Solubility Measurement of Natural Gas in Reservoir Formation Water under (333.2 to 393.2) K and (15.0 to 43.6) MPa

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ABSTRACT: The solubility of five groups of natural gas in reservoir formation water was measured under (333.2 to 393.2) K and (15.0 to 43.6) MPa. The formation water and corresponding natural gas were sampled in situ from a China oilfield. The range of total dissolved solids (TDS) of the reservoir formation water samples is from (8744 to 80634) mg·kg^{-1}. The mole fraction of methane in natural gas ranges from 0.7575 to 0.9449. The experimental results show that, with the increase of temperature and pressure, the solubility of natural gas in formation water goes through a minimum value under the experimental conditions. The solubility of natural gas in formation water was also influenced by a composition of gas phase and TDS of liquid phase. The salt effect becomes more significant in the high-pressure region.

INTRODUCTION

In petroleum reservoirs, formation water always coexists with natural gas, and they are doubtless transported subterraneously from high to low pressure regions.[1-6] The solubility of natural gas in formation water cannot be neglected under the special conditions of high pressure and temperature. Its value may decide the natural gas reserves and operating conditions.[7,8]

Typical examples of one or several components of gas dissolving in water include: pure hydrocarbon in water or brines,[1,3,9-18] nitrogen or carbon dioxide in water or brines,[1,19-23] and gas mixture in water or brines.[24-28] However, the solubility data of natural gas in formation water are limited due to the difficulty of sampling formation water and the corresponding natural gas in situ. Many factors affect the solubility of natural gas in formation water, such as temperature, pressure, composition of natural gas, and total dissolved solids (TDS), that is, the total amount of mineral salts dissolved in 1 kg formation water. Some theoretical models were developed[29-41] to calculate the solubility of gas in electrolyte solution, but few of them can satisfy for calculating solubility of natural gas in formation water due to the deficiency of the corresponding experimental data for stratum fluids under high temperature and high pressure conditions.[14,16,24,30,42,43] The water content in the gas phase under high temperature cannot be neglected during the development of solubility model.[1,4,16,44]

In this work, five groups of formation water samples and the corresponding natural gas were collected in situ from five oil wells in China oilfield using a bottom hole sampler. A RUSKA high-pressure equipment was used to measure the solubility data of natural gas in formation water. The solubility measurement was performed at a temperature range of (333.2 to 393.2) K and a pressure range of (15.0 to 43.6) MPa.

EXPERIMENTAL SECTION

Apparatus. A RUSKA PVT unit made in USA was used to measure the solubility of natural gas in formation water in this work. The schematic diagram of the experimental apparatus was
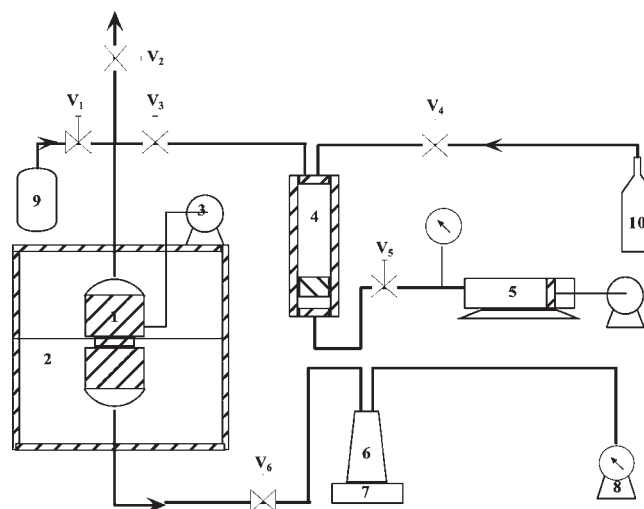

Figure 1. Schematic flow diagram of the apparatus for measuring gas solubility. 1, equilibrium cell; 2, oil bath; 3, mechanical rocking device; 4, buffer tank; 5, motor-driven pump; 6, flash vessel; 7, analytical balance; 8, gas meter; 9, formation water bottle; 10, natural gas cylinder.

