

Effect of methanol on carbonate equilibrium and calcite solubility in a gas/methanol/water/salt mixed system

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ABSTRACT. Methanol is a common industrial solvent and is added to water to enhance hydrocarbon solubility and to prevent solid hydrate from forming, as well as other applications. One of the side effects of methanol addition to water is to greatly reduce the solubility of ionic solids, particularly divalent solids. The effect of methanol on ionic solubility has been reported for only few isolated conditions. A self-consistent activity model is proposed to describe the effect of methanol on carbonate equilibrium and calcite solubility in gas/methanol/water/salt solutions. The model is semi-empirical in nature, which uses the Pitzer theory to model the effect of salt and a Born-type equation to model the effect of methanol. The model parameters are derived from experimental studies at 0-3 m ionic strength, 4-25 °C, and 0 - 0.75 mole fraction methanol. The experimentally determined methanol activity coefficients, with respect to dissolved CO₂, bicarbonate, carbonate, and calcium, are determined as a function of temperature and ionic strength. Excellent agreements between the model predictions and

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experimental results are presented. From model predictions, significant scaling problems can be anticipated with as low as 20% (by volume) of methanol.

Introduction

Methanol is one of the most common industrial solvents. It is used in many industrial, household and environmental applications. In oil and gas industries, methanol is often used to inhibit gas hydrate formation during production. Gas hydrate is a crystalline solid consisting of gas molecules surrounded by a cage of water molecules, which forms at certain high pressure and low temperature regimes. In deep ocean waters, massive amounts of natural gas is trapped and cold water hydrates are also being studied as a method of CO₂ sequestration. Gas hydrate formation is particularly troublesome for offshore gas wells where the producing temperature is low due to both adiabatic expansion of gas and seawater cooling. Once gas hydrate forms, it can plug up the well and prevent further production. One economic solution to prevent hydrate formation is to inject a large quantity of methanol. However, methanol may cause adverse scaling problems in the associated brine solution, which often contains high concentrations of dissolved minerals. The solubility of these mineral salts can be severely reduced in the presence of methanol.

There is little research on the solubility of mineral salts in methanol/water/salt solutions. The problem concerning activity effects in alcohol/water/salt mixture is very complex^{1,2}. Conventionally, the non-ideal behavior of an aqueous solution due to the presence of salt is modeled with the concept of activity effects, e.g, Pitzer theory of specific ion interactions³. A generally accepted relationship is well established for describing single-ion activity coefficients and the corresponding parameters. Unfortunately, this is not the case for the treatment of solutions containing nonelectrolytes. Only limited sets of Pitzer parameters for nonelectrolytes are reported in the literature^{4,5}. There is not a known set of Pitzer parameters for the binary and ternary interaction between ions and nonelectrolytes, especially when the mole fraction of nonelectrolyte is large.

The formula for the activity coefficients of electrolyte solutions is integrated via the Gibbs-Duhem equations from infinite dilution in pure water to the ionic strength and concentration of the final

solution, i.e., the reference state is: a molality (moles of solute/kg of water) concentration scale referenced to pure water. As Bates¹ emphasized, the goal is to use a single reference state of pure water for all ions and compositions; if this could be done, ionic equilibrium constants would only be a function of temperature and nonaqueous solvent effects would all be treated as activity coefficient correction. The approach used here is similar to that of Chen et al⁶. An excellent discussion of Chen's model was presented in Tester and Modell⁷.

Extending the concept of activity effects to mixed solvents, the “reference state” for activity coefficients has to be reexamined¹. When both alcohol and salt water are present in the solution, the overall activity coefficient for an ion, or the free energy change of the ion due to solution composition, can be written as follows:

$$\begin{aligned}\Delta G^{\text{ex.}} &= RT \ln \gamma_{\text{overall}} \\ &= \Delta G_{\text{al/w}}^{\text{ex.}} + \Delta G_{\text{salt}}^{\text{ex.}} \\ &= RT \ln \gamma_{\text{al/w}} + RT \ln \gamma_{\text{salt}}\end{aligned}\tag{1}$$

where $\Delta G^{\text{ex.}}$ is the molar excess free energy change due to overall change in solution composition from pure water to alcohol/water and then to salt solution in the alcohol/water mixture. $\Delta G_{\text{al/w}}^{\text{ex.}}$ and $\Delta G_{\text{salt}}^{\text{ex.}}$ are the molar excess free energy changes for the reference state ion transfer from pure water to pure alcohol/water mixture and from alcohol/water mixture to alcohol/water/salt solution and $\gamma_{\text{al/w}}$ and γ_{salt} are the corresponding activity coefficients. The fundamental problem is that, to date, there is no theory that can be used to calculate the free energy of transfer of an ion from pure water to the pure alcohol/water mixed solvent (See Bates or Stokes and Robinson for a discussion of these effects)^{1,8}. The primary difficulty that prevents using a single pure-water reference state arises from attempting to calculate the free energy change for the reference state proton ion, H^+ , from pure water to the pure alcohol/water mixture. Since the pure-water reference state is most commonly used for the thermodynamic properties of aqueous electrolyte solutions, a semi-empirical approach is proposed that incorporates the alcohol effect in the standard pure-water reference state.

To understand the solubility of calcite, the carbon dioxide partitioning and carbonic acid dissociation chemistry must be understood. In this paper, the influence of salt on ion activity is estimated from Pitzer's theory of ion interaction. The free energy change, $\Delta G_{\text{al/w}}^{\text{ex.}}$, is estimated from a Born-type equation for electrostatics, based upon the difference in the dielectric constant, etc., for the two solutions. The Born equation is strictly approximate at all alcohol concentrations, but at greater than 50 to 80 %, w/w alcohol, the error can increase substantially⁸, and therefore, the Born equation (listed below) is used only as a model template to suggest a semi-empirical functional form. The reasonableness of this assumption lies in how well it is able to represent the solution chemistry of species of interest as a function of salt, methanol, composition, and temperature. A rationale for this assumption can be found in any of several texts on the molecular nature of ions in mixed alcohol/water solutions in that the water is selectively concentrated around the ions^{1,7,8}.

Self-Consistent Activity Coefficients in Alcohol/water/salt

A self-consistent set of activity coefficient-type equations for mineral ions of interest to oil field brine versus salt and methanol concentration is proposed. First, it is assumed that, in each case, $\gamma_{\text{overall}} = \gamma^{\text{S}} \cdot \gamma^{\text{N}}$; where γ^{S} is the activity coefficient due to the salt effect in water and γ^{N} is the activity coefficient due to the alcohol effect. For example, it is assumed that the activity coefficient of aqueous carbon dioxide, $\gamma_{\text{CO}_2, \text{aq}}$, can be written as a product of the effect of salt and of neutral methanol, $\gamma_{\text{CO}_2, \text{aq}} = \gamma_{\text{CO}_2, \text{aq}}^{\text{S}} \cdot \gamma_{\text{CO}_2, \text{aq}}^{\text{N}}$. The value of γ^{S} is calculated by conventional methods for activity coefficients, e.g., the Pitzer theory, with all concentration units as “aqueous molality,” (moles of solute) per (kilogram of water). The term, γ^{N} , is a curve fitted parameter obtained using an equation similar to the Born equation. The concentration of all aqueous species is expressed in units of aqueous molality (moles/kg of water). It is important to emphasize that all concentrations are expressed as moles per kilogram of water, even in the presence of a substantial quantities of methanol; this is as required for conventional activity coefficient calculations, e.g., Pitzer theory, which uses pure water as the reference state in all conditions. Note that the pH response of a glass electrode in a mixed solvent has to be corrected for medium effect due to

methanol and salt by an alcohol-specific correction term (δ) and a salt correction term for the junction potential (ΔpH_j)^{1,9}.

The following equations illustrate the activity coefficient relationships; the numerical values are at 25 °C and 1 atm¹⁰:

$$K_H = 10^{-1.47} \frac{\text{molal}}{\text{atm}} = \frac{a_{\text{CO}_2, \text{aq}}}{f_{\text{CO}_2, \text{g}}} = \frac{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}}{P_{\text{CO}_2, \text{g}} \cdot \gamma_{\text{CO}_2, \text{g}}} = \frac{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{g}}^S \cdot \gamma_{\text{CO}_2}^N}{P_{\text{CO}_2, \text{g}} \cdot \gamma_{\text{CO}_2, \text{g}}} \quad (2)$$

$$K_1 = 10^{-6.35} = \frac{a_{\text{H}^+}^* \cdot a_{\text{HCO}_3^-}}{a_{\text{CO}_2, \text{aq}}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta \text{pH}_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}}{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta \text{pH}_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N}{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}^S \cdot \gamma_{\text{CO}_2, \text{aq}}^N} \quad (3)$$

$$K_2 = 10^{-10.33} = \frac{a_{\text{H}^+}^* \cdot a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta \text{pH}_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}}{[\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta \text{pH}_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N}{[\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N} \quad (4)$$

$$K_{\text{sp}} = 10^{-8.36} = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}^S \cdot \gamma_{\text{Ca}^{2+}}^N \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N \quad (5)$$

where $[\]$ represents the concentration of each species in moles of solute per kg of water and $P_{\text{CO}_2, \text{g}}$ in unit of atm. Note that 1 atm = 1.03 bar. When solution phase total calcium concentration is large (e.g., 0.1 m, or greater) and in substantial methanol concentration (>0.4 mole fraction), it is necessary to include a stability constant for CaHCO_3^+ ion pair formation - see below. The value of $\gamma_{\text{CO}_2, \text{g}}$ in Eq. 2 can be calculated using an equation of state for carbon dioxide, but at room temperature and pressure it can be taken to be one (1.00). $\text{pH}_{\text{meter reading}}$ in Eqs. 3 and 4 refers to the observed pH response in the mixed solvent when the pH electrode has been calibrated using normal aqueous buffers¹. The term $a_{\text{H}^+}^*$ refers to the activity of the hydrogen ion in the mixed solvent. Since no practical method has yet been devised to convert mixed solvent $a_{\text{H}^+}^*$ into pure water activities, a_{H^+} , the constants in Eqs. 2-5 must be regarded as "mixed" or semi-empirical constants and their usefulness should be judged by how well they can be used to calculate measurable quantities, such as calcite solubility in mixed solvents and

salts. The value of $a_{H^+}^*$ in a mixed solvent in the presence of salt can be related to the pH-meter reading taken with a glass electrode, as suggested by Bates¹.

$$-\log(a_{H^+}^*) = \text{pH}_{\text{meter reading}} + \Delta\text{pH}_j - \delta_{\text{MeOH}} \quad (6)$$

where “ $\text{pH}_{\text{meter reading}}$ ” is the meter reading when the glass electrode has been calibrated against normal aquatic NIST standard buffers, ΔpH_j is the salt correction (see below); and δ_{MeOH} is the mixed-solvent correction term suggested by Bates. In the absence of methanol, $-\log(a_{H^+}^*)$ is simply the solution pH. The ΔpH_j term is the correction term to represent the changes in electrode response due to the presence of salt. The magnitude of ΔpH_j is between 0.07 to 0.23 for a salinity of 0.1 to 3 m NaCl solution (see Results and Discussion section for detail). δ_{MeOH} is the correction term used to represent the changes in electrode response due to methanol, which is less than 0.1 pH unit when methanol concentration is less than 40% by weight. In this paper, ΔpH_j and δ_{MeOH} are assumed to be independent of temperature.

