

# Prediction of thermodynamic properties using a modified UNIFAC model: application to sugar industrial systems

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## Abstract

A modified UNIFAC model recently proposed in the literature is used to predict thermodynamic properties of aqueous solutions containing different sugars, commonly used in food industries (D-galactose, D-mannose, D-xylose, maltose and lactose), and for which the experimental information available is not sufficient in order to allow the application of UNIQUAC based models. Moreover, the new model is successfully extended to the prediction of the water activity of industrial sugar solutions (e.g., honey and fruit juices), which is used in quality control of foods and processed foods. A comparison with the results obtained from another UNIFAC based model for these solutions is also presented. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Carbohydrate solutions; Modified UNIFAC model; Sugar industrial solutions

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## 1. Introduction

Carbohydrate solutions are very important in several industries, mainly those related with the preservation of processed foods. In fact, sugars, poli-alcohols, and salts, among others, are commonly used in these industries to adjust the water activity and the pH, in order to reduce the growth of contaminated microorganisms [1].

A considerable number of deteriorative reactions occurring in different foods are related to the water activity value. For instance, in the case of honey, the crystallization of some sugars during its storage contributes to the decreasing of the concentration of the solute in the liquid phase, changing the water activity in the mixture. The concentration gradient resulting may lead to the local growth of osmophilic yeasts, and therefore to undesired fermentations [2]. Foods with high content of soluble

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solids, as fruits and juices, may be transformed in intermediate moisture foods (IMF) by concentration (drying, evaporation, freezing) of the soluble constituents, mainly sugars. The microbial and the physico-chemical stability of foods and the shelf life of IMF are highly dependent of both water activity (values between 0.65 and 0.90) and pH values.

Therefore, the prediction of this and other thermodynamic properties of sugar solutions is most relevant in food process development, allowing a better understanding of how food components interact with water. A modified UNIFAC group–contribution method developed recently and used with success to aqueous and non-aqueous sugar solutions [9], is used to describe experimental thermodynamic properties of different sugar mixtures of industrial and academic interest, as well as, experimental information concerning industrial sugar solutions (e.g., honey and juices [2–4]). Moreover, a comparison with the results obtained from other UNIFAC and UNIQUAC based models [5–8] is given.

## 2. Modified UNIFAC model

The modified UNIFAC model proposed in a previous study [9] is used in this work. The combinatorial contribution of this model is the one introduced by Larsen et al. [10] with the modification of Kikic et al. [11]. The equation for the residual contribution is the original one, as proposed by Fredenslund et al. [12]. Moreover it should be noticed that the groups used to build each sugar molecule ('PYR', 'FUR', '-O-' and 'OH<sub>ring</sub>') and the respective UNIFAC parameters are those given by Peres and Macedo [9], using a database that includes only experimental information for D-glucose, D-fructose and sucrose.

Table 1 gives the new UNIFAC groups from which the three sugar molecules included in this work (D-galactose, maltose and lactose) are built; for the other five sugars also studied (D-glucose, D-fructose, D-xylose, D-mannose and sucrose), the groups are the same adopted by Peres and Macedo [9].

## 3. Phase equilibria studies

Two kinds of phase equilibria of sugar aqueous systems are studied—vapor–liquid equilibria (VLE) and solid–liquid equilibria (SLE)—: water activities, osmotic coefficients, vapor pressures, freezing temperatures and solubilities in water.

Table 1  
UNIFAC functional groups present in sugar molecules

Sugars	UNIFAC groups						
	PYR1	PYR2	FUR1	FUR2	-O-	CH <sub>2</sub>	OH <sub>ring</sub>
D-Galactose	0	0	1	0	0	2	5
Lactose	0	0	2	0	1	4	8
Maltose	2	0	0	0	1	2	8

The equations needed to describe the VLE and SLE of aqueous solutions containing one or more sugars are the same used by Peres and Macedo [8]. However, it should be emphasized that, the equation used for the calculation of the solubilities of the sugars in water is based on the symmetric convention for the calculation of the activity coefficients, i.e., the pure liquid at the solution temperature is the standard state for the sugar, and it uses fusion enthalpy and melting temperature data for the sugars [13–15].

