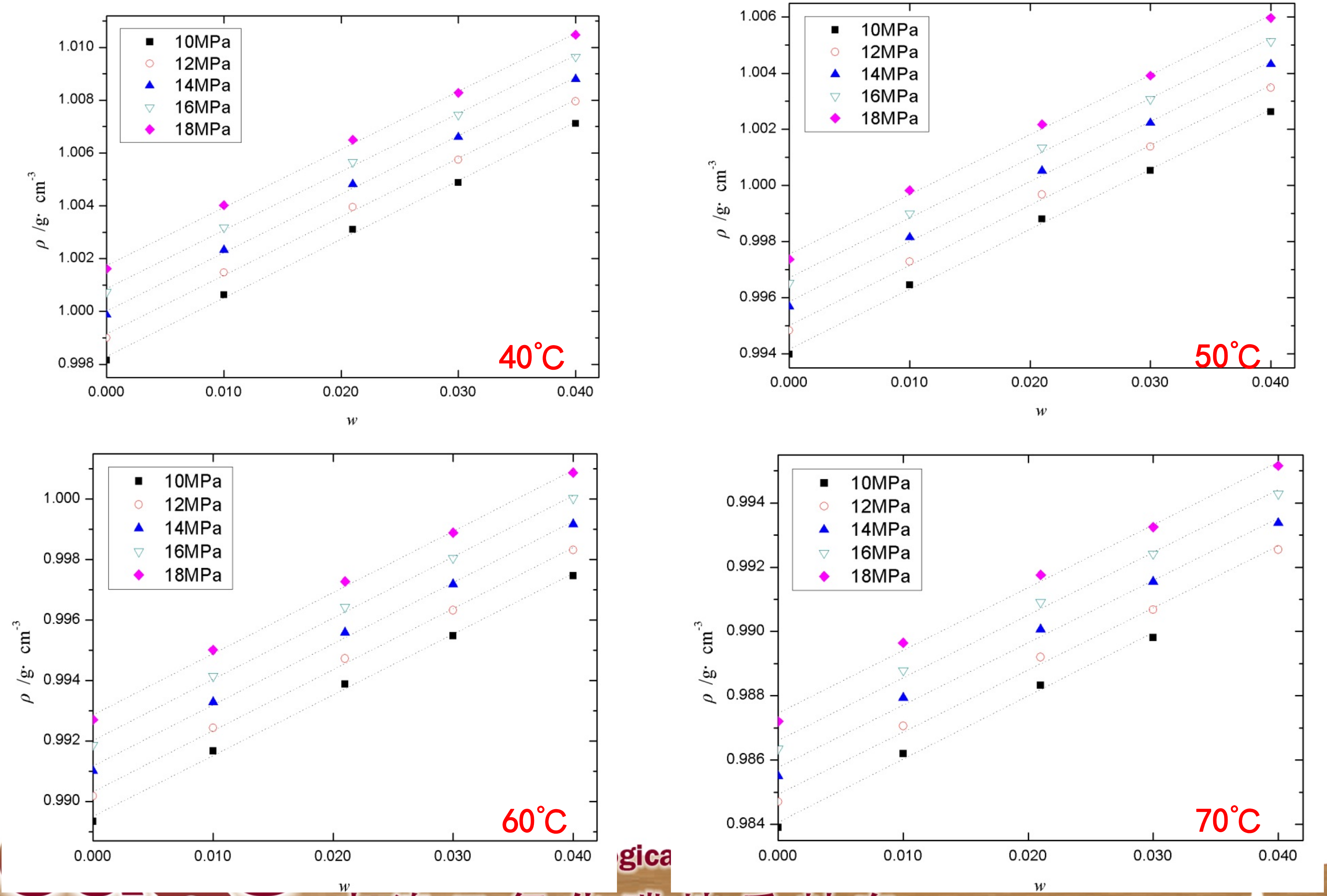


The density of CO_2 brine solution increases linearly with an increase of pressure, and the rate of increase is almost the same.

Discussions

- With the increase of pressure, the density of CO2 aqueous solutions showed linearly increasing
- With the increase of temperature, the density of CO2 aqueous solutions showed decreasing
- The slope of the CO2 brine solution density vs pressure are the same at different temperature

3.4 CO_2-brine density change with CO_2 mass fraction



Discussions

- With the increase of CO2 mass fraction, the density of CO2 aqueous solutions also showed an increasing trend.
- The slope of the CO2 brine solution density vs CO2 mass fraction is closely related to temperature; it decreases from 0.220 to 0.183 as temperature increases from 40 to 70℃.
- Formations with higher temperatures are less suitable for CO2 storage than cooler formations, if all other conditions remain unchanged.

3.5 Error analysis of our experiment

- Random Error

the measurement error of temperature ±0.01℃,

pressure ±0.01bar and CO_2 mass fraction ±0.05%

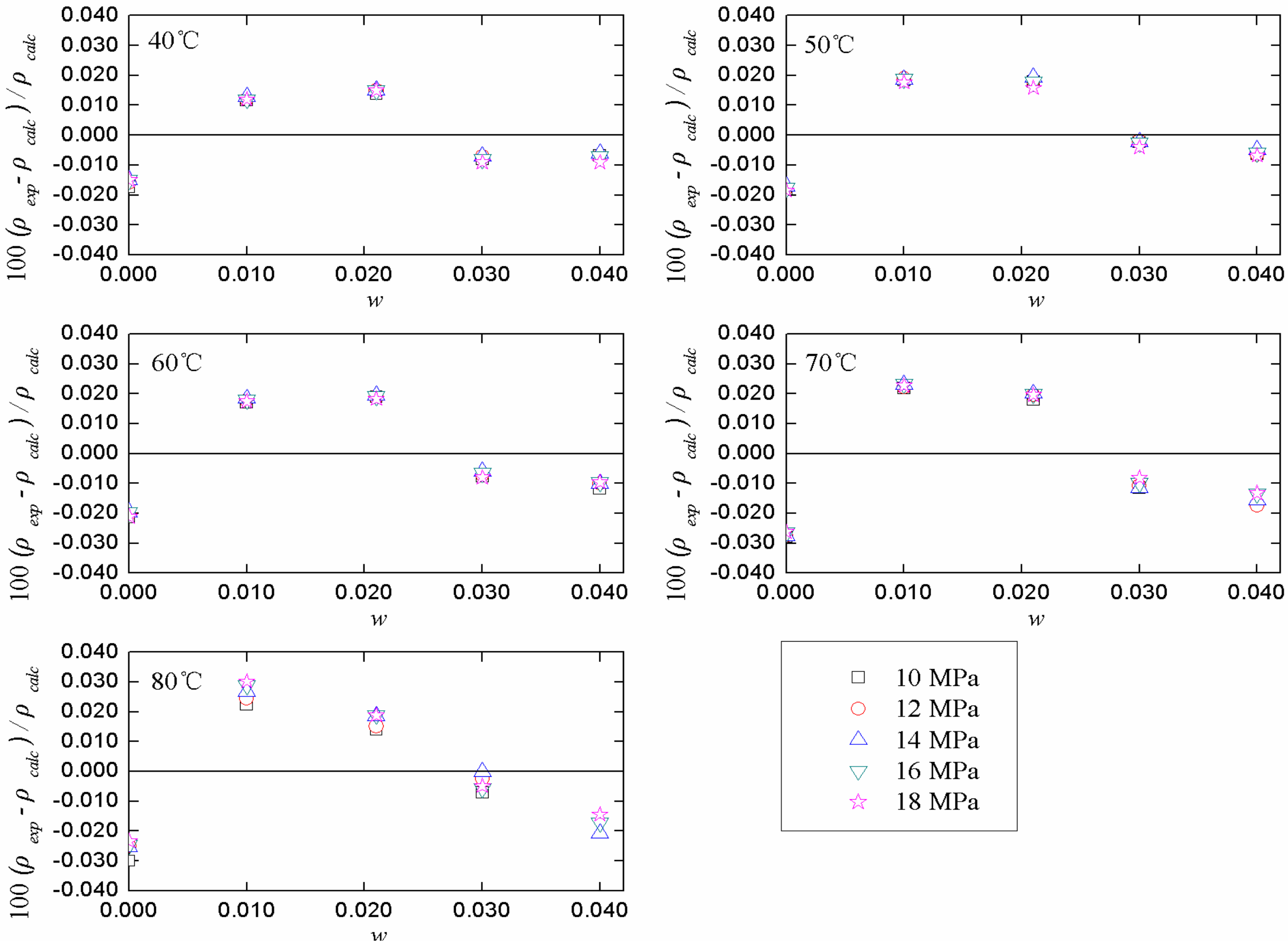
- systemic error
  - The transfer error of MSB, usually be neglected
  - the corrected volume of sinker, less than 0.001%

