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Carbon Dioxide Solubility and Monoethylene Glycol (MEG) Degradation at MEG Reclaiming/Regeneration Conditions

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ABSTRACT: Monoethylene glycol (MEG) is a gas hydrate inhibitor. The large amounts used in gas field industry impose the need for MEG regeneration. During this process the water−MEG mixture is heated at low pressure to remove most of the water. It is important to know the carbon dioxide equilibria under MEG regeneration conditions to prevent problems related to mineral precipitation and scale formation. The equilibrium amount of total CO_2 in solution was therefore examined in water−MEG solutions at typical MEG regeneration conditions [(50 to 98) % wt MEG, (80 to 140) °C, (50 or 100) mmol·kg^{-1} total alkalinity]. A CO_2/N_2 mixture of known composition (0.200 % or 0.050 % mol CO_2) controlled the CO_2 pressure in the reaction vessel. Discoloration was observed in some experiments, and ion chromatography showed that glycolic and formic acids were the dominating MEG degradation products. Data for the total CO_2 concentration at equilibrium are reported together with a discussion describing why common acid titration is still a valid analysis method although significant amounts of organic acids were present.

INTRODUCTION

Transporting hydrocarbons and water in long subsea flow lines from satellite fields to a platform or to shore results in new challenges to control hydrates, corrosion, and mineral scale. As the fluids cool down, water will condense, and gas hydrates will form, unless an inhibitor such as monoethylene glycol (MEG) is present.

Due to the large amounts of MEG being used for hydrate control, it is usually necessary to recycle it. The main processes for recycling of MEG are the regeneration and reclamation processes. The former implies that the incoming water−MEG solution "rich-MEG" is simply heated in a distillation column to remove most of the water. Typical conditions will be ambient pressure and 120 °C. The bottom product is the desired "lean MEG" of around 90 wt % MEG. Salts or other contaminants will consequently follow this "lean MEG" phase. In a reclamation process the water−MEG solution (either "lean" or "rich MEG") is evaporated to remove salts and other contaminants. This is typically achieved under vacuum and at (120 to 150) °C.

Sodium bicarbonate is usually added to avoid corrosion in the pipelines. The added bicarbonate will end up in the MEG recycle facility, and to control scale in such a facility it is necessary to have knowledge of the carbonic acid equilibria in eqs 1 and 2.

$$2HCO_3^- \rightarrow CO_2(g) + CO_3^{2-} + H_2O \tag{1}$$

$$CO_3^{2-} + H_2O \rightarrow CO_2(g) + 2OH^- \tag{2}$$

In regeneration/reclamation units the CO_2 partial pressure is low, and the reactions, eqs 1 and 2, will be driven to the right releasing CO_2 and increasing pH.

According to the definition of alkalinity[1] as the sum of all titratable bases, alkalinity (A_T) for the carbonate system in an aqueous solution (eqs 1 and 2) is given in eq 3 where m denotes concentration (mol·kg^{-1} solvent). The total dissolved CO_2 content ($m^{tot}_{CO_2}$) for this system is described in eq 4 where $CO_2(aq)$ is negligible at the conditions of interest.

$$A_T = m_{HCO_3^-} + m_{OH^-} + 2m_{CO_3^{2-}} - m_{H^+} \tag{3}$$

$$\begin{aligned} m^{tot}_{CO_2} &= m_{HCO_3^-} + m_{CO_3^{2-}} + m_{CO_2(aq)} \\ &\approx m_{HCO_3^-} + m_{CO_3^{2-}} \end{aligned} \tag{4}$$

In reclamation units, the alkalinity can be up to 1000 mmol·kg^{-1}. In this work a lower alkalinity [(50 to 100) mmol·kg^{-1}] typical for regeneration units was chosen.

