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Measurement of CO_2 diffusivity in synthetic and saline aquifer solutions at reservoir conditions: the role of ion interactions

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Abstract Storage and disposal of CO_2 as the main component of greenhouse gases in saline aquifers require careful measurement of diffusivity for predicting rate of transfer and cumulative amount of trapped gas. Little information is available on diffusion of CO_2 in highly concentrated saline aquifers at reservoir conditions. In this study, diffusivity of CO_2 was measured into different solutions, including saline aquifer taken from oil field, distilled water and synthetic solutions prepared from four most common ions, Mg^{2+}, Ca^{2+}, K^+, Na^+. The roles of salvation effect and hydration phenomenon were studied on diffusivity of dissolved CO_2. Synthetic solutions were prepared at concentration ranges of 83–200 g/l. Experimental measurements were reported at temperature and pressure ranges of 30–40 °C and 5,880–6,265 kPa, respectively. Results show that both type and concentration of ion affect CO_2 diffusivity. Diffusion coefficient was found dependent on effective radius of hydrated ions. Also, CO_2 diffusivity increase by increasing strength of bonds between ion and neighbor water molecules. Also, presence of ions in water solution creates hydration competition between solution metal ions and aqua ions from diffusive gas. The Mg^{2+} cation, which has strongest hydration competition among other ions, has an increasing effect on gas diffusivity into saline aquifer. However, increasing ion concentration in solution decreases diffusivity of CO_2 due to growth in fraction of contact ion pairs. Results of this study provide unique measures of CO_2 diffusion coefficient in saline aquifer at high pressure and temperature conditions and conceptual information about effect of each common saline formation ion on gas diffusivity.

List of symbols

C^*	Equilibrium concentration of CO_2 in brine (kmol/m^3)
D	Diffusion coefficient (m^2/s)
K_h	Henry's law constant (kPa.m^3/kg)
L	Height of gas in diffusion cell (m)
m_d	Diffused gas into the saline aquifer (kg)
M	Molecular mass of gas (kg/kmol)
N	Normality
P	Pressure (kPa)
R	Universal gas constant
S	Weight fraction of sodium chloride
t	Time (s)
T	Temperature (K or °C)
Z	Compressibility factor

Subscripts

E	Equilibrium value
I	Initial value

1 Introduction

Human-based activities contribute to a major source of greenhouse gas (GHG) emissions worldwide. CO_2 is the main gas which constitutes most of the greenhouse effect in atmosphere. Dealing with CO_2 has been a primary concern for many researchers who try to properly sequestrate and effectively remove it from atmosphere. Saline aquifers are found as natural sinks with large capacity for CO_2 storage as a carbon capture and sequestration (CCS) project [1]. High concentration of salt makes these formations inappropriate for irrigation, nor for drinking purposes. The main

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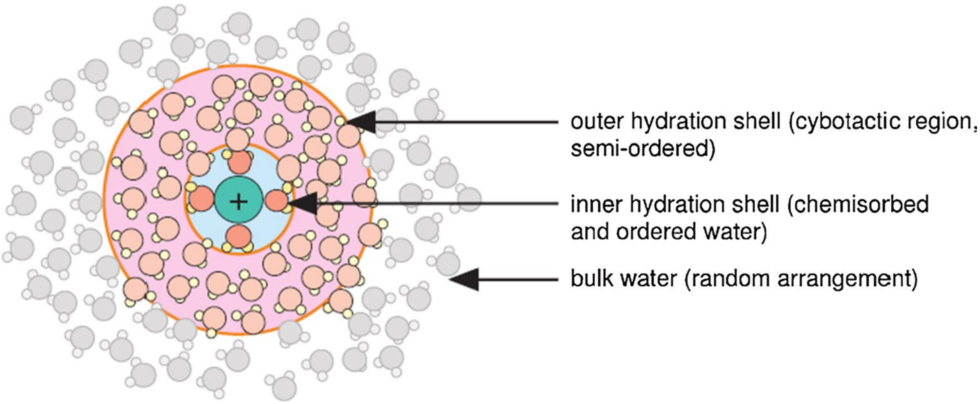

Fig. 1 An ion in aqueous solution with its hydration shells [2]

mechanisms of mass transfer during CO_2 injection into saline aquifers is molecular diffusion, followed by convection and mineral precipitation. Thus, knowledge of CO_2 diffusivity in aquifer as a function of temperature, pressure, solvent property (viscosity, density, composition) and molecular property of the solute (size, shape and hydration) is crucial for proper design of a CCS project, along with biological, geochemical, and medical applications.

