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Solid–liquid equilibrium of α -lactose in ethanol/water

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Abstract

Solubilities of α -lactose in water–ethanol solvent mixtures were obtained using an accurate analytical method, at 25, 40 and 60°C in a concentration range from 0 to 100 sugar-free wt.% of water. The α -lactose solubility is a strong function of the water concentration in the solvent mixture. It increases monotonically with temperature and with water concentration. The experimental data were correlated using a UNIQUAC-based model and were predicted using two different UNIFAC-based models. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: α -Lactose; Data; Modified UNIQUAC; Modified UNIFAC

1. Introduction

Carbohydrate solutions are important in a variety of areas, such as biological and food industries. They are often involved in crystallization processes. An increased interest in systems containing the biological molecules found in carbohydrate solutions has made evident the need for both, experimental information on thermodynamic properties of mixtures containing sugars, and proper thermodynamic models able to represent them.

In spite of the well recognized importance of sugar-containing systems, as demonstrated by the growing number of publications on the subject [1–7], there is still a lack of experimental information on the solid–liquid equilibrium of aqueous and non aqueous multicomponent solvent mixtures containing common sugars. These systems are present in many processes in the food, chemical and pharmaceutical industries.

A variety of approaches are available for modeling these highly complex systems. The UNIQUAC model [8] was used by Le Maguer [9] to describe only the excess Gibbs energy and excess enthalpy of five binary aqueous carbohydrate systems. Catté et al. [10] applied the modified UNIQUAC model [11]

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to correlate eight different thermodynamic properties of three binary water/sugar systems and to predict the osmotic coefficient and water activity of two sugars in aqueous solutions at 25°C. However, the use of the unsymmetric convention by Catté et al. [10] hinders the application of their model in the case of mixed solvents. Peres and Macedo [12] proposed a modified UNIQUAC model that is able to correlate and predict vapor–liquid and solid–liquid equilibria of aqueous solutions containing more than one sugar.

The solubility of a single sugar in mixed solvents has been the focus of some contributions too. Bockstanz et al. [3] used a Redlich–Kister equation, in a purely empirical way, to correlate the solubility of D-glucose in water–ethanol mixtures at 35°C. Based on their earlier work [12], Peres and Macedo [6] proposed three UNIQUAC-based models for the solubility of sucrose and D-glucose in mixed solvents.

Also, a number of predictive group-contribution methods have been proposed to describe this kind of systems. Achard et al. [13], used the modified UNIFAC [11] model to predict water activities, boiling temperatures and freezing points of one or more sugars in water. Because this model uses the original UNIFAC group definitions, it is not capable to represent sugar solubilities accurately enough. The representation of sugar solubilities at a quantitative level requires the definition of special groups for sugar molecules (e.g. [14,15]).

Abed et al. [14] and Gabas and Laguérie [15], defined new groups for the UNIFAC model [16] and estimated new interaction parameters from binary and ternary solubility data. They used these parameters to predict solid–liquid phase equilibria in ternary systems of two sugars in water at a fixed temperature (25 or 70°C). Catté et al. [17], proposed a new model which, using a modified UNIFAC equation [11], makes possible to discriminate between carbohydrate isomers. These authors used this model to describe some thermodynamic properties of seven water/sugar systems. The limitations of this approach have been discussed elsewhere [18]. Peres and Macedo [18,19], proposed a modified UNIFAC model to predict thermodynamic properties of systems containing water and/or non-aqueous solvents, and one or more sugars. More recently, Spiliotis et al. [20] presented, without providing information on the values of the interaction parameters, a new UNIFAC approach for the description of partition coefficients of sugars in solvent mixtures.

α -Lactose is the major sugar in milk and is widely used in industry. The α -lactose is used as an alternative sweetening agent for sucrose. It is also used as a solid support for active substances in pharmaceutical formulations. Crystallization of α -lactose is a potential route for α -lactose removal from food products specially aimed to people suffering from lactose-intolerance. There is a lack of data concerning properties of α -lactose in a single or mixed solvents solutions [1,21–24]. The optimization and design of new processes in the industry requires knowledge of solid–liquid and liquid–vapor equilibria for these mixtures. In this work solid–liquid equilibrium data for α -lactose in mixtures of water and ethanol at 25, 40 and 60°C have been obtained, using a simple and accurate analytical apparatus. These solubility experimental data were correlated with the modified UNIQUAC model proposed by Peres and Macedo [6,12], and were compared with predictions obtained from a modified UNIFAC method by the same authors [18,19] and from the UNIFAC model by Gabas and Laguérie [15]. From the discussion in previous paragraphs these are the most suitable models for the problem of interest here.

