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Solubility of carbon dioxide in ternary and quaternary mixtures of water, CO_2, malic acid and glucose: experimental results and phase equilibrium modeling

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An experimental apparatus was set up to measure the CO_2 solubility in ternary mixtures of water-CO_2-glucose, water-CO_2-malic acid and in a quaternary mixture of water-CO_2-malic acid-glucose at different concentrations of malic acid (0.01 and 2.68 g in 100 g of water) and of glucose (4 and 12 g in 100 g of water). The range of pressure tested was between 7.5 and 15.0 MPa at 40 and 50°C.
The experimental results were compared with the equilibrium conditions evaluated by applying different thermodynamic models by means of the process simulation software Aspen Plus®. The Peng – Robinson – Wong – Sandler (PRWS), the electrolytic non-random two liquids (ELECNRTL) and the completely predictive Soave-Redlich-Kwong (PSRK) thermodynamic models were applied to solve the equilibrium.
The experimental results show that the CO_2 solubility strongly depends on glucose concentration, decreasing when it increases in the system. On the contrary it is only slightly affected by the malic acid concentration. The solubilities predicted by the PRWS model exhibit a good agreement with the experimental data in the pressure and temperature range tested, once main coefficients of binary interaction are derived from ternary systems at one reference condition.

1. Introduction

For more than two decades, HPCD has been proposed as an alternative cold pasteurization for liquid foods. This method presents some advantages due to the mild conditions employed, particularly because it allows processing at lower temperatures than those used in thermal pasteurization. It can reduce the microbial count of foods while preserving heat sensitive nutrients and the product quality, including flavor, color and texture. In the HPCD technique, food is contacted with pressurized sub or supercritical CO_2 for a certain amount of time in a batch, semi – batch or continuous manner. Carbon dioxide (CO_2) is used because of its low critical temperature and pressure that allow supercritical at conditions which minimize damage to biological

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compounds, of its low cost, and of its availability in purified form. Other reasons which make carbon dioxide suitable in food treatments are its chemical inertia, its nontoxicity and the fact that it is a natural component of many foods. The exact microbial inactivation mechanism that occurs during HPCD is not yet completely understood. However, carbon dioxide action, is in the liquid phase and, therefore, its solubilization is a fundamental step to be described for the correct interpretation of the experiments and for the application of reliable process and apparatus design procedures. Solubility of gases in liquids has been studied since the early 19th century (Battino and Clever, 1965). While there are many vapor-liquid equilibrium data available for the binary systems CO_2-water (Wiebe and Gaddy, 1940) and CO_2-ethanol as well as for the ternary system CO_2-ethanol-water, little data have been produced for systems including water, carbohydrates and CO_2. Recently Calix *et al.* (2008) evaluated the CO_2 solubility in water–glucose–malic acid and water–glucose–citric acid solutions. In view of this situation, a high pressure apparatus was tested for obtaining reliable phase equilibrium data in the ternary systems glucose-water-CO_2, malic acid-water-CO_2 and the quaternary system glucose-water-malic acid-CO_2 at temperatures of 40 and 50°C and pressures in the range 7.5-15.0 MPa. This work describes the experimental technique employed, presents the experimental results obtained for the systems mentioned above and discusses the ability of different thermodynamic models to describe the experiments.

2. Material and Methods

2.1 Experimental equipments

The equipment employed can be used for the treatment of liquid and solid food with CO_2 under pressure. The vessel (Parr Stirred Reactor, FKV srl, Bergamo, Italy), 100 mL of volume, is able to withstand a maximum pressure of 20.0 MPa. A four – bladed impeller magnetically coupled to a DC motor allowed adjustable mixing speed, and a fixed thermocouple (Type J) was used for temperature measurement inside the vessel. The liquid CO_2 was pumped into the reactor with a CO_2 pump through an on-off valve that was kept closed after pumping for the time required for the experiments. The time required for the pressurization of the reactor and for heating was about 5 minutes. The depressurization step of the reactor required only few seconds and occurred by opening the on – off valve on the vessel outlet line. The vessel was jacketed to keep the system at the desired experimental temperature, by recirculating water from an external heated water bath. In addition a valve at the bottom of the vessel was designed to perform the solubility experiments.

