

Calcium Carbonate Precipitation and pH Variations in Oil Field Waters. A Comparison between Experimental Data and Model Calculations

Manoochehr Abtahi,[†] Baard Kaasa, Jens E. Vindstad and Terje Østvold*

Institute of Inorganic Chemistry, The Norwegian Institute of Technology, N-7034 Trondheim, Norway

Abtahi M., Kaasa B., Vindstad J. E. and Østvold T., 1996. Calcium Carbonate Precipitation and pH Variations in Oil Field Waters. A Comparison between Experimental Data and Model Calculations. – Acta Chem. Scand. 50: 114–121 © Acta Chemica Scandinavica 1996.

A Peng–Robinson equation of state (PR EOS) gives reliable data for CO₂ fugacities in CO₂–CH₄ gas mixtures over large composition, temperature (0 < T/°C < 200) and pressure (0 < P_{tot}/bar < 400) ranges. By introducing the PR EOS in a scale prediction model to be used for oil field waters, we are able to calculate the amount of CaCO₃ precipitated and pH in water solutions. Experimental data at 25 and 50 °C at CO₂ pressures of 0.5 and 1 bar showed good agreement with calculated pH (SD = 0.034 pH units) and precipitated CaCO₃ (SD_{rel} % ≈ 5). Literature data on pH measurements and solubility of CO₂(g) and CaCO₃ also agree well with model predictions. Even at 35 °C and below and at very high CO₂ pressures (300 bar) experimental CO₂ solubilities agreed with model calculations within a few %. pH measurements under pressures of up to 40 bar CO₂ also compare well with model calculations within 0.1 pH units. Experimental data predicted an increase in pH of about 0.2 pH units when pure CO₂ was substituted by a mixture of CO₂ and CH₄ at a constant partial pressure of CO₂. The calculated pH, however, only showed a very small increase owing to the change in the CO₂ fugacity coefficient.

In five previous communications we have discussed scale formation from oil field waters based on chemical equilibrium^{1–3} and chemical kinetics.^{4,5} Using a simple hydrodynamic model for liquid transport in a model reservoir, we were able to simulate precipitation and dissolution of the major scale-forming minerals in the reservoir itself.^{1,3} In a North Sea well where BaSO₄ had precipitated, our scale prediction model was able to calculate the BaSO₄ precipitation profile from the bottom to the top over a length of 2800 m with reasonable accuracy.⁴ Moreover, results from an experimental investigation of the kinetics of BaSO₄ and SrSO₄ precipitation in 16-m long steel tubing indicated that the precipitation of these minerals could be modelled satisfactorily.⁵ The concentration of the ions in the flowing supersaturated solution along the tubing was very close to the model data, and the calculated amount of precipitate on the tubing wall was only underestimated slightly close to the site where the metal ions (Ba²⁺ and Sr²⁺) were mixed with the SO₄^{2–}-containing solution.⁵

These results are very promising and have led us to

improve the scale prediction model further. The reason for this improvement is related to the need for the oil industry to be able to calculate pH at down-hole conditions and to calculate pH and CaCO₃ precipitation at low temperatures and high CO₂ pressures where measurements cannot be performed easily. These aspects have not been considered in detail in our earlier model, and new and preliminary tests showed that our calculations at low temperatures and high CO₂ pressures gave erroneous predictions owing to a lack of precision in the EOS used to describe the CO₂-containing gas phase.

We also wanted to test the influences of organic acids in the waters on CaCO₃ precipitation, since many oil field waters contain such acids. No data were available to compare with our calculations, and measurements had to be performed. To improve our model at low temperatures and high CO₂ pressures we decided to look more closely on the equation of state used to calculate thermodynamic data for CO₂ both in the gas and in the aqueous phases.

Solubility model for CaCO₃

In two previous papers^{1,2} a solubility model for the minerals FeCO₃, CaCO₃, BaSO₄, SrSO₄, CaSO₄ and

[†] Present address: Institute of Petroleum Technology, The Norwegian Institute of Technology, N-7034 Trondheim, Norway.

* To whom correspondence should be addressed.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was presented. This model was able to predict solubilities of the above minerals from water solutions containing the components: OH^- , H^+ , CO_2 (aq), HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^- , Br^- , A^- , Na^+ , K^+ , Fe^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} (A^- being the organic anion of an acid HA with $K_{\text{HA}} = 10^{-5}$) in the temperature and pressure ranges $0 < T/^\circ\text{C} < 175$ and $0 < P/\text{bar} < 400$. In this model all possible equilibria are considered simultaneously. Activities are calculated as a function of water composition and temperature according to the formalism developed by Pitzer.⁶ The pressure dependence of activities and equilibria are calculated using the partial molar volume approach.¹ Stoichiometric equilibrium constants are calculated as function of temperature, pressure and composition. Equilibrium is first calculated without precipitation before supersaturated salts are precipitated one by one until the correct solution is found. Every time a concentration is changed, new stoichiometric equilibrium constants has to be calculated, and Newton iteration is used to find the final solution. The equation of state used for CO_2 (g) to obtain CO_2 fugacities, however, was not very accurate at temperatures below 70°C when the CO_2 pressure was above 50 bar. This resulted in somewhat erroneous pH and CaCO_3 solubility predictions at low temperatures and high CO_2 pressures. To remedy this situation we have substituted in our model the old equation of state with a new equation which reproduces experimental data better. There are many equations of state which can predict thermodynamic properties over a wide range of temperatures and pressures. Two of the most commonly used are given by Soave, Redlich and Kwong (SRK)⁷ and Peng and Robinson (PR).⁸ Both equations can be used for pure CO_2 and for mixture of gases by applying 'mixing rules'.

