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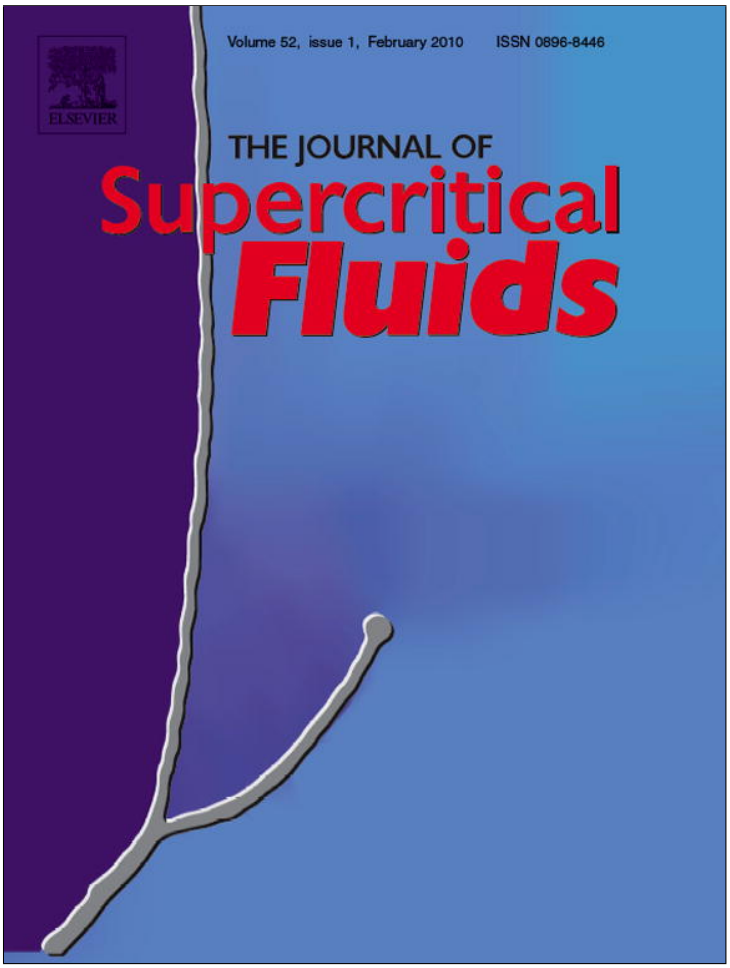


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# Measurement and prediction of $CO_2$ solubility in sodium phosphate monobasic solutions for food treatment with high pressure carbon dioxide

Giovanna Ferrentino[a,*], Diego Barletta[a], Murat Omer Balaban[b], Giovanna Ferrari[a,c], Massimo Poletto[a]

[a] Dipartimento di Ingegneria Chimica e Alimentare, Università degli Studi di Salerno, Via Ponte Don Melillo, I-84084 Fisciano (SA), Italy
[b] Fishery Industrial Technology Center, University of Alaska Fairbanks, 118 Trident Way, Kodiak, AK 99615, USA
[c] ProdAl S.c.ar.l.- Centro Regionale di Competenza sulle Produzioni Agroalimentari, via Ponte Don Melillo, I-84084 Fisciano (SA), Italy

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ABSTRACT

Two experimental systems were designed and tested to measure the $CO_2$ solubility in pure water and sodium phosphate monobasic solutions (0.240, 2.40 and 4.80 g/100 g water) at different pressures (7.5 and 15.0 MPa) and temperatures (35, 40 and 50 °C).

The solubility experimental results were compared with the equilibrium conditions evaluated by applying three different thermodynamic models by means of the process simulation software Aspen Plus®: (1) the Peng–Robinson equation of state (EOS), with the Wong and Sandler mixing rules (PRWS) and the excess Gibbs free energy calculated according to the UNIFAC method; (2) the Electrolytic Non-Random Two Liquids (ELECNRTL) with the Redlich–Kwong equation of state for aqueous and mixed solvent applications; (3) the completely predictive Soave–Redlich–Kwong (PSRK) equation of state.

$CO_2$ solubility appeared to be a strong function of sodium phosphate monobasic concentrations. The predictions of the PRWS EOS agreed well with the experimental data in the pressure and temperature ranges tested. Larger differences between experimental and predicted results were observed for conditions close to the $CO_2$ critical point and for low sodium phosphate monobasic concentrations. Predictions of thermodynamic models 2 and 3 had much larger deviations from experimental data.

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## 1. Introduction

Carbon dioxide ($CO_2$) is preferred as a supercritical solvent for extraction because of its low critical temperature and pressure that minimize damage to biological compounds, its low cost, and its availability in purified form. In the food and health industries $CO_2$ is used because it is inert, nontoxic and is a natural component of many foods. The decaffeination of coffee beans is an example [1] of this application. For many chemical processes that are conducted at high pressures, knowledge of the phase behavior of $CO_2$ is of special interest. In particular the growing interest for the high pressure carbon dioxide (HPCD) treatment used for the pasteurization and sterilization of liquid foods emphasizes the importance of a better understanding of the physical behavior of systems made of water based liquid food and carbon dioxide. In fact, it has been verified that the process inactivation kinetics of microorganisms in liquid foods treated with HPCD can be described with a unified model based on $CO_2$ solubility and temperature, almost independently from the composition of the suspending medium and the pressure used [2].

There are several review articles presenting equipments and procedures used to obtain high pressure phase equilibrium data [3,4]. Experimental equilibrium data are important, even when thermodynamic models are used to calculate the phase behavior of a mixture. In fact, thermodynamic models can help to reduce the number of experimental data points needed for a special design problem but, in general, at least some experimental data points are needed to evaluate binary or higher order interaction parameters of models [5], or to assess the model predictive ability.

