J. Chem. Eng. Data **2007,** *52,* 135−140

Density Calculation of Sugar Solutions with the SAFT Model

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Density is one of the key physicochemical properties for sugar solutions. The objective of this work is to model the density of sugar solutions. The density calculation has been carried out by applying statistical associating fluid theory (SAFT) equations of state. This new method made use of critical temperature, pressure, and volume as well as normal boiling temperature to determine the SAFT parameters for sugars and is now extended to determine the SAFT parameters for D-xylose, sucrose, and sorbitol. The critical properties and normal boiling temperature of sugars are estimated based on information of molecular structure. The densities of sugar solutions including binary systems of D-glucose/H_2O, D-fructose/H_2O, D-xylose/H_2O, sucrose/H_2O, and sorbitol/H_2O; ternary systems of D-fructose/H_2O/ethanol and sucrose/sorbitol/H_2O; and quaternary systems of D-glucose/D-fructose/H_2O/ethanol have been calculated without using binary interaction parameters. Results with high accuracy have been obtained. Finally, the water activity of sorbitol/water and xylitol/water and the normal boiling temperature of glucose/water and fructose/water have been modeled.

Introduction

In the food technology and sugar industries, the density of sugar solutions is an important control parameter. Accurate modeling of the density of sugar solutions is very useful for process design, control, and operation. Some calculations of density were carried out using empirical equations for binary systems,[1] and generally, a high number of coefficients were required. However, these type of equations, due to lack of a theoretical basis, are very difficult or impossible to extend to multicomponent systems. The aim of this work is to model the density of sugar solutions. The thermodynamic model applied is the statistical associating fluid theory (SAFT) equation of state.[2] The SAFT models[3,4] are versatile tools and have been applied to a wide variety of fluids.[5] In a previous work,[2] the SAFT model was applied to describe the sugar solubility in water and in mixed solvents, which was accomplished by developing a new method to determine the SAFT parameters. In this work, we will apply the SAFT equation of state to predict the density of sugar solutions by using the new method developed to determine the SAFT parameters of sugars.

Determination of the SAFT Parameters for Sugars

The SAFT equation of state we have applied is the version of Huang and Radosz.[6,7] For describing sugars, five parameters are required by the SAFT model, namely, the segment number m, segment volume υ^{00}, and segment−segment interaction energy u^0/k, association energy ϵ^{AB}/k, and association volume κ^{AB}.

The method of parameter determination previously developed[2] is extended to determine the SAFT parameters for sugars. There are three steps for the parameter determination. First, both the parameters segment volume υ^{00} and association volume κ^{AB} are set to a value; the parameters of m, u^0/k, and ϵ^{AB}/k are taken as the three variables in eqs 1 to 3 (the three equations are expressed by the SAFT model), which are the pressure at the critical temperature T_c; the first derivative of pressure with respect to density at T_c, P_c, and V_C; and the second derivative of pressure with respect to density at T_c, P_c, and V_c, respectively.

$$P|_{T_c} = P_c \tag{1}$$

$$\left[\frac{\partial P}{\partial \rho}\right]_{T_c} = 0 \tag{2}$$

$$\left[\frac{\partial^2 P}{\partial \rho^2}\right]_{T_c} = 0 \tag{3}$$

By making use of the critical properties of temperature, pressure, and volume, the three equations can be solved, and then the parameters of m, u^0/k, and ϵ^{AB}/k are determined. Second, with the five parameters (three of them are determined as mentioned above), the SAFT model is used to calculate normal boiling temperature. If the normal boiling temperature is calculated correctly, then we say the early value given to the parameter κ^{AB} is the correct one. Otherwise, κ^{AB} is adjusted to a new value, and the above procedures (fist and second steps) are repeated until the normal boiling temperature is calculated correctly. Third, with the above five parameters (four of them have been obtained through the determination steps), the SAFT model is used to calculate the density of sugars at room temperature and atmospheric pressure. If the density is calculated with a small deviation from the crystal density of the sugar at room temperature (the crystal density is taken as a reference density of the sugar, assumed to be in an amorphous state at room temperature), then the early value given to the parameter υ^{00} is the correct one. Otherwise, the parameter υ^{00} is set to a new value, and the procedures of parameter determination mentioned above are repeated. In this way, the SAFT parameters are determined finally. During the process of parameter determination, the association number should be carefully chosen. On the one hand, the association number affects the solving of eqs

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10.1021/je060310i CCC: $37.00

Table 1. Critical Properties and Normal Boiling Points

substance	T_c K	P_c bar	V_c $cm^3 \cdot mol^{-1}$	T_B K
D-fructose[a]	820.00	55.05	425.5	669.68
D-glucose[a]	846.00	48.00	478.5	691.13
sucrose[a]	1309.79	46.26	782.5	1030.18
xylose[a]	749.22	50.59	390.5	607.18
sorbitol[b]	868.00	46.40	483.0	704.00

[a] Estimated through group contribution method. [b] Aspen plus.