In two recent papers the temperature dependent coefficients of SRK and PR were improved.^{9,10} EOS for gas mixtures are discussed in several papers.¹¹⁻¹⁶

Both the SRK and PR give fugacity coefficients of pure CO_2 with acceptable errors, but the PR equation has one advantage which is important. It is more stable near the CO_2 critical point than the SRK. The PR equation was therefore chosen by us. In order to verify if this equation was useful for pH and CaCO_3 precipitation calculations in oil field waters, we decided to test if the equation would predict experimental data. The predominant gases present during oil production are CO_2 and CH_4 . We therefore wanted to test if our model calculation predicted available data related to pure CO_2 gas and CO_2 and CH_4 gas mixtures.

Figure 1 shows the fugacity coefficient of pure CO_2 at varying temperatures and pressures. The break in the -3°C line shows the dew point of CO_2 (44 bar); thus for higher pressures the lowest line shows the fugacity coefficient in liquid CO_2 . The other temperatures are all above the critical temperature (31°C) and show no discontinuity. Good agreement between IUPAC¹⁷ data and model calculations may be observed even in the critical region.

Figure 2 shows calculated and experimental¹⁸ fugacity

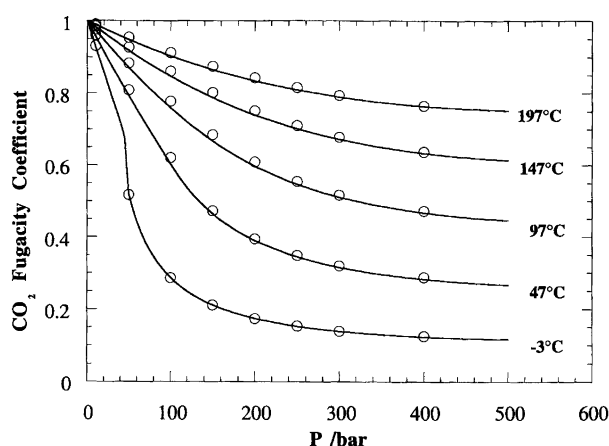


Fig. 1. Fugacity coefficients of pure CO_2 (g) at varying temperatures and pressures. \circ , IUPAC data;¹⁷ (—) PR EOS.

coefficients of CO_2 in a mixture of 90 mol% CH_4 and 10 mol% CO_2 at 100 and 200°C as a function of pressure.

Owing to a lack of experimental fugacity coefficients in mixed systems, especially at low temperatures and high pressures, we had to compare calculated and experimental compressibility factors instead. Comparisons at different temperatures, pressures and compositions are shown in Fig. 3.

With the new PR EOS we are now able to calculate reliable pH and CaCO_3 solubility data over a wider temperature and pressure regime than before. Accurate experimental data in the low-temperature and high-pressure area for comparison with model calculations are not available. Some experimental pH measurements up to 40 bars CO_2 pressure are, however, published.²⁰ These data together with new CaCO_3 solubility data²¹ at low CO_2 pressures can be used to test the model. In addition, we have performed precipitation experiments from supersaturated CaCO_3 solutions with $P_{\text{CO}_2}/\text{bar} = 0.5$ and 1 at

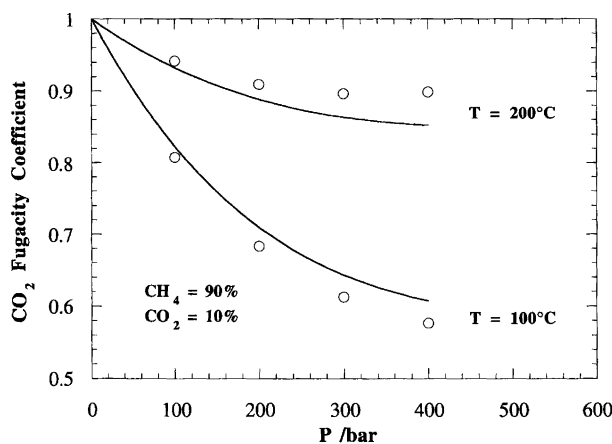


Fig. 2. Fugacity coefficients of CO_2 for the CO_2 (10 mol%)- CH_4 (90 mol%) mixture at 100 and 200°C and varying pressures. \circ , Experimental,¹⁸ (—) PR EOS.

