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Effect of Carbon Dioxide in Seawater on Desalination: A Comprehensive Review

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Effect of Carbon Dioxide in Seawater on Desalination: A Comprehensive Review

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Abstract: The two main methods of removing salt from ocean water currently in use for large scale applications are: distillation using thermal desalination and membrane reverse osmosis separation. A detailed knowledge of the CO_2 solubility in the seawater at the conditions prevailing in the system is required for the modeling of CO_2 release in the multi-stage flash distillers. The measurement of the solubility of CO_2 in pure water has been extensively studied in the literature, whereas there is a lack of saline solutions studies. Several studies have investigated the solubility of CO_2 in seawater under different temperatures and pressures without covering the conditions that prevailed in the desalination plants for example low pressures and high temperatures. The gas solubility can be theoretically estimated by considering the ionic strength and the salting-out parameter in the low-pressure regime, i.e., near atmospheric pressure. The measurements of gas solubility can be made as a function of the seawater temperature and salinity at low pressure where effect of pressure can be considered negligible. Alkaline scale formation causes fouling in the MSF plants and it is known that the rate of formation of calcium carbonate and magnesium hydroxide in seawater depends on a number of parameters such as temperature, pH, concentration of bicarbonate ions, rate of CO_2 release, concentration of Ca^{2+} and Mg^{2+} ions, and total dissolved solids. This review shows an overview of the carbon dioxide solubility in the high concentrated saline water, carbonate equilibriums in the seawater and the various correlations used to characterize the CO_2-seawater system.

Keywords: Desalination, salt separation, CO_2 solubility in seawater, carbonate equilibriums, fouling

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INTRODUCTION

The multi-stage flash (MSF) procedure is the most common technique for desalination, found mostly in the Middle East countries. The techniques worldwide capacity adds up to about 48 percent of the total number of bigger plants having a capacity greater than 4,000 m^3/day. Among other evaporation techniques, the multi-effect distillation (MED) may be mentioned here, either with vertical or horizontal smooth tubes or doubly fluted tubes. The vapor compression course is very popular for remote locations, resort areas, islands, etc. These two techniques, though not widely used, are promising as far as good water quality, simple application, reliability, and efficiency are concerned. Membrane processes, mainly reverse osmosis (RO), are currently the fastest-growing techniques in water desalination (1, 2). Challenges, however, still exist to produce desalinated water at affordable costs.

The presence of dissolved non-condensable (NC) gases in process water is a serious problem in thermal desalination of seawater, which can deteriorate the performance and efficiency of the whole desalination plant, and hence cause a cost increase in most commercial units. Even low concentrations of NC gases can significantly reduce the overall heat transfer coefficient and hence the performance of desalination evaporators. CO_2 dissolves in the condensate and lowers its pH value. In the presence of O_2, this may cause corrosion of the condenser tubes.

Also, the release of CO_2 from the evaporating brine in seawater distillers considerably influences concentrations of HCO_3^-, CO_3^{2-}, H^+ and OH^- ions in the carbonate system of the brine and thus plays an important role in alkaline scale formation. Furthermore, an accumulation of NC gases may disturb the brine flow through the flash chambers of multi-stage flash (MSF) distillers. Most often neither a deaerator nor a decarbonator is provided to alleviate the problem of NC gases that is caused by the leakage of ambient air through flanges, man-holes, instrumentation nozzles, etc. into the parts of the evaporator operating under vacuum and the release of dissolved gases from the evaporating brine. Molecularly dissolved gases such as O_2, N_2 can be removed by adequate venting. In contrast to that, CO_2 chemically reacts in seawater and is produced during the desalination process itself. Under the alkaline conditions prevailing in seawater only a small proportion of the total inorganic carbon content in seawater is present as molecular CO_2, the major proportion is chemically combined in HCO_3^- and CO_3^{2-} ions (3–8).

Literature data regarding solubility of CO_2 in different solvents and combinations thereof are rather abundant. However solubility in saline water at or near conditions prevailing in the thermal desalinations processes is lacking. Thus, considerable uncertainty exists in predicting the total CO_2 absorption or release rates in distillers. This study is essentially aimed at reviewing the solubility of CO_2 in the saline water under the conditions prevailing in the multi-stage flash evaporators, since the solubility of CO_2 in brine is an important parameter for modelling the behaviour of CO_2, especially on the production of the alkaline scales.

THEORY: CO_2 SOLUBILITY IN SEAWATER AND CARBONATE EQUILIBRIUM

Seawater is a complex mixture of ions and the major composition of seawater is controlled by a number of chemical reactions and physicochemical processes usually take place in seawater such as: acid-base reactions, gas absorption and desorption processes, precipitation and dissolution of solids and adsorption processes at interfaces. Characteristic for seawater is the high salinity that may vary between average limits of 7 g/kg (Baltic Sea) and 43 g/kg (Arabian Sea). The seawater pH is buffered by a set of reactions that take place between CO_2 and water, which is usually in the range from 7.7 to 8.3 in surface waters. Table 1 shows the composition of standard seawater with a salinity of 35 g/kg (7–11).

Carbon dioxide-carbonate system is certainly one of the most complex equilibrium systems and as CO_2 dissolves in seawater, it reacts with seawater to produce H^+ and various negatively charged forms of dissolved carbon. The carbonate system is a weak acid-base system, which exists in seawater results from the dissolution of carbon dioxide in seawater. Carbon dioxide first reacts with the water molecule (H_2O) to form carbonic acid (H_2CO_3). Not all the CO_2 dissolved in seawater reacts to make carbonic

Table 1. The composition of standard seawater with S = 35 g/kg, TA = 2.3×10^{-3} mol/kg and pH = 8.1 at 25°C

	Concentration		
Species	[$g \cdot kg^{-1}$ seawater]	[$mol \cdot kg^{-1}$ seawater]	Specific concentration [$g \cdot kg^{-1}$] $\cdot S^{-1}$
Na^+	10.78	0.469	0.308
Mg^{2+}	1.28	0.0528	0.0367
Ca^{2+}	0.412	0.0103	0.0118
K^+	0.400	0.0102	0.0114
Sr^{2+}	0.0079	0.00009	0.000227
Cl^-	19.35	0.546	0.553
SO_4^{2-}	2.71	0.0282	0.0775
HCO_3^-	0.107	0.00175	0.00306
Br^-	0.0672	0.00084	0.00192
CO_3^{2-}	0.016	0.00027	0.000459
$B(OH^-)_4$	0.0079	0.00010	0.000225
F^-	0.0013	0.000068	0.000037
$B(OH)_3$	0.0193	0.00031	0.000551
Σ	35.171	1.12	1.005

acid and therefore seawater contains dissolved gaseous CO_2. According to Henry's Law, in a simple aqueous solution it would be expected that the concentration of CO_2 in the air to be proportional to that in the solution of carbonic acid. Carbonic acid will split up into its constituents, releasing an excess of H^+ to solution and so driving pH towards lower values. Carbonic acid splits up by adding one H^+ to solution along with HCO_3^- (a bicarbonate ion), this increase in H^+ causes some CO_3^{2-} (carbonate ion) to react with H^+ to become HCO_3^-. Thus, the net effect of the dissolution of CO_2 in seawater is to increase concentrations of H^+, H_2CO_3 and HCO_3^-, while decreasing concentrations of CO_3^{2-}.

The decrease in carbonate ion concentration $[CO_3^{2-}]$ has important consequences for the formation and dissolution of carbonate minerals. Because the dissolution of CO_2 in seawater decreases $[CO_3^{2-}]$, this reaction will lead to impeding the formation of carbonate minerals and promoting their dissolution. Dissolution of carbonate minerals provides carbonate ions that can react to consume H^+, thus, the dissolution of carbonate minerals tends to decrease $[H^+]$ (increase pH), counteracting some of the pH effects of added CO_2. As a consequence of these reactions it is often necessary to consider all three phases, aqueous, gas and solid, in order to describe the response of the system to external influences (12–15).

Many investigators such as (6, 7, 9, 10, 12, 13, 16, 17) have given an overview of the carbonate system in seawater and they have summarized the following, the solubility of CO_2 in seawater, the chemical equilibriums, the mechanisms, the orders and the rates of reactions involved in CO_2 release. Also, they described the effects of temperature, pressure and ionic strength on the solubility, the chemical equilibriums and the reaction rates. To accurately predict the amount of CO_2 released at high temperatures in the desalination plants there is a real need for experimental data of CO_2 solubility in seawater at high temperatures. Since, CO_2 solubility data in seawater at high temperatures is obtained usually by extrapolating and fitting a limited set of experimental data obtained at 40°C or by using models to calculate CO_2 solubility coefficient in water at high temperatures and assuming that the seawater has no effect on the CO_2 dissolution.

