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Laboratory measurements of ultrasonic velocities in CO_2 saturated brines

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Abstract

The acoustic velocities in CO_2-saturated brines were investigated and compared with velocities measured in pure brines in the range of temperatures (30 - 70°C), pressures (2 - 38 MPa) and salinities (0 -100,000 ppm). It has been found that CO_2 dissolution significantly changes the acoustic properties of brine. This change can be accounted for by a simple linear empirical equation.

Keywords: CO2, brine, mixture, ultrasonic, bulk modulus

1. Introduction

Precise knowledge of the acoustic velocities in CO_2 saturated brines is of crucial importance for obtaining bulk moduli of fluids and therefore for estimating the seismic properties of hydrocarbon reservoirs, for optimization of the enhanced oil recovery (EOR) processes, and also for CO_2 plume monitoring in saline aquifers and depleted reservoirs often used for carbon geological storage.

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Batzle and Wang [1] summarized all available at the time data on ultrasonic velocities in brines and derived empirical relations between acoustic velocities, pressures, temperatures and salinities. Recently Han *et al*. [2] reported experimental results on the acoustic properties of pure CO_2 measured at pressures up to 100 MPa and at temperatures up to 200°C. Sun and Han [3] reported first results on acoustic measurements of mixtures of CO_2 with distilled water. However, despite numerous data sets of ultrasonic velocities in water and brines at elevated temperatures and pressures throughout the years, very limited information about acoustic properties of brines saturated with carbon dioxide is available in open literature. This paper is an attempt to fill the gap in the experimental study of the acoustic properties of brines. Here we are reporting the results of measurements of ultrasonic velocities in brines fully saturated with CO_2 as a function of pressure, temperature and salinity.

2. Experimental set-up and procedure

The measurement apparatus used in this study includes a test vessel, temperature and pressure control systems, and an acquisition system. The test vessel was modified from a Hoek cell designed for 1 inch cores (Fig.1). the total volume of the pressure cell was 0.15 L. To measure ultrasonic wave velocity two acoustic transducers (V103-RM, Panametrics) with a central frequency of 1 MHz are attached to both flat sides of the test vessel. The transducers are connected to a pulser/receiver (5077PR, Olympus). The waveforms of the signals are recoded using a digital oscilloscope (TDS 3034C, Tektronix). The pressure in the test vessel is controlled by two pumps, namely LA-20 (Shimazu *Ltd*.) for liquids and isco-260D (Teledyne Ltd) for CO_2. Flexible heaters are wrapped around the test vessel and all pipes that connect the pumps with the test vessel. The temperature is monitored at four points using digital temperate controllers with accuracy of 0.25°C. Acoustic velocities are computed using the time-of-flight method. The travel path of the wave was measured with accuracy 0.1 %, uncertainties in the measurements of wave arrival was 0.3%. The system was calibrated by measurement of velocities in distilled water at various pressures and temperatures. The commercial grade CO_2 (purity 99.8%) was used in this study.

The procedure of the measurements was as follows. After vacuuming of the test vessel, brine was pumped into the vessel. Acoustic velocities of brines were measured at a given temperature as a function of pressure up to 38 MPa with a step of 4 MPa. At this stage the pressure inside the test vessel is maintained by a "liquid" pump. Then pressure was decreased to 6 MPa and 20% of volume of brine in the vessel was replaced by CO_2. The test

Fig. 1. The testing vessel taken apart. P-wave transdusers are glued to two platens, shown in the bottom.
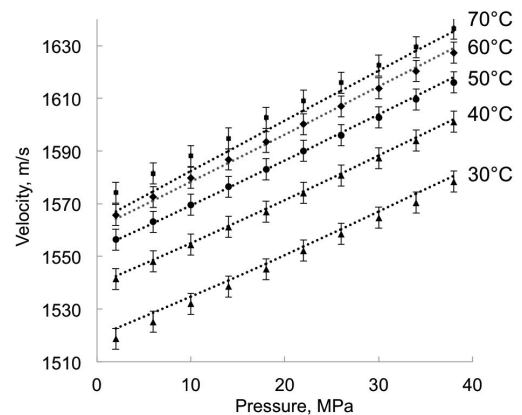

