COMPATIBILITIES AND INTERACTIONS

SECTION B2
SOLUBILITY OF GASES IN FORMATE BRINES

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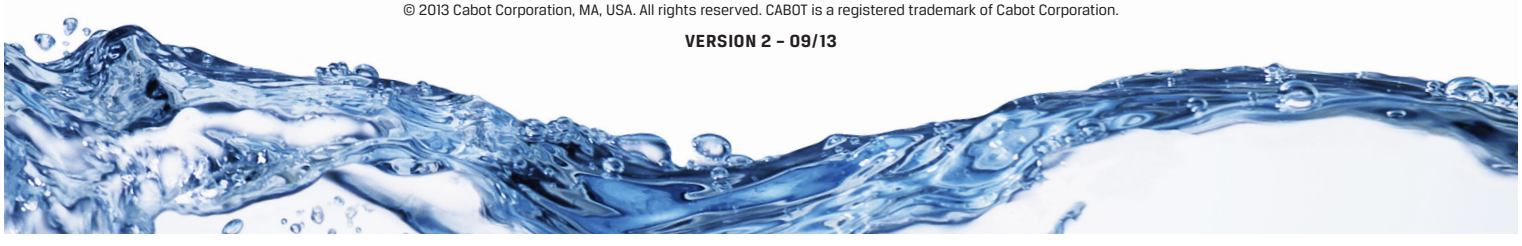
VERSION 2 – 09/13



B2.1 Introduction

Low solubility of reservoir gases in well construction fluid is important for well control purposes. Changes in volume and density as a consequence of gas influx can have severe consequences. The solubility of typical reservoir gasses in formate brines has been shown to be very low, and significantly lower than in water.

Henry's Law states that the solubility of gases in a liquid is proportional to the partial pressure of that gas in contact with the liquid.

B2.2 Solubility of methane, CH_4

The solubility of methane gas is known from literature to be much lower in water than in oil-based fluids and even lower in brines than in water.

A 2.09 g/cm^3 / 17.43 lb/gal cesium / potassium formate brine (buffered, standard blend) has been tested for methane solubility by Westport Technology Center International [1].

The tests were carried out with a visual phase behavior cell rated to 103 MPa / 15,000 psia and 177°C / 350°F. Water was used as pressurizing fluid, separated by a piston. This allowed the cell to be completely inverted, which caused considerable mixing between the gas and liquid phases. This is necessary to achieve equilibrium in these low-solubility systems. The system has a small sample volume, which makes the procedure more cumbersome and time consuming for low-solubility systems. The experimental procedure called for loading the cell with 50 mL of formate brine and charging an additional 10 mL of methane gas at high pressure. The cell was then taken to temperature and the contents pressurized by water injection. The cell contents were vigorously mixed by inverting the cell. This procedure was repeated until the pressure remained constant, indicating that solubility equilibrium had been achieved. At constant pressure, excess gas was bled out of the system, and a known volume of the liquid phase collected in a metal pycnometer. A single-stage flash of the liquid sample into a small volume glass ball using routine procedures gave the reported GOR. Methane gas solubility was similar, yet slightly lower, than in sodium chloride brine. Methane solubilities in water, *NaCl* (20%) and 2.09 g/cm^3 / 17.43 lb/gal cesium formate brine are shown in Figure 1.

The effect of pressure and temperature on solubility of methane in formate brines is shown in Figure 2 and Figure 3. As can be seen, solubility increases with higher pressure and temperature. An increase with temperature is very unusual. In most solvents, methane solubility is known to decrease with temperature.

The effect of solubilized methane on fluid density is important for well control. Density decreases as solubility of methane gas increases. This is important for tracking change in the fluid's hydrostatic while drilling. Figure 4 shows how dissolved methane influences brine density. As can be seen, the effect of dissolved methane on fluid density is less than 1% for most of the pressure and temperature range.

