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STRONTIUM CARBONATE SOLUBILITY DATA IN AQUEOUS MIXTURES OF MONOETHYLENEGLYCOL UNDER A CARBON DIOXIDE ATMOSPHERE

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Abstract - In order to inhibit natural gas hydrate formation, monoethyleneglycol (MEG) is usually injected into producing well heads. The MEG regeneration process is continuously performed at the platform. Scaling problems usually occur due to the presence of chlorides and carbonates. This work presents salt solubility data for the aqueous system with strontium carbonate, MEG and carbon dioxide. A specific analytical method was developed. Thus, experimental data for strontium carbonate ($SrCO_3$) solubility at various carbon dioxide pressures are reported. Solubilities of $SrCO_3$ in water were measured from 760 to 1610 mmHg at 278.15. 288.15. 298.15 and 323.15 K. For the mixed solvent (ms) conditions, solubilities were measured at 298.15 K and four isobars, i.e., 760, 1210, 1410 and 1520 mmHg. Experimental data were correlated and demonstrated to be accurate for thermodynamic modeling and process simulation.

Keywords: Strontium Carbonate, Salt Solubility, Monoethyleneglycol, Regeneration Process.

INTRODUCTION

Among several problems faced by the oil industry, natural gas hydrate formation turned out to be a challenge. Hydrates are crystal structures produced by the contact of water, contained in fluids, or from the reservoir itself, with low molecular weight gases and short chain hydrocarbons in an environment of high pressures and low temperatures. The major consequences caused by the formation of hydrates are fouling of the production lines and plant shut down in the worst case. Thus, there may be productivity losses by blocking the flow in drilling stages or completion, large power consumption, equipment and staff impairment, and high cost related to stopping production in order to unclog and clean the equipment. Many solutions can be applied to prevent the problem such as reduce the amount of water in the system by dehydration, keeping the temperature and pressure low, and the injection of inhibitors. These inhibitors are injected at the wellhead and should be processed with gas and condensate fluid in the production unit

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where the separation and recovery process should be performed.

MEG is a high dosage type of inhibitor and acts thermodynamically by reducing the temperature of hydrate formation by altering the water chemical potential (Carroll, 2003). Regarding the inhibitor selection, the choice of MEG was based on its excellent properties such as high hydrophilicity and solubility of salts. Moreover, MEG presents low toxicity, viscosity and solubility in liquid hydrocarbons, facilitating its recovery, which makes it more economic. Compared to methanol, it is less efficient, but as methanol is quite volatile, toxic and requires large quantities to have an effect. MEG becomes more favorable and it is usually applied as hydrate inhibitor.

The MEG regeneration process basically consists of the removal of water and salts, and thereby corrosion and mineral scaling are problems to be considered in the process (Figueiredo *et al.*, 2015). The aim of this work is to report new solubility data of strontium carbonate in aqueous mixtures of MEG under a carbon dioxide atmosphere. Salt solubilities were evaluated as a function of CO_2 pressure, temperature and MEG concentration. A CO_2 atmosphere is an important variable in this work because, without its presence, strontium carbonate is practically insoluble in water and MEG. Thus, CO_2 addition to the system is vital for the salt solubility experiments. Analysis and correlation of the experimental data were provided with empirical equations. The salting-out effect was also described with the Setchenov equation for all mixed solvent data sets, $SrCO_3$ solubility isobars.

MATERIALS AND METHODS

Strontium carbonate solubilities were determined experimentally in aqueous mixtures of MEG, under different pressures of carbon dioxide at constant temperature by a specially designed analytical method (Chiavone-Filho and Rasmussen. 1993) specially designed. MEG and strontium carbonate (analytical grade) were supplied by Merck. Carbon dioxide (99% purity grade) was supplied by Linde. The solutions were prepared gravimetrically with deionized water (Milli-Q). The species mixing was provided with the aid of vortex stirrer and closed test tube. Care was constantly taken to avoid samples contamination due to air humidity in the mixing operations.

