

The solution and exsolution characteristics of natural gas components in water at high temperature and pressure and their geological meaning

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Abstract: The processes of solution in, and exsolution from, formation water influence the component content of natural gas by contrasting the relative contents of components before the natural gas dissolves in water and those after exsolving from water under different conditions of high temperatures and pressures. Compared with the composition of original natural gas, the relative content of methane and nitrogen increased after the natural gas dissolved in water. The increase of nitrogen content exceeds that of methane, but the content of ethane, propane, pentane etc reduced. At the same temperature and with pressure increasing the content of methane increased and that of heavier hydrocarbons reduced. At the same pressure the content of methane increased quickly from 90°C to 120°C, and the content of heavier hydrocarbons reduced. But at even higher temperatures, the increase of methane slowed down and the content of heavier hydrocarbons increased slightly. At the same temperature and different pressures, heavier hydrocarbons reduced much more with increasing carbon atom number, while with temperature increasing the content difference of heavier hydrocarbons reduced. Therefore, the influence of the solution and exsolution should be considered in the study of the migration and accumulation mechanism of natural gas.

Key words: Methane, heavier hydrocarbon, nitrogen, formation water, exsolution

1 Introduction

Compared with liquid petroleum, natural gas has a high solubility in water. The layers of gas-bearing basins are fully filled with formation water. After natural gas is generated in the source rock, it will inevitably encounter formation water in the process of primary migration. Hereby, formation water is an important medium in the process of the natural gas migration. At underground temperatures and pressures, some natural gas will dissolve in water and in the course of the migration of formation water, the values of temperature and pressure will change, which will impact on the solubility of natural gas in the water at the same time. If the content of natural gas exceeds the saturation level, some dissolved gas will exsolve from the formation water. Some experiments have been done on the dissolution of natural gas in water, but the majority of them focused on the study of solubility (McAuliffe, 1963; Price, 1976; Bonham, 1978). They mainly measured the solubility of natural gas and analyzed the controlling factors (Sultanov et al, 1972; Висоцкий, 1986;

Hao and Zhang, 1993; Gao et al, 1996; Fu et al, 1996). The controlling factors included temperature, pressure, natural gas content and salinity. The solubility of C₁-C₉ hydrocarbons in water was determined, and it is thought that the lower the carbon number of the hydrocarbon, the higher its solubility (McAuliffe, 1963). Oil and gas origins and primary migration were analyzed by experiments determining solubility in water (Price, 1976). Methane solubility in water was determined at elevated temperature and pressure (Bonham, 1978). Natural gas solubility experiments in water at pressures of 10-40 MPa and temperatures of 60-140°C, determined the relation of solubility with formation water salinity, water type, temperature and pressure and water solution gas resource was evaluated in the Langgu and Baxian sags of the Jizhong Depression (Hao and Zhang, 1993). New natural gas solubility equipment enabled measurements at high temperature (up to 150°C) and high pressure (up to 60 MPa). The methane solubility in NaHCO₃ solution was determined by modified PT function fitting to electrolyte systems. As a result there is a good uniformity between the calculated and experiment results when pressure is lower than 40 MPa and there is a bigger deviation at higher temperature (Gao et al, 1996). Based on analysis of the dissolution mechanism

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of natural gas in salt solution, a solubility equation whose temperature scope between 0 and 150°C and pressure between 0 and 60 MPa was established (Fu et al, 1996). There were also some experiments to study the characteristics of the solubility of non-hydrocarbons such as carbon dioxide (Diamond and Akinfiev, 2003; Spycher et al, 2003; Chapoy et al, 2004; Portier and Rochelle, 2005; Ji et al, 2007). On the study of the solubility of natural gas components, some scholars have discussed the difference of composition and carbon isotopes of nonassociated gas from the gas dissolving in the water of the gas field (Zorking, 1984). Some other scholars analyzed the influence of the dissolution in water on components of natural gas through analogous experiments (Fu et al, 1997; Liu et al, 2004; Lu et al, 1991; Chen and Li, 1994; Shi et al, 2005). The temperature and the pressure covered in past experiments were generally very low, pressure was mostly below 50 MPa and the temperature was mainly below 140°C. Gas reservoirs are being discovered at increasingly greater depths with higher temperatures and pressures. In order to understand the dissolution and exsolution characteristics of the components of natural gas in formation water under deep geologic conditions with high temperature and pressure, experiments on the dissolution and exsolution of natural gas have been done, and the exsolution characteristics of different components of natural gas after dissolving in formation water have been analyzed, which will be helpful for the deep exploration of natural gas.