Carbonate equilibria in MEG−water solutions have been studied in literature mainly in connection with salt precipitation. Fosbøl et al.,[2] Gärtner et al.,[3] and Oosterhof et al.[4] provide elaborate data sets on the solubility of the different species in the $NaHCO_3-Na_2CO_3$−MEG−water system. Sandengen[5] obtained data for the solubility of sparingly soluble carbonates $CaCO_3$, $BaCO_3$, $SrCO_3$, and $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, while Flaten et al[6] examined the polymorphism of calcium carbonate under MEG reclamation conditions. Thus salt solubility data are available in the literature, but to predict precipitation one obviously also need to know the equilibrium constants of eqs 1 and 2.

Hayduk and Malik[7] published a series of data for the whole range of MEG fractions at 25 °C. Later Sandengen[5] extended the range to (25 to 90) °C, with and without NaCl in solution. Recently, Kan and Lu[8] conducted experiments at (3 to 70) °C investigating the salt effect (NaCl) on CO_2 partitioning for this system. However in these studies the partial pressure of CO_2 is a lot higher ($P_{CO_2} \sim 10^5$ Pa) than in reclaiming and regeneration

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processes. Data to determine these equilibria at high temperature, high MEG content, alkaline solutions, and low CO_2 partial pressure are to our knowledge not available in the literature. The current work was therefore initiated with the aim of acquiring data for the total amount of CO_2 (eq 4) in solution at a given alkalinity and CO_2 pressure.

A secondary objective of this paper is to present results of MEG degradation under regeneration/reclamation conditions and how the degradation products influence the determination of alkalinity and the total dissolved CO_2 content. Acid titration is commonly used for monitoring MEG regeneration units and the degradation of MEG will always take place to some extent in these facilities. In the study of Rossiter et al.[9] aerated and deaerated MEG solutions were heated at 100 °C for 15 days and showed that MEG degradation took place due to thermal oxidation. They identified the major products as mainly glycolic acid ($HOCH_2COOH$), formic acid (HCOOH), and oxalic acid (HOOCCOOH). Rudenko et al.[10] confirmed that the thermal decomposition without oxidation is possible only above 157 °C. Acid titration may lead to false results in the presence of the unexpected acids and consequently result in incorrect conclusions for the operator.

EXPERIMENTAL SECTION

Materials. Monoethylene glycol (MEG) and all of the salts were supplied by Merck (analytical grade quality). Specifically, MEG purity was more than 99.5 mol %, and the salts were used without any drying. For the gas phase, two different concentrations of CO_2 in N_2 were examined, 0.050 mol % and 0.200 mol %. Any impurity in the gas was certified by the supplier (Yara Praxair) to be less than 0.001 mol %. The working solutions were made gravimetrically from MEG and deionized water (50 to 98 wt % MEG). The alkalinity (50 or 100 $\text{mmol}\cdot\text{kg}^{-1}$ of solvent) was introduced gravimetrically by the use of either $NaHCO_{3(s)}$, $Na_2CO_{3(s)}$, or $NaOH_{(aq)}$.

Equilibrium Apparatus. The equilibrium cell consisted of a round-bottom glass flask (250 cm^3 or 600 cm^3) placed in an oil bath with a glass condenser [(4 to 8) °C cooling water] connected on top. Gas was introduced through polytetrafluoroethylene (PTFE) tubing and a stainless steel filter (SS/2F/K4/05, NUPRO) to efficiently disperse it into the solution. The gas flow rate was regulated by a manual needle valve connected after the gas bottle reduction valve. Prior to the experiment a sampling tube (PTFE) and a thermocouple was inserted into the flask. A magnetic stirrer was used for mixing.

Two experimental setups were considered:

- The one used herein where a dry gas was passed directly into the reaction vessel and a glass spiral condenser was used to minimize evaporation.
- Prewetting the gas with MEG and water to avoid loss of solvent in the reaction vessel and to ensure that the gas leaving the reaction vessel was saturated with solvent vapor.

The second setup was discarded because of condensation problems in the tubing between the gas scrubbing bottle and the reaction vessel and concerns over the time it would take for the scrubbing solution to reach CO_2 saturation. The decision to pass dry gas directly into the solution was made as it was considered more important to know the exact CO_2 to N_2 gas ratio entering the reaction vessel rather than being sure the gas was saturated with MEG and water.