A large number of experimental studies have been conducted with different techniques to measure the $CO_2$ solubility in water and more complex aqueous solutions. Complete surveys of these works can be found in recent reviews [6–8]. The presence of substances dissolved in water solution could have a positive or negative effect on $CO_2$ solubility [9,10]. The relevance for carbon sequestration in deep saline aquifers motivated several studies, which were recently reviewed by Ji et al. [8], on the solubility of $CO_2$ in water with salts (mainly NaCl) present in seawater. Among these studies Bando et al. [11] measured the $CO_2$ solubility in aqueous solutions of NaCl. The experimental apparatus was designed to dissolve $CO_2$ in $H_2O$–NaCl solution in a pressurized vessel. From the evaluation of the mass of the sample and the pressure of the dis-

* Corresponding author. Tel.: +39 089964028; fax: +39 089964168.
*E-mail addresses:* gferrentino@unisa.it (G. Ferrentino), dbarletta@unisa.it (D. Barletta), mob@sfos.uaf.edu (M.O. Balaban), gferrari@unisa.it (G. Ferrari), mpoletto@unisa.it (M. Poletto).

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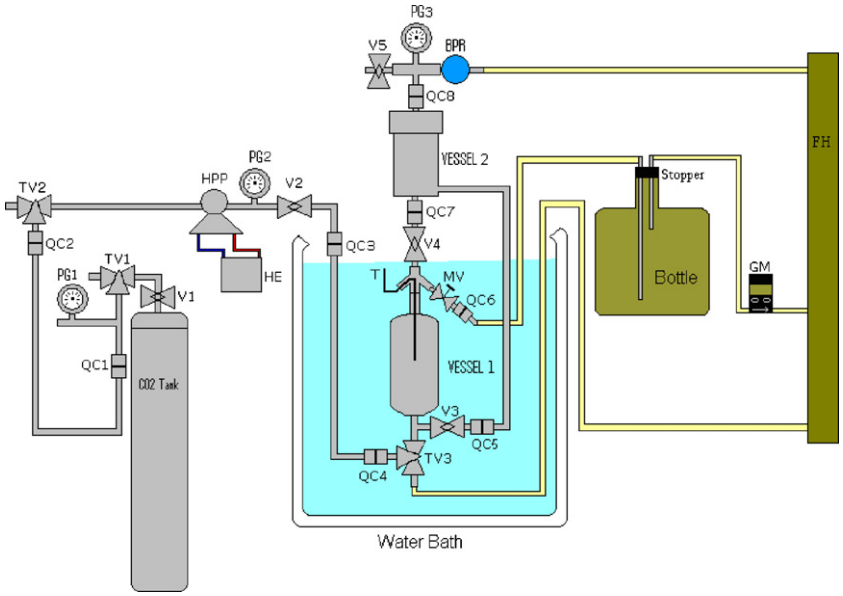


**Fig. 1.** Schematics of the high pressure continuous $CO_2$ solubility apparatus [25].

solved gas of the saturated solution removed from the vessel it was possible to calculate $CO_2$ solubility. Results showed that increasing the mass fraction of NaCl in the solutions from 0.01 to 0.03 at 303–333 K and 10–20 MPa the $CO_2$ solubility decreases. Some other studies assessed the effect of other salts (nitrates, acetates) on the $CO_2$ solubility in the temperature ranges from 313 to 433 K and at pressures up to 10 MPa [9,12]. The results showed that while the presence of $NaNO_3$ negatively affects the $CO_2$ solubility in water, $NH_4NO_3$, NaOH, sodium acetate, ammonium acetate and acetic acid have a salting in effect. The effect of species other than salts has been studied too. Dohrn et al. [13] designed a high pressure apparatus for obtaining reliable phase equilibrium data in the glucose–water–$CO_2$ and glucose–water–ethanol–$CO_2$ system at temperature up to 343 K and pressure up to 30 MPa. These data showed that the $CO_2$ solubility in water decreased in the presence of the glucose and that ethanol acted as a polar co-solvent and determined a substantial increase in the solubility of glucose in the vapor phase at high pressure. Bamberger et al. [14] designed an apparatus based on the flow technique to obtain binary phase equilibrium data for carbon dioxide–water and carbon dioxide–acetic acid systems. The results extended the database for the high pressure phase equilibrium of these systems confirming an increase in the $CO_2$ solubility in water–acetic acid solutions with respect to pure water. Calix et al. [15] designed an experimental system to measure the carbon dioxide solubility in ascorbic acid–sugars–water, citric acid–sugars–water solutions and in commercial orange and apple juice as a function of pressure (7.58–15.86 MPa) at 40 °C showing that $CO_2$ solubility in these solutions and in the real juices was always lower than for pure water, due to the presence of solutes.

Modeling of the vapor liquid phase equilibria of the $CO_2$–$H_2O$ system has been extensively studied with different approaches based either on a single type of equation of state for all the phases ($\phi-\phi$ models) or on an equation of state combined with an excess Gibbs free energy model for the liquid phases ($\gamma-\phi$ models) [16–19]. Carroll and Mather [16] used the Krichevsky–Kasarnovsky equation of state which is reliable at temperatures lower than 100 °C. Shyu et al. [18] used a model based on the Peng–Robinson equation of state [20] with the Wong–Sandler mixing rules. In particular, the van Laar model was used to calculate the excess Gibbs energy with three parameters, two energy parameters for the liquid phase and one interaction parameter for the gas phase. The results were accurate over a wide range of temperatures 25–350 °C and pressures 1–100 MPa. Also Valtz et al. [19] combined the Peng–Robinson equation of state with the Wong–Sandler mixture combining rule to model binary $CO_2$–$H_2O$ systems at a temperature and pressure of 5–45 °C and 0.464–7.963 MPa with the NRTL (Non-Random Two Liquid) local composition model used to obtain the excess molar Gibbs free energy. The calculated results for the vapor composition were accurate, especially at low temperatures.