2 Experimental conditions and steps

Natural gas sample used in this experiment is the gas from the Penglaizhen group of the Jurassic system in well Mapeng 3 in the west of the Sichuan Basin, China. The

volume content of natural methane is 95.19% and the heavier hydrocarbon contents are low and the amount of nitrogen is small (0.64%). In the heavier hydrocarbons, the ethane concentration is 1.86%, propane 0.90%, isobutane 0.20%, *n*-butane 0.10%, isopentane 0.09% and *n*-pentane 0.07%. So the gas is classified as dry gas.

The pressures used in this experiment were 20, 40, 60, 80, 100 and 120 MPa and the corresponding temperatures were 90, 120, 150, 175 and 200°C. In this experiment we measured the relative content of different components of natural gas in formation water at different temperature and pressure conditions. The formation water used is of the NaHCO₃ type and its salinity is 34,567 mg/L.

The equipment used in this experiment (Fig. 1) includes vacuum pump, condenser, formation water chamber, gas sample, booster pump, dissolution chamber, water-measuring cylinder, gas-metering device, gas chromatograph, constant-pressure pump and thermostat. Among them, the vacuum pump is used to pump out of the air in the system before the dissolving experiment to ensure avoiding the influence of air on the analyzed natural gas samples. The constant pressure pump is used to maintain constant pressure within the system. The gas chromatograph is used to analyze the relative content of natural gas components. The booster bump is used to add formation water or gas into dissolution chamber. The volume of dissolution chamber is 1,500 mL, and the allowed working pressure is up to 150 MPa, the allowed working temperature is up to 250 °C. The maximum working pressure of the constant speed and pressure pump is 150 MPa with a controlled accuracy of 0.1 MPa. The gas chromatograph is an HP-6890 (Agilent Technologies, USA) and its working temperature range is from 0 to 399°C with the highest sensitivity of 1×10^{-12} A/mV.

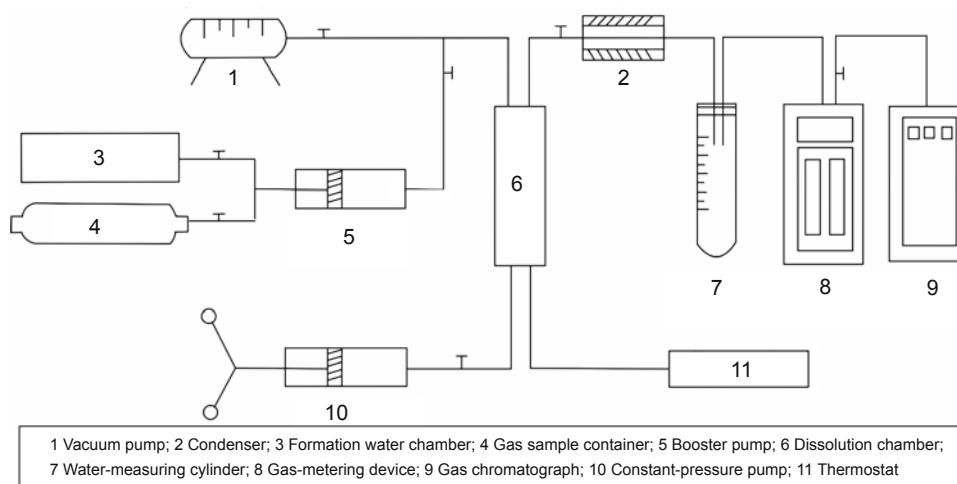


Fig. 1 Working principle diagram of the natural gas solution and exsolution experiments

Experimental process is as follows:

1) Sample introduction: First, the air in the system was pumped out by the vacuum pump; then formation water was injected into the dissolution chamber by the booster bump; next, gas was introduced into the dissolution chamber. Some gas was dissolved in the formation water.

