### A Research Note

# Relationship Between Freezing Point Depression and Solute Composition of Fruit Juice Systems

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## ABSTRACT

Freezing points of orange juices and model sugar-acid-water systems at various solute concentrations were investigated using models of solution theory. The observed freezing point depression values of citrus juice were less than those of the model system of comparable average molecular weight. The differences were characterized by a parameter which accounted for the solute-solvent interactions. Models with generalized values were presented which allowed the prediction of equilibrium freezing curves of fruit juices based on proximate sugar-acid composition.

## INTRODUCTION

FRUIT JUICE CONCENTRATES are not preserved by commercial sterilization, but instead by a combination of pasteurization, freezing and high concentration of soluble solids. Concentration and freezing are, therefore, two important operations in fruit juice processing. A knowledge of freezing point depression (FPD) at various solute concentrations is needed for calculating refrigeration requirements (Riedel, 1951) and for analysis of a food freezing or thawing process (Chen et al., 1984; Schwartzberg et al., 1977; Hayakawa, 1977).

A plot of freezing point vs solute concentration is called an equilibrium freezing curve (EFC). Variations of the observed EFC can be expected for different fruit juices due to differences in solute composition (Chen, 1988).

Our work investigated the depression of freezing points in relation to solute composition of fruit juice systems.

## MATERIALS & METHODS

### Proximate composition analysis

Concentrated orange juice (COJ) samples previously used in FPD determination (Chen, 1988) were analyzed for percent acid by titration (Ting and Rouseff, 1986) and for °Brix by refractometer (corrected for temperature and acid). The Brix value represents all the soluble solids in the juice. A commercial medium invert sugar solution (Amalgamated Sugar Co., Kansas, MO) was also analyzed.

Sugar composition was determined by gas-liquid chromatography (GLC) (AOAC, 1980) using a modified procedure (Braddock and Marcy, 1985). The concentrates of juices and invert sugar were diluted to 11.8°Brix. The sugars were silylated before injection. The GLC analyses included triplicate injections of duplicate samples. The six data points were averaged. Peak areas were automatically integrated and compared with 0.001 mg/mL standard solutions of fructose, glucose and sucrose. The areas of fructose, glucose and sucrose peaks were determined. The area percentage of each component was calculated.

### Freezing point determination

Solutions of fructose:glucose:sucrose with a ratio of 1:1:2 were prepared from reagent grade materials. Samples of these solutions were mixed with citric acid to prepare samples of 15:1 sugars/acid ratio. These model samples simulated citrus juice systems. Freezing point depression of these samples were determined by Beckman differential thermometer as described by Chen (1988).

## RESULTS & DISCUSSION

### Composition and effective molecular weight

Fruit and vegetable juice extracts are solutions of carbohydrates, with suspensions of nonsoluble components. In citrus juices, soluble components include sugars, organic acids and the soluble salts of organic acids. Complex carbohydrates such as pectins, hemicellulose and cellulose comprise only a very slight amount of total juice carbohydrates (Ting and Rouseff, 1986). Considering citrus juices as a multicomponent system of fructose-glucose-sucrose-citric acid-water (i.e., sugar-acid model), the effective molecular weight can be calculated from the average molecular weight of a mixture (Bonnar et al., 1958):

$$M = \sum_{i}^{n} X_i / \sum_{i}^{n} (X_i/M_i); \qquad i = 1, 2, ..., n \qquad (1)$$

where M is the effective molecular weight of all constituent solutes; X is mass fraction of solutes; i denotes i-component.

The results of proximate composition analysis and calculated effective molecular weights are presented in Table 1. The calculated M = 238 for Florida Valencia OJ agreed with M = 239.4 ± 28.3 determined by the FPD method. Similarly, the calculated M = 233 for Mexican Corriente OJ was also in agreement with M = 232.9 ± 13.1 determined by the FPD method (Chen, 1988). These results indicated that the sugar-acid constituents can account for the effective molecular weight of citrus juices. The effects of other constituents, such as pectic substances, on the calculated molecular weight are negligible. The effective molecular weights of some fruit juices calculated from the typical data of sugar-acid composition are also included in Table 1 for a comparison.

### Equilibrium freezing curves

Two semi-empirical FPD equations were investigated to characterize the EFC. Chen (1988) employed the following approximate FPD equation of bound water theory of a binary system:

$$\Delta t = -\frac{K_o}{M}\ln\left[\frac{1 - X - bX}{1 - X - bX + EX}\right] \approx \frac{K_o X}{(1 - X - bX)\,M} \qquad (2)$$

where $\Delta t = T_o - T$ is the FPD, K; $T_o$ is the FP of pure water ($T_o$ = 273.1 K); T is the FP of solution, K; $K_o$ is the Van't Hoff's constant ($K_o$ = 1860 K·kg/kg-mole or °C·g/g-mole); b is mass of bound water per unit mass of solutes (Schwartzberg, 1976). E is the ratio of the molecular weight of water ($M_w$) to