2.2 Experimental procedure

The vessel was loaded with the liquid sample and then carefully closed. The external jacket was connected to the water bath and the system was brought to the temperature chosen for the experiments. After the system reached the desired temperature, CO_2 was pumped until the system pressure reached the set-point value. Since this moment, an equalization period of one more hour was allowed to the system to reach thermodynamic equilibrium. In all tests the same stirring speed (approx. 850 rpm) was used to promote the dissolution of CO_2 in the liquid phase. After the equalization period a plastic syringe (60 mL) was connected to the bottom valve of the vessel and the liquid

phase was spilled, slightly opening the valve located at the bottom of the vessel. The operation was not longer than few seconds and a very small amount of liquid was spilled in order to keep the system at pressure and temperature as much constant as possible. Assuming within the syringe a complete vaporization of the CO_2 in the sampled solution and standard conditions, the volume defined by the displacement of the syringe piston was related to the amount of CO_2 in the original sample, accounting also for the volume of the liquid estimated from the weight of the liquid collected into the syringe. Both the amounts of gaseous CO_2 and liquid water found in the syringe concurred to the determination of the carbon dioxide solubility within the vessel (Ferrentino, 2009).

2.3 Vapor-liquid equilibrium simulation

The block RGibbs of the process simulation software Aspen Plus® version 2004.1 (Aspen Technology, Inc., Burlington, MA) was used to solve the equations for the vapor – liquid equilibrium by choosing the pressure and temperature of the system and the thermodynamic model. The data obtained with this procedure were the molar fractions of the two phases at the equilibrium conditions. Three thermodynamic models were tested: 1) the Peng – Robinson – Wong – Sandler (PRWS) thermodynamic model with the Peng-Robinson equation of state (EOS), where the *a* and *b* parameters were evaluated with the Wong and Sandler mixing rules and the activity coefficients were defined using the functional groups with the modified UNIFAC method; 2) the electrolytic non-random two liquids (ELECNRTL) thermodynamic model with the Redlich-Kwong equation of state for aqueous and mixed solvent applications; 3) the completely predictive Soave-Redlich-Kwong (PSRK) thermodynamic model where the equilibrium calculations were solved with the Soave – Redlich – Kwong equation of state with the modified UNIFAC method (Holderbaum *et al*. 1993). The first model requires the user to provide the coefficient of binary interactions, while the latter two models are fully predictive.

2.4 Sample preparation

Solubility experiments were performed for carbon dioxide – glucose – water system at two different concentrations of glucose: 4 and 12 g of glucose in 100 g of water. For the carbon dioxide - malic acid – water system, the solubility experiments were carried out at two different concentrations of malic acid: 0.01 and 2.68 g in 100 g of water. Further solubility experiments were carried out on a quaternary solution of carbon dioxide – malic acid – glucose – water and the concentration of the solution was: 0.01 g of malic acid and 12 g of glucose in 100 g of water. The range of pressure tested was between 7.5 and 15.0 MPa at 40 and 50°C.

3. Result and Discussion

3.1 CO_2 solubility in water: performance of PRWS, ELECNRTL and PSRK thermodynamic models

Figure 1 reports the experimental solubility results at 40°C in pure water. The values were compared with the literature results of Wiebe and Gaddy (1940).Comparison shows that the experimental procedure proposed in this work was able to give solubility results very close to the literature values.

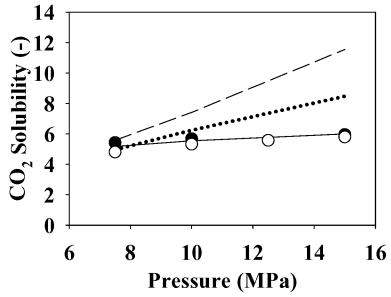

Figure 1 CO_2 solubility (g CO_2/100g H_2O) in pure water at 40°C: ●, experimental data, ○, Wiebe and Gaddy (1940) data; --- PSRK model; ·····, ELECNRTL model; —, PRWS model.

In the same figure, the PRWS, ELECNRTL and PSRK thermodynamic model values are shown in the range of pressures 7.5 – 15.0 MPa and at 40°C. Both the ELECNRTL and the PSRK thermodynamic models, which are totally predictive, did not show a good agreement with the experimental CO_2 solubility values, with a deviation that is more evident at high pressures. The same behavior was observed by Calix *et al.* (2008) applying the ELECNRTL model to pure water and solutions of water–glucose–malic acid and water–glucose–citric acid.

Instead, the PRWS thermodynamic model exhibited a very good agreement with the experimental data, provided the best fit value of the coefficient of binary interaction between H_2O and CO_2. This finding is in agreement with the results reported by Shyu *et al.* (1997) and Valtz *et al.* (2004) who studied 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), and were able to accurately model the solubility of CO_2 in water.

3.2 Effect of glucose and malic acid concentration on the CO_2 solubility

Solutions were prepared to determine the CO_2 solubility of binary water – glucose and water – malic acid mixtures. The experiments were carried out at 40°C and with solutions at different concentrations of glucose and malic acid respectively. Figure 2 shows the results for both systems. Inspection of the figure suggests that the CO_2 solubility value decreases significantly for the water – glucose system compared with the pure water system at the same conditions of pressure and temperature. Moreover, an increase in the glucose concentration from 4 g to 12 g in 100 g of water causes a marked drop in the CO_2 solubility value. The results confirm experiments reported by Dohrn *et al.* (1993). For the malic acid – water system (Figure 2 (b)) the results show no dependence of the CO_2 solubility value on the malic acid concentration in the solutions. Also comparing the CO_2 solubility values with those in pure water, no significant

Table 1 Coefficients of binary interaction evaluated for the PRWS model.