2) Increasing pressure and temperature: The temperature is increased to the desired temperature by the thermostat and

then it maintains constant temperature. The gas pressure in the dissolution chamber is set to the desired pressure by the booster bump.

3) Solution and balance: The gas sample and formation water reached dissolution equilibrium by interaction in the designed temperature and pressure conditions. Tests showed that 6 hours was enough to achieve equilibrium.

4) Sampling: After equilibrium, the gas exit valve was

opened and about 10 mL of formation water with dissolved gas was released. The volume of formation water and dissolved gas were measured under atmospheric conditions and the solubility (the ratio of gas to water) was calculated. Last, the composition of the gas at different temperatures and pressures was analyzed by gas chromatograph.

In order to ensure the accuracy and precision of experimental results, parallel solubility experiments of the same long time have been done respectively at 20 MPa and 90°C and 60 MPa and 150°C. It is found that at the same temperature and pressure, the highest error of solubility data in different time is less than 5.2%, which shows that instrument accuracy and the experiment results are reliable.

3 Discussion

Compared with the original natural gas sample, at the conditions of different temperatures and pressures, the relative content of methane with the lowest molecular weight has completely increased in the exsolved gas. The relative content of methane of the original samples is 95.19%. The content of methane in the gas exsolving from water is commonly above 96.9% (Fig. 2) and the highest content has increased by 2.81%. When the pressure is increasing, the content of methane is increasing at the same temperature. When the temperature is increasing, the methane is also increasing at the same pressure. But when the temperature reaches 120°C and above, the increasing extent will reduce significantly at the same pressure. Fig. 2 shows that the content of methane increases rapidly from 90°C to 120°C, but after that the rate of increase slows down.

Compared with the content of methane, the relative contents of heavier hydrocarbons in the exsolved natural gas have reduced (Fig. 3). As the temperature rises, the content of heavier hydrocarbons reduces at first and then increases slightly at the same pressure. When the pressure

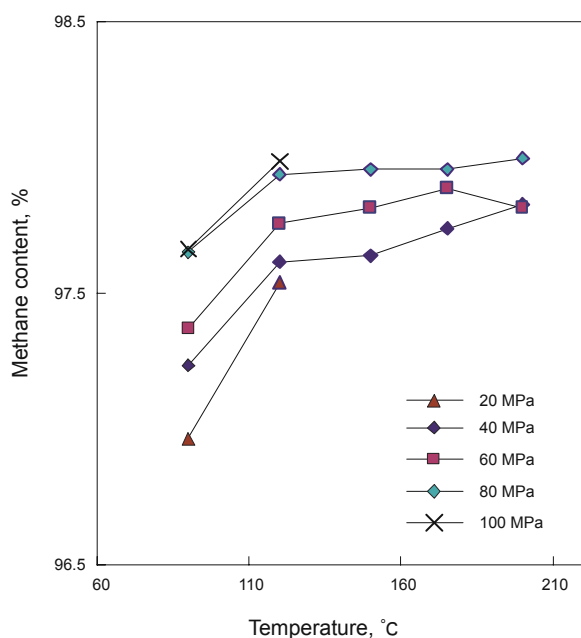


Fig. 2 Relationship of the exsolved gas methane content to temperature and pressure

ranges from 20 MPa to 60 MPa, the decreasing extent of heavier hydrocarbons is very large from 90°C to 120°C. When the pressure ranges from 80 MPa to 100 MPa and the temperature is 90°C, the content of the heavier hydrocarbons reduces obviously. Then the temperature rises continuously, the decreasing extent of the content of heavier hydrocarbons decreases. When the pressure is 80 MPa and the temperature passes 175°C, it rises slightly (Fig. 3).