Only few attempts have been carried out to model vapor liquid equilibria of $CO_2$–$H_2O$ system including other components. The majority of the modeling studies have been developed for aqueous solutions with salts present in seawater [17,21,8]. Kiepe et a1. [17] successfully predicted the gas solubility in the $CO_2$–$H_2O$–NaCl system from 313.15 to 353.15 K and from 0.006 to 10 MPa by coupling the PSRK EOS with the group contribution model LIFAC. This approach was applied by Kiepe et al. [17] to other electrolyte system over wider ranges of temperature (288–523 K) and pressure (0.01–70 MPa) with good results especially below 10 MPa. Duan and Sun [21] calculated the solubility of $CO_2$ in aqueous solutions with NaCl and in more complex solutions at temperatures from 273 to 533 K and pressures from 0 to 200 MPa, and ionic strength from 0 to 4.3 mol $L^{-1}$ using a model based on the excess Gibbs energy equation by Pitzer [22] for the liquid phase and the equation of state of Duan et al. [23] for the vapor phase. A similar approach for the liquid phase coupled with a truncated virial equation of state for the vapor fugacity coefficients was applied to aqueous solutions containing a single solute among sodium nitrate, ammonium nitrate [10], sodium hydroxide [24], sodium acetate and ammonium acetate [12]. With concern to more complex solutions, Calix et al. [15] tried to model the phase equilibrium of ascorbic acid–sugars–water and citric acid–sugars–water solutions with the Electrolytic Non-Random Two liquids (ELECNRTL) thermodynamic model with the Redlich–Kwong equation of state for aqueous and mixed solvent applications but the calculated gas solubility showed large discrepancies from the experimental data.

This paper is a part of a wider project aiming at finding an engineering approach for the design of high pressure carbon dioxide treatment processes for liquid foods. In particular, the project focuses on the definition of simple modeling and experimental procedure to be used in designing HPCD process [2]. The objective of this work was to set up a simple experimental procedure to

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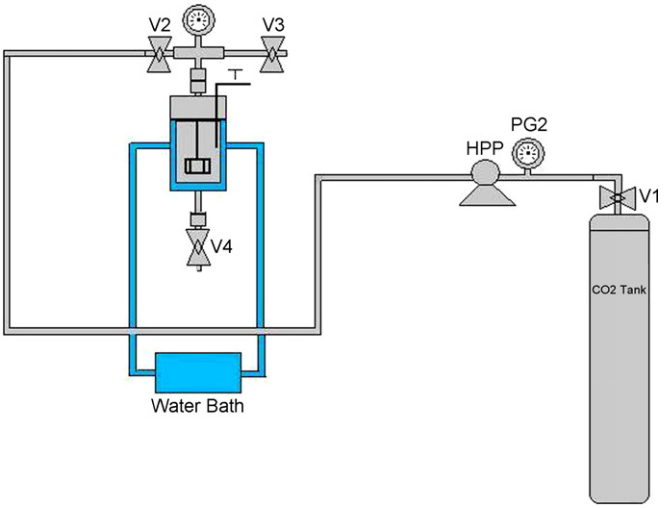


**Fig. 2.** Schematics of the high pressure batch $CO_2$ solubility apparatus [26].

measure $CO_2$ solubility in buffer solutions and to verify the ability of the existing thermodynamic models to predict experimental results. $CO_2$ solubility was measured with two different setups using water solutions of monobasic sodium phosphate ($NaH_2PO_4$) at different concentrations. Three different thermodynamic submodels available in Aspen Plus® process flowsheeting software (Aspen Technology, Inc., Burlington, MA) were used to predict $CO_2$ solubility in the experimental conditions tested.

## 2. Materials and methods

### 2.1. Experimental setup

#### 2.1.1. Semi-continuous equipment

The measurement of $CO_2$ solubility was performed using a semi-continuous apparatus designed in the Food Science and Human Nutrition Department, University of Florida, Gainesville, FL, in order to put in contact a continuous gas stream with a stationary liquid phase. A schematic of the experimental setup is shown in Fig. 1. The objective was to saturate a known amount of liquid with $CO_2$ under controlled pressure and temperature conditions, collect a sample of the liquid at equilibrium and measure the dissolved gas by letting it expand at atmospheric pressure. The system was composed of two vessels. The lower vessel (vessel 1) had a capacity of approximately 150 mL, the upper vessel (vessel 2) had a capacity of approximately 55 mL. The apparatus was submerged in a water bath with a capacity of about 60 L. The water in the bath was recirculated through a plastic tube to a small high precision thermally controlled bath (model 6035, Hart Scientific, American Fork, UT) that was set in the range 46–50 °C (maximum uncertainty of about ±0.1 °C) to maintain a constant temperature within the vessel. To recirculate the water a Masterflex peristaltic pump (model 7553-50, Cole Parmer, Chicago, IL) was used. Thermocouples, used in the water bath (Omega® Engineering Inc., Stamford, CT), and inside the lower vessel (Omega® Engineering, part # TQSS-116G-12 and QC# PL040052) monitored the system temperature [15] with a maximum uncertainty of about ±0.1 °C.

Carbon dioxide was pumped to the bottom of vessel 1 by a high pressure pump model X-10 (Milton Roy, Ivyland, PA). Pump head was cooled to about −15 °C by a 50/50 water and antifreeze solution thermostated in a cooling bath (Fisher Scientific, model 900). Carbon dioxide exited from the system through a back pressure valve. A side recirculation tube connecting the bottom of vessel 2 to the bottom of vessel 1 allowed the liquid from vessel 2 to recirculate to vessel 1 by gravity and the gas in vessel 1 to bubble up to vessel 2. This recirculation allowed good contact between phases and a well mixed uniform liquid phase in equilibrium with the gas phase at the end of the gas–liquid contact operation. During this operation gas exited from the top of vessel 2 through a back pressure valve BPR, in which $CO_2$ was depressurized to the atmosphere and sent to the stack. Valves V3, TV3 and V4 allowed isolating vessel 1 and the dissolved $CO_2$ in it was depressurized through the metering valve MV to a liquid trap connected to a gas meter discharging to the stack [25].

