# The Effect of Ethanol–Sucrose Interactions on Specific Gravity. Part 2: A New Algorithm for Estimating Specific Gravity<sup>1</sup>

James J. Hackbarth,<sup>2</sup> The Gambrinus Company, San Antonio, TX

#### **ABSTRACT**

J. Am. Soc. Brew. Chem. 69(1):39-43, 2011

One method for the estimation of specific gravity is the Tabarie equation:  $SGv = 1 + \Sigma(SGv_i - 1)$ , which combines volume-adjusted binary solution specific gravities (SGv<sub>i</sub>) independently. In a previous study, the Tabarie equation was found to be within the observed 95% confidence level for solute concentrations below 5% sucrose and 18% ethanol (by weight). However, when ethanol exceeds 7 mol% the deviation from observation is extreme. In this region, ternary solutions appear to expand because the mixing collapse of hydrogen-bonded bulk water is overestimated by the Tabarie model. In this paper, a new algorithm is proposed that assumes that change in solution volume during mixing is related only to change in water structure or the specific gravity of water in the presence of solutes. The model then takes the form of an ideal solution:  $SG = (\Sigma w_i / SG_i)^{-1}$ , where  $w_i$  is the mass fraction of species i. Ethanol-sucrose aqueous solutions were prepared by weight, mixed via sonication, and analyzed for density across the full range of sucrose solubility. Least squares regression analysis was used to fit the difference between the experimental specific gravity and theoretical ideal solution using polynomial cross-products of solute concentration (adjusted  $R^2 = 0.998$ ; SE =  $2.9 \times 10^{-5}$ ; and n = 153).

Keywords: Apparent extract, Ideal solution, Specific gravity, Tabarie equation, Ternary solution

#### RESUMEN

Un método para la estimación de la gravedad específica es la ecuación Tabarie: SGv =  $1 + \Sigma(SGv_i - 1)$ , que combina los volumen-ajustado solución binario gravedades específica ((SGv<sub>i</sub>) de forma independiente. En un estudio anterior, la ecuación Tabarie se encontró entre el nivel de confianza del 95% observado para las concentraciones de soluto por debajo del 5% de sacarosa y 18% de etanol (en peso). Sin embargo, cuando el etanol se excede 7% en moles la desviación desde la observación es extrema. En esta región las soluciones ternarias parece que ampliar debido a la contraer de la mezcla de puentes de hidrógeno de agua a granel está sobreestimada por el modelo Tabarie. En este trabajo, un nuevo algoritmo se propone que se supone que el cambio en el volumen de la solución durante la mezcla se refiere únicamente a los cambios en la estructura del agua o la gravedad específica del agua en presencia de solutos. El modelo a continuación, toma la forma de una solución ideal:  $SG = (\Sigma w_i / SG_i)^{-1}$ , donde  $w_i$ es la fracción de masa de la especie i. Soluciones acuosas de etanol sacarosa se prepararon en peso, mezcladas a través de ultrasonidos, y se analizó para la densidad en toda la gama de la solubilidad de la sacarosa. Análisis de regresión lineal se utiliza para ajustar la diferencia entre la gravedad experimentales específicas y la solución ideal teórico utilizando polinomio productos cruzados de la concentración de soluto ( $R^2$  ajustado = 0.998; SE =  $2.9 \times 10^{-5}$ ; and n = 153).

Palabras claves: Ecuación Tabarie, Extracto aparente, Gravedad específica, Solución ideal, Solución ternaria

#### The Tabarie Model

The determination of alcohol by indirect means was first described in 1830 by French Chemist M. Emile Tabarie. "The principle consists in boiling the wine or any spirituous liquor into the open air,

doi:10.1094/ASBCJ-2010-1207-01

© 2011 American Society of Brewing Chemists, Inc.

allowing the alcohol to escape, and making up the 'volume' of the residue by the addition of pure water. The difference between the specific gravity of this mixture (SGEv) and the original liquid (SGV) indicates the quantity of alcohol which was present (SGAv)" (22). This specific gravity relationship is known as the Tabarie equation by volume because the distillation fractions are adjusted to the original volume:

$$SGV = SGAv + SGEv - 1$$
 (eq. 1)