The solubility of CO_2 in seawater occur as a result of a number of reactions taking place when carbon dioxide dissolves in seawater (8, 11, 13, 18). In the presence of gaseous CO_2, The dissolved CO_2 exchanges with CO_2 gas can be represented by series of equilibriums. Henry's law describes only the physical equilibrium between the phases and may only be applied to the fraction of the gas that is molecularly dissolved and not chemically bound (19–24). Henry's law coefficient depends on the type of the gas and the solvent, the temperature, the total pressure and in case of salt solutions it also depends on the ionic strength of the solution. Gas solubility in salt or electrolyte solutions is usually smaller than the gas solubility $K_{G,o}$ in pure water (salting-out effect). The effect of the molar salt concentration c_s can be described in the form of Setchenow equation (25). Danckwerts (20) related the Henry's law coefficient in the salt solution to that in water at the same temperature on the basis of a method originally proposed by Setchenow (8). Furthermore, the activity coefficient of CO_2 in seawater can be considered as the ratio of its solubility in water to the CO_2 solubility in seawater. The application to the solubility of CO_2 in seawater has lead to the formulation of an empirical correlation which is shown elsewhere (26–28).

Yasunishi and Yoshida (29) determined the solubility of CO_2 in aqueous solutions of 16 electrolytes and found that the empirical Setchenow equation was not applicable to some electrolyte systems. But researches (26–28) research presented an empirical model for the prediction of gas solubilities in electrolyte solutions which described the data with greater accuracy, the observed influence of the salt type on the gas specific part of the Setchenow constant was considered in their model. The model presented in (27) has a simple structure and is consistent when applied to mixed electrolyte solutions. The parameters values evaluated for this model allowed to estimate the effects of 20 cations and 19 anions on the solubilities of 15 gases including CO_2, further work was carried out by (28) to study the effect of temperature on the model and they extended the model to the temperature range of 273 K to 363 K, and assumed that the gas-specific constant to be linear function of the temperature. This model was used to evaluate Setchenow constants for different gas/salt/temperature combinations in the range of 273 K to 363 K, and they observed linear decrease of the Setchenow constant with temperature in most cases.

The ionic strength can be related to salinity S and as it is known that NaCl is the main constituent of seawater and it accounts for 73% of seawater ionic strength, the ion specific parameters of Na^+ and Cl^- are the only considered parameters.

Teng et al. (22), presented a theory of CO_2-gas solubility in seawater, and in their paper they investigated the CO_2-water binary system and CO_2-gas solubility in seawater. They carried out a complete mathematical derivation of the CO_2-water binary system, and CO_2-gas solubility in seawater, and they have obtained an expression to calculate the solubility coefficient for the CO_2-water binary system and CO_2-gas solubility in seawater similar to that obtained by (30). The solubility of CO_2 in seawater was measured by (30–33). The latter work of (30) supported the accuracy of the measurements of (31) and led to the formulation that is used to calculate Henry's law constant, K_o for seawater as a function of salinity (S) and temperature (T, K). This equation is derived from the integrated van't Hoff equation and the logarithmic Setchenow salinity dependence, and ‰has the form given by (30):

$$\begin{aligned}\mathrm{Ln}K_o &= -60.24 + 93.45\ (100/\mathrm{T}) + 23.36\ \mathrm{Ln}\,(\mathrm{T}/100) \\ &\quad + S‰\,[0.0235 - 0.0236\ (\mathrm{T}/100) + 0.0047\ (\mathrm{T}/100)^2] \quad (1)\end{aligned}$$

All of these measurements were made on acidified seawater equilibrated with pure CO_2, and with a certain temperature range and salinity range ($T = 0$ to

40°C and $S‰ = 0$ to 40). The extrapolation of Equation (1) for higher temperatures and salinities doesn't give reliable results. The more recent measurements of (34) indicate that the K_o measurements by (30) are consistent with their K_oK_1 measurements to ± 0.0003 in log K_o.

Since the extrapolation of equation (1) for higher temperatures and salinities doesn't give reliable results, many researchers such as (5) determined Henry's law coefficient of CO_2 in the brine by using equation (5) and using the correlation for Henry's law coefficient in pure water given by (35), which is valid up to 334°C:

$$\mathrm{Ln}K_{G,o} = 108.38 + 0.0198\mathrm{T} - 6919/\mathrm{T} - 40.45\log\mathrm{T} + 669000/\mathrm{T}^2 \quad (2)$$

However, Duan and Sun (36) proposed a more recent thermodynamic model for the solubility of carbon dioxide in pure water and in aqueous NaCl solutions for temperatures from 273 to 533 K, for pressures from 0 to 2000 bar. Their CO_2 solubility model was based on the equation of state (EOS) of Duan et al. (37) and the theory of Pitzer (38, 39):

$$\begin{aligned}\mathrm{Ln}\, m_{\mathrm{CO2}} = {} & \mathrm{Ln}\, y_{\mathrm{CO_2}}\, \varphi_{\mathrm{CO_2}}\, P - \mu^{l(0)}_{\mathrm{CO_2}}/\mathrm{R}T \\ & - 2\lambda_{\mathrm{CO_2-Na}}(m_{\mathrm{Na}} + m_K + 2m_{Ca} + 2m_{mg}) \\ & - \zeta_{\mathrm{CO_2-Na-Cl}} m_{cl}(m_{\mathrm{Na}} + m_{\mathrm{K}} + m_{\mathrm{mg}} + m_{\mathrm{Ca}}) + 0.7m_{SO4} \quad (3)\end{aligned}$$

where, m molality of CO_2 or salts in the liquid phase, T absolute temperature in Kelvin, P total pressure $= P_{\mathrm{CO_2}} + P_{\mathrm{H_2O}}$ in bar, y mole fraction of CO_2 in vapor phase, R universal gas constant; $=0.083145\ \mathrm{bar\ L\ mol^{-1}\ K^{-1}}$, φ fugacity coefficient, μ chemical potential, $\lambda_{\mathrm{CO2\text{-}ion}}$ interaction parameter, $\zeta_{\mathrm{CO2\text{-}Na\text{-}Cl\text{-}cation\text{-}anion}}$ interaction parameter in v vapor, l liquid, 0 standard state and aq aqueous solution. The Duan and Sun (36) model was able to predict CO_2 solubility in seawater-type brine and compared to experimental data obtained by Murray and Riley (32) with great accuracy (only 3% deviation from experimental data). But, this model relies on a complex virial EOS that needs to be solved iteratively.

Solubility of gases in the seawater is a function of their molecular weight, temperature and salinity, Table 2 (6, 8, 11) shows the concentrations of the gases dissolved in seawater with a salinity of 35 g/kg in equilibrium with the atmosphere at 25°C and from this table we can see that CO_2 is more soluble than O_2, N_2 and Ar. The Henry's law coefficient of CO_2 decreases with increasing temperature passes through a minimum at 170°C and increases again. The Henry's law coefficient also decreases with increasing salinity. The effect of salinity is less obvious at high temperatures.

The dissociation of H_2CO_3 in water, the dissociation of water obeys the equilibrium conditions and are important parts of carbonic acid equilibria (8, 11, 13, 18), Where, the equilibrium conditions are quantified by the

Table 2. Solubility data of the gases dissolved in seawater with S = 35 g/kg in equilibrium with the atmosphere at 25°C

Gas	Partial pressure in atmosphere [bar]	Henry's law coefficient [mol/(m^3 bar)]	Concentration in seawater [μmol/kg SW]	[mg/kg SW]
Co_2	0.00033	29.3	9.45	0.4
N_2	0.7808	0.5	383.4	10.7
O_2	0.2095	1.0	206.3	6.6
Ar	0.00934	1.1	10.11	0.4

dissociation or acidity constants:

$$K_1 + [H^+][HCO_3^-]/[H_2CO_3] \tag{4}$$

$$\text{and } K_2 + [H^+][CO_3^{2-}]/[HCO_3^-] \tag{5}$$

$$H_2O \longleftrightarrow H^+ + OH^-, \quad \text{where; } K_W + [H^+][OH^-] \tag{6}$$

The carbonate system in seawater is characterised by the interaction of major cations (Na^+, Mg^{2+}, Ca^{2+} and K^+) and major anions (Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}). These interactions can be described in terms of an ion association formalism and, more recently, in terms of a specific interaction theory (6, 8, 9, 11, 40).

$$Na^+ + CO_3^{2-} \longleftrightarrow NaCO_3^-, Ca^{2+} + HCO_3^- \longleftrightarrow CaHCO_3^+,$$
$$Mg^{2+} + OH^- \longleftrightarrow MgOH^+ \tag{7}$$

$$H^+ + SO_4^{2-} \longleftrightarrow HSO_4^-, H^+ + F^- \longleftrightarrow HF \tag{8}$$

Additionally insoluble calcium carbonate and magnesium hydroxide can be formed (41, 42). Figure 1, was presented by (8) and showed a schematic representation of the carbonate system in gas, liquid and solid phases.

