

# Characterization of pH in Aqueous CO<sub>2</sub>-Systems

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The applications of pH measurement range from pharmaceutical to food industries, from cosmetics to sewage treatments. Accurate measurements of pH at high pressure which are necessary for applications in various areas like process control, reaction equilibrium and kinetics have given scope to a lot of research to develop methods for measuring pH in-situ at high pressure in the past decade. This work engages with the measurement of pH of aqueous systems under CO<sub>2</sub> pressure up to 70 bar. Two in-line methods of pH measurement are presented: the Dual Wavelength UV/VIS spectrophotometric method and the high pressure pH electrode method. These two methods were integrated together into a single instrumental set-up and calibrated at different temperatures. pH values were measured for the systems carbon dioxide / water, carbon dioxide / buffer solution, and carbon dioxide / aqueous protein solution for temperatures between 30 and 50°C and pressures in the range of 10 to 70 bar by both methods experimentally and the results were compared with theoretical values. Due to the reaction of water and CO<sub>2</sub> to carbonic acid the pH of aqueous solutions is decreasing under CO<sub>2</sub> pressure depending on pressure, temperature, and buffer efficiency.

## INTRODUCTION

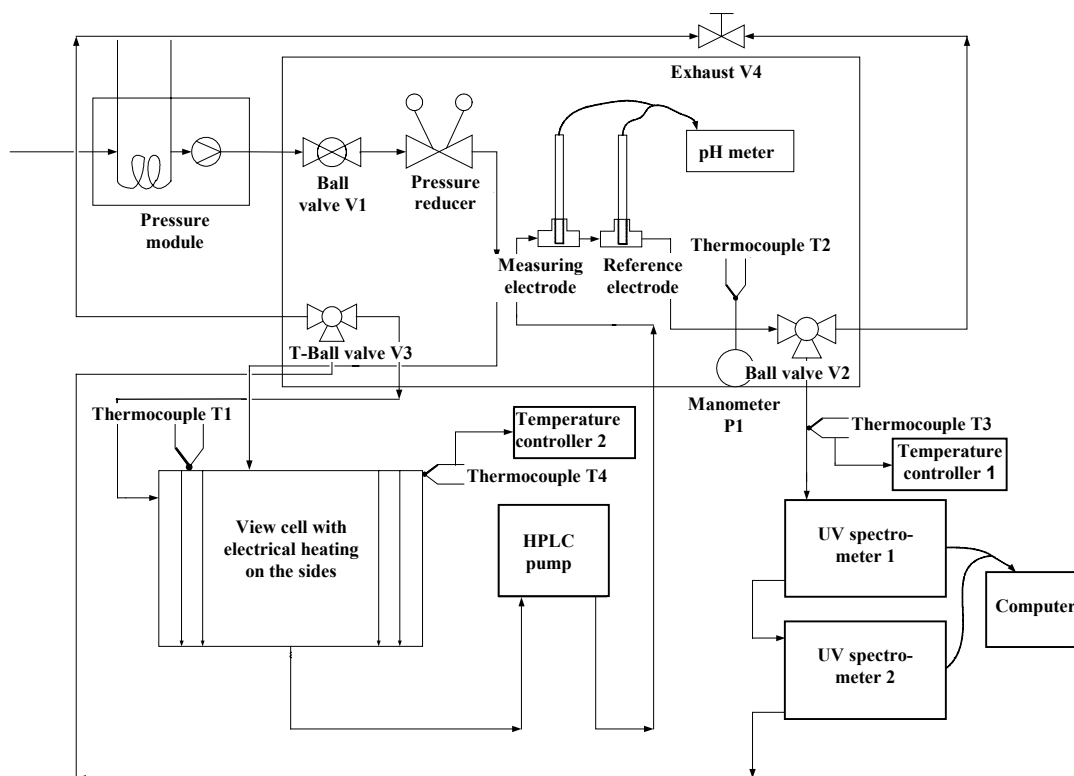
Various researches have been worked in the past decade on methods for reducing the pH of aqueous solutions by applying pressurized carbon dioxide. “High pressure” research in food industries should take into consideration the variation of pH with pressure especially for pH dependant reactions such as enzyme activity or protein denaturing. Protein denaturing processes could be used to inactivate vegetative cells or microbial spores to increase the shelf life of food products. Both thermal and pressure treatments can be applied for such purposes. Pressure treatments often have advantages over heat treatments as the former has a milder effect on taste, colour, odour and nutritional qualities of the food product. Also many vitamins which are easily destroyed by heat can survive high pressure treatments [1]. The conformation of molecules as well as the dissociation constants of pH sensitive substances in the solution change with pH while pH varies with pressure. Hence a detailed knowledge has to be realized to understand chemical or biochemical behaviour of various systems under high pressure treatments [2].