Table 2. Parameters of the SAFT Equation

substance	m	u/k K	v^{00} $cm^3 \cdot mol^{-1}$	ϵ^{AB} K	κ^{AB}	N_{assoc}[a]
D-fructose[b]	5.026	215.67	12.0	7867	0.00025	4
D-glucose[b]	5.238	199.18	12.0	7654	0.0007	4
sucrose[c]	2.583	206.054	55.0	7297.7	0.0055	6
xylose[c]	5.025	167.486	10.0	6490.55	0.0012	4
sorbitol[c]	4.096	189.526	16.0	7295.76	0.0014	4
water[b]	1.165	194.29	8.0	3229	0.052	3
ethanol[d]	2.457	213.48	12.0	2759	0.0292	2

[a] N_{assoc}, number of association sites. For D-fructose, D-glucose, xylose, and sorbitol, the four association sites are distributed on two OH groups. Each has one on oxygen and one on hydrogen. For sucrose, the six association sites are distributed on three OH groups. Each has one on oxygen and one on hydrogen. For water, two association sites on oxygen and one on hydrogen. [b] From ref 1. [c] This work. [d] From ref 6.

1 to 3, whereas on the other hand, the association number affects reproduction of the normal boiling temperature.

For sugars, the critical properties of temperature, pressure, and density, as well as the normal boiling temperature are estimated using Joback's modification of Lydersen's method,[8] as shown in eqs 4 to 7:

$$T_c = T_B[0.584 + 0.965\sum\Delta T - (\sum\Delta T)^2]^{-1} \tag{4}$$

$$P_c = [0.113 + 0.0032n_A - \sum\Delta P]^{-2} \tag{5}$$

$$V_c = 17.5 + \sum\Delta V \tag{6}$$

$$T_B = 198 + \sum\Delta b \tag{7}$$

How to calculate ΔT, ΔP, ΔV, and Δb has been described in detail by Reid et al.[8]

On the basis of the group contribution method and using molecular structure information, the critical properties of temperature, pressure, and volume as well normal boiling temperatures have been estimated. The values are listed in Table 1. Using the method of parameter determination described above, the SAFT parameters have been determined and are listed in Table 2.

Modeling of Density of Sugar Solutions

For the calculation of the density of sugar solutions including binary, ternary, and quaternary systems, the SAFT parameters used are listed in Table 2. The calculations are carried out without using binary interaction parameters.

Binary Systems. Figure 1 shows density calculations for the system D-fructose/H_2O containing up to 6.4 % D-fructose. Figure 2 shows the relative deviations of the density calculation, which are from (0.97 to 2.18) % at 5 °C, from (−0.15 to 1.39) % at 15 °C, from (−1.14 to 1.39) % at 25 °C, and from (0.8 to −2.14) % at 35 °C.

Figure 3 shows density calculations for D-xylose/H_2O containing up to 6.6 % D-xylose. As can be seen in Figure 4, the relative deviations of the density calculations are from (0.88 to 1.0 9) % at 5 °C, from (−0.23 to 0.24) % at 15 °C, from (−1.24 to −0.56) % at 25 °C, and from (−2.13 to −1.29) % at 35 °C.

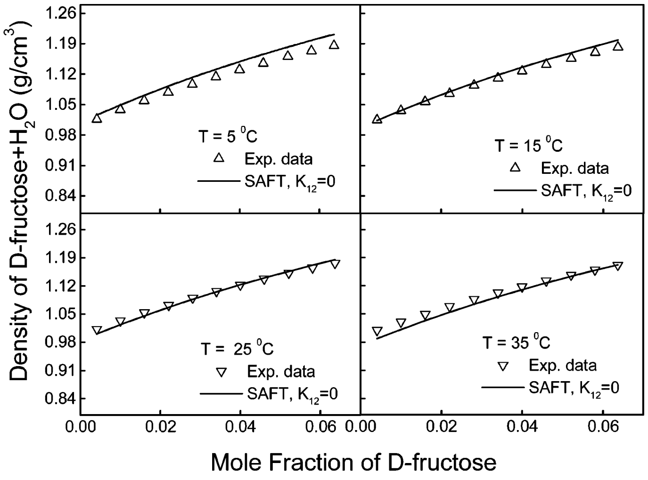

Figure 1. Density of the aqueous solution of D-fructose/H_2O at (5, 15, 25, and 35) °C. Comparison of SAFT calculation to experimental data.[9]