To ensure the gas was vapor-saturated in the chosen setup, the gas flow rate was kept low after the initial stage of the experiment. It was assumed that vigorous stirring together with the dispersion filter should lead to equilibrium between the water + MEG saturated gas phase and the solution inside the reaction vessel, that is, that the partial pressure of carbon dioxide could be calculated from eq 5, where P denotes pressure and y is mole fraction. This assumption was not further investigated.

$$P_{CO_2} = P_{tot} \cdot y_{CO_2} = P_{tot} - P_{water} - P_{MEG} - P_{N_2} \qquad (5)$$

No elaborate screening of the optimal gas rate was performed. It was observed that at high temperatures and a high gas rate (~100 $\text{cm}^3\cdot\text{min}^{-1}$) smoke, believed to be condensed MEG, formed at the outlet of the condenser. Thus it was decided to use a gas rate of (10 to 20) $\text{cm}^3\cdot\text{min}^{-1}$, where smoke could no longer be observed. The slow gas flow rate both ensured that the gas phase was saturated with water vapor and minimized water evaporation. However, as carbon dioxide had to be transferred between the phases (solution and gas) this low gas flow rate should yield a longer time to reach equilibrium.

In experiments run for a long time at high temperature, degradation of MEG was a concern. Exclusion of O_2 by the CO_2 + N_2 gas flow through the reaction cell was believed to be an effective measure to prevent degradation; however during most of the experiments the solution turned slightly yellow, which is a sign of degradation.

Experimental Procedure. The working solution was weighed [(250 to 600) g] into the round flask and heated [(25, 80, 120, and 140) °C] under reflux and continuous gas flow [(10 to 100) $\text{cm}^3\cdot\text{min}^{-1}$]. Equilibrium was approached both with solutions under- and supersaturated with CO_2, that is, with $NaHCO_3(s)$, $Na_2CO_3(s)$, or NaOH(aq) as the initial salt. Samples [(3 to 8) g] were withdrawn with a syringe, weighed, and immediately diluted in cold deionized water (~100 cm^3). Analysis was performed by acid titration (0.01 M HCl) using a Mettler Toledo DL 50 titrator. The alkalinity[1] and the total amount of CO_2 in the solution were found from the two inflection points on the titration curve. The experiment was stopped when the total carbon dioxide concentration was constant for several days. Samples of the remaining solution were capped and stored at room temperature awaiting organic acid analysis. An AS15 column on a Dionex ICE 3000 ion chromatograph was used for glycolic and acetic acids, while an AS-11-HC column was used for the other acids. For some of the solutions, the density was measured (DMA 5000 M from Anton Paar) to estimate the MEG concentration at the end of the experiment.

Uncertainties. The experiments were completed at atmospheric pressure (min 960 hPa, max 1020 hPa). The gas flow rate was measured volumetrically at the end of each experiment with an uncertainty of ± 1 $\text{cm}^3\cdot\text{min}^{-1}$. The temperature varied ± 1 °C. Measurements of density, which is an accurate method to estimate MEG concentration in an aqueous solution, showed that, for experiments with 90 wt % MEG, the MEG concentration had increased up to 94.5 wt % by the end of the experiment due to evaporation. For the experiments with initial 95 and 98 wt %, MEG concentrations increased to 98 and 98.5 wt %, respectively.

RESULTS AND DISCUSSION

The results will be discussed in the following context:

- Determination of carbonate equilibria,
- MEG degradation,
- Validity of the acid titration method in solutions with MEG degradation.