It is often more convenient to work with the corresponding "conditional" equilibrium constants wherein all activity coefficient are set equal to unity, except for the hydrogen ion.

$$K'_H = [\text{CO}_{2,\text{aq}}] / P_{\text{CO}_{2,\text{g}}} \quad (7)$$

$$K'_1 = a_{H^+}^* \cdot [\text{HCO}_3^-] / [\text{CO}_{2,\text{aq}}] \quad (8)$$

$$K'_2 = a_{H^+}^* \cdot [\text{CO}_3^{2-}] / [\text{HCO}_3^-] \quad (9)$$

$$K'_{\text{sp}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] \quad (10)$$

$$K_{\text{st}}^{\text{CaHCO}_3^+} = \frac{[\text{CaHCO}_3^+]}{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]} \quad (11)$$

Normally (as is done in this work), the hydrogen ion term is left as an activity-based term, because that is directly related to what the pH meter reads.

The conditional stability constant of CaHCO_3^+ ($K_{\text{st}}^{\text{CaHCO}_3^+}$) is determined from the Fuoss theory of ion pair formation⁸. Eq. 12 is modified from that of Morel and Hering¹¹ for outer-sphere complexes.

$$K_{st}^{CaHCO_3^+} = \frac{[CaHCO_3^+]}{[Ca^{2+}] \cdot [HCO_3^-]} = \frac{4000\pi Na^3}{3} \exp\left[\frac{-z_M z_L e^2}{4\pi\epsilon_0 \epsilon kTa}\right] \exp\left[\frac{z_M z_L e^2 \kappa}{4\pi\epsilon_0 \epsilon kT(1 + \kappa a)}\right] \quad (12)$$

where [], in this equation, represent concentration in units of moles of solute/Kg of solvent, z_M and z_L are charges of cation and ligand, e is the elementary charge ($=1.6 \times 10^{-19}$ coulomb), N is the Avogadro constant ($= 6.02 \times 10^{23} \text{ mol}^{-1}$), k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), ϵ_0 is the vacuum permittivity ($= 8.854 \times 10^{-12} \text{ J}^{-1} \cdot \text{C}^2 \cdot \text{m}^{-1}$), ϵ is the unitless dielectric constant of the mixed solvent, I is the ionic strength of the mixed solution (moles/Kg solvent) and "a" is the distance of closest approach ($a = 2.4 \times 10^{-10} \text{ m}$, see below) and κ is the Debye-Hückel ion atmosphere parameter:

$$\kappa = \left(\frac{2000e^2 NI}{\epsilon_0 \epsilon kT} \right)^{0.5} = \left(\frac{2000e^2 N}{\epsilon_0 k} \right)^{0.5} \cdot \left(\frac{I}{\epsilon T} \right)^{0.5} \quad (13)$$

The $CaHCO_3^+$ stability constant in water ($K_{st}^{CaHCO_3^+} = 13.3$ at $I = 0$), calculated from Eq. 12 with the above constants is similar to that reported by Plummer and Busenberg¹².

Experimental Section

In the following, the experimental procedures used to determine the activity coefficients of methanol ($\gamma_{CO_{2,aq}}^N, \gamma_{HCO_3^-}^N, \gamma_{CO_3^{2-}}^N, \gamma_{Ca^{2+}}^N$) are briefly discussed. The experiments were systematically varied over a wide range of parameters, i.e., 0-3 m NaCl, 0-0.75 mole fraction methanol, and 4-25 °C temperature. Specific parameters for each experiment are listed in the Tables 1-7 in the Results and Discussion section. The experimental procedures were first tested in duplicate and triplicate with 0 - 1 M NaCl as background electrolyte in the absence of methanol. Excellent reproducibility was observed for all procedures and the data are consistent with that reported in the literature (See results section).

Carbon dioxide partition in gas/liquid (methanol/water/salt) phases. The partition of CO_2 between the gas phase and a liquid phase, consisted of methanol/water/salt solution, was determined by measuring the pressure changes upon the addition of HCl (1 N) to a methanol/salt solution containing a fixed concentration of bicarbonate. Approximately 100 g of solution containing various concentrations of methanol, NaCl, and water was added to a reaction bottle. The solution also contained approximately

4 mm NaHCO_3 . The reaction bottle was a ~305 ml Pyrex bottle capped with an open-top cap, a stainless steel septum and rubber gasket (Columbia Instrument). The stainless steel septum was connected to a digital pressure gauge (Omega Engineering M3359, ± 15 psig, 0.25% accuracy, full scale) and an acid injection port via a 1/8" PFA tubing and a ball valve (Swagelok). At the beginning of the experiment, the bottle was evacuated to a sub-ambient pressure (~0.5 psia) to allow water and methanol to saturate the gas phase. The pressure of the gas phase was re-established at ~7 psia by allowing some influx of air. The reaction bottle was then submerged completely into a jacketed water bath and the bath was connected to a heat/refrigeration circulator (Neslab) and monitored for 30 minutes to establish a constant background pressure. The jacketed water bath was positioned on top of a magnetic stirring motor for continuous mixing. A small aliquot of HCl (1 N) was then injected into the bottle via the injection port to a final concentration of ~5 mM, followed by 1 ml DI water to rinse the injection tubing. The pH of the mixed solution is between 1.7-2.8 pH. The effect of pressure increase due to added liquid volume was corrected from the pressure reading. The net pressure changes due to CO_2 dissolution were recorded after the acid/bicarbonate reaction reached equilibrium, in less than 1.5 hrs.

Carbonic acid dissociation in methanol/water/salt solution. The bicarbonate equilibrium chemistry was determined by measuring pH of a solution containing approximately equal concentrations of dissolved CO_2 and bicarbonate in a closed bottle with negligible headspace. A 250 ml glass bottle, fitted with a Teflon-faced (24 mm) septa and screw cap, was used. In the center of the septa, a hole (~10 mm ID) was cut to accommodate an Orion Ross[®] combination electrode. A needle size vent hole was inserted in the septa to prevent pressure built-up, yet avoid convective gas exchange. At the beginning of the experiment, methanol and NaCl- NaHCO_3 solutions were degassed and weighed into the bottle before the bottle was capped. High purity NaCl (99.999%, Sigma) was used. A known quantity of HCl (1N), equivalent to a final concentration of ~5 mM, was injected into the closed bottle with a syringe and stirred. The pH of the solution was recorded after it reached a constant pH in a few minutes. The solution phase concentration of neutral carbon dioxide was kept sufficiently low that free

phase gas bubbles would not form spontaneously, i.e., the solution phase bubble point was always less than one atmosphere.

Similarly, the carbonate equilibrium chemistry was determined by measuring the pH of a solution containing approximately equal concentrations of bicarbonate and carbonate in a closed bottle with negligible headspace. At the beginning of the experiment, methanol and NaCl-NaHCO₃ were degassed and weighed into the bottle before the bottle was capped. A known quantity of NaOH (1.0 N), equivalent to a final concentration of ~ 5 mm, was added into the closed bottle with constant stirring. The pH of the solution was recorded after it reached a constant pH value, within a few minutes.

Solubility of calcite in methanol/water/salt solution (no gas phase). In these experiments, a serum bottle, containing 0.5 g CaCO₃ salt, was filled with a salt solution containing methanol (0-0.8 mole fraction), water, NaCl (1-3 m), and NaHCO₃ (0.02 m). The solution was then acidified with a known amount of approximately 0.02 m HCl. After one day of thorough mixing, an aliquot of the solution was filtered with a 0.2 µm filter (Acrodisc polysulfone membrane filter) and analyzed for Ca concentration.

Solubility of calcite in methanol/salt solution (with gas phase). These experiments were done using the same reaction bottle as described in CO₂ partition experiments. At the beginning of the experiment, excess CaCO₃ (1 g) was added to the reaction bottle containing 200 g solution of either (A) methanol (0-0.3 mole fraction), water, NaCl (1 m), NaHCO₃ (0.04 m) or (B) Methanol (0.16 mole fraction), water, NaCl (1 m), and CaCl₂·2H₂O (0.1 m). First, the bottle was evacuated to a sub-ambient background pressure using the same procedure as discussed in the CO₂ partition experiment. After the background pressure was established, an aliquot of 1N HCl was added to the reaction bottle to cause calcium carbonate dissolution. After ~20 hours equilibrium time, the pressure change was determined. The bottle was opened and as a quality control check the pH of the solution was immediately measured (less than 10 sec.). The solution was then transferred to a 140 ml syringe and filtered through a 0.2 µm filter to separate undissolved CaCO₃ from solution. Total calcium and bicarbonate concentrations of the filtered solution were measured.

Medium effect on an Orion-Ross combination pH electrode. In this research, the differences in junction potential of an Orion Ross[®] combination pH electrode, in solutions of high salinity versus buffer standards, were measured. The electrode was first calibrated with 0.05 M phthalate and 0.01 M borax standard solutions. The experiments were done by measuring the EMF of $\sim 1 \cdot 10^{-3}$ m HCl in solutions of 0 - 3 m NaCl, where the high purity NaCl (99.999%, Sigma) was used. Similarly, the effect of methanol (52.1%, w/w) on the pH of a borax solution (4.996 mM borax and 9.992 mM KCl) was measured and compared with the literature value.

Ca and bicarbonate analysis. Solution phase total Ca concentration was determined by EDTA (0.8 N) titration to a Calmagite end point (HACH). Total bicarbonate concentration was determined by titrating the solution with 1.6 N H₂SO₄ to 3.5pH. The bicarbonate concentration is determined from the concentration of H₂SO₄ needed to reach the titration end point. No interference from methanol was observed for either total Ca or bicarbonate analysis. The error of duplicate analyses is generally less than 2%.

Data Interpretation

In principle, the free energy of transfer from a solution of one dielectric constant to another dielectric constant ($\Delta G_{al/w} = \Delta G_{tr}$) can be calculated via the Born equation and this in turn is the primary medium-effect activity coefficient, $\gamma_{al/w}$ ^{6,7}:

$$\Delta G_{al/w}^{ex.} = RT \ln(\gamma_{al/w}) = \frac{N \cdot z_i^2 \cdot e^2 \cdot 10^{-10}}{8 \cdot \pi \cdot r \cdot \epsilon_0} \left(\frac{1}{\epsilon_{al/w}} - \frac{1}{\epsilon_w} \right) (\text{J/mole}) \quad (14)$$

where z_i is the ion charge, T is temperature (°K), r is the ion radius (Å), $\epsilon_{al/w}$ and ϵ_w are the dimensionless dielectric constant of the mixed solvent and water, respectively. It is observed that

$\left(\frac{1}{\epsilon_{al/w}} - \frac{1}{\epsilon_w} \right)$ is a second order function of methanol concentration as mole fraction, x_{MeOH} ($r^2 = 0.999$).

