AN ASSOCIATION UNIFAC MODEL FOR AQUEOUS AND ALCOHOL SOLUTIONS OF SUGARS

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SUMMARY
In this work, a modified UNIFAC model [1] that explicitly takes into account association effects is applied to mixtures containing common sugars, alcohols and water.

Following the same strategy adopted before [2], four residual groups were defined to represent the sugars family: the pyranose ring (PYR), the furanose ring (FUR), the osidic bond (-O-) and the hydroxyl ring group (OH_{ring}) [2]. For the association term, a general two sites OH associating group is used to represent association effects in these solutions, allowing a straightforward extension to multicomponent mixtures. Correlation of both solvent activity properties (water activities, vapor pressures, boiling and freezing points of aqueous D-glucose and D-fructose solutions) and sugars (D-fructose, D-glucose and sucrose) solubility in water, ethanol and methanol give very good results. Satisfactory predictions are obtained for vapor-liquid equilibrium and solid-liquid equilibrium of ternary and quaternary mixtures of sugars in mixed solvents.

INTRODUCTION
The UNIFAC group contribution method has been used for the prediction of thermodynamic properties of mixtures containing sugars and polar solvents like water and alcohols [2-9].There is one UNIFAC model that explicitly takes into account hydrogen bonding: the physical chemical UNIFAC developed by Catté and coworkers [8], for aqueous solutions of sugars. The authors introduce a chemical part to model conformational and solvation equilibria between water and sugars. The physical part is given by the modified UNIFAC model proposed by Larsen et al. [10]. However, the fact that there is neither enough available information for the conformers composition in wide ranges of temperature, nor about the influence on that equilibrium of more than one solvent or sugar in the solution, makes the use of this method very difficult.

In this work, a modified UNIFAC model [1] is applied. This model was derived by adding an association term to the traditional UNIFAC residual and combinatorial contributions to the activity coefficients. The group association term is based on the Wertheim's theory for fluids with highly directed attractive forces [11-14]. This model was successfully used for the representation of phase equilibria in mixtures containing alcohols and water, by using the same hydroxyl OH associating group, to take into account hydrogen bonding in all alcohols and water. With this approach it is possible to solve the self- and cross-association problem present in multicomponent mixtures of alcohols, water and inert components, by solving a self-association problem that has an explicit solution for the activity coefficients as a function of the global mixture composition.

THE A-UNIFAC MODEL
a. Association term

It is known that sugars form hydrogen bonding with water and alcohols. In order to limit the number of adjustable parameters and keep the simplicity of the model, it was decided to use the same OH associating group already defined for alcohols and water. Then, for each sugar, the number of OH associating groups was set equal to the number of OH groups that are in equatorial position or not directly attached to a carbon ring. As result, no new association parameters were estimated from thermodynamic data of sugar mixtures.

b. Residual Term

The sugar molecules are decomposed in the following groups: pyranose and furanose ring PYR/FUR (with subgroups PYR1, PYR2, FUR1 and FUR2), the osidic bond (-O-) and the ring hydroxyl group (OH_{ring}) [2]. D-glucose and D-fructose are represented by the conformer in majority in water. For maltose and lactose, the structures that better represent the data were selected. Table 1 presents the structural groups considered in this work.

Table 1. Structural groups used in the A-UNIFAC model for sugars

	PYR1	PYR2	FUR1	FUR2	-O-	CH_3	CH_2	OH	OH_{ring}	H_2O
D-glucose	1	0	0	0	0	0	1	0	5	0
D-frutose	0	1	0	0	0	0	2	0	5	0
Lactose	0	0	2	0	1	0	4	0	8	0
Maltose	2	0	0	0	1	0	2	0	8	0
Sucrose	1	0	1	0	1	0	3	0	8	0
Water	0	0	0	0	0	0	0	0	0	1
Ethanol	0	0	0	0	0	1	1	1	0	0
Methanol	0	0	0	0	0	1	0	1	0	0

The experimental database included the one used by Peres and Macedo [6]. In order to estimate the interactions between the sugar groups (PYR-FUR and OH_{ring}) and the residual alcohol groups, ternary data of D-glucose in water/ethanol mixtures were added to increase the scarce available binary solubility data in alcohols. Also ternary data of sucrose in water/ethanol mixtures were used to estimate interactions between the alcohol groups and the osidic bond. Table 2 gives the interaction parameters obtained. Due to the lack of experimental data, the interactions between the FUR/PYR groups and the other groups were considered to be the same. Also, some interactions were set equal to zero.