The dissociation constant of water, the stoechiometric equilibrium constant of water in seawater K_w^{sw} can be expressed as:

$$K_w^{sw} = K_w/(\gamma^{sw}H + \gamma^{sw}OH^-) = [H^+]^{sw}[OH^-]^{sw} \tag{9}$$

Culberson and Pytkowicz, Dickson and Riley, Hansson and Mehrbach et al. (43–46) measured the equilibrium constant of water in seawater for temperatures up to 35°C and salinities up to 44 g/kg. Another correlation to calculate the equilibrium constant of water in seawater K_w^{sw} can be found in reference (44).

Basically all values of solubility and dissociation constant are temperature dependent. However, the K values also depend on the solute concentrations, because the formation of ion complexes between the carbonic ions

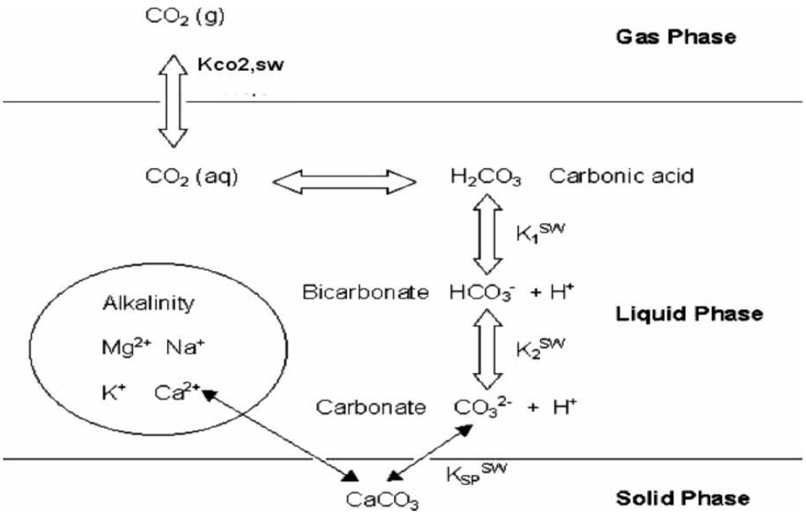

Figure 1. Schematic representation of the carbonate system.

and molecules and ions in the solution hinder the dissolved carbonic molecules and ions to take part in the thermodynamic equilibrium reactions. Therefore, in the thermodynamic equation, the concentrations have to be replaced by their activities that are smaller than the concentrations. The thermodynamic solubility constant is:

$$K_o = \gamma_a[H_2CO_3]/P_{CO_2} \tag{10}$$

where, in general the activity coefficients $\gamma > 1(\gamma = 1$ for an ideal solution, i.e., with zero solute concentrations or zero ionic strength).

In the non-ideal solutions of seawater and brackish water it is more practical to describe the relation between the real, measurable concentrations by the apparent solubility constant. Full details of the correlations to calculate the solubilities and dissociation constants are given by Fig. 2 and can be cited elsewhere (6, 13, 15, 17, 47).

For practical reasons the values of the dissociation constants are generally given as: $pK = -{}^{10}\log\ K\ or\ K = 10^{-\mathrm{pK}}$. Many investigators such as (34, 44–46, 48–51) presented Various correlations of the dissociation constants K_1^{sw} and K_2^{sw} of carbonic acid in seawater. (7, 47, 52, 53) investigated the parameters used to study the carbonate system such as pH, Total alkalinity (TA), f_{CO2} (fugacity) and $T\mathrm{CO}_2$, since combination of at least two of these parameters is needed to characterize the carbonate system. Millero (7) suggested two correlations for calculating the stoichiometric dissociation constants $K_1^{sw}$and K_2^{Sw} and these correlations

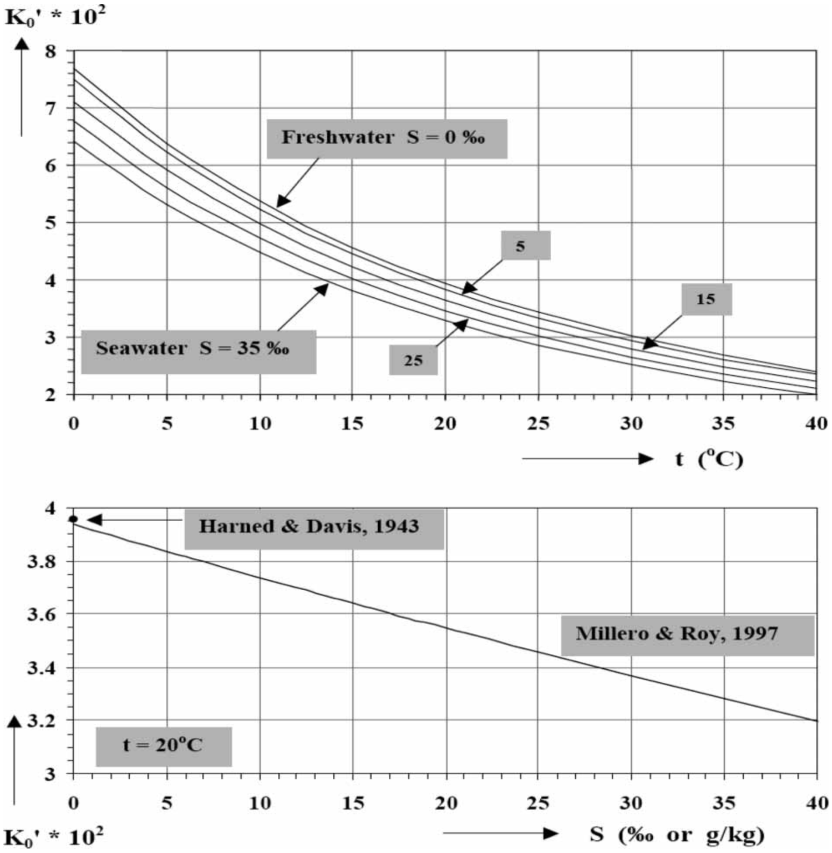

Figure 2. The solubility constants (=solubilities in M/L.atm) for CO_2 in freshwater, seawater and brackish water as a function of temperature at salinities of 0, 5, 15, 25, and 35‰ (=g of salt per kg of water) (upper graph) and as a function of salinity at 20°C (lower graph). All values are according to (7, 94), at higher salinities similar to (30) (Eq. (7); the values for freshwater are similar to those of (95).

are based on the experimental data of (34, 49):

$$\begin{aligned}\text{Ln } K_1^{sw} &= 2.189 - 2275/\text{T} - 1.4691\text{Ln T} + (-0.138 - 9.333/\text{T})\ \text{S}^{0.5} \\ &\quad + 0.0726\text{S} - 0.00574\text{S}^{1.5} \qquad (11)\end{aligned}$$

$$\begin{aligned}\text{Ln } K_2^{Sw} &= -0.842 - 3741/\text{T} - 1.437\ \text{Ln T} + (-0.128417 \\ &\quad - 24.41239/\text{T})\text{S}^{0.5} + 0.1195\text{S} - 0.00913\text{S}^{1.5} \qquad (12)\end{aligned}$$

where, K_1^{sw} and K_2^{Sw} are on the basis mol/kg seawater, T is in K and S is in g/kg. Figures 3 and 4 show the change of the acidity constants with temperature.

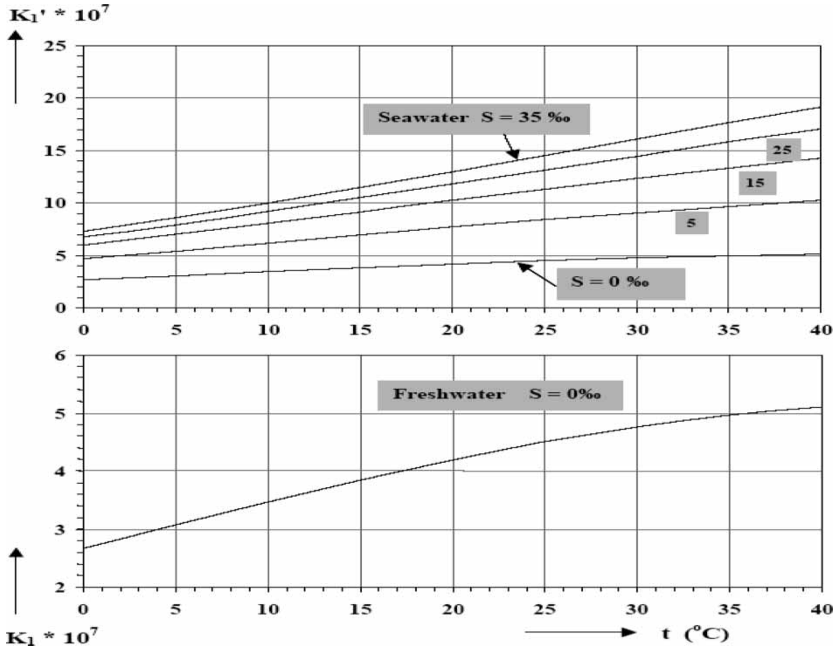

Figure 3. The acidity constants for the first dissociation of carbonic acid in freshwater and seawater as a function of the water temperature at salinities of 0, 5, 15, 25, and 35‰. The values are according to (7, 94). The freshwater values are equal to those of (95), the marine values are in good agreement with those reported by (46) as discussed by (48).