The general form for the Tabarie relationship is SGV = 1 + $\Sigma(SGv_i - 1)$ , where  $SGv_i$  is the specific gravity of binary solution i. The implication is that binary solutions can be combined independently, but a review of the Tabarie equation by Hackbarth (6) in 2009 required the addition of a solute interaction correction (SGX). Figure 1 depicts a moderate correction for most beer, but when ethanol concentrations exceed 7 mol%, the correction becomes excessive. When equation 1 is algebraically multiplied by the density of water and volume of distilled solution, the result is a mass balance equation. Mass balance for these volumetric distillation fractions is only true when SGX equals zero. As seen in Figure 1B, this occurs when one or both solutes are infinitely dilute or near 7 mol% ethanol where SGX changes sign. The change in sign has been related to an inflection point in the binary specific gravity-concentration curve for aqueous ethanol at 16.4% (wt/wt) (6) or 10.2% (wt/wt) ethanol when 40% (wt/wt) sucrose is included. The Tabarie model fails when solutes are present at higher concentrations because the implied requirement for mass balance is false, and the mixing collapse of hydrogen-bonded bulk water is overestimated. For example, a (50:50) ethanol/sucrose "solution" (%, wt/wt) has no water, yet the Tabarie distillation model would combine the specific gravity of two aqueous solutions by volume, predicting a large water volume collapse with a specific gravity of 1.09. Sucrose is nearly insoluble in ethanol, so the actual specific gravity would be <1.05. The Tabarie model always overestimates the collapse of water in component binary solutions. The Tabarie equation appears to work for low extract beer and wine in Figure 1B, but it is coincidence that the Tabarie error and the SGX correction in this region are directionally the same. High-extract beer and wine, ready-todrink mixers, liqueurs, and distilled spirits (G. Spedding, Brewing and Distilling Analytical Services, personal communication, 2010) differ significantly from the Tabarie model.

#### The Vdovenko Model

An alternative equation begins with an isopiestic mixing rule for electrolytes first observed in 1936 by Zdanovskii (24) and later extended to nonelectrolytes by Stokes and Robinson (21), which is now referred to as the ZSR rule: "Binary solutions having the same water activity are mixed without any variation of this water activity value." Water activity ( $a_{\rm w}$ ) is the effective mole fraction of water or "free" water available for solute hydration, defined as  $a_{\rm w} = \lambda_{\rm w} X_{\rm w} = p/p_o$ , where  $\lambda_{\rm w}$  is the activity coefficient of water,  $X_{\rm w}$  is the mole fraction of water, and  $p/p_o$  is the equilibrium partial pressure of solution water relative to pure water. Vapor pressure is a colligative property of solutions that depends only on the number of solute particles in solution and not on their identity. The ZSR rule connects the molality (mol solute/kg of solvent) of the mixture ( $m_i$ ) with its binary components ( $m_{bi}$ ) for species i:

<sup>&</sup>lt;sup>1</sup> Original work was completed at The Spoetzl Brewery.

<sup>&</sup>lt;sup>2</sup> Corresponding author. E-mail: jhackbarth@gambrinus.com; Phone +1.210.490. 9128; Fax: +1.210.489.8180.

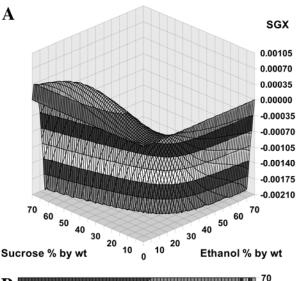
 $\Sigma_i m_i / m_{bi} = 1$ , where  $a_w$  is constant and  $0 \le m_i / m_{bi} \le 1$ 