Table 1. Total Amount of CO_2 in Solution ($m_{CO_2}^{tot}$) at a Specified Temperature (T) and Initial Alkalinity (A_T)[a]

	t	MEG	MEG_f	A_T	CO_2		$m_{CO_2}^{tot}$
no.	°C	% wt	% wt	mmol·kg^{-1}	mol %	salt	mmol·kg^{-1}
1 and 2	80 ± 1	90	94.5	49.5 ± 0.1	0.05	NaOH and Na_2CO_3	25.6 ± 0.3
3	80 ± 1	98	98.5	49.4 ± 0.1	0.05	Na_2CO_3	25.0 ± 0.1
4 and 5	80 ± 1	60		50.1 ± 0.5	0.20	$NaHCO_3$ and Na_2CO_3	38.0 ± 0.5
6	80 ± 1	60		49.6 ± 0.1	0.05	Na_2CO_3	25.2 ± 0.2
7 and 8	80 ± 1	90	94.5	49.9 ± 0.1	0.20	$NaHCO_3$ and Na_2CO_3	39.6 ± 0.6
9 and 10	80 ± 1	98	98.5	49.7 ± 0.1	0.20	Na_2CO_3 and $NaHCO_3$	40 ± 1
11 and 12	120 ± 1	90	94.5	49.8 ± 0.4	0.05	NaOH and Na_2CO_3	5.8 ± 0.3
13 and 14	120 ± 1	90	94.5	100.4 ± 0.4	0.05	Na_2CO_3 and NaOH	13.3 ± 0.6
15 and 16	120 ± 1	95	98.0	49.5 ± 0.1	0.05	NaOH and Na_2CO_3	6.0 ± 0.4
17	120 ± 1	95	98.0	50.0 ± 0.1	0.05	Na_2CO_3	*b*
18 and 19	120 ± 1	98	98.5	50.6 ± 0.8	0.05	NaOH and Na_2CO_3	6.4 ± 0.4
20 and 21	140 ± 1	95	98.0	50.4 ± 0.6	0.05	NaOH and Na_2CO_3	3 ± 0.1
22 and 23	140 ± 1	98	98.5	49.7 ± 0.1	0.05	Na_2CO_3 and NaOH	3.5 ± 0.2

[a] MEG concentration in starting solution (MEG) and in the solution at the end of the experiment (MEG_f) are given as wt % in solvent. CO_2 corresponds to the dry gas feed. Salt corresponds to the salt used to introduce the alkalinity. [b] The experiment was stopped before equilibrium was reached because significant discoloration and precipitation was observed.

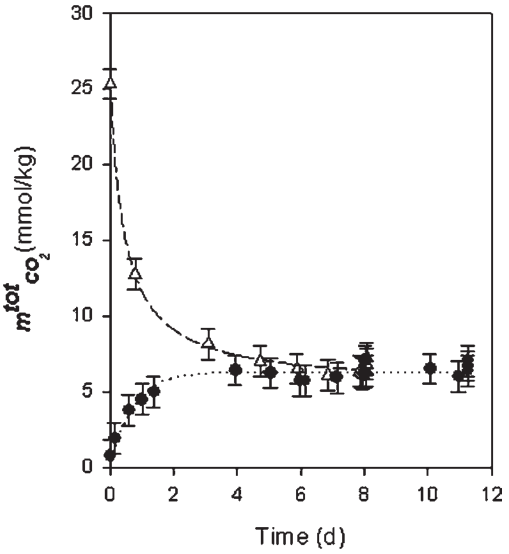

Figure 1. Total amount of CO_2 ($m_{CO_2}^{tot}$) in a solution of 98 % wt MEG and 50 mmol·kg^{-1} alkalinity at 120 °C versus time (expts 18 and 19). Alkalinity initially introduced by Na_2CO_3 (△) and NaOH (●).

Carbonate Equilibria. The solubility of carbon dioxide was determined in solutions of high MEG concentrations as presented in Table 1. At the low gas rate with 0.05 mol % CO_2 in the supplied gas only ~(0.3 to 0.6) mmol·d^{-1} of CO_2 was supplied to the vessel. It was decided to approach equilibrium both by depleting CO_2 from the solution and by supplying CO_2 from the gas phase. For the latter case NaOH was used as starting material, while in the former $NaHCO_3$ or Na_2CO_3 were used. Figure 1 shows a comparison of these two approaches. The type of starting material states whether CO_2 was supplied or removed from the solution. This way the risk of not reaching equilibrium because of insufficient carbon dioxide supply is eliminated. Plots equivalent with Figure 1 were used to determine the equilibrium values presented in Table 1.