Saline aquifers are ionic solutions that contain ions such as K^+, Na^+, Mg^{2+} and Ca^{2+}. These are the four common cations in almost any aquifer solution with Na^+ being the predominant component in solution, although their composition may vary from one point to another. The aquifer systems are characterized by high concentration of common ions and relatively high reservoir pressure and temperature. Understanding the interaction of each ion with neighboring ions and water molecules, as well as the individual and combined role of ions on gas diffusivity requires a careful, conceptual analysis of such a complex system. Relaxation effect, electrophoretic effect and salvation effect are three active phenomena which make analysis of diffusion into ionic solutions more difficult in comparison to non-electrolyte solutions [2, 3]. The relaxation effect is due to change in the atmosphere of an ion when it moves. The ion atmosphere stands for the excess charge of ions with opposite sign surrounding an individual ion. When an ion moves, the ion atmosphere changes and relaxes to become centered on the new position of ion, and motion of ion itself slows down. Electrophoretic effect implies that ions of the opposite charge move in the opposite direction and can slow the ion motion. The salvation effect occurs when ions compete with each other to attract solvent molecules [2].

In ionic solutions, the ionic structure is disoriented and cations and anions are released and distribute throughout the solvent (water). Hereby water molecules aggregate around ions mainly due to ionic-dipole interaction and form water clusters. Actually, two hydration shells around an ion can be distinguished. In the first shell, the force containing water molecules is ionic-dipole interaction, while in the second shell, water molecules tend to join and make chains through hydrogen bonds. The size of hydrated ions will significantly influence structure of the system, as well as particle diffusion coefficients [4]. It should be noted that first and second shells are separated according to the type of interaction forces and water molecules can transfer between first and second shells. This phenomenon is shown schematically in Fig. 1. In this way, diffusion coefficient may depend on effective radius of hydrated ions.

Composition of saline aquifer plays an important role in the diffusivity of CO_2 during CCS. It is well documented that water salinity and type of salt affects gas diffusivity, especially at high salt concentration. The valence of dominating cation present in salt solution is important while studying diffusion phenomenon in saline aquifer. Monovalent NaCl or KCl solutions with the same salt concentration absorb more CO_2 than their divalent $CaCl_2$ or $MgCl_2$ counterparts [5]. The pattern of CO_2 diffusion in a concentrated aqueous solution like saline aquifers is rather complicated, as the local viscosity of water in the neighborhood of a diffusing ion may be decreased appreciably by distortion in the structure of water caused by the presence of other ions [6].

Zeebe [7] addressed a number of diffusion experiments coupled with geochemical reactions which pointed at measurement of CO_2 diffusivity in sea water. He points that measurement of diffusion coefficients for bicarbonate and carbonate ions are important as well as for CO_2 itself, and have been reported traditionally using conductivity measurements for solutions with infinite dilution. He also provided a literature review on the experimental and theoretical studies which dealt with such fundamental concepts as hydration, hydrogen bonding, salvation, calcite growth and thermodynamic equilibrium and their critical roles on the diffusion of CO_2 in ion-bearing environments. Garcia et al. [8] proposed a correlation based on molecular dynamic (MD) simulation for the self-diffusion coefficient of CO_2 in terms of the rotational relaxation time which can ultimately be used to estimate the mutual diffusion coefficient of CO_2

in brine composed of Na^+ and Cl^- ions. Another (MD) simulation study was reported by Zeebe [7] for predicting diffusion coefficient of dissolved CO_2, HCO_3^-, and CO_3^{2-} and their dependence on temperature. He proposed equations for calculating diffusion coefficients of the dissolved carbonate species in the range of 0–100 °C.

In spite of direct relationship between solubility of CO_2 in saline aquifer and its salinity, Garcia et al. [8] indicate that no clear dependency of diffusion coefficient is identified with salinity or with CO_2 mol fraction, if the system is overall dilute. Moreover, they did not observe dependency of diffusion coefficient on pressure in their molecular dynamic simulation.