Compound	Water	Glucose	Malic acid
CO_2	0.238	1.905	1.05
Water	-	1.5	1.2
Glucose	1.5	-	-
Malic acid	1.2	-	-

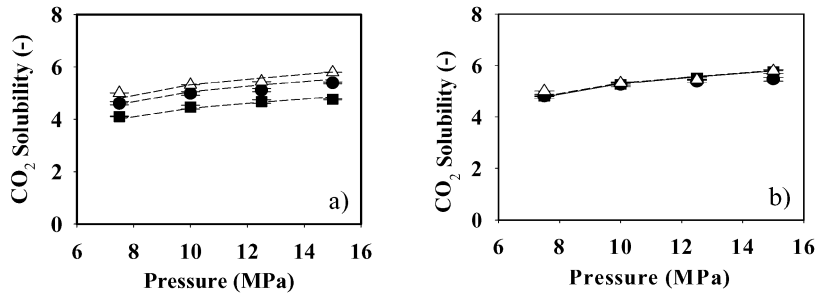

Figure 2 CO_2 solubility (g CO_2/100g H_2O) for the water – glucose system (a) and the water – malic acid system (b) at different concentrations: ●, 4 g glucose (a), 0.01 g malic acid (b); ■, 12 g glucose (a), 2.68 g malic acid (b). Symbols are experimental values; short dash line is the PRWS thermodynamic model. For comparison CO_2 solubility values for the water system (△) are reported.

differences are detected in the range of pressure tested. The equilibrium of the two ternary systems was also modeled using the Aspen Plus software with the implementation of the same PRWS thermodynamic model used for the CO_2–water system. The values of the coefficients of binary interaction between H_2O and each of the two solutes and between CO_2 and each of the two solutes were determined by searching the best fit of experimental equilibrium data at fixed concentration of glucose (12g/100g H_2O) or malic acid (2.68g/100g H_2O). These values are reported in Table 1. The model with the obtained values of the coefficients was used to predict the other experimental equilibrium points yielding results in very good agreement (as shown in Figure 2).

3.3 Effect of temperature on the CO_2 solubility of water – glucose – malic acid solutions

To simulate the composition of a fruit juice, CO_2 solubility was measured in a water–malic acid–glucose system. The results are shown in Figure 3. The composition of the mixture was 12 g of glucose and 0.01 g of malic acid in 100 g of water and the experiments were performed at two experimental temperatures. An increase of the experimental temperature determines a decrease of CO_2 solubility value. Also for this

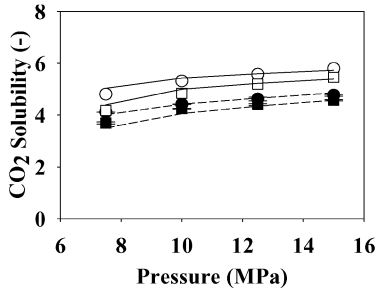

Figure 3 CO_2 solubility (g CO_2/100g H_2O) for the water – malic acid – glucose system at different temperatures: ●, 40°C; ■, 50°C. For comparison CO_2 solubility values for the water system are reported: ○, 40°C;□, 50°C. Symbols are experimental values; short dash line corresponds to the PRWS thermodynamic model results.

quaternary system the solubility data were simulated with the PRWS thermodynamic model, by using the values of the binary interaction coefficient obtained from the fitting of the ternary systems and reported in Table 1. Inspection of Figure 3 reveals that the model is able to well predict the experimental data, showing the possibility to describe the equilibrium in a juice model system.

4. Conclusions

The experimental results show that the CO_2 solubility strongly depends on glucose concentration, while it is only slightly affected by malic acid concentration. In water-glucose systems CO_2 solubility is lower than in pure water at the same conditions of pressure and temperature, and decreases when the glucose concentration increases.
On modeling grounds, the fully predictive thermodynamic models ELECNRTL and PSRK exhibited significant deviations from experimental data. The experimental solubility results were accurately predicted by the PRWS thermodynamic model. In particular, once the main coefficients of binary interaction were obtained by a best fit procedure for a single reference condition, the model was able to predictively describe the full range of pressure, temperature and composition tested for ternary and quaternary systems.
The combined use of simple solubility experiments and model equilibrium calculation offers a promising instrument for the experimental interpretation and the design of applications involving the high pressure carbon dioxide.

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