shown in Figure 1. The main part of the unit is an equilibrium cell of 600 cm^3 which is immersed in a silicone oil bath and can be rocked by a mechanical device to quicken the equilibrium process during the solubility experiment. It was made of stainless steel, and the maximum working temperature and pressure are 423.2 K and 68.0 MPa, respectively. A buffer tank and a RUSKA motor-driven pump with an accuracy of 0.002 mL are used to maintain the pressure in the equilibrium cell during the gas dissolving and liquid sampling process. The volume of the buffer tank is 1500

Table 1. Property of Formation Water for Five Groups of Oil Well Samples

| | formation water | | | | | | | | | | |
| | ρ^a | TDS^b | | | amount of ions of formation water/mg·kg^{-1} | | | | | | |
oil well no.	g·cm^{-3}	mg·kg^{-1}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	others
1	1.041	60163	131.8	36167.4	6050.1	78.3	43.0	10.8	17188.4	454.9	38.3
2	1.004	8744	268.5	3870.9	1476.2	279.2	63.4	34.0	2368.1	320.1	63.5
3	1.020	31915	189.5	19198.2	2855.1	165.2	66.3	23.3	8657.0	660.2	100.2
4	1.056	80634	88.2	39656.1	15348.9	62.5	72.2	8.8	23635.1	1671.6	90.7
5	1.033	50267	104.9	28889.0	6107.3	79.9	71.1	10.7	13917.3	1029.7	57.1

^{a} ρ is the density of formation water, measured by a density bottle at 293 K and atmospheric pressure, and its error is lower than 0.01 %. ^{b} TDS is the total dissolved solids of formation water, measured using the gravimetric method (SL 79-1994). The accuracy of TDS was 1 mg·kg^{-1}.

Table 2. Composition of Natural Gas for Five Oil Well Samples

| | mole fraction of natural gas components | | | | | | | |
oil well no.	CH_4	C_2H_6	C_3H_8	C4	C5	C6+	CO_2	N_2
1	0.8227	0.0966	0.0318	0.0118	0.0323		0.0048	
2	0.8586	0.0771	0.0247	0.0098	0.0027		0.0118	0.0153
3	0.7575	0.1150	0.0859	0.0295	0.0038		0.0083	
4	0.9449	0.0249	0.0020	0.0025	0.0012		0.0025	0.0220
5	0.8349	0.0522	0.0095	0.0118	0.0071	0.0122	0.0063	0.0660

cm^3, and the maximum working temperature and pressure are 423.2 K and 83.0 MPa, respectively. The formation water sample after being flashed is weighed by an analytical balance with an accuracy of 0.1 mg. The volume of natural gas flashed is measured by a RUSKA gas meter with an accuracy of 1 cm^3. All of the temperature controllers were calibrated with a 25 Ω reference platinum thermometer (TINSLEY precision instrument). The pressure gauges were calibrated at different temperatures using a pressure balance (model 21000, Desgranges & Huot). The accuracy of temperature and pressure was 0.1 K and 0.01 MPa, respectively.

Samples. The formation water and the corresponding natural gas were sampled in situ simultaneously using a bottom hole sampler from five oil wells in a China oilfield. On the ground, the formation water was sealed in a bottle under atmosphere pressure while the corresponding natural gas was sealed in a high-pressure gas cylinder, both of which were stored at room temperature and kept in a dark place. The ion concentrations were analyzed by high-performance ion-exchange chromatography (HPIC) with two ion-exchange columnd (NJ-3A-4A, 250 mm × 4.6 mm; Grace609121268, 100 mm × 4.6 mm) and a suppressed conductivity detection. The minimum detection limit of the HPIC was 0.05 mg·kg^{1-}. The composition of gas mixtures was analyzed by a HP 6890 gas chromatograph equipped with a thermal conductive detector (TCD) and three analytical columns (Porapak Q, molecular sieve, and sebaconitrile). The gas chromatograph was calibrated by injecting standard gases in advance, and its minimum detection limit was 200 ppmv. A high-pressure gas sampler (50 cm^3, 65 MPa, 423.2 K) equipped with a reducing valve was used to transport natural gas into the gas chromatograph. For each gas sample, it was measured at least three times, and the average value was used as the composition of natural gas. TDS, amount of ions of formation water, and the composition of natural gas for five samples of different oil wells are shown in Tables 1 and 2, respectively. The density (ρ) of the