3.6 Eos of CO2-brine density

$$\rho = \sum_{i=0}^{2} \left(c_i + d_i p + e_i w'\right) T^i$$

i	c_i	d_i	e_i
0	8.255116E-01	6.453167E-04	3.300099E-03
1	1.463710E-03	-1.401649E-06	1.380885E-06
2	-2.954866E-06	2.218350E-09	-1.567212E-08

Compared with the experiment data, the maximum relative error of the brine model and CO2-brine model is 0.004 % and 0.03%.



The prediction deviation of the EOS compared with experimental data

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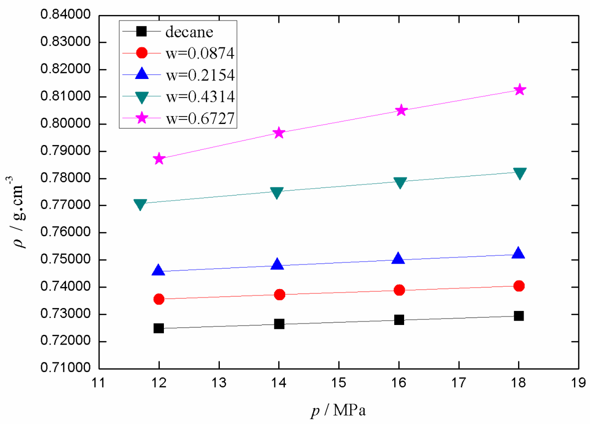
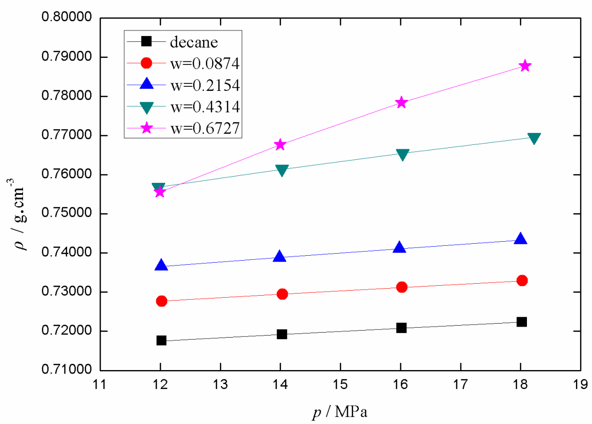
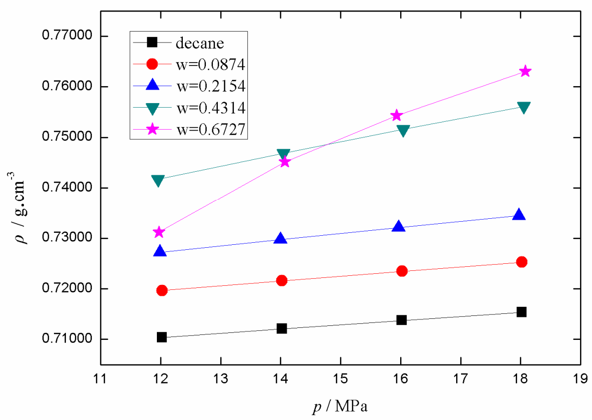
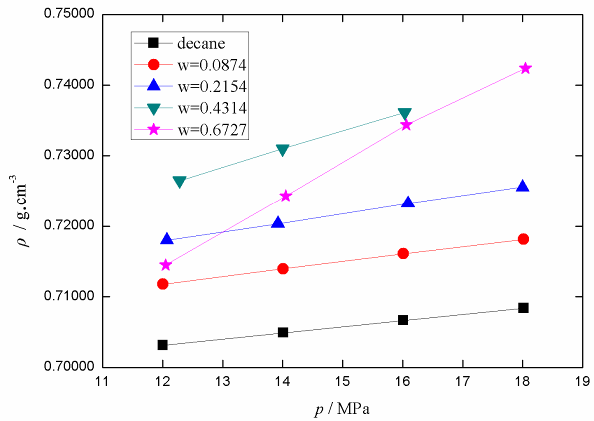
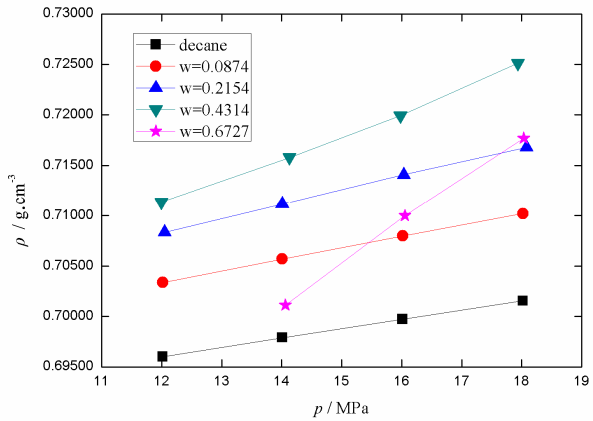
4.1 CO2-decane density change with pressure