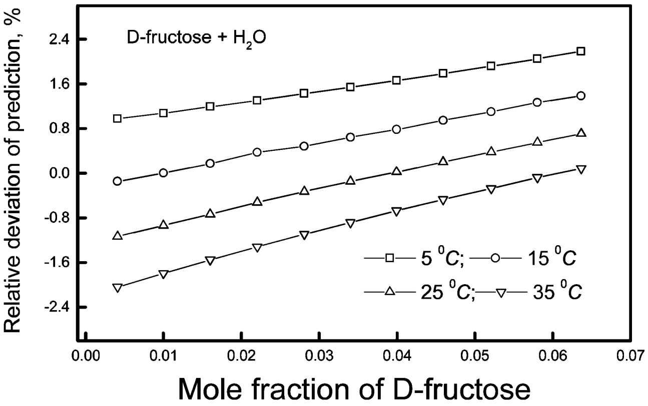

Figure 2. Relative deviation of the density calculation at deferent temperatures for D-fructose/H_2O.

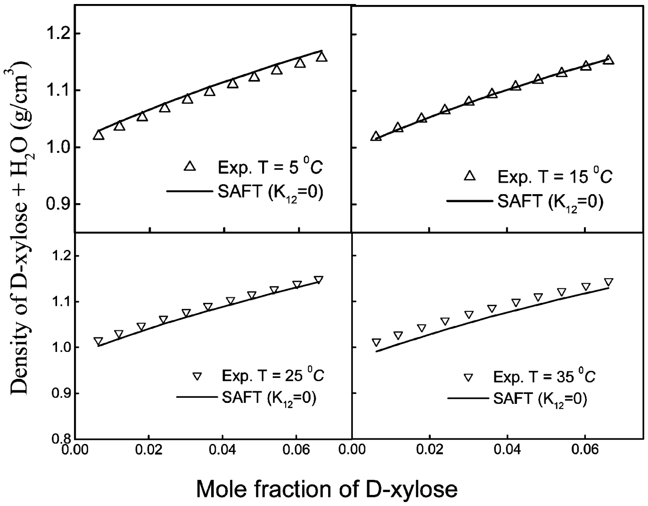

Figure 3. Density of the aqueous solution of D-xylose/H_2O at (5, 15, 25, and 35) °C. Comparison of SAFT calculation to experimental data.[9]

In Figure 5, the density calculations for the system sucrose/H_2O containing up to 7.0 % sucrose are presented. As shown in Figure 6, the relative deviations of the density calculation are from (1.06 to 1.38) % at 5 °C, from (−0.002 to 0.8) % at 15 °C, from (−0.9 to 0.40) % at 25 °C, and from (−1.8 to −0.026) % at 35 °C.

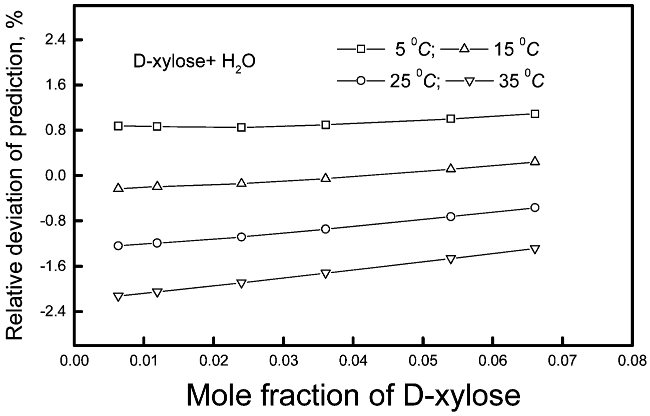

Figure 4. Relative deviation of the density calculation at deferent temperatures for D-xylose/H_2O.