Studies on formation water properties have mostly focused on NaCl and KCl, two most common salts in connate water and saline aquifer solutions [9]. There is a few data reported for diffusion coefficient of CO_2 into saline aquifer at high pressure. Rather, many experiments have been conducted at atmospheric conditions in either pure water or synthetic brines mostly containing a single salt. For example, Unver and Himmelblau [10], Thomas and Adams [11], Tamimi et al. [12], Frank et al. [13] and Jähne et al. [14] studied diffusivity of CO_2 into pure water in the different range of temperature. All above studies were conducted at atmospheric pressure and pure water. Effect of pressure on diffusion coefficient was reported by Hirai et al. [15], where they measured diffusion coefficient of CO_2 in pure water at 13 °C and 29,400 and 39,200 kPa. Tewes and Boury [16], conducted their study in fixed temperature of 40 °C and pressure range of 3,000–9,000 kPa. Renner [17] measured diffusivity of CO_2 into 0.25 N NaCl brine at 38 °C for a pressure range of 1,544–5,833 kPa and recorded $D_{CO2-H2O}$ in the range 3.07–7.35 × 10^{-9}m^2/s. Wang et al. [18] performed a set of tests with condition same as Renner [17], but with different pressure in range of 1,524–5,178 kPa. In another study, Bahar and Liu [19] measured diffusion of CO_2 at 2,580 kPa and 83 °C in synthetic brine of 2 % NaCl, which was corresponding to field conditions of Otway Basin in southeastern Australia. They proposed an empirical correlation for diffusivity of CO_2 in brine as a function of molecular weight, volume, and viscosity of liquid phase, as well as pressure and temperature. In another study, Yang and Gu [20] studied mass transfer of CO_2 in reservoir brine taken from Instow oil field in Saskatchewan, Canada. They reported diffusivity of CO_2 in the pressure range of 2,600–7,500 kPa and at two different constant temperatures of 27 and 58 °C. The effective diffusivity was determined to be in the range of 170.7–183.2 × 10^{-9} m^2/s at $T = 27$ °C and 250.2–269.8 × 10^{-9} m^2/s at $T = 58$ °C. Moghaddam et al. [21] published a set of CO2 diffusivity data into 200 gr/l NaCl brine at 25 °C and pressure range of 2,200–5,900 kPa. Recently, Azin et al. [22] reported diffusivity values of CO_2 into a real saline aquifer taken from an oil field which was measured and modelled in the temperature and pressure ranges of 32–50 °C and 5,900–6,900 kPa, respectively. Based on their measurements, diffusivity of CO_2 varies between 3.52–5.98 × 10^{-9} m^2/s for 5,900 kPa and 5.33–6.16 × 10^{-9} m^2/s for 6,900 kPa initial pressure. In this study has been asserted that diffusion coefficients increase with temperature at a given pressure. Also, increasing pressure will result in a higher diffusion coefficient at isothermal conditions. Table 1 summarizes reported diffusivity data for CO_2 into saline aquifer and synthetic solution systems.

The objective of this paper is to measure the diffusion coefficient of CO_2 into different aqueous ionic solutions, ranging from synthetic solutions to saline aquifer samples collected from an oil field. Conceptual information on diffusivity of CO_2 in ionic aquifer solutions will be obtained through careful investigation and analysis of the role played by every single present ion in saline aquifer. Also, the salvation effect and hydration mechanism of each ion present

Table 1 Summary of experimental studies on CO_2 diffusivity into brine and synthetic solution

Temperature range (°C)	Pressure range (kPa)	Solution (gr/l)	No. of points	D × 10^9 (m^2/s)	Reference
6–65	100	Pure water	5	1.15–4.29	[10]
18.5–75.1	90	Pure water	7	1.95–5.4	[11]
20–95	100	Pure water	7	1.76–8.2	[12]
25–55	100	Pure water	4	1.97–3.67	[13]
10–35	100	Pure water	6	1.26–2.47	[14]
13	29,000–38,700	Pure water	2	1.35–1.45	[15]
40	3,000–9,000	Pure water	7	0.47–1.8	[16]
38	1,544–5,833	NaCl (5.844)	4	3.07–7.35	[17]
38	1,524–5,178	NaCl (5.844)	5	2.93–4.83	[18]
25	2,186–5,861	NaCl (200)	5	9.07–9.86	[21]
27–58	2,600–7,500	Brine	6	170.7–269.8	[20]
32–50	5,900–6,900	Brine	6	3.52– 613	[22]

in aquifer and their impact on diffusivity of dissolved CO_2, HCO_3^-, and CO_3^{2-} will be studied.