In 1965, Vdovenko and Ryazanov (23) demonstrated that the thermodynamic properties of mixtures can be calculated when the ZSR rule holds. Kappenstein et al (9) used this model to calculate the volume (V) and specific gravity (SG) of a ternary mixture from the molal concentration  $(m_{bi})$  and specific gravity (SG<sub>bi</sub>) of the binary components and the molal concentration of the mixture  $(m_i)$  for solute i.  $M_i$  is the molar mass (g/mol) for solute i:

$$V = \sum_{i} m_{i} / m_{bi} (M_{i} m_{bi} + 1000) / SG_{bi}$$
  
SG =  $(\sum_{i} M_{i} m_{i} + 1000) / V$ 

When the ternary solution parameters (SG,  $M_i$ , and  $m_i$ ) are known, the ZSR rule can be applied to solve for  $m_i/m_{bi}$ . The ZSR rule defines the water partition between binary solutes if a binary pair exists with the same  $a_w$  as the mixture. If  $m_i/m_{bi}$  is the fraction of water ( $f_w$ ) in the first binary solution then  $1 - f_w$  would be the water in the second binary solution. The initial value for  $f_w$  assumes a constant  $a_w$  during mixing, an activity coefficient of one, and, therefore, a molar fraction of water in the binary solution that is equal to the molar fraction of water in the mixture ( $X_w$ ):

$$f_{\rm w}$$
 initial value =  $m_1/m_{b1} = m_1/[(1 - X_{\rm w})/X_{\rm w} \cdot 1000/M_{\rm w}]$ 



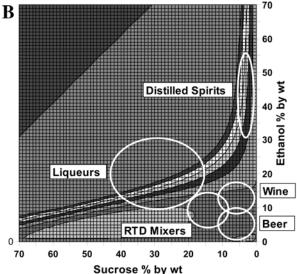


Fig. 1. A, Specific gravity–solute interaction correction (SGX) for Tabarie equation. B, Specific gravity–solute interaction contour map of  $\bf A$ .

The basic idea when combining binary solutions is that instead of consisting of bare particles dissolved in solvent, the solution really consists of solvated particles dissolved in the remaining "free" solvent. Because the outer surface of the solvated particle consists of solvent molecules, the solvent–solvated solute interactions are essentially reduced to solvent–solvent interactions to form practically ideal solutions (14). The Vdovenko equation can be converted to sucrose extract in the mix and binary solution (%, wt/wt) (E and E<sub>b</sub>, respectively) and ethyl alcohol in the mix and binary solution (%, wt/wt) (A and A<sub>b</sub>, respectively):

$$E_b = E \cdot 100/[E + f_w (100 - E - A)]$$

$$A_b = A \cdot 100/[A + (1 - f_w) (100 - E - A)]$$

$$SG = (E/E_b/SGE_b + A/A_b/SGA_b)^{-1}$$

The Vdovenko model does converge on a value for  $f_{\rm w}$  when solutions are <14% sucrose and <16% alcohol (by weight), but the inability to converge at higher concentrations is evidence of specific solute–solute interaction. The failure of the Tabarie equation and the ZSR rule for high concentrations of sucrose and ethanol leads to a model independent of atypical water-partitioning calculations.

#### The New Model

Because mass is conserved during mixing, a change in density is observed as a change in volume. An ideal solution has a volume that is equal to the sum of its premixed component volumes (V =  $\Sigma V_i$ ). Solution volume can also be expressed as mass per unit density or specific gravity (1/SG =  $\Sigma w/SG_i$ ), where  $w_i$  is the mass fraction of species i. In the Vdovenko model, two simple binary aqueous solutions with the same  $a_w$  retain their original volume when mixed as a ternary solution. Similarly, each ideal binary solution volume could be separated as the volume of pure solute and water that has collapsed in the presence of that solute.

The ideal solution specific gravity (SG) is calculated in equation 2. First, the ternary solute concentration is converted to a pair of binary concentrations by removal of the second solute. Unlike the Tabarie model that over-dilutes each binary solution and then corrects by subtracting one volume of pure bulk water or the Vdovenko model that under-dilutes by splitting the water between solutes, these binary solutions contain the same mass of water as the ternary solution. For now, variable *Z*, which corrects for solute interaction will be set to zero and solved later. Next, the specific gravity of water is calculated for binary solutions of sucrose (SGWE), ethanol (SGWA), and ternary solution (SGW). Specific gravity equations for extract (fe(E)) and alcohol (fa(A)) are covered in the next section as equations 3 and 4. Finally, the ternary solution specific gravity (SG) is calculated as the ratio of total mass to combined pure component volumes:

```
\begin{split} E_b &= E \cdot 100/(100-A) + Z \\ A_b &= A \cdot 100/(100-E) + Z \\ SGWE &= (100-E_b)/[100/fe(E_b) - E_b/fe(100)] \\ SGWA &= (100-A_b)/[100/fa(A_b) - A_b/fa(100)] \\ SGW &= SGWE \cdot SGWA \\ SG &= 100/[E/fe(100) + A/fa(100) + (100-E-A)/SGW] \end{split}  eq. (2)
```