#### 4. Estimation of new $\Delta A$ and $\Delta B$ parameters for maltose and lactose

The cyclic structures of the new sugars studied in this work (D-galactose, D-mannose, D-xylose, maltose and lactose) can be represented by the UNIFAC groups available in the literature [9]. Therefore, the activity coefficients of these molecules in aqueous solutions can also be predicted using the UNIFAC parameters previously estimated [9]. So, in this work it was only necessary to optimize the  $\Delta A$  and  $\Delta B$  parameters of the sugars other than D-glucose, D-fructose and sucrose, whenever the experimental data available in the literature is sufficient enough to allow the estimation procedure.

Unfortunately, from the five new sugars studied, only for the two disaccharides, maltose and lactose, there is a number of experimental points that allows the estimation of the  $\Delta A$  and  $\Delta B$  parameters [16–18]. Therefore, for D-galactose, D-mannose, D-xylose, the respective  $\Delta A$  and  $\Delta B$  were set equal to zero. Table 2 presents the estimated parameters as well as the enthalpy and fusion temperature data needed for the calculations, which were estimated using a finite difference Levenberg–Marquardt algorithm.

#### 5. Results and discussion

Before discussing the results obtained in this work it seems important to make a brief comment regarding the groups chosen in this work to build the sugar molecules.

Seven of the eight sugars that are being studied (except sucrose) present conformational equilibria in solution and so, they exist as an equilibrium of different structures: pyranose and furanose rings. The model adopted in this work does not take into account the conformational equilibria, due to the lack of knowledge about the percentage of each anomer present at equilibrium in water or in other solvent mixtures, as previously discussed [9]. Therefore, it was necessary to establish the configuration of these sugars in solution. For D-glucose, D-fructose, D-mannose, D-xylose and sucrose this was already done taking into account the structure that allowed a better description of the thermodynamic

Table 2

Experimental data of the enthalpy ( $\Delta H_f$ ) and the temperature ( $T_f$ ) of fusion, and estimated  $\Delta A$  and  $\Delta B$  parameters for maltose and lactose

Sugars	Thermodynamic data			
	$T_f$ (K)	$\Delta H_f$ (J mol <sup>-1</sup> )	$\Delta A$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta B$ (J mol <sup>-1</sup> K <sup>-2</sup> )
Maltose	438.15 <sup>a</sup>	43130 <sup>c</sup>	626.9634 <sup>d</sup>	-8.3940 <sup>d</sup>
Lactose	496.15 <sup>b</sup>	75240 <sup>b</sup>	277.8296 <sup>d</sup>	-1.1099 <sup>d</sup>

<sup>a</sup>Weast [19]; <sup>b</sup>Raemy and Schweizer [13]; <sup>c</sup>Roos [15]; <sup>d</sup>Estimated parameters.

Table 3

Experimental information used: number of data points (1st line), temperature (2nd line) and concentration ranges (3rd line), for each system and property; and AAD values (4th line) calculated from the modified UNIFAC model and the UNIFAC model proposed by Gabas and Laguérie [6], respectively