Accurate measurement of pH at high pressure finds applications in various areas like process control, reaction equilibrium and kinetics, environmental research to monitor seawater chemistry and natural water quality, biomedical research and in oilfields [3]. Such requirements have given scope to a lot of research to develop methods to measure pH in-situ at high pressure in the past decade. Spectrofluorometry was applied to a high pressure bomb reactor by Hayert et al. to check the variation of pH on acid and buffer solutions under pressure [2]. Spectroscopic methods with a mixture of multiple dyes for measurement of pH during high pressure treatment of food have been investigated by Stippl et.al [1]. One of the commonly used indicators for measuring pH in aqueous solution is bromophenol blue [4, 5] which has a colour transformation within a pH span of 3.0 to 4.6.

In this work, two methods of in-line measurement of pH of solutions at higher pressures and various temperatures have been suggested: Dual wavelength UV/VIS spectrophotometric method and high pressure electrode method. Both methods were integrated to form one experimental set-up including a view cell where the contact between the carbon dioxide phase and the aqueous solution phase could be observed. Each of the methods has been calibrated, verified and applied to investigate the pH behaviour of aqueous carbon dioxide systems at higher pressures and different temperatures.

## MATERIALS AND METHODS

Bromophenol blue from Merck KGaA (Darmstadt, Germany) was used as an indicator. A set of buffer solutions supplied by CARL ROTH GmbH+Co. KG (Germany) were used for calibration. For the measurement of pH for buffer / CO<sub>2</sub> systems, buffer solutions of pH 4, 5, 6, and 7 were prepared from disodium citrate, hydrochloric acid, sodium hydroxide, citric acid and disodium hydrogenphosphate. Albumin fraction V from bovine serum (BSA) for biochemistry from Merck KGaA (Darmstadt, Germany) was used to prepare an aqueous protein solution. Carbon dioxide (purity > 99.9 %) was supplied by Yara Industrial GmbH (Germany).



**Figure 1:** Schematic sketch of the main experimental set-up

The measurement of the pH value of the aqueous carbon dioxide systems at different pressures and temperatures was carried out using the apparatus shown in Figure 1. CO<sub>2</sub> was supplied to the apparatus using a pressure module (NWA GmbH, Germany). The custom-made high-pressure view cell, which consists of a stainless steel vessel with two glass windows, has an internal volume of 200 ml. A HPLC pump (K-1001, Knauer GmbH, Germany) was used to deliver the liquid phase into the view cell. The high-pressure pH electrodes, which consist of a measuring and a reference electrode, were obtained from Corr Instruments (LLC, San Antonio, TX, USA). The view cell and the pipelines were equipped

with an electrical heating system (Horst GmbH, Germany) in order to maintain a constant temperature in the system.

Two UV/VIS spectrophotometric detectors (SPD-6AV) manufactured by Analytical Instruments Division of Shimadzu Corporation (Duisburg, Germany) were used. Each spectrophotometer was set at a certain wavelength (590 and 430 nm), thereby, the two together, enabling a dual wavelength spectroscopy. Data were collected with the help of a software (Gynkosoft from Softron GmbH, Germany).

With the apparatus describes, measurements of pH value were done for water samples pressurized with gaseous carbon dioxide at three different temperatures: 30, 40 and 50°C and for pressures between 10 and 70 bar. First, the “baseline” was determined by pumping distilled water in open system at the desired temperature and atmospheric pressure until the signals at the high-pressure electrodes and the spectrophotometers were constant. Then the spectrophotometers were set to zero. For measurements, 100 mL of distilled water spiked with 0.5 mL of bromophenol blue solution were placed in the pressure cell. The water solution was recirculated and the view cell closed in order to pressurize the system. Once the desired temperature was reached, the pressure was increased by a first pressure step of about 10 bar. The system was let to equilibrate for around 40 minutes. Then the measured values of the high-pressure electrodes and the spectrophotometers were recorded. After that the pressure again was increased by additional 10 bar. This procedure was repeated up to a final pressure of 70 bar.

The procedure for the measurement of pH of buffer solution / carbon dioxide was carried out as described above for the measurement of pH of water / carbon dioxide system, but instead of water buffer solutions of pH 4 to 7 were analyzed. The experiment was performed for every buffer solution at 30, 40 and 50°C from about 7 to 60 bar with the high pressure electrode.