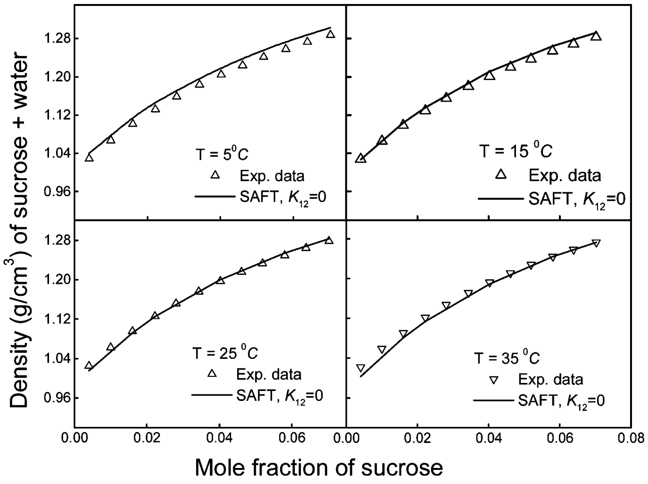

Figure 5. Density of the aqueous solution of sucrose/H_2O at (5, 15, 25, and 35) °C. Comparison of SAFT calculation to experimental data.[9]

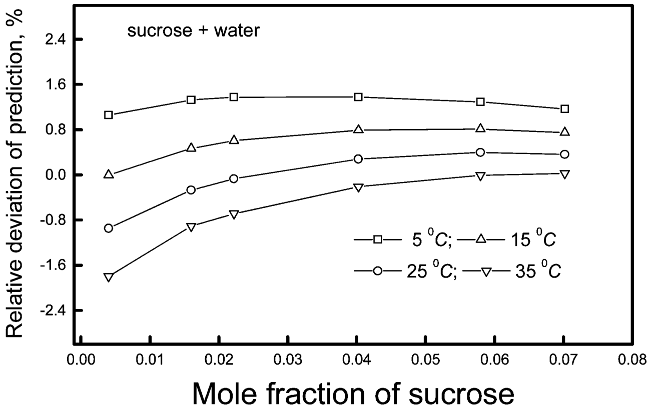

Figure 6. Relative deviation of the density prediction at deferent temperatures for sucrose/H_2O.

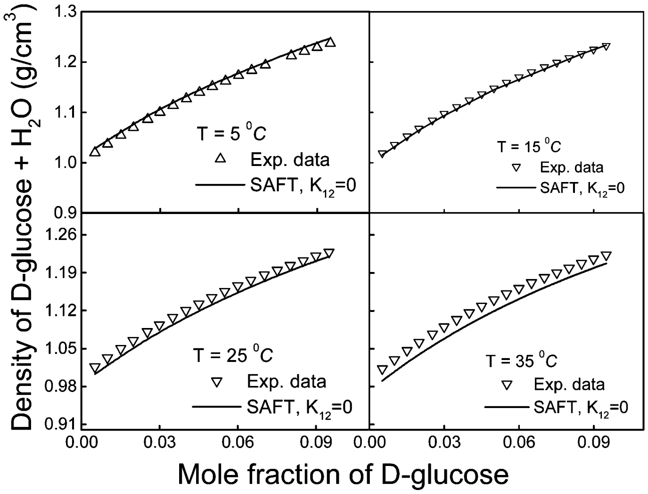

Figure 7. Density of the aqueous solution of D-glucose/H_2O at (5, 15, 25, and 35) °C. Comparison of SAFT calculation to experimental data.[9]

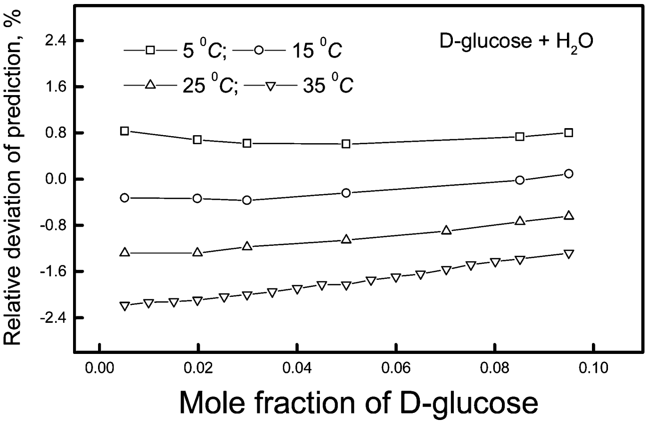

Figure 8. Relative deviation of the density calculation at deferent temperatures for D-glucose/H_2O.