#### 2.1.2. Batch equipment

This equipment was originally built for the treatment of liquid and solid food with $CO_2$ under pressure at the Department of Chemical and Food Engineering of the University of Salerno (Fig. 2). The vessel (100 mL) was a modified version of a Parr Stirred Reactor (FKV s.r.l., Bergamo, Italy). It reached a maximum pressure of 20.0 MPa. A four-bladed impeller magnetically coupled to a DC motor (model no. A1120HC6) allowed adjusting the mixing speed, and a fixed thermocouple (Type J) was used to measure the temperature inside the vessel. All the connections for the inlet and the outlet lines, the stirrer and the thermocouple were fitted on the removable head of the vessel. This head could be removed to clean the system and to introduce the liquid samples used in the batch experimental procedure. It was equipped with a calibrated rupture disc for surcharge pressure relief. A pressure gauge, fitted on the reactor head, displayed the pressure inside the system. The $CO_2$ pump was a Jasco model PU-1580 for chromatography with flow control based on volume displacement or on the output pressure. Liquid $CO_2$ for the pump (99.99% purity, SOL SpA, Italy) was withdrawn from a cylinder. An on–off valve on the feed line between the pump and the vessel that was turned closed after pumping to avoid back flow during experiments. The time required for the pressurization of the reactor and for heating was about 5 min. The vessel had a jacket to circulate water coming from an external thermally controlled bath and keep the system at the desired temperature. A valve at the vessel bottom was used to withdraw liquid samples in the solubility experiments. At the end of the experiments the system could be easily depressurized by opening the on–off valve on the vessel outlet line.

### 2.2. Sample preparation

Both experimental systems were used to measure the $CO_2$ solubility in solutions of water and sodium phosphate monobasic. Pure de-ionized water was used with a volume of 100 mL per run for the batch and 500 mL per run for the semi-continuous apparatus. For the preparation of the sodium phosphate monobasic solutions 0.240, 2.40 and 4.80 g of $NaH_2PO_4$ (certified ACS reagent, Sigma–Aldrich, St. Louis, MO, USA) were weighted on an analytic balance (maximum uncertainty of about ±0.1 mg) and were dissolved in 100 g of pure de-ionized water to obtain solutions with molarities of 0.02, 0.20 and 0.40, respectively. The experiments were performed at temperatures of 35, 40 and 50 °C and pressures of 7.58, 10.34, 13.10 MPa. Each experiment was performed in triplicate.

### 2.3. Experimental procedure

#### 2.3.1. Solubility experiments with the semi-continuous equipment

After the desired temperature was reached throughout the system, about 500 mL of sample was pumped by the peristaltic pump through a plastic tube connected to the stem connection of QC3 in place of the gas feeding system shown in Fig. 1. The thermocouple inside the reactor was used to read the sample temperature with

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a maximum uncertainty of about ±0.1 °C. The temperature of the water in the jacket was regulated in the range 46–50 °C to keep the vessel at the desired temperature. After reconnection of the $CO_2$ feeding system, liquid $CO_2$ was pumped into the system by turning on the high pressure pump. Valves V1 and V2 were opened while the back pressure regulator was adjusted to increase pressure. When the pressure reached about 1.5–2.0 MPa (read with a maximum uncertainty of about ±1 MPa) above the desired value, the $CO_2$ flow rate of the high pressure pump was reduced to about 37% of the original flow rate. The high pressure pump remained on for 70 min to allow the liquid to be saturated by $CO_2$. At the end of this period, the high pressure pump was turned off and the valve V1 was closed. After letting some time to allow the gas to bubble up and out of vessel 1, valves V3, TV3 and V4 were closed to isolate vessel 1 while the remaining parts of the system were depressurized to the atmosphere. At this stage it was assumed that in vessel 1 there was only the liquid phase saturated with $CO_2$. The metering valve (MV) was opened for depressurization of vessel 1, until all the dissolved gas came out of the system and the volumetric flow rate read by the mass flow meter (GM) was null. The $CO_2$ was measured using the mass flow meter from Alicat Scientific (Tucson, AZ, USA), model number M-1SLPM-D, calibrated for $CO_2$. The GM accurately measures the volumetric flow in standard liters per minute (SLPM) at a standard temperature and pressure (0.1 MPa and 25 °C) and with an accuracy of up to +/- (0.4% of reading +0.2% of full scale). The liquid inside vessel 1, in the trap, and in the connecting tubing was collected and measured with a 100 mL cylinder (scale divisions of 1 mL). This amount was considered as the basis for the solubility calculations which taking into account all uncertainties in the measured variables showed that the maximum relative uncertainty in $CO_2$ solubility is about ±0.1 g $CO_2$/100 g solution.

#### 2.3.2. Solubility experiments with the batch equipment

The batch vessel was opened and loaded with the liquid mixture and then carefully closed. The external jacket was connected with the water bath and the system was heated to the experimental temperature. Next, $CO_2$ was pumped until experimental pressure was reached. The temperature and pressure inside the vessel were monitored with the thermocouple and the pressure gauge. The experimental pressure is controlled by the high pressure pump (PU-1580-$CO_2$ pump, Jasco s.r.l., LC, Italy) which transferred the $CO_2$ from the tank to the reactor and had a precision of 0.1 MPa. The experimental temperature is controlled by the water bath (DC-10 thermostatic bath, Enco s.r.l., VE, Italy) equipped with a Pt1000 thermocouple with a maximum uncertainty of about ±0.01 °C. When the pressure reached the desired level, the system was stirred for almost 1 h to reach thermodynamic equilibrium. In all the tests the same stirring speed (approximately 850 rpm) to promote the dissolution of $CO_2$ in the liquid phase was used.

After 1 h, time required to reach the saturation in the liquid phase, a plastic syringe (60 mL syringe catheter) with scale divisions of 1 mL was connected to the bottom valve of the vessel through an on–off valve. Before sampling, the piston of the syringe was pushed all the way to the front in order to remove all the air from it. A small amount of liquid phase was drawn by opening the bottom valve. The operation was short and the small amount of liquid that was drawn did not change significantly the pressure and temperature of the pressurized reactor. The syringe expansion took into account the volume of $CO_2$ and that of the liquid solution. The syringe was then disconnected from the vessel and weighted on a high precision balance (Laboratory electronic balance, Gibertini Elettronica s.r.l., MI, Italy) with a maximum uncertainty of about ±0.1 mg to obtain the mass of the sampled liquid. The total volume expansion in the syringe was read. The total weight took into account the grams of liquid. From the density of the liquid mixture the volume of the liquid was calculated and subtracted from the total volume to find the $CO_2$ volume. Multiplying the $CO_2$ density and the $CO_2$ volume the grams of $CO_2$ were obtained. The ratio between the grams of $CO_2$ and the grams of liquid gave the solubility value [26]. A calculation taking into account all uncertainties in the measured variables showed that the maximum relative uncertainty in $CO_2$ solubility is about ±0.099 g $CO_2$/100 g solution.