For methanol, Eq 15 can be derived from Eq. 14:

$$\begin{aligned} \log(\gamma_{al/w}^N) &= \Delta G_{al/w}^{ex.} / (2.303 \cdot R \cdot T) \\ &= 3.628 \cdot 10^4 \cdot \frac{z_i^2}{r \cdot T} (0.0115 \cdot x_{MeOH} + 0.0068 \cdot x_{MeOH}^2) \end{aligned} \quad (15)$$

The functional form of Eq. 15 ($\log \gamma_{\text{al/w}}^{\text{N}} = a \cdot x_{\text{MeOH}} + b \cdot x_{\text{MeOH}}^2$) will be used to correlate all γ^{N} values to methanol concentration. The ionic radius is assumed to be unchanged at different methanol concentrations. Experimentally, the first term represents the majority of the observed data up to about $0.3 \cdot x_{\text{MeOH}}$. At higher methanol concentrations, it has been demonstrated that the experimental data often deviates from the prediction of Born equation^{1,8,13}. In this study, it has been shown that, at high methanol concentrations, some activity coefficients increase and some decrease, and both can be represented with a second term, quadratic in x_{MeOH} .

Interpretation of carbon dioxide partition data. By assuming the conservation of CO_2 mass and assuming $\text{CO}_{2,\text{aq}}$ is the only solution species, $\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}}$ can be calculated by rearranging Eq. 2:

$$\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}} = K_{\text{H}} \cdot P_{\text{CO}_{2,\text{g}}} \cdot \gamma_{\text{CO}_{2,\text{g}}} / \{ [\text{CO}_{2,\text{aq}}] \cdot \gamma_{\text{CO}_{2,\text{aq}}}^{\text{S}} \} \quad (16)$$

At any particular methanol and salt concentration all the terms on the right hand side of equation 16 are either known (K_{H} and $\gamma_{\text{CO}_{2,\text{g}}} = 1.00$), measured (P_{CO_2} and $[\text{CO}_{2,\text{aq}}]$), or calculated ($\gamma_{\text{CO}_{2,\text{aq}}}^{\text{S}}$ from Pitzer theory). After $\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}}$ at various methanol concentrations was determined, the activity coefficients were correlated to the methanol concentrations using PSI-Plot statistical software¹⁴.

Interpretation of carbonic acid dissociation data. By measuring total carbonate and pH vs. methanol and salt concentrations, the value of activity coefficient effect due to methanol, $\gamma_{\text{HCO}_3^-}^{\text{N}}$, can be calculated by rearranging Eq. 3:

$$\gamma_{\text{HCO}_3^-}^{\text{N}} = K_1 \cdot [\text{CO}_{2,\text{aq}}] \cdot \gamma_{\text{CO}_{2,\text{aq}}}^{\text{S}} \cdot \gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}} / \{ 10^{-(\text{pH} + \Delta\text{pH}_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^{\text{S}} \} \quad (17)$$

Similarly, by measuring total carbonate and pH vs. methanol and salt concentrations, the value of activity coefficient effect due to methanol, $\gamma_{\text{CO}_3^{2-}}^{\text{N}}$, can be calculated from Eq. 4:

$$\gamma_{\text{CO}_3^{2-}}^{\text{N}} = K_2 \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^{\text{S}} \cdot \gamma_{\text{HCO}_3^-}^{\text{N}} / \{ 10^{-(\text{pH} + \Delta\text{pH}_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^{\text{S}} \} \quad (18)$$

Interpretation of calcite solubility experiments-closed system. In these experiments, the total carbonate concentration (T_{CO_3}) is equal to the sum of added NaHCO_3 and carbonate that dissolved from

calcite. The Ca and bicarbonate concentrations are low enough that CaHCO_3^+ complex formation can be ignored, see below. By carbonate mass balance, it can be shown that the concentration of carbonate and bicarbonate are functions of K_1 , K_2 , activity coefficients and hydrogen ion activity (Eq. 19 and 20).

$$\begin{aligned} T_{\text{CO}_3} &= [\text{CO}_{2,\text{aq}}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = T_{\text{CO}_3}^0 + [\text{Ca}^{2+}] \\ [\text{CO}_3^{2-}] &= T_{\text{CO}_3} \cdot f \end{aligned} \quad (19)$$

$$[\text{HCO}_3^-] = \frac{T_{\text{CO}_3} \cdot f \cdot a_{\text{H}^+}^* \gamma_{\text{CO}_3}^S \gamma_{\text{CO}_3}^N}{K_2 \gamma_{\text{HCO}_3}^S \gamma_{\text{HCO}_3}^N} \quad (20)$$

where $f = 1 / \{ a_{\text{H}^+}^* \gamma_{\text{CO}_3}^S \gamma_{\text{CO}_3}^N / K_1 K_2 \gamma_{\text{H}_2\text{CO}_3}^S \gamma_{\text{H}_2\text{CO}_3}^N + a_{\text{H}^+}^* \gamma_{\text{CO}_3}^S \gamma_{\text{CO}_3}^N / K_2 \gamma_{\text{HCO}_3}^S \gamma_{\text{HCO}_3}^N + 1 \}$ and $T_{\text{CO}_3}^0$ is the total bicarbonate concentration added to the solution at the beginning of the experiment. From the charge balance equation, the following equation can be used to find the hydrogen ion activity ($a_{\text{H}^+}^*$) that would satisfied Eq. 21.

$$\begin{aligned} &[\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{H}^+] - [\text{Cl}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \\ &= [\text{Na}^+] + 2[\text{Ca}^{2+}] + a_{\text{H}^+}^* - [\text{Cl}^-] - T_{\text{CO}_3} \cdot f \cdot \{ a_{\text{H}^+}^* \gamma_{\text{CO}_3}^S \gamma_{\text{CO}_3}^N / K_2 \gamma_{\text{HCO}_3}^S \gamma_{\text{HCO}_3}^N + 2 \} = 0 \end{aligned} \quad (21)$$

Where both $[\text{H}^+]$ and $[\text{OH}^-]$ are negligibly small. Once $a_{\text{H}^+}^*$ is determined, $\gamma_{\text{Ca}^{2+}}^N$ can be calculated.

$$\gamma_{\text{Ca}^{2+}}^N = K_{\text{sp}} / \{ [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}^S [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N \} \quad (22)$$

Calcite solubility in the presence of a gas phase. In the calcite dissolution experiments with a gas phase present, the initial condition was used to predict the reaction endpoint with Eqs. 2-19. In these experiments, the T_{Ca} was often large enough to expect significant ion pair formation. The total calcium concentration measured at the end of the experiment is equal to the calcium concentration of the initially added solution ($[T_{\text{Ca}}^0]$) and that dissolved from calcite ($[m_{\text{calcite}}]$, moles of calcite dissolved/Kg H_2O) and it is also equal to the sum of Ca^{2+} and CaHCO_3^+ in the solution after equilibrium, i.e.,

$$[T_{\text{Ca}}^0] + [m_{\text{calcite}}] = [\text{Ca}^{2+}] + [\text{CaHCO}_3^+]. \quad (23)$$

Similarly, the total carbonate concentration is equal to the bicarbonate concentration of the added solution ($[T_{CO_3}^0]$) and that dissolved from calcite ($[m_{\text{calcite}}]$) and it is also equal to the sum of all CO_2 species in both the gas phase and liquid phase:

$$[T_{CO_3}^0] + [m_{\text{calcite}}] = [CO_{2,g}] + [CO_{2,aq}] + [HCO_3^-] + [CO_3^{2-}] + [CaHCO_3^+] \quad (24)$$

where $[CO_{2,g}]$ on the right hand side is given by $[CO_{2,g}] = P_{CO_2,g} V_g / (RT m_{H_2O})$ and m_{H_2O} is the mass of water (Kg). The charge balance of the system dictates that

$$[Na^+] - [Cl^-] + 2[Ca^{2+}] + [CaHCO_3^+] - [HCO_3^-] - 2[CO_3^{2-}] + [H^+] - [OH^-] = 0 \quad (25)$$

From the mass balance and the charge balance equations the values of $P_{CO_2,g}$ and $a_{H^+}^*$ can be calculated from initial condition values, i.e., $[T_{Ca}^0]$, $[T_{CO_3}^0]$, $[Na^+]$, $[Cl^-]$. Once $P_{CO_2,g}$ and $a_{H^+}^*$ are calculated, the concentrations of all other species in solution can be calculated and this permits several quality control checks to be performed.

Results and Discussion

Medium effect on pH measurement. In this study, an Orion Ross® combination electrode calibrated with the NBS pH standards was used to measure pH. When pH is measured with this type of electrode, the measured pH has to be corrected for the difference in the electrode responses in different solution media. First the methanol correction term of Bates¹ was confirmed in the laboratory by measuring the pH of a solution containing 47.9% (w/w) of a borax solution (4.996 mM borax and 9.992 mM KCl) and 52.1% (w/w) methanol. The pH meter was calibrated against the phosphate (pH = 6.86 @ 25°C) and borax buffer (pH = 9.18 @ 25 °C) standards with a combination Ross electrode. The pH meter reading was pH = 9.563. After correcting by $\delta = 0.13$ at $x_{MeOH} = 0.36^1$, $pa_{H^+}^* = 9.433$, which compares very well to the literature value for this solution ($pa_{H^+}^* = 9.432^8$). Even though this approach of using known aqueous buffers reproduces reported non aqueous buffer values to ± 0.001 pH, it should be noted the nonaqueous buffer pH* standards are also available⁸. Alternatively, $pa_{H^+}^*$ may be measured via a

hydrogen electrode¹⁵⁻¹⁷. Eq. 26 is curve fitted from the δ terms given as a function of methanol mole fraction using the data in Bates¹:

$$\delta = x_{\text{MeOH}}^2 \cdot \left\{ -0.0897 \cdot \exp(3.262 \cdot x_{\text{MeOH}}^2) + 1.309 \cdot \exp(-4.008 \cdot x_{\text{MeOH}}^3) \right\} \quad r = 0.9999 \quad (26)$$

The effect of salt on electrode response is evaluated by measuring the pH of a series of solutions containing a fixed concentration of HCl, typically about 10^{-3} m HCl, and various concentrations of NaCl. When the only variable of these solutions is NaCl concentration, the change in junction potential (ΔE_j) is a function of the difference in EMF measurements and the hydrogen ion activity coefficients of the different solutions (Eq. 27).

$$\Delta E_j(x \text{ m NaCl}) = s \cdot \frac{2.303RT}{F} \log \gamma_{\text{H}^+}^{0 \text{ m NaCl}} - s \cdot \frac{2.303RT}{F} \log \gamma_{\text{H}^+}^{x \text{ m NaCl}} - E^{0 \text{ m NaCl}} + E^{1 \text{ m NaCl}} \quad (27)$$

where F is the Faraday constant, R is the gas constant ($\text{moleJ}^{-1}\text{K}^{-1}$), T is temperature ($^{\circ}\text{K}$), s is the ratio of the electrode response to the theoretical Nernst slope ($=2.303RT/F$) determined using standard buffers (typically, $s = 0.98$ to 1.00) and $\gamma_{\text{H}^+}^{0 \text{ m NaCl}}, \gamma_{\text{H}^+}^{x \text{ m NaCl}}$ are the hydrogen ion activity coefficients in 0 and x m NaCl solutions. Note that ΔpH_j in Eqs. 3 and 4 is derived from ΔE_j , as shown in Eq. 28.

$$\Delta \text{pH}_j = \frac{\Delta E_j}{s \cdot 2.303RT/F} \quad (28)$$

In Table 1 is listed the EMF measurements of six HCl solutions containing various amount of NaCl, and $\gamma_{\text{H}^+}^{x \text{ m NaCl}}$ calculated from Pitzer coefficients. The ΔE_j values of this study are consistent with others¹⁸. As shown in Table 1, the pH response of an electrode in a high salinity solution can be in error by up to a few tenths of a pH unit.