In the following sections, the experimental setup and materials are described first. Next, experimental results are presented and analysed. Effects of ion hydration, salvation effect and ion concentration on diffusion coefficient of dissolved gas will be discussed in detail. Concluding remarks will appear at the end of paper.

2 Materials and methodology

2.1 Mathematical modeling

To evaluate and interpret the experimental data, the method proposed by Sheikha et al. [23] was used. This method works based on gas pressure decline and interface mass balance as gas diffuses into liquid. The following assumptions are made when using this method:

1. Diffusion process is one-dimensional.
2. Dissolved CO_2 fraction in brine is often less than 3 wt%; therefore, change in concentration of CO_2 in brine has a small effect on diffusion coefficient.
3. Due to relatively low experiment time, effect of chemical reaction on diffusion is negligible.
4. Swelling of brine due to CO_2 dissolution is negligible.
5. Evaporation of liquid phase is negligible in the experimental conditions. Therefore, the gas phase is assumed as pure during tests.
6. Henry's law was applied to calculate equilibrium concentration of CO_2 in gas–liquid interface.
7. Gas phase compressibility factor is assumed constant during tests.

Assumptions 4 and 7 were approved by Azin et al. [22] for the same system.

Using the Fick's second law of diffusion in the liquid phase with implementation of above assumptions and following initial and boundary conditions result in pressure solution proposed by Sheikha et al. [23], as shown in Eqs. (1–5).

$$\frac{\partial C}{\partial t} = D_{AB}\frac{\partial^2 C}{\partial x^2} \tag{1}$$

$$P = K_h C \ @\ x = 0 \tag{2}$$

$$C = 0 \ @\ x \to \infty \tag{3}$$

$$C = 0 \ @\ t = 0 \tag{4}$$

$$\mathrm{P(t)} = \mathrm{P_i} \exp\left(\frac{\sqrt{\mathrm{D}}\mathrm{ZRT}\sqrt{\mathrm{t}}}{\mathrm{LMK_h}}\right)^2 \mathrm{erfc}\left(\frac{\sqrt{\mathrm{D}}\mathrm{ZRT}\sqrt{\mathrm{t}}}{\mathrm{LMK_h}}\right) \tag{5}$$

The simplified relation to interpret the pressure decay data was suggested by Sheikha et al. [23]:

$$\frac{\mathrm{d}(\mathrm{erfc}^{-1}\{\mathrm{P(t)}/\mathrm{P_i}\})}{\mathrm{d}(\sqrt{\mathrm{t}})} = \frac{\sqrt{\mathrm{D}}\mathrm{ZRT}}{\mathrm{K_h LM}} \tag{6}$$

A plot of $erfc^{-1}\{\frac{P(t)}{P_i}\}$ versus $\sqrt{t}$ gives diffusion coefficient. This plot starts with a nonlinear part, followed by a linear one. The slope of linear part can be used to determine diffusion coefficient of gas in liquid, as shown in Eq. (7).

$$\frac{\sqrt{D}}{K_h} = m\left(\frac{LM}{ZRT}\right) \tag{7}$$

2.2 Set-up description

The experimental setup, shown schematically in Fig. 2, was used for conducting diffusion experiments. Details of experimental setup are described by [22].

2.3 Materials

CO_2 cylinder with 99.9 % purity was prepared from domestic source. Saline aquifer was collected from Gachsaran oilfield located in the southwest of Iran. Its salinity amounts to 182,000 mg/l. Four synthetic solutions of $MgCl_2$, $CaCl_2$, NaCl, KCl salts and distilled water were prepared to study the role of individual solute ion in CO_2 diffusivity. Also, N_2 was used for leakage test. Complete analysis of synthetic solutions and detailed ion analysis of saline aquifer are shown in Tables 2 and 3, respectively.