The amount of liquid and $CO_2$ in the samples obtained from the batch and the continuous equipment were very different. About 0.75 g of liquid and 0.035 g of $CO_2$ were collected from the batch equipment while 170 g of liquid and 8.5 g of $CO_2$ were collected from the semi-continuous one. In particular quantities in the samples taken in the batch equipment suggest that even small experimental errors could influence the measurement. For this reason each experiment was run in triplicate and the experimental procedure was tested several times to perform a good repetition of the results.

### 2.4. Vapor–liquid equilibrium simulation

The process simulation software Aspen Plus® version 2006.5 (Aspen Technology, Inc., Burlington, MA) was used to study the vapor–liquid equilibrium of the system. In particular, the $R_{Gibbs}$ simulation block of Aspen Plus® was used to solve the equations for the vapor–liquid equilibrium, once the user had chosen the pressure and temperature of the system and the thermodynamic model, by minimizing the Gibbs free energy of the system [27]. Data were obtained in terms of molar fractions of the two phases at the equilibrium conditions. During this study three thermodynamic models were considered:

(1) The Peng–Robinson–Wong–Sandler (PRWS) thermodynamic model. This model is based on the Peng–Robinson equation of state (PR-EOS) with the Wong and Sandler [28] mixing rule. Thus, it is a $\phi - \phi$ thermodynamic model used to describe the non-ideality of both the $CO_2$-rich phase and $H_2O$-rich phase with an equation of state. In particular, the Wong–Sandler mixing rule combines the Peng–Robinson equation of state with a free energy model to obtain the $a$ and $b$ parameters of the PR-EOS for a mixture.

The excess Gibbs free energy $G^E_\gamma$, appearing in the equations of this thermodynamic model, can be calculated with any excess Gibbs free energy model. In the present work the group contribution method UNIFAC [29] was used. As a result, the binary interaction parameters $k_{ij}$, appearing in the equation which links the $a$ and $b$ coefficients, are adjustable parameters which make the model not fully predictive. Wong and Sandler [28] proposed to find out the proper $k_{ij}$ values by searching the best fitting at low pressure between the excess Gibbs free energy predicted by the combined EOS-free energy method (in this case PRWS), $G^E_{EOS}$, and one evaluated according to the excess Gibbs free energy model $G^E_\gamma$. In this study, the $k_{ij}$ values were evaluated by the best fitting of experimental VLE values at a single reference condition. In order to calculate the $NaH_2PO_4$ activity coefficients used for the evaluation of $G^E_\gamma$, it was necessary to define the structure of the molecule as composed by two ionic groups $Na^+$ and $H_2PO_4^-$. The relevant values of the surface and volume parameters proportional to the van der Waals surface areas and volumes of the groups necessary for the evaluation of the activity coefficients according to the UNIFAC method were evaluated by the Bondi's method, as reported by the work of Haghtalab and Mokhtarani [30]. The surface parameters were 0.176 and 1.329, while the volume parameters were 0.315 and 1.210 for $Na^+$ and $H_2PO_4^-$, respectively.

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**Table 1**
Experimental $CO_2$ solubility in pure water obtained with the semi-continuous and the batch equipment compared to the literature data and the thermodynamic models.

| Temperature (°C) | Pressure (MPa) | Semi-continuous equipment | | Batch equipment | | PRWS model (g/100 g[a]) | ELECNRTL model (g/100 g[a]) | PSRK model (g/100 g[a]) | Literature data (g/100 g[a]) |
|---|---|---|---|---|---|---|---|---|---|
| | | Experimental solubility (g/100 g[a]) | St. dev.[b] (g/100 g[a]) | Experimental solubility (g/100 g[a]) | St. dev.[b] (g/100 g[a]) | | | | |
| 35 | 7.58 | 5.41a | 0.12 | 5.45a | 0.04 | 5.28 | 4.96 | 5.71 | 5.43[c]–5.36[d] |
| | 10.34 | 5.68b | 0.21 | 5.72b | 0.05 | 5.66 | 6.23 | 7.65 | 5.68[c]–5.61[d] |
| | 13.10 | 5.81c | 0.05 | 5.85c | 0.11 | 5.90 | 8.53 | 9.81 | 5.82[c]–5.85[d] |
| 40 | 7.58 | 4.71a | 0.15 | 5.01d | 0.02 | 4.89 | 4.64 | 5.22 | 4.81[c]–5.00[d] |
| | 10.34 | 5.51b | 0.20 | 5.32e | 0.19 | 5.35 | 5.65 | 6.54 | 5.32[c]–5.40[d] |
| | 13.10 | 5.72c | 0.08 | 5.54f | 0.05 | 5.59 | 6.74 | 8.30 | 5.65[c]–5.80[d] |
| 50 | 7.58 | 4.38a | 0.04 | 4.45a | 0.03 | 4.24 | 4.07 | 4.40 | 4.40[c]–4.45[d] |
| | 10.34 | 5.01b | 0.12 | 4.96b | 0.02 | 4.92 | 4.54 | 5.12 | 5.00[c]–4.86[d] |
| | 13.10 | 5.25c | 0.18 | 5.31c | 0.05 | 5.29 | 4.75 | 5.48 | 5.22[c]–5.25[d] |

Different letters in mean values between semi-continuous and batch experiments mean significant difference in $CO_2$ solubility ($p < 0.05$).
[a] Grams of $CO_2$/100 g of liquid.
[b] Standard deviation.
[c] Data taken from [36].
[d] Data taken from [37].