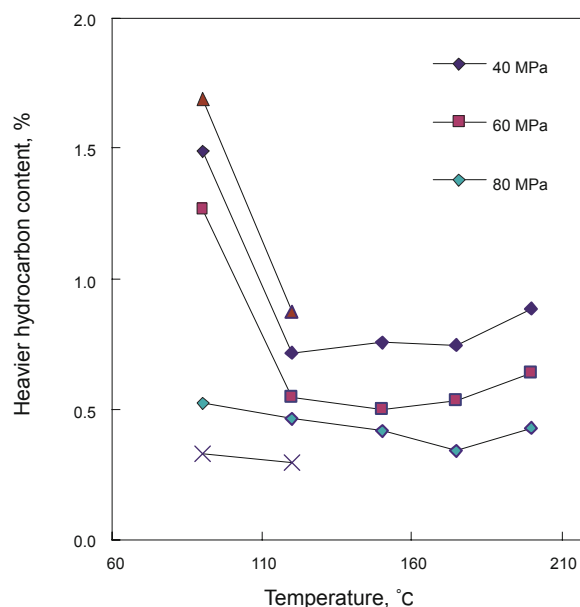


Fig. 3 Relationship of the exsolved gas heavier hydrocarbons content to temperature and pressure

When the temperature is the same and the pressure is different, compared with the content of original gas sample, the decreasing extent of heavier hydrocarbon content increases with the rise of carbon number of heavier hydrocarbons exsolving from water. The more the pressure rises, the more the content of heavier hydrocarbon reduces. The difference between the exsolved gas and the original gas sample is becoming bigger and bigger, but when the temperature keeps raising, the difference in the content of heavier hydrocarbons decreases (Fig. 4 and Fig. 5).

Fig. 5 shows the relationship of the relative content ratio of the exsolved natural gas components to the original gas at different temperatures and pressures. It is found that the relative content ratio of the exsolved gas components to the original gas rises with the rise of pressure at different temperatures (Fig. 5). In fact it shows that the content of methane increases with the rise of pressure. When the temperature rises, the content of methane will increase too at the same pressure. But after the temperature exceeds 120°C, the increasing extent will slow down (Fig. 5). At different temperatures, with the rise of pressure, the contents of heavier hydrocarbon components in the exsolved gas all show a decreasing trend which becomes more and more obvious with the carbon number of hydrocarbons increasing. In heavier hydrocarbons, ethane has the highest content and its change characteristic is the most obvious. When the pressure is below 80 MPa and the temperature is 90°C, the content of