The effect of partial pressure on CO_2 solubility was determined by using two different feed gases: 0.20 mol % CO_2 and 0.05 mol %. As expected, the solubility of carbon dioxide decreased with increasing temperature (Table 1), and the trend of increasing carbon dioxide solubility with increasing MEG concentration is in good agreement with literature.[5,7,8] This can be attributed to the higher affinity of CO_2 to MEG than to water. Increased alkalinity also results in higher CO_2 solubility.

The lack of literature data for direct comparison with the data in Table 1 is probably largely due to experimental issues. The main challenge for this kind of experiment is to minimize evaporation while at the same time knowing the partial pressure of CO_2. In retrospect, our approach partly failed to meet this demand. As water is the most volatile component, it will inevitably leave the solution and cause an increase in MEG concentration with time. The solution that condenses in the cooler will consist of mainly water; hence the vapor pressure of water at the cooler outlet will be nearly that of pure water at the given temperature. Calculations showed that at ~(4 to 8) °C and a gas rate of (10 to 20) cm^3·min^{-1} an evaporation of ~(0.1 to 0.2) g of water per day was expected. As samples were withdrawn, the amount of solution decreased. As an experiment could last for several weeks, the percentage of water lost was higher than anticipated. It was also believed that, if significant evaporation had taken place, it would have been detected as an increase in measured alkalinity. Alkalinity, however proved to be a poor indicator as any increase due to evaporation was masked by MEG oxidation. This is discussed further below. Despite the uncertainties evaporation introduced, these are the best, or indeed only, available data of the CO_2 solubility under regeneration/reclamation conditions. The data are also in accordance with unpublished data from a MEG reclamation pilot plant.[12] Thus, these data can still be used to qualitatively check model predictions of the equilibria eqs 1 and 2 during MEG regeneration.

MEG Degradation Products. The results of MEG degradation are presented in Table 2. The main products were glycolic and formic acid, both a result of oxidation; see eqs 6 and 7. The most likely explanation is air ingress during the experiment.

Table 2. Organic Acid Analysis ($\mathrm{mmol \cdot kg^{-1}}$) at the End of the Experiment[a]

no.	glycolic	acetic	formic	oxalic	acid$_{tot}$	$B - A_T^0$
1	4.5	0.1	3.0		7.5	5.2
2	0.7	0.1	2.3		3.1	0.9
3	1.9	0.1	0.9		2.9	0.4
4	0.0	0.0	0.3		0.4	−0.7
5	0.1	0.0	0.0		0.2	0.8
6	0.3	0.1	0.6		1.0	0.4
7	0.5	0.1	1.5		2.1	0.1
8	0.7	0.1	2.1		2.9	0.2
9	0.1	0.1	0.2		0.4	0.2
10	6.4	0.0	1.9		8.3	−1.4
11	3.5	0.1	1.7		5.3	0.4
13	10	0.1	6.8		17	−4.5
14	8.4	0.1	3.4		12	−2.5
15	2.7	0.0	1.1		3.8	−0.4
16	10	0.0	3.8		14	−25.4
17	18	0.0	5.2	0.1	24	−18.3
18	3.8	0.0	0.8		4.6	−1.8
19	2.0	0.2	0.7		2.9	−2.0
20	1.7	0.0	2.2		3.9	−3.9
21	1.6	0.1	2.0		3.7	−4.7
22	1.8	0.1	0.7		2.6	−7.9
23	2.2	0.1	0.7		3.0	−4.4

[a] Acid$_{tot}$ corresponds to total acid concentration determined by ion chromatography. B ($\mathrm{mmol \cdot kg^{-1}}$) denotes the base concentration from the second equivalence point, and A_T^0 denotes the initial alkalinity.