Table 2. Interaction parameters.

	PYR/FUR	-O-	OHring	CH_2	OH	H_2O
PYR/FUR	0.0	0.0[a]	0.0[a]	-209.5	371.9	-118.6
-O-	0.0[a]	0.0	0.0[a]	748.5	0.0[a]	-311.2
OHring	0.0[a]	0.0[a]	0.0	250.3	461.2	-172.8
CH_2	-127.6	558.3	439.7	0.0	14.0[b]	381.9[b]
OH	-459.0.0	0.0[a]	36.3	125.9[b]	0.0	-333.6[b]
H_2O	89.9	86.1	110.8	220.0[b]	156.7[b]	0.0

a: set equal zero; b: estimated, in a previous work, using binary γ_∞, VLE and LLE data of mixtures containing water, n-alcohols and n-alkanes.

For the solid-liquid equilibrium calculations, some physical properties of the pure sugar are needed, namely, the melting temperature, enthalpy of fusion and the estimated two parameters ΔA and ΔB used to calculate the difference between the heat capacities of the pure solid and the pure liquid. These two parameters were estimated using solubility data of the corresponding sugar in water. The pure component data used in this work is presented in Table 3.

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ugars

	OH_{ring}	H_2O
)	5	0
)	5	0
)	8	0
)	8	0
)	8	0
)	0	1
I	0	0
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›H	H_2O
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).0[a]	-311.2
ı61.2	-172.8
4.0[b]	381.9[b]
ı.0	-333.6[b]
56.7[b]	0.0

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Table 3. Estimated ΔA and ΔB coefficients, number of associating groups ν^{OH} and experimental melting temperature T_m and enthalpy of fusion ΔH_f used to describe the solid-liquid equilibrium with the A-UNIFAC model.

Sugars	D-Glucose	D-Fructose	Sucrose	Maltose	Lactose
ΔH_f (J/mol)	32432[a]	32428[a]	46187[d]	43130[f]	75240[a]
T_m (K)	423.15[a]	378.15[a]	459.15[d]	438.15[e]	496.15[a]
ΔA(J mol^{-1} K^{-1})	122.30[b]	240.00[b]	410.08[b]	632.20[b]	225.19[b]
ΔB(J mol^{-1} K^{-2})	0[c]	0[c]	-2.5000[b]	-7.7691[b]	0.0000[b]
ν^{OH}	4	4	7	7	7

a: [16]; b: estimated; c: set equal zero; d: [5]; e: [17]; f: [18].

RESULTS AND DISCUSSION

Good results were obtained in the correlation of water activities, osmotic coefficients, vapor pressures, boiling and freezing points of D-glucose and D-fructose in water; solubilities of D-glucose, D-fructose, sucrose, maltose and lactose in water and solubilities of D-glucose and D-fructose in ethanol and methanol. Figure 1 shows the results for the solubility of D-glucose, D-fructose and sucrose in water. Figure 2 presents some of the results obtained for the freezing temperatures of binary mixtures of aqueous solutions of D-glucose and maltose.

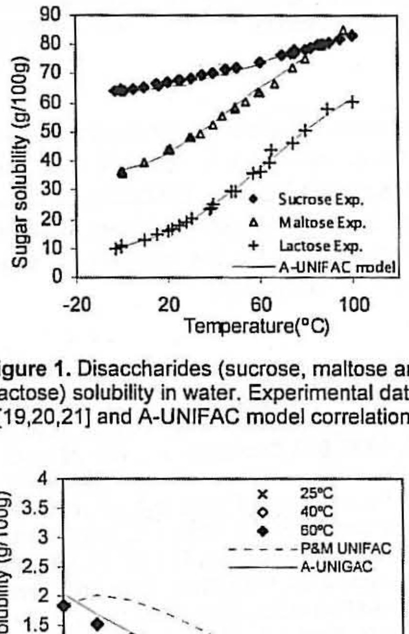

Figure 1. Disaccharides (sucrose, maltose and lactose) solubility in water. Experimental data [19,20,21] and A-UNIFAC model correlation.