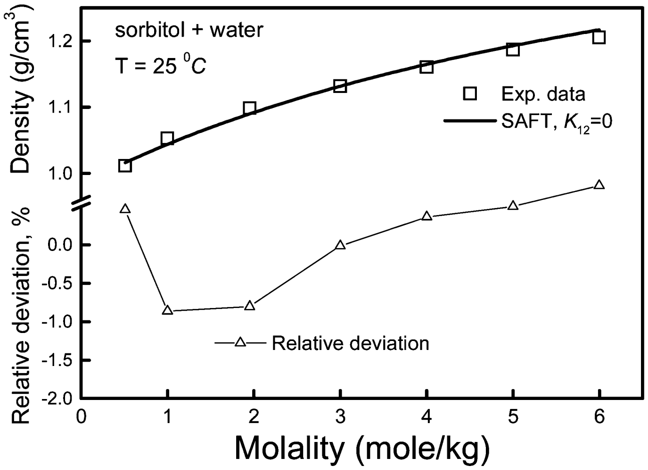

Figure 9. Density of the aqueous solution of sorbitol/H_2O at 25 °C. Comparison of SAFT calculation to experimental data.[10]

Figure 7 presents the density calculation for D-glucose/H_2O containing up to 9.5 % D-glucose. In Figure 8, the relative deviations of the density calculation are shown, which are from (0.61 to 0.83) % at 5 °C, from (−0.37 to 0.09) % at 15 °C, from (−0.64 to 1.28) % at 25 °C, and from (−1.28 to 2.18) % at 35 °C.

At 25 °C, the densities of sorbitol/H_2O with the molality of sorbitol up to 6.0 are calculated. The results and the relative deviations of the density calculation are presented in Figure 9. The relative deviations are from (−0.86 to 0.98) %.

Ternary Systems. At 40 °C, Figure 10 shows the density calculation and the relative deviation of the density calculations for the solutions of D-fructose/water/ethanol containing up to 50 % D-fructose. The relative deviations are from (1.53 to 3.31) % at the ratio of ethanol to water of 7.5:1, from (1.67 to 3.01) % at the ratio of ethanol to water of 6:1, and from (1.03 to 2.98) % at the ratio of ethanol to water of 4.5:1.

In Table 3, for the solutions of sorbitol/sucrose/water, the results of the density calculation and relative deviations are listed. For the 29 cases with varying weight concentrations of

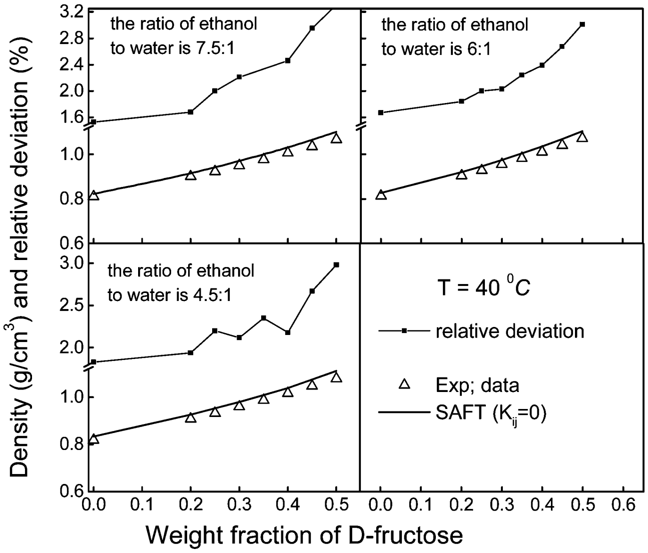

Figure 10. Density of D-fructose/water/ethanol with varying ratios of ethanol to water. Comparison of SAFT calculation to experimental data.[11]

Table 3. Density Prediction by the SAFT Model for Sorbitol (1) + Sucrose (2) + Water (3) at 25 °C

molality/(mol·kg^{-1})		density/(g·cm^{-3})		relative deviation
sorbitol	sucrose	experimental[10]	predicted	%
0.2065	0.1969	1.02302	1.02399	0.09
0.2591	0.2608	1.03665	1.03495	−0.16
0.3036	0.3064	1.04590	1.04288	−0.30
0.5104	0.1168	1.03256	1.03106	−0.15
0.3895	0.2372	1.04160	1.03919	−0.23
0.2643	0.3619	1.05096	1.04736	−0.34
0.1344	0.4912	1.06070	1.05554	−0.49
0.3560	0.3422	1.05386	1.04985	−0.38
0.4017	0.3862	1.06180	1.05724	−0.43
0.6731	0.1507	1.04989	1.04401	−0.56
0.5157	0.3078	1.05915	1.05412	−0.47
0.3513	0.4719	1.06886	1.06426	−0.43
0.1797	0.6432	1.07885	1.07441	−0.41
0.8748	0.1910	1.06750	1.05902	−0.79
0.6731	0.3923	1.07763	1.07123	−0.60
0.4601	0.6040	1.08825	1.08338	−0.45
0.2371	0.8275	1.09892	1.09563	−0.30
0.6482	0.6607	1.10120	1.09730	−0.35
0.8125	0.8258	1.12037	1.11915	−0.11
1.6842	0.4681	1.12326	1.12160	−0.15
1.0316	1.0588	1.14364	1.14630	0.23
2.1968	0.3037	1.12836	1.12674	−0.14
1.2288	1.2069	1.15868	1.16373	0.44
2.5006	0.1267	1.12569	1.12291	−0.25
2.2167	0.4812	1.13996	1.14281	0.25
0.5267	2.0098	1.18918	1.19562	0.54
0.2519	2.5619	1.21206	1.21957	0.62
1.5059	1.6160	1.18896	1.19820	0.78
1.8125	1.8036	1.20601	1.21638	0.86

sorbitol and sucrose, the relative deviations are from (−0.79 to 0.86) %.