Figure 2A shows the specific gravity-concentration curves for binary aqueous solutions of sucrose (SGE) from equation 3, ethanol (SGA) from equation 4, and water (SGWE and SGWA) from equation 2. Note that when solute volumes are based on pure compounds, the density of water for single-solute aqueous solutions always increases as solute concentration increases. In his 1865 doctoral dissertation, Mendeleev (13) observed inflection points in the derivative of the ethanol curve and related them to specific ethanol hydrates. Figure 2B contains the first derivative curves for solute equations 3 and 4. Inflection points are marked by the position of

solute/water molar ratios. Inflection points reveal bound water hydrate structures or combinations of hydrate structures that determine physical properties. Bound water can be supercooled and freezes at a lower temperature than bulk water, because hydrates break the percolating hydrogen-bonded water network.

# Specific Gravity of Binary Solutions

Aqueous sucrose conversion between concentration E (%, wt/wt) and true specific gravity (SGE) at 20/20°C is based on AOAC Plato tables (1). Polynomial regression statistics are adjusted  $R^2 = 1.000$ ; SE =  $1.6 \times 10^{-6}$ ; and n = 501.

$$\begin{aligned} & \text{SGE} = \text{fe}(\text{E}) = 1 + \sum_k m_k (\text{E}/100)^k, \text{ where } k = 1 \text{ to } 10 & \text{eq. (3)} \\ m_1 &= +0.3875135555 & m_5 = +5.591472292 & m_9 = +4.387787019 \\ m_2 &= +0.09702881653 & m_6 = -11.00667976 & m_{10} = -0.7995558730 \\ m_3 &= +0.3883357480 & m_7 = +13.62230734 \\ m_4 &= -1.782845295 & m_8 = -10.33082001 \end{aligned}$$

Aqueous ethanol conversion between concentration A (%, wt/wt) and true specific gravity (SGA) at 20/20°C is based on the OIML alcohol equation (18).

SGA = fa(A) = 
$$1 + \sum_k m_k / m_0 (A/100)^k$$
, where  $k = 1$  to 11 eq. (4)  
 $m_0 = +0.99820123$   $m_4 = +13.52215441$   $m_8 = +747.0172998$   
 $m_1 = -0.1929769495$   $m_5 = -88.29278388$   $m_9 = -547.8461354$   
 $m_2 = +0.3891238958$   $m_6 = +306.2874042$   $m_{10} = +223.4460334$   
 $m_3 = -1.668103923$   $m_7 = -613.8381234$   $m_{11} = -39.03285426$ 

# Specific Gravity of Ternary Solutions Using the Tabarie Equation

Three functions are defined that rely on convergent iteration to convert the ternary solute concentration (%, wt/wt) to specific gravity. The iteration loop is repeated until successive answers are  $<10^{-7}$ . The first two functions (equations 5A and B) convert solute concentrations Av and Ev (%, vol/vol) to solute concentrations E and A (%, wt/wt) and then to specific gravity using equations 3 and 4. A third function (equation 5C) calculates the Tabarie equation by volume (SGV) from the solute concentrations (%, wt/wt) using equations 5A and B:

#### **EXPERIMENTAL**

# Sample Preparation

Samples (120 mL) were prepared by weight directly from pure sucrose (S2-212, Fischer Scientific), 92.41% (wt/wt) ethanol (190 proof, 95% [vol/vol] Everclear), and distilled water. Mass was recorded on an analytical balance to the nearest 0.1 mg in a tared and capped 250-mL clear bottle (Nalgene). Dissolving and mixing the solutes was facilitated with an ultrasonic bath (fs30, Fischer Scientific). Sonicated samples produced more stable density measurements especially when solute concentrations were high. In addition to sucrose solvation, sonication causes cavitation and the collapse of microscopic bubbles. Samples were sonicated with swirling until sucrose particulates were dissolved and bubble formation ceased. Samples then were held in a separate 20°C water bath, typically for <1 hr, until analyzed.