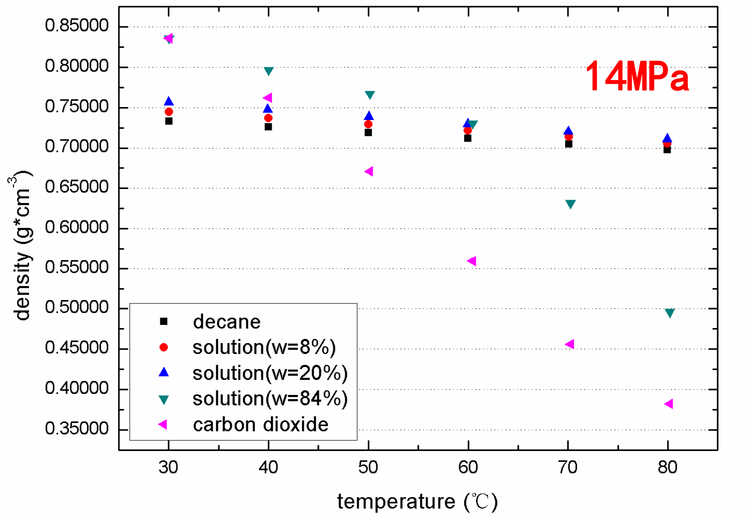


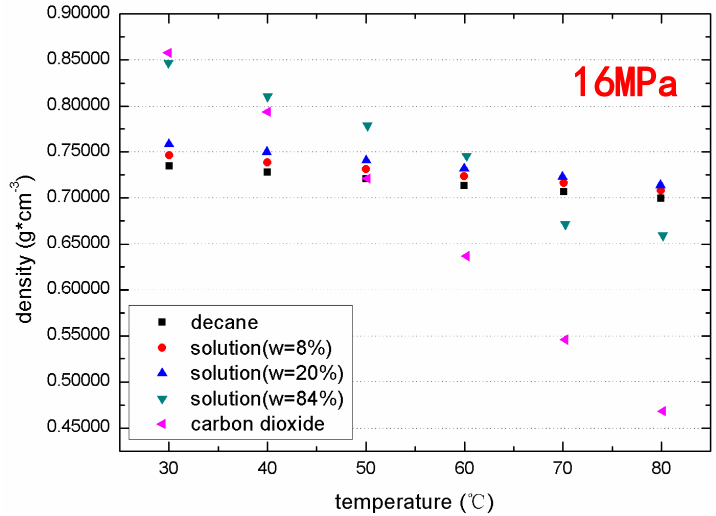


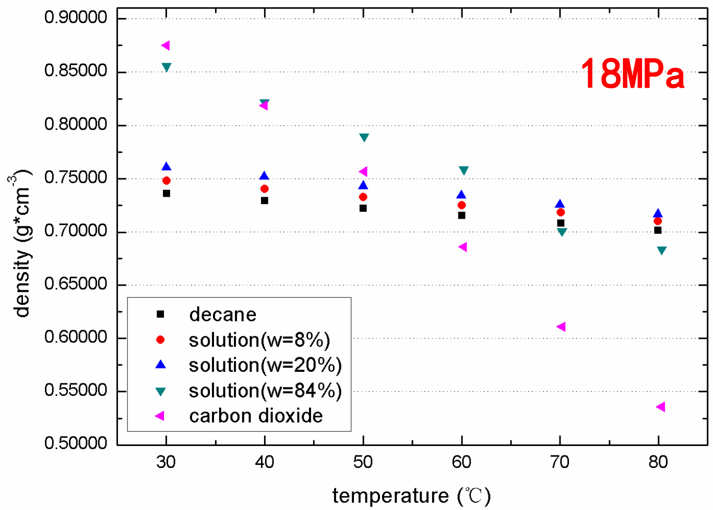
Disscussions

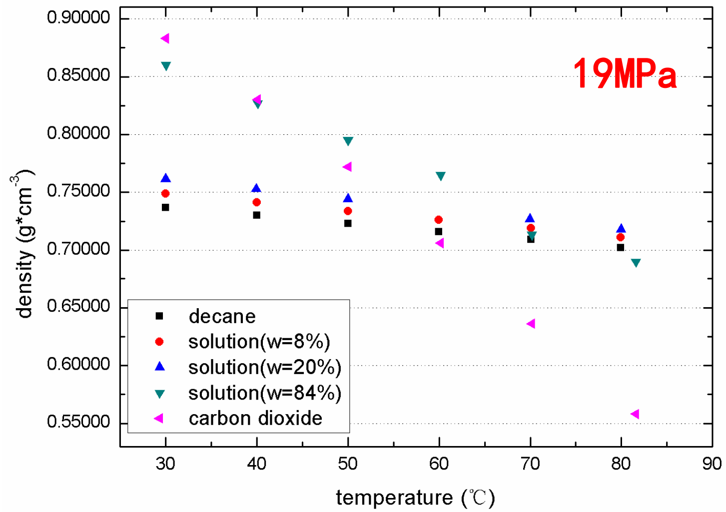
- When CO_2 mass fraction in the solution is small such as 8% and 24%, the change of CO_2-decane density is small and similar with decane.
- When more CO_2 dissolved, the solution density has a remarkable increase and similar with CO_2.
- A crossover is appeared between different CO_2 mole fraction, the pressure of the crossover reveal a increase trend.