Figure 1 shows the solubility constants (=solubilities in M/L · atm) and stoichiometric dissociation constants K_1^{sw} and K_2^{Sw} for CO_2 in freshwater, seawater and brackish water as a function of temperature and salinities.

Because sea water has high ionic strength, then the ionic strength can be related to salinity, S, and as it is known that NaCl is the main constituent of seawater and it accounts for 73% of seawater ionic strength, the ion specific parameters of Na^+ and Cl^- are the only parameters considered. The activity coefficients in reality are complex functions of the composition of the aqueous solution and it is central to the description of the chemical behavior of the ions dissolved in seawater. In electrolyte solutions, the activity coefficients are influenced mainly by electrical interactions. Much of their behavior can be correlated in terms of the ionic strength, defined by:

$$I = 1/2 \sum z_i^2 m_i \tag{13}$$

In general, model equations that express the dependence of activity coefficients on solution composition only in terms of the ionic strength are restricted in applicability to dilute solutions. Al-Rawajfeh (8) has summarized the

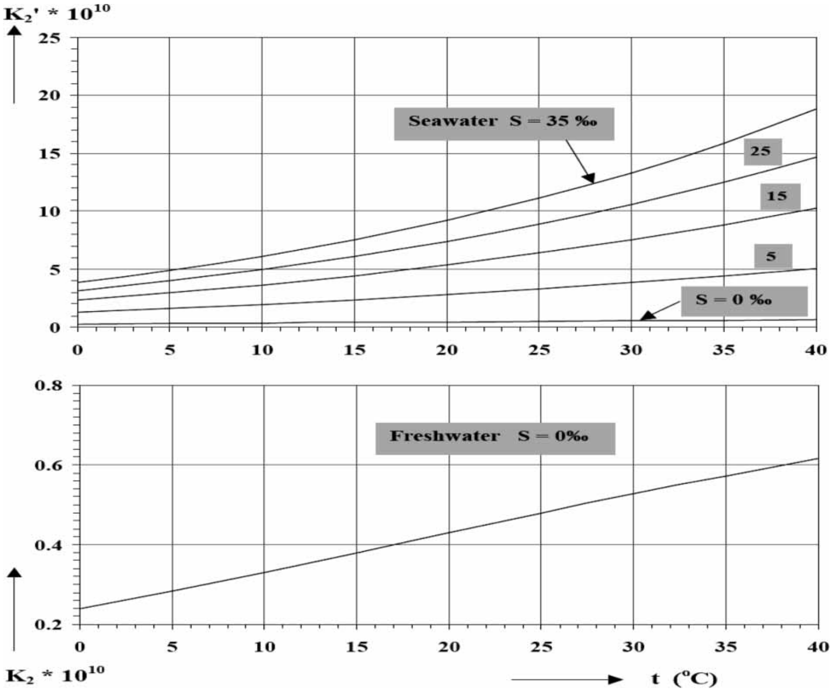

Figure 4. The acidity constants for the second dissociation of carbonic acid in freshwater and seawater as a function of the water temperature at salinities of 0, 5, 15, 25, and 35‰. The values are according to (94). The freshwater values are equal to those of (95), the marine values are in good agreement with those reported by (46) as reported by (48).

theoretical expressions for the activity coefficients in Table 3 (6, 12, 19, 25, 54–59). Figure 5 shows the variation of the acidity constants with salinity.

Many researchers such as (8, 60) have used the Davies equation to describe the concentration dependence of activity coefficients:

$$\text{Log}\,\gamma_i = -A_\gamma z_i^2[(\sqrt{}I/(1+\sqrt{}I)) - 0.2I] \qquad (14)$$

It should be noted that many other workers have replaced the value of 0.2 with 0.3 value. The Davies equation is normally only used for temperatures close to 25°C. It is only accurate up to ionic strengths of a few tenths molal in most solutions. With *zi* as the charge of the ion and (61) presented an interpolation formula to calculate A the Debye-Hückel constant:

$$A = 0.4819 + 0.0011T \qquad (14a)$$

where T is the temperature in °C, which is valid for $I < 0.5$ mol/kg, has the advantage that it needs no adjustable ion size parameter. The Davies equation (21) is used in many of the chemical equilibrium systems because

Table 3. Expressions for activity coefficients with z_i as the charge of the ion, A as the Debye-Hückel parameter which depends on the dielectric constant of the solvent and on the temperature

Approximation	Equation	Applicability
Debye-Hückel	$\log\gamma_i = -A\, z_i^2 \sqrt{I}$	$I < 0.005$ mol/kg
Extended Debye-Hückel	$\log\gamma_i = -A\, z_i^2 \sqrt{I}/(1+B\, a_i\sqrt{I})$	$I < 0.1$ mol/kg
"WATEQ"-Debye-Hückel	$\log\gamma_i = -A\, z_i^2 \sqrt{I}/(1+B\, a_i\sqrt{I}) + b_i I$	$I < 1$ mol/kg
Davies	$\log\gamma_i = -A\, z_i^2(\sqrt{I}/(1+\sqrt{I}) - 0.21)$	$I < 0.5$ mol/kg
Güntelberg	$\log\gamma_i = -A\, z_i^2 \sqrt{I}/(1+\sqrt{I})$	$I < 0.1$ mol/kg useful for mixed electrolytes

For water at 25°C $A = 0.509\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$; B as temperature-dependent parameter; a_i and b_i as ion specific parameters.

of its simplicity. In this version of the Debye-Hückel equation, a simple term, linear in I, was added at the end of the equation. This term improves the empirical fit to higher ionic strength but it has no theoretical justification (8, 58, 60, 62, 63). The activity coefficients for seawater ($I = 0.72$ mol/kg)

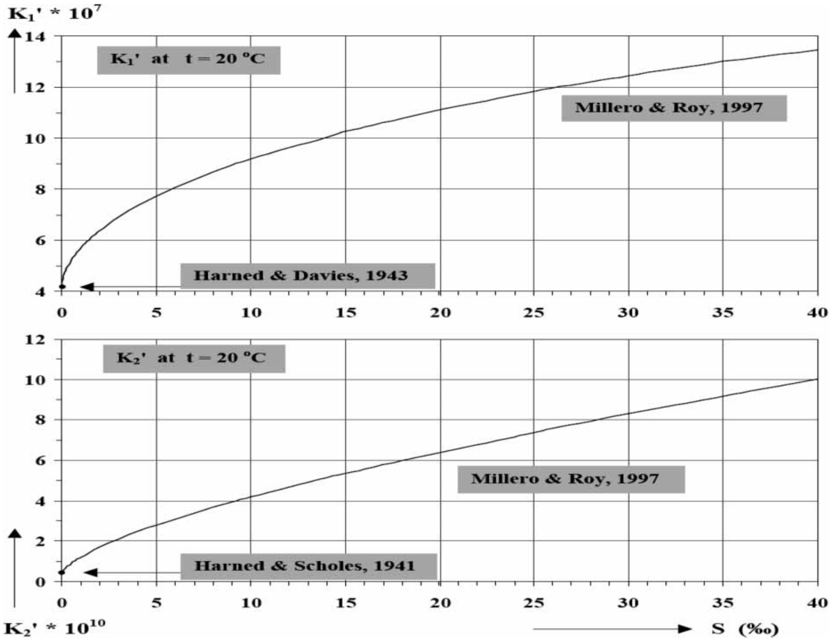

Figure 5. Values for the first and second dissociation constants of dissolved carbonic acid as a function of the salinity. The values are valid for a water temperature of 20°C. Values for the first and second dissociation constants of dissolved carbonic acid as a function of the salinity (7, 94).

Table 4. Activity coefficients for some species in seawater (S = 35 g/kg) at 25°C

	Activity coefficient in seawater (I = 0.72 mol/kg)	
Species	Loewenthal and Marias [Loe84]	Davies equation [Dav38]
Na^+	0.693	0.69
Ca^{2+}	0.248	0.23
HCO_3^-	0.669	0.69
CI^-	0.649	0.69
CO_3^{2-}	0.203	0.23
CO_2	1.17 [Mil96]	

are for monovalent ions $\gamma_i = 0.69$, for divalent ions $\gamma_i = 0.23$ and for trivalent ions $\gamma_i = 0.04$ (Table 4). Loewenthal and Marais (15) concluded that these values are realistic even though seawater ionic strength is outside the valid range of this equation.