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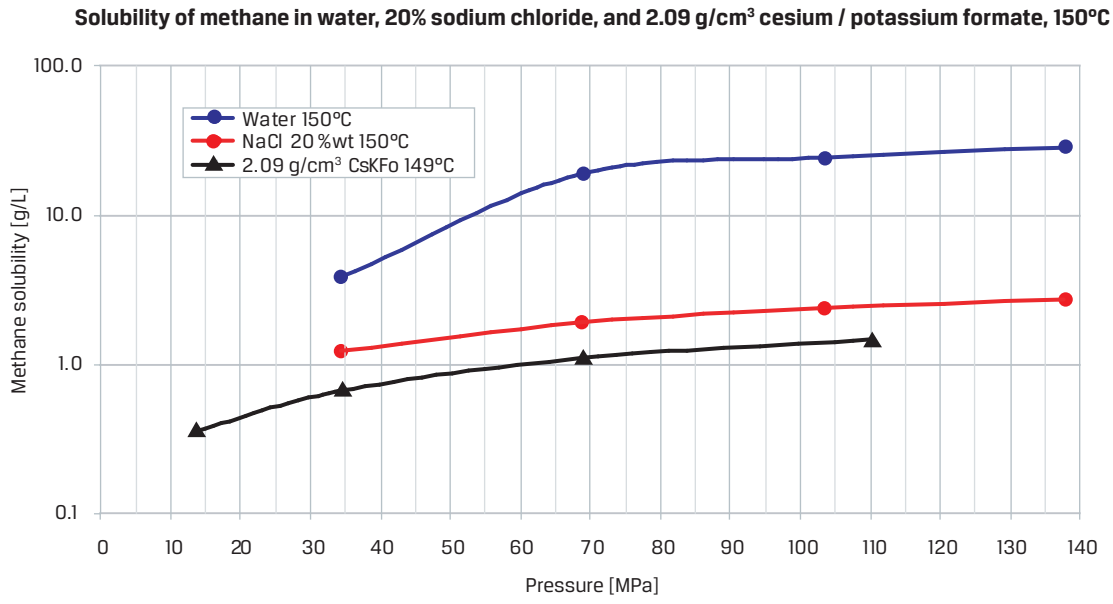

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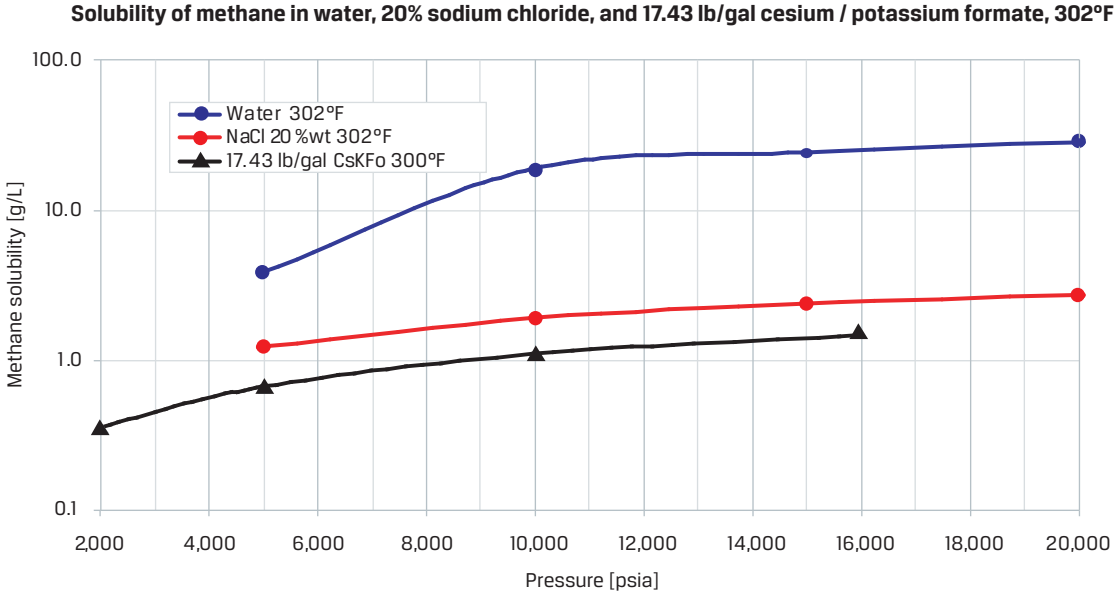

Figure 1 Solubility of methane in water, *NaCl* (20%), and buffered cesium / potassium formate brine (2.09 g/cm³ / 17.43 lb/gal).