formation water measured at 293.2 K and atmospheric pressure is also listed in Table 1.

Experimental Procedure. First, the whole system was evacuated, and about 50 cm^3 of formation water was injected into the equilibrium cell. The corresponding natural gas was introduced to the equilibrium cell until the system pressure attained a specified value using the motor-driven pump. During the injection of natural gas, the gas cylinder was heated to ensure that no condensate exists. Then the temperature of oil bath was set to the specified value. When the temperature was stable, the rock of the equilibrium cell was started by the mechanical rocking device. During the process of gas dissolving into water, the system pressure was maintained constant by the buffer tank and the motor-driven pump, while the temperature of the buffer tank was kept at the same with that of the oil bath. At least 24 h was needed to attain gas−liquid equilibria under agitation conditions. Afterward, the equilibrium cell was kept still for 3 h to ensure that the equilibrium temperature/pressure condition was stable. Then the liquid back pressure valve (V6) was opened and adjusted slightly, and about (10 to 20) cm^3 liquid was slowly charged to the flash vessel where it was flashed under atmospheric pressure and room temperature. During the sampling process, the system pressure was maintained constant using the motor-driven pump. The amount of formation water obtained after flashing was weighed by the analytical balance. The amount of flashed gas was measured by the RUSKA gas meter and then transformed to standard conditions. If neglecting the solubility of natural gas in formation water or the water content in natural gas at atmosphere temperature and pressure, the solubility of natural gas in formation water at elevated temperature and pressure was therefore calculated by the following formula.

$$x = \frac{n_g}{\sum n_i} \tag{1}$$

where n_g refers to the mole number of natural gas flashed from the sampled formation water, which is calculated from the volume of

Table 3. Methane Solubility x in 0.02 Mass Fraction of Sodium Bicarbonate Solution

T/K	this work		data reported by Gao et al.[45]		absolute relative deviation /%
	P/MPa	$x \cdot 10^4$	P/MPa	$x \cdot 10^4$	
324.2	5.66	8.02	5.35	8.29	3.37
	10.32	11.50	10.20	11.87	3.22
	20.03	19.76	20.40	20.35	2.99
	30.73	25.72	30.73	26.76	4.04
	40.60	30.02	40.60	31.42	4.66
374.2	5.05	7.96	5.20	8.13	2.14
	10.50	11.81	10.40	12.14	2.79
	20.10	19.62	20.20	19.20	2.14
	30.15	25.13	30.40	26.21	4.30
	40.60	29.60	40.50	30.77	3.95
403.2	5.42	8.22	5.40	8.57	4.26
	10.40	12.34	10.60	12.74	3.24
	20.05	19.09	20.30	19.62	2.78
	30.16	26.08	30.20	26.75	2.57
	40.52	31.43	40.30	32.27	2.67