The reaction kinetics of the CO_2 solubility in seawater has a very important influence on the oceanic system and many authors such as Johnson (64) reported measurements of the hydration and dehydration rate constants (K_{CO_2}, K_{OH^-}, K_d, $K_{\overline{HCO}_3}$) of carbon dioxide in seawater and compared the results with other determinations in dilute solutions. Also, Johnson (64) examined the salinity dependence of the rate constants in terms of transition state theory and the rate constants for hydration and dehydration of CO_2 corrected to infinite dilution at 25°C using certain equations that can be sited in the same paper (64). Other studies were done by other authors such as (6, 12, 33, 65–68) described the reaction mechanisms and reaction rates of the hydration and dehydration of CO_2 in aqueous bicarbonate-carbonate solutions. These studies have presented parallel reaction mechanisms and many correlations to calculate the reaction rate constant and reaction time.

The carbonate system in seawater have been described by (6, 7, 13, 51, 52, 69–72) by the following six quantities:

1. Concentration of dissolved CO_2 $[CO_2]$
2. Concentration of bicarbonate ions $[HCO^{3-}]$
3. Concentration of carbonate ions $[CO_3^{2-}]$
4. *pH* value or concentration of H^+ ions $[H^+]$ or concentration of OH^- ions $[OH^-]$, For seawater samples, three pH scales have been proposed (seawater scale, total proton scale, and free proton scale) that can be sited elsewhere (59, 73–75)
5. Total carbon dioxide content *TC*:

$$TC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] + [H_2CO_3] \qquad (15)$$

6. Total alkalinity, *TA*:
   The alkalinity is a practical quantity, following from the conservation of electroneutrality in solutions where the metal-ion concentrations (Na, Ca, Mg) and pH are constant, the concentration of all bases that can accept a proton when seawater is titrated to the pH end point of carbonic acid:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [\text{other weak acid anions}] \tag{16}$$

in which concentrations of other weak acids may be included in the interest of high precision, such as humic acids in freshwater or borate, $[B(OH)_4^-]$, in seawater. Alkalinity and total carbon dioxide are both conservative properties (i.e., salinity is conservative).

Figure 6 illustrates the proportion of the different ions obtained when CO_2 dissolved in seawater at different pHs, salinities and temperatures. Stumm and Morgan (40) related the total alkalinity, TA, to chlorinity, Cl, and it is known

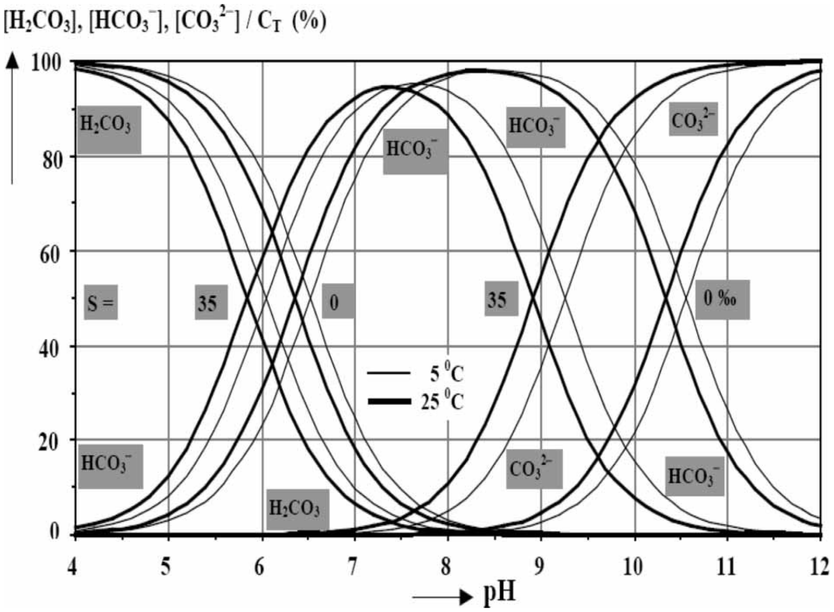

Figure 6. Distribution of the carbonic acid fractions as a percentage of the total carbon content, C_T. The values are calculated at temperatures of 5 and 25°C and for salinities of 0 and 35‰ as a function of the pH. Seawater has pH values around 8.2. However, the carbon distributions are shown for an (unrealistic) wider range of pH values, to illustrate the dependence of the carbon distribution on salinity (7, 94, 96).

that TA and TC vary as a result of any changes in salinity due to mixing, evaporation or dilution, so to remove these variations (17) presented the normalized values, NTA and NTC, which are defined as follows:

$$\mathrm{NTA} = \mathrm{TA} \times (35/\mathrm{S}) \tag{17}$$

$$\text{and } \mathrm{NTC} = \mathrm{TC} \times (35/\mathrm{S}) \tag{18}$$

with NTA, NTC, TA and TC in mol/kg and S in g/kg.

FOULING, ALKALINE SCALE FORMATION AND SOLUBILITY PRODUCT OF CALCIUM CARBONATE

Fouling is the accumulation of undesired solid materials at the phase interfaces. Buildup of fouling film leads to an increase in resistance and deteriorates the performance of process equipment such as membranes and heat exchangers and is costing industries billions of dollars annually. One of the major fouling phenomena encountered in the aqueous systems is scale formation due to precipitation of salts present in the water. Alkaline scale formation in seawater distillation occur as a result of the decomposition hydrolysis of seawater bicarbonate ion as process temperature is increased (76). In real-life situations, scale deposits are formed mainly through thermal effects, in fact, heating of the water has the consequence that carbon dioxide solubility decreases, carbon dioxide released, pH increases and finally alkaline scale such as calcium carbonate precipitates according to equation (19).

Berthold and Rafal et al. (59, 77) developed a computer software to simulate and predict the behavior of electrolyte systems, they based their calculations on chemical electrolyte approach. The commercial name for this software is OLI electrolyte software which is today the industry-leading tool for both phase/solution equilibria and prediction of scaling tendencies. Table 5, shows examples of the OLI electrolyte applications (59, 77).

Multi-stage flash (MSF) plants usually operate at temperatures as high as 120°C, and multiple effect evaporation (MED) plants operate at temperatures lower than 70°C. Consequently, the major risk of scaling is for minerals whose solubility decreases with increasing temperature. The mostly observed scales that occur in multistage flash (MSF) distillers are found to be either $CaCO_3$ or $Mg(OH)_2$. The two are commonly referred to as alkaline scale. The formation of the alkaline scales $CaCO_3$ and $Mg(OH)_2$ strongly depends on temperature, pH, the release rate of CO_2 as well as the concentrations of HCO_3^-, CO_3^{2-}, Ca^{2+}, and Mg^{2+} ions, and on the metal cations and anions that exist naturally in the water (2, 4, 70, 78–84).

Al-Sofi (4) made an attempt based primarily upon visual and reported observations of fouling in various parts along the flow path of brine solutions in MSF distillers and proposed certain sequence of scale forming reaction steps, also suggested certain experiments that could verify the

Table 5. Examples of OLI electrolyte applications

- Emergency chlorine scrubber
- Caustic wash tower
- Acid stream neutralization
- Manufacture of KF
- Dynamic pH control
- Removal of fluoride ions from waste water
- Scrubbing refinery process streams with DEA
- Chlor-alkali brine treatment
- Ahlstron NSSC "Stora" process
- Tower scale control
- Foul feed stripper
- Multi-effect evaporator
- Cooling tower
- Coke oven gas
- Ammonia still
- Organic acid removal in brines
- BTEX stripper
- MSF desalination plant
- Removal of chlorobenzene with Biological treatment
- Dregs washer and clarifier
- CO_2 corrosion
- Corrosion rates in acids
- Inhibitor squeeze in oil/gas reservoirs
- Corrosion in LiBr refrigeration brines
- Thermodynamic analysis of corrosion inhibitors
- Electrostatic precipitator separation H_2S/CO_2 corrosion productsunder gas pipeline conditions
- Hazzardous waste deep well disposal
- Contaminated groundwater management

validity of his proposed reaction mechanism. Meanwhile, the presence of hydroxyl ions will be short lived primarily due to the formation of $Mg(OH)_2$. The proposed steps support $CaCO_3$ precipitation ahead of $Mg(OH)_2$. The abundance of magnesium ions and the extreme low solubility of magnesium hydroxide will rapidly then lead to its formation. However, scale precipitation inside tubes are not only from initial scale formation under pressure inside the tubes but also due to nucleates recirculation from flash chambers back into heat gain exchanger tubes because of brine recycling. Recent analysis of variation in coloration of water boxes came as a strong support to this hypothesis. It is worth noting that the end results of various reaction mechanisms are almost the same in the cited ones also the same to the proposed overall reaction.