Finally the procedure was applied to the measurement of pH of protein (BSA) solution / carbon dioxide with the high pressure electrode at three different temperatures: 35, 40 and 45°C and for pressures between 1 and 65 bar.

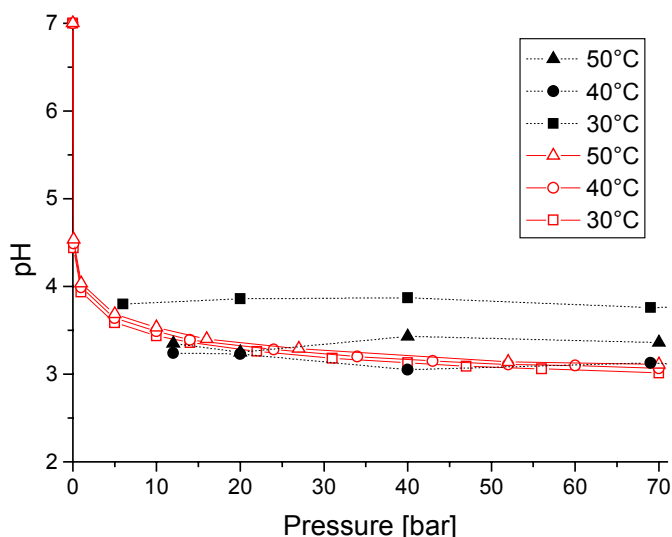
## RESULTS AND DISCUSSION

Carbon dioxide as gas dissolves in water and as a first approximation the phenomena can be explained according to Henry's law. For the system  $\text{H}_2\text{O} / \text{CO}_2$ , equilibrium reaction and mass balances can be written. An empirical expression for Henry's constant was taken from Edwards et al. for the calculation [6]. The equilibrium step of dissolved carbon dioxide to carbonic acid and the dissociation step of the latter one can be expressed together with a single overall constant,  $K_1$ , which value is obtained from the empirical equation [6, 7]. The values of the water ionization constant,  $K_w$ , at 30, 40 and 50°C were obtained from literature [8].

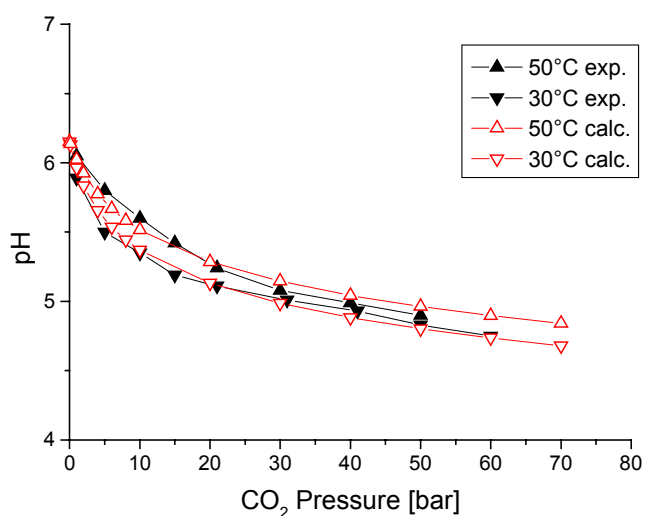
Theoretical calculations for water /  $\text{CO}_2$  system were performed in order to compare the results of the measurement obtained. The influence of pressure and temperature on pH can be seen in Figure 2 and Figure 3. With increasing pressure, the amount of carbon dioxide that dissolves in water increases, thus leading to a decrease in pH value. A decrease in temperature leads to a slight decrease in pH value. Additionally, in Figure 2 the experimental data measured by the UV/VIS spectrophotometric method are shown as a function of pressure for different temperatures. The experimental data differ from calculated values but the

experimental data by this method show large variances due to only small differences in absorbance.

A good agreement of experimental and calculated data was obtained for measurements with the high pressure electrodes as shown in Figure 3 for a buffer solution of pH of 6.

