

## COMMUNICATIONS

### A Study of Water Activity Prediction for Molasses Solutions

This work reports on the experimental determination of water activity in solutions of molasses ("blackstrap") and its comparison with sucrose. An attempt is made to predict the water activity of molasses from the knowledge of its main nonelectrolyte components, namely, sucrose, invert sugar, and natural acids. The results show that the prediction gives reasonably good results for  $a_w$  below  $\sim 0.92$ ; at higher water activities electrolytes present in molasses also play a role in  $a_w$  depression; allowance for this contribution has to be made to accurately predict the behavior of molasses.

Molasses ("blackstrap") can be broadly defined as the final mother liquor remaining after all of the sucrose that is possible to remove (by practical means) from the juice of sugar cane has been removed. Generally, molasses will contain from 50 to 75% total sugars (sucrose and invert sugar) and variable amounts of ash and nonsugar organic materials. Molasses is an important commodity in the food industry and has extensive use in the baking industry in such products as breads, cakes, cookies, pie fillings, and so on. Additional food applications include incorporation into candies, sauces, condiments, and table syrups (Morano, 1976).

One of the functional properties of molasses that has a direct effect on its shelf life and that of an end product is the water activity ( $a_w$ ). Water activity is the single most important factor affecting the shelf life of intermediate moisture foods ( $a_w$  between 0.65 and 0.90) and molasses belongs to this category. Troller (1979) has thoroughly discussed the effect of  $a_w$  on microbial stability of intermediate moisture foods. At present, molasses is not widely used to control water activity, probably because little is known about its water activity. Some data indicate that molasses could be at least as effective as sucrose in lowering water activity, but no detailed study of this behavior has been done (Morano, 1976).

The composition of molasses depends not only upon cane variety, climate, and soil condition but also on the method and extent of processing conditions. By this reason it would be important to be able to predict the  $a_w$  of molasses from knowledge of its composition (reducing and nonreducing sugars and nonsugar materials).

This work reports on the experimental determination of water activity in solutions of molasses (blackstrap) and its comparison with sucrose. An attempt is also made to predict the  $a_w$  of molasses from the  $a_w$ -lowering characteristics of its main components.

#### EXPERIMENTAL SECTION

**Materials.** A commercial ("Melrico", Abuin & Co.) molasses from Tucumán, Argentina, was used in this study.

**Analytical Methods.** Solids content was determined by a vacuum oven method at 65 °C over magnesium perchlorate. Protein, ash, and reducing (invert) and nonreducing (sucrose) sugars were determined according to the procedures described in AOAC (1980). Acidity was determined by titration with 0.1 N NaOH and expressed as malic acid. The percent of nonsugar, nonprotein organic materials was calculated by difference.

**Determination of Water Activity.** The  $a_w$  of molasses solutions was determined by using the  $a_w$ -Wert Messer

Table I. Composition of Molasses Used<sup>a</sup>

	% (w/w)
moisture	23.3
ash	9.7
sucrose	40.4
invert sugar	12.1
protein ( $N \times 6.25$ )	2.5
acidity (as malic acid)	1.9
other nonsugar, nonprotein organic materials	10.1

<sup>a</sup> pH 6.

manufactured by Firma Lufft, Stuttgart, West Germany. The instrument was calibrated at 25 °C with five different standard saturated salt solutions in the  $a_w$  range of interest to this study ( $\sim 0.80$ – $0.97$ ). The instrument was operated following the procedure described in detail by Chirife and Ferro Fontán (1980).

Water activity of dilute molasses solutions was derived from measuring freezing points (Ferro Fontán et al., 1981). Freezing points were determined on an Advanced Instruments Milk Cryoscope 4 DII which was calibrated against sodium chloride standard solutions. All measurements were made in triplicate.