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*Table 1—Sugar-acid composition of various juice systems and calculated effective molecular weights*

| Juice systems | Sugar content (% by wt)<br>Reducing sugars<br>Glucose | <br><br>Fructose | <br><br>Sucrose | <br>Total sugars | Acid (% by wt) | Sugars/acid ratio | Effective mol wt |
|---|---|---|---|---|---|---|---|
| **Tested samples** | | | | | | | |
| Florida Valencia OJ | 15.80 | 12.50 | 33.78 | 62.08 | 4.6 | 13.5 | 238 |
| Mexican Corriente OJ | 22.36 | 9.61 | 32.68 | 64.65 | 5.0 | 12.9 | 233 |
| Medium invert sugar solution | 25.64 | 13.88 | 38.48 | 75.00 | 0.0 | – | 235 |
| Fructose-Glucose-Sucrose model solution | 15.00 | 15.00 | 30.00 | 60.00 | 0.0 | – | 236 |
| Fructose-Glucose-Sucrose Citric acid model solution | 15.23 | 15.23 | 30.47 | 60.93 | 4.1 | 15.0 | 233 |
| **Typical data**[a] | | | | | | | |
| Apple juice | 7.95 | | 2.95 | 10.90 | 0.02 | – | 207 |
| Pineapple juice | 4.50 | | 8.95 | 13.45 | 0.80 | 16.8 | 258 |
| Orange juice | 4.20 | | 4.10 | 8.30 | 0.95 | 8.7 | 230 |
| Grapefruit juice | 4.25 | | 2.15 | 6.40 | 1.15 | 5.6 | 211 |
| Grape juice | 15.40 | | 1.25 | 16.65 | 1.20 | 13.9 | 184 |

[a] Tressler and Joslyn (1971).

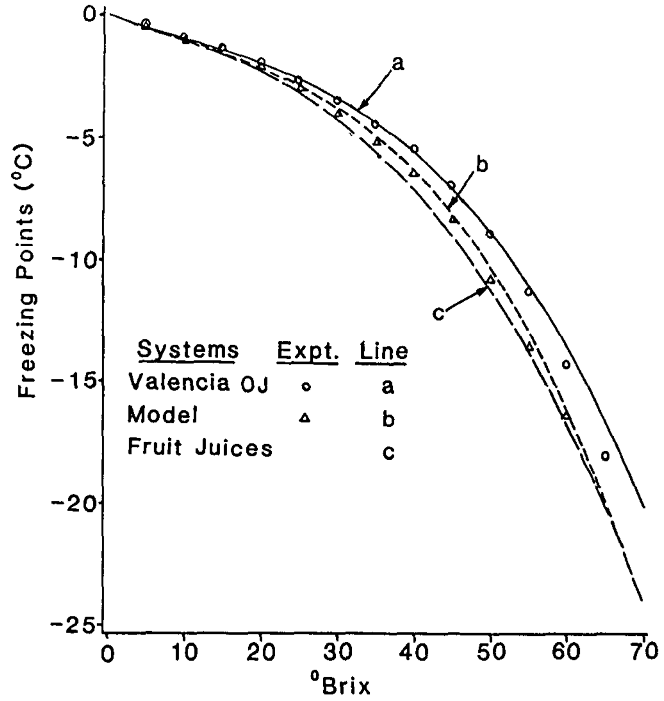

*Fig. 1—Comparison of experimental and calculated freezing points for citrus juice and model systems: line a - Eq. (4) using M = 238 and C = 0.25; line b - Eq. (4) using M = 233 and C = 0.56; line c - Riedel's equation.*

the molecular weight of solutes (M). The applicability of Eq. (2) is subject to the following limitation:

$$X < \frac{1}{1+b} \tag{3}$$

Equation (2) can be applied for the associated solutions such as the sucrose solution.

An alternative semi-empirical FPD equation for a binary system was proposed by Chen and his co-workers (Chen, 1987; Chen and Nagy, 1987):

$$\Delta t = \frac{K_oX\,(1 + CX)}{(1 - X)\,M} \tag{4}$$

where C is the coefficient of solute-solvent (water) interaction. Equation (4) can be applied for the solutions of nonelectrolytes and weak acids and it has no discontinuity of the variable X.

## Characterization of solute-water interaction

When b = 0 and C = 0, both Eq. (2) and Eq. (4) reduce to the Van't Hoff's FPD equation of an ideal solution. The parameters b and C provide the characteristics of solute-water interaction for the systems. By rearrangement, the values of b and C can be calculated from the following equations, respectively:

$$b = \frac{1}{X}\left[1 - X - \frac{K_oX}{M\Delta T}\right] \tag{5}$$

and

$$C = \frac{1}{X}\left[\frac{M\,(1 - X)\,\Delta T}{K_oX} - 1\right] \tag{6}$$

The calculated values of b for citrus juices and medium invert sugar solution varied from 0.12 to 0.16 and for the model system was 0.23 ± 0.06. The calculated values of C for citrus juices and medium invert sugar solution varied from 0.25 to 0.27 and for the model system was 0.56 ± 0.13. Both models can be used to describe the EFC and the characteristic parameter b or C can be used to quantify the deviation from the ideal system.

## Comparison of generalized models

Riedel (1951) used a generalized empirical EFC model and developed a heat content (enthalpy) diagram for fruit, vegetables and juices which has been widely adopted in standard references (e.g., Dickerson, 1968; ASHRAE, 1981). Riedel's equation assumes all juices completely frozen at −60°C and is expressed as:

$$\Delta t = 10X + 50X^3 \tag{7}$$

As a comparison, Eq. (2) assumes the existence of a definite amount of unfreezable water at any temperature, whereas Eq. (4) assumes a factor of solute-water interaction. Both Eq. (2) and Eq. (4) imply that juices cannot be completely frozen at a finite temperature. Both Eq. (2) and Eq. (4) are semi-empirical models which require one empirical constant for predicting changes in FPD for different values of molecular weights. The EFC given by Riedel's model compared closely to M = 202 and b = 0.20 or C = 0.25 using Eq. (2) or (4), respectively (Chen, 1986).

Experimental and calculated freezing points for citrus juices and model systems are compared in Fig. 1. The root mean square errors of the predicted results of Eq. (4) were 4–6% for 0–65 °Brix. Note that, for a comparable M, the EFC of the citrus juice was different from that of the model system as

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