Fig. 2. Velocities of 50% KCl 50% NaCl brine of 10,000 ppm salinity at different pressures and temperatures: Points - experimental results (this paper), dotted lines- empirical relationship by Batzle and Wang (1992) for 100% NaCl brines.

vessel was oriented horizontally to allow the acoustic transduces to be immersed into the liquid phase. As density of CO_2 is less than that of brines CO_2 phase was accumulated in the top of the vessel and gradually dissolves into brine. At that stage the pressure inside the test vessel is regulated by a "gas" pump. For that purpose the CO_2 supply line has been kept open, and extra amount of CO_2 is able to enter the test vessel if pressure in the vessel decreases due to dissolution of CO_2 into the brine. Such "open for CO_2" system guarantees that the concentration of CO_2 dissolved into the brine will reach the maximum possible at given temperature and pressures value and thus the two phases system (i.e. CO_2 / brine) will be in the thermodynamic equilibrium. There was no enforced mixing equipment to stimulate dissolution of CO_2 into brine used in these experiments. The test vessel was kept at a constant temperature while pressure inside was changed up to 38 MPa with an increment of 4 MPa. The system was kept for 10 min at each stage before velocity was measured. As the pressure reached 38 MPa the experiment was terminated and the system was cleaned. At the next step, fresh brine was injected into the test vessel to perform experiment at a different temperature. No density measurements of brine/CO_2 mixture have been performed in this study.

3. Results and discussion

3.1. *Acoustic* velocity in 50% NaCl /50% KCl brines.

Ultrasonic velocities in brines composed of 50% *KCl* and 50% *NaCl* and salinities of 0, 10,000, 20,000, 40,000 and 100,000 ppm were measured at pressures from 2 MPa to 38 MPa in order to obtain the "reference" points for experiment with CO_2/brine mixtures. Fig. 2 shows the results of velocity measurement for the brine with salinity of 10,000 ppm at temperatures from 30° to 70°C as a function of pressure compared with empirical relationship by Batzle and Wang [1]. Differences between the results of the measurements and the predictions of the Batzle-Wang empirical formula under the same conditions (P, T and salinity) are less than 5 m/s over the entire range of the measurements. Such small differences demonstrate the reliability of the experimental system.

3.2. *CO_2 dissolution into brine: Time effect*

Fig. 3 shows acoustic velocity evolution due to CO_2 dissolution into brine with 10,000 ppm salinity for different temperatures at a fixed pressure of 6 MPa. At low temperatures (30°C and 40°C), dissolution of CO_2 increases the velocity of the mixture, while at a higher temperature (70°C) the velocity decreases with increasing amount of CO_2.

Fig. 4 presents acoustic velocity evolution due to dissolution of CO_2 in brines of different salinities. It is observed
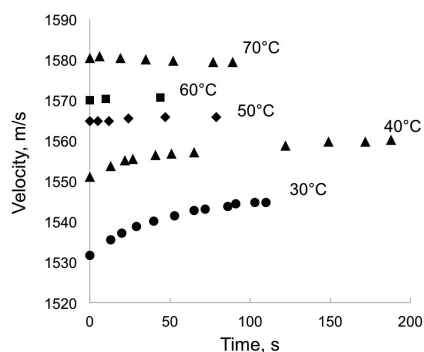