4.2 CO2-decane density change with temperature





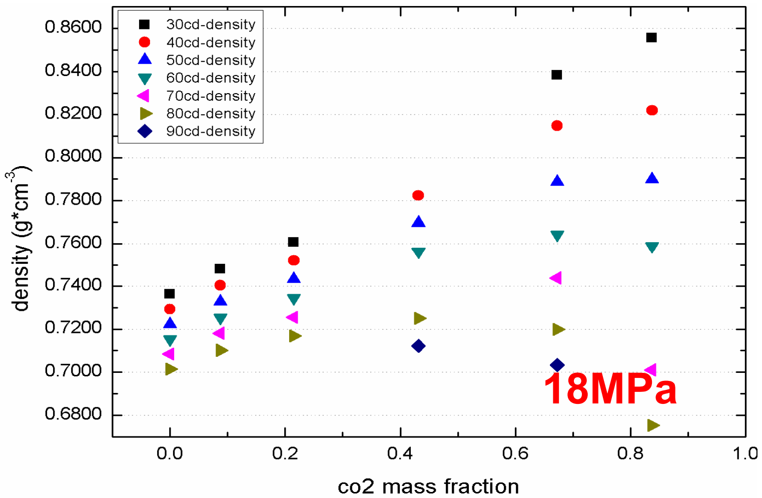


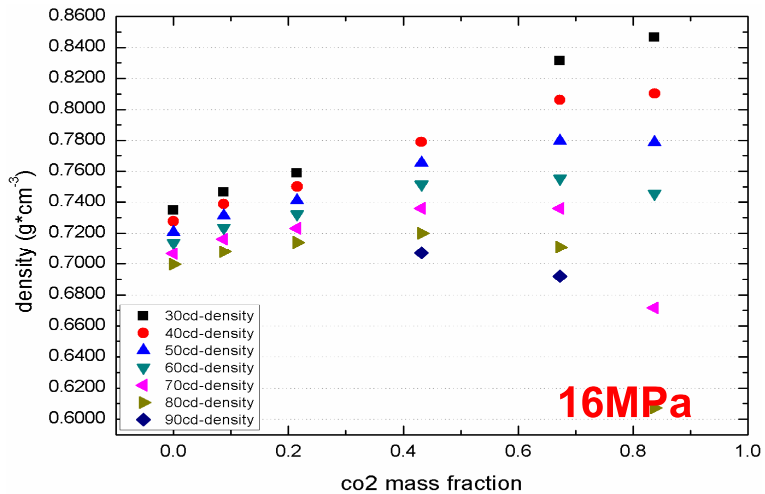


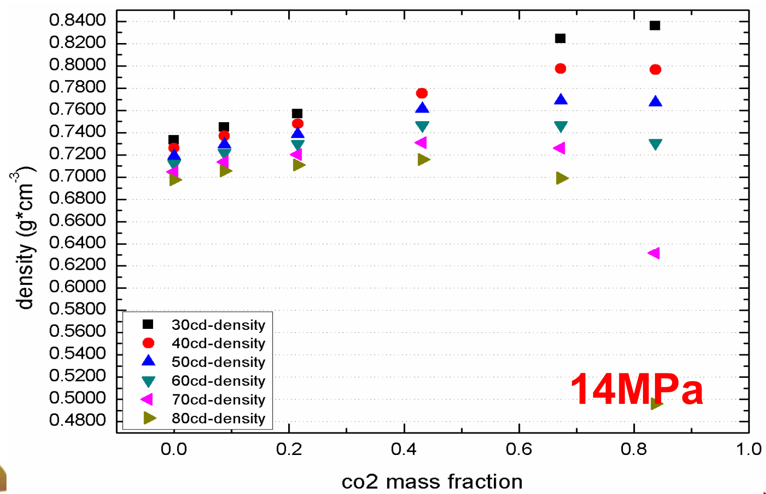
Disscussions

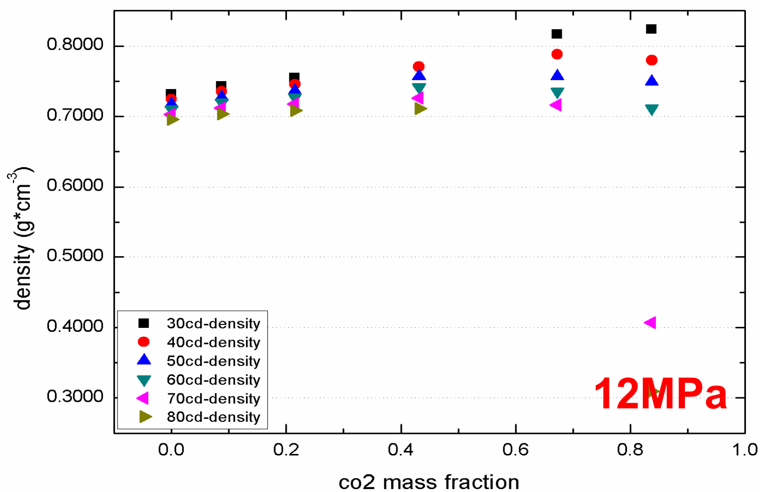
- The density of CO_2 decane solution decreases linearly with increasing temperature
- The drop in the solution density is small when CO_2 concentration is small. When more CO_2 dissolved the drop is obvious.
- This is due to the solution properties are more closer to CO_2 when the CO_2 concentration is high.

4.3 CO2-decane density change with CO2 mass fraction









Disscussions

- The density of CO_2 decane solution reveal first increase and then decrease with increase CO_2 mass fraction in general
- When temperature is low, the density of CO_2 decane solution show increase trend; when temperature is higher, it reveals increase first and decrease then
- The Boundary temperature of the two phenomenon are not the same with different pressure

4.4 EOS of CO2 decane density

$$\rho = \frac{c_3 - \left(c_4 / T + c_5 / T^{1/3} \right) + p}{c_1 + c_2 p}$$

ρ ----density of CO2 decane solution；

p ----pressure， MPa；

T ----temperature， K;

c_1, c_2, c_3, c_4, c_5 are the regression coefficient

This model was proposed by Abel Zúñiga et al. in 2005, have been widely used to predict the density of CO2-hydrocarbon system

The regression coefficient of EOS

	w =0	w =0.0874	w =0.2154	w =0.4314	w =0.6727
T_{min}/K	313.13	303.15	313.06	313	313.23
T_{max}/K	353.13	353.13	353.13	353.26	352.99
p_{min}/MPa	12	12	11.99	11.96	11.97
p_{max}/MPa	19.02	19.02	19.12	18.23	18.08
$\rho_{min}/g\cdot cm^{-3}$	0.69601	0.703371	0.708348	0.711359	0.673066
$\rho_{max}/g\cdot cm^{-3}$	0.73002	0.748641	0.753046	0.782427	0.812622
number	25	30	24	18	19
$c_1/MPa\cdot kg^{-1}\cdot m^3$	1.768084E+02	8.329398E+01	1.043577E+02	1.836682E+01	7.672652E+01
$c_2/kg^{-1}\cdot m^3$	1.174453E+00	1.245383E+00	1.165817E+00	1.230709E+00	-3.749935E+00
c_3/MPa	-1.852536E+02	-1.376241E+02	-2.208307E+02	-1.587045E+02	1.226821E+00
$c_4/K\cdot MPa$	2.854577E+04	1.947300E+04	3.063676E+04	1.931232E+04	6.089254E+03
$c_5/MPa\cdot K^{1/3}$	-2.735088E+03	-1.766095E+03	-2.681794E+03	-1.589299E+03	-6.309829E+02
AAD/%	0.001	0.0021	0.0037	0.1308	0.6202

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5. The volume character of CO_2 solution

- **Excess molar volume**

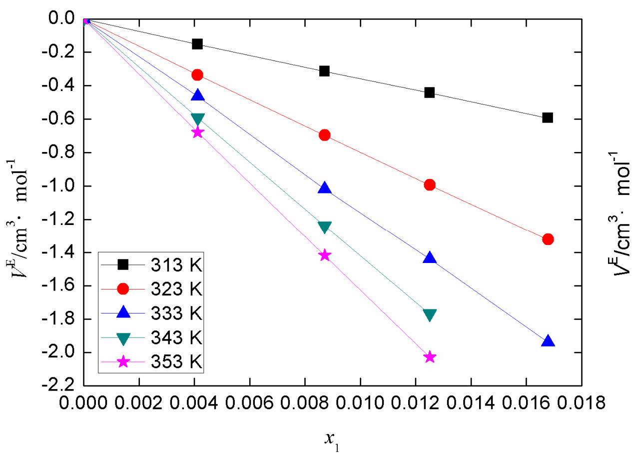
shows the difference between the actual character and the ideal character

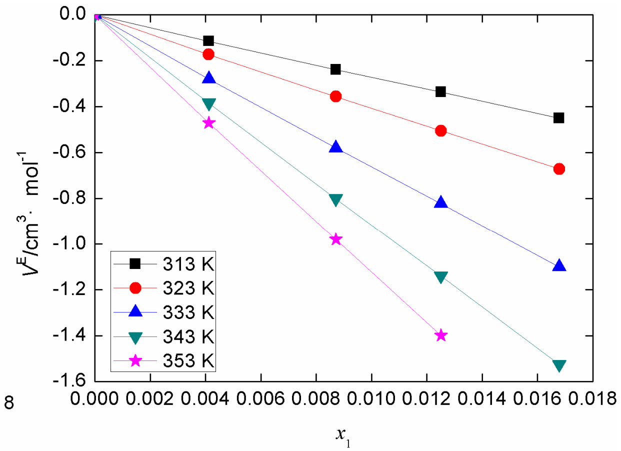
$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right)$$

