

Research Article

Measurement and Prediction of Hydrate Phase Equilibrium of Orange Juice + CO₂, C₂H₄ or C₂H₆ for Orange Juice Concentration

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Abstract: Phase equilibrium data for hydrates formed in CO₂ + orange juice system, C₂H₄ + orange juice system and C₂H₆ + orange juice system were measured in pressures range of (0.68 to 4.40 MPa) and temperatures range of (274.8 to 283.3 K). The experimental data were generated using an isochoric pressure-search method. The effects of orange juice on the hydrate equilibrium conditions were studied. The hydrate equilibrium conditions were calculated by using the Redlich-Kwong-Soave equation of state with a modified version of the Huron-Vidal mixing rule. It is found that the orange juice exhibited an inhibition effect on hydrate formation. The results of the predicted three-phase equilibrium conditions for the CO₂, C₂H₄ and C₂H₆ hydrate formation in water and orange juice were in good agreement with the experimentally data.

Keywords: Carbon dioxide, concentration, ethane, ethylene, hydrate, orange juice, phase equilibrium

INTRODUCTION

To reduce packaging, storage and transport cost, fruit juices are usually subjected to concentration (Jiao *et al.*, 2009; Jesus *et al.*, 2007; Guignon *et al.*, 2012; Aider and de Halleux, 2008). Concentration by gas hydrate formation is recognized as a novel way to separate water from solution (Javanmardi and Moshfeghian, 2003; Park *et al.*, 2011; Ngan and Englezos, 1996; Chun *et al.*, 2005; Aydođan *et al.*, 2007; Bayraktar *et al.*, 2008; Li *et al.*, 2014). Clathrate hydrates are crystalline inclusion compounds which form through the temperature and elevated pressure conditions. Within the clathrate lattice, water molecules form a network of hydrogen bonded cavity structures that enclose the guests. Of more than 130 compounds that are known to form clathrate hydrates with water molecules, the majority form sI, sII, or sH (Sloan and Koh, 2008). As early as the 1960s, Huang *et al.* (1966) utilized CH₃Br and CCl₃F hydrate to concentrate apple, orange and tomato juices. Purwanto *et al.* (2011) proposed concentration of coffee solutions by use of xenon hydrate. Andersen and Thomsen (2009) investigated the possibility of using gas hydrates for

concentration of sugar juice. Most recently, Purwanto *et al.* (2014) designed a novel higher pressure container to concentrate coffee solution by formation of Xe hydrate. The ingenious designs of the higher pressure container could contribute to the development of separation process continuously. Although increasing attention has been given to juice concentration by hydrate formation, there is no report on measurement and prediction of hydrate phase equilibrium of orange juice + CO₂, C₂H₄ or C₂H₆ for juice concentration orange.

Therefore, the purpose of this work is to measure and predict CO₂ (C₂H₄, or C₂H₆) hydrate phase equilibrium in the presence of orange juice and the results could provide guidance for juice concentration by hydrate formation.

MATERIALS AND METHODS

Materials: C₂H₄ (99.95%) and C₂H₆ (99.99%) were purchased from Dalian GuangMing Special Gas Products Co., Ltd (China). CO₂ (99.99%) was supplied by Beijing AP BAIF Gases Industry CO., Ltd (China) and orange juice was supplied by Beijing Huiyuan Group (China). The contents of reducing sugars, total

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Table 1: The contents of reducing sugars, total acid, vitamin C, soluble solid and water content of orange juice used in this study

Orange juice Content	Reducing sugar (g/100 g)	Total acid (g/kg)	Vitamin C (mg/100 g)	Soluble solid	Water cut
	4.42	6.08	49.96	10.5%	87.7%

Table 2: Optimized kihara potential parameters for CO₂, C₂H₂ and C₂H₆+ water interaction

Gas	$\sigma_g/\text{\AA}$	$(\epsilon_g/k)/\text{K}$	$a_g/\text{\AA}$	ω
CO ₂	3.407	506.25	0.677	0.225
C ₂ H ₄	3.819	354.33	0.534	0.097
C ₂ H ₆	4.036	393.20	0.574	0.105

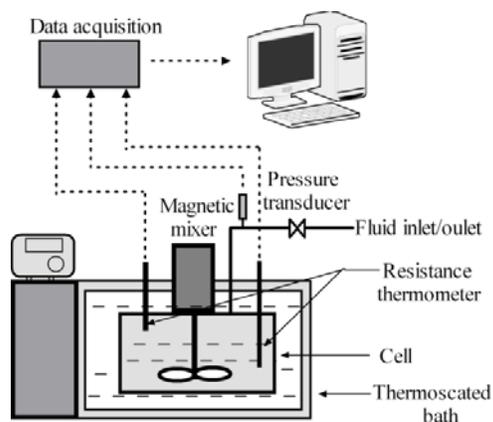


Fig. 1: Schematic of the experimental apparatus used for phase equilibrium measurements

acid, vitamin C, soluble solid and water content of orange juice are listed in Table 1.