2. Experimental

2.1. Materials

For the solubility measurements deionized water, supplied by Paracélcia, Porto, Portugal and ethanol with a minimum purity of 99.8% vol. supplied by Merk, Germany were used. The monohydrated α -lactose

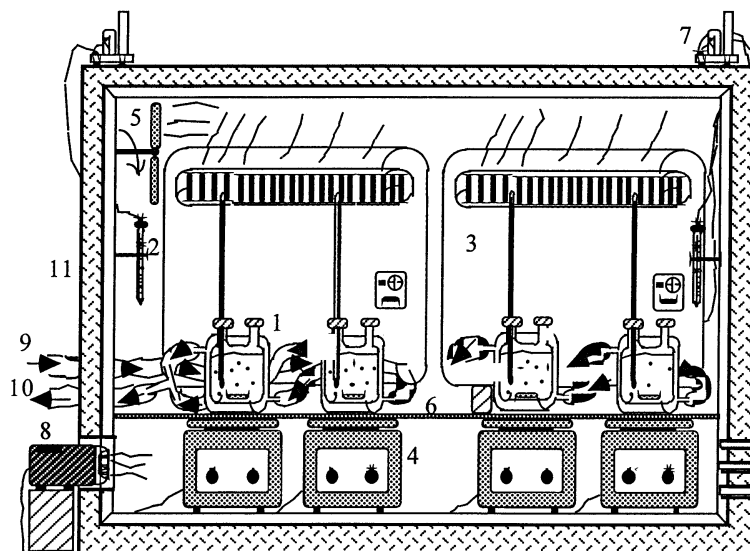


Fig. 1. Schematic representation of the experimental apparatus. 1 – Equilibrium cell; 2 – Contact thermometer; 3 – Heater; 4 – Magnetic stirrer; 5 – Fan; 6 – Insulating block; 7 – Controller; 8 – Cooling fan; 9 – Thermostated water entrance; 10 – Thermostated water exit; 11 – Insulated box.

used was supplied by Sigma (L8783), Spain, with a minimum purity of 99.5%, and dried in a vacuum oven at 55°C before being used.

2.2. Solubility-apparatus and procedure

The solubility of α -lactose in ethanol–water mixtures was determined according to an isothermal method, described in detail previously [5,6]. It is well-known [18,19] that at equilibrium α -lactose can be partially converted to β -lactose. The conversion degree depends on temperature and solvent composition. In our experiments we did not track this complicated phenomenon. Hence, the solubilities reported in this work are characterized by the described experimental technique. Some conversion from α -lactose into β -lactose must have surely taken place. Therefore, the solubilities given here have to be regarded as effective α -lactose solubilities.

Fig. 1 presents a schematic representation of this apparatus. Four jacketed glass cells of about 80–100 cm³ each are loaded with different ethanol–water mixtures. Each mixture is prepared by weighing the desired amount of each solvent in a 0.1 mg precision balance. Once the desired temperature is reached by the system, dried α -lactose is added to the solution in a small excess over the expected solubility.

The temperature in each cell is controlled by thermostated water circulating through the jacket and can be considered to be accurate within ± 0.1 K.

At constant temperature, the liquid and solid phases are stirred for 48 h and allowed to stand for about 24 h to enable any finely dispersed solids to settle down. All four glass cells are kept inside an insulated box, specially projected with the purpose of maintaining the air temperature inside it constant. In this way it was possible to keep the temperature at the desired value during all the experiments.

The sampling procedure is as follows. From each equilibrium cell, samples of the clear supernatant liquid are carefully withdrawn using pipettes with a slightly higher temperature than the solution temperature in order to avoid any precipitation. The solubility is determined by slow evaporation of the solvent mixture from a previous weighed sample of the saturated solution (5–10 cm³) and by weighing the precipitated sugar regularly until a constant value is achieved. The drying procedure has two steps: first the sample is allowed to dry slowly at ambient temperature to avoid the loss of any solid until the majority of the solvent mixture has been evaporated. Then, the remaining sample is dried in a vacuum oven at 55°C. Each experimental point is an average of three different results obeying to one of the following criteria: if the experimental solubility is <0.2 wt.% then the maximum deviation allowed (from the average), must be <3%; if the experimental solubility is between 0.2 and 10 wt.%, then the standard deviation (σ) of the three measurements should be <0.005; for solubilities higher than 10 wt.%, then 2σ /solubility should be <0.001 [25].