The experiments were carried out in a specially designed apparatus with two jacketed glass cells (approximately 50 mL each) coupled to a thermostatic bath, a buffer tank, a CO_2 cylinder and valve system, or manifold, as illustrated in Figure 1. Cells were maintained at the same conditions of pressure and temperature during the experiment. An excess of strontium carbonate was added to the liquid phase to ensure constant presence of the solid phase and provide conditions for the salt saturation in the cell during the experiment. The system was maintained at constant temperature by circulating water from a thermostatic bath. Pressure was also fixed by providing an atmosphere of carbon dioxide with the aid of the buffer tank. Suspension mixing was conducted with a magnetic stirrer during two hours. By monitoring the pH during the kinetic experiment, it was possible to determine the required time to reach the equilibrium state. In that state, carbon dioxide and strontium carbonate dissolutions achieve a constant value after approximately two hours of experiment. The microcrystal thermal maturation effect was applied. For each equilibrium temperature, for example, 298.15 K, the start was at 293.15 K. Considering that lowering the temperature increases CO_2 dissolution (Serpa *et al.*, 2017), with subsequent lowering of pH, and thereby salt dissolution is favored and increased. Shortly after stirring the mixture, the cells were left to stand at rest for 1 hour under the same temperature and pressure conditions before sampling. The procedure to withdraw the sample used a surgical needle to perforate the septum. This method ensures that the solution equilibrium is not disturbed. The solubility results are based on reproducibility of the process considering two samples for each experiment, obtaining the final result as the average of these two values. In case of dispersion above the expected accuracy (~1%), different for each pressure and temperature applied to the system, the experiment was repeated. In order to avoid strontium carbonate precipitation, samples were diluted in HNO_3 solution before analysis. HNO_3 addition enables analytical determination of strontium carbonate solubility. The concentration of nitric acid was found to be adequate for analysis in the ratio of 1:200. Thus, it is possible to verify that, to ensure carbonate dissolution, the solution must be acid. This acidification procedure was applied to the samples of saturated solutions to determine solubility. The strontium amount in the samples was analyzed by atomic absorption (Varian model AA240). For the $SrCO_3$ analysis samples were also diluted to within the equipment range of reading concentration. After the solubility experiments of strontium carbonate in water, the experimental procedure began with addition of MEG, i.e., with the mixed solvent (ms) system. The same procedure performed for water solubility of carbonates was repeated but with the addition of

Figure 1: Experimental $SrCO_3$ solubility test apparatus and scheme in water under a CO_2 atmosphere.

different concentrations of salt free MEG (5 to 80 wt % was prepared gravimetrically).

RESULTS AND DISCUSSION

As mentioned before, the solubility experiments were carried out under a carbon dioxide atmosphere. At first, experiments without carbon dioxidewere performed to study its influence on the system, see Table 1 and Figure 2. Measurements of the pH of the saturated solutions were recorded and the average was 7.8.

It may be noted in Figure 2 that the absence of dioxide carbon provides a considerable decrease in the solubility of strontium carbonate as compared to the data in the presence of the same gas (Figure 6). This occurs because carbon dioxide dissolves in the solution, decreasing the pH and, therefore, promotes favorable conditions for the dissolution of the salt. This could be observed in the temporal variation of the pH, conducted to determine the behavior and mainly the time required to attain equilibrium conditions, see Figure 3.

It may be observed in Figure 3 that there was indeed carbonate saturation after ca. 2 hours of the solubility experiment, indicated by the stabilization of the pH. The behavior of the decrease in pH reflects the gradual increase of CO_2 dissolution ,so that carbonates are also dissolved. In other words, CO_2 dissolution generates carbonic acid, reducing the pH, and dissolving carbonates. Thus, a solid-liquid-gas equilibrium is attained at the stabilization.

Previous experiments applying the same methodology were performed with calcium carbonate. It was possible to compare the results with the literature

Table 1: $SrCO_3$ solubility data in salt free aqueous MEG and at 298.15 K; average pH = 7.8.