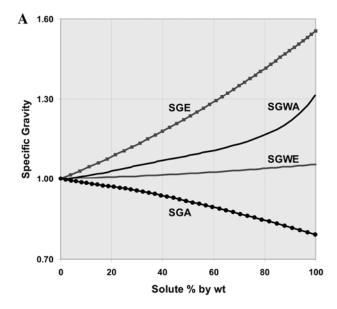
### **Specific Gravity Analysis**

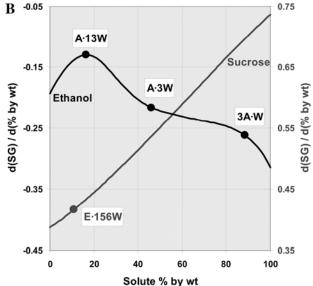
Specific gravity was measured using an oscillating U-tube densitometer (DMA5000, Anton Paar). True specific gravities were recorded to the nearest 10<sup>-5</sup> at 20/20°C corrected for air buoyancy to weight in vacuo. Incomplete mixing might be observed as drift

during the density measurement because high frequency U-tube oscillations achieve mixing similar to sonication. Shift between replicates occurred with high concentrations of sucrose where liquid exchange within the U-tube was presumed incomplete. Replicate sampling continued until three contiguous samples changed  $<10^{-4}$ . Triplicate samples were averaged before model analysis.

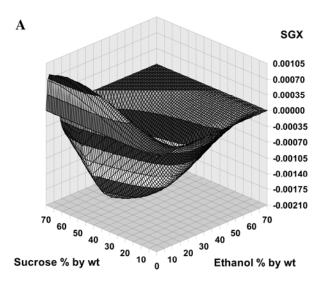
#### RESULTS AND DISCUSSION

Data points included 111 ternary solutions from Hackbarth's previous paper (6) and 42 additional solutions to fill gaps in the new emerging pattern. The solute interaction cross-product (*Z*) in equation 2 was solved by inverse interpolation. Inverse interpolation is an iterative method of convergence for solving nonlinear equations. Least squares regression was used to estimate *Z* values with polynomial cross-products of sucrose (E) and ethanol (A) (%, wt/wt). When either solute is missing, *Z* is calculated as zero, and equation





**Fig. 2. A,** Specific gravity for solutions of sucrose (SGE), ethanol (SGA), and water (SGWE and SGWA) in the presence of those solutes. **B,** Derivative of specific gravity with respect to solute concentration calculated using equations 3 and 4. Ethanol has three inflection points shown with related hydrate structures. Sucrose may have one rising inflection point.



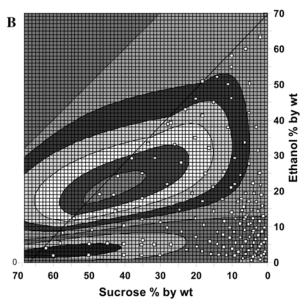


Fig. 3. A, Specific gravity-solute interaction correction (SGX) for equation 2. **B**, Specific gravity–solute interaction contour map of **A**.

2 is solved as a binary solution. Regression statistics for equation 2 with Z are adjusted  $R^2 = 0.998$ ; SE = 2.9 × 10<sup>-5</sup>; and n = 153. The standard error (SE) for this model is the same magnitude as the pooled standard deviation for replicate density measurements. Coefficients and variables for calculating Z are listed in equation 6:

$$\begin{split} Z &= -1.020733575\ 10^{-2}\ E^1\cdot A^{0.5} + 6.223951696\ 10^{-4}\ E^2\cdot A^{0.5} \\ &- 3.463023825\ 10^{-6}\ E^3\cdot A^{0.5} + 7.234029153\ 10^{-3}\ E^1\cdot A^1 \\ &- 4.496851490\ 10^{-4}\ E^1\cdot A^2 + 9.045618812\ 10^{-6}\ E^1\cdot A^3 \\ &- 5.427265684\ 10^{-8}\ E^1\cdot A^4 - 1.719663278\ 10^{-4}\ E^2\cdot A^1 \\ &+ 2.302760700\ 10^{-9}\ E^3\cdot A^3 \end{split} \tag{eq. 6}$$

Bubnik and Kadlec (2) reported sucrose solubility for six points from 66.72% (wt/wt) in pure water to 47.43% with 20% (wt/wt) ethanol at 20/20°C. The boundary for sucrose solubility follows a linear relationship: sucrose solubility E = 66.72 - 0.962A. Soluble sucrose in equation 6 is limited to this maximum. This allows approximate calculation of Z and prediction of SG for ternary solutions beyond sucrose saturation.