2.4 Set- up validation

Validation of experimental set-up and implemented measurement method was checked by reproducing selected data points from literature. The data point was taken from Wang et al. [18] for CO_2/Brine (NaCl 0.25 N) at 5,178 kPa and 38 °C, who reported diffusion coefficient as 4.83×10^{-9} m^2/s. measured Diffusion coefficient of CO_2 at the same conditions was 4.34×10^{-9} m^2/s, which has a good agreement with reported value.

3 Results and discussion

As stated earlier, salvation phenomenon is one of the main active mechanisms in highly concentrated ionic solutions. Salvation phenomenon, occurring as ions have to compete with each other to attract solvent molecules, can affect the hydration number of solvent ions and diffusing ions. Also, structure of the solution system will be significantly influenced by ion concentration and the size of each hydrated ion. In this way, diffusion coefficient into ionic solution

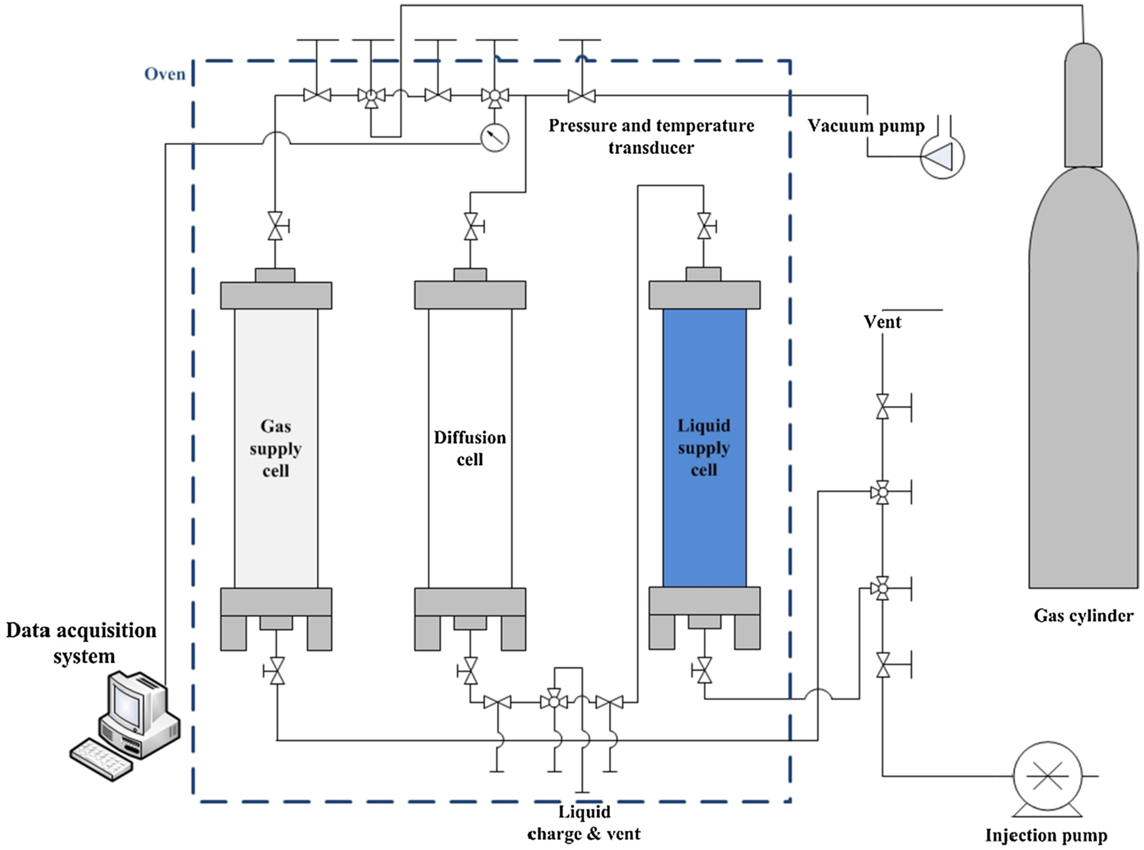

Fig. 2 Schematic of experimental set-up

Table 2 Properties of synthetic and actual brine solutions at experimental conditions