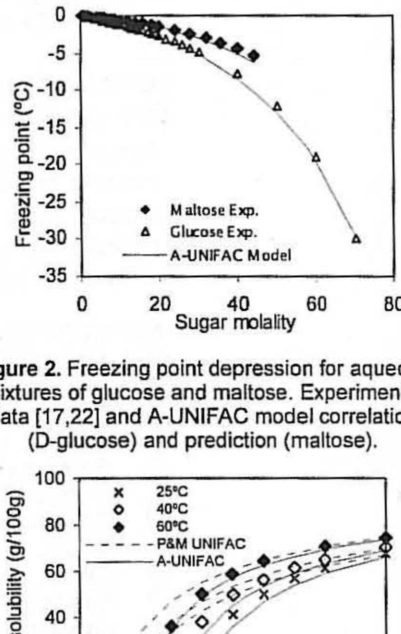

Figure 2. Freezing point depression for aqueous mixtures of glucose and maltose. Experimental data [17,22] and A-UNIFAC model correlation (D-glucose) and prediction (maltose).

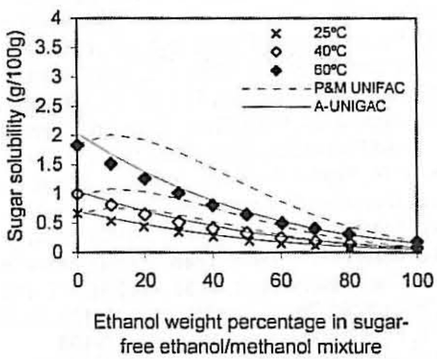

Figure 3. Experimental [23] and calculated sucrose solubility in ethanol/methanol mixtures.

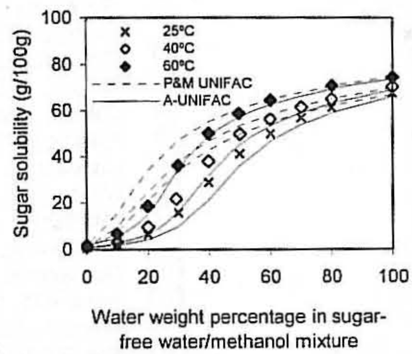

Figure 4. Experimental [23] and calculated sucrose solubility in ethanol/water mixtures.

Figures 3 and 4 show the predictions of the solubility of sucrose in mixed solvents using the A-UNIFAC model (for comparison, the results obtained with the P&M UNIFAC model are also presented).

Figure 5 shows the predictions, with the A-UNIFAC method, of the normal boiling point for a quaternary mixture of D-glucose, D-fructose and sucrose in water. Finally, on figure 6, the predictions for the water activities in binary mixtures of D-fructose-water and sucrose-water are presented. The predicted water activity for an apple juice (containing 14.8 wt% of D-glucose, 62.4 wt% of D-fructose and 22.7wt% of sucrose) is also shown.

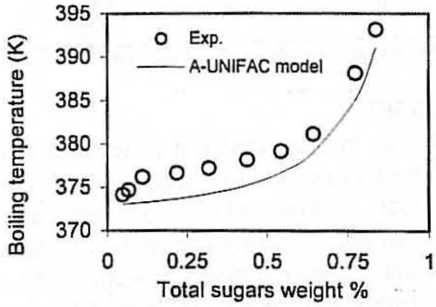

Figure 5. Experimental [24] and calculated normal boiling point of quaternary aqueous solutions of D-glucose, D-fructose and sucrose.

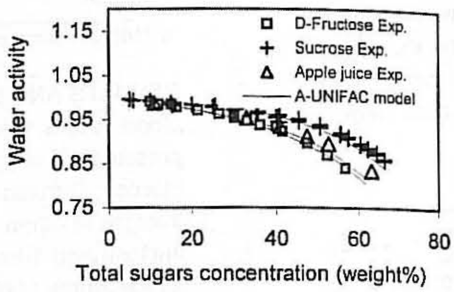

Figure 6.. Experimental [25-28] and calculated water activity for solutions containing D-fructose or sucrose and for an apple juice (14.8 wt% D-glucose, 62.4 wt% D-fructose,22.7wt% sucrose).