Fig. 3. Time evolution of velocity in brine due to CO_2 dissolution at different temperatures: salinity 10,000 ppm, pressure 6 MPa.
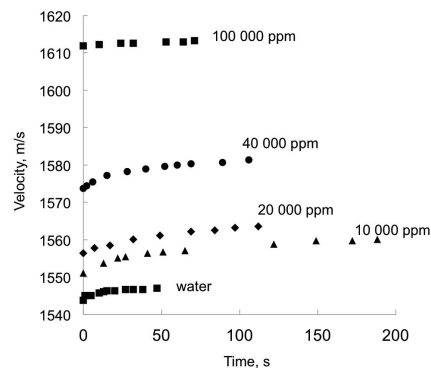
Fig. 4. Velocity evolution due to CO_2 dissolution in brine at different salinities: pressure 6 MPa, temperature 40°C
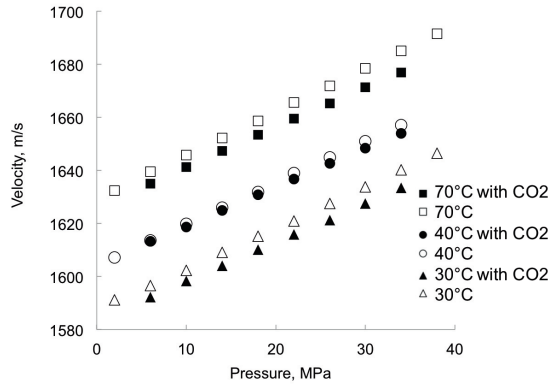
Fig. 5. Velocities of brine (open symbols) and CO_2 / brine mixtures (solid symbols) at different temperatures. Salinity is 100,000 ppm.
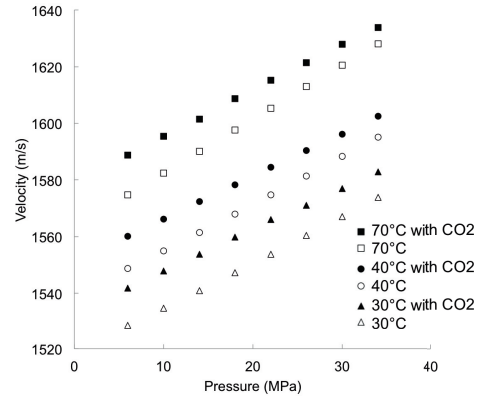
Fig. 6. Velocities of brine (open symbols) and CO_2 brine mixtures (solid symbols) at different temperatures. Salinity is 10,000ppm.

that at a temperature of 40°C and pressure of 6 MPa, CO_2 dissolved in brine increases the acoustic velocity of the mixture. No change in velocity within experimental errors was observed after 10 min of the experiment. It can be concluded that system CO_2 / brine came to a thermodynamic equilibrium in less than 10 min for our experimental set-up.

3.3. CO_2 / brine mixtures: Pressure effect

Fig. 5 shows pressure dependence of acoustic velocity of 100,000 ppm brines and CO_2 saturated brines (with the same salinity of 100,000 ppm) at different temperatures. Velocities of brines and brines with dissolves CO_2 are linearly increase with the pressure (at temperature up to 70°C, pressures up to 38 MPa). For high salinity brine, velocity decreases with dissolution of CO_2 at all temperatures. On the contrary, results for low salinity brine (10,000 ppm) presented in the Fig. 6 demonstrate that the acoustic velocity increases with increase of dissolved CO_2.

3.4. CO_2 / brine mixtures: Temperature effect

Fig. 7 shows temperature dependence of velocities for fresh water and high salinity brine (100,000 ppm) at two different pressures. The acoustic velocity increases with the growth of temperature (up to 70°C). Dissolution of CO_2 into pure water increases the acoustic velocity for all pressures and temperatures used in the experiments; however the dissolution of CO_2 in high salinity brine decreases the acoustic velocity, as illustrated by Fig 8.

3.5. Empirical correction on CO_2 dissolution.

Based on experimental data set (full data set is available in the Appendix A) we have correlated measured velocity in thermodynamically equilibrated brine / CO_2 mixture ($V_{B,CO2}$) with acoustic velocity in brine obtained by Batzle and Wang (1992). After fitting of the experimental data the first order empirical relationship can be written as:

Fig. 8. Difference between acoustic velocity in brines calculated by empirical relationship Batzle and Wang [1] and measured velocity of CO_2 saturated brines.