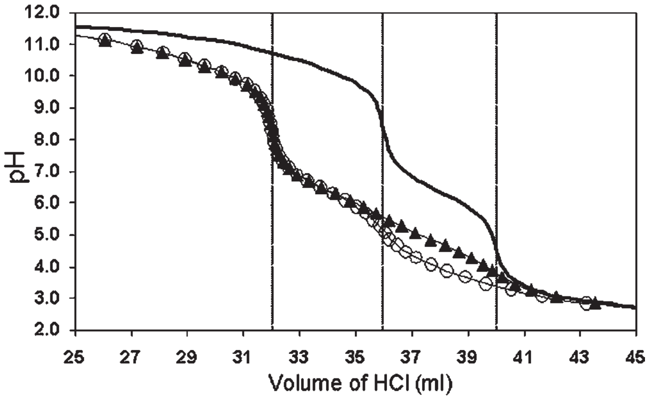

Figure 2. Simulated titration curves for solutions of $A_T = 50\ \mathrm{mmol \cdot L^{-1}}$ and $m_{CO_2}^{tot} = 5\ \mathrm{mmol \cdot L^{-1}}$. —, no organic acids; ○, 5 $\mathrm{mmol \cdot L^{-1}}$ glycolic acid; and ▲, 5 $\mathrm{mmol \cdot L^{-1}}$ acetic acid. The HCl concentration was 25 $\mathrm{mmol \cdot L^{-1}}$, and the sample size was 20 mL. The vertical lines mark the equivalence points.

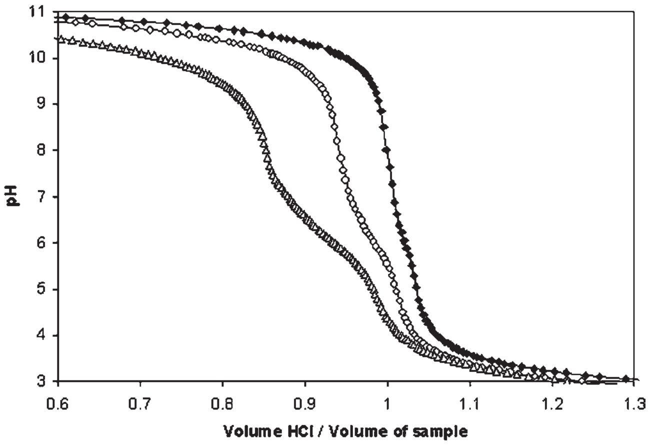

Figure 3. Titration curves from experiment no. 18 (see Tables 1 and 2) ♦, after 2 h; ○, after 1 day; and △, after 11 days. The alkalinity was initially introduced by NaOH. After 2 h enough CO_2 had been taken up from the gas phase to be detectable by titration.

In many experiments a small amount of acetic acid was also detected.

$$HOCH_2CH_2OH + O_2 \rightarrow HOCH_2COOH + H_2O \qquad (6)$$

$$HOCH_2CH_2OH + \frac{3}{2}O_2 \rightarrow 2HCOOH + H_2O \qquad (7)$$

This corresponded well with the work of Rossiter et al.[9] who found that glycolic and formic acid were the main products of MEG degradation. They reported (5 to 10) $\mathrm{mg \cdot kg^{-1}}$ at (86 to 101) °C after 20 days in deaerated solutions of 59.64 wt % MEG. Some of the solutions in this work showed much higher degradation than this, which can be attributed to the higher MEG content in the present study.

Acid Titration Validity in Solutions of Oxidized MEG. A simulated acid titration curve[11] of a carbonate/bicarbonate solution without any MEG decomposition products is illustrated in Figure 2 as a solid line. The total CO_2 concentration corresponds to the amount of acid added between the first and the second equivalence point indicated with vertical lines, (36 and 40) mL, respectively. The total alkalinity corresponds to the second point.