$[SrCO_3]$ (ppm)	$100\ w'_{MEG}$ (wt%)	$[SrCO_3]$ (ppm)	$100\ w'_{MEG}$ (wt%)
188.63	0.00	144.06	60.00
176.30	10.03	117.51	80.02
170.61	20.05	85.27	99.79
157.34	39.98		

Data uncertainties: $u(T)$ = 0.02 K; $u([SrCO_3])$ = 3.62 ppm; $u(100\ w'_{MEG})$ = 0.01 wt%.

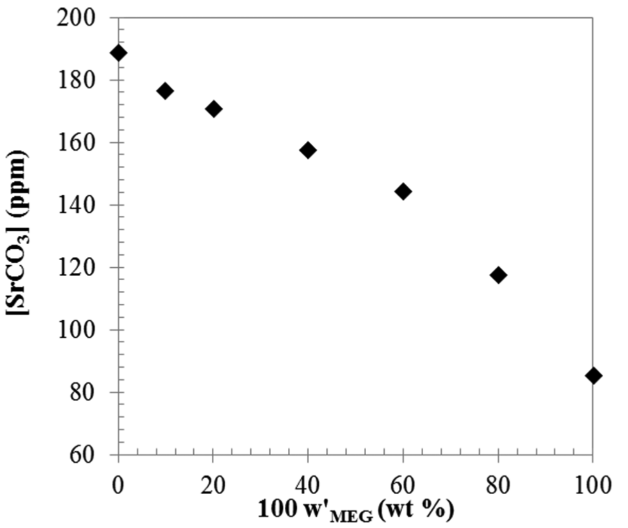

Figure 2: $SrCO_3$ solubility without carbon dioxide at 298.15 K; Average pH = 7.8.

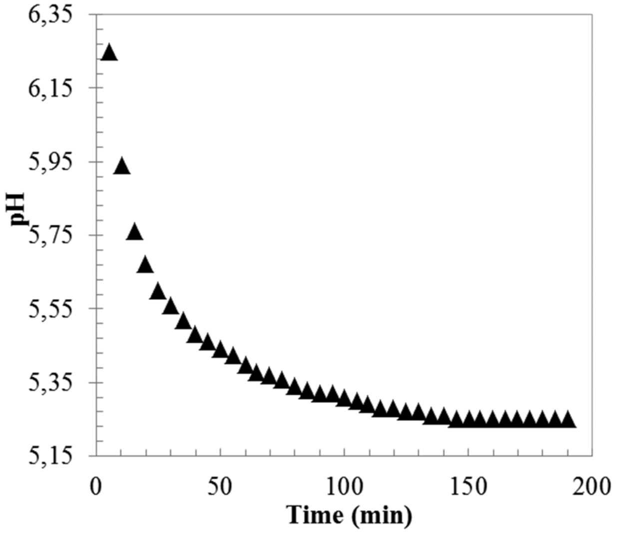

Figure 3: pH measurement during the $SrCO_3$ solubility test at 288.15 K and 1610 mmHg.

Table 2: $CaCO_3$ solubility experimental data and those of Frear and Johnston (1929) in water as a function of CO_2 partial pressure at 298.15 K.

Pressure (mmHg)	$[CaCO_3]_{exp}$ (ppm)	Pressure (mmHg)	$[CaCO_3]_{lit}$ (ppm)
1610	1335.51	760	900.78
1410	1234.57	76	390.34
1210	1118.42	7.6	170.15
1010	1003.22	0.76	78.07
760	849.83	0.243	53.05

Data uncertainties: $u_{exp}(T) = 0.02$ K; $u_{exp}(P) = 10$ mmHg; $u_{exp}([CaCO_3]) = 3.42$ ppm.