3. Modeling

3.1. Phase equilibria

Two kinds of phase equilibria of sugar-containing systems are studied: vapor–liquid equilibria (VLE) and solid–liquid equilibria (SLE). The properties considered are water activity, vapor pressure, freezing temperature and sugar solubility either in pure water or in mixtures of ethanol and water.

The equations needed to describe the VLE and SLE are those used by Peres and Macedo [12]. We repeat here, the equation to calculate the solubility of α -lactose in water or in mixed solvent mixtures:

$$\ln(x_{\text{sug}}\gamma_{\text{sug}}) = \left[-\frac{\Delta H_f}{R} + \frac{\Delta C_p}{R}T_m + \frac{\Delta B}{2R}(T_m)^2 \right] \left(\frac{1}{T} - \frac{1}{T_m} \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T}{T_m} \right) + \frac{\Delta B}{2R}(T - T_m) \quad (1)$$

with

$$\Delta C_p = \Delta A + \Delta B(T - T^0) \quad (2)$$

where x_{sug} and γ_{sug} are respectively, the sugar mole fraction and the sugar activity coefficient; R the universal gas constant and T the mixture temperature; T^0 is an arbitrary temperature which was, in this work, set equal to 298.15 K; T_m the melting temperature of the sugar; ΔH_f is the enthalpy of fusion of the sugar at T_m ; and ΔA and ΔB are two temperature independent parameters that allow the calculation of the difference between the heat capacities (ΔC_p) of the pure sugars in the liquid and the solid phase, assumed to be a linear function of the temperature in the range $[T - T_m]$.

The activity coefficients needed for the calculation of the solubilities were, in this work, evaluated using a modified UNIQUAC model and two UNIFAC based methods.

3.2. Modified UNIQUAC model

The modified UNIQUAC model proposed in a previous study [6,12] was used. Accordingly, the activity coefficient can be obtained from the following equations:

$$\ln(\gamma_i) = \ln(\gamma_i^C) + \ln(\gamma_i^R) \quad (3)$$

The combinatorial contribution used is the same proposed by Larsen et al. [11], and is defined as:

$$\ln(\gamma_i^C) = \ln\left(\frac{\varphi_i}{x_i}\right) + 1 - \frac{\varphi_i}{x_i} \quad (4)$$

where φ_i is a modified molecular volume fraction of component i :

$$\varphi_i = \frac{x_i(R_i)^{2/3}}{\sum_j x_j(R_j)^{2/3}} \quad (5)$$

R_i is the volume parameter of component i , and x_i is the mole fraction.

The residual contribution is the same as in the original UNIQUAC equation [8] with the same linear temperature dependency for the interaction parameters introduced by Hansen et al. [26]:

$$a_{ij} = a_{ij}^0 + a_{ij}^t(T - T^0) \quad (6)$$

a_{ij}^0 and a_{ij}^t are two temperature independent parameters, T is the system temperature in Kelvin; and T^0 is a reference temperature, which was set to 298.15 K.

3.3. Modified UNIFAC models

The modified UNIFAC method proposed by Peres and Macedo [18,19] was also used in this work. The combinatorial term is the same suggested by Larsen et al. [11]. According to the definition of groups in this model, α -lactose is constituted by two FUR1 groups, eight OH_{ring} groups, four CH₂ groups and one –O– group [19]. The residual contribution is the original one, proposed by Fredenslund et al. [16]. All UNIFAC parameters used here for α -lactose/ethanol/water calculations were those of Peres and Macedo [18,19].

For comparison purposes, the UNIFAC method proposed by Gabas and Laguérie [15] was also used. These authors used the same combinatorial and residual expressions from the original UNIFAC model [16]. The calculations with this model were performed using the same groups, UNIFAC parameters, volume and surface area parameters, and enthalpies and temperatures of fusion defined and/or estimated by those authors [14,15,27]. Thus, α -lactose is built up with the groups G, O and F introduced in their work, as already pointed out [19].