Solution system	Solution formulation	Temperature (°C)	Initial pressure (kPa)	Prepared concentration in lab (gr/l)	Ionic strength (mol/l)	Solution viscosity (mPas)	Solution density (kg/m^3)	Notes
A	NaCl	40	5,880	200	3.422	0.63	1,115	Synthetic Solution
B	NaCl	30	6,265	100	1.711	0.772	1,061.3	Synthetic Solution
C	KCl	30	6,244	128	1.717	0.772	1,061.2	Synthetic Solution
D	$CaCl_2$	30	6,182	95.68	2.586	0.77	1,030.4	Synthetic Solution
E	$MgCl_2$	30	6,141	82	2.583	0.77	1,030.3	Synthetic Solution
F	H_2O	30	6,100	–	–	0.76	997	Distilled Water
G	H_2O	40	5,880	–	–	0.62	995	Distilled Water
H[γ]	Gachsaran	30	6,155	182.513	3.579	0.772	1,071	Saline Aquifer
I[γ]	Gachsaran	40	5,880	182.513	3.579	0.62	1,068	Saline Aquifer

[γ] Ion analysis of aquifer is reported in this table

may depend on effective radius of hydrated ions, ion charge and ion concentration. Synthetic solutions, making up four common aquifers ions, were used to evaluate the effect of each relevant phenomenon on gas diffusivity.

Table 4 summarizes all experimental conditions and measured diffusion coefficients. Solubility of gas in liquid was estimated using Henry's law, and the Duan and Sun [24] model was used to estimate Henry's constant.

3.1 Hydration effect

3.1.1 Metal ion size and charge effect

Table 4 shows measured diffusion coefficient of CO_2 in all solutions. Systems B and C represent diffusion coefficient of CO_2 into NaCl and KCl solutions prepared at the same concentration and ionic strength. Molecular ionic solution

Table 3 Ion analysis of aquifer used in this work

Composition	Concentration (mg/l)
Na^+	66,068
Ca^{2+}	4,000
Mg^{2+}	729
Cl^-	110,050
SO_4^{2-}	1,300
HCO_3^-	366
Total	182,513

properties are reported in Table 5. Comparing CO_2 diffusivity in these systems imply a significant dependency of CO_2 diffusivity to effective metal ion radius. This was also observed for $CaCl_2$ and $MgCl_2$ (systems D and E) solutions. As mentioned before, the aqua ion is associated with water molecules through hydrogen bond in a secondary salvation shell. Water molecules in the first hydration shell can exchange with molecules in the second salvation shell, as well as molecules in the bulk liquid. Movement of water molecules from hydration shells to water bulk increases the number of free water molecules in solution. Consequently, possibility of CO_2 ions hydration increases. Increasing the hydration of CO_2 ions will result in smaller CO_2 diffusion coefficient into ionic solution.

The high charge on the cation polarizes water molecules in the first salvation shell to an extent that they form hydrogen bonds with molecules in the second shell. The hydrogen bonds in this shell are strong enough to form a more stable entity [27]. Also, the strength of bonds between metal ion and water molecules in the first salvation shell increases with electrical charge on the metal ion and decreases as its radius increases [28]. This is the impressive phenomena to determine the diffusion coefficient of CO_2 into ionic solution. As the strength of bonds between metal ion and neighbour water molecules increase, the possibility of structure deformation for hydrated metal ions during diffusion of CO_2 molecules and its relevant ions into ionic solution reduces. As a result, temptation of water molecule to attract metal ions increases and in contrast, possibility of CO_2 ions hydration decreases. Decreasing the hydration of CO_2 ions will result in greater CO_2 diffusion coefficient into ionic solution.