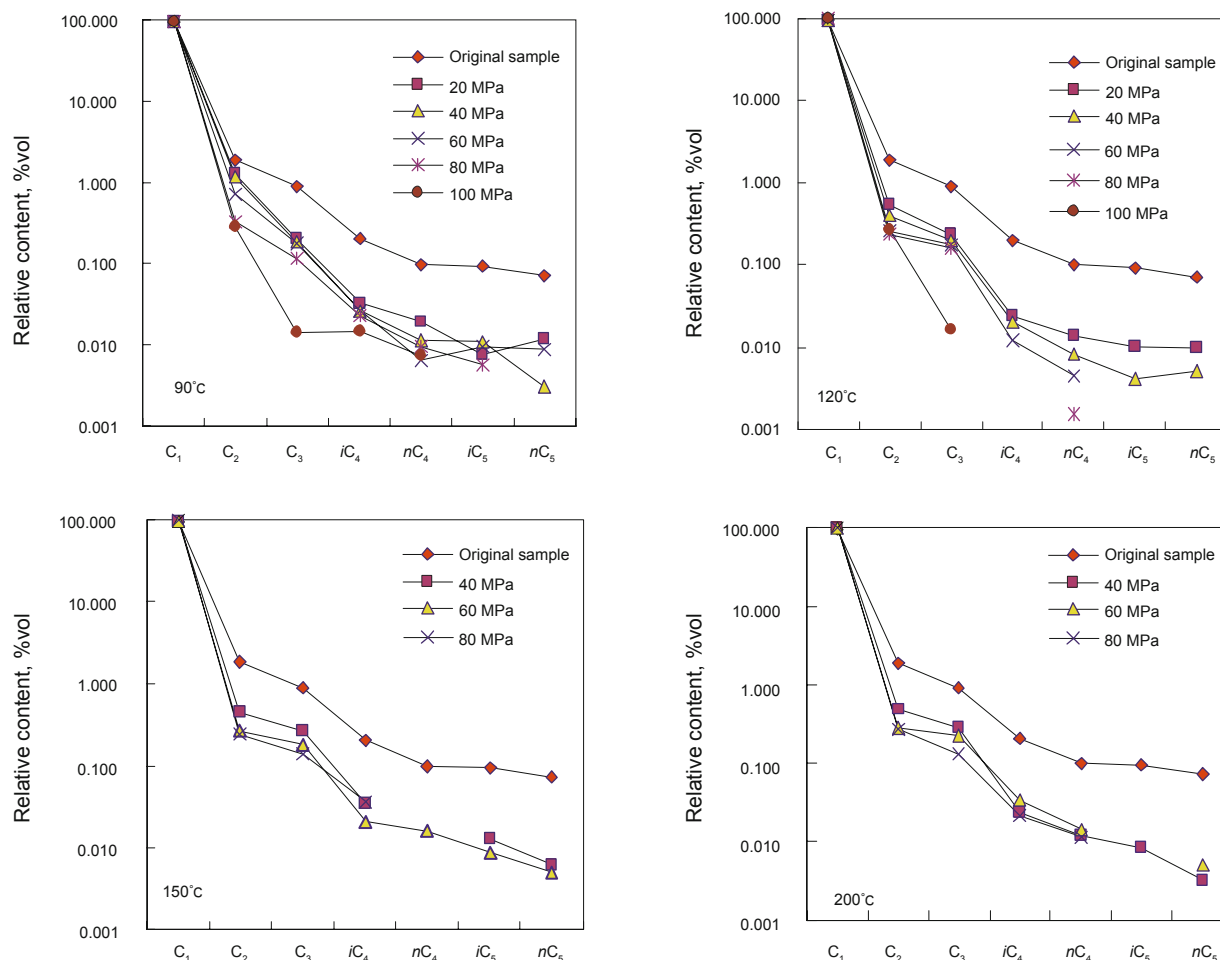


Fig. 4 Comparison of the composition of exsolved natural gas to that of the original natural gas sample at different temperatures and pressures

ethane is obviously higher than that at other high temperature points, but the content of ethane is close at each high point and will decrease with the increase of pressure. Eventually the content of ethane in the exsolved gas generally tends to a fixed value around 14.9% of its level in the original natural gas at different temperatures, the variation of propane and other heavier hydrocarbons at different temperatures cannot be reliably estimated due to their low content. But at the same temperature, the decrease trend of the component content of the exsolved gas is very obvious with increasing pressure.

The relative content of different hydrocarbon isomers will also change at different temperatures and pressures (Fig. 6). Among them, *n*-butane (nC_4) vs. iso-butane (iC_4), *n*-pentane (nC_5) vs. isopentane (iC_5) are two important heavier hydrocarbon isomers. Compared with the original gas samples, the ratio iC_4/nC_4 is higher at pressures from 40 MPa to 80 MPa, and its highest value corresponds to a pressure of 60 MPa, whose corresponding temperature is mainly 90°C and 120°C. At a pressure of 60 MPa and a temperature of 200°C, the value of iC_4/nC_4 is also higher than that in the original gas sample. The corresponding pressure of the highest value of iC_5/nC_5 has reduced a little mainly at the pressure of 40 MPa. The value of iC_5/nC_5 is the highest at the pressure of 40 MPa and the temperature of 90°C (Fig. 6). The appearance of the pressure difference of the highest value

may have a particular relation with the molecular weight. Overall it is found that the change of the ratios of different hydrocarbon isomers has a close relationship with pressure and temperature.