Fig. 7. Velocity of CO_2-saturated brines (solid lines) and pure brine (dashed lines): (a) salinity is 100,000 ppm; (b) fresh water (0 ppm). Arrows show change in velocity due to CO_2 dissolution. Note different vertical scales.
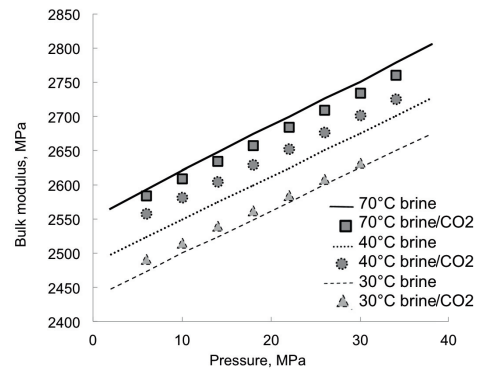
Fig. 9. Bulk modulus of brine and CO_2 dissolved in brine dependence on pressure at different temperatures. Salinity is 40,000ppm.

$$V_{B,CO2} = V_{BW} + 20.42 - 0.08377 \cdot T - 0.18 \cdot P - 0.0004173 \cdot S \qquad (1)$$

where, V_{BW} (in m/s) is a velocity of brine calculated using Batzle and Wang (1992) empirical relationship, T is temperature (in °C), P is pressure (in MPa), and S is salinity of brine (in ppm).

This empirical relationship is valid in the range of pressures of 2 MPa-38 MPa, temperatures of 30°C - 70°C; and salinities of 0 - 100,000 ppm.

3.6. Solubility and bulk modulus

Bulk modulus (K_{fluid}) of the CO_2/brine mixture fluid can be obtained from acoustic velocity and density,

$$K_{B,CO2} = \rho_{B,CO2} V_{B,CO2}^2 \tag{2}$$

where $\rho_{B,CO2}$ is the density of brine/CO_2 mixture,

Density of CO_2/brine was estimated using the empirical relationship proposed by Bachu and Adams [4]:

$$\rho_{B,CO2} = \frac{\rho_B}{1 - X^{CO2}\left(1 - V_\varphi \rho_W / M_2\right)} \tag{3}$$
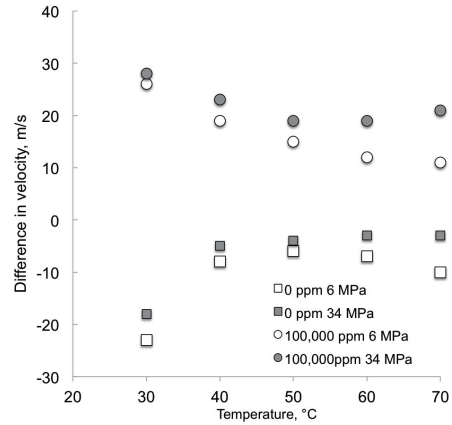
where ρ_W and ρ_B are the densities of water and brine, respectively, M_2 is a molecular weight of solute (44 g/mol for CO_2), X^{CO2} is the CO_2 mass fraction, and V_ϕ is apparent molar volume of CO_2 in pure water (Garcia [5]):

$$V_\varphi = 37.51 - 9.585 \cdot 10^{-2} T + 8.74 \cdot 10^{-4} T^2 - 5.044 \cdot 10^{-7} T^3 \tag{4}$$

The densities of brine ρ_B and fresh water ρ_W were calculated using empirical expressions presented by Batzle and Wang [1].

Fig. 9 shows the bulk moduli of brine (salinity 40,000 ppm) and brine / CO_2 mixtures as a function of pressure for different temperatures. Bulk moduli were calculated using densities obtained from equation (3). The difference in moduli exceeds errors of the measurements and density calculations. The maximum observed difference in bulk moduli measured in pure brine and in brine with dissolved CO_2 was 2.3% (at pressure 6 MPa, temperature 30°C, and salinity 0 ppm).

4. Conclusion

1) Our experiments confirm that empirical formula of Batzle and Wang (1992) (which was derived for for NaCl brines) can be applied for brines with salt composition 50% NaCl / 50% KCl in the range of pressures of 6 MPa – 38 MPa, temperatures of 30-70°C, and salinities of 0 - 100,000 ppm.