Figure 3A illustrates the specific gravity difference for equation 2 with and without Z. Figure 3B is a contour map of that same surface down the SGX axis. Also shown are the experimental data points and a boundary line for sucrose solubility. Note that each band represents a specific gravity change of 0.00035 or 12 times the standard error of the model.

A few observed specific gravity values (SGobs) are compared to calculated values in Table I. The data include various alcohol levels near 10% (wt/wt) sucrose. The Tabarie equation value (SGV) was calculated using equation 5C, and the new model was calculated using equation 2 without (SG0) and with (SGZ) the solute interaction cross-product (Z). Equation 2, with or without Z, is closer to the observed value than the Tabarie equation.

The proposed model for estimating the specific gravity of a ternary solution from component binary solutions presumes that any departure from ideal mixing is due to changes in water structure. The unusual physical properties of water (viscosity, surface tension, heat capacity, expansion on freezing, etc.) that attenuate earth's climate and determine protein structure and intracellular function, making life on earth possible, depend largely on hydrogen bonds (HB). HBs in water are the electrostatic dipole-dipole interactions between electronegative oxygen ( $\delta$ -) and the positive hydrogen ( $\delta$ +) of a nearby water molecule. Each HB proton is involved with two tetrahedral sp<sup>3</sup>-hybridized orbitals, one lone electron pair from the acceptor oxygen forming the HB, and one shared valence pair from the donor oxygen forming a covalent bond. Liquid water is not a homogeneous structure at the molecular level, and it is "structure" from materials research that describes the 3-D arrangement of molecules that control its properties (20). Martin Chaplin's remarkable website on water structure (3) describes liquid water as heterogeneous, forming an infinite hydrogen- bonded network of localized and structured clustering composed of bicyclo-octamers, cyclic pentamers, and tricyclo-decamers that further cluster to form highly symmetric 280-molecule icosahedra. In pure water <0.2\% of water molecules are not connected (10). This structure allows water to convert between high- and low-density states. The simplicity of the water molecule belies its complex behavior as a chemical compound. Pauling's (19) prediction of electron resonance across the HB in the 1930s was not confirmed until 1999 by Isaacs et al (8), who used the ESRF in Grenoble France to confirm that the HB is 90% electrostatic and 10% covalent and resonates on a picosecond time scale. Eaves et al (4) found that nonhydrogen-bonded (NHB) water molecules are intrinsically unstable, reforming HBs within 200 fsec (10<sup>-15</sup> sec). This is on a time scale of water's fastest intermolecular motions; as a result, NHBs are an insignificant species often reforming bonds with the same oxygen. HB separation in water is approx. 15% closer than if only van der Waals forces were involved, but the directional nature of hydrogen-bonding restricts water to its four nearest neighbors (3). Clearly, the net effect is that hydrogenbonding in bulk water creates structure, increases intermolecular separation, and decreases density.

Both ethanol and sucrose contain the permanent dipole hydroxyl group (-OH), which also engage in hydrogen bonds with water and each other (15,17). In fact, any aqueous solute containing a polar group or contributing ions can be considered a water structure breaker (7,11,16).