The authors of these two studies (76, 85) concluded that scaling occur as a result of the thermal decomposition of bicarbonate ions (HCO_3^-) at high temperatures (above 45°C). This causes the precipitation of $CaCO_3$ once its solubility limits are reached and the presence of the resulting OH^- ions will lead to the precipitation of $Mg(OH)_2$. El-Dahshan (85) also concluded that pitting corrosion and fatigue were attributed to the oxygenated carbonic acid which occur because of the presence of the non-condensable gases such as CO_2.

A number of other studies were done by (3, 8, 42, 86) to analyze scale formation in seawater distillers which is mainly caused by crystallization of the inversely soluble salts calcium carbonate, magnesium hydroxide, and calcium sulfate. The release of CO_2 from the evaporating brine shifts the pH to higher values and considerably influences the concentrations of HCO_3^- and CO_3^{2-} ions in the brine. Thus, it plays an important role in alkaline scale formation. CO_2 release and alkaline scale formation in seawater distillers are closely related to the carbonate system in the brine. Researchers (3) proved that the model developed by (3, 8, 18, 70, 86) is very useful to calculate the CO_2 release rates and the HCO_3^-, CO_3^{2-}, CO_2, H^+, and OH^- concentrations in the brine on its flow path through multiple-effect distillers. It is known that $CaCO_3$ formation results in the release of CO_2 according to the following reaction:

$$Ca^{2+} + 2HCO_3^- \longleftrightarrow CaCO_3(S) + CO_2 + H_2O \tag{19}$$

Many researchers such as (87) conducted studies on the removal of alkaline scale from the industrial desalination plants by acidification. Ellis et al. (87) in their work injected carbon dioxide in the desalination boilers at high temperatures and monitored the pH and scale composition. The results of this work showed that as more carbon dioxide was injected the formation of alkaline scale such as $CaCO_3$ and $Mg(OH)_2$ was reduced but this technique has not, however, been applied on large-scale plants.

Whereas, Azaroual et al. (88) presented a thermokinetic geochemical calculation program (SCALE2000) based on Pitzer's ion interaction model, which can take into account the fluid flow effect using a specific approach based on a scheme of serially connected homogeneous reactors. According to the authors (60, 88) SCALE2000 is well adapted to perform scaling risk prediction applied to industrial desalination facilities and the authors tested the reliability of the SCALE2000 results against measurements of individual mineral solubility and kinetics data derived from the literature. Calcium carbonate $CaCO_3$ dissolves according to the following equation:

$$CaCO_{3(S)} \longleftrightarrow Ca^{2+} + CO_3^{2-} \tag{20}$$

The solubility product of calcium carbonate is given by

$$K_{sp}^{sw} = K_{sp}/(\gamma^{sw}Ca^{2+}\gamma_{CO_3^{2-}}^{sw}) = [Ca^{2+}]^{sw}\ [CO_3^{2-}]^{sw} \tag{21}$$

where K_{SP} is the thermodynamic solubility product and $[i]^{SW}$ and γi^{SW} are the concentration and the activity coefficient of the component i, respectively. K_{sp}^{sw} of calcite and aragonite, respectively, can be calculated from correlations reported by (48, 84, 88–90) for a salinity between 5 and 45 g/kg and a temperature between 5 and 40°C at 1 atm total pressure. K_{sp}^{sw} values increase with pressure and salinity but decrease with temperature. At $T = 30°C$, $S = 60$ g/kg and $p = 10$ bar, the values of K_1^{sw}, K_2^{Sw} and K_w^{sw} differ from the values at 1 bar by 1%, 0.3% and 0.3%, respectively (12). K_{sp}^{sw} differs from the values at 1 bar by 0.3%. Thus, for small and moderate pressures, the pressure dependence of the equilibrium constants can be neglected.

VAPOR-LIQUID EQUILIBRIUM AND GAS SOLUBILITY APPARATUS PREVIOUSLY USED

Many researchers have tested different experimental equipments to measure the gas solubility in alkaline and saline solutions under different experimental conditions. Yasunishi et al. (29) and Tokunaga, (91) used an apparatus that comprised from an absorption chamber, gas burettes, manometer and a stirrer of magnet coated with glass inside. They determined the solubility of CO_2 in aqueous solutions of 16 electrolytes by using the gas volumetric method at 1 atm (1 bar) and temperatures of 15, 25, and 35°C. They evaluated the CO_2 solubility by the Ostwald coefficients, L and concluded that the empirical Setschenow equation was not applicable to some systems. The data of those systems were correlated by a two-parameter equation within a deviation of 2%. A bubble column reactor has been designed by (92) to study the uptake of gas in liquid and they concluded that this technique has an applicability wider than the determination of solubilities and simple reaction rates. The device, for example, has a unique utility in studying interactions at the gas-liquid interface.

However, others such as (47) designed an apparatus that consisted of an equilibrator and vacuum extraction system to achieve complete and stable thermodynamic equilibrium of CO_2 between the gas and solution phases in a closed system and to provide for sampling of the gas and solution without disturbing the equilibrium. The partial pressure of carbon dioxide in the ocean's surface waters, precisely expressed as the fugacity $f CO_2$ is determined from dissolved inorganic carbon DIC and total alkalinity TA.

A PVT apparatus was designed by (93), where they employed a technique for liquid sample withdrawal and shown to provide accurate and reproducible gas solubility measurements at temperatures up to 200°C and pressure up to 10 MPa. They found that CO_2 solubility is slightly lower in a 1 wt % NaCl solution than in pure water due to the salting-out effect.

It is clear from the previous studies conducted on the CO_2 solubility in alkaline solutions that there are many more different designs of gas solubility equipments that can be used for the measurement of CO_2 absorption in alkaline and saline solutions. If a study of CO_2 solubility is to be carried out for conditions similar to those in MSF plants, careful consideration should be taken into account for the effect of temperature, pressure, salinity, and pH.

CONCLUSIONS

The resulting survey of the literature has shown that there are different models to measure the solubility of CO_2 in seawater under different conditions and many workers have suggested certain reaction mechanisms trying to better understand the reaction kinetics that takes place in these conditions. Generally, the solubility of a gas in water decreases as the water warms and it is known that high temperature conditions usually encountered in desalination plants. Due to high temperatures encountered in the desalination plants pH rise caused by the carbon dioxide loss, involves alkaline scale formation for example, calcium carbonate precipitation.

In the MSF desalination plants fouling occur as a result of CO_2 release and alkaline scale formation in seawater distillers. Therefore, there is a need for in-depth knowledge of solubility of CO_2 in seawater.

NOMENCLATURE

A	Debye-Hückel constant
aq	dissolved phase
c_i	concentration of the ion, i (kmol/m^3)
Cl	chlorine content (g/kg)
g	gaseous phase
h	summation of ion specific parameters of the positive ions *(h+)*, negative ions *(h−)* and the gas specific parameter *(hG)*
h_i	ion-specific parameter (m^3/kmol)
h_G	gas-specific parameter (m^3/kmol)
H_G	gas-specific part of the Setchenow constant (m^3/kmol)
I	ionic strength (mol/kg)
K_1	first dissociation or acidity constants
K_2	second dissociation or acidity constants
K_{CO2},K_{OH-}, K_d & $K_{\overline{HCO3}}$	rate constants for the hydration and dehydration steps of CO_2 in seawater
K_W	thermodynamic equilibrium constant of water
K_w^{sw}	stoichiometric equilibrium constant of water in seawater (mol/kg seawater)
K_o & K_G	gas solubility coefficient in salt solution (mol L^{-1} atm^{-1}) or (moles kg^{-1} atm^{-1})
$K_{G,o}$	gas solubility in water (moles kg^{-1} atm^{-1})
$K_{G,o}/K_G$	ratio of the gas solubility in water to that in a salt solution
mi	molality of the ion, i
$n_i = c_i/c_s$	index of ion, i
P_{CO_2}	atmospheric CO_2 partial pressure, P_{CO2}(atm)
S	salinity of the seawater (g/kg)
T	system temperature (°C or K)
TA	total alkalinity (mol/kg)
TC	total carbon dioxide content
zi	charge of the ion, i
$[i]^{sw}$	concentration of the component, i
$[H_2CO_3]$	dissolved CO_2 concentration in mol/kg of water

Greek Letters

$\gamma_{co2,sw}$	activity coefficient of carbon dioxide
γ_i^{sw}	activity coefficient of the component i that is free or involved in ion pairing