2) It was experimentally verified that acoustic velocity of CO_2 saturated brines is significantly different from velocities of pure brines: CO_2 dissolved into low salinity brines increases the acoustic velocities, whereas for higher salinity brines the acoustic velocities decrease.

3) An empirical formula for CO_2 / brine mixture under thermodynamical equilibrium was derived.

Appendix A. Results of measurements

T- temperature, S –salinity of brines, P –pressure, V - velocity of brines with dissolved CO_2, VB&W velocity obtained for brines using of Batzle and Wang (1992) empirical relationship

T (°C)	S (ppm)	P (MPa)	V (m/s)	VB&W (m/s)
30	0	6	1541±5	1518
30	0	10	1547±5	1524
30	0	14	1552±5	1531
30	0	18	1558±5	1537
30	0	22	1563±6	1543
30	0	26	1569±5	1550
30	0	30	1575±7	1557
30	0	34	1581±5	1563
40	0	6	1547±5	1539
40	0	10	1553±5	1545
40	0	14	1559±5	1552
40	0	18	1565±5	1558
40	0	22	1571±5	1565
40	0	26	1577±5	1572
40	0	30	1583±5	1578
50	0	6	1560±5	1554
50	0	10	1566±5	1560
50	0	14	1573±5	1567
50	0	18	1580±7	1574
50	0	22	1586±5	1580
50	0	26	1594±9	1588
50	0	30	1599±6	1595
50	0	34	1606±5	1602
60	0	6	1570±5	1563
60	0	10	1577±5	1570
60	0	14	1583±5	1577
60	0	18	1590±6	1584
60	0	22	1596±5	1591
60	0	26	1603±5	1599
60	0	30	1609±5	1606
70	0	6	1576±5	1566
70	0	10	1582±5	1574
70	0	14	1589±5	1582
70	0	18	1595±5	1589
70	0	22	1602±5	1597
70	0	26	1609±5	1604
70	0	30	1615±5	1612
70	0	34	1622±5	1619
30	10000	6	1542±5	1529
30	10000	10	1548±5	1535
30	10000	14	1554±5	1541
30	10000	18	1560±5	1547
30	10000	22	1566±5	1554
30	10000	26	1571±5	1560
30	10000	30	1577±5	1567
30	10000	34	1583±5	1574
40	10000	6	1560±5	1549
40	10000	10	1566±5	1555
40	10000	14	1572±5	1561
40	10000	18	1578±5	1568
40	10000	22	1584±6	1575
40	10000	26	1590±6	1581
40	10000	30	1596±5	1588
40	10000	34	1602±7	1595
50	10000	6	1566±5	1563
50	10000	10	1572±5	1569
50	10000	14	1579±5	1576
50	10000	18	1585±5	1583
50	10000	22	1591±5	1590
50	10000	26	1598±5	1597
50	10000	30	1604±5	1604
50	10000	34	1610±5	1611
60	10000	6	1574±5	1571
60	10000	10	1580±5	1578
60	10000	14	1587±5	1585
60	10000	18	1593±5	1593
60	10000	22	1599±6	1600
60	10000	26	1606±5	1607
60	10000	30	1613±5	1614
60	10000	34	1619±5	1622
70	10000	6	1589±5	1575
70	10000	10	1595±5	1582
70	10000	14	1602±5	1590
70	10000	18	1609±5	1598
70	10000	22	1615±5	1605
70	10000	26	1621±5	1613
70	10000	30	1628±6	1621
70	10000	34	1634±7	1628
30	20000	6	1553±5	1539
30	20000	10	1559±5	1545
30	20000	14	1565±6	1551
30	20000	18	1570±5	1557
30	20000	22	1576±5	1563
30	20000	26	1582±5	1571
30	20000	30	1588±6	1577
30	20000	34	1593±6	1584
40	20000	6	1566±5	1559
40	20000	10	1573±5	1565
40	20000	14	1579±5	1571
40	20000	18	1585±5	1578
40	20000	22	1590±5	1585
40	20000	26	1597±5	1591
40	20000	30	1603±5	1598
40	20000	34	1609±7	1605