As mentioned above, organic acids formed in several of the experiments and a shift in the second equivalence point in these cases were also observed. This is illustrated in Figure 3, where titration curves from an experiment with sodium hydroxide as starting material are shown. The curves are from samples taken at the beginning of the experiment (2 h), after one day where no discoloration was apparent and at the end of the experiment (11 days) when the solution had turned yellow. After 2 h the presence of CO_2 is already visible, and the second equivalence point corresponds well with the initial total alkalinity. After a day, more CO_2 has been absorbed, but the second equivalence point has shifted toward the left. After 11 days, the second equivalence point is still clearly visible and has moved further to the left.

This shift cannot be explained by a decrease in alkalinity. The degradation products of MEG according to eqs 6 to 7 do not change alkalinity, defined in eq 8, as they do not add any extra sodium.

$$\begin{aligned} A_T^0 &= m_{NaHCO_3}^o + 2m_{Na_2CO_3}^o + m_{NaOH}^o = m_{Na^+} \\ &= m_{HCO_3^-} + m_{OH^-} + 2m_{CO_3^{2-}} \\ &\quad + m_{HOCH_2COO^-} + m_{HCOO^-} - m_{H^+} \\ &\approx m_{HCO_3^-} + m_{OH^-} + 2m_{CO_3^{2-}} + m_{HOCH_2COO^-} \\ &\quad + m_{HCOO^-} \end{aligned} \qquad (8)$$

However, they change the titration course. The acids formed in these experiments (glycolic and formic) are relatively strong acids compared with bicarbonate and therefore remain dissociated between the first and second equivalence points, giving a titration

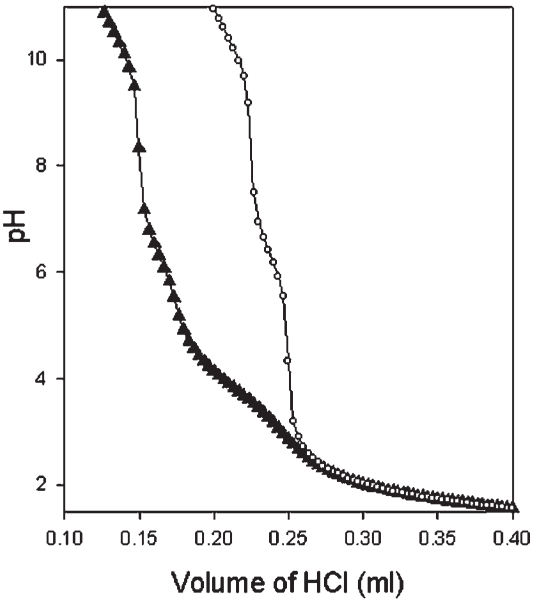

Figure 4. Simulated titration curves for a solution with an A_T = 50 mmol·L^{-1} and $m_{CO_2}^{tot}$ = 5 mmol·L^{-1}. —○—, no organic acids; —▲—, 15 mmol·L^{-1} glycolic acid. The HCl concentration was 1 mol·L^{-1}, and the sample size was 5 mL.

curve similar to the one indicated by the circles in Figure 2. There is still untitrated base left at the second equivalence point, though. This means that the total CO_2 can be determined by acid titration but the method is no longer valid for alkalinity measurement. If the same solution was titrated with a more concentrated acid, then the untitrated base would be titrated, and a third equivalence point would be present. This would correspond to the correct alkalinity, as indicated in the simulated titration curve shown in Figure 4 for a mixture of carbonate and glycolic acid. The volume of acid needed to reach these three equivalence points is much too low for practical use, however. The curve further validates titration as a good method to determine total CO_2 concentration, though, provided only acids significantly stronger than bicarbonate are formed by MEG oxidation. Acetic acid and oxalic acid, which are the other two decomposition products, might hide the second equivalence point, as indicated by the triangles in Figure 2. In both this work and that of Rossiter et al.,[9] only negligible amounts of these acids formed.