Table 4. Natural Gas Solubility x in Formation Water for Five Oil Wells

oil well no.	T/K	P/MPa	$x \cdot 10^4$
1	333.2	15.20	15.67 (0.76)
	348.2	20.30	15.12 (0.63)
	363.2	26.00	16.83 (0.58)
	378.2	32.40	23.56 (0.54)
	393.2	43.00	27.65 (0.62)
2	333.2	15.00	22.48 (0.45)
	348.2	20.70	19.24 (0.47)
	363.2	25.70	20.85 (0.47)
	378.2	32.30	26.18 (0.66)
3	333.2	15.50	15.51 (0.49)
	348.2	19.00	14.38 (0.44)
	363.2	26.00	15.44 (0.70)
	378.2	32.30	25.10 (0.47)
	393.2	43.60	29.25 (0.56)
4	333.2	15.60	20.69 (0.55)
	348.2	20.80	18.09 (0.56)
	363.2	26.50	20.06 (0.50)
	378.2	33.00	21.40 (0.46)
	393.2	42.20	24.00 (0.50)
5	333.2	15.50	19.21 (0.59)
	348.2	19.00	17.83 (0.47)
	363.2	26.00	19.67 (0.52)
	378.2	32.30	23.89 (0.46)

flashed gas at room condition. $\sum n_i$ refers to the sum of mole number of all species in the sample formation water, including natural gas and aqueous solutions.

For guaranteeing the data quality, at least two parallel runs were conducted. The average value was adopted as the solubility of natural gas in formation water. Thereafter, the above experimental procedure was repeated for other specified temperature and pressure of the same oil well or other oil well samples.

During the gas solubility measurement, only about 50 cm³ of formation water was injected into the equilibrium cell with a volume of 600 cm³, and a buffer tank was also connected with the equilibrium cell. At the experimental pressure conditions, the gas—liquid ratio was very high. In contrast, the gas solubility in formation water was very low. Therefore, the gas composition was assumed constant during the solubility measurement. This was also confirmed by comparing the measured natural gas composition before/after the gas—liquid equilibrium.

■ RESULTS AND DISCUSSION

Validation of the Test System. For checking the reliability of the apparatus and experimental procedure used in this work, the solubility data of methane in 0.02 mass fraction of sodium bicarbonate aqueous solution were measured. Three groups of temperature (324.2 K, 374.2 K, and 403.2 K) were chosen, and the experimental pressure was between (5.05 and 40.60) MPa, which was very close to the experimental conditions of Gao et al.[45] The obtained solubility data (x) of methane in sodium bicarbonate solution are listed in Table 3, in which the gas solubility was expressed in mole fraction. The corresponding literature data reported by Gao et al.[45] are also listed in Table 3 for comparison. It could be found that the deviation between the measured solubility data in this work and the data reported by Gao et al.[45] was below 5 %.

Solubility of Natural Gas in Formation Water. The solubility data (x) of five groups of natural gas in different reservoir formation water samples collected in this work are tabulated in Table 4. TDS of the formation water samples was in a range of

(8744 to 80634) mg·kg^{1-}. The range of CH_4 mole fraction in the corresponding natural gas was from 0.7575 to 0.9449. The uncertainty of the measured solubility in Table 4 according to error analysis was marked in the parentheses after the corresponding value.

Figure 2 showed the variation of natural gas solubility data with temperature and pressure for five groups of oil well samples. For each oil well sample, the solubility was measured at the same four or five groups of temperature, but the corresponding pressure was a little different. The pressure fluctuation range for five well samples at the same temperature was also shown in Figure 2. It can be found that there exists a minimum value for the solubility of natural gas in formation water under the experimental conditions. It is known that the heat of solution includes two effects: a positive heat of cavitation and a negative heat of hydrophobic interaction between gas and water. These two effects counteract each other at the minimum temperature. The heat of cavitation becomes the dominant effect when the temperature is larger than the minimum value.[18,44,46] Therefore, the solubility of hydrocarbon or hydrocarbon mixtures in water increases with an increase in pressure but shows a minimum with an increase in temperature.[24] In the present work, when the temperature is low, the positive effect of pressure cannot compensate the negative effect of temperature, resulting in a minimum solubility value at about 348.2 K.