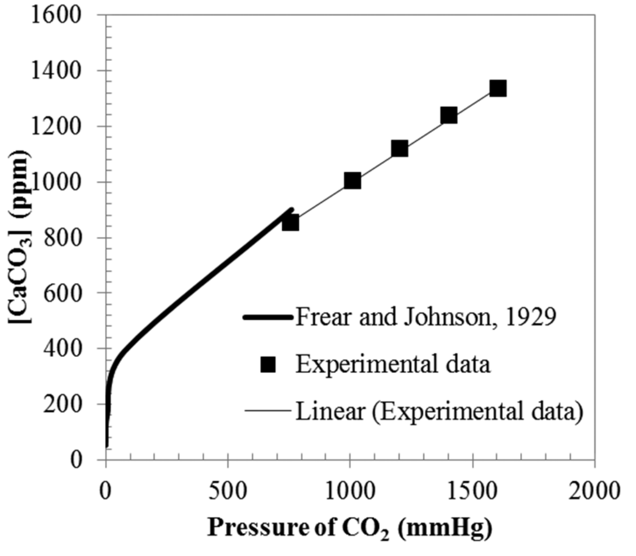

Figure 4: $CaCO_3$ solubility experimental data and those of Frear and Johnston (1929) in water as a function of CO_2 partial pressure at 298.15 K.

(Frear and Johnston, 1929), see Table 2 and Figure 4. Through this analysis, strontium carbonate solubility could be predicted under the same conditions as calcium carbonate and the experimental procedure was validated within acceptable deviations, considering the availability of solubilities in the literature.

Analyzing Figure 4, it is possible to observe the increase in calcium carbonate solubility with pressure in the system. The literature data obtained were developed at lower pressures. However, the carbon dioxide effects in both cases are similar, providing validation for the applied experimental methodology. Furthermore, the deviation relative to the literature at 760 mmHg was 0.6 %.

$SrCO_3$ experimental solubility data comparison with the literature was not feasible because of the lack of information. Strontium carbonate is slightly soluble in water, around 0.01 g per liter. Thus, the analytical method should be accurate to describe properly the effects on solubility. Strontium carbonate solubilities were measured in water and in the presence of carbon dioxide, as shown in Table 3 and Figure 5.

To correlate the experimental data, an empirical model was used (Equation 1). This model describes strontium carbonate solubility as a linear function of CO_2 partial pressure and temperature without the influence of MEG. Table 4 presents the empirical parameters used in equation 1.

$$[SrCO_3] = A + B * P_{CO_2} + C * (T - 298.15) \qquad (1)$$

The error of confidence interval presented in Table 4 was provided by STATISTICA®, during the correlation of the experimental data.

It can be seen that $SrCO_3$ solubility increases with CO_2 pressure, as expected. On the other hand, the temperature effect on $SrCO_3$ solubility is reversed, i.e., salt solubility decreases with increasing temperature due to the fact that CO_2 aqueous solubility also decreases with temperature (Figueiredo *et al*., 2014).

The calculated values of solubility, and consequently its deviation in relation to the experimental data, can be seen in Figure 6.

Figure 6 shows a low dispersion between experimental and calculated data, which demonstrates the quality of the applied correlation.

Table 5 presents $SrCO_3$ solubility data as a function of CO_2 partial pressure and salt-free aqueous MEG concentration at 298.15 K.

Another correlation was performed with Setchenov's model (Equation 2) for the three isobars

Table 3: $SrCO_3$ solubility data in water as a function of CO_2 partial pressure and temperature.

Temperature (K)	Pressure (mmHg)	$[SrCO_3]$ (ppm)	Temperature (K)	Pressure (mmHg)	$[SrCO_3]$ (ppm)
278.15	1610	1036.55	298.15	1610	875.87
	1410	1027.18		1410	833.52
	1210	1010.64		1210	778.29
	1010	918.25		1010	731.80
	760	863.00		760	675.58
288.15	1610	915.00	323.15	1610	651.19
	1410	910.23		1410	598.76
	1210	876.76		1210	575.93
	1010	813.18		1010	521.82
	760	735.90		760	459.24

Data uncertainties: $u(T) = 0.02$ K; $u(P) = 10$ mmHg; $u([SrCO_3]) = 4.88$ ppm.

Table 4: Empirical parameters for equation (1).