CO₂ partition, carbonate chemistry, and calcite solubility in the absence of methanol. To confirm that the experimental procedure would yield true equilibrium conditions, control experiments were conducted in the absence of methanol and the data were compared with the literature reported equilibrium constants of pK_H , pK_1 , pK_2 , and pK_sp . In Table 2 is listed the initial experimental conditions (T , and NaCl, NaHCO_3 , HCl, and CaCO_3 concentrations), the measurements ($P_{\text{CO}_2, \text{g}}$, pH, Ca^{2+}), and

calculated activity coefficients from Pitzer theory. Also listed in Table 2 are the conditional equilibrium constants (pK'_H , pK'_1 , pK'_2 , and pK'_{sp}). The observed pK' values are quite reasonable as compared with literature reported values (e.g., $pK'_H = 1.51$, $pK'_1 = 6.04$, $pK'_2 = 9.57$, and $pK'_{sp} = 6.93$ in 1 m NaClO₄ at 25 °C)¹⁹. In the last three columns of the table are listed: 1. the "experimental" pK values, 2. the thermodynamic pK values and 3. the deviation between the two values (Δ = thermodynamic pK values - experimentally determined pK values). The "experimental" pK values are that calculated from Eqs. 2-5 using the measured parameters and Pitzer activity coefficients with $\gamma^N = 1$, since no methanol was added to these solutions. The thermodynamic pK values at different temperatures are from that of Langmuir²⁰. As shown in Table 2, experimentally determined pK values compare closely to the thermodynamic pK values with mean standard deviation of the errors (Δ) less than ± 0.04 . Both the temperature and ionic strength dependence of the experimental results agreed with literature values and Pitzer activity coefficient corrections.

CO₂ partition, carbonate chemistry, and calcite solubility in the presence of methanol. In Tables 3-6 are listed the experimental conditions and results of CO₂ partitioning, carbonic acid dissociation and calcite dissolution experiments at various temperatures in the presence of various amounts of methanol and NaCl. Overall, added methanol increases the CO₂ partition into the aqueous phase, while it decreases carbonic acid dissociation and calcite solubility. For example, pK'_H decreases by 1.2 log-units between 0 to 0.67 mole fraction methanol; pK'_1 increases by 1.8 log-units between 0 and 0.75 mole fraction methanol; pK'_2 increases by 1.3 log-units between 0 and 0.85 mole fraction methanol; and pK'_{sp} increases by 2.6 log-units between 0 and 0.76 mole fraction methanol at 25 C and 1 m I. For the same range of conditions, the corresponding $\gamma^N_{CO_{2,aq}}$ varies from 1 to 0.06; $\gamma^N_{HCO_3^-}$ varies from 1 to 2; $\gamma^N_{CO_3^{2-}}$ varies from 1 to 40; and $\gamma^N_{Ca^{2+}}$ varies from 1 to 11. While there are no literature data available regarding the carbonic acid dissociation and calcite solubility in alcohol/water solutions, there are two reports on CO₂ solubility in alcohol/water^{21,22}. The literature data are in unit of Bunsen absorption

coefficients. After converting the data to pK'_H , our data are in good agreement with the literature results (See Figure 1).

In Figures 2 are plotted pK'_H , pK'_1 , pK'_2 , and pK'_{sp} versus the methanol concentrations, where the solid and open squares are at 1 m I, the solid and open triangles are at 3 m I and the solid and open circles are at 2 m I. In all plots, the solid symbols are the 25 °C data and the open symbols are the 4 °C data, with all ion concentrations set by using molality standard state in water and methanol concentration in mole fraction of methanol on methanol/water basis (i.e., salt concentration is not included in x_{MeOH} calculation). As discussed earlier, the differences in pK' values at $x_{MeOH} = 0$ reflects the expected temperature and ionic strength dependence and can be corrected with Pitzer activity coefficient and temperature dependence of the equilibrium constants. If the lines in Figure 2 are parallel to each other, no additional T and I correction is needed for methanol activity term. Interestingly, the lines in the plots of pK'_H , pK'_1 , and pK'_2 are nearly parallel to each other, while there is a stronger dependence of pK'_{sp} with both temperature and ionic strength.

When the experimentally determined values of $\gamma_{CO_{2,aq}}^N$, $\gamma_{HCO_3^-}^N$, $\gamma_{CO_3^{2-}}^N$, and $\gamma_{Ca^{2+}}^N$ are correlated with methanol concentration using the functional form of Eq. 15, the following four equations are obtained:

$$\log(\gamma_{CO_{2,aq}}^N) = \{-6.029 + 1444.9/T(^{\circ}K)\} \cdot x_{MeOH} - 1.170 \cdot x_{MeOH}^2 \quad r = 0.995 \quad (29)$$

One standard deviations for the three parameters are 0.612, 175.4, and 0.135, respectively.

$$\log(\gamma_{HCO_3^-}^N) = \{-3.338 + 955.9/T(^{\circ}K)\} \cdot x_{MeOH} + 0.565 \cdot x_{MeOH}^2 \quad r = 0.849 \quad (30)$$

One standard deviations for the three parameters are 0.929, 260.8, and 0.211, respectively. Note that even though the fit is not as good, it appears that the error in each $\log(\gamma_{HCO_3^-}^N)$ is about ± 0.05 to ± 0.1 (see Table 4).

$$\log(\gamma_{CO_3^{2-}}^N) = \{-1.957 + 1580.9/T(^{\circ}K)\} \cdot x_{MeOH} - 1.601 \cdot x_{MeOH}^2 \quad r = 0.994 \quad (31)$$

One standard deviations for the three parameters are 0.520, 150.9, and 0.097, respectively.

$$\log(\gamma_{\text{Ca}^{2+}}^{\text{N}}) = \{19.343 - 4714.2/T(^{\circ}\text{K}) - 0.333 \cdot I\} \cdot x_{\text{MeOH}} - 2.519 \cdot x_{\text{MeOH}}^2 \quad r = 0.967 \quad (32)$$

One standard deviations for the four parameters are 0.861, 247.2, 0.0316 and 0.189, respectively.

In Figure 3 is plotted the $\log(\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}})$, $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$, $\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$, and $\log(\gamma_{\text{Ca}^{2+}}^{\text{N}})$ calculated from Eqs. 29-32 versus that determined from experimental measurement using Eqs. 16-18, and 22. The correlations between the calculated and observed $\log(\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}})$, $\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$, and $\log(\gamma_{\text{Ca}^{2+}}^{\text{N}})$ are excellent with no systematic deviation of any set of temperature and ionic strength data. The correlation for the calculated and observed $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$ is not as good, but the total variation in $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$ is small. Note that the value of the methanol-effect activity coefficient for bicarbonate ($\gamma_{\text{HCO}_3^-}^{\text{N}}$) is derived from fitting the experimental data to Eq. 3 and 17, which contains the quotient ($\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}}/\gamma_{\text{HCO}_3^-}^{\text{N}}$). The deviation in $\gamma_{\text{HCO}_3^-}^{\text{N}}$ appears larger because the total variation in $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$ is smaller than $\log(\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}})$ and yet the two are directly coupled as a quotient, see Eq. 3. Note that pK_1' and pK_H' have similar but opposite dependence on methanol concentration. In eq.17, most of the correction needed for pK_1 is accounted by the variation in $\gamma_{\text{CO}_{2,\text{aq}}}^{\text{N}}$ and therefore, the values of $\gamma_{\text{HCO}_3^-}^{\text{N}}$ are closer to one. Even so, there is no systematic error in $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$ in all four sets of temperature and ionic strength data.

Self-consistency of the proposed activity coefficients in alcohol/water/salt solution - a critical test.

In Table 7 is listed the experimental conditions (top seven rows) and analysis results (bottom seven rows) of the calcite dissolution experiments in the presence of a gas phase. As explained in the Data Interpretation section, the end products of these calcite dissolution experiments can be predicted, apriori, from initial conditions via the proposed model as would be done in an application. Therefore, a comparison of experimental results to calculations via Eqs. 23 to 25 provides an independent validation of our activity model. Both measured and calculated reaction end products are compared. All four measured parameters ($P_{\text{CO}_{2,\text{g}}}$, T_{Ca} , T_{HCO_3} , and $\text{pa}_{\text{H}^+}^*$) compare well with the calculated values. Typical

errors between the calculated values to the measured values are less than 5%, except for the bicarbonate concentration of Exp. 4 (8%).

Often, the activity model is used to predict whether the ions in the solution will form scale, this is done using the supersaturation index (SI), where SI is defined as the logarithm of the ratio of ion activity product to calcite solubility product, Eq. 33.

$$SI = \log \left\{ \frac{[Ca^{2+}] \cdot [HCO_3^-]^2 \cdot \gamma_{Ca}^S \cdot \gamma_{Ca}^N \cdot \gamma_{HCO_3^-}^S{}^2 \cdot \gamma_{HCO_3^-}^N{}^2 \cdot K_2}{P_{CO_2,g} \cdot \gamma_{CO_2,g} \cdot K_H \cdot K_1 \cdot K_{sp}} \right\} \quad (33)$$

In Eq. 33, the SI is determined from measured T_{Ca} , T_{HCO_3} , and $P_{CO_2,g}$ values. SI can also be calculated from the T_{Ca} , T_{HCO_3} , and $pa_{H^+}^*$ values or T_{Ca} , $P_{CO_2,g}$, and $pa_{H^+}^*$. However, $pa_{H^+}^*$ based SI values are typically less accurate than $P_{CO_2,g}$ based SI since $P_{CO_2,g}$ can be more accurately measured than $pa_{H^+}^*$. In Eq. 33, all γ^S values are determined by ScaleSoftPitzer[®] and γ^N values are from Eqs. 29 and 32. For the four experiments in Table 7, the theoretical SI should be equal to 0 since the solution is at equilibrium with calcite. The deviation of the reported SI values from zero (0.00) is a good estimate of the overall error expected for scale prediction using this model. When γ^N values calculated from Eqs. 29 and 32 are used to determine SI, the experimental SI values deviate from theoretical values by -0.08 to 0.1 SI unit. These deviations from zero are similar to what is typically obtained in the absence of methanol, again supporting the overall model approach and experimental results.

Field implication. The potential impact of methanol on calcite scale formation in realistic field conditions of a natural gas producing well can be illustrated with the following example using the scale-prediction software specifically written for oil field application (ScaleSoftPitzer[®]). Eqs. 29-32 has been incorporated into ScaleSoftPitzer[®] V.4.0. Details of the software, which is a Microsoft Excel[®] program, have been discussed in earlier papers by the authors^{23,24}. Prediction of scaling in the presence of methanol has been simulated for a typical set of well conditions: the produced brine is assumed to contain 4,750 mg/L Ca, 840 mg/L bicarbonate alkalinity, 71,779 mg/L total dissolved solids (total molar ionic strength), equilibrated with 1% CO₂ in the gas phase, at 55 °F and 2,940 psig pressure. These

conditions made the brine near saturation in the absence of methanol (See Figure 4). In Figure 4 is plotted the predicted change in saturation index of calcite versus the methanol concentration (% vol). The simulation shows that a significant amount of calcite will precipitate in the presence of as little as 20% methanol (by volume) in the system.