Thermodynamic properties	Binary aqueous systems				
	D-Galactose	D-Mannose	D-Xylose	Maltose	Lactose
Water activity	n.a.	n.a.	n.a.	n.a.	4 <sup>f</sup> 25°C 0.03–0.25 mol kg <sup>-1</sup> 0.2%; 0.2%
Osmotic coefficient	18 <sup>a</sup> 25°C 0.1–3.5 mol kg <sup>-1</sup> 1.6%; 8.2%	23 <sup>b</sup> 25°C 0.1–6.0 mol kg <sup>-1</sup> 1.9%; 13.0%	9 <sup>c</sup> 25°C 0.56–3.5 mol kg <sup>-1</sup> 7.2%; 6.9%	32 <sup>d</sup> 25°C 0.1–3.0 mol kg <sup>-1</sup> 10.3%; 5.8%	n.a.
Vapor pressure	n.a.	n.a.	n.a.	n.a.	6 <sup>g</sup> 50 to 100°C 1.3–6.3 mol kg <sup>-1</sup> 0.9%; 1.9%
Freezing point (°C)	n.a.	n.a.	n.a.	22 <sup>e</sup> –0.03 to –5.4°C 0.01–2.3 mol kg <sup>-1</sup> 5.2%; 7.8%	19 <sup>h</sup> –0.02 to –1.03°C 0.01–1.6 mol kg <sup>-1</sup> 3.6%; 4.1%
Total	18 25°C 0.1–3.5 mol kg <sup>-1</sup> 1.6%; 8.2%	23 25°C 0.1–6.0 mol kg <sup>-1</sup> 1.9%; 13.0%	9 25°C 0.56–3.5 mol kg <sup>-1</sup> 7.2%; 6.9%	54 –0.03 to 25°C 0.01–3.0 mol kg <sup>-1</sup> 8.3%; 6.2%	29 –0.02 to 100°C 0.01–6.3 mol kg <sup>-1</sup> 2.6%; 3.1%

n.a. Not available; <sup>a,b</sup>Miyajima et al. [20]; <sup>c,d</sup>Uedaira and Uedaira [22], <sup>d</sup>Miyajima et al. [21]; <sup>e</sup>Weast [19]; <sup>f</sup>Lerici et al. [4]; <sup>g,h</sup>Hudson [16], <sup>h</sup>Weast [19].

data available in the literature [9]. This same philosophy was used to fix the structures of D-galactose, maltose and lactose in solution (Table 1).

A similar procedure has been followed in order to use the UNIFAC model proposed by Gabas and Laguérie [5,6]. In these works four new UNIFAC groups were proposed ('G', 'F', 'X' and '-O-') and the related new interaction parameters were estimated from solubility experimental data for binary and ternary systems containing D-glucose (G-OH), D-fructose (F-OH), D-xylose (X) and sucrose (G-O-F). Since for this model there were also different possibilities to represent the other sugar molecules, it was decided to choose the one that allows a better agreement between experimental and predicted values: D-mannose (X-CH<sub>2</sub>-OH), D-galactose (X-CH<sub>2</sub>-OH), maltose (G-O-F), and lactose (G-O-F).

It should also be remarked that a comparison between the results obtained with the modified UNIFAC model and those calculated by means of other models available in the literature is performed whenever possible. Moreover, for the literature UNIQUAC based models [7,8] this kind of comparison is only possible for systems containing D-glucose, D-fructose and sucrose, since for the other sugars treated in this work the sugar/water interaction parameters are not available.

### 5.1. Correlation results

The modified UNIFAC model [9] together with the new  $\Delta A$  and  $\Delta B$  parameters estimated here, were able to describe accurately the experimental solubility data [16–18] available in the literature, for the systems maltose/water (with an AAD of 1.8%) and lactose/water (with an AAD of 1.4%).