CONCLUSIONS

A modified UNIFAC that accounts explicitly for association effects was successfully applied to mixtures of sugars with water, ethanol and methanol. Good correlation results for binary data of mixtures of water and a sugar (D-fructose, D-glucose or sucrose) are obtained. Predictions for the solid-liquid equilibrium and vapor-liquid equilibrium of ternary and quaternary mixtures of the previous components in water and for the solubility of sugars in mixed solvents containing ethanol and methanol are very satisfactory.

REFERENCES

[1] Mengarelli A.C., Brignole E.A.and Bottini,S.B., Fluid Phase Equilibria, **1999**, 163, 195-207.

[2] Peres, A.M., Macedo, E.A., Fluid Phase Equilibria, **1997**, 139, 47-74.

[3] Achard C., Gros J. B., Dussap C.G., Ind. Agric. Aliment., **1992**, 109, 93-101.

[4] Gabas N., Laguérie C., 1990, Bull. Soc. Chim. Fr., 127, 391-395.

[5] Gabas N., Laguérie C., 1992, European Symposium on Computer Aided Process Engineering Communication - ESCAPE 2, Toulose, France, 5-7 October **1992**.

[6] Gabas N., Laguérie C., J. Crytal Growth, **1993**, 128, 1245-1249.

[7] Abed Y., Gabas N., Delia M. L., Bounahmidi T., Fluid Phase Equilibria, **1992**, 73, 175-184.

[8] Catté M., Dussap C.-G., Gros J.-B-, Fluid Phase Equilibria, **1995**, 105, 1-25.

[9] Spiliotis-N; Tassios-D, Fluid Phase Equilibria. **2000**, 173 (1), 39-55.

[10] Larsen B. L., Rasmussen P., Fredenslund Aa., Ind. Eng. Chem. Res., **1987**, 26, 2274-2286.

[11] Wertheim M., Journal of Statistical Physics, **1984**, 35(1/2), 19-34.

[12] Wertheim M., Journal of Statistical Physics, **1984**, 35(1/2), 35-47.

[13] Wertheim M., Journal of Statistical Physics, **1986**, 42(3/4), 459-476.

[14] Wertheim M., Journal of Statistical Physics, **1986**, 42(3/4), 477-492.

[15] Peres, A.M., Macedo, E.A., Fluid Phase Equilibria, **1996**, 123, 71-95.

[16] Raemy A., Schweizer T. F., J. Therm. Anal.,**1983**, 28, 95-108.

[17] Weast R.C. Ed., CRC Handbook of Chemistry and Physics, 53^{rd} ed., The Chemical Rubber Co., Cleveland, **1972-73**.

[18] Roos Y., Carbohydr. Res., 238, 39-48, **1993**.
[19] Young F. E., Jones F. T., J. Phys. Chem., **1949**, 53, 1334-1350.
[20] Mullin J. W., *Crystallisation*, Butterworths, 2ª Ed., Londres, **1972**.
[21] Stephen and Stephen, *Binary Systems*, Vol.I, Parts 1 and 2, Pergamon Press, Oxford,**1963**.
[22] Young F. E., J. Phys. Chem., **1957**, 61, 616-619.
[23] Peres, A.M., Macedo, E.A.,Carbohydr. Res., **1997**, 303, 135-151.
[24] Abderafi S., Bounahmidi T. , Fluid Phase Equilibria, **1994**, 93, 337-351.
[25] Rüegg M., Blanc B., Lebensm.-Wiss. u.-Technol., **1981**, 14, 1-6.
[26] Lerici C. R., Piva M., Rosa M. D., J. Food Sci., **1983**, 48, 1667-1669.
[27] Chuang L., Toledo R. T., J. Food Sci., **1976**, 41, 922-927.
[28] Fontán C. F., Chirife J., Boquet R., J. Food Technol., **1981**, 18, 553-559.
[29] Fontán C. F., Chirife J., 1981, J. Food Technol., **1981**, 16, 21-30.