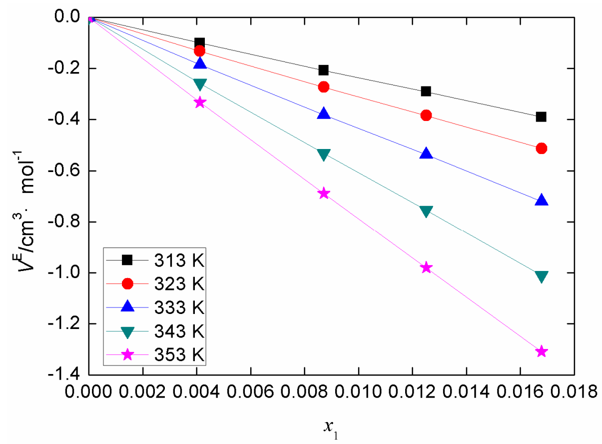
- **Apparent molar volume**

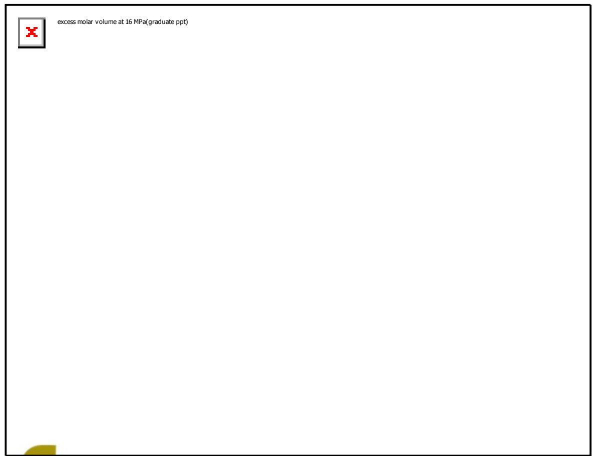
$$V_\phi = \frac{1000(\rho_0 - \rho)}{m \rho_0 \rho} + \frac{M}{\rho}$$