Eqs 29 to 32 can be used in conjunction with any other scale prediction equations or softwares. In Figure 5 is a nomogram, to estimate the γ^N values and dielectric constant of the solvent for any methanol concentrations (vol%, wt%, mole fraction). The nomograms are calculated for 1 m I and 25 °C. For example, to determine the γ^N -values at 50 vol% methanol concentration, draw a horizontal line from the 50% mark on the lower Y-axis to intercept curved Line 1, i.e., the vol% vs. mole fraction curve. Then, draw a vertical line through the intercept of the horizontal line and Line 1. The intercept of the vertical line and X-axis shows the corresponding mole fraction of methanol. The intercepts of the vertical line through curved Lines 2-7 yield the corresponding methanol concentration in wt%, dimensionless dielectric constant (ϵ), $\gamma_{\text{CO}_2, \text{aq}}^N$, $\gamma_{\text{HCO}_3^-}^N$, $\gamma_{\text{Ca}^{2+}}^N$, and $\gamma_{\text{CO}_3^{2-}}^N$ values, respectively. Figure 5 can also serve as an estimate of γ^N values for other conditions, since the temperature and ionic strength dependence of γ^N -values are relatively small. Combining γ^N with common activity coefficient calculations for the electrolytes, the solubility and saturation index of calcite at different methanol concentrations can be predicted.

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Table 1. EMF measurements of six solutions which contain HCl (0.919 mM) and various NaCl concentrations, all at 25 °C.

NaCl (m)	$\gamma_{\text{H}^+}^{\text{x m NaCl a}}$	EMF (mv)	ΔE_j (mv)	ΔpH_j
0.000	0.991	233.7	0.00	0.00
0.100	0.803	232.3	3.95	0.07
0.500	0.792	234.2	6.21	0.11
1.000	0.881	238.6	7.90	0.13
2.000	1.179	248.4	10.27	0.18
3.000	1.641	259.7	13.17	0.23

a Activity coefficient is calculated based on Pitzer theory of electrolyte interaction using a Microsoft Excel Visual Basic program - ScaleSoftPitzer®.

Table 2. Experimentally determined pK_H , pK_1 , pK_2 , for carbonate equilibrium and pK_{sp} for calcite at 1-3 m ionic strength and 4-25 °C. Data were compared with the literature reported equilibrium constants after correction with activity coefficients calculated with Pitzer theory of ion interaction^a and temperature.

1. CO2 solubility													
T (C)	NaCl (m)	NaHC O ₃ (m)	HCl (m)	PCO ₂ (psia)	CO ₂ , _{aq} (m)	pK _H [']	γ _{CO₂,aq} ^S	Exp. pK _H	pK _H ^b	Δ ^c			
25	0.94	0.038	0.040	5.17	0.010	1.55	1.15	1.49	1.47	-0.02			
25	0.00	0.039	0.046	4.88	0.011	1.47	1.01	1.46	1.47	0.00			
25	2.80	0.037	0.050	4.92	0.007	1.65	1.50	1.48	1.47	-0.01			
4	0.94	0.037	0.046	3.77	0.014	1.25	1.15	1.19	1.18	-0.02			
4	2.80	0.037	0.050	4.14	0.011	1.41	1.50	1.24	1.18	-0.06			
2. First carbonic acid dissociation constant													
T (C)	NaCl (m)	NaHC O ₃ (m)	HCl (m)	CO ₂ , _{aq} (m)	HCO ₃ ⁻ (m)	pH	pa _{H⁺} [*]	pK ₁ [']	γ _{CO₂,aq} ^S	γ _{HCO₃⁻} ^S	Exp. pK ₁	pK ₁ ^b	Δ ^c
24	1.00	0.01	0.005	0.0050	0.0049	5.95	6.08	6.09	1.16	0.56	6.41	6.36	-0.04
24	3.00	0.01	0.005	0.0049	0.0050	5.65	5.88	5.87	1.53	0.49	6.37	6.36	0.00
4	1.00	0.01	0.005	0.0050	0.0049	6.02	6.17	6.17	1.15	0.53	6.52	6.53	0.01
4	3.00	0.01	0.005	0.0050	0.0050	5.68	5.92	5.92	1.53	0.43	6.47	6.53	0.06
3. Second carbonic acid dissociation constant													
T (C)	NaCl (m)	NaHC O ₃ (m)	NaOH (m)	HCO ₃ ⁻ (m)	CO ₃ ²⁻ (m)	pH	pa _{H⁺} [*]	pK ₂ [']	γ _{HCO₃⁻} ^S	γ _{CO₃²⁻} ^S	Exp. pK ₂	pK ₂ ^b	Δ ^c
24	1.00	0.01	0.005	0.0050	0.0050	9.48	9.61	9.61	0.56	0.10	10.37	10.35	-0.02
24	1.00	0.01	0.005	0.0050	0.0050	9.47	9.61	9.60	0.56	0.10	10.36	10.35	-0.01
24	2.00	0.01	0.005	0.0050	0.0050	9.20	9.38	9.38	0.51	0.06	10.31	10.35	0.04
24	2.00	0.01	0.005	0.0050	0.0050	9.23	9.41	9.41	0.51	0.06	10.33	10.35	0.01
24	3.00	0.01	0.005	0.0050	0.0050	9.09	9.32	9.32	0.49	0.04	10.38	10.35	-0.04
4	1.00	0.01	0.005	0.0051	0.0050	9.80	9.94	9.95	0.53	0.10	10.67	10.57	-0.10
4	2.00	0.01	0.005	0.0050	0.0050	9.47	9.66	9.66	0.46	0.06	10.58	10.57	-0.01
4. CaCO ₃ solubility product													
T (°C)	NaCl (m)	NaHC O ₃ (m)	HCl (m)	Ca ²⁺ (m)	HCO ₃ ⁻ (m)	pa _{H⁺} [*]	pK ₂ [']	pK _{sp} [']	γ _{Ca²⁺} ^S	γ _{HCO₃⁻} ^S	Exp. pK _{sp}	pK _{sp} ^b	Δ ^c
24	1.00	0.020	0.021	0.011	0.021	6.37	9.59	6.85	0.22	0.56	8.51	8.47	-0.04
24	1.00	0.020	0.020	0.011	0.022	6.43	9.59	6.78	0.22	0.56	8.43	8.47	0.04
24	2.95	0.020	0.023	0.012	0.021	6.19	9.28	6.67	0.34	0.50	8.51	8.47	-0.04
24	2.95	0.020	0.023	0.012	0.021	6.15	9.28	6.73	0.34	0.50	8.56	8.47	-0.09
4	1.00	0.020	0.020	0.012	0.025	6.73	9.83	6.63	0.23	0.54	8.28	8.39	0.11
4	2.96	0.020	0.020	0.012	0.024	6.48	9.51	6.55	0.33	0.44	8.46	8.39	-0.07

^a Activity coefficient is calculated based on Pitzer theory of electrolyte interaction using a Microsoft Excel Visual Basic program - ScaleSoftPitzer[®]. ^b The temperature dependence of the thermodynamic equilibrium constants were that of Langmuir²⁰. ^c $\Delta = pK - \text{Exp. } pK$

Table 3. Partition of CO_{2(g)} between gas and methanol/water/salt solution: Experimental condition and results. Concentrations are in terms of moles of solute per Kg of water in the solution.

I (m)	T (°C)	MeOH (wt%)	MeOH (mole fraction)	NaCl (m)	NaHCO ₃ (m)	HCl (m)	P _{CO2} (psia)	CO _{2, aq} (m)	pK' _H	log($\gamma_{CO_2, aq}^N$)	Pred. ^a log($\gamma_{CO_2, aq}^N$)
0.98	25	0.00	0.00	0.94	0.038	0.040	5.17	0.010	1.55	0.02	0.00
0.04	25	0.00	0.00	0.00	0.039	0.046	4.88	0.011	1.47	0.00	0.00
0.98	25	0.00	0.00	0.93	0.037	0.048	4.71	0.010	1.51	-0.01	0.00
0.98	25	9.96	0.06	0.93	0.037	0.053	4.28	0.011	1.43	-0.10	-0.07
0.98	25	20.29	0.13	0.93	0.037	0.050	3.58	0.011	1.33	-0.20	-0.17
0.98	25	30.03	0.19	0.94	0.037	0.048	3.11	0.012	1.25	-0.28	-0.27
0.98	25	39.68	0.27	0.94	0.037	0.050	2.56	0.013	1.12	-0.41	-0.40
0.98	25	49.60	0.36	0.94	0.037	0.048	2.02	0.015	0.96	-0.57	-0.57
0.98	25	59.07	0.45	0.94	0.037	0.046	1.55	0.017	0.80	-0.73	-0.76
0.95	25	78.55	0.67	0.91	0.036	0.044	0.59	0.022	0.27	-1.26	-1.33
2.84	25	0.00	0.00	2.80	0.037	0.050	4.92	0.007	1.65	0.01	0.00
2.84	25	20.81	0.13	2.79	0.037	0.052	3.90	0.009	1.47	-0.18	-0.17
2.84	25	33.47	0.22	2.79	0.037	0.052	2.99	0.010	1.31	-0.34	-0.32
2.85	25	40.23	0.27	2.80	0.037	0.050	2.75	0.012	1.20	-0.44	-0.41
2.83	25	51.34	0.37	2.79	0.037	0.052	1.94	0.014	0.97	-0.67	-0.60
2.85	25	59.30	0.45	2.81	0.037	0.049	1.62	0.016	0.83	-0.81	-0.77
0.98	4	0.00	0.00	0.94	0.037	0.046	3.77	0.014	1.25	0.02	0.00
0.98	4	21.02	0.13	0.94	0.037	0.048	2.95	0.015	1.13	-0.11	-0.13
0.98	4	29.89	0.19	0.94	0.037	0.050	2.49	0.015	1.05	-0.19	-0.20
0.98	4	39.45	0.27	0.93	0.037	0.049	2.17	0.016	0.97	-0.26	-0.30
0.98	4	50.14	0.36	0.93	0.037	0.051	1.67	0.017	0.82	-0.42	-0.45
0.98	4	59.95	0.46	0.93	0.037	0.052	1.17	0.020	0.61	-0.63	-0.62
0.98	4	79.68	0.69	0.93	0.037	0.054	0.43	0.025	0.07	-1.16	-1.11
2.84	4	0.00	0.00	2.80	0.037	0.050	4.14	0.011	1.41	0.06	0.00
2.84	4	0.00	0.00	2.80	0.037	0.050	4.14	0.011	1.40	0.05	0.00
2.82	4	22.30	0.14	2.78	0.037	0.056	2.90	0.011	1.24	-0.11	-0.14
2.83	4	31.59	0.21	2.79	0.037	0.053	2.52	0.013	1.14	-0.21	-0.22
2.84	4	42.22	0.29	2.80	0.037	0.056	2.13	0.013	1.04	-0.31	-0.34
2.82	4	54.18	0.40	2.77	0.037	0.057	1.64	0.014	0.91	-0.44	-0.51
2.82	4	61.42	0.47	2.77	0.037	0.055	1.18	0.018	0.64	-0.71	-0.65

^a Predicted from Eq. 29.

Table 4. Experimental condition for determination of bicarbonate-methanol interaction activity coefficient ($\gamma_{\text{HCO}_3^-}^{\text{N}}$).