Quaternary System of D-Glucose/D-Fructose/H_2O/Ethanol. The quaternary systems are the solutions of D-glucose/D-fructose/H_2O/ethanol with varying ratios of D-glucose to D-fructose.

Figure 11 presents the density calculations for the solutions containing up to 70 % total sugar, and the mixed solvent containing 40 % ethanol. Figure 12 shows that the relative deviations of the density calculation are from (−1.60 to 1.82) % at the ratio of D-glucose to D-fructose of 1:1, from (−2.02 to 0.57) % at the ratio of D-glucose to D-fructose of 2:1, and from (−1.48 to 2.41) % at the ratio of D-glucose to D-fructose of 1:2.

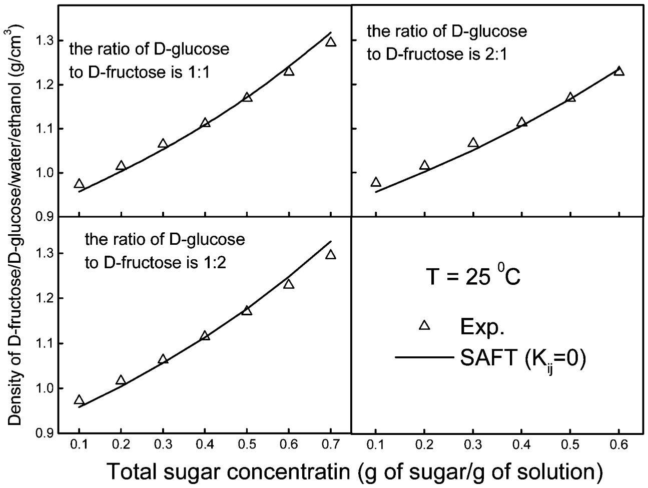

Figure 11. Density of D-fructose/D-glucose/water/ethanol with varying ratios of D-glucose to D-fructose. The mixed solvent contains 40 % ethanol. Comparison of SAFT calculation to experimental data.[12]

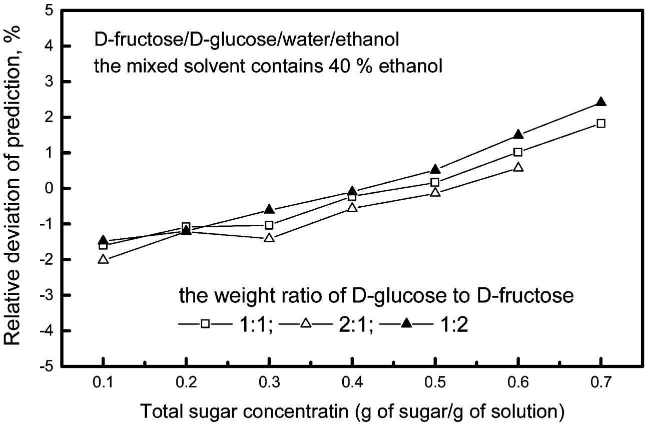

Figure 12. Relative deviation of the density prediction for D-fructose/D-glucose/water/ethanol.

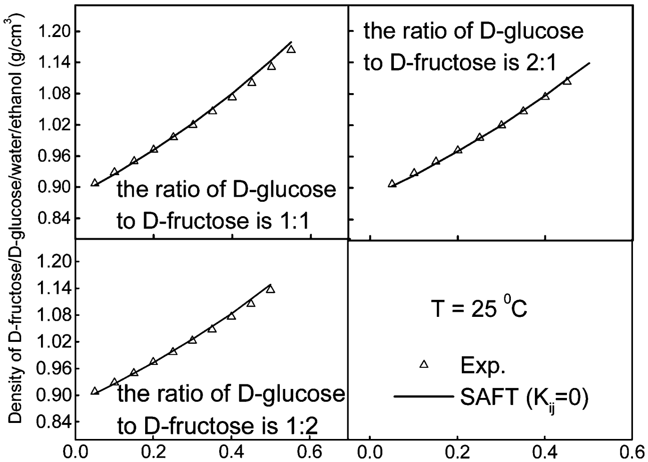

Figure 13. Density of D-fructose/D-glucose/water/ethanol at the ratio of ethanol to water 60:40 and varying ratios of D-glucose to D-fructose. Comparison of SAFT calculation to experimental data.[12]