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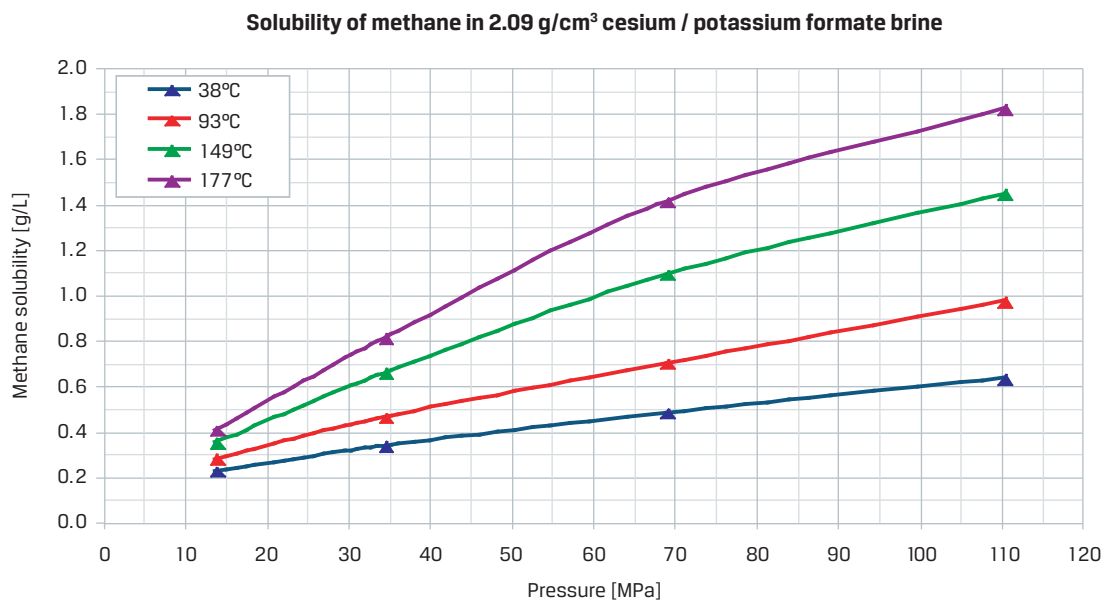

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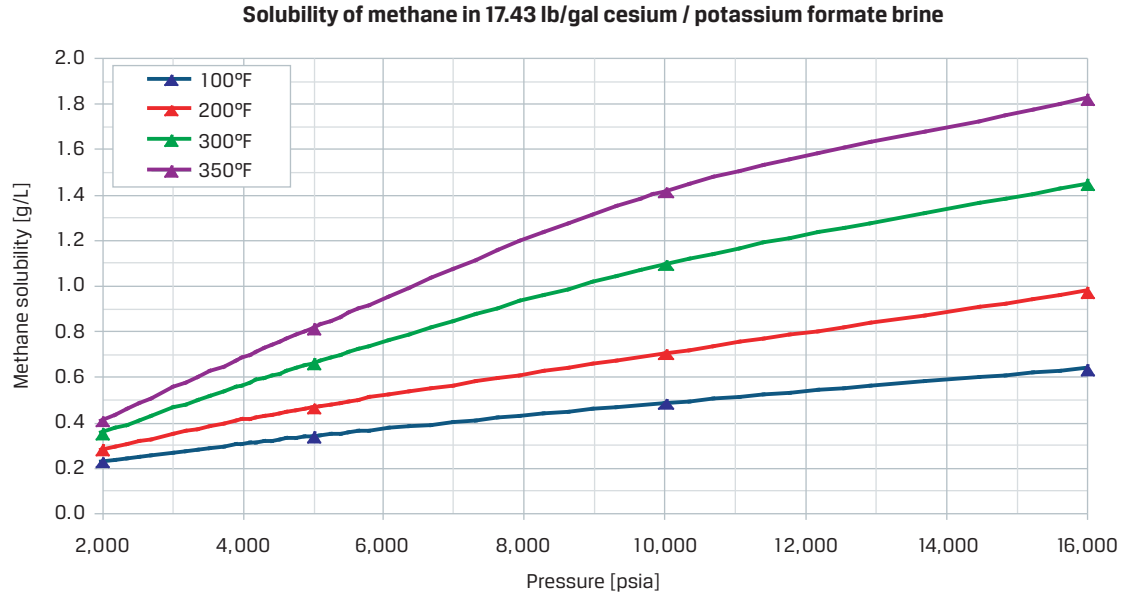

Figure 2 Effect of pressure on solubility of methane in buffered 2.09 g/cm³ / 17.43 lb/gal cesium / potassium formate brine.