4. Results and discussion

4.1. Experimental results

The data on the solubility of α -lactose in water–ethanol solvent mixtures and the corresponding standard deviations are presented in Tables 1–3. Fig. 2 shows the experimental ternary phase diagram for the system α -lactose/ethanol/water at the three temperatures studied. It can be seen that the solubility increases monotonically both with water concentration and with temperature.

Table 1
Experimental data of α -lactose solubility in water–ethanol mixtures at 25°C

%m water ^a	Solubility (g/100 g solution)	σ^b
20.035	0.0536	0.001
30.053	0.3343	0.002
40.084	0.5695	0.001
50.004	1.7835	0.003
59.957	3.2782	0.005
70.048	5.2428	0.005
80.041	8.5048	0.002
90.063	13.2557	0.005
100.000	18.9049	0.008

^a %m is the water mass percentage in the sugar-free solvent mixture.

^b σ is the standard deviation of the experimentally measured α -lactose weight percentage.

4.2. Modeling results

4.2.1. UNIQUAC model

4.2.1.1. Lactose/water system. The temperature-dependent interaction parameters for the binary system α -lactose/water, and ΔA and ΔB for α -lactose were estimated simultaneously based on α -lactose/water experimental data of diverse nature, according to Table 4.

The volume (R_i) and the surface area (Q_i) parameters for the α -lactose, water and ethanol are presented in Table 5. They were calculated using the size parameters of the groups involved in each molecule and these were taken from the UNIFAC parameter tables [28].

The regressed UNIQUAC parameters are presented in Table 6. The ΔA and ΔB values estimated are shown in Table 7, together with the enthalpy of fusion and the melting temperature values used in this work. The values for these two properties were taken from Peres and Macedo [19].

Table 2
Experimental data of α -lactose solubility in water–ethanol mixtures at 40°C

%m water ^a	Solubility (g/100 g solution)	σ^b
0.000	0.0111	0.0002
10.076	0.0595	0.001
20.077	0.2213	0.003
30.155	0.6955	0.004
40.036	1.7382	0.003
50.089	3.6248	0.001
60.006	6.0474	0.005
69.995	10.004	0.005
80.039	14.6029	0.007
90.065	20.1463	0.029
100.000	25.1484	0.007

^a %m is the water mass percentage in the sugar-free solvent mixture.

^b σ is the standard deviation of the experimentally measured α -lactose weight percentage.

Table 3
Experimental data of α -lactose solubility in water–ethanol mixtures at 60°C

%m water ^a	Solubility (g/100 g solution)	σ^b
0.000	0.0270	0.0003
10.023	0.0919	0.0001
20.001	0.4732	0.002
29.991	1.6093	0.004
40.172	4.1926	0.002
49.989	8.4758	0.003
60.044	14.3462	0.007
70.108	20.7072	0.009
79.982	27.3234	0.010
89.958	33.6975	0.011
100.000	37.2149	0.012

^a %m is the water mass percentage in the sugar-free solvent mixture.

^b σ is the standard deviation of the experimentally measured α -lactose weight percentage.

The correlation results obtained with the modified UNIQUAC model compare favorably with the experimental data available in the literature for the binary system studied. Table 4 shows that the model is able to describe the properties with a maximum AAD value smaller than 2%. This can also be seen from Figs. 3–6, where the model results are compared with experimental data for the four properties used for fitting the parameters.

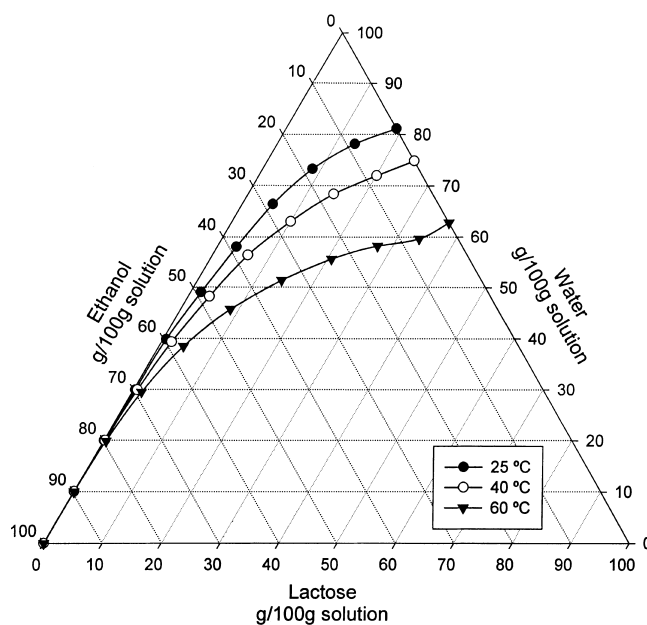


Fig. 2. Experimental ternary phase diagram for the system α -lactose/ethanol/water.