From Figure 2, it can be found that there exists intersection between some of the solubility lines of different well samples. For these data points of the five groups of well samples, both temperature and pressure are close. Therefore, those intersections should be attributed to the composition difference of gas phase and liquid phase. The solubility of pure gas in water is different, and the order is: $CO_2 > CH_4 > N_2 > C_2H_6 > C_3H_8 > C4 > C5 > C6$.[17,23,47] The solubility of light hydrocarbon in water is

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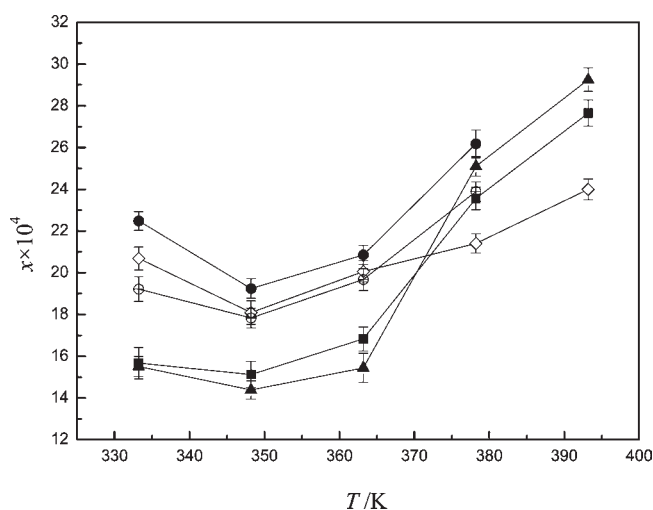dx.doi.org/10.1021/je1010246 |*J. Chem. Eng. Data* 2011, 56, 1025–1029

Figure 2. Solubility of natural gas in formation water for five oil well samples. -■-, Well 1; -●-, Well 2; -▲-, Well 3; -◇-, Well 4; ⊕, Well 5. For each group of temperature, the pressure is a little different for five oil well samples. The pressure fluctuation range for five groups of temperature is as follows: 333.2 K: (15.0 to 15.6) MPa; 348.2 K: (19.0 to 20.8) MPa; 363.2 K: (25.7 to 26.5) MPa; 378.2 K: (32.3 to 33.0) MPa; 393.2 K: (42.2 to 43.6) MPa.

low due to the hydrophobic effect which increases rapidly with the increase of size of the solute.[48] For gas mixture, the solubility of hydrocarbon−carbon dioxide mixtures in water is always lower than that of pure carbon dioxide at the same temperature and pressure.[25,28] For the case of solubility of hydrocarbon gas mixtures in water, it is in general considered that the solubility of hydrocarbon mixtures was lower than that of pure methane at the same temperature and pressure,[27,45,49] although the opposite view also existed.[24] For the influence of liquid phase, the increase of TDS suppresses the solubility of natural gas in formation water.[50,51] Particularly, the salt effect becomes more significant in high pressure regions.[1,4,45]

For Well 2 in this work, it has the lowest TDS of formation water and the highest content of carbon dioxide; therefore, the solubility of natural gas for Well 2 is always the highest among the five oil well samples for the whole experimental temperature and pressure range. For other four groups of oil well samples, when at lower pressure region (lower than about 26 MPa), the solubility of Well 4 is larger than that of Well 1, Well 3, and Well 5 due to its highest mole fraction of methane in the gas phase. However, with the increase of pressure, the influence of TDS increases. From Figure 2, it can be found that the magnitude order of solubility of five groups of oil well samples is reverse to that of TDS of formation water when the pressure is larger than 32 MPa.

CONCLUSIONS

The solubility of natural gas in reservoir formation water was measured under elevated pressures and temperatures. The experimental results show that the solubility of natural gas in formation water increases with an increase in pressure and there exists a minimum solubility value with an increase in temperature. The solubility of natural gas in formation water is related to the content of methane and carbon dioxide in gas phase. It increases with the increase of methane mole fraction in natural gas, if without regard to the influence of carbon dioxide. TDS also has a great effect on the solubility of natural gas in formation

water, and the salt effect becomes more significant in high pressure ranges.

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