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REFERENCES

1. Semiat, R. (2000) Desalination: Present and future. *Water Intl.*, 25 (1): 54–65.
2. Quteishat, K., Abu Arabi, M.K., and Reddy, K.K. (2003) Review of MEDRC R&D projects. *Desalination*, 156: 1–20.
3. Al-Rawajfeh, A.E., Glade, H., and Ulrich, J. (2005) Scaling in multiple-effect distillers: the role of CO_2 release. *Desalination*, 182: 203–213.
4. Al-Sofi, M.A. (1999) Fouling phenomena in multi stage flash (MSF) distillers. *Desalination*, 126: 61–76.
5. Glade, H. and Genthner, K. (2000) The problem of non-condensable gas releases in evaporators. In *Encyclopedia of Desalination and Water Resources*; AlGobaisi, D.M.K. (ed.), EOLSS Publishers Co. Ltd.: Oxford.
6. Hunter, K.A. (1998) Acid-base Chemistry of Aquatic Systems: An introduction to the chemistry of acid-base equilibria with emphasis on the carbon dioxide system in natural waters. Cited 10 May 2005, available from: http://neon.otago.ac.nz/chemistry/research/mfc/pubs/misc/acidbasebook.pdf.
7. Millero, F.J. (1995) Thermodynamics of the carbon dioxide system in the oceans. *Geochim. Cosmochim. Acta*, 59: 661–677.
8. Al-Rawajfeh, A.E. (2004) Modelling and simulation of CO_2 release in multiple-effect distillers for seawater desalination. In *Mathematisch-Naturwissenschaftlich-Technische Fakultät*; Martin-Luther-University Halle-Wittenberg, avail. Online http://sundoc.bibliothek.uni-halle.de/diss-online/04/04H141/of_index.htm.
9. Millero, F.J. (1996) *Chemical Oceanography*, 2nd ed.; CRC Press: Boca Raton, FL.
10. Millero, F.J. (1974) *The Physical Chemistry of Seawater*; Annual Reviews, www.annualreviews.org/aronline.
11. DOE (1994) *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*, A.G.D.C.G. version 2, Dickson, A.G. and Goyet, C. (eds.), ORNL/CDIAC-74 Editor.
12. Glade, H. (2001) *Transport und Reaktion von Kohlendioxid in Entspannungsverdampfern zur Meerwasserentsalzung*; University of Bremen, 2001, VDI Fortschritt-Berichte, Series 3, No. 699. VDI Verlag: Düsseldorf.
13. IAEA (2003) *Chemistry of Carbonic Acid in Water*. [cited 2005 21 March 2005]; Available from: http://www.iaea.org/programmes/ripc/ih/volumes/vol_one/cht_i_09.pdf.
14. Kurz, F., Rumpf, B., and Maurer, G. (1996) Simultaneous solubility of ammonia and carbon dioxide in aqueous solutions of ammonium sulfate and (ammonium

sulfate + sodium sulfate) at temperatures from 313 K to 393 K and pressures upto 10 MPa. *J. Chem. Thermodynamics*, 28: 497–520.

15. Loewenthal, R.E. and Marais, G.v.R. (1984) *Carbonate Chemistry of Aquatic Systems. Volume 2; High Salinity Waters*; Butterworths: Boston.
16. Follows, M.J., Ito, T., and Dutkiewicz, S. (2006) On the solution of the carbonate chemistry system in ocean biogeochemistry models. *Ocean Mode.*, 12: 290–301.
17. Millero, F.J., Degler, E.A., O'Sullivan, D.W., Goyet, C., and Eischeid, G. (1998) The carbon dioxide system in the Arabian Sea. *Deep Sea Res. II*, 45: 2225–2252.
18. Al-Rawajfeh, A.E., Glade, H., and Ulrich, J. (2003) CO_2 release in multiple-effect distillers controlled by mass transfer with chemical reaction. *Desalination*, 156: 109–123.
19. Prausnitz, J.M. (1969) *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, New Jersey.
20. Danckwerts, P.V. (1970) *Gas-liquid Reactions*; McGraw-Hill: New York.
21. Wilhelm, E., Battino, R., and Wilcock, R.J. (1977) Low-pressure solubility of gases in liquid water. *Chem. Rev.*, 77 (2): 219–262.
22. Teng, H., Masutani, S.M., Kinoshita, C.M., and Nihous, G.C. (1996) Solubility of CO_2 in the ocean and its effect on CO_2 dissolution. *Energy Conv. Mgmt.*, 37 (6–8): 1029–1038.
23. IUPAC (1998) *Introduction to the Solubility Data Series: Solubility of Gases in Liquids*; The SSED's Solubility Data Project. [cited; Available from: http://www.unileoben.ac.at/ ~ IUPAC/gl-intro.html.
24. Garcia, J.E. (2003) Fluid dynamics of carbon dioxide disposal into saline aquifers. In *Engineering–Civil and Environmental Engineering*; University of California, Berkeley: Los Angeles- Berkeley., 150.
25. Corti, H.R., Krenzer, M.E., Pablo, J., and Prausnitz, J.M. (1990) Effect of a dissolved gas on the solubility of an electrolyte in aqueous solution. *Ind. Eng. Chem. Res.*, 29: 1043–1050.
26. Hermann, C., Dewes, I., and Schumpe, A. (1995) The estimation of gas solubilities in salt solutions. *Chem. Eng. Sci.*, 50 (10): 1673–1675.
27. Schumpe, A. (1993) The estimation of gas solubilities in salt solutions. *Chem. Eng. Sci.*, 48 (1): 153–158.
28. Weisenberger, S. and Schumpe, A. (1996) Estimation of gas solubilities in salt solutions at temperatures from 273 K to 363 K. *AIChE J*, 42 (1): 298–300.
29. Yasunishi, A. and Yoshida, F. (1979) Solubility of carbon dioxide in aqueous electrolyte solutions. *J. Chem. and Eng. Data*, 24 (7): 11–14.
30. Weiss, R.F. (1974) Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Mar. Chem.*, 2: 203–215.
31. Li, Y.H. and Tsui, T.F. (1971) The solubility of CO_2 in water and seawater. *J. Geophys. Res.*, 76: 4203–4207.
32. Murray, C.N. and Riley, J.P. (1971) The solubility of gases in distilled water and seawater–IV. Carbon dioxide. *Deep-Sea Res.*, 18: 533–541.
33. Stewart, P.B. and Munjal, P. (1970) Solubility of carbon dioxide in pure water, synthetic sea water, and synthetic sea water concentrates at −50 to 250°C and 10- to 45-atm. pressure. *J. Chem. Engi. Data*, 15 (1): 67–71.
34. Roy, R.N., Roy, L.N., Vogela, K.M., Porter-Moore, C., Pearson, T., Good, C.E., Millero, F.J., and Campbell, D.M. (1993) The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mari. Chem.*, 44: 249–267.
35. Plummer, L.N. and Busenberg, E. (1982) The solubility of calcites, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the

aqueous model for the system $CaCO_3$-CO_2-H_2O. *Geochim. Cosmochim. Acta*, 46: 1011–1040.

36. Duan, Z. and Sun, R. (2003) An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology*, 193: 257–271.
37. Duan, Z., Moller, N., and Weare, J.H. (1992) An equation of state for the CH_4-CO_2-H_2O system: I. Pure systems for 0 to 1000°C and 0 to 8000 bar. *Geochim. Cosmochim. Acta*, 56: 2605–2617.
38. Pitzer, K.S. (1973) Thermodynamics of electrolytes: I. Theoretical basis and general equations. *J. Phys. Chem.*, 77: 268–277.
39. Pitzer, K.S., Perper, J.C., and Busey, R.H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data*, 13: 1–103.
40. Stumm, W. and Morgan, J.J. (1981) *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*; 2nd edition; John Wiley: New York.
41. Mubarak, A. (1998) A kinetic model for scale formation in MSF desalination plants. Effect of antiscalants. *Desalination*, 120 (1–2): 33–39.
42. Shams El Din, A.M. and Mohammed, R.A. (1994) Brine and scale chemistry in MSF distillers. *Desalination*, 99 (1): 73–111.
43. Culberson, C.H. and Pytkowicz, R.M. (1973) Ionization of water in seawater. *Mar. Chem.*, 1: 309–316.
44. Dickson, A.G. and Riley, J.P. (1979) The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water—Kw. *Mar. Chem.*, 7: 89–99.
45. Hansson, I. (1973) A new set of acidity constants for carbonic acid and boric acid inseawater. *Deep-Sea Res.*, 20: 461–478.
46. Mehrbach, C., Culberson, C.H., Hawley, J.E., and Pytkowicz, R.M. (1973) Measurement of the apparent dissociation constants of the carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.*, 18: 897–907.
47. Lueker, T.J., Dickson, A.G., and Keeling, C.D. (2000) Ocean pCO_2 calculated from dissolved inorganic carbon, total alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Mar. Chem.*, 70: 105–119.
48. Dickson, A.G. and Millero, F.J. (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Res. A*, 34 (10): 1733–1743.
49. Goyet, C. and Poisson, A. (1989) New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep. Sea. Res.*, 36: 1635–1654.
50. Copin-Montegut, C. (1988) A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. *Marine Chemistry*, 25: 29–37.
51. Hunter, K.A. (1998) The temperature dependance of pH in surface seawater. *Deep-Sea Res.*, 45: 1919–1930.
52. Millero, F.J., Purkerson, D.G., Steinberg, P., Peltola, E., Lee, K., Edwards, C., Goen, J., and Roche, M.. *The Carbon Dioxide System in the Ross Sea During the JGOFS Southern Ocean Process Study*; available from: http://usjgofs.whoi.edu/PI-NOTES/southern/Millero-TCO2.html.
53. Park, P.K. (1969) Oceanic CO_2 system: An evaluation of ten methods of investigation. *Limnol. Oceanogr.*, 14 (2): 179–186.
54. Reid, R.C., Prausnitz, J.M., and Poling, B.E. (1987) *The Properties of Gases and Liquids*; 4th ed.; McGroaw-Hill Book Company: New York.