3.1.2 *Effect of metal–oxygen (M–O) distance*

The metal–oxygen (M–O) distance is defined as the distance between a hydrated metal ion and the first neighbour water molecule in an aqueous solution. Values of metal ion radius and M–O distance are shown in Table 5 for common ions (Mg^{2+}, Ca^{2+}, Na^+ and K^+) in aquifer solutions. According to this table, there is a direct relation between ion radius and M–O distance. In other words, increasing anion radius in the same column of periodic table results in larger M–O for all ions dissolved in water. Figure 3 shows measured CO_2 diffusivity into ionic solution versus M–O distance for four synthetic ionic solutions. According to this figure, diffusivity of CO_2 into ionic solutions is inversely related to effective radius of hydrated metal ions. As can be observed, a sharp decrease exists for diffusion coefficient of CO_2 into ionic solutions from NaCl to $CaCl_2$ at almost same salt concentration (systems B and D) and operating conditions. According to reported data in Table 5, there is a relation between M–O distance and coordination number in aqua complex ions. Mg^{2+} and Na^+ generate aqua complexes with six coordinated water and M–O distance values of 2.1 and 2.43, respectively. In contrast, Ca^{2+} and K^+ complexes are made up with eight coordinated water and M–O distance values equal to 2.46 and 2.86, respectively. The gas diffusivity in six-coordinated-water ions solution with less M–O distance are larger those with eight-coordinated-water ions. This behaviour can refer to inverse relation between M–O distance and strength of the bonds between metal ion and neighbour water molecules. Reduction in M–O distance corresponds to stronger ion-water bonds and so ions can form a less widespread cluster. Then, the possibility of deforming hydrated metal ion structures

Table 4 Summarized experimental conditions and CO2 diffusion Coefficient in results

Test	Solution system	Solution (gr/l)	Initial pressure (kPa)	Temperature (°C)	Equilibrium pressure (kPa)	Kh (KPa m^3/kg)	D (m^2/s)
1	A	NaCl(200)	5,880	40	5,583	235.06	2.59e−9
2	B	NaCl(100)	6,265	30	5,955	176.70	4.68e−9
3	C	KCl(128)	6,244	30	5,803	176.95	1.71e−9
4	D	$CaCl_2$(95.68)	6,182	30	5,996	181.06	3. 20e−9
5	E	$MgCl_2$(82)	6,141	30	5,858	179.41	2.33e−8
6	F	H_2O	6,100	30	5,831	123.38	6.78e−10
7	G	H_2O	5,880	40	5,652	129.08	7.32e−10
8	H	Gachsaran	6,155	30	6,100	221.36	4.42e−09
9	I	Gachsaran	5,880	40	5,459	158.64	4.50e−09

Table 5 Molecular ionic solution properties used in this study [25, 26]

Solution System	Solution	Aqua complex	M^{n+}'s ion radius/Å	M–O distance/A
B	NaCl	$Na(H_2O)_6^+$	1.09	2.43
C	KCl	$K(H_2O)_8^+$	1.5	2.84
D	$CaCl_2$	$Ca(H_2O)_8^{2+}$	1.12	2.46
E	$MgCl_2$	$Mg(H_2O)_6^{2+}$	0.76	2.1

and hydration of diffused CO_2 aqua ions into ionic solution will be reduced.

3.2 Metal ion concentration effect

Measurement of CO_2 diffusion coefficient into pure water, system G, and NaCl solutions at different concentration (systems A and B) are reported in Table 4. Results show that CO_2 diffusivity in NaCl solution at low concentration (100 gr/l, system A) is larger than that for pure water with same operating conditions. Also, by increasing ion concentration from system A to B, diffusivity of CO_2 into ionic solution decreases. This difference may be justified in accordance with ionic solution features and special molecule–ion behaviors such as hydration phenomenon. Aqua ions are subject to hydrolysis. This process can help to make up the more regular structure for water molecules in ionic solutions. Also, presence of metal ions in water solution creates a competition between solution metal ions and aqua ions from diffusive gas for hydration. This event can be effective in hydration structure around the diffusive ion and then hydrolyzed ion size. For a diffusive ion having a weak hydration structure, the diffusivity increases as the hydration structure becomes weaker. Einstein's early studies of diffusion in solutions assert same findings [29]. In contrast, by increasing ion concentration the fraction of contact ion pairs increase and that of solvent separated ion pairs decrease. In concentrated solutions, some water molecules occupy interstitial positions and, as a result, no well-defined second hydration shell is found around a central molecule.