Apparatus: Figure 1 shows the schematic diagram of the apparatus used to determine the phase equilibrium conditions. It mainly consisted of a stainless-steel reactor (volume 300 mL) equipped with a magnetic stirrer (Nantong Feiyu Science and Technology exploitation CO., China). The reactor can be operated at pressure up to 25 MPa. The reactor was submerged into a thermostat (Tianheng THCD-306) with a stability of ± 0.01 K to control the temperature. Two Pt-100 resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy placed in the middle and bottom of the reactor respectively were used to monitor the temperature of the reactor. A pressure transducer (Senex DG-1300) with the accuracy of 0.01 MPa was used to measure the pressure inside the reactor. The pressures and temperatures of the reactor were recorded by data logger (Agilent 34972A).

Method: The hydrate phase equilibrium conditions were measured with an isochoric pressure search method. The cell containing liquids (approximately 150 mL) was immersed into the temperature-controlled bath. Hydrate formation gas (such as CO₂, C₂H₄ or C₂H₆) was then supplied from a gas cylinder through a pressure-regulating valve into the evacuated cell until the pressure inside the cell (p) was increased to the desired level. After Temperature (T) and p stabilized, the valve in the line connecting the cell and cylinder was closed. Subsequently, temperature was decreased to form the hydrate. Hydrate formation in the cell was detected by a

decrease in p and an increase in T . The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was held constant for 4 h to achieve equilibrium state in the cell. In this way, a p - T diagram was obtained for each experimental run, from which the hydrate dissociation point was determined. Consequently, the point at which the slope of the p - T curve plots sharply changed was considered as the hydrate dissociation point at which all hydrate crystals have dissociated.

Thermodynamic model: The phase equilibrium calculations of clathrate hydrate system are based on the equality of the fugacity of water and hydrate-forming component in hydrate phase and vapor phase:

$$f_i^H = f_i^L = f_i^V$$

where, H is the hydrate phase, L is the liquid phase and V is the vapor phase. The fugacities of hydrate-forming component in the vapor and liquid phases were calculated using the Redlich-Kwong-Soave equation of state (Soave, 1972) with a modified version of the Huron-Vidal mixing rule (Michelsen, 1990). The UNIFAC group-contribution model (Fredenslund and Sørensen, 1993) was used with the excess Gibbs energy model of the Huron-Vidal mixing rule. The fugacity of water in the hydrate phase, f_w^H based on the van der Waals and Platteeuw (1959) is given by the following equation:

$$f_w^H = f_w^{MT} \exp\left(\frac{-\Delta\mu_w^{MT-H}}{RT}\right) = f_w^{MT} \exp\left(-\sum_m V_m \ln\left(1 + \sum_j C_{mj} f_j^V\right)\right)$$

where, V_m is the number of cavities of type m per water molecule in the hydrate phase, C_{mj} is the Langmuir constant of component j on cavity type m and f_j^V is the fugacity of component j in the vapor phase with which the hydrate phase is in equilibrium. The Langmuir constant (Chun and Lee, 1998) describes the guest-host interaction inside the cage and is given by:

$$C_{mj} = \frac{4\pi}{kT} \int_0^{R-a} \exp\left[\frac{-\omega(r)}{kT}\right] r^2 dr$$

The final optimized Kihara potential parameters of the CO₂, C₂H₄ and C₂H₆-water interaction needed for calculating the spherically symmetrical cell potential, $\omega(r)$ are presented in Table 2, where r is the radial distance from the center of the cavity (Chun and Lee, 1998).

The fugacity of water in the empty hydrate lattice, f_w^{MT} , is given by:

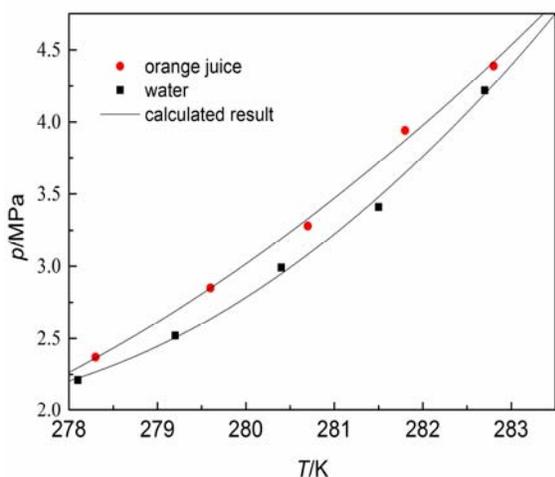


Fig. 2: Hydrate phase equilibria of water + CO₂ and orange juice + CO₂ system

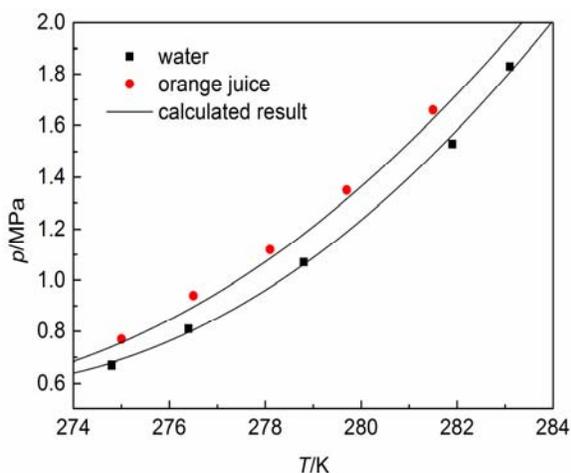


Fig. 3: Hydrate phase equilibria of water + C₂H₄ and orange juice + C₂H₄ system

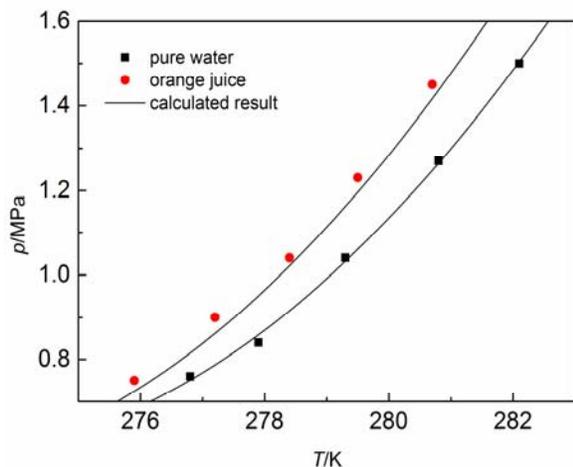


Fig. 4: Hydrate phase equilibria of water + C₂H₆ and orange juice + C₂H₆ system

$$f_w^{MT} = f_w^L \exp\left(\frac{\Delta\mu_w^{MT-L}}{RT}\right)$$

where, the chemical potential difference of water between the empty hydrate and liquid phases, $\Delta\mu_w^{MT-L}$ was calculated by the method of Holder *et al.* (1980):

$$\frac{\Delta\mu_w^{MT-L}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{MT-L} + \Delta h_w^{fus}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{MT-L} + \Delta v_w^{fus}}{RT} dP$$

According to the van der Waals and Platteeuw (1959) model, the fugacities of guest components in the vapor phase are in equilibrium with that in the hydrate phase. The equality between the fugacity of water in the hydrate and that in the liquid phase was further checked to yield a final equilibrium condition for the hydrate-forming system given below:

$$\sum_m v_m \ln(1 + \sum_j C_{mj} f_j^V) = \frac{\Delta\mu_w^{MT-L}}{RT} - \ln a_w$$

RESULTS AND DISCUSSION

Figure 2 shows measured and calculated hydrate dissociation conditions of the water + CO₂ and orange juice + CO₂ system, respectively. It is found that the orange juice exhibited an inhibition effect on CO₂ hydrate formation. As shown in Fig. 2, calculated results obtained using thermodynamic model are fitted better with experimental data of water + CO₂ system and orange juice + CO₂ system.

Figure 3 and 4 show measured and calculated hydrate dissociation conditions of the water + C₂H₄, orange juice + C₂H₄, water + C₂H₆ and orange juice + C₂H₆ system, respectively. It is also found that the orange juice exhibited inhibition effect on C₂H₄ or C₂H₆ hydrate formation. As shown in Fig. 3 and 4, calculated results obtained using thermodynamic model are fitted better with experimental data of water + C₂H₄ system and water + C₂H₆ system. However, there are little disagreement between the calculated result and the experimental data in the presence of orange juice. The deviation might be caused by the interactions of C₂H₄ or C₂H₆ with some constituents of orange juice.

CONCLUSION

Hydrate phase equilibrium conditions of orange juice + CO₂, C₂H₄ or C₂H₆ were measured by isochoric pressure search method. It is found that the orange juice exhibited an inhibition effect on hydrate formation. The hydrate equilibrium conditions were calculated by using the Redlich-Kwong-Soave equation of state with a modified version of the Huron-Vidal mixing rule. The results of the predicted three-phase equilibrium conditions for the CO₂, C₂H₄ and C₂H₆ hydrate

formation in water and orange juice were in good agreement with the experimentally data.

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