Engberts and Blandamer (5) have identified a camouflage effect for chemical reactions in the presence of carbohydrates. The stereochemistry of carbohydrates allows the hydrophilic -OH groups to fit into the 3-D hydrogen-bonded network of water molecules. Consequently, these -OH groups are camouflaged by the solvent water from reactant molecules. Reactant molecules then respond to the remaining hydrophobic -CH groups as if the hydration properties are hydrophobic. This camouflage effect may explain the large positive solute interaction seen in Figure 3A. The addition of ethanol to aqueous sucrose first collapses water in the hydrophobic hydration shell surrounding sucrose, which increases water density. As additional ethanol is added, there is hydrogen bonding between sol-

Z A  $\mathbf{E}$ **SGobs** SGV SG<sub>0</sub> SGZ Error SGV Error SG0 Error SGZ 0.92398 58.0639 10.0001 0.92748 -0.29940.92379 -365 4 0.92383 -1446.0167 9.9990 0.95390 0.95695 0.95438 -0.67330.95387 -305-48 3 37.8983 10.9480 0.97891 0.97685 -0.77810.97612 -280-74-10.97611 29.2987 8.9852 0.98772 0.98911 0.98835 -0.48200.98774 -138-2 -633 20.8400 10.1983 1.00707 1.00757 1.00746 -0.27081.00704 -50-39 -2 13.8752 10.0062 1.01679 1.01675 1.01686 -0.03431.01680 4 -7 1 9.6710 10.5521 1.02527 1.02508 1.02517 0.0609 1.02526 19 10 6.7455 10.4871 1.02968 1.02946 1.02951 0.0877 1.02963 21 17 5 1.03236 3.6414 9.8531 1.03238 1.03228 1.03228 2 0.0614 10 10 1.03293 1.03293 1.03295 1.5802 9.0617 1.03296 0.0162 2 2 1

TABLE I
Ethanol-Sucrose Specific Gravity Calculations<sup>a</sup>

utes (dehydration of sucrose) that releases bound water, decreases the probability of solute interaction with water, promotes HBs between water molecules, and decreases density relative to the density in component binary solutions.

# CONCLUSIONS

A theoretical model for estimating the specific gravity of ternary solutions of sucrose, ethanol, and water at 20/20°C has been proposed that isolates and predicts solute–solute interactions. This model (equation 2) is an improvement over the Tabarie model (equation 1). Both methods rely on published binary density concentration data. Although the Tabarie equation is not well known in the Americas, it is recommended by MEBAK (Central European Analytical Methods) as verification of distillation (12) and is used in instruments such as the Anton Paar Alcolyzer to estimate extract (R. Benes, Anton Paar GmbH, personal communication, 2009). The Tabarie model is adequate for dilute solutions of <18% ethanol and <5% sucrose (by weight), but grossly overestimates specific gravity above 7 mol% ethanol. This error can be assigned to the construction of the Tabarie model, which incorrectly implies mass balance in a volumetric distillation. As solute concentrations increase, so does departure from an ideal solution. The new model is more accurate for all solute concentrations and is increasingly important for high-extract beer and wine, ready-to-drink mixers, liqueurs, and distilled spirits.

#### ACKNOWLEDGMENTS

I thank The Gambrinus Company President Carlos Alvarez for allowing this work to be undertaken and published. Thanks also to Brewery Director Jaime Jurado and Spoetzl Brewery QA Manager Peter Takacs for support and to Roderick Read, Carolyn Hackbarth, and Melissa Todd for laboratory work.

# LITERATURE CITED

- AOAC International. Official Methods of Analysis. Table 942.33: Degrees Brix, specific gravity, and degrees Baumé of sugar solutions (Plato table). The Association, Gaithersburg, MD, 2005.
- Bubnik, Z., and Kadlec, P. Sucrose solubility. In: Sucrose Properties and Applications. M. Mathlouthi and P. Reiser, eds. Chapman and Hall. Vol. 5, p. 120, 1995.
- 3. Chaplin, M. Water Structure and Science. Published online at www. lsbu.ac.uk/water/. London South Bank University, London, 2009.
- Eaves, J. D., Loparo, J. J., Fecko, C. J., Roberts, S. T., Tokmakoff, A., and Geissler, P. L. Hydrogen bonds in liquid water are broken only fleetingly. *Proc. Natl. Acad. Sci. U.S.A.* 102:13019-13022, 2005.
- Engberts, J. B. F. N., and Blandamer, M. J. Reactant-solute encounters in aqueous solutions studied by kinetic methods: Hydration cosphere overlap and camouflage effects. *J. Phys. Org. Chem.* 11:841-846, 1998.