3.3 Combined effect of ions

Figure 4 compares pressure decay versus time for synthetic NaCl solution and saline aquifer solution with composition given in Table 2. The concentration of synthetic solution was similar to that of aquifer sample. Also, the operating conditions were the same for both experiments. Calculated Gas diffusion coefficient in saline aquifer solution (systems I) and synthetic NaCl solution (systems A), reported in Table 4, are 4.5×10^{-9} and 2.59×10^{-9} m^2/s respectively. It is clear that gas diffusivity into synthetic NaCl solution is lower than that for saline aquifer. This difference indicates that presence of some metal ions among Mg^{2+}, Ca^{2+} and K^+ in solution may accelerate the diffusion process. As mentioned before, each metal ion shows a different behavior in solution due to its M–O distance and hydration competition with other solution metal, as well as carbonate and bicarbonate ions. Calculated diffusivities for synthetic solutions shows that $MgCl_2$ solution has the largest gas diffusivity among synthetic solutions at almost same experimental conditions, as reported in Table 4. The Mg^{2+} has the strongest hydration competition with other ions and also firmest hydration structure. Therefore, presence of such an

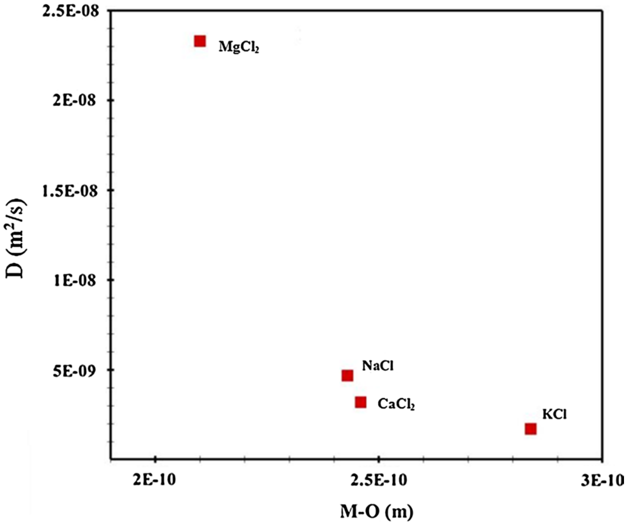

Fig. 3 CO_2 diffusion coefficient in ionic solution versus first neighbor ion–water distance at experimental condition

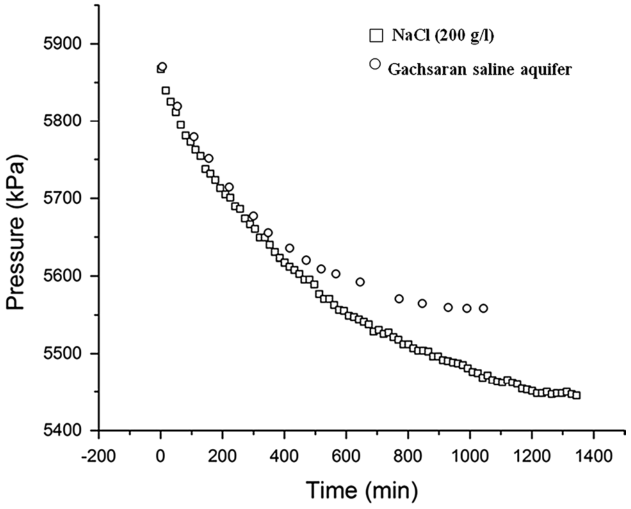

Fig. 4 Pressure decay graphs at equal initial pressure (5,880 kPa) and temperature (40 °C)

ion in saline aquifer has an increasing effect on gas diffusivity. In contrast, K^+ and Ca^{2+} have decreasing effect on gas diffusivity.

4 Conclusion

In this paper, an experimental setup was employed to measure diffusivity of CO_2 into high salinity saline aquifer and synthetic solutions at reservoir conditions. The role of each common metal ion in CO_2 diffusivity into synthetic solutions and saline aquifer were studied based on the salvation effect and hydration mechanism of each ion. Also, the combined effect of ions on diffusivity of dissolved CO_2 were studied. The following conclusions can be drawn from this study:

- Hydration process is an effective mechanism in the diffusion process of CO_2 into aqueous solution.
- Diffusivity of CO_2 into ionic solutions is inversely related to effective radius of hydrated metal ions.
- The CO_2 diffusion coefficient in low concentration NaCl solution is larger than that for pure water at the same operating conditions.
- The CO_2 diffusion coefficient in high concentration NaCl solution is lower than that for pure water with same operating conditions.
- Each metal ion has a different behavior in solution related to its solution properties and its hydration competition with other solution metal ions and aqua ions from diffusive gas.
- The Mg^{2+} cation which has strongest hydration competition among other ions, has a increasing effect on gas diffusivity into saline aquifer.

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