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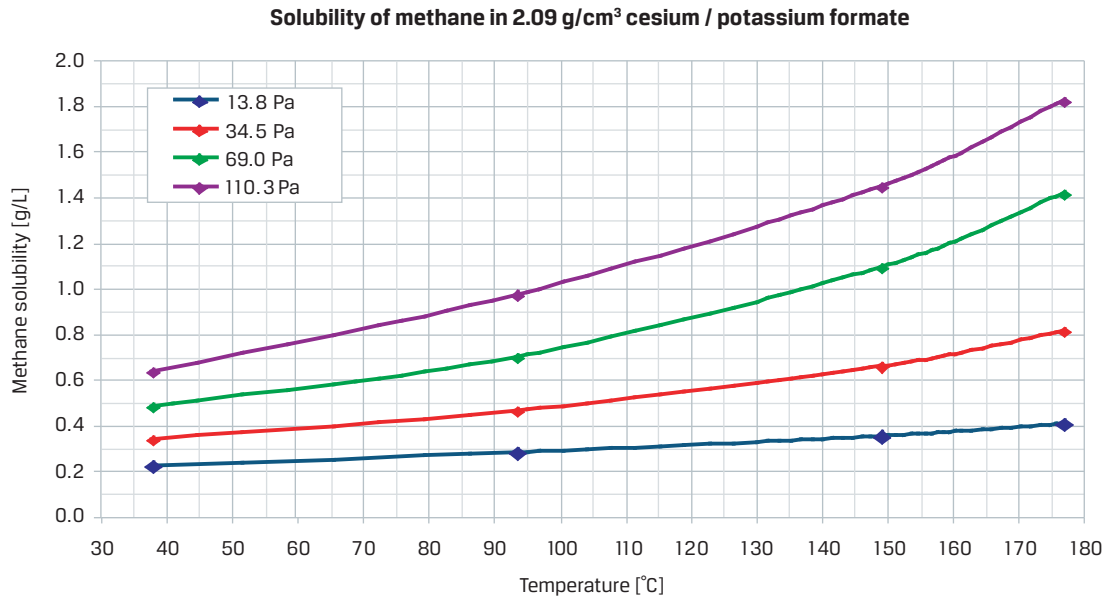

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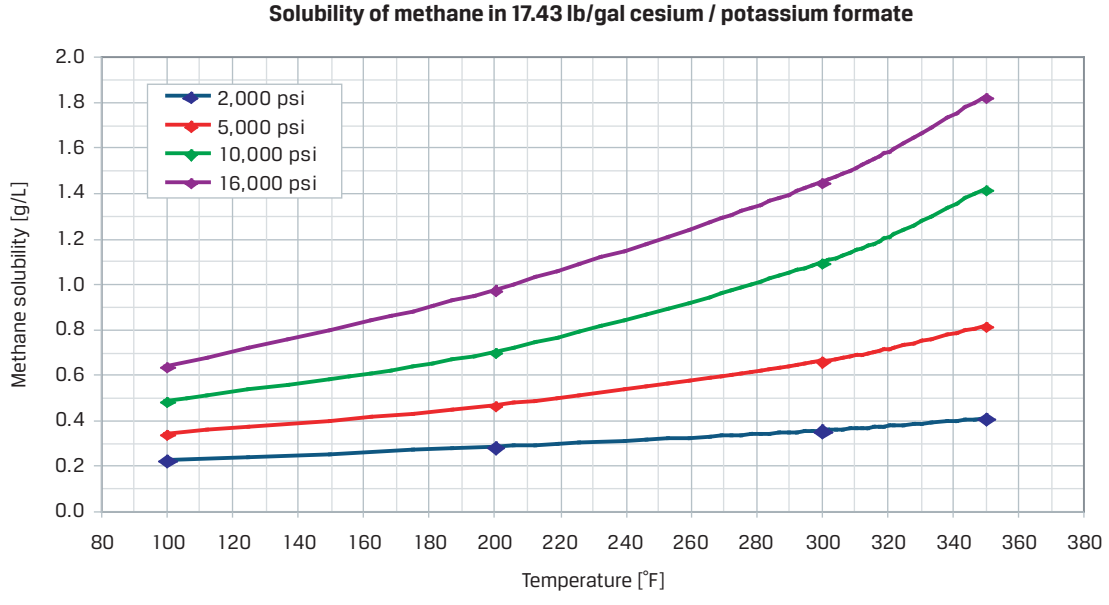

Figure 3 Effect of temperature on solubility of methane in buffered 2.09 g/cm³ / 17.43 lb/gal cesium / potassium formate brine.