A		$B_{(PCO_2)}$		$C_{(T)}$	
Estimated	**Error**	**Estimated**	**Error**	**Estimated**	**Error**
512.1508	19.36443	0.2217	0.01556	-8.8217	0.26906

Exp. data points: $n = 79$; ΔS_{med}*: 10.46 ppm; ΔS_{max}: 42.7 ppm.
*$\Delta S_{med} = 1/n\sum|y_{ca}\,l - y|$

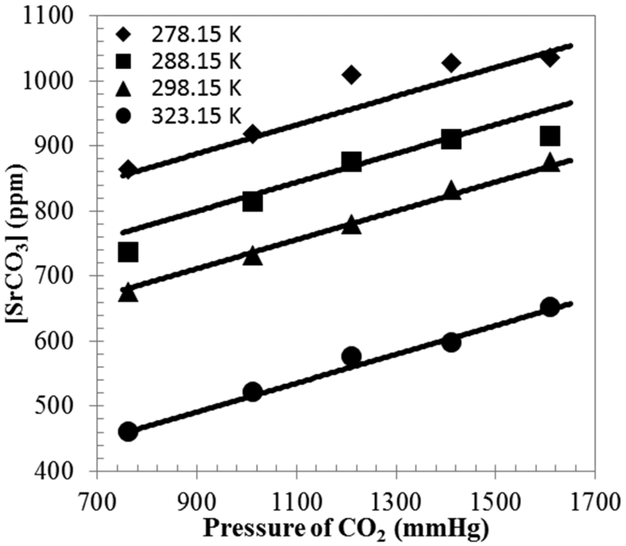

Figure 5: $SrCO_3$ solubility data in water vs. CO_2 partial pressure; calculated lines from equation (1).

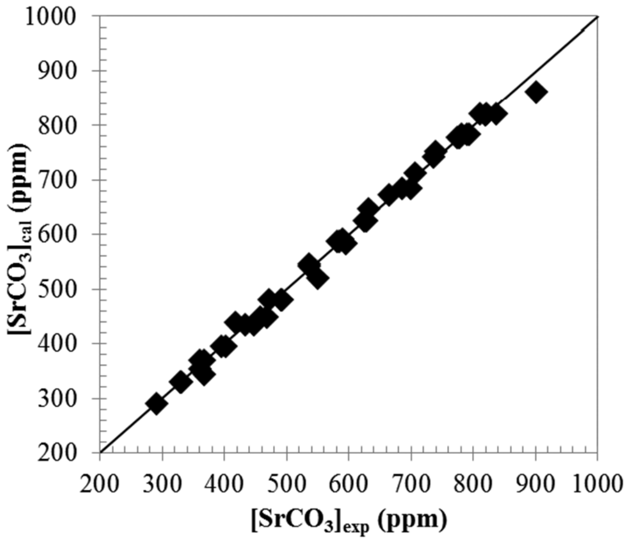

Figure 6: $SrCO_3$ solubility data dispersion using equation (1).

Table 5: $SrCO_3$ solubility data as a function of CO_2 partial pressure and salt-free aqueous MEG concentration at 298.15 K.

Pressure (mmHg)	**[$SrCO_3$] (ppm)**	**100 w'_{MEG} (wt %)**	**Pressure (mmHg)**	**[$SrCO_3$] (ppm)**	**100 w'_{MEG} (wt %)**
760	700.12	0.00	1350	484.56	60.05
	690.83	5.02		397.05	79.98
	620.30	10.25		329.97	99.79
	572.93	18.10	1410	833.52	0.00
	462.39	40.20		827.91	5.13
	367.64	60.09		787.17	10.04
	309.74	80.12		705.29	20.07
	255.87	99.78		586.77	40.07
1170	534.88	40.13	1520	875.87	0.00
	290.84	99.78		900.31	5.03
1210	778.29	0.00		814.55	10.07
	775.08	5.23		739.74	20.05
	734.32	10.19		625.69	40.01
	663.57	20.11		548.14	59.99
	415.92	60.09		439.56	79.98
	360.88	79.92		363.23	99.87

Data uncertainties: $u(T) = 0.02$ K ; $u(P) = 10$ mmHg; $u([SrCO_3]) = 1.35$ ppm; $u(100\ w'_{MEG}) = 0.007$ wt%.