(2) The Electrolytic Non-Random Two liquids (ELECNRTL) thermodynamic model with the Redlich–Kwong equation of state for aqueous and mixed solvent applications. It is a $\gamma - \phi$ model where the Redlich–Kwong EOS [31] is used to describe the non-ideality of the vapor $CO_2$-rich phase and Henry's law or the electrolyte NRTL model [32], an excess molar Gibbs free energy model, is used to describe the non-ideality of the liquid $H_2O$-rich phase. The model takes into account the ionic species formed by the dissociation of the compounds and requires the interaction parameters between all the species in the solution. In this case all the binary parameters values for the electrolyte NRTL model were retrieved from the database available in Aspen Plus®. The simulation software solved the mass and energy balances of the defined system together with the thermodynamic equations and gave the molar fractions of $H^+$, $CO_2$, $HCO_3^-$ and $CO_3^{2-}$ and of the other electrolytes deriving from the dissociation of the $NaH_2PO_4$. The value of the mass fraction of $CO_2$ dissolved in the liquid gave the solubility of the system at a fixed temperature and pressure.
(3) The completely predictive Soave–Redlich–Kwong (PSRK). In this thermodynamic model the equilibrium calculations are solved with the Soave–Redlich–Kwong EOS [33] with the modified UNIFAC method [29]. The UNIFAC method was used to describe the activity coefficient through the Holderbaum and Gmehling [34] predictive mixing rules, a modified form of the Huron and Vidal [35] mixing rules.

The Gibbs free energy $G^E$ is calculated with the UNIFAC model. These equations do not include any adjustable parameters and do not need any experimental data to be retrieved by model fitting. This makes the model completely predictive. All the parameters in the mathematical expressions of PSRK model were obtained with the method of the functional groups. The same surface and volume parameters of the ionic groups $Na^+$ and $H_2PO_4^-$ forming the $NaH_2PO_4$ molecular structure, considered for the PRWS thermodynamic model, were also used for this calculation.

The three thermodynamic models were applied to the experimental data. With concern to the PRWS, data at a certain temperature and pressure were used to evaluate the coefficients of binary interactions $k_{ij}$ with a best fitting procedure. After that the model was applied to predict the $CO_2$ solubility values at different temperatures, pressures and solute concentrations.

### 2.5. Statistical analysis

Analysis of variance (ANOVA) and means separation were performed to evaluate the difference between experimental solubilities at different conditions of pressure, composition and temperature. The statistical data analysis was conducted by performing a Tukey (HSD) test, with $p < 0.05$. The software program used was Statistica, version 7.0 (StatSoft Inc., Tulsa, OK).

## 3. Results and discussion

### 3.1. Validation of the experimental equipments and procedures with the literature results

To demonstrate the accuracy and precision of the high pressure $CO_2$ solubility equipments and measurement procedures, the experimental results of $CO_2$ solubility in pure water were compared with the values presented in the literature. The $CO_2$ solubility charts developed by Wiebe and Gaddy [36] and Dodds et al. [37] were used as a reference.

Table 1 reports the experimental solubility values in pure water at 35, 40 and 50 °C obtained with the semi-continuous and the batch

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**Table 2**
Solubility of $CO_2$ in 0.02 M sodium phosphate monobasic solutions (0.240 g/100 g water) at 40 °C.

| Pressure (MPa) | Solubility (g/100 g[a]) | St. dev.[b] (g/100 g[a]) | PRWS model | ELECNRTL model | PSRK model |
|---|---|---|---|---|---|
| Semi-continuous equipment | | | | | |
| 7.58 | 4.74a | 0.02 | 4.85 | 4.68 | 5.21 |
| 10.34 | 5.20b | 0.03 | 5.31 | 5.70 | 6.54 |
| 13.10 | 5.44b | 0.07 | 5.65 | 6.80 | 8.30 |
| Batch equipment | | | | | |
| 7.58 | 4.73a | 0.025 | 4.85 | 4.68 | 5.21 |
| 10.34 | 5.16b | 0.031 | 5.31 | 5.70 | 6.54 |
| 13.10 | 5.36b | 0.055 | 5.65 | 6.80 | 8.30 |

Different letters in mean values mean significant difference in $CO_2$ solubility ($p < 0.05$).
[a] Grams of $CO_2$/100 g of liquid.
[b] Standard deviation.

**Table 3**
Solubility of $CO_2$ in 0.2 M sodium phosphate monobasic solutions (2.40 g/100 g water) at 40 °C.

| Pressure (MPa) | Solubility (g/100 g[a]) | St. dev.[b] (g/100 g[a]) | PRWS model | ELECNRTL model | PSRK model |
|---|---|---|---|---|---|
| Semi-continuous equipment | | | | | |
| 7.58 | 4.43a | 0.04 | 4.54 | 4.40 | 5.23 |
| 10.34 | 4.75b | 0.09 | 4.97 | 5.36 | 6.56 |
| 13.10 | 4.96c | 0.03 | 5.23 | 6.40 | 8.70 |
| Batch equipment | | | | | |
| 7.58 | 4.41a | 0.01 | 4.54 | 4.40 | 5.23 |
| 10.34 | 4.79b | 0.09 | 4.97 | 5.36 | 6.56 |
| 13.10 | 5.16c | 0.04 | 5.23 | 6.40 | 8.70 |

Different letters in mean values mean significant difference in $CO_2$ solubility ($p < 0.05$).
[a] Grams of $CO_2$/100 g of liquid.
[b] Standard deviation.

equipment. Inspection of the table suggests that both the high pressure equipments are able to reproduce accurate solubility results which are very close to the experimental results reported in previously published works. A statistical analysis was also performed showing there are not significant differences ($\alpha = 0.05$) between the experimental and the literature values.