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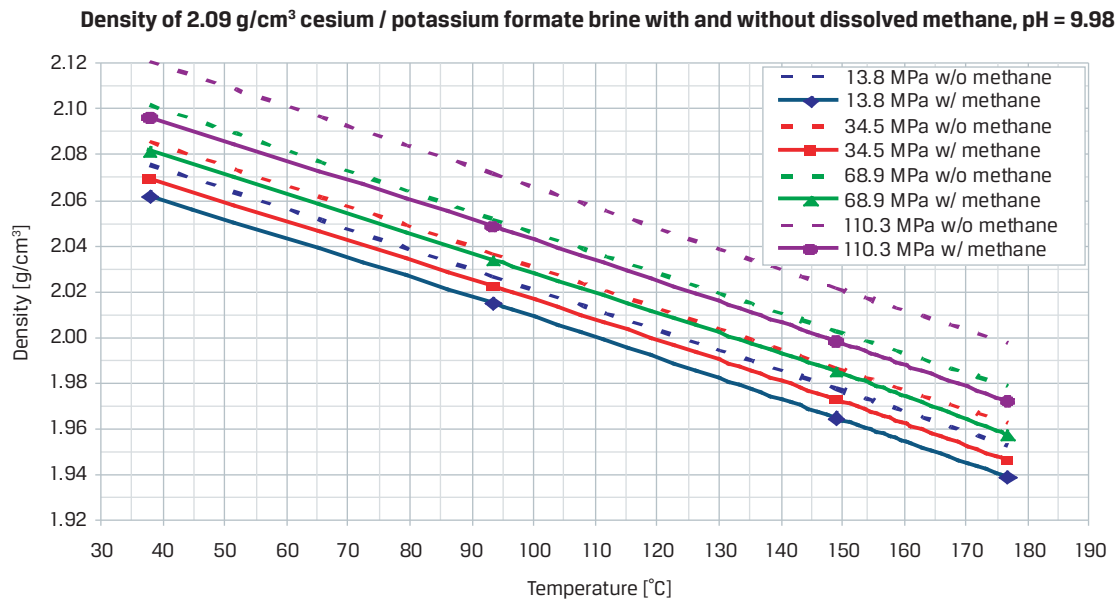

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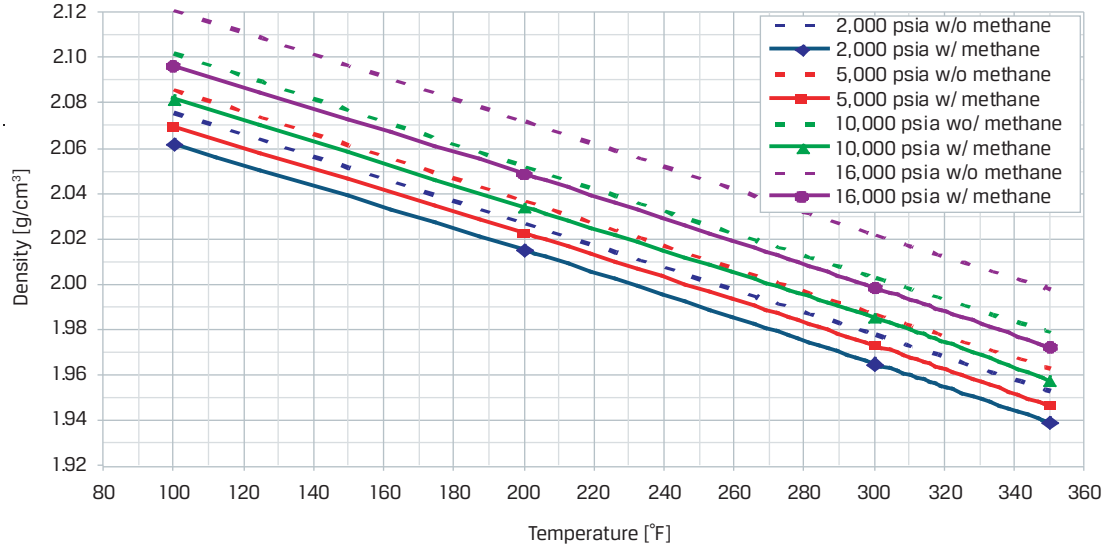

Figure 4 Effect of pressure and solubilized methane on density of buffered 2.09 g/cm³ / 17.43 lb/gal cesium / potassium formate brine.