Table 4
Experimental information on α -lactose/water used for the UNIQUAC model

Thermodynamic properties	NDE ^c	Temperature range (°C)	Concentration range	AAD (%) ¹
Water activity ^a	4	25	0.0295/0.2543 (mol kg ⁻¹)	0.189
Vapor pressure ^b	6	50/100	0.0224/0.1023 mole fraction	0.708
Freezing temperature ^c	19	-1.03/-0.02	0.341/16.134 (g/100 g solution)	1.914
Solubility ^d	25	-3/100	10.09/61.027 (g/100 g solution)	1.637
Total	54			

^a Lericci et al. [21];

^b Hudson [22];

^c Hudson [22], Weast [24];

^d Stephen and Stephen [1], Hudson [22], Mullin [23], this study.

^e This is given by

$$\text{AAD}(\%)^1 = \frac{\sum_n |(V_n^{\text{exp}} - V_n^{\text{calc}})/(V_n^{\text{exp}})|}{\text{NDE}} \times 100;$$

where NDE is the number of data points, V is any of the properties of the first column of the table.

Table 5
Structural parameters (R_i and Q_i) for the α -lactose, water and ethanol

	R_i	Q_i
α -Lactose	12.5265	12.2280
Water	0.9200	1.400
Ethanol	2.5755	2.588

4.2.1.2. *Lactose/ethanol/water system.* Using the α -lactose/water parameters obtained in the first step, the UNIQUAC interaction parameters for the pairs α -lactose/ethanol and water/ethanol were estimated from the measured data for α -lactose/water/ethanol at 25, 40 and 60°C. Only the data measured in this work were used, since, to our knowledge, no other experimental information for phase equilibria of α -lactose in mixed solvents is available. The interaction parameters were considered to be temperature independent (e.g. a_{ij}^t in Eq. (6) equal to zero). Table 6 also presents the fitted interaction parameters for the

Table 6
New UNIQUAC parameters for all the components of the system α -lactose in water–ethanol mixtures: first row a_{ij}^0 in Kelvin; second row a_{ij}^t

i/j	Interaction parameters		
	α -Lactose	Ethanol	Water
α -Lactose	0.000	-7.666	11.853
	0.000	0.000	1.455
Ethanol	163.58	0.000	-351.37
	0.000	0.000	0.000
Water	11.529	391.18	0.000
	-1.422	0.000	0.000

Table 7

Values of ΔA and ΔB estimated and values of fusion enthalpy and melting temperature, for α -lactose, used in this work

Thermodynamic data	α -Lactose
T_f (K)	223.00
ΔH_f (J mol ⁻¹)	75240.00
ΔA (J mol ⁻¹ K ⁻¹)	182.4097
ΔB (J mol ⁻¹ K ⁻²)	0.9809

pairs α -lactose/ethanol and ethanol/water. It is worth mentioning that the available UNIQUAC parameters, published by Gmehling and Onken [29], for ethanol/water were not used here. In fact, as shown by Peres and Macedo [5], although they may lead to satisfactory results, they present two major disadvantages: (a) none of the parameters given by Gmehling and Onken [29] was estimated simultaneously at the experimental pressure and temperature conditions of the present experimental study, i.e., ambient pressure and temperatures from 25 to 60°C; (b) in the books by Gmehling and Onken [29] it is possible to find 55 different pairs of values for the ethanol/water interaction parameters. Hence, the choice of the optimum pair to be used here becomes very difficult. Fig. 7 presents a comparison between the experimental data and the correlation results obtained with the modified UNIQUAC model. The AAD (%) values for the solubilities in Fig. 7 are 14.7, 11.0 and 9.0% for 25, 40 and 60°C, respectively. It is possible to conclude