I (m)	T (°C)	MeOH (wt fr)	MeOH (x)	PH _{meter} reading	pa _{H⁺} [*]	H ₂ CO ₃ (mm)	HCO ₃ ⁻ (mm)	pK ₁ [']	$\gamma_{\text{CO}_2, \text{aq}}^{\text{N}}$ ^a	$\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$	Pred. $\log(\gamma_{\text{HCO}_3^-}^{\text{N}})$ ^b
1.01	24	0.00	0.00	5.95	6.08	5.02	4.91	6.05	1.00	0.04	0.00
1.01	24	0.16	0.10	6.18	6.26	5.01	4.92	6.27	0.75	0.09	0.01
1.01	24	0.31	0.20	6.34	6.40	5.02	4.89	6.41	0.52	0.08	0.03
1.01	24	0.50	0.36	6.70	6.69	5.10	4.81	6.72	0.27	0.10	0.08
1.01	24	0.65	0.51	7.02	6.97	5.08	4.80	6.99	0.12	0.04	0.16
1.01	24	0.76	0.63	7.26	7.26	5.21	4.64	7.31	0.06	0.05	0.24
1.01	24	0.84	0.75	7.60	7.84	5.22	4.57	7.90	0.03	0.32	0.33
1.01	4	0.00	0.00	6.02	6.17	5.02	4.91	6.17	1.00	-0.01	0.00
1.01	4	0.16	0.10	6.14	6.29	5.02	4.91	6.30	0.81	0.02	0.03
1.01	4	0.31	0.20	6.33	6.45	5.04	4.87	6.46	0.62	0.07	0.07
1.01	4	0.50	0.36	6.68	6.73	5.10	4.80	6.76	0.36	0.12	0.17
1.01	4	0.65	0.51	6.98	6.99	5.08	4.80	7.01	0.19	0.10	0.28
1.01	4	0.76	0.63	7.22	7.29	5.29	4.56	7.35	0.10	0.18	0.39
1.01	4	0.84	0.75	7.52	7.83	5.22	4.57	7.89	0.05	0.43	0.51
3.01	24	0.00	0.00	5.65	5.88	4.94	4.99	5.87	1.00	0.00	0.00
3.01	24	0.15	0.09	5.77	5.99	5.02	4.90	6.00	0.77	0.01	0.01
3.01	24	0.30	0.20	5.97	6.15	5.01	4.91	6.16	0.53	0.02	0.02
3.01	24	0.50	0.36	6.34	6.45	5.05	4.85	6.47	0.27	0.03	0.08
3.01	24	0.65	0.51	6.70	6.77	5.02	4.86	6.79	0.13	0.02	0.15
3.01	24	0.75	0.63	6.95	7.07	5.19	4.66	7.12	0.06	0.06	0.23
3.01	24	0.84	0.75	7.27	7.64	5.21	4.58	7.70	0.03	0.29	0.33
3.01	4	0.00	0.00	5.68	5.92	4.97	4.96	5.92	1.00	-0.06	0.00
3.01	4	0.15	0.09	5.86	6.15	5.01	4.91	6.15	0.82	0.09	0.03
3.01	4	0.30	0.20	5.97	6.23	5.01	4.91	6.24	0.62	0.05	0.07
3.01	4	0.50	0.36	6.38	6.58	4.96	4.94	6.58	0.36	0.15	0.17
3.01	4	0.65	0.51	6.71	6.86	5.03	4.85	6.87	0.19	0.17	0.28
3.01	4	0.75	0.63	7.18	7.38	5.02	4.83	7.39	0.11	0.44	0.38

^a Calculated from eq. 29. ^b Predicted from eq. 30.

Table 5. Experimental condition and determination of carbonate-methanol interaction activity coefficient ($\gamma_{\text{CO}_3^{2-}}^{\text{N}}$).

I (m)	T (C)	MeOH (wt fr)	MeOH (x)	PH _{meter} reading	pa _{H⁺} [*]	pK ₂ '	$\gamma_{\text{HCO}_3^-}^{\text{N}}$ ^a	$\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$	Pred. ^b $\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$
1.01	24	0.00	0.00	9.47	9.60	9.60	1.00	0.01	0.00
1.00	24	0.00	0.00	9.48	9.61	9.61	1.00	0.02	0.00
1.00	24	0.16	0.10	9.83	9.94	9.94	0.99	0.34	0.32
1.01	24	0.16	0.10	9.85	9.96	9.96	0.99	0.36	0.32
1.00	24	0.28	0.18	10.10	10.19	10.18	0.99	0.59	0.56
1.01	24	0.28	0.18	10.11	10.20	10.20	0.99	0.61	0.56
1.00	24	0.37	0.25	10.31	10.37	10.37	1.01	0.79	0.74
1.01	24	0.37	0.25	10.31	10.37	10.37	1.01	0.78	0.74
1.00	24	0.44	0.31	10.46	10.49	10.49	1.04	0.92	0.88
1.01	24	0.44	0.31	10.45	10.49	10.49	1.04	0.92	0.88
1.00	24	0.50	0.36	10.55	10.56	10.56	1.07	1.00	0.99
1.01	24	0.50	0.36	10.56	10.58	10.58	1.07	1.02	0.99
1.00	24	0.54	0.40	10.63	10.63	10.63	1.10	1.08	1.09
1.01	24	0.54	0.40	10.64	10.65	10.64	1.10	1.10	1.09
1.01	24	0.70	0.57	10.81	10.79	10.79	1.30	1.32	1.40
1.01	24	0.73	0.61	10.88	10.88	10.88	1.37	1.43	1.45
1.00	24	0.73	0.61	10.85	10.85	10.85	1.37	1.39	1.45
1.01	24	0.78	0.67	10.78	10.86	10.86	1.48	1.44	1.53
1.01	24	0.81	0.70	10.81	10.95	10.94	1.56	1.55	1.57
1.00	24	0.81	0.70	10.74	10.87	10.87	1.56	1.48	1.57
1.01	24	0.85	0.76	10.69	10.99	10.98	1.71	1.63	1.63
1.00	24	0.85	0.76	10.62	10.92	10.92	1.71	1.56	1.63
1.01	4	0.00	0.00	9.80	9.94	9.94	1.00	0.10	0.00
1.01	4	0.16	0.10	10.17	10.21	10.21	1.12	0.41	0.36
1.01	4	0.28	0.18	10.43	10.44	10.45	1.23	0.69	0.63
1.01	4	0.37	0.25	10.62	10.61	10.61	1.32	0.89	0.83
1.01	4	0.44	0.31	10.76	10.72	10.73	1.41	1.03	1.00
1.01	4	0.50	0.36	10.87	10.81	10.82	1.49	1.14	1.13
1.01	4	0.54	0.40	10.95	10.88	10.89	1.56	1.23	1.24
1.01	4	0.74	0.61	11.18	11.11	11.12	1.98	1.57	1.69
1.01	4	0.81	0.70	11.11	11.17	11.18	2.20	1.67	1.84
1.01	4	0.85	0.76	11.00	11.22	11.23	2.34	1.75	1.92

Table 5. Experimental condition and determination of carbonate-methanol interaction activity coefficient ($\gamma_{\text{CO}_3^{2-}}^{\text{N}}$), cont'l.

I (m)	T (C)	MeOH (wt fr)	MeOH (x)	PH _{meter} reading	pa _{H⁺} [*]	pK ₂ [']	$\gamma_{\text{HCO}_3^-}^{\text{N}}$ ^a	$\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$	Pred. ^b $\log(\gamma_{\text{CO}_3^{2-}}^{\text{N}})$
2.01	24	0.00	0.00	9.23	9.41	9.41	1.00	-0.01	0.00
2.01	24	0.00	0.00	9.20	9.38	9.38	1.00	-0.04	0.00
2.01	24	0.17	0.10	9.59	9.77	9.77	0.99	0.34	0.32
2.01	24	0.17	0.10	9.56	9.74	9.74	0.99	0.31	0.32
2.01	24	0.29	0.18	9.83	9.99	9.99	0.99	0.56	0.56
2.01	24	0.29	0.18	9.80	9.96	9.96	0.99	0.54	0.56
2.01	24	0.37	0.25	10.01	10.15	10.15	1.01	0.73	0.75
2.01	24	0.37	0.25	10.00	10.13	10.13	1.01	0.71	0.75
2.01	24	0.44	0.31	10.17	10.28	10.28	1.04	0.87	0.89
2.01	24	0.44	0.31	10.17	10.28	10.28	1.04	0.87	0.89
2.01	24	0.50	0.36	10.27	10.36	10.36	1.07	0.96	1.00
2.01	24	0.50	0.36	10.28	10.37	10.36	1.07	0.97	1.00
2.01	24	0.54	0.40	10.39	10.46	10.46	1.10	1.08	1.09
2.01	24	0.54	0.40	10.37	10.44	10.44	1.10	1.06	1.09
2.01	24	0.74	0.62	10.69	10.77	10.77	1.39	1.49	1.47
2.01	24	0.74	0.62	10.70	10.79	10.79	1.39	1.51	1.47
2.01	24	0.81	0.71	10.62	10.85	10.85	1.58	1.62	1.58
2.01	24	0.81	0.71	10.66	10.89	10.89	1.58	1.66	1.58
2.01	24	0.85	0.77	10.57	10.97	10.97	1.73	1.78	1.64
2.01	24	0.85	0.77	10.55	10.95	10.95	1.73	1.76	1.64
2.01	4	0.00	0.00	9.47	9.66	9.66	1.00	0.01	0.00
2.01	4	0.17	0.10	9.84	10.02	10.01	1.04	0.38	0.36
2.01	4	0.29	0.18	10.11	10.26	10.26	1.09	0.65	0.63
2.01	4	0.37	0.25	10.31	10.44	10.44	1.16	0.85	0.84
2.01	4	0.44	0.31	10.48	10.58	10.58	1.23	1.01	1.01
2.01	4	0.50	0.36	10.60	10.68	10.68	1.30	1.14	1.14
2.01	4	0.54	0.40	10.72	10.78	10.78	1.37	1.26	1.25
2.01	4	0.74	0.62	11.11	11.18	11.19	1.93	1.82	1.70
2.01	4	0.81	0.71	11.03	11.25	11.26	2.30	1.97	1.85
2.01	4	0.85	0.76	10.92	11.30	11.31	2.60	2.07	1.93
3.01	24	0.00	0.00	9.09	9.32	9.32	1.00	0.04	0.00
3.01	24	0.18	0.11	9.47	9.64	9.65	0.99	0.36	0.35
3.01	24	0.30	0.20	9.72	9.87	9.88	1.00	0.59	0.60
3.01	24	0.39	0.27	9.92	10.05	10.05	1.02	0.77	0.79
3.01	24	0.46	0.33	10.07	10.17	10.17	1.05	0.91	0.93
3.01	24	0.52	0.38	10.18	10.26	10.26	1.08	1.01	1.04
3.01	24	0.57	0.42	10.25	10.31	10.32	1.12	1.08	1.14

^a Calculated from Eq. 30. ^b Predicted from Eq. 31.

Table 6. Experimental condition and result of calcite dissolution experiments in the absence of gas phase.