T (°C)	S (ppm)	P (MPa)	V (m/s)	V$_{B\&W}$ (m/s)	T (°C)	S (ppm)	P (MPa)	V (m/s)	V$_{B\&W}$ (m/s)
50	20000	6	1592±5	1572	60	40000	22	1621±5	1626
50	20000	10	1599±6	1579	60	40000	26	1628±5	1633
50	20000	14	1604±5	1585	60	40000	30	1634±5	1640
50	20000	18	1609±5	1592	60	40000	34	1640±7	1647
50	20000	22	1616±5	1599					
50	20000	26	1623±5	1606	70	40000	6	1600±5	1600
50	20000	30	1629±5	1613	70	40000	10	1606±5	1607
50	20000	34	1634±5	1620	70	40000	14	1613±5	1615
					70	40000	18	1619±5	1622
60	20000	6	1597±5	1580	70	40000	22	1626±5	1630
60	20000	10	1604±5	1587	70	40000	26	1632±5	1638
60	20000	14	1610±6	1594	70	40000	30	1638±5	1645
60	20000	18	1616±5	1601	70	40000	34	1645±5	1652
60	20000	22	1622±5	1608					
60	20000	26	1628±5	1616	30	100000	6	1592±5	1618
60	20000	30	1635±5	1623	30	100000	10	1598±5	1623
60	20000	34	1641±5	1630	30	100000	14	1604±5	1629
					30	100000	18	1610±5	1635
70	20000	6	1589±5	1583	30	100000	22	1616±5	1642
70	20000	10	1595±5	1591	30	100000	26	1621±5	1648
70	20000	14	1601±5	1598	30	100000	30	1628±6	1655
70	20000	18	1609±5	1606	30	100000	34	1633±6	1661
70	20000	22	1615±5	1614					
70	20000	26	1621±5	1621	40	100000	6	1613±5	1632
70	20000	30	1628±5	1628	40	100000	10	1618±5	1638
70	20000	34	1634±6	1636	40	100000	14	1624±5	1644
					40	100000	18	1630±5	1651
30	40000	6	1559±5	1559	40	100000	22	1637±5	1657
30	40000	10	1565±5	1565	40	100000	26	1643±5	1664
30	40000	14	1571±5	1571	40	100000	30	1648±5	1670
30	40000	18	1577±5	1579	40	100000	34	1654±5	1677
30	40000	22	1583±5	1584					
30	40000	26	1588±5	1591	50	100000	6	1627±5	1642
30	40000	30	1594±5	1598	50	100000	10	1633±5	1648
					50	100000	14	1639±5	1654
					50	100000	18	1645±5	1661
40	40000	6	1582±5	1577	50	100000	22	1652±5	1667
40	40000	10	1588±5	1584	50	100000	26	1658±5	1674
40	40000	14	1594±5	1590	50	100000	30	1663±5	1680
40	40000	18	1600±5	1597	50	100000	34	1669±6	1688
40	40000	22	1606±5	1603					
40	40000	26	1612±5	1610	60	100000	6	1634±5	1646
40	40000	30	1618±5	1617	60	100000	10	1640±6	1653
40	40000	34	1624±5	1624	60	100000	14	1646±5	1660
					60	100000	18	1652±5	1667
48	40000	6	1591±5	1588	60	100000	22	1658±5	1674
48	40000	10	1597±5	1594	60	100000	26	1664±5	1681
48	40000	14	1603±5	1601	60	100000	30	1669±6	1688
48	40000	18	1609±5	1608	60	100000	34	1676±8	1695
48	40000	22	1615±5	1614					
48	40000	26	1622±5	1621	70	100000	6	1635±5	1646
48	40000	30	1628±5	1628	70	100000	10	1641±5	1654
48	40000	34	1634±5	1635	70	100000	14	1647±5	1661
					70	100000	18	1653±5	1668
60	40000	6	1596±5	1597	70	100000	22	1659±6	1676
60	40000	10	1603±5	1604	70	100000	26	1665±7	1683
60	40000	14	1609±5	1611	70	100000	30	1671±7	1690
60	40000	18	1615±5	1618	70	100000	34	1677±7	1698

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