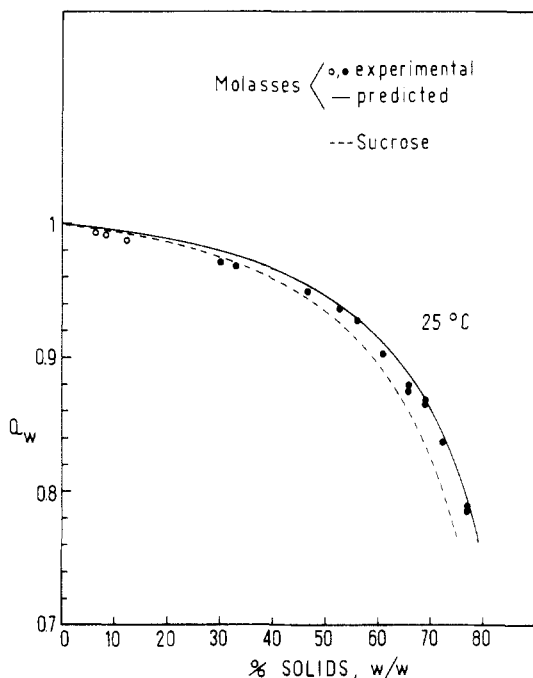
#### RESULTS AND DISCUSSION

The expressible juice from sugar cane is the precursor of molasses, this juice being the aqueous solution circulating in the living plant and carrying materials required for growth and metabolism. It is therefore extremely complex in its composition (Morano, 1976) but characteristically high in sucrose. Table I shows the composition of the molasses used in this study; as expected, sucrose constitutes the main component (52.7% of the dry solids). However, sizable amounts of invert sugar, ash, and nonsugar organic materials are also present. Although malic acid is not the only natural acid in molasses, acidity was expressed on that basis for the sake of simplicity.

Previous work by Chirife et al. (1980) has shown that the water activity of nonelectrolytes can be very well correlated using the equation

$$a_w = X_1 \exp(-KX_2^2) \quad (1)$$

where  $X_1$  and  $X_2$  are molar fractions of water and solute, respectively, and  $K$  is the correlating constant. Chirife et al. (1980) and Chirife and Ferro Fontán (1980) reported  $K$  values for various nonelectrolytes of interest to this study, namely, sucrose, glucose (or invert sugar), and malic acid. As a first approximation we may simply consider that molasses constituents which depress water activity are



**Figure 1.** Comparison of measured and predicted water activity in molasses solutions at 25 °C.

sucrose, glucose, and organic acids; nonsugar organic materials may be considered to contribute very little to water activity lowering due to its presumed high molecular weight. The role of ash constituents (i.e., inorganic salts) is not considered at this time. Ferro Fontán et al. (1981) have shown that for a mixture of nonelectrolytes, eq 1 still holds but using a "mean" molecular weight,  $\bar{M}$ , and correlating constant,  $K'$ , defined as

$$\bar{M} = \left[ \sum_s (C_s/M_s) \right]^{-1} \quad (2)$$

$$K' = \sum_s [K_s C_s (\bar{M}/M_s)] \quad (3)$$

where  $C_s$  is the weight fraction (dry basis) of the  $s$  component, and  $M_s$  and  $K_s$  are the molecular weight and correlating constant of each solute. Values of  $\bar{M}$  and  $K'$  for molasses can now be readily evaluated from the composition shown in Table I and the reported  $K_s$  values for sucrose, glucose, and malic acid (Chirife et al., 1980; Chirife and Ferro Fontán, 1980). Calculated values for molasses were found to be  $\bar{M} = 385.86$  and  $K' = 4.72$ .

Figure 1 shows experimental and predicted  $a_w$  data for molasses solutions at the temperature of 25 °C and also literature data for sucrose solutions (Chirife et al., 1980). Experimental data for molasses at high  $a_w$  (above 0.98) were obtained from freezing point measurements; the freezing point depression ( $\theta_F$ ) was transformed to  $a_w$  according to (Ferro Fontán and Chirife, 1981)

$$-\ln a_w = (9.6934 \times 10^{-3})\theta_F + (4.761 \times 10^{-6})\theta_F^2 \quad (4)$$

It is noteworthy that for the  $a_w$ 's involved in these experiments ( $a_w$  above 0.98), molasses may be considered to behave ideally and thus  $a_w$  at the freezing point is equal

to that at 25 °C (Raoult's law).

Various observations can be made about the results shown in Figure 1. (1) On an equal solids basis at  $a_w$  less than 0.97, molasses is less effective than sucrose in lowering water activity; at  $a_w$  above 0.97 this is reversed and molasses is somewhat more effective. (2) The predicted curve is in (good agreement with experimental data for  $a_w$  less than 0.92, although the measurements are always somewhat below the predicted curve. (3) For  $a_w \geq 0.92$ , the experimental data significantly deviate from the predicted curve and do not follow the typical pattern shown by nonelectrolyte species (Chirife et al., 1980). This may be attributed to the  $a_w$ -lowering contribution of electrolyte species, mainly inorganic salts present in molasses and evidenced as ash in the chemical analysis. It is noteworthy that data for molasses at high  $a_w$  seem to follow the same trend exhibited by some inorganic salts, like phosphates (Benmergui et al., 1979), which are likely to be present in molasses (Furia, 1972).

It may be concluded that an approximate prediction of  $a_w$  in molasses solutions may be done from knowledge of its sugar-organic acid composition, but for a more precise estimation, allowance has to be made of the contribution of inorganic salts present.

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