From the above experiment, it is found that after natural gas experiences the process of dissolving in water and exsolving from water, the content of methane and nitrogen will increase and that of heavier hydrocarbons will decrease generally. Besides, the increase extent of nitrogen is bigger than that of methane. In a gas-containing basin, natural gas formed in source rocks will first get into the unblocked transport layer or the reservoir. Because the medium which the natural gas first contacts with is the formation water, at specific temperature and pressure, some natural gas inevitably dissolves in the formation water. When formation water which has dissolved natural gas moves, dissolved natural gas will migrate in the formation water. When migrating, some of the dissolved natural gas will exsolve from the formation water due to changes of temperature and pressure. The temperature and pressure in different depths are different, so the relative content of exsolved natural gas components is also different. Compared with the original natural gas, the contents of the natural gas components in a gas reservoir which has experienced the migration process have changed. The result is that the content of nitrogen and methane has increased

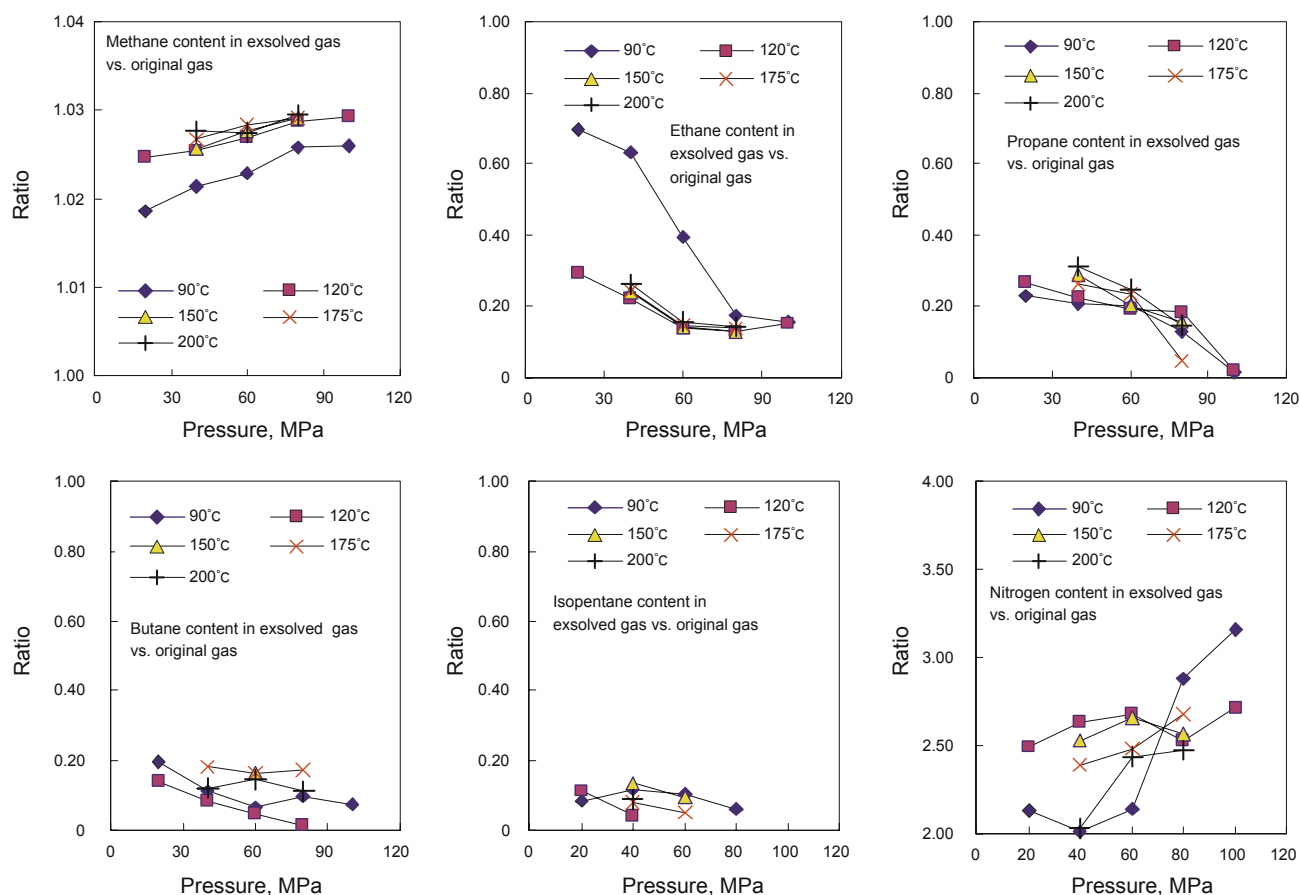


Fig. 5 Relationship of the ratio of different components content in natural gas to that of the original gas at different temperatures