to describe the $SrCO_3$ solubility data in mixed solvent for each studied isobar.

$$\log[SrCO_3]_{ms} = \log[SrCO_3]_{water} + K\,[MEG]' \qquad (2)$$

Through Setchenov's model, it was possible to estimate the K values correlating strontium carbonate solubility experimental data in water (S_o) and in aqueous mixtures of MEG (S), see Table 6. Using these parameters, it is possible to calculate strontium carbonate solubility values and compare them to the experimental data for the three studied pressures (Figure 7).

In this case, as observed in Figure 7, when the MEG content is increased, $SrCO_3$ solubility decreases. Higher CO_2 partial pressures increase strontium carbonate solubility and thus inhibit salt precipitation. Similar behavior has also been observed with two other carbonates, $CaCO_3$ and $FeCO_3$ (Figueiredo *et al*., 2016), studied in the laboratory. This information is relevant to the MEG regeneration process in *offshore* oil and gas production.

CONCLUSIONS

A series of salt solubility experiments were conducted on the $SrCO_3 + H_2O$ system under carbon dioxide atmosphere. Experimental data demonstrate

Table 6: Setchenov's parameters and correlation coefficients* for $SrCO_3$ solubilities in mixtures of water and MEG for three CO_2 partial pressures at 298.15 K

Pressure (mmHg)							
1520		1410		1210		760	
K	R²	K	R²	K	R²	K	R²
-0.38	0.996	-0.41	0.999	-0.44	0.996	-0.44	0.999

*$R^2 \equiv \sum (y_{cal} - y_{med})^2 / \sum (y_{exp} - y_{med})^2$

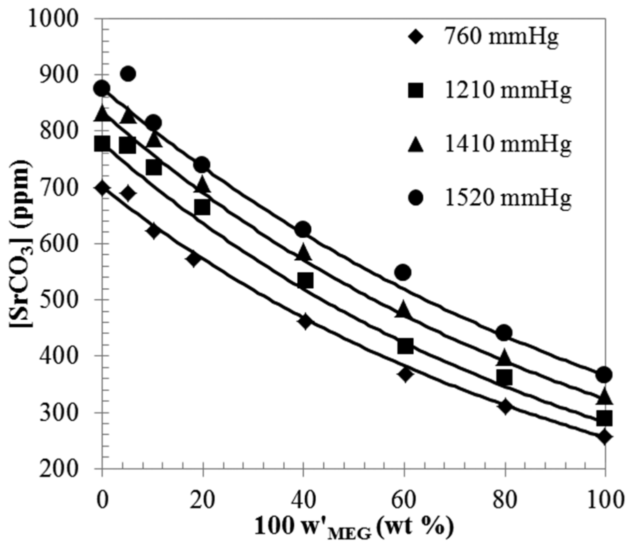

Figure 7: $SrCO_3$ solubilities as a function of MEG content in water at 298.15 K and under CO_2 atmosphere.

the thermodynamic behavior of these complex solutions.

The temperature dependence of strontium carbonate solubility was described at 278.15, 288.15, 298.15 and 323.15 K. It was observed that increasing the temperature implies a decrease in the salts solubility. Solubility is also dependent on carbon dioxide dissolution and pH. In order to explain this behavior, carbon dioxide is dissolved and the pH is reduced, promoting simultaneously strontium carbonate dissolution. Thus, an increase in carbon dioxide partial pressure leads to a gradual increase of $SrCO_3$ solubility.

The experimental procedure was demonstrated to be adequate for carbonate salts and a series of strontium carbonate solubility measurements is now available.

Strontium carbonate solubility experiments with MEG were also performed at 298.15 K at different pressures, and it was concluded that increasing the MEG concentration in the system decreases carbonate solubility. The increase in carbon dioxide partial pressure causes an increase in carbonate solubility. Experimental data were correlated with two empirical models, allowing process applications with accuracy as a function of temperature, MEG content and carbon dioxide pressure.

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