In Figure 13, the predicted densities are presented for sugar solutions containing up to 55 % total sugar, and the mixed solvent containing 60 % ethanol. In Figure 14, the relative deviations of the density calculations are from (−0.40 to 1.29) % at the ratio of D-glucose to D-fructose of 1:1, from (−0.37 to 0.45) % at the ratio of D-glucose to D-fructose of 2:1, and from

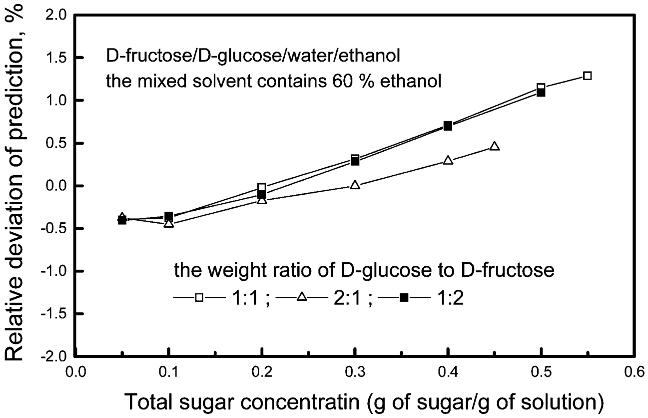

Figure 14. Relative deviation of the density calculation for the sugar solutions with the mixed solvent containing 60 % ethanol.

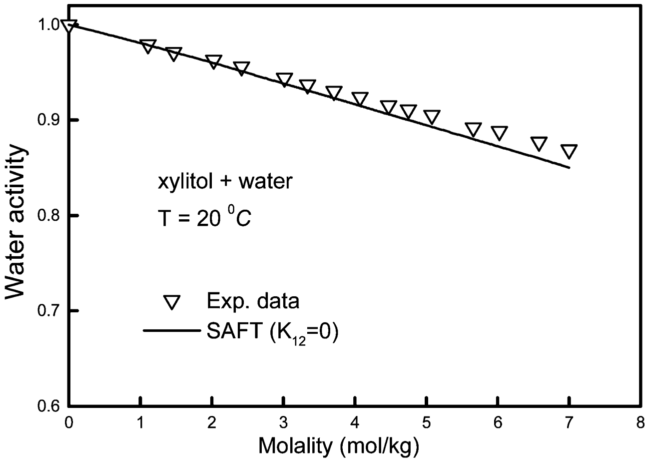

Figure 15. Water Activity of the system xylitol + water. Comparison of SAFT calculation to experimental data.[13]

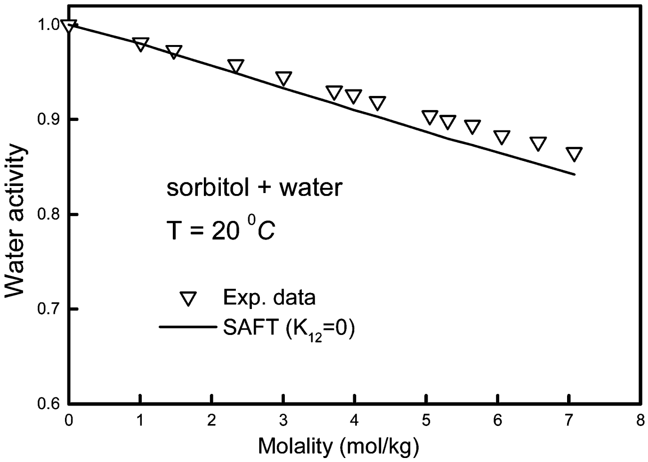

Figure 16. Water Activity of the system sorbitol + water. Comparison of SAFT calculation to experimental data.[13]

(−0.41 to 1.09) % at the ratio of D-glucose to D-fructose of 1:2.

Water Activity and Normal Boiling Temperature. The water activity of sorbitol/water and xylitol/water has been calculated by SAFT without using binary interaction parameters as shown in Figures 15 and 16. The normal boiling temperatures of glucose/water and fructose/water are presented in Figures 17 and 18. In Figure 17, the result is predicted without using a binary interaction parameter, and in Figure 18, the normal boiling temperature is calculated both without and with a binary interaction parameter of $K_{12} = 0.13$.