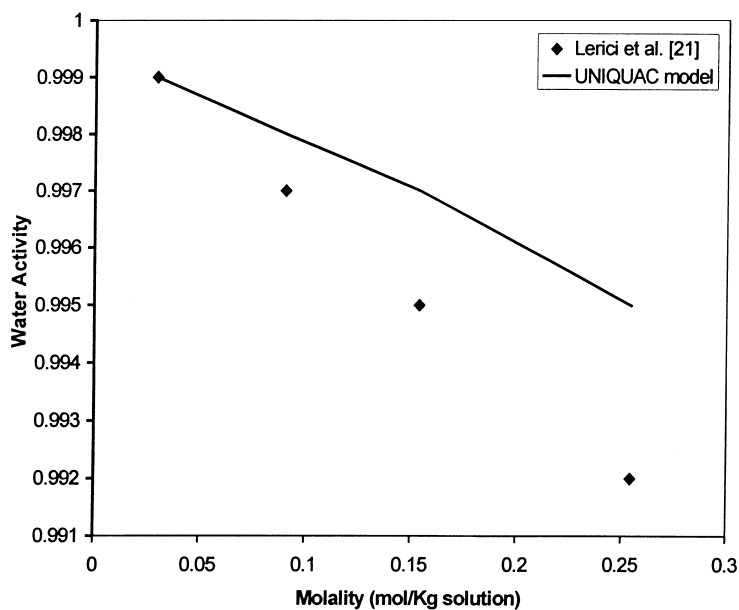


Fig. 3. Water activity: comparison between modeling results with the modified UNIQUAC model and experimental data for the α -lactose/water system.

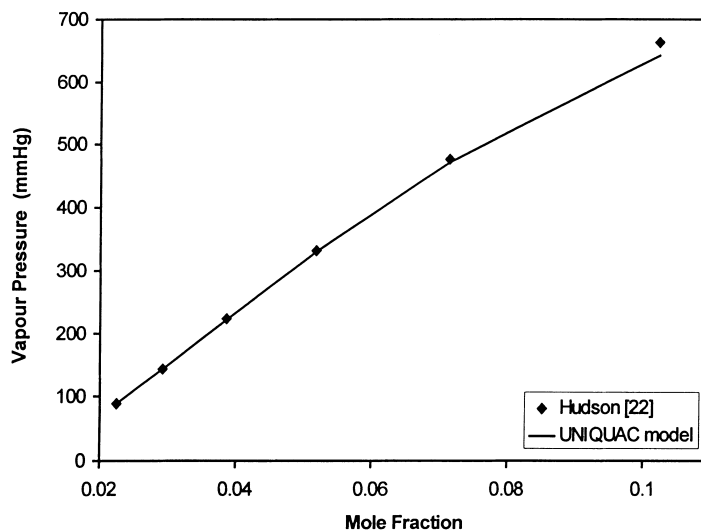


Fig. 4. Vapour pressure: comparison between modeling results with the modified UNIQUAC model and experimental data for the α -lactose/water system.

that the model gives acceptable results for this system. The description of the experimental data is only fair because the α -lactose/ethanol interaction parameters were set independent from temperature. However, the number of experimental data points available does not justify the introduction of a temperature dependent parameters, as in the case of α -lactose/water.

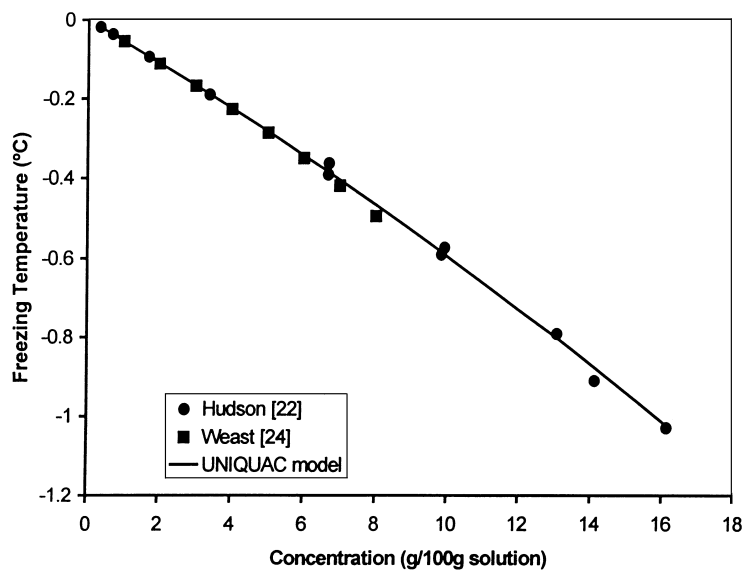


Fig. 5. Freezing temperature: comparison between modeling results with the modified UNIQUAC model and experimental data for the α -lactose/water system.

