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Phase equilibria of D-glucose and sucrose in mixed solvent mixtures: Comparison of UNIQUAC [1]-based models

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Abstract

Solid–liquid equilibrium measurements of ternary sucrose–mixed solvent mixtures at 25, 40, and 60 °C are carried out, using a simple and accurate analytical method. A search for a reliable activity coefficient model for sugar liquid mixtures is performed: three UNIQUAC-based models are investigated—modified UNIQUAC, entropic free-volume and original Flory–Huggins. New UNIQUAC interaction parameters are estimated based on the aqueous and non-aqueous experimental data presented in this work together with those available in the literature. The solubility calculations were carried out using an equation based on fusion enthalpy data for the sugars. Although the UNIQUAC-based models investigated give in general a quite satisfactory representation of different thermodynamic properties of aqueous solutions containing D-glucose, D-fructose, and/or sucrose, it is shown that only the modified UNIQUAC model is able to accurately describe the ternary solubility data of D-glucose and sucrose in mixed solvent mixtures. © 1997 Elsevier Science Ltd.

Keywords: Sugar solution equilibria; Solid–liquid equilibria; Phase equilibria; UNIQUAC; Ternary solubility

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1. Introduction

Thermodynamics of carbohydrate systems play an important role and are often a key factor for the design and operation of crystallization processes of common sugars. An increased interest in this kind of biological molecules, together with the considerable lack of information concerning the solid–liquid equilibrium (SLE) data of common sugars in water [1], and especially in mixed solvents, has shown a need for the determination of thermodynamic properties of solutions containing sugars.

As far as multicomponent solvent mixtures are concerned, only a few experimental studies are available in the literature [2–6]. Therefore, in this work, an effort to overcome the scarcity of the available experimental data has been made: the solubilities of sucrose in water–ethanol, water–methanol, and ethanol–methanol at 25, 40, and 60 °C were measured using a simple and accurate analytical apparatus.

Concerning the models used for the description of these complex systems, a literature survey has shown

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[1] UNIQUAC = Universal Quasi Chemical.

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that UNIQUAC- or UNIFAC-based methods were successfully used for the representation of the solubilities of one or more sugars in water: Gabas and Laguérie [7,8]; Abed et al. [9]; Catté et al. [10,11]; and Peres and Macedo [12], among others. Unfortunately, less attention has been given to the description of the solubilities of one sugar in mixed solvents: only two approaches were presented in the literature [4–6]. Bockstanz et al. [4] used a Redlich–Kister equation to describe the solubility of D-glucose in water–ethanol mixtures at 35 °C. In previous works [5,6] a systematic study of the solid–liquid equilibria of D-glucose in water–ethanol, water–methanol and ethanol–methanol mixtures at 40 and 60 °C was carried out, and new D-glucose–alcohol and solvent–solvent UNIQUAC interaction parameters were estimated based on those data.

This work undertakes to evaluate the performance of three UNIQUAC-based activity coefficient models —a modified UNIQUAC model [13,14], an entropic free-volume model [15], and the original Flory–Huggins model [16–19]—to describe simultaneously the new experimental solubility data measured in this work for sucrose and the data already available in the literature for D-glucose in water–ethanol, water–methanol, and ethanol–methanol at 40 and 60 °C [5,6]. The first model has proved to be able to describe well this kind of systems [5,6]. The other two models are chosen in order to evaluate the importance of the free-volume contribution that for other solutions, as in the case of polymers, are too important to be neglected [15,20]. In order to use the entropic free-volume and the