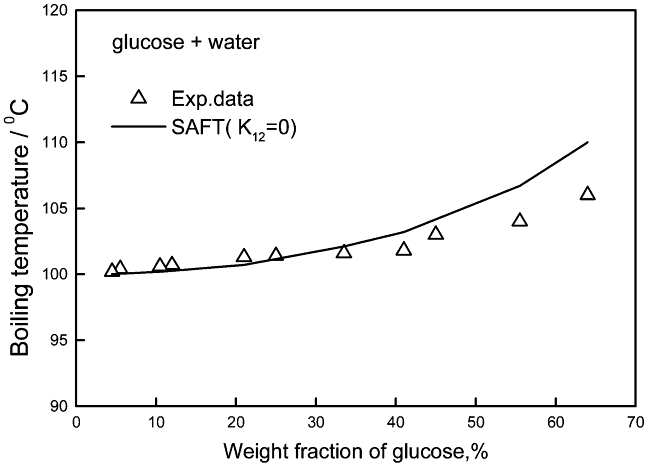

Figure 17. Boiling temperature of glucose/water. The solid line is calculated by SAFT without using a binary interaction parameter. Comparison of SAFT calculation to experimental data.[14]

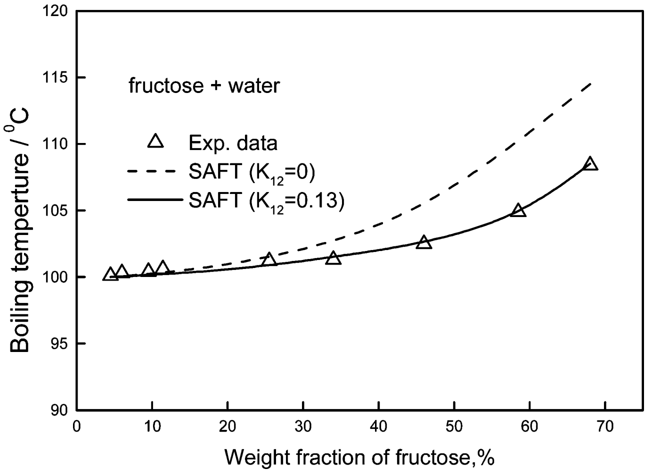

Figure 18. Boiling temperature of fructose/water. The dashed line is calculated by SAFT without using a binary interaction parameter, the solid line with $K_{12} = 0.13$. Comparison of SAFT calculation to experimental data.[14]

Conclusions

With the new method previously developed to determine the SAFT parameters for sugars, density calculations of sugar solutions using the SAFT equation of state has been accomplished. The determination of the SAFT parameters is based on information of molecular structure. Binary interaction parameters are not required when carrying out the density calculations. For the binary aqueous solutions including D-glucose, D-fructose, D-xylose, sucrose, and sorbitol, the largest relative deviation (absolute value) of the density calculation is 2.18 % in the temperature range of (5 to 35) °C. For the ternary systems of D-fructose/water/ethanol, the largest relative deviation of the density calculation is 3.31 %. For the systems of sorbitol/sucrose/water, the densities predicted present excellent agreement with experimental data. For the quaternary systems of D-glucose/D-fructose/water/ethanol containing up to 70 % total sugar, the largest relative deviation is 2.41 %. All the results of density calculations of sugar solutions show that the modeling of density has been accomplished with a very good accuracy. During the parameter determination, the crystal density of sugar at room temperature, taken as the reference density of sugar in an assumed amorphous state, was used for determining the parameter of the segment volume. This may be the reason that the density calculation is more accurate around room temperature, for example, at (25 and 15) °C, than at other temperatures.

The water activity of sorbitol/water and xylitol/water has been calculated well without using binary interaction parameters. For the solution glucose/water, the normal boiling temperature has been predicted well without using a binary interaction parameter. For the solution fructose/water, the predicted normal boiling temperature is large at high concentrations of fructose, and the correlated result has good agreement with experimental data.

Glossary

m	segment number
P	pressure
T	temperature (K)
u/k	temperature-dependent dispersion energy of interaction between segments (K)
υ^{00}	temperature-independent segment volume ($cm^3 \cdot mol^{-1}$)

Greek Symbols

κ^{AB}	volume of interaction between sites A and B
ϵ^{AB}/k	association energy interaction between sites A and B

Subscripts

c	critical
B	boiling point

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Received for review July 9, 2006. Accepted October 21, 2006. This work was supported by the National Science Foundation of China (Grants 20676014, 20676009, and 20576013) and the Liuxue Foundation of The Ministry of Education of China.

JE060310I