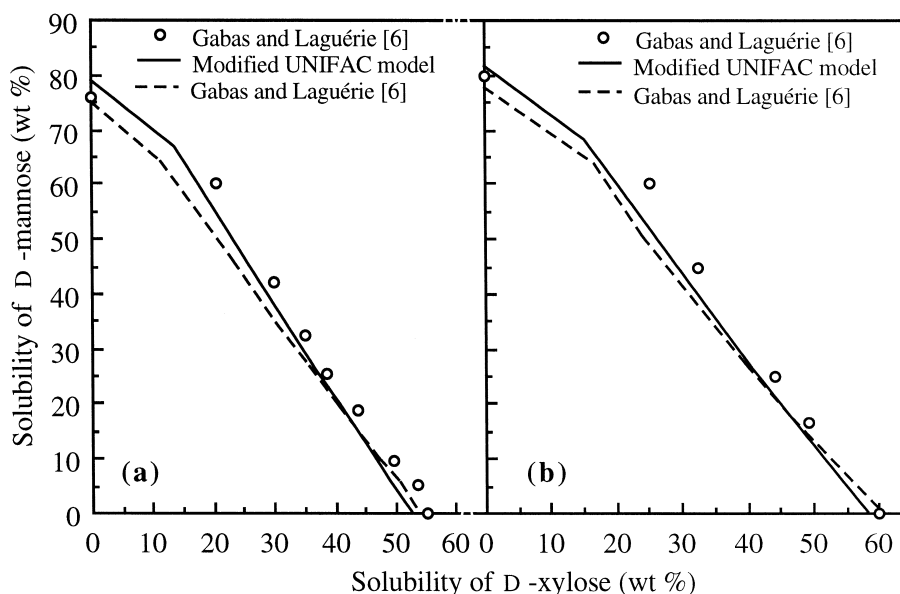


Fig. 1. SLE for D-xylose/D-mannose/water at (a) 25°C and (b) 35°C: comparison between experimental data and predicted values from different models.

However, the model proposed by Gabas et al. [5,6] completely fails when trying to predict these experimental data: AADs equal to 26.0 and 50.5% for maltose and lactose, respectively. For this model, the pairs of experimental fusion data used were those of Roos [15] and Weast [19] for maltose; and the ones of Raemy and Schweizer [13] for lactose.

## 5.2. Prediction results

The predictive capabilities of the modified UNIFAC model are tested using three kinds of available experimental data: (i) water activity, osmotic coefficient, vapor pressure and freezing point of aqueous sugar solutions containing D-galactose, D-mannose, D-xylose, maltose and lactose; (ii) solubility of D-xylose and D-mannose in water; and (iii) water activity in industrial mixtures (juices and synthetic honey).

From the point of view of colligative properties, fruit juice concentrates and synthetic honey can usually be considered as a mixture of D-glucose, D-fructose, sucrose and water, or of these components and maltose, respectively [2,3]. Therefore, thermodynamic models developed for sugar solutions can be easily applied to the prediction of important properties of these industrial mixtures. In this work, the water activity of juices and honey solutions is predicted. The importance of this fact is due since this thermodynamic property is industrially used as an indicator of the quality of foods and processed foods.

### 5.2.1. Sugar / water solutions

Four thermodynamic properties (water activity, osmotic coefficient, vapor pressure and freezing temperature) of aqueous D-galactose, D-mannose, D-xylose [20], maltose [19,21,22] and lactose [4,16,19] mixtures have been satisfactorily predicted using the model proposed by Peres and Macedo [9]. Moreover, the results given in Table 3 clearly show that this model gives, in general, a better prediction than the UNIFAC model proposed by Gabas and Laguérie [6].

### 5.2.2. Sugars / water solutions

The modified UNIFAC model has been already successfully used for the prediction of SLE of sugars/water systems [9]: D-glucose/sucrose/water and D-fructose/sucrose/water [23]. In this work, this model is used to accurately predict the solubilities of D-xylose and D-mannose in water [6]. A comparison with the results obtained with the model proposed by Gabas and Laguérie [6] is also performed, and clearly indicates that, although this model [6] was developed using experimental data

Table 4  
Sugar proportions in fruit juices

Fruit juices	Proportion of each sugar (g sugar/100 g sugars)		
	D-Fructose	D-Glucose	Sucrose
Grape	35.8	64.2	0.0
Apple	62.4	14.8	22.7

Table 5

Water activities in apple and grape juices: comparison between experimental data and models predictions

Models	Water activity	
	Apple juice (AAD, %)	Grape juice (AAD, %)
UNIQUAC model (Catté et al. [7])	0.12	0.39
Modified UNIQUAC model (Peres and Macedo [8])	0.32	0.41
UNIFAC model (Gabas and Laguérie [6])	1.26	0.57
Modified UNIFAC model (Peres and Macedo [9])	0.34	0.37

of D-xylose, the modified UNIFAC model gives better predictions—Fig. 1. This conclusion is identical to that found in a previous work [9], regarding the prediction of SLE data of D-xylose and D-mannose in water/ethanol mixtures.