- Hackbarth, J. J. The effect of ethanol–sucrose interactions on specific gravity. J. Am. Soc. Brew. Chem. 67:146-151, 2009.
- 7. Hribar, B., Southall, N. T., Vlachy, V., and Dill, K. A. How ions affect the structure of water. *J. Am. Chem. Soc.* 124:12302-12311, 2002.
- Isaacs, E. D., Shukla, A., Platzman, P. M., Hamann, D. R., Barbiellini, B., and Tulk, C. A. Covalency of the hydrogen bond in ice: A direct X-ray measurement. *Phys. Rev. Lett.* 82:600-603, 1999.
- Kappenstein, A.-C., Moisy, P., Cote, G., and Blanc, P. Contribution of the concept of simple solutions to calculation of the stoichiometric activity coefficients and density of ternary mixtures of hydroxylammonium or hydrazinium nitrate with nitric acid and water. *Phys. Chem. Chem. Phys.* 2:2725-2730, 2000.
- Lenzi, F. An upper bound to the mole fraction of unbonded H<sub>2</sub>O in liquid water at 25°C. Can. J. Chem. 50:1088, 1972.
- Lerbret, A., Bordat, P., Affouard, F., Descamps, M., and Migliardo, F. How homogeneous are the trehalose, maltose, and sucrose water solutions? An insight from molecular dynamics simulations. *J. Phys. Chem. B* 10:11046-11057, 2005.
- MEBAK. Mitteleuropäische Brautechnische Analysenkommission (Central European Brewing Technology Analysis Commission). Vol. 2, Method 2.13.4. MEBAK, Freising-Weihenstephan, Germany, 1993.
- 13. Mendeleev, D. The compounds of ethyl alcohol with water. *J. Chem. Soc.* 51:778, 1887.
- 14. Miller, D. G. On the Stokes-Robinson hydration model for solutions. *J. Phys. Chem.* 60:1296-1299, 1956.
- Molinero, V., Cagin, T., and Goddard, W. A., III. Sugar, water and free volume networks in concentrated sucrose solutions. *Chem. Phys. Lett.* 377:469-474, 2003.
- Nose, A., and Hojo, M. Hydrogen bonding of water-ethanol in alcoholic beverages. *J. Biosci. Bioeng.* 102:269-280, 2006.
- Noskov, S. Y., Lamoureux, G., and Roux, B. Molecular dynamics study of hydration in ethanol-water mixtures using a polarizable force field. *J. Phys. Chem. B.* 109:6705-6713, 2005.
- OIML. International recommendation 22: International alcoholometric tables. Published online at www.oiml.org/publications/R/R022-e75.pdf.
   Organisation Internationale de Métrologie Légale (International Organisation of Legal Metrology), Paris, 1973.
- Pauling, L. The Nature of the Chemical Bond., 3rd ed. (Ed. I, 1939 from 1930s series in J. Am. Chem. Soc.). Cornell University, Ithaca, NY. Vol. 12, p. 452, 1960.
- Roy, R., Tiller, W. A., Bell, I., and Hoover, M. R. The structure of liquid water; novel insights from materials research; potential relevance to homeopathy. *Mater. Res. Innovat.* 9:577-608, 2005.
- Stokes, R. H., and Robinson, R. A. Interactions in aqueous nonelectrolyte solutions. I. Solute-solvent equilibria. *J. Phys. Chem.* 70:2126-2130, 1966.
- Tabarie, E. Nouvel oenomètrè. Poggendorff's Ann. Chim. Phys. P. 223, 1830.
- Vdovenko, V. M., and Ryazanov, M. A. Activity coefficients in systems with multiple components. II. Importance of Zdanovskii rule for calculating the thermodynamic properties of mixed solutions. Sov. Radiochem. 7:368-474, 1965.
- Zdanovskii, A. B. Trudy Solvanoi Laboratorii (Trans. Salt Laboratory). Akad. Nauk. SSSR, No. 6, 1936.

<sup>&</sup>lt;sup>a</sup> Error between observed specific gravity (SGobs) and specific gravity calculated by the Tabarie equation (SGV) or the new model without Z (SG0) and with Z (SGZ) was multiplied by  $10^5$  for solutions of ethanol (A) and sucrose (E) (%, wt/wt).