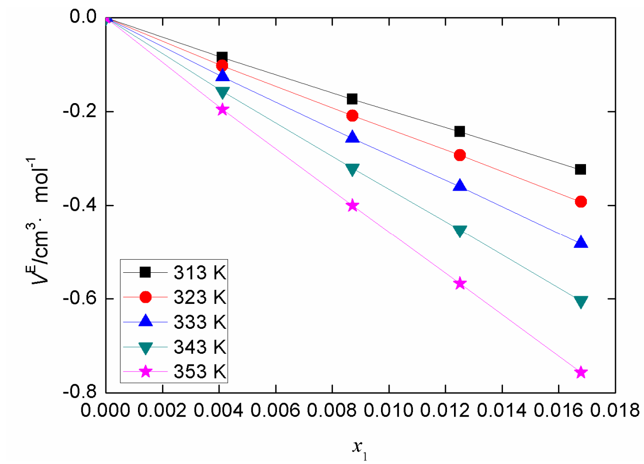
5.1 Excess molar volume of CO2 brine

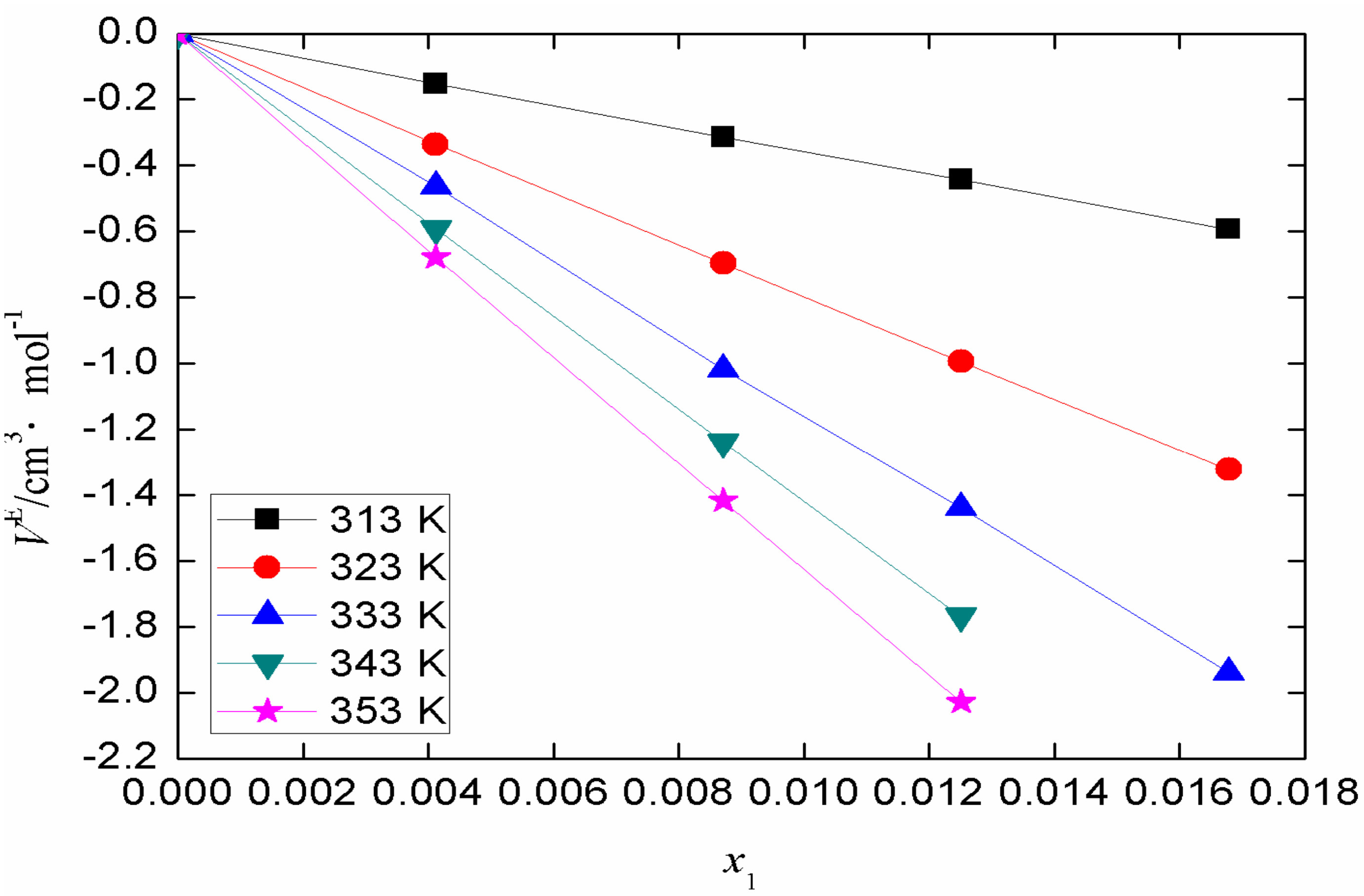










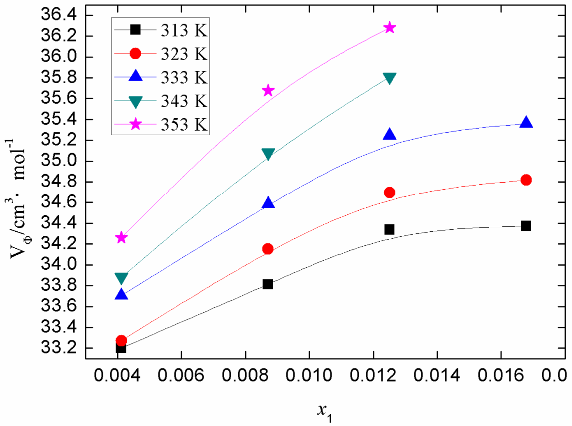


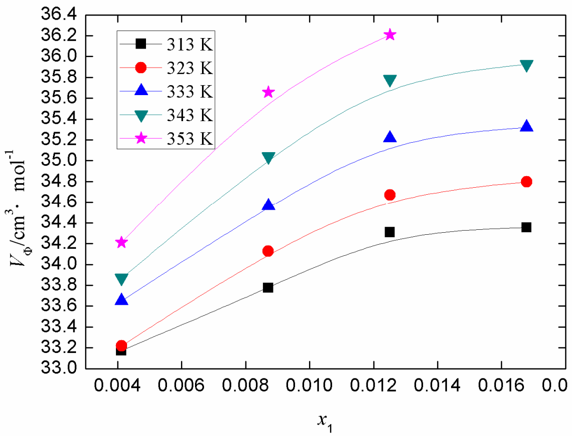
Excess molar volume decrease with increase CO2 mole fraction, the higher the temperature, the lower the excess molar volume

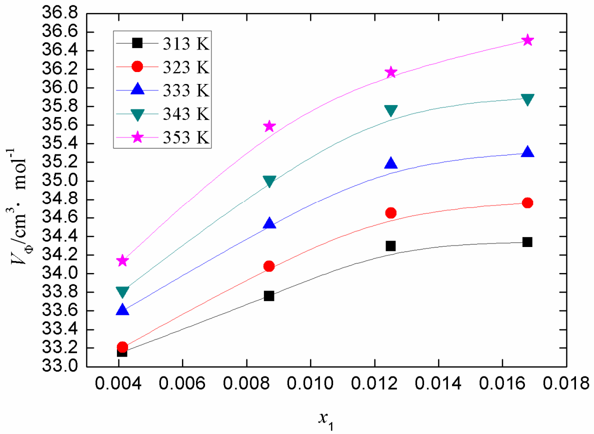
Discussions

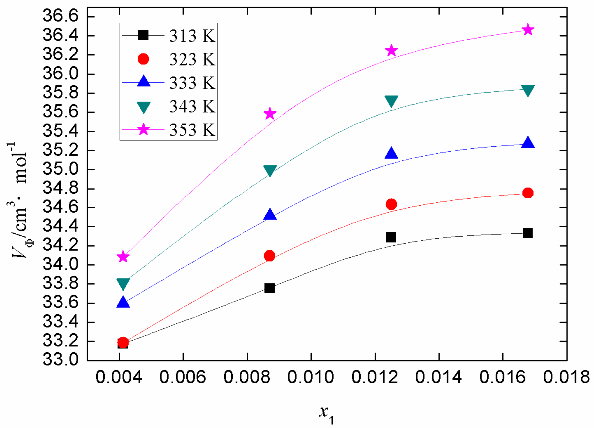
- The excess molar volume of CO2 aqueous solutions decrease linearly with increase CO2 mole fraction ＆pressure
- The excess molar volume of CO2 aqueous decrease with increase temperature
- Show the free volume between molecules decrease with increase temperature