Any shift in the second equivalence point should directly correspond to the amount of organic acids present in the sample, and the difference $B - A_T^0$, where B is the total amount of base titrated at the second equivalence point and $A_T{}^0$ is initial alkalinity, should correspond with the total acid concentration detected by ion chromatography (Table 2). Although it is not a good match, the values correspond qualitatively. The reason for this is probably that the change is a sum of the lowering effect of oxidation, explained above, and an increased alkalinity due to water evaporation. The acid concentration is therefore given by eq 10.

$$m_{\text{acids}} = A_T^0 \cdot \frac{M^0}{M^0 - M^{\text{evaporated}}} - B \qquad (10)$$

where M^0 is the initial solvent weight and $M^{\text{evaporated}}$ is the mass of water evaporated. In the cases where evaporation was measured by density measurements, eq 10 was shown to be valid.

CONCLUSIONS

New equilibrium data have been obtained for the carbon dioxide equilibrium under typical MEG reclamation/regeneration conditions [(80 to 140) °C and (60 to 98) wt % MEG]. The equilibrium was approached both from undersaturated and supersaturated conditions. The degradation of MEG was observed, and the main products were glycolic and formic acid. A review of the acid titration method in the presence of these species showed that the method is still valid for determination of total CO_2 content, while the measured total alkalinity will be affected.

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REFERENCES

(1) Kaasa, B.; Østvold, T. What Alkalinity is and How it is Measured. *SPE 37277 Int. Symp. Oil field scale*, Houston, TX, Feb 18−21, 1997.

(2) Fosbøl, Ph.; Thomsen, K.; Stenby, E. Solubility Measurements in the Mixed Solvent Electrolyte System Na_2CO_3−$NaHCO_3$−Monoethylene Glycol−Water. *Ind. Eng. Chem. Res.* **2009**, *48* (4), 2218–2228.

(3) Gärtner, R.; Marcelo, S.; Witkamp, G. Solid Phases and Their Solubilities in the System Na_2CO_3 + $NaHCO_3$ + Ethylene Glycol + Water from (50 to 90) °C. *J. Chem. Eng. Data* **2004**, *49*, 116–125.

(4) Oosterhof, H.; Witkamp, G. J.; Van Rosmalen, G. M. Some antisolvents for crystallisation of sodium carbonate. *Fluid Phase Equilib.* **1999**, *155*, 219–227.

(5) Sandengen, K. Prediction of mineral scale formation in wet gas condensate pipelines and in MEG (monoethylene glycol) regeneration plants. *Ph.D. Thesis*, Norwegian University of Science and Technology, Trondheim, Norway, 2006.

(6) Flaten, E. M.; Seiersten, M.; Andreassen, J. P. Polymorphism and morphology of calcium carbonate precipitated in mixed solvents of ethylene glycol and water. *J. Cryst. Growth* **2009**, *311* (13), 3533–3538.

(7) Hayduk, W.; Malik, V. K. Density, Viscosity, and Carbon Dioxide Solubility and Diffusivity in Aqueous Ethylene Glycol Solutions. *J. Chem. Eng. Data* **1971**, *16* (2), 143–146.

(8) Kan, A. T.; Lu, H. Effects of Monoethylene Glycol on Carbon Dioxide Partitioning in Gas/Monoethylene Glycol/Water/Salt Mixed Systems. *Ind. Eng. Chem. Res.* **2010**, *49* (12), 5884–5890.

(9) Rossiter, W. J., Jr.; Brown, P. W.; Godette, M. The determination of acidic degradation products in aqueous ethylene glycol and propylene glycol solutions using ion chromatography. *Sol. Energy Mater.* **1983**, *9*, 267–279.

(10) Rudenko, A. I.; Gershuni, A. N.; Kalabina, L. V. Some characteristics of ethylene glycol as a heat-transfer agent for closed two-phase systems. *J. Eng. Phys. Thermophys.* **1997**, *70* (5), 799–804.

(11) Gutz, I. G. R. *CurTiPot-pH and Acid−Base Titration Curves: Analysis and Simulation software*, version 3.5.4; http://www2.iq.usp.br/docente/gutz/Curtipot_.html (accessed March 24, 2011).

(12) Kaasa, B. Statoil, Norway. Private communication, June 2011.