T (°C)	MeOH (x)	NaCl (m)	NaHCO ₃ (m)	HCl (m)	Ca ²⁺ (m)	HCO ₃ ⁻ (m)	pa _{H⁺} ^a	pK _{sp} [*]	log(γ_{Ca}^N)	Pred. ^b log(γ_{Ca}^N)
24	0.000	1.00	0.020	0.021	0.0111	0.0209	6.37	6.85	0.04	0.00
24	0.000	1.00	0.020	0.020	0.0111	0.0218	6.43	6.77	-0.04	0.00
24	0.061	1.00	0.020	0.020	0.0084	0.0164	6.27	7.40	0.38	0.18
24	0.061	1.00	0.020	0.020	0.0091	0.0173	6.30	7.31	0.29	0.18
24	0.127	1.00	0.020	0.021	0.0082	0.0150	6.27	7.64	0.42	0.36
24	0.128	1.00	0.020	0.021	0.0082	0.0147	6.26	7.67	0.45	0.36
24	0.200	1.00	0.020	0.022	0.0073	0.0126	6.27	7.98	0.55	0.53
24	0.201	1.00	0.020	0.021	0.0069	0.0128	6.29	7.98	0.55	0.53
24	0.369	1.00	0.020	0.020	0.0045	0.0085	6.40	8.62	0.77	0.81
24	0.369	1.00	0.020	0.020	0.0046	0.0086	6.41	8.60	0.75	0.81
24	0.465	0.99	0.019	0.030	0.0079	0.0051	6.26	8.89	0.86	0.91
24	0.466	1.00	0.020	0.022	0.0041	0.0061	6.45	8.91	0.87	0.91
24	0.637	1.00	0.020	0.020	0.0023	0.0038	6.74	9.26	0.95	0.98
24	0.764	1.00	0.020	0.022	0.0021	0.0020	6.86	9.52	1.06	0.93
24	0.000	2.95	0.020	0.023	0.0122	0.0214	6.19	6.67	0.04	0.00
24	0.000	2.95	0.020	0.023	0.0121	0.0207	6.15	6.72	0.09	0.00
24	0.068	2.95	0.020	0.022	0.0104	0.0180	6.13	7.10	0.26	0.16
24	0.067	2.95	0.020	0.022	0.0099	0.0172	6.10	7.17	0.33	0.16
24	0.139	2.95	0.020	0.022	0.0097	0.0166	6.17	7.34	0.28	0.30
24	0.139	2.95	0.020	0.024	0.0096	0.0153	6.10	7.46	0.39	0.30
24	0.217	2.95	0.020	0.022	0.0086	0.0144	6.21	7.64	0.35	0.42
24	0.218	2.95	0.020	0.023	0.0086	0.0142	6.19	7.66	0.37	0.42
24	0.393	2.95	0.020	0.022	0.0062	0.0100	6.35	8.17	0.47	0.59
24	0.393	2.95	0.020	0.022	0.0062	0.0097	6.33	8.21	0.50	0.59
24	0.493	2.95	0.020	0.023	0.0055	0.0080	6.46	8.37	0.49	0.61
24	0.492	2.95	0.020	0.023	0.0055	0.0078	6.46	8.39	0.49	0.61
24	0.660	2.95	0.020	0.023	0.0039	0.0044	6.68	8.74	0.58	0.54
24	0.660	2.94	0.019	0.028	0.0060	0.0038	6.57	8.71	0.56	0.54
24	0.785	2.95	0.020	0.025	0.0038	0.0026	6.87	8.81	0.53	0.40
24	0.786	2.95	0.020	0.024	0.0036	0.0031	6.96	8.69	0.41	0.40
4	0.000	1.00	0.020	0.020	0.0123	0.0245	6.73	6.63	-0.10	0.00
4	0.061	1.00	0.020	0.022	0.0115	0.0211	6.59	7.07	0.12	0.11
4	0.201	1.00	0.020	0.019	0.0082	0.0166	6.63	7.73	0.30	0.30
4	0.366	1.00	0.020	0.020	0.0065	0.0126	6.74	8.23	0.34	0.39
4	0.467	1.00	0.020	0.020	0.0051	0.0097	6.82	8.56	0.42	0.38
4	0.467	1.00	0.020	0.019	0.0050	0.0103	6.87	8.50	0.35	0.38
4	0.632	1.00	0.020	0.020	0.0038	0.0067	7.08	8.80	0.33	0.25
4	0.627	1.00	0.020	0.020	0.0037	0.0071	7.11	8.76	0.29	0.26
4	0.765	1.00	0.020	0.020	0.0032	0.0061	7.49	8.59	-0.09	0.05
4	0.000	2.96	0.020	0.020	0.0124	0.0241	6.48	6.55	0.07	0.00
4	0.068	2.96	0.020	0.021	0.0115	0.0217	6.43	6.92	0.19	0.08
4	0.217	2.96	0.020	0.020	0.0093	0.0184	6.52	7.45	0.23	0.17
4	0.394	2.96	0.020	0.020	0.0074	0.0142	6.68	7.91	0.21	0.13
4	0.491	2.96	0.020	0.021	0.0067	0.0120	6.79	8.08	0.14	0.05
4	0.650	2.94	0.019	0.028	0.0090	0.0091	7.01	8.04	-0.20	-0.19
4	0.650	2.96	0.020	0.020	0.0047	0.0093	7.12	8.20	-0.03	-0.20
4	0.780	2.95	0.020	0.024	0.0061	0.0080	7.44	7.90	-0.52	-0.49
4	0.791	2.96	0.020	0.020	0.0049	0.0094	7.61	7.76	-0.68	-0.52

^a Calculated from eq. 6. ^b Predicted from eq. 32.

Table 7. Calcite solubility in methanol/salt/water solution with gas phase

A. Experimental condition												
Exp No.	I (m)	T (°C)	MeOH (x)	NaCl (m)	NaHCO ₃ (m)	CaCl ₂ (m)	HCl (m)	CaCO ₃ (g)				
1	1.04	24	0.00	0.95	0.0380	0.000	0.0466	1.00				
2	1.02	24	0.16	0.95	0.0380	0.000	0.0428	1.01				
3	1.01	25	0.32	0.95	0.0380	0.000	0.0430	1.00				
4	1.31	22	0.17	0.95	0.0000	0.093	0.0426	1.00				
B. Observed and calculated results												
Exp. No.	P _{CO2} ^b (atm)			T _{Ca} ^b (m)			T _{HCO3} ^b (m)			pa _{H⁺} ^b		SI ^d
	Meas	Calc	error ^a (%)	Meas	Calc	error ^a (%)	Meas ^c	Calc	error ^a (%)	Meas	Calc	New
1	0.53	0.58	4.55	0.0152	0.0166	3.80	0.0248	0.0242	5.21	6.19	6.18	-0.08
2	0.41	0.40	0.93	0.0101	0.0104	1.46	0.0175	0.0160	1.92	6.17	6.15	-0.05
3	0.27	0.27	0.01	0.0078	0.0077	0.32	0.0123	0.0102	1.45	6.22	6.14	0.07
4	0.24	0.23	2.72	0.1200	0.116	1.69	(0.0048)	0.0041	8.17	5.90	5.79	0.10

a % error = (Meas. - Calc.)/(Meas.+Calc.)*100. b For each parameter, Meas. is the measured quantity; Calc is the calculated quantity (Eqs.23-25). c Measured total bicarbonate concentration are either determined by charge balance or by H₂SO₄ titration (in parentheses). d SI is calculated from Eq. 33 where SI values are calculated with γ^N values determined by Eqs. 29-32.

Figure captions:

Figure 1. Plot of the observed conditional Henry's law constant for CO₂ (pK'_H) versus alcohol concentrations of this study and two sets of literature data, where our data are the methanol data at 1 m ionic strength and 25 °C, the literature data are from Sada et al.²¹ (methanol data at 0 m ionic strength and 25 °C) and Stephen and Stephen²² (ethanol data at 0 m ionic strength and 20 °C).

Figure 2. Plot of the conditional equilibrium constants ($pK'_H, pK'_1, pK'_2, pK'_{sp}$) versus methanol concentrations (mole fraction) using the data listed in Tables 3-6.

Figure 3. Plot of the calculated vs. measured values of $\log(\gamma_{CO_2,aq}^N, \gamma_{HCO_3^-}^N, \gamma_{CO_3^{2-}}^N, \text{ and } \gamma_{Ca^{2+}}^N)$. The predicted values are calculated from Eqs. 29-32 and the observed values are listed in Tables 3-6.

Figure 4. Plot of calcite SI (the right axis) and the concentration of calcite (mg/L) that will precipitate (the left axis) versus methanol concentration (vol%), where the simulation is calculated with a Pitzer theory based program, ScaleSoftPitzer[®], under realistic oil and gas well conditions. In this simulation, the brine is assumed to contain 4750 mg/L Ca, 840 mg/L bicarbonate, 71,779 mg/L TDS, at equilibrium with 1%CO₂ in the gas phase, and at 55 °F and 2940 psig pressure.

Figure 5. Plot of methanol (1) vol% concentration, (2) wt% concentrations, (3) mixed solvent dielectric constants, (4) $\gamma_{CO_2,aq}^N$, (5) $\gamma_{HCO_3^-}^N$, (6) $\gamma_{CO_3^{2-}}^N$, and (7) $\gamma_{Ca^{2+}}^N$ versus methanol mole fraction concentration, where $\gamma_{CO_2,aq}^N, \gamma_{HCO_3^-}^N, \gamma_{CO_3^{2-}}^N, \gamma_{Ca^{2+}}^N$ is calculated from Eqs. 29-32 at 25 °C and 1 m I. The mixed solvent dielectric constant is from Sen et al.²⁵.

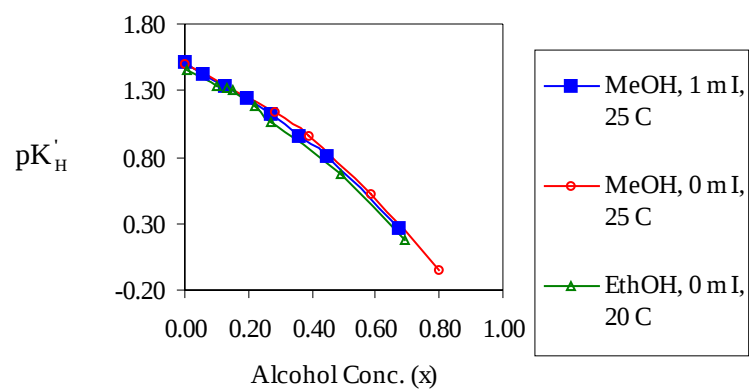


Figure 1.