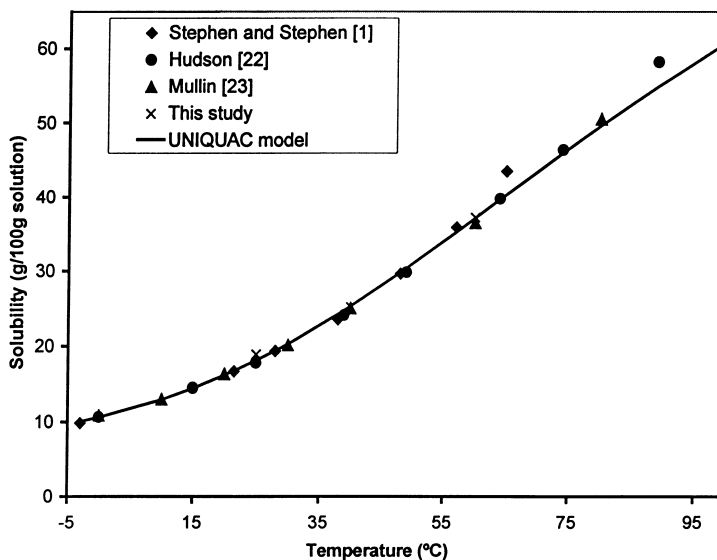


Fig. 6. Solubility: comparison between modeling results with the modified UNIQUAC model and experimental data for the α -lactose/water system.

4.2.2. UNIFAC models

The experimental ternary data for α -lactose/ethanol/water at 25, 40 and 60°C were predicted using the modified UNIFAC model proposed by Peres and Macedo [18,19]. The groups definition for α -lactose, as well as all the information needed to carry out the calculations are available elsewhere [18,19].

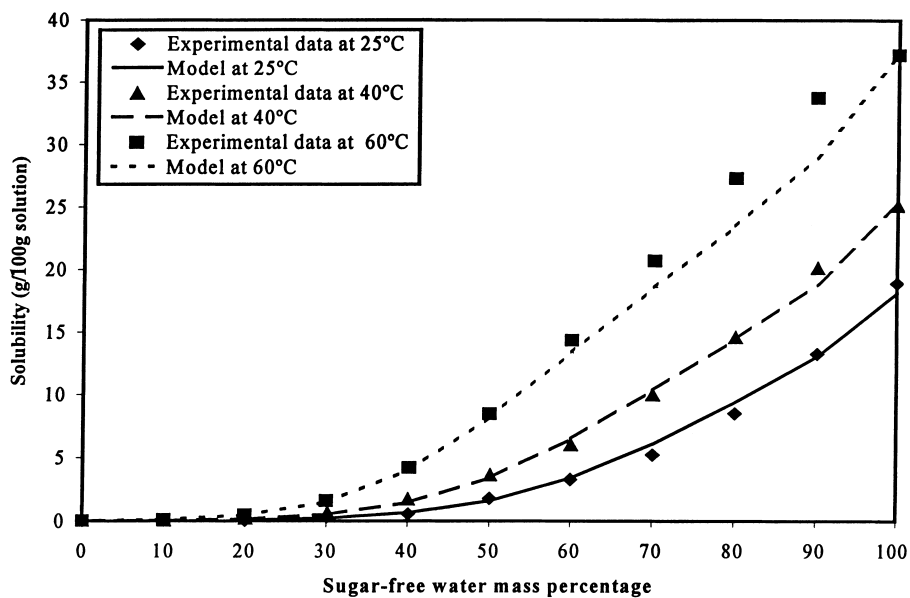


Fig. 7. Correlated and experimental results for α -lactose/water/ethanol system at 25, 40 and 60°C.