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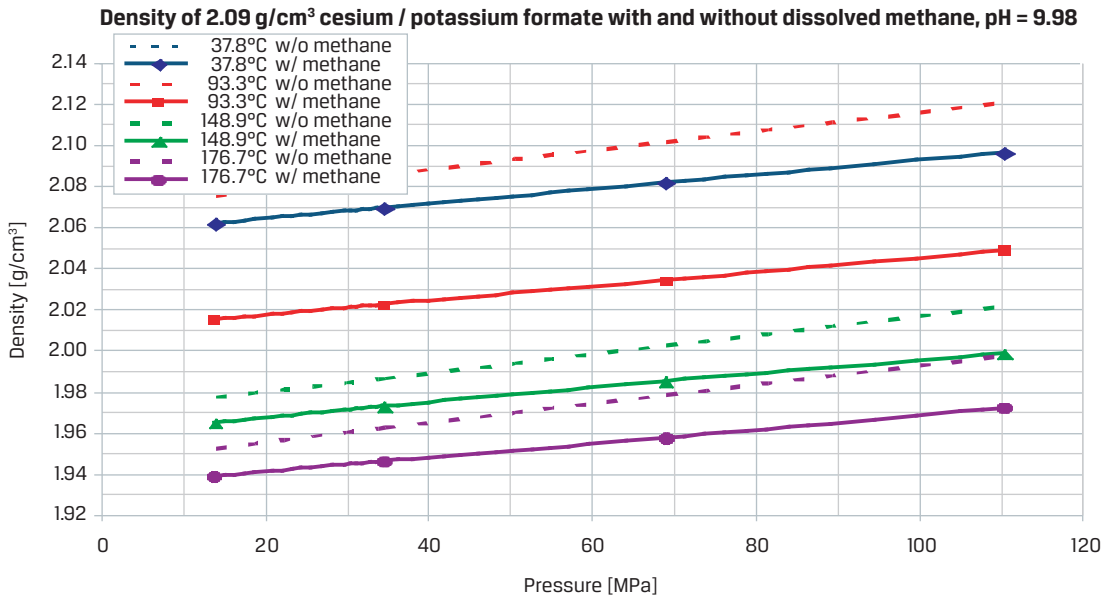

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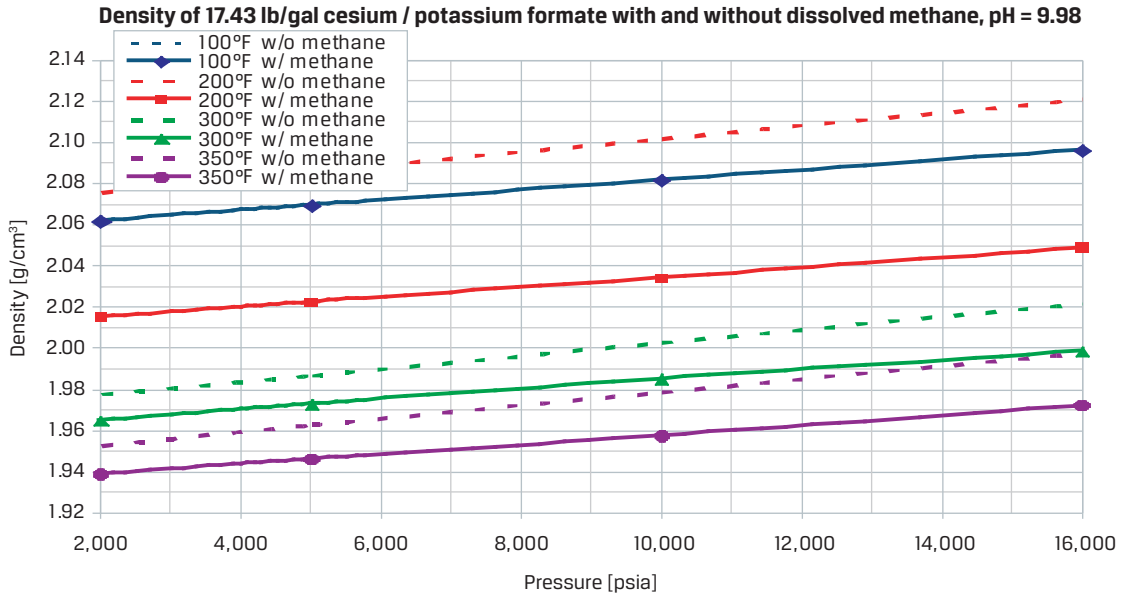

Figure 5 Effect of temperature and solubilized methane on density of buffered 2.09 g/cm³ / 17.43 lb/gal cesium / potassium formate brine.