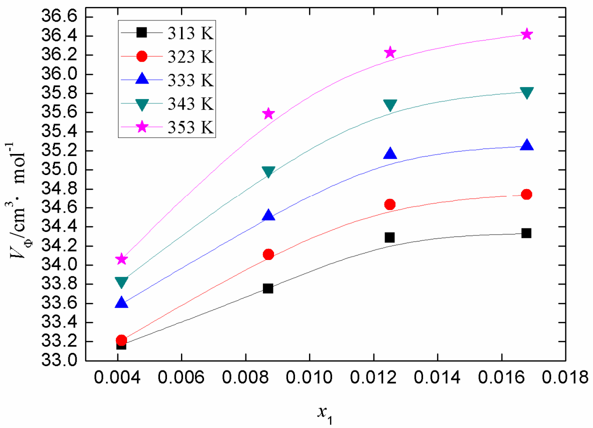
5.2 Apparent molar volume of CO2 brine

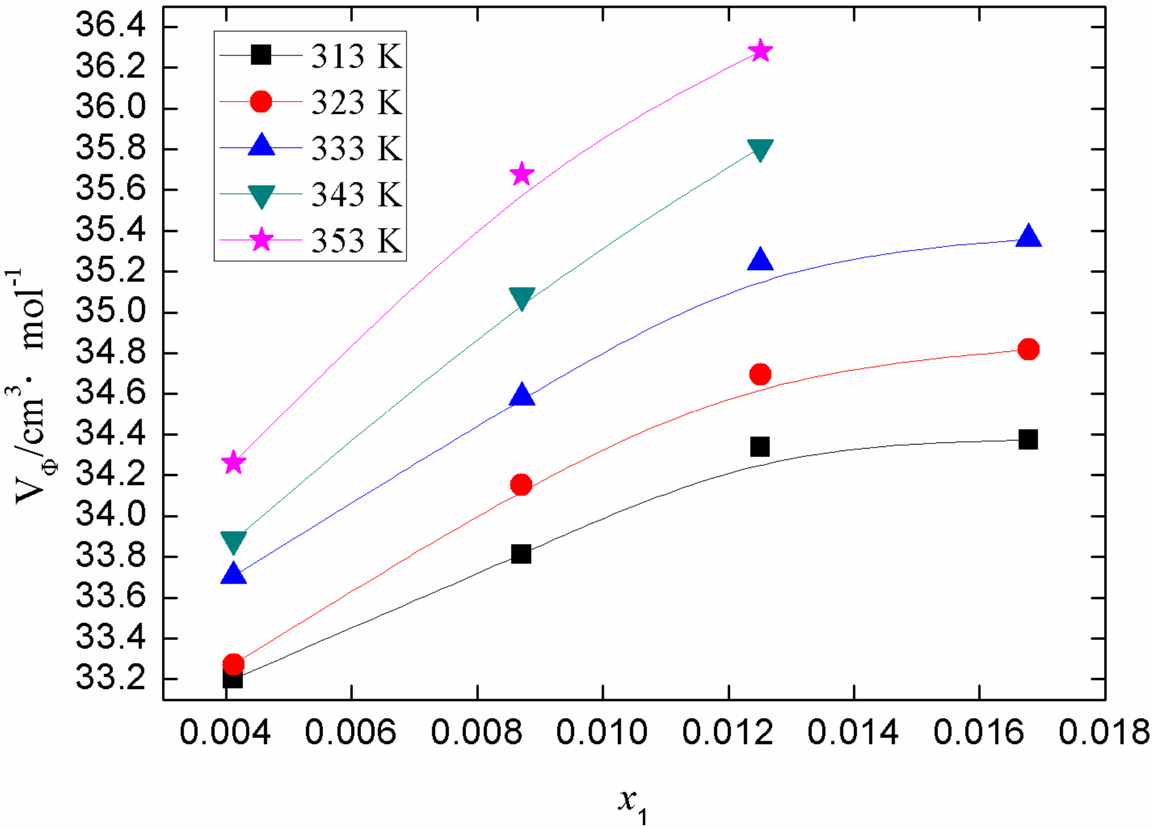






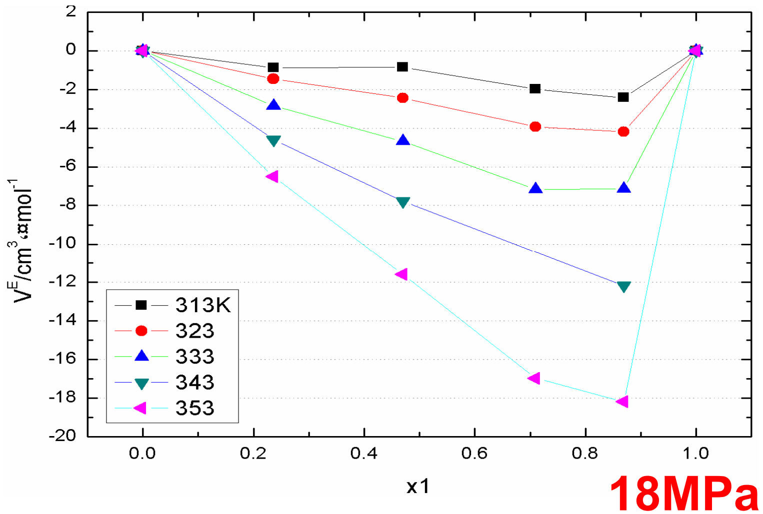




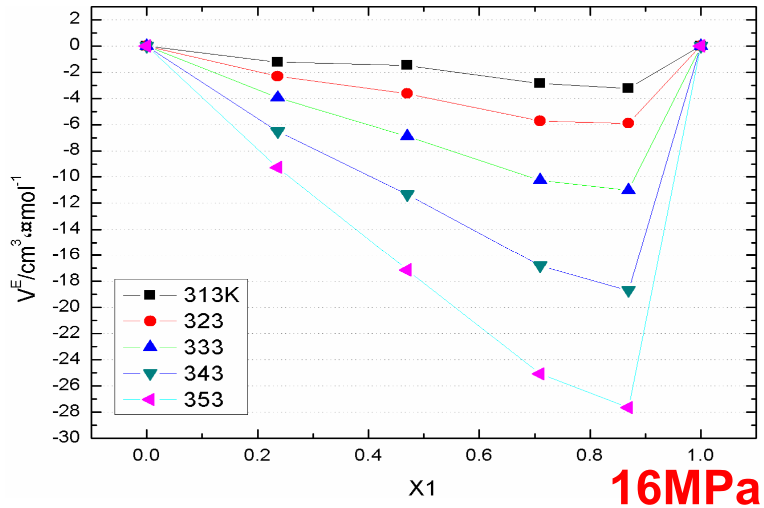


Apparent molar volume increase with CO2 concentration, the increase trend slow down gradually; the higher the temperature, the larger the apparent molar volume