55. Walas, S.M. (1984) *Phase Equilibiria In Chemical Engineering*; Butterworth-Heinemann: Boston.
56. Salminen, J. (2004) *Chemical Thermodynamics of Aqueous Electrolyte Systems for Industrial and Environmental Applications, in Department of Chemical Technology,Laboratory of Physical Chemistry and Electrochemistry*; Helsinki University of Technology: Espoo, Finalnd.
57. Khoshkbarchi, M.K. and Vera, J.H. (1996) Measurement and correlation of ion activity coefficients in aqueous solutions of mixed electrolyte with a common ion. *Fluid Phase Equil.*, 121: 253–265.
58. Thomsen, K. (1997) *Aqueous Electrolytes: Model Parameters and Process Simulation, in Department of Chemical Engineering*; Technical University of Denmark: DK-2800 Lyngby, Denmark.
59. Berthold, J. (2006) *An Overview of Data Analysis and Data Entry for OLI Programs*; OLI Systems Inc. Date accessed: 23 May 2006: www.olisystems.com.
60. Kervévan, C., Azaroual, M., and Durst, P. (2005) Improvement of the calculation accuracy of acid gas solubility in deep reservoir brines: Application to the geological storage of CO_2. *Oil & Gas Sci. Technol.–Rev. IFP.*, 60 (2): 357–379.
61. Helgeson, H.C. and Kirkham, D.H. (1974) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye-Hüchel parameters for activity coefficients and relative partial molal properties. *Am J. Sci.*, 274: 1199–1261.
62. Davies, C.W. (1938) The extent of dissociation of salts in water part VIII. An equation for the mean ionic acidity coefficient of an electrolyte in water, and a revision of the dissociation constant of some sulphates. *J. Chem. Soc.*, 32: 2093–2098.
63. Byrne, R., Kester, D., Millero, F., and Luther, F. (1998) *Physical Chemistry of Seawater*; F.o.O.C.i.t.U.S.W. (FOCUS).
64. Johnson, K.S. (1982) Carbon dioxide hydration and dehydration kinetics in seawater. *Limnol. Oceanogr.*, 27 (5): 849–855.
65. Astarita, G. (1967) *Mass Transfer with Chemical Reaction*; Elsevier: Amsterdam.
66. Astarita, G., Savage, D.W., and Longo, J.M. (1981) Promotion of CO_2 mass transfer in carbonate solutions. *Chem. Eng. Sci.*, 36: 581–588.
67. Wall, H.H. (1966) *Absorption and Desorption of Carbon Dioxide in Carbonate-Bicarbonate Buffer Solutions*; University of Delaware: Newark, Delaware.
68. Emerson, S. (1975) Chemically enhanced CO_2 gas exchange in a eutrophic lake: A general model. *Limnol. Oceanogr.*, 20: 743–753.
69. Lewis, E. and Wallace, D. (1998) *Program Developed for the CO_2 System Calculations*; http://cdiac.esd.ornl.gov/ftp/co2sys.
70. Glade, H. and Ulrich, J. (2003) Influence of solution composition on the formation of crystalline scales. *Chem. Eng. Technol.*, 26 (3): 277–281.
71. Andersen, C.B. (2002) Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems. *J. Geosci. Edu.*, 50 (4): 389–403.
72. Frankignoulle, M. and Borges, A.V. (2001) Direct and indirect pCO_2 measurements in a wide range of pCO_2 and salinity values (the Scheldt estuary). *Aqua. Geochem.*, 7: 267–273.
73. Dickson, A.G. (1993) The measurement of sea water pH. *Mar. Chem.*, 44: 131–142.
74. Ternon, J.F., Oudot, C., Gourlaouen, and V. Diverres, D. (2001) The determination of pH_T in the equatorial Atlantic Ocean and its role in the sound absorption modeling in seawater. *J. Mar. Syst.*, 30 (1–2): 67–87.

75. Lefrvre, N., Ciabrini, J.P., Michard, G., Brient, B., DuChaffaut, M., and Merlivat, L. (1993) A new optical sensor for Pco_2 measurements in seawater. *Mar. Chem.*, 42: 189–198.
76. Shams El Din, A.M., El-Dahshan, M.E., and Mohammed, R.A. (2002) Inhibition of the thermal decomposition of HCO_3^-; A novel approach to the problem of alkaline scale formation in seawater desalination plants. *Desalination*, 142: 151–159.
77. Rafal, M., Berthold, J., and Linz, D.; *Introduction to OLI Electrolytes*; Date accessed: 23 May 2006: www.olisystems.com.
78. Chong, T.H. and Sheikholeslami, R. (2001) Thermodynamics and kinetics for mixed calcium carbonate and calcium sulfate precipitation. *Chem. Eng. Sci.*, 56: 5391–5400.
79. Gal, J.-Y., Fovet, Y., and Gache, N. (2002) Mechanisms of scale formation and carbon dioxide partial pressure influence. Part I. Elaboration of an experimental method and a scaling model. *Water Res.*, 36: 755–763.
80. Gal, J.-Y., Fovet, Y., and Gache, N. (2002) Mechanisms of scale formation and carbon dioxide partial pressure influence. Part II. Application in the study of mineral waters of reference. *Water Res.*, 36: 764–773.
81. Glade, H., Meyer, J.-H., and Will, S. (2005) The release of CO_2 in MSF and ME distillers and its use for the recarbonation of the distillate: A comparison. *Desalination*, 182: 95–106.
82. Marion, G.M. (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system. *Geochim. Cosmochim. Acta*, 65 (12): 1883–1896.
83. Patel, S. and Finan, M.A. (1999) New antifoulants for deposit control in MSF and MED plants. *Desalination*, 124: 63–74.
84. Sheikholeslami, R. and Ong, H.W.K. (2003) Kinetics and thermodynamics of calcium carbonate and calcium sulfate at salinities up to 1.5 M. *Desalination*, 157: 217–234.
85. El-Dahshan, M.E. (2001) Corrosion and scaling problems present in some desalination plants in Abu Dhabi. *Desalination*, 138: 371–377.
86. Al-Rawajfeh, A.E., Glade, H., Qiblawey, H.M., and Ulrich, J. (2004) Simulation of CO_2 release in multiple-effect distillers. *Desalination*, 166: 41–52.
87. Ellis, R.D., Glater, J., and McCutchan, J.W. (1971) Alkaline scale abatement by carbon dioxide injection. *Environ. Sci. Technol.*, 5 (4): 350–356.
88. Azaroual, M., Kerrevan, Ch., Durance, M.-V., and Durst, P. (2004) SCALE2000: Reaction-transport software dedicated to thermokinetic prediction and quantification of scales. Applicability to desalination problems. *Desalination*, 165: 409–419.
89. Mucci, A. (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Amer. J. Sci.*, 283: 780–799.
90. Zuddas, P. and Mucci, A. (1994) Kinetics of calcite precipitation from seawater: I. A classical chemical kinetics description for strong electrolyte solutions. *Geochim. Cosmochim. Acta*, 58 (20): 4353–4362.
91. Tokunaga, J. (1975) Solubilities of oxygen, nitrogen, and carbon dioxide in aqueous alcohol solutions. *J. Chem. Eng. Data*, 20 (1): 41–46.
92. Shorter, J.A., De Bruyn, W.J., Hu, J.H., Swartz, E., Davidovits, P., Worsnop, D.R., Zahniser, M.S., and Kolb, C.E. (1995) Bubble column apparatus for heterogeneous chemistry studies. *Environ. Sci. Technol.*, 29: 1171–1178.

93. Nighswander, J.A., Kaiogerakis, N., and Mehrotra, A.K. (1989) Solubilities of carbon dioxide in water and 1 wt% NaCl solution at pressures up to 10 MPa and Temperatures from 80 to 200°C. *J. Chem. Eng. Data*, 34: 355–360.
94. Millero, F.J. and Roy, R.N. (1997) A chemical equilibrium model for the carbonate system in natural waters. *Croatia Chem. Acta*, 70: 1–38.
95. Harned, H.S. and Davis R., Jr (1943) The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0° to 50°C. *J. Am. Chem. Soc.*, 65: 2020–2037.
96. Langmuir, D. (1997) *Aqueous Environmental Geochemistry*; Prentice Hall: Englewood Chiffs, New Jersey.