B2.3 Solubility of carbon dioxide, CO_2

The solubility of carbon dioxide in formate brines is also a function of temperature, pressure, and salinity. Solubility of CO_2 in fresh water is known to increase with increasing pressure and decreasing temperature.

When carbon dioxide is dissolved in water-based fluid, the following reaction takes place:

$$CO_2\,(g) \longleftrightarrow CO_2\,(aq) \quad (1)$$

Aqueous CO_2 then reacts with water to form carbonic acid (H_2CO_3):

$$CO_2\,(aq) + H_2O \longleftrightarrow H_2CO_3\,(aq) \quad (2)$$

Carbonic acid dissociates in water to form carbonate and bicarbonate ions depending on pH:

$$H_2CO_3\,(aq) \longleftrightarrow H^+\,(aq) + HCO_3^-\,(aq) \quad (3)$$

$$HCO_3^-\,(aq) \longleftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \quad (4)$$

In formate brine, solubility of CO_2 is complicated by the carbonate / bicarbonate buffer. As long as there is carbonate (CO_3^{2-}) present in the brine, carbonic acid formed reacts with carbonate to form bicarbonate, according to the following equation:

$$H_2CO_3\,(aq) + CO_3^{2-}\,(aq) \rightarrow 2HCO_3^-\,(aq) \quad (5)$$

First, when the entire concentration of carbonate is consumed, does carbon dioxide gas start to dissolve according to equations 3 and 4 above.

The solubility of carbon dioxide (CO_2) in concentrated cesium formate brine has been measured by Westport Technology Center International [2]. Testing was carried out at two temperatures (148.9°C / 300°F and 176.7°C / 350°F) in the pressure range 0.83 – 38 MPa / 120 – 5,415 psia.

In order not to confuse absorption of CO_2 by the carbonate buffer with solubility, brines with only the bicarbonate portion of the added buffer were tested. Bicarbonate buffers brine at pH 6.35, but does not interfere with CO_2 dissolution reactions (equations 3 and 4).

A 2.156 g/cm^3 / 21.3 lb/gal cesium formate brine with pH of 7.98 (undiluted) was tested at various temperatures and pressures.

The tests were carried out according to the following experimental procedure: A known weight of cesium formate brine was charged in a high-pressure and high-temperature cylinder. A known amount [moles] of carbon dioxide was then added to the cylinder. The mixture of cesium formate and CO_2 was equilibrated at target temperature and high pressure. A constant composition expansion (CCE) was then conducted on the equilibrated solution of cesium formate and CO_2. From the CCE test, the bubble point of the equilibrated mixture was measured. At the experimental temperature and bubble point of the mixture, solubility of CO_2 in cesium formate brine was defined.

Table 1 and Figure 6 show the measured solubility of CO_2 in the concentrated cesium formate brine as a function of temperature and pressure.

Table 1 CO_2 solubility in a concentrated cesium formate brine.

Solution	Temperature		Pressure		CO_2 solubility x 10^5
	[°C]	[°F]	[MPa]	[psia]	[moles/g]
Cesium formate with HCO_3^- 2.156 g/mL	148.9	300	1.937	281	3.0034
			9.908	1,437	10.1727
			22.23	3,224	20.3851
	176.7	350	11.96	1,734	2.9900
			19.53	2,832	6.5918
			37.34	5,415	14.1938

References

[1] "Methane Solubility in Cesium Potassium Formate Solution", report # R-04-166, Westport Technology Center International, April 2004.

[2] "CO_2 solubility in cesium formate", report R-03-141, Westport Technology Center International, June 2003.