### 5.2.3. Industrial sugar mixtures

The modified UNIFAC model was used to predict the water activities of some sugar solutions of industrial interest: fruit juice concentrates and synthetic honey. As was already discussed, since these solutions can be well represented by mixtures of sugars and water, the application of UNIFAC based models is easy and direct.

Fruit juices, e.g., lemonade, orange, prune, grape, apple, pineapple, may be considered as a mixture of two or three sugars (D-glucose, D-fructose and sucrose) and water. Table 4 shows the sugar proportions in apple and grape juices. Since for these common sugars there are UNIQUAC parameters available in the literature [7,8] it has been possible to extend the comparison. The results obtained show that the four models investigated are able to accurately predict the water activities in apple and grape juices at 25°C [3,4] (Table 5) for a total sugar concentration between 10 and 60 wt.%.

The UNIFAC based models were also used for the prediction of the water activities of synthetic honey at 25°C [2], for a total sugar concentration between 72 and 84 wt.%. Since this industrial

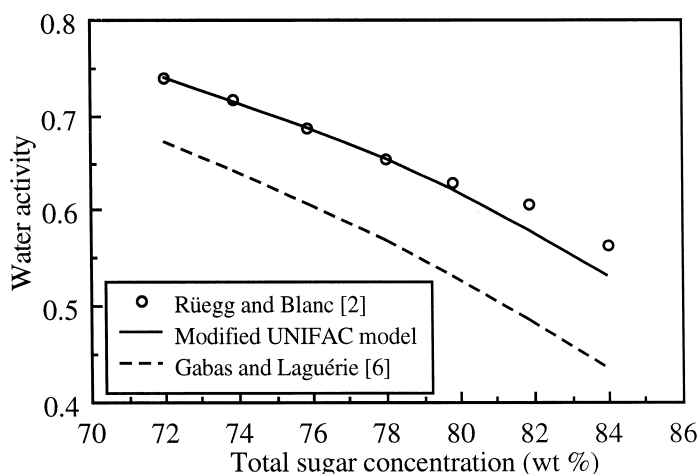


Fig. 2. Water activities in synthetic honey at 25°C: comparison between modeling results and experimental data.

solution can be represented by an aqueous mixture of D-glucose, D-fructose, maltose and sucrose—proportion of each sugar (g sugar/100 g sugars): 48%, 40%, 10% and 2% respectively—, only these two models can be applied to this kind of mixtures, as already discussed. The calculated results show that only the model proposed by Peres and Macedo [9] is able to correctly predict this thermodynamic property for honey, with an AAD of 1.7%, against the 14.6% obtained with the model of Gabas and Laguérie [6].

The better performance of the modified UNIFAC model is clear from the observation of Fig. 2.

## 6. Conclusions

The modified UNIFAC model proposed in a previous work [9] is used with good achievement for the correlation and prediction of experimental thermodynamic properties of aqueous sugar solutions. The capability to describe VLE and SLE of sugar systems for which the reduced number of experimental data does not allow the application of UNIQUAC models constitutes a significant advantage. Moreover, it has been shown that this new model is more accurate than the other UNIFAC based model available in the literature, being a considerable improvement. It should also be noticed that for the first time this kind of models are applied with success to the prediction of important thermodynamic properties of sugar mixtures of industrial interest (e.g., concentrated fruit juices) being the modified UNIFAC model the only one that may be accurately extended to the description of the water activity of honey solutions.

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