### 3.2. Effect of the sodium phosphate monobasic concentration on the $CO_2$ solubility

Tables 2–4 report experimental values of the $CO_2$ solubility in water–sodium phosphate monobasic solutions obtained with the continuous and the batch equipment at 40 °C. Each table gives the results for a fixed concentration of the buffer in water. Comparing the results with the $CO_2$ solubility in pure water [36,37] these values were lower and decreased with increasing concentrations of the buffer in the solutions at the same pressure and temperature. Both the continuous and the batch equipment at the same pressure and temperature gave results that were not significantly different ($\alpha = 0.05$). At low sodium phosphate monobasic concentration (0.240 g/100 g water) a significant increase ($\alpha = 0.05$) in solubility values was observed when increasing the pressure from 7.58 to 10.34 MPa while from 10.34 to 13.10 MPa a slight but not significant increase was observed. At high concentrations (2.40 g and 4.80 g/100 g water) a significant increase in solubility values was observed when increasing the pressure from 7.58 to 10.34 and also from 10.34 to 13.10 MPa. The increase in the amount of the solutes in the solution influenced the $CO_2$ solubility. The values obtained had different significant changes increasing the pressure depending on the amount of the solute. Literature data on the solubility of $CO_2$ in solutions containing $NaH_2PO_4$ are absent. For this reason the comparison with the literature data was performed considering the effect of other salts in solutions on the $CO_2$ solubility. Bando et al. [11] performed experiments on aqueous mixtures of NaCl and demonstrated that increasing the mass fraction of NaCl in the solutions from 0.01 to 0.03 at 30–60 °C and 10–20 MPa the $CO_2$ solubility decreases. In particular considering the experimental results they reported a reduction of $CO_2$ solubility, compared to the value in pure water, of about 2.6% per gram of NaCl dissolved in the aqueous solution at 40 °C and 10.0 MPa. In the same experimental conditions we obtained a solubility reduction of about 22.7% per gram of $NaH_2PO_4$ dissolved in solution. This suggested that the

**Table 4**
Solubility of $CO_2$ in 0.4 M sodium phosphate monobasic solutions (4.80 g/100 g water) at 40 °C.

| Pressure (MPa) | Solubility (g/100 g[a]) | St. dev.[b] (g/100 g[a]) | PRWS model | ELECNRTL model | PSRK model |
|---|---|---|---|---|---|
| Semi-continuous equipment | | | | | |
| 7.58 | 4.11a | 0.03 | 4.21 | 4.11 | 5.24 |
| 10.34 | 4.53b,c | 0.08 | 4.66 | 5.01 | 6.58 |
| 13.10 | 4.82c | 0.07 | 4.85 | 5.99 | 8.74 |
| Batch equipment | | | | | |
| 7.58 | 4.27a | 0.03 | 4.21 | 4.11 | 5.24 |
| 10.34 | 4.61b | 0.06 | 4.66 | 5.01 | 6.58 |
| 13.10 | 4.86c | 0.09 | 4.85 | 5.99 | 8.74 |

Different letters in mean values mean significant difference in $CO_2$ solubility ($p < 0.05$).
[a] Grams of $CO_2$/100 g of liquid.
[b] Standard deviation.

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decrease in $CO_2$ solubility is affected by the chemical compound dissolved in the liquid matrix.

### 3.3. Performance of the PRWS, ELECNRTL and PSRK thermodynamic models for the $CO_2$–water solutions and the $CO_2$–water–sodium phosphate monobasic solutions

Table 1 reports the PRWS, ELECNRTL and PSRK thermodynamic model predictions for the $CO_2$ solubility in pure water in the range of pressures 7.58–13.10 MPa and of temperatures 35–50 °C. At 35 and 40 °C, the ELECNRTL and the PSRK thermodynamic models are not in good agreement with the experimental $CO_2$ solubility values. The difference between the experimental data and the predictions of both models is more evident at high pressures. At 50 °C both thermodynamic models are able to fit the experimental data with better agreement. The same behavior was observed by Calix et al. [15] applying the ELECNRTL model to pure water and solutions of water–glucose–malic acid and water–glucose–citric acid.

Kiepe et al. [17] calculated gas solubilities (isothermal $P-x$ data) for the $CO_2$–$H_2O$ system at temperatures and pressures of 40–120 °C and 0–10 MPa by coupling the predictive Soave–Redlich–Kwong (PSRK) group contribution EOS with the LIFAC model where the activity coefficient was calculated as the sum of an electrostatic contribution, a contribution for ion dipole effects based on Pitzer's theory and a short-range contribution (using UNIFAC). The prediction was in good agreement with the experimental data considering that the PSRK was not completely predictive. In this study the PSRK thermodynamic model is completely predictive and it was not able to describe the equilibrium properly.

**Table 5**
Coefficients of binary interaction evaluated for the PRWS thermodynamic model for the water–sodium phosphate monobasic solutions.

| Coefficient of binary interaction $k_{ij}$ | | |
|---|---|---|
| Component | Water | Sodium phosphate monobasic |
| Carbon dioxide | 0.240 | 5 |
| Water | – | 2.843 |

The PRWS thermodynamic model applied the UNIFAC model to calculate the excess Gibbs free energy $G^E_\gamma$. A single value for the coefficient of binary interaction $k_{ij}$ for the water–carbon dioxide system, as reported in Table 5, was used for all the three tested temperatures. The fitting of the experimental data was good for each temperature over the investigated pressure range. Good results were obtained with the PRWS thermodynamic model also by Shyu et al. [18] and Valtz et al. [19]. In particular, Shyu et al. [18] modelled the phase behavior for the $CO_2$–$H_2O$ system over a wide range of temperatures (25.15–350.15 °C) and pressures (1–100 MPa) using the van Laar model to calculate $G^E_\gamma$. The calculated solubility of $CO_2$ in water was accurate, but required two additional parameters for the van Laar model. Valtz et al. [19], instead, used the NRTL local composition model to calculate $G^E_r$ by adjusting the values of three parameters ($k_{ij}$ and two NRTL parameters) for each temperature