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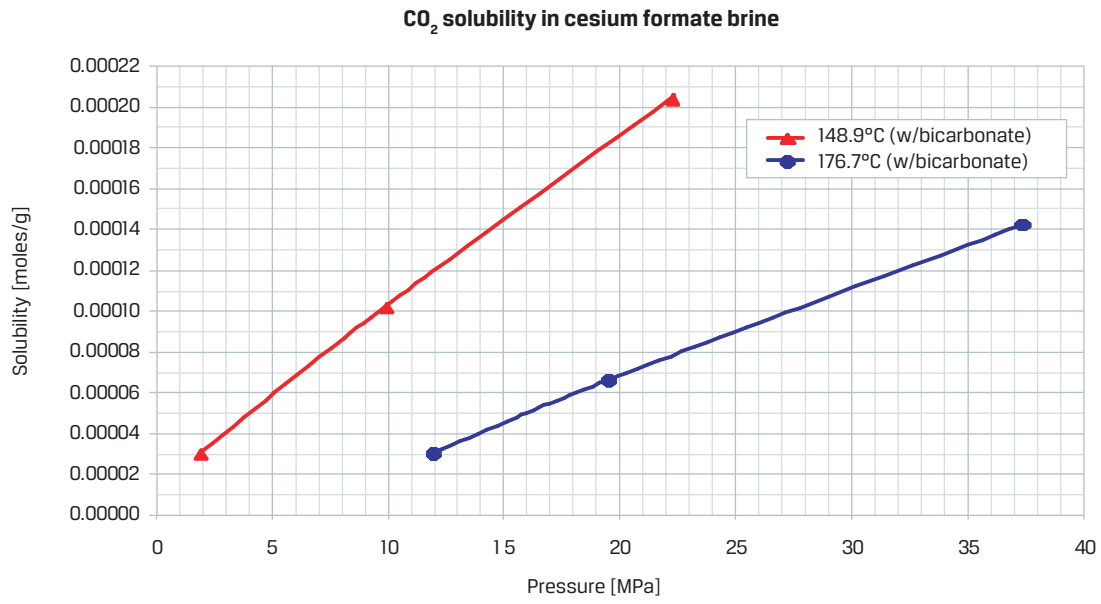

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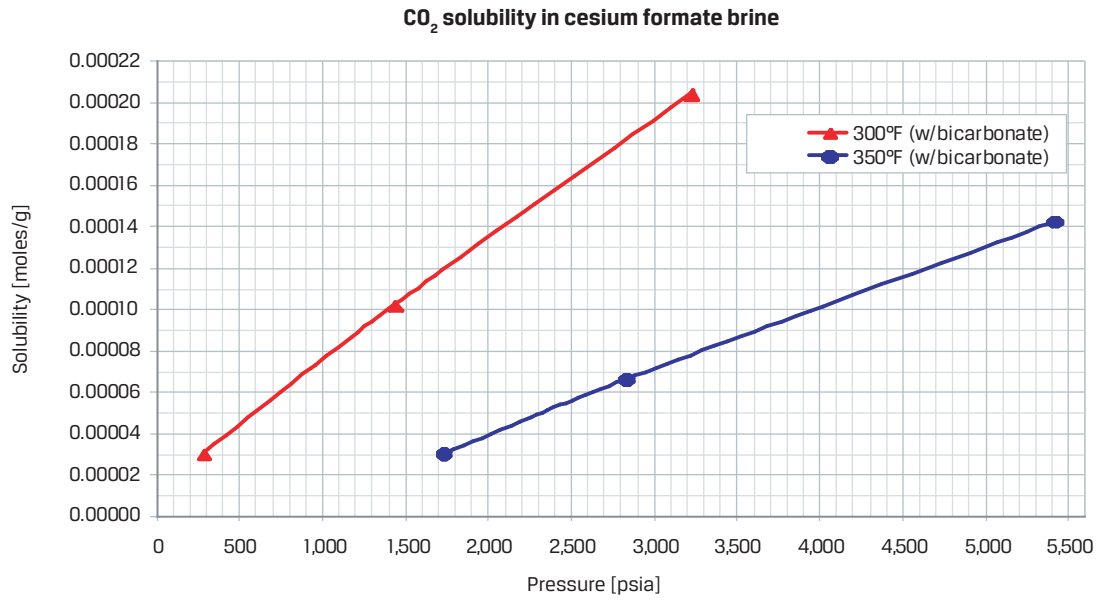

Figure 6 CO_2 solubility in concentrated cesium formate brines.