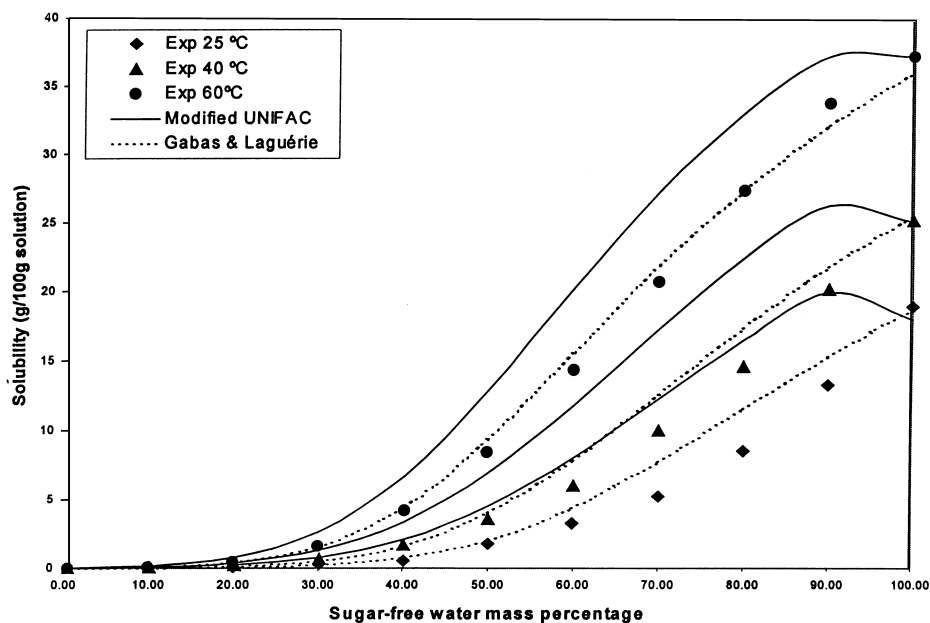


Fig. 8. Predicted and experimental results for α -lactose/water/ethanol system at 25, 40 and 60°C.

The predictive performance of the UNIFAC model proposed by Gabas and Laguérie [15] was also tested.

A comparison between the experimental data and the predictions from the two models is given in Fig. 8. Table 8 shows the corresponding values of AAD (%). It can be seen that the model of Gabas and Laguérie [15] gives lower deviations than the model of Peres and Macedo [18,19]. One of the possible reasons for the better performance of the model of Gabas and Laguérie [15] could be the fact that the model parameters were regressed from both binary and ternary data, while Peres and Macedo [18,19] only used binary data for the parameter estimation. The model of Peres and Macedo [18,19] predicts a maximum in solubility at high sugar-free water concentration. Though a solubility maximum has no actual existence for the system of Fig. 8, the presence of maxima in real systems is not particularly unusual [30].

Table 8

Comparison between the AAD (%) values calculated in this work using two modified UNIFAC models for the system α -lactose/ethanol/water

UNIFAC models	Temperature (°C)		
	25	40	60
Peres and Macedo [18,19]	142	60.5	42.3
Gabas and Laguérie [15]	25.2	24.7	8.3

5. Conclusions

In the present paper we report new experimental data on solubilities of α -lactose in water–ethanol solvent mixtures, at 25, 40 and 60°C, in a concentration range from 0 to 100 sugar-free wt.% of water. The variation of the α -lactose solubility in this concentration range is of two orders of magnitude. The solubility increases with temperature and with water concentration.

The experimental data were successfully correlated using a UNIQUAC-based model. Prediction results using two different group-contribution UNIFAC-based models were only fair.

List of symbols

$a_{ij}, a_{ij}^0, a_{ij}^t$	UNIQUAC interaction parameters, Eq. (6) (K)
Q	group area parameter
R	group volume parameter, gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	absolute temperature (K)
x	mole fraction

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γ	activity coefficient
ΔA	temperature-independent parameter ($\text{J mol}^{-1} \text{K}^{-1}$)
ΔB	temperature-independent parameter ($\text{J mol}^{-1} \text{K}^{-2}$)
ΔC_p	difference between the heat capacities of the pure liquid and the pure solid sugar ($\text{J mol}^{-1} \text{K}^{-1}$)
ΔH_f	enthalpy of fusion (J mol^{-1})
σ	standard deviation
φ	molecular volume fraction

Subscripts

i	component i
j	component j
m	melting
sug	sugar

Superscripts

C	combinatorial
R	residual
⁰	reference temperature, set equal to 298.15 K

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