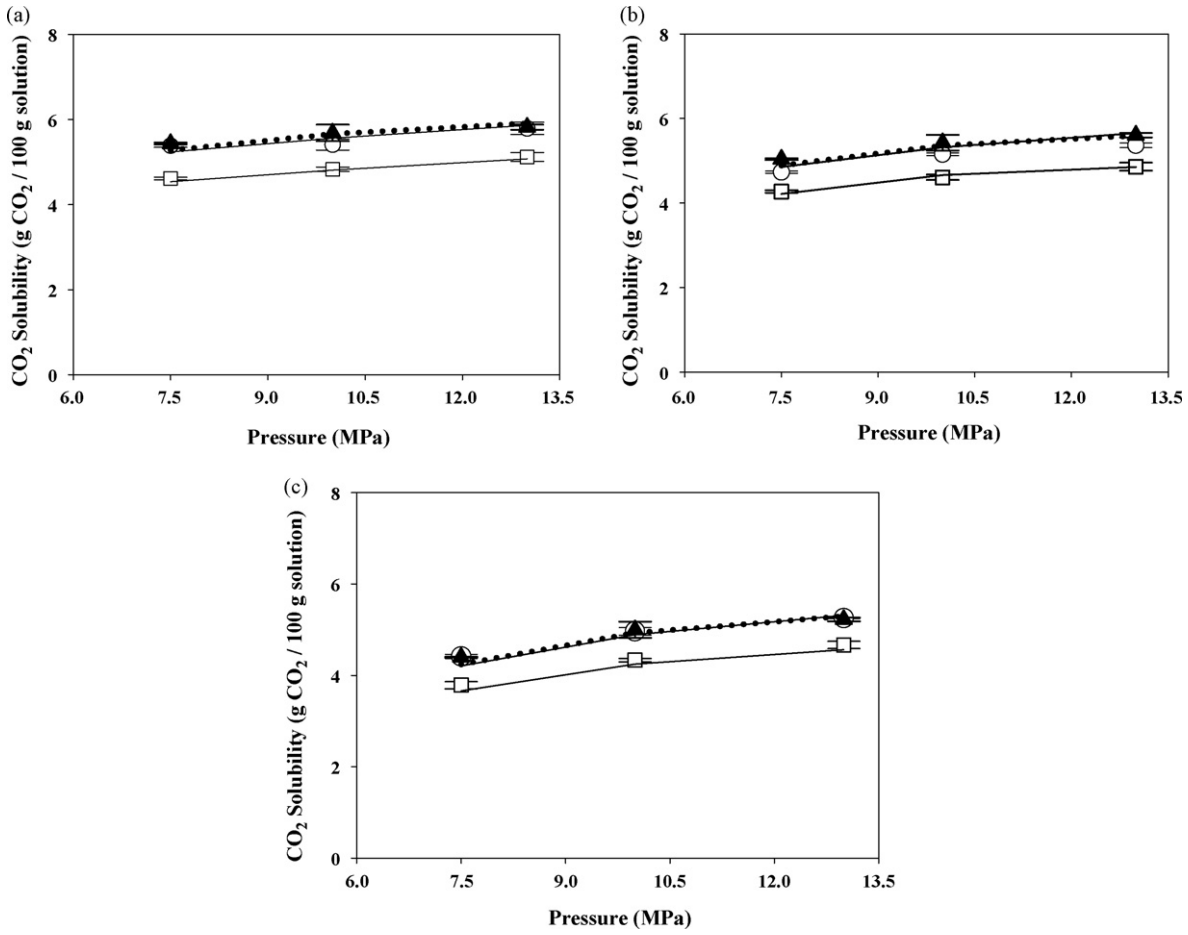


**Fig. 3.** $CO_2$ solubility for the water–sodium phosphate monobasic solutions at different temperatures (a) 35 °C, (b) 40 °C, and (c) 50 °C. Symbols are experimental values at different phosphate concentrations: 0.240 g (○) and 4.80 g (□), in 100 g water. Continuous lines are the PRWS thermodynamic model predictions for water–sodium phosphate monobasic solutions while dotted lines are the PRWS thermodynamic model predictions for pure water. Experimental values were obtained with the batch equipment. Experimental data for pure water (▲) are also included for comparison.

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value (in the range 5.2–45.2 °C) to obtain results in very good agreement with the experimental $CO_2$ solubilities in the pressure range between 0.464 and 16 MPa.

Tables 2–4 also show the comparison between the $CO_2$ solubility results of PSRK, ELECNRTL and PRWS thermodynamic models and the experimental results for water–sodium phosphate monobasic solutions at different concentrations (0.240, 2.40 and 4.80 g/100 g water) at 40 °C. For this system the ELECNRTL model significantly overpredicts the $CO_2$ solubility at all concentration values over the investigated pressure range. The PSRK model results are closer to experimental ones, but a greater discrepancy arises with increasing pressure. As in the case for pure water, the PRWS was able to predict with good agreement the experimental solubility data in buffer solutions. In this case $k_{ij}$ for the water–carbon dioxide pair was kept unchanged with respect to that obtained in the experiments with pure water. Experimental results of Tables 2–4 were used to find out the values of $k_{ij}$ for the water–monobasic sodium phosphate and carbon dioxide–monobasic sodium phosphate pairs by a best fitting procedure. The obtained values are also reported in Table 5. These coefficients of binary interaction were kept constant to simulate the thermodynamic equilibrium for the same system at different conditions of pressure, temperature and monobasic sodium phosphate concentration. In this way the predictive ability of the PRWS thermodynamic model for this system was tested. Fig. 3 shows the predictions of the model at 0.240 and 4.80 g of sodium phosphate monobasic in 100 g of water at 35, 40 and 50 °C. The model was able to predict with good agreement the experimental data for the range of pressure, temperature and solute concentration used in this study. A higher scatter between the experimental and the predicted results was observed for the conditions close to the critical point where the $CO_2$ properties changed drastically and due to the unstable equilibrium between the vapor and the liquid phase and to the possibility to have a part of liquid $CO_2$ in the system which could affect the experimental values.

## 4. Conclusions

The two different experimental procedures to evaluate $CO_2$ solubility in sodium phosphate monobasic solutions using the batch and the semi-continuous equipments described in this study independently produced very similar results, suggesting a reasonable accuracy for both experimental procedures tested. As a result, both equipments are suitable to accurately measure $CO_2$ solubility in water solutions.

The Peng–Robinson equation of state with the Wong and Sandler mixing rules (PRWS) and the excess Gibbs free energy calculated by the UNIFAC method predicted with good agreement the experimental $CO_2$ solubility data both in water and in buffer solutions. In particular, after the evaluation of only three binary interaction coefficients by a best fitting procedure on a set of experimental data at reference conditions, the PRWS thermodynamic model was able to predict well the $CO_2$ solubility values at different temperature values. This suggests that by using the prediction of the PRWS thermodynamic model in conjunction with some experimental data, it is possible to predict $CO_2$ solubility with a reasonable accuracy over a wider range of experimental conditions than those used to derive the binary interaction parameters values. These capabilities will be used in the HPCD microbial inactivation kinetics [2], to evaluate the amount of $CO_2$ dissolved in the food for a better and more realistic correlation with microbial lethality.

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