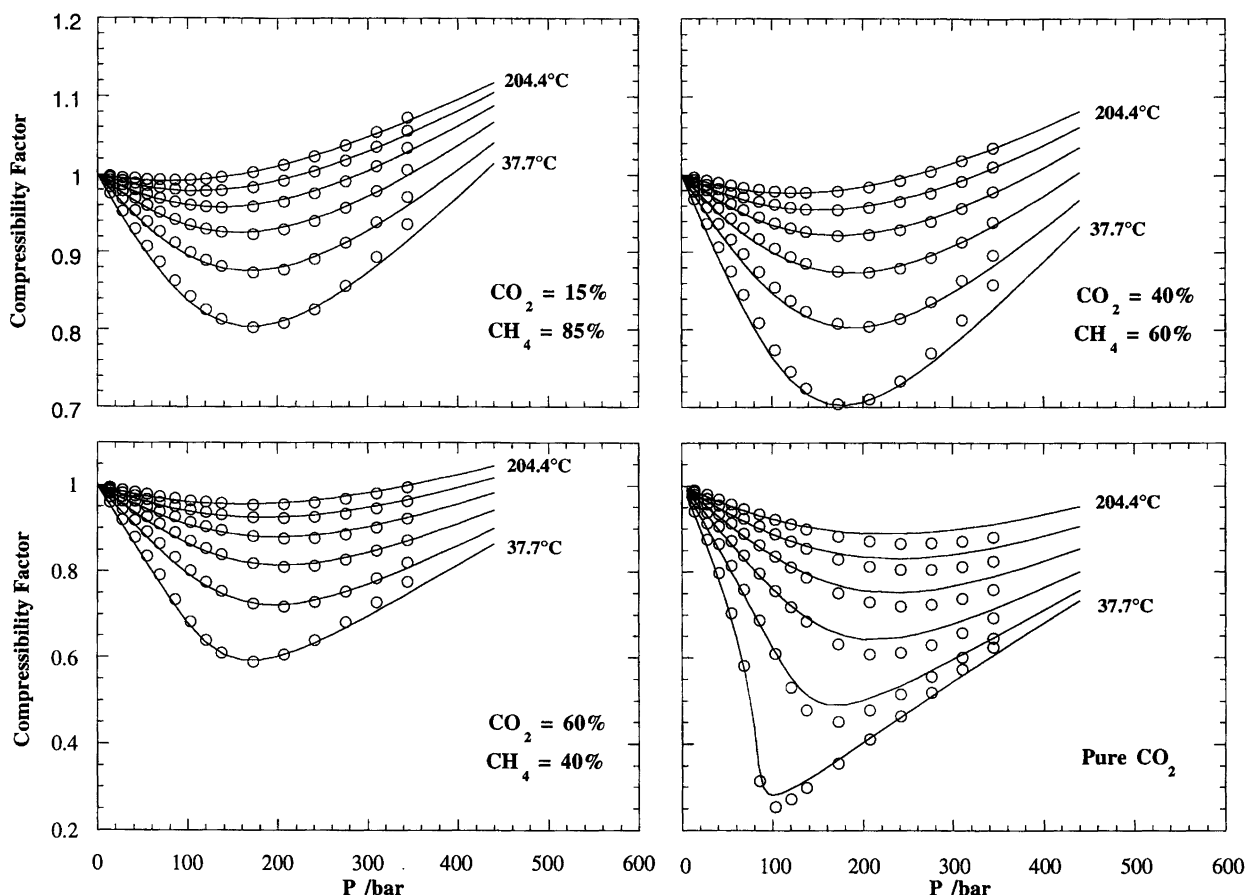


Fig. 3. Compressibility factors for the $\text{CO}_2\text{-CH}_4$ system at varying temperatures and pressures. \circ , Experimental;¹⁹ (—) PR EOS.

25 and 50 °C with varying amounts of acetic acid in the solution to compare with model calculations.

Experimental

Chemicals. The chemicals used in the experiments are listed in Table 1.

Procedures. All experiments were performed in 250 ml Pyrex beakers contained in a constant-temperature ($\pm 0.1^\circ\text{C}$) water bath. The beakers were fitted with a lid through which pH-electrodes and gas inlet and outlet tubes were connected. The solutions were made by dissolving the appropriate amounts of NaCl, CaCl_2 and CH_3COOH in distilled water. Then NaHCO_3 was added,

and a stream of either pure CO_2 (350 ml min^{-1}) or a 50% mixture of $\text{CO}_2 + \text{N}_2$ (600 ml min^{-1}) was bubbled through a gas dispersion tube immersed in the solution. Magnetic stirring at a rate of 450 r.p.m. was used. The duration of each run lasted until a constant pH (± 0.01) was observed during 30 min. The time needed to reach this state varied with the concentration of Ca^{2+} , CO_2 pressure and temperature. A reasonable reproducibility in the precipitated amount of CaCO_3 was observed using this technique to determine the equilibrium state.

When the precipitation reaction was completed, the solution was rapidly forced through a $0.22\ \mu\text{m}$ filter. The filtration system was kept at experimental temperature. The precipitated CaCO_3 on the filter paper was dried at 105°C for 3–4 h, cooled in a desiccator to room temperature and weighed.

Table 1. Chemicals.