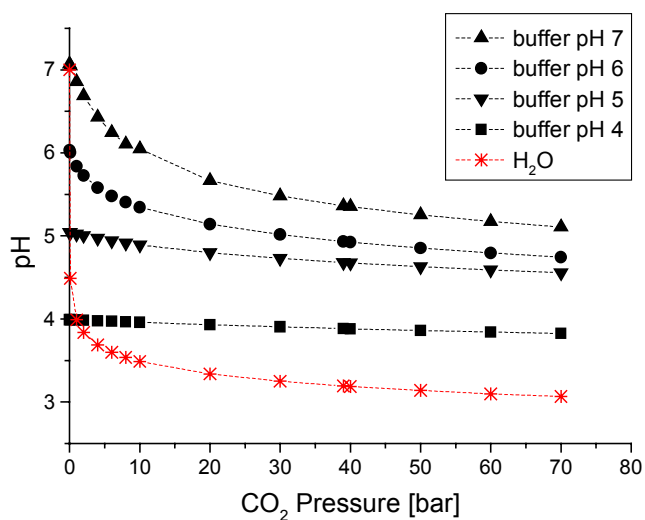


**Figure 2:** pH of water in equilibrium with CO<sub>2</sub> for different temperatures measured by UV/VIS spectrophotometers (open symbols represent the predicted values, while solid symbols represent experimental values).

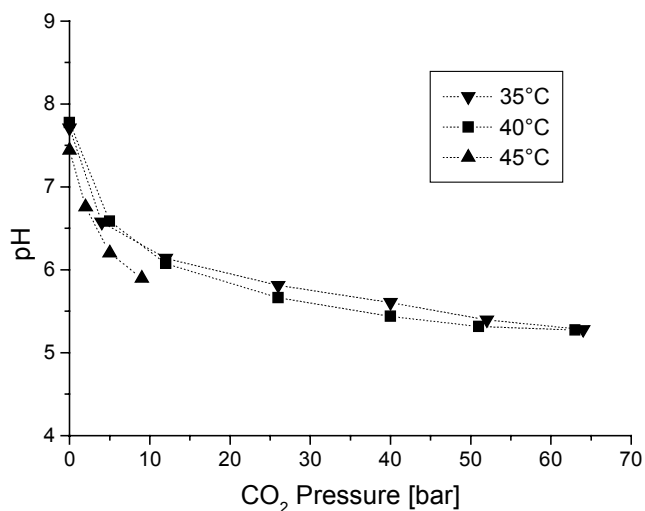


**Figure 3:** pH of buffer solution pH 6 in equilibrium with CO<sub>2</sub> measured by high pressure pH electrodes for T=30°C and 50°C (open symbols represent the predicted values, while solid symbols represent experimental values).

For the calculation of buffer solution / CO<sub>2</sub> system, the procedure is more complex. In this work calculations for the buffer solution were done with a freeware program called “CurTiPot” which is a comfortable tool for pH calculation [9, 10]. The results of the calculations of pH of different buffer solutions in contact with CO<sub>2</sub> are shown in Figure 4 as a function of pressure for T=40°C. The pH of the system buffer solution / CO<sub>2</sub> decreases with increasing pressure and comes to constant values at higher pressure. In the presence of buffer the decrease of pH with increasing pressure is lower compared to pure H<sub>2</sub>O. It can be observed that the higher the pH of the buffer solution is, the larger the decrease is in the beginning when the CO<sub>2</sub> is applied to the system. The absolute decrease of pH is lower the lower the starting pH of buffer solution.



**Figure 4:**  
pH of different buffer solutions in equilibrium with CO<sub>2</sub> calculated with CurTiPot (T=40°C)



**Figure 5:**  
pH of protein solution (200 mg BSA/ml) in equilibrium with CO<sub>2</sub> measured by high pressure pH electrodes for three temperatures

Results of the measurement of an aqueous protein solution (200 mg BSA/ml) in equilibrium with CO<sub>2</sub> is shown in Figure 5 as a function of pressure for different temperatures. Similar to buffer solutions the pH of the system protein solution / CO<sub>2</sub> decreases with increasing pressure and comes to constant values at higher pressure, namely the behavior of BSA solution is similar to the one of buffer solution at starting pH 7. The influence of temperature is marginal. However it has to be mentioned that the protein in the solution precipitates at higher pressures depending pressure, temperature and concentration of protein.

## CONCLUSION

Two methods of in-line measurement of pH of solutions at higher pressures and various temperatures have been investigated in this work. In this work the method of measurement by high pressure electrodes shows more reliable results than the measurement by UV/VIS spectrophotometry. Theoretical calculations were obtained based on electrochemical equilibrium of carbon dioxide in water and Henry's law. Experimental data were compared

with calculated values, showing the trend of pH to decrease as carbon dioxide pressure increases and to increase with increasing temperature. Determination of the influence of pressurization with carbon dioxide on the pH of buffer solutions was performed with the high pressure electrode and the results were compared with calculated ones. With increasing pressure, the pH of buffer solutions decrease to a constant value. A similar behaviour was found for an aqueous protein solution. The study showed successful in-line measurements of pH of aqueous solutions at higher pressures and temperatures.

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