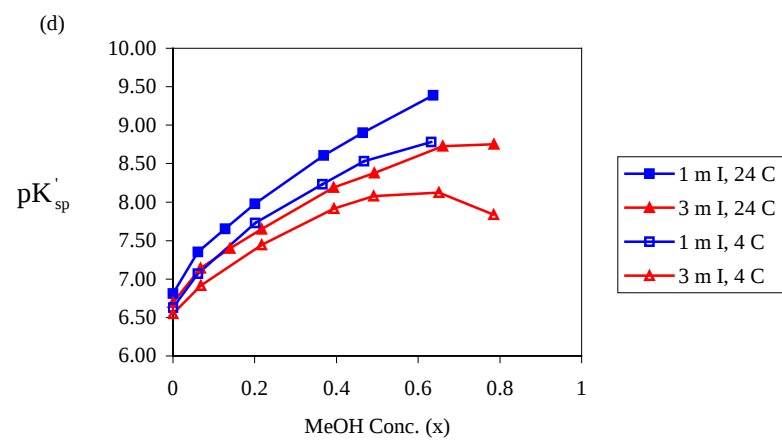
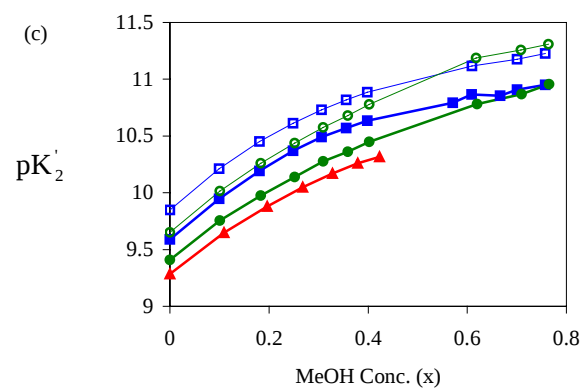
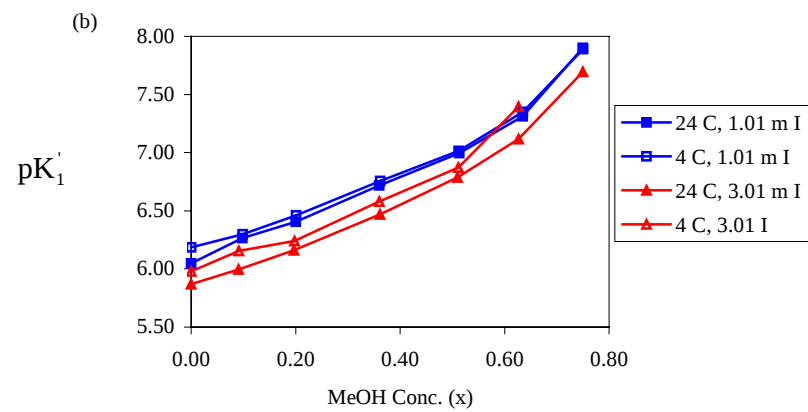
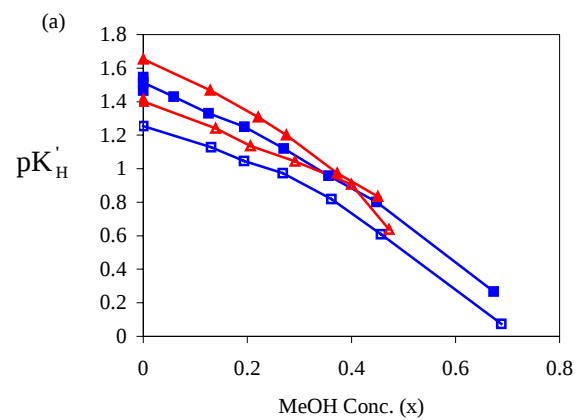


Figure 2.

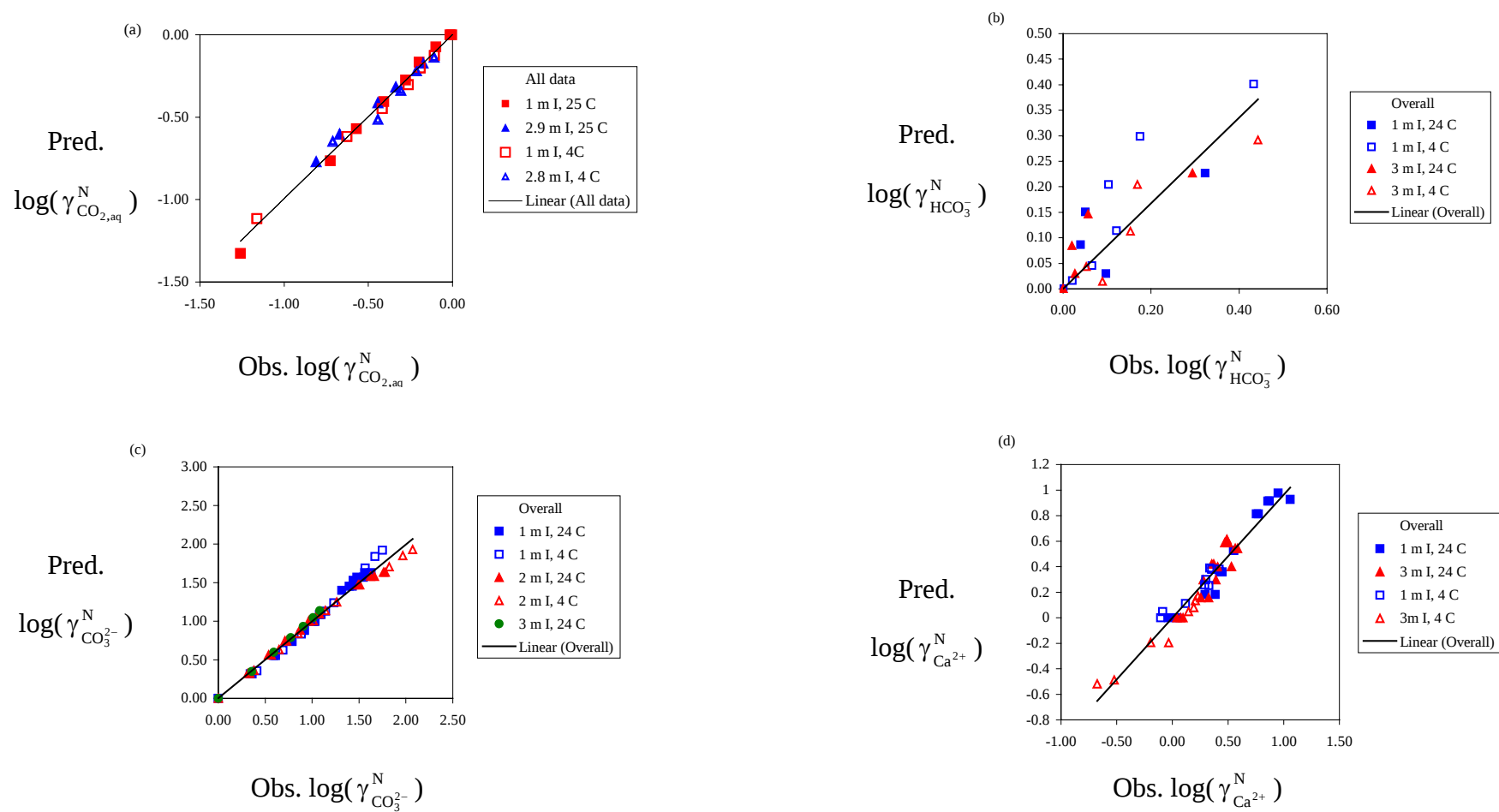


Figure 3.

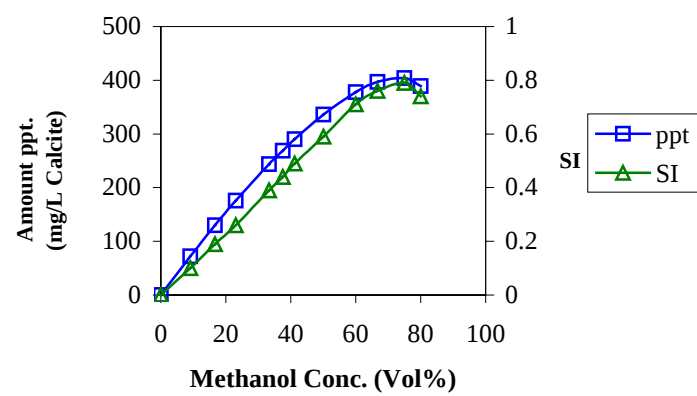


Figure 4.

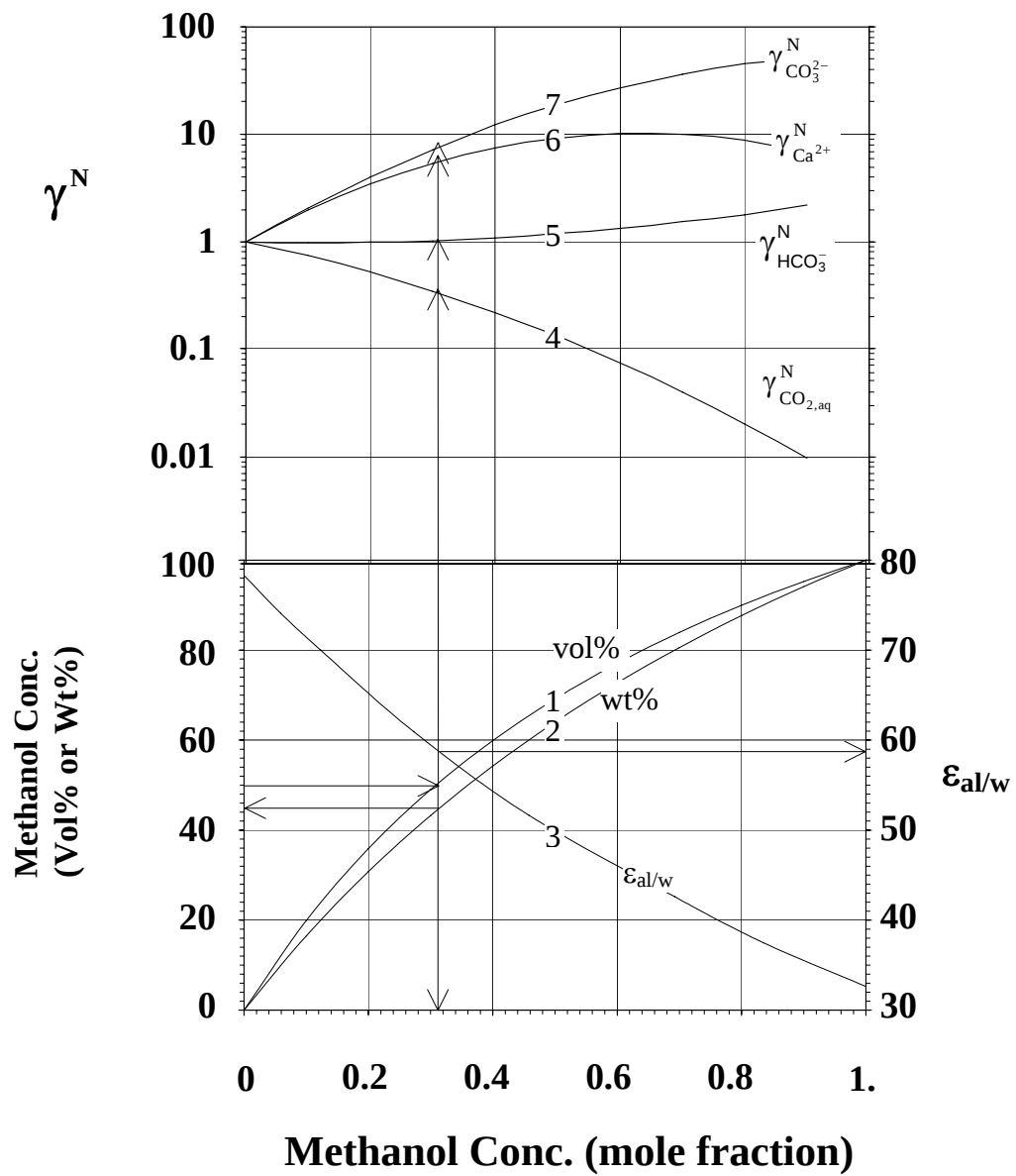


Figure 5.

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