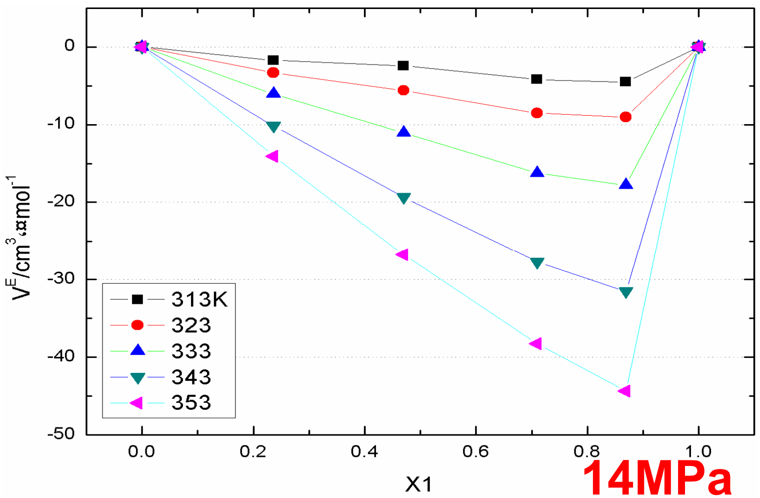
5.3 Excess molar volume of CO2 decane



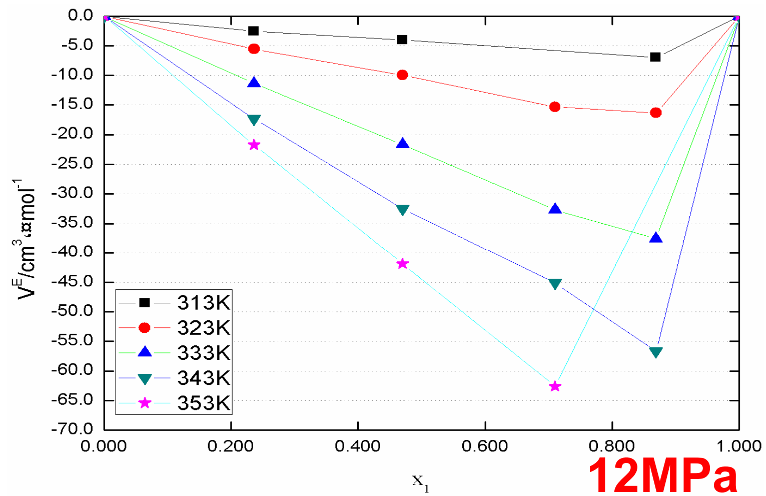
18MPa



16MPa



14MPa

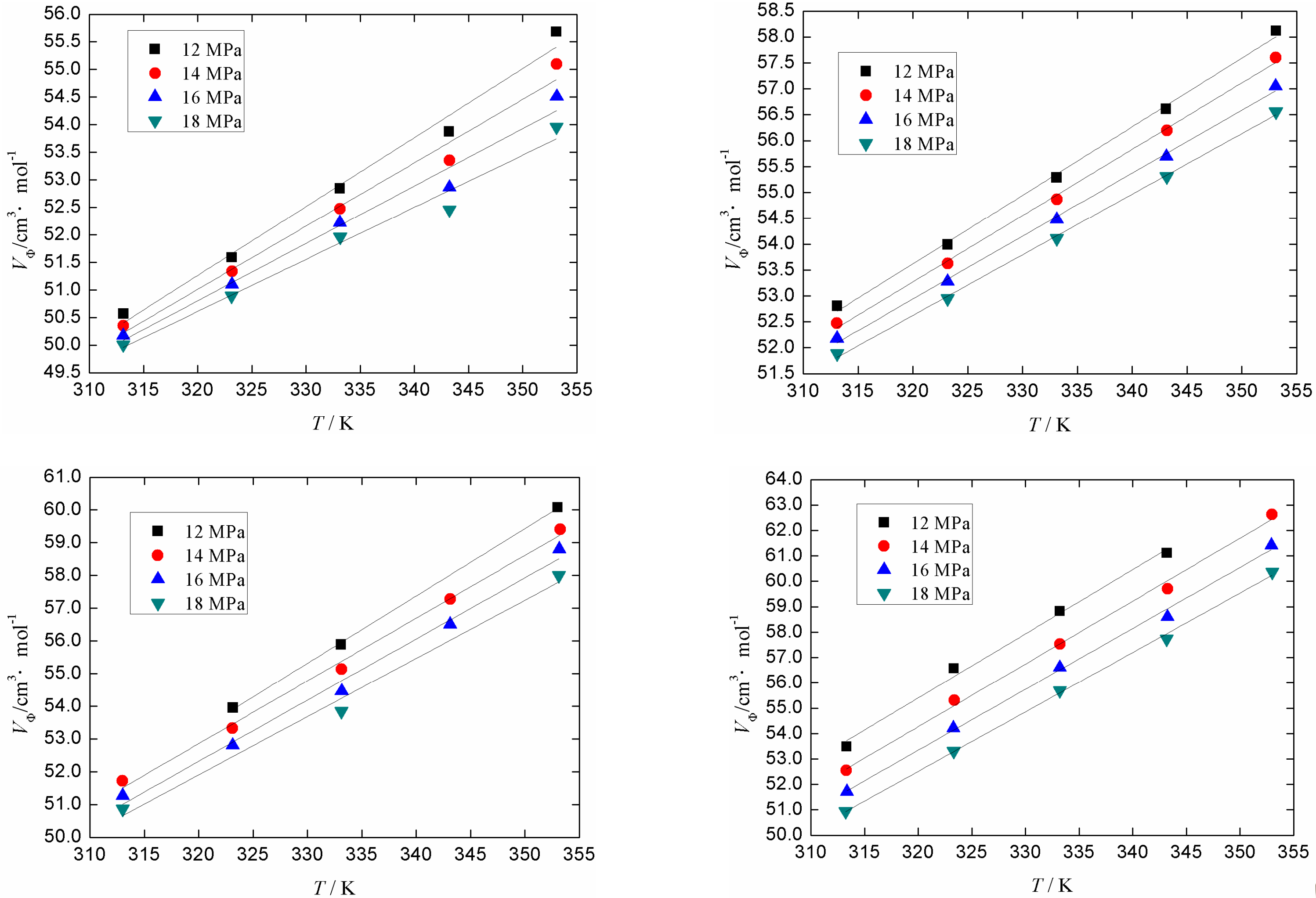


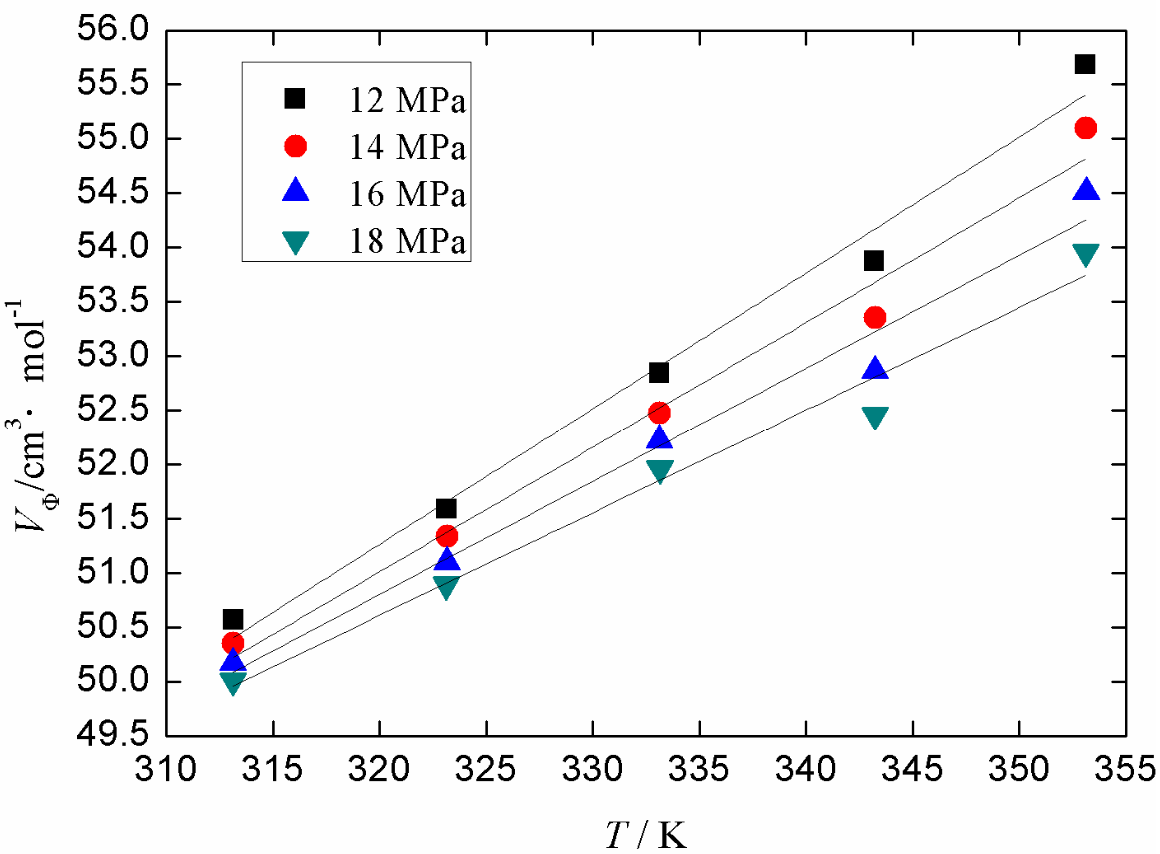
12MPa

Disscussions

- At a certain pressure, excess molar volume of CO2 decane solution shows decrease first and then increase with increase CO2 mole fraction
- When the temperature is higher, the volume change is more than low temperature
- It reveals that the lower the temperature, the more CO2 dissolve

5.4 Apparent molar volume of CO2 brine





Apparent molar volume increase linearly with temperature; the higher the pressure, the larger the apparent molar volume

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6. Conclusions & Discussions

- Density of CO2-saline system increases linearly with pressure and mass fraction of CO2 at different temperature.
- Density of CO2-brine system decreases with temperature.
- Density of CO2-decane system increase with temperature, decrease with temperature, a crossover appear among different CO2 mass fraction.
- The research on volume character of the CO2 solution is meaningful for physical character and the interaction between molecular.

Thank you for your attention!