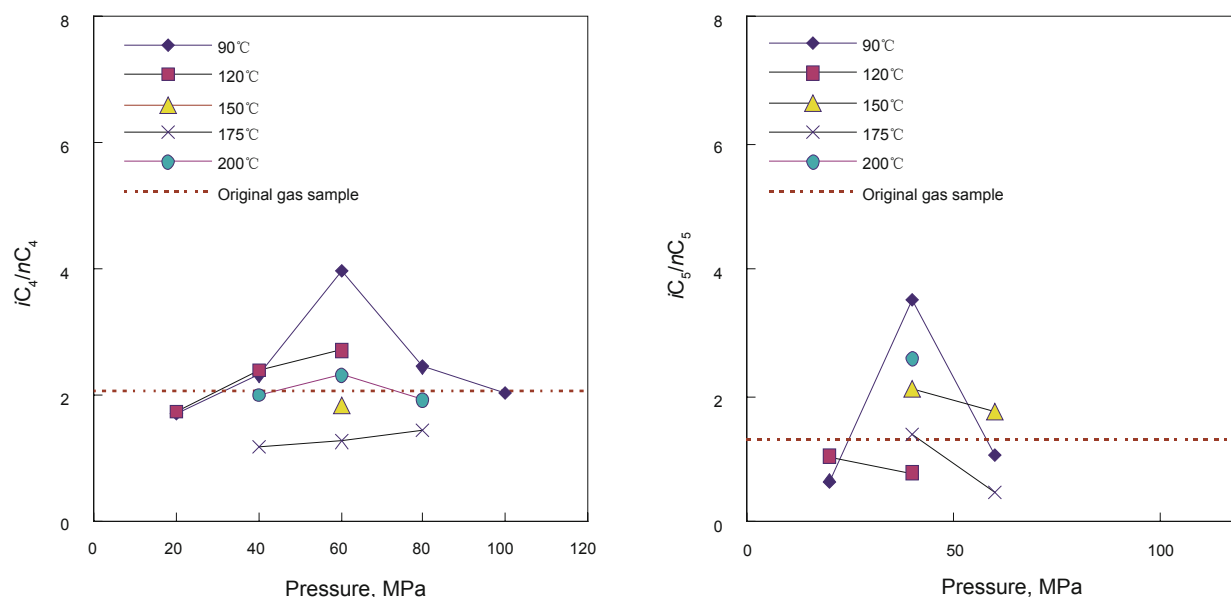


Fig. 6 Relationship of the content of different hydrocarbon isomers in exsolved gas to pressure at different temperatures

and the content of heavier hydrocarbons has decreased. In some oil and gas-containing basins, the gas source rocks are very deep. With the depth reducing, the trend of methane and nitrogen contents increasing and the decrease of heavier hydrocarbons content are due to gas dissolving in water and then later exsolving. It is clear that the effect of water solution should be taken into consideration when research of source correlation and migration direction is undertaken.

4 Conclusions

The solution of natural gas in formation water is universal in oil and gas-containing basins. When the temperature and pressure conditions change, the supersaturated part of natural gas which has dissolved in formation water will exsolve from formation water and form gaseous natural gas, thus gaseous natural gas will migrate and accumulate. Compared with

the gas before solution, the relative content of methane and nitrogen increases in the exsolution gas, the relative content of heavier hydrocarbons decreases and the relative contents of different hydrocarbon isomers also vary. The solution and differentiation of natural gas in formation water should be considered when natural gas composition changes, gas-source correlation and natural gas migration are analyzed in gas-bearing basins.

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