Compound	Quality	Producer
NaHCO_3	p.a.	E. Merck, Germany
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	p.a.	E. Merck, Germany
NaCl	p.a.	E. Merck, Germany
CH_3COOH (100%)	p.a.	E. Merck, Germany
H_2O (distilled), $\text{CO}_2(\text{g})$, $\text{N}_2(\text{g})$	Commercial quality, typically 99.9%	

Results

In Fig. 4 a typical pH versus time curve is shown indicating equilibrium for CaCO_3 precipitation after 120 min. The calculated pH (5.83) is slightly lower than the measured value (5.86), indicating that equilibrium is not completely established. The amount of precipitate formed was 532 mg, while the calculated amount was 543 mg, in

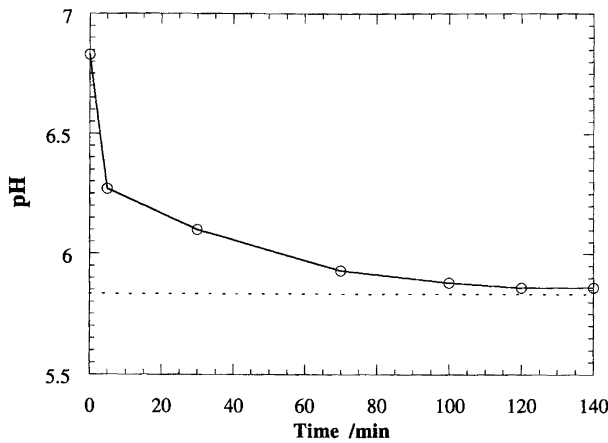


Fig. 4. pH versus time for a CaCO_3 precipitation experiment. $C_{\text{Na}^+}^\circ = 18385 \text{ mg l}^{-1}$, $C_{\text{Cl}^-}^\circ = 33075 \text{ mg l}^{-1}$, $C_{\text{HCO}_3^-}^\circ = 1000 \text{ mg l}^{-1}$, $C_{\text{Ca}^{2+}}^\circ = 3000 \text{ mg l}^{-1}$ and $T/^\circ\text{C} = 50$. (—) Experimental; (---) calculated.

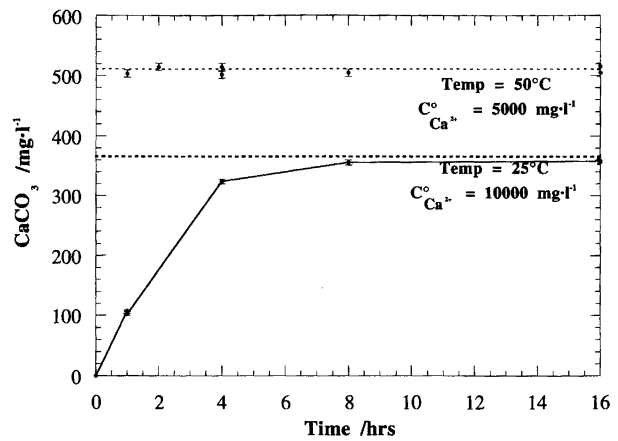


Fig. 5. CaCO_3 precipitation versus time. $C_{\text{Na}^+}^\circ = 18000 \text{ mg l}^{-1}$, $C_{\text{HCO}_3^-}^\circ = 1000 \text{ mg l}^{-1}$, $C_{\text{Ca}^{2+}}^\circ = 5000/10000 \text{ mg l}^{-1}$ and $T/^\circ\text{C} = 50/25$. $P_{\text{CO}_2} = 1.0 \text{ atm}$. (—) Experimental; (---) calculated.

agreement with the above observation. For most runs this trend was observed, indicating that the time needed to reach true equilibrium was probably somewhat longer than indicated by a constant pH of ± 0.01 for 30 min. Especially at the lower temperature of 25°C , large positive differences were sometimes observed between the calculated and measured amounts of CaCO_3 precipitated. Reproducibility experiments were performed to check further the experimental technique. Results are shown in Fig. 5, indicating a satisfactory agreement between the calculated and measured amount of precipitate with a standard deviation in the measured data of 1.2% for the measurements at 50°C and 1.9% at 25°C (two samples for 16 h). It is, however, quite evident from Fig. 5 that long equilibration times are needed at low temperatures.

In Fig. 6 the pH is shown as a function of temperature for varying initial Ca^{2+} concentrations and varying amounts of organic acid at $P_{\text{CO}_2} = 0.5$ and 1.0 atm . The agreement between calculated and measured pH values is, as can be observed, not the best. The reason for this deviation is quite obviously due to inaccuracies in the experimental data. The calculated standard deviation of the fit between experimental and theoretical data is $\text{SD}(\text{pH}) = 0.034$. There is almost an overlap between calculated pH values for 0, 100 and 200 mg l^{-1} concentrations of acetic acid as it should be when the solutions are saturated with CaCO_3 . Figure 6 shows that increasing the temperature reduces the pH owing to a lower solubility of CaCO_3 at higher temperature, and a decreasing pH is observed with increasing initial Ca^{2+} concentration. This decrease is due to the increasing precipitation of CaCO_3

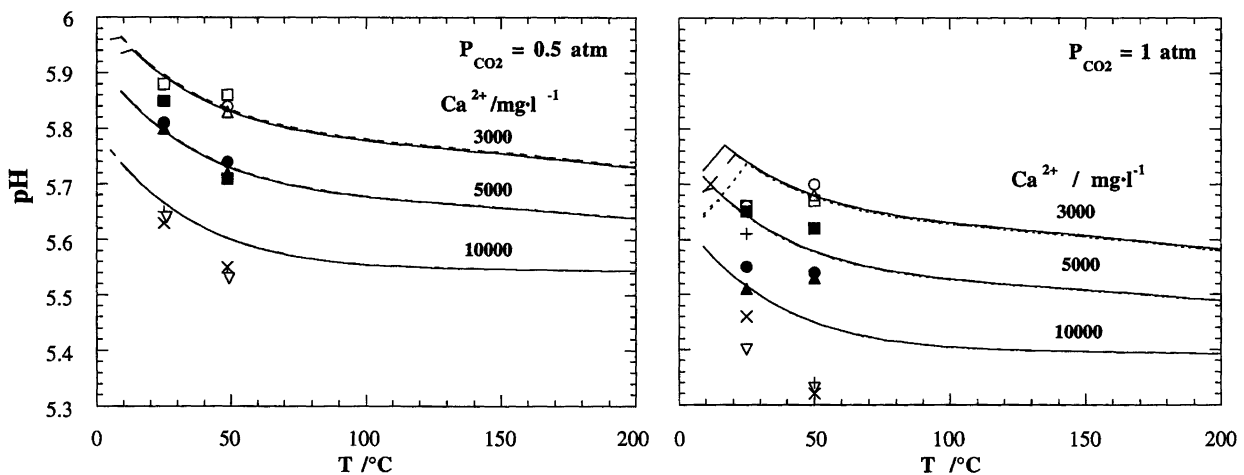


Fig. 6. pH at equilibrium as a function of temperature and initial Ca^{2+} concentration at $P_{\text{CO}_2} = 0.5$ and 1.0 atm . $\square, \circ, \Delta, 0, 100, 200 \text{ mg l}^{-1} \text{ CH}_3\text{COOH}$ at $C_{\text{Ca}^{2+}}^\circ = 3000 \text{ mg l}^{-1}$; $\blacksquare, \bullet, \blacktriangle, 0, 100, 200 \text{ mg l}^{-1} \text{ CH}_3\text{COOH}$ at $C_{\text{Ca}^{2+}}^\circ = 5000 \text{ mg l}^{-1}$; $\nabla, +, \times, 0, 100, 200 \text{ mg l}^{-1} \text{ CH}_3\text{COOH}$ at $C_{\text{Ca}^{2+}}^\circ = 10000 \text{ mg l}^{-1}$; (—), (---), (···), calculated for 0, 100 and 200 $\text{mg l}^{-1} \text{ CH}_3\text{COOH}$ and $C_{\text{Ca}^{2+}}^\circ = 3000, 5000$ and 10000 mg l^{-1} , respectively.

for high Ca^{2+} concentrations and thus a significant reduction in pH according to eqn. (1):



Figure 7 shows a summary of our experimental results together with model calculations. A reasonable agreement is observed between calculated and experimental data. The amount of CaCO_3 precipitated varied between 0 and

600 mg. The calculated standard deviation of the fit between measured and calculated precipitation was 13 mg (18 mg at 25°C and 9 mg at 50°C).

To test our new model, experiments should have been made at much higher CO_2 pressures and at lower temperatures. For practical reasons this is not yet possible, but we hope to have access to the necessary high-pressure equipment in the near future.

We may, however, test our model using some new lit-

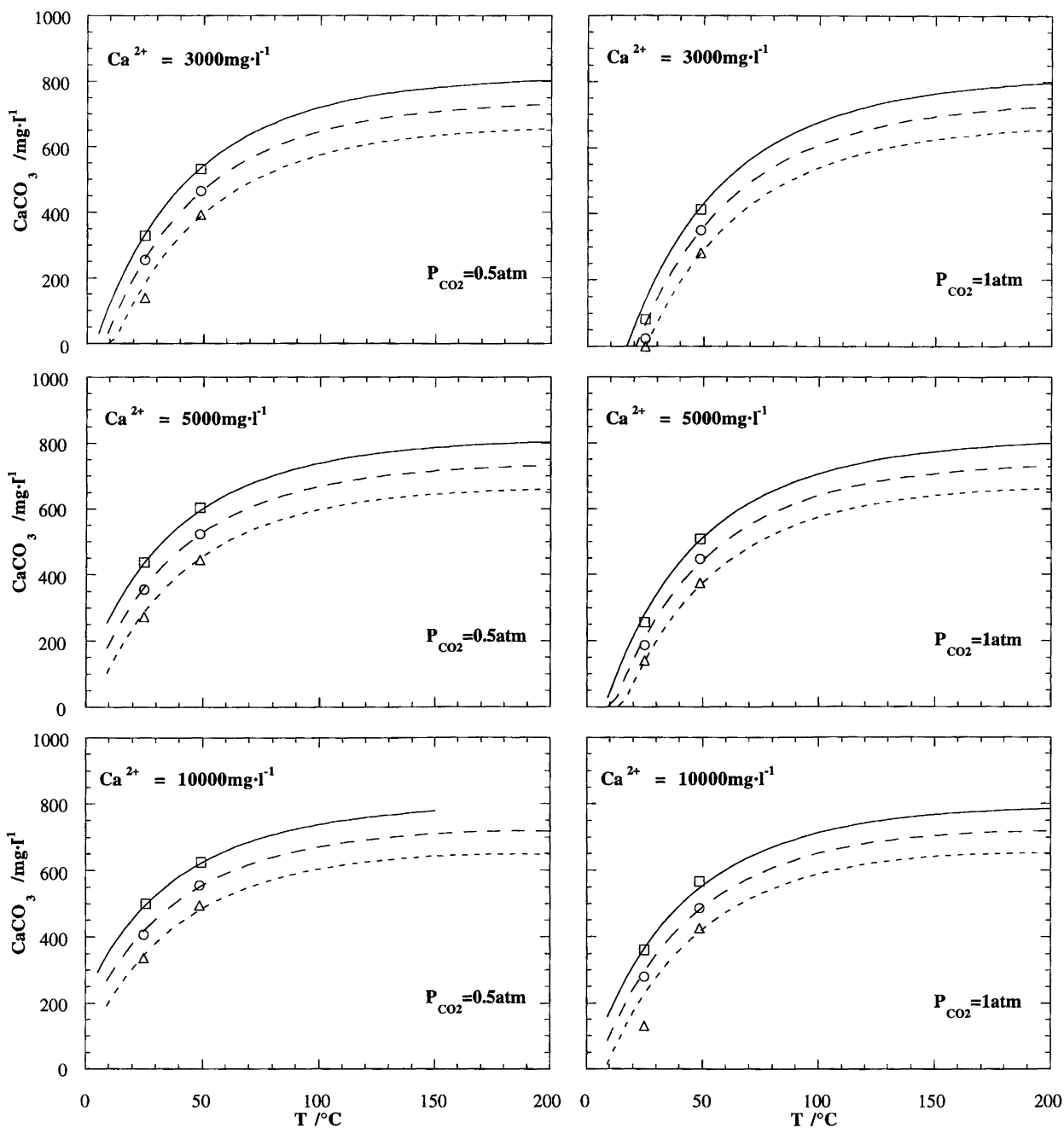


Fig. 7. CaCO_3 precipitated at equilibrium as a function of temperature at different amounts of organic acid and different initial Ca^{2+} concentrations at $P_{\text{CO}_2}=0.5$ and 1.0 atm. \square , \circ , \triangle , Measured for 0, 100 and 200 $\text{mg}\cdot\text{l}^{-1}$ CH_3COOH ; —, ---, ..., calculated for 0, 100 and 200 $\text{mg}\cdot\text{l}^{-1}$ CH_3COOH .

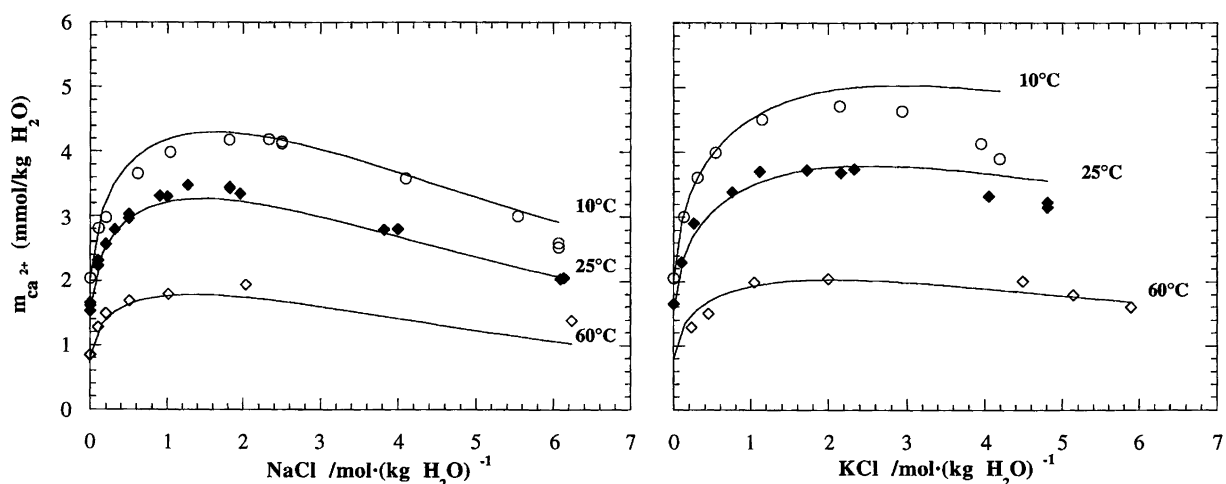


Fig. 8. CaCO_3 solubilities as function of (a) NaCl concentration and (b) KCl concentration at varying temperatures. \circ , \blacklozenge , \triangle , Measured²¹ and (—) calculated.

erature data for CaCO_3 solubilities not available when we first published our model. The calcite solubilities in NaCl and KCl solutions at low CO_2 pressures and relatively low temperatures, published by Wolf and Puk,²¹ agree well with our model calculations, as can be seen from Fig. 8.

CO_2 solubilities for the CO_2 - H_2O system published by Wiebe²² at high pressures and low temperatures also compare very well with our model (Fig. 9). The data of Wiebe at 35 and 12°C did not fit at all with our previous model.¹⁻⁵

In 1983 Crolet and Bonis²⁰ published a paper in which acid corrosion in oil field wells was addressed. The pH was measured in some NaCl-containing solutions at varying temperatures up to a CO_2 pressure of 40 bar. In Fig. 10 some of the data of Crolet and Bonis are compared with our model calculations. Within the experimental accuracy (± 0.2 pH units) as indicated by Crolet and

Bonis²⁰ there is good agreement between measured and calculated data. However, when CO_2 - CH_4 mixtures were used instead of pure CO_2 , the data of Crolet and Bonis indicated higher pH values than those obtained with pure CO_2 at the same CO_2 partial pressures. Calculations also showed an increase in pH, but much smaller than the increase indicated by Crolet and Bonis. The calculated increase in pH is due to a decrease in the fugacity coefficient of CO_2 caused by the increase in the total pressure when CH_4 is added to the gas phase. It is, however, difficult to understand how the addition of CH_4 can increase the pH as much as that given by Crolet and Bonis, especially at pressures below 10 bar where the gas mixture is close to ideal.

A unit for pH measurements at high pressures is under construction, and we will in the future measure the influence of CO_2 and CO_2 - CH_4 gas mixtures on the pH of oil field waters.

Concluding remarks

The improved equation of state for CO_2 gas in our model, used for calculations of CaCO_3 precipitation and pH of water solutions of interest for the oil industry, seems to work satisfactorily even at low temperatures and high CO_2 pressures. The influence of CH_4 on the CO_2 fugacity, and thereby on the CaCO_3 precipitation and the aqueous pH, is included in the model. However, there are no data available in the literature at high pressures and low temperatures with which to test the model thoroughly. We hope to provide such data in the future.

Acknowledgement. Financial support from Norsk Hydro and Statoil is gratefully acknowledged. The experimental part of this work was performed at the Norsk Hydro Research Centre in Bergen and benefited from the guidance of Dr. Scient. Kari Ramstad.

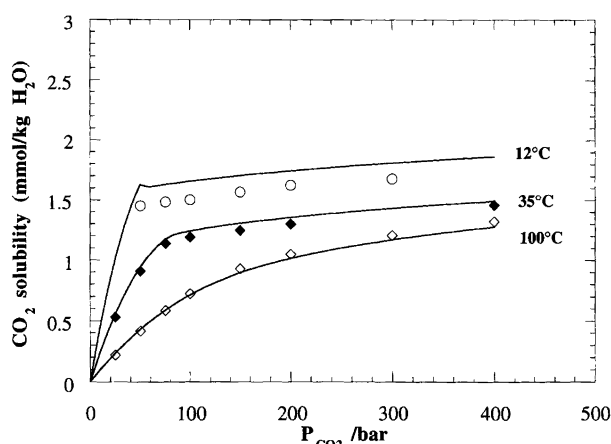


Fig. 9. CO_2 solubilities in H_2O at varying pressures and temperatures \circ , \blacklozenge , \triangle , Measured²² and (—) calculated.

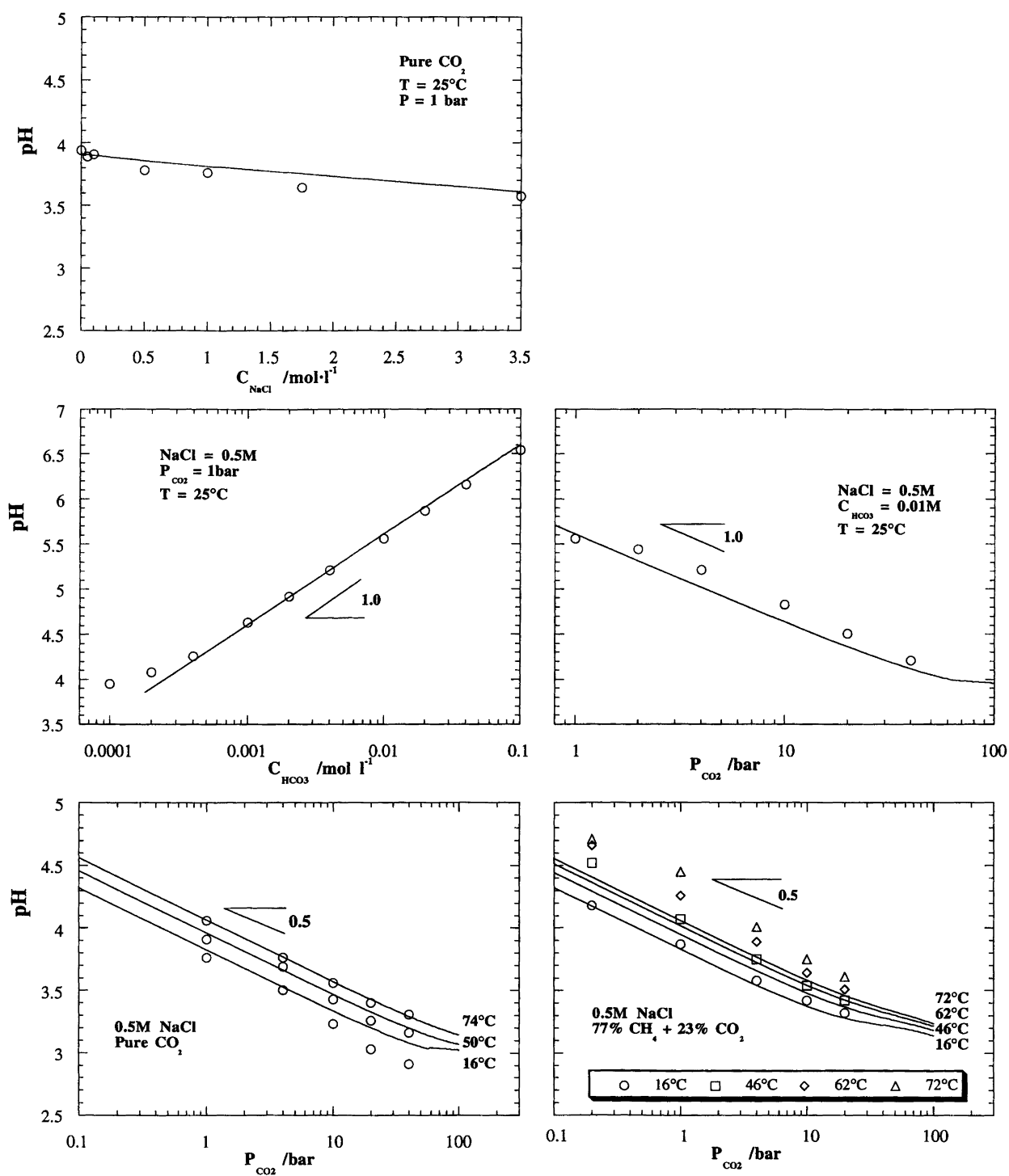


Fig. 10. Measured and calculated pH of some aqueous solutions under CO₂ and CO₂+CH₄ pressures, respectively. Open symbols, measured data;²⁰ lines, calculated. The slope of the lines are indicated at the figures.

References

1. Haarberg, T., Seim, I., Granbakken, D. B., Østvold, T., Read, P. and Schmidt, T. *SPE Prod. Eng.* (1992) 75.
2. Haarberg, T., Jakobsen, J. E. and Østvold, T. *Acta Chem. Scand.* 44 (1990) 907.
3. Haarberg, T. *Thesis* Dept. of Inorganic Chemistry, Norwegian Institute of Technology, Trondheim, Norway 1989.
4. Granbakken, D. B., Haarberg, T., Rollheim, M., Østvold, T., Read, P. and Schmidt, T. *Acta Chem. Scand.* 45 (1991) 892.

5. Rollheim, M., Shamsili, R. G., Østvold, T. and Siamos, A. *Acta Chem. Scand.* 47 (1993) 358.
6. Pitzer, K. S. in Pitzer, K.S., Ed., *Activity coefficients in electrolyte Solutions*, Chap. 3 2nd Edn., CRC-Press Boca Raton, FL 1991.
7. Soave, G. *Chem. Eng. Sci.* 27 (1972) 1197.
8. Peng, D. and Robinson, D. B. *Ind. Eng. Chem., Fundam.* 15 (1976) 59.
9. Soave, G., Barolo, M. and Bertucco, A. *Fluid Phase Equilibria* 391 (1993) 87.
10. Daridon, J. L., Lagourette, B., Saint-Guirons, H. and Xans, P. *Fluid Phase Equilibria* 91 (1993) 31.
11. Ohe, S. *Phys. Sci. Data* 42 (1990).
12. Nishiumi, H. and Arai, T. *Fluid Phase Equilibria* 42 (1988) 43.
13. Søreide, I. and Whitson, C. *Fluid Phase Equilibria* 77 (1992) 217.
14. Jacobs, G. K. and Kerrick, D. M. *Geochim. Cosmochim. Acta* 45 (1981) 607.
15. Han, S. J., Lin, H. M. and Chao, K. C. *Chem. Eng. Sci.* 43 (1988) 2327.
16. Oellrich, L., Plöcker, U., Prausnitz, J. M. and Knapp, H. *Int. Chem. Eng.* 21 (1981) 1.
17. IUPAC, *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Angus, S., Armstrong, B. and de Reuck, K. M. Eds., 1973.
18. Duan, Z., Møller, N. and Weare, J. H. *Geochim. Cosmochim. Acta* 56 (1992) 2619.
19. Reamer, H. H., Olds, R. H., Sage, B. H. and Lacey, W. N. *Ind. Eng. Chem.* 36 (1944) 88.
20. Crolet, J. L. and Bonis, M. R. *Corrosion* 39 (1983) 39.
21. Wolf, M., Breitung, O. and Puk, R. *Chem Geol.* 76 (1989) 291.
22. Wiebe, R., *Chem. Rev.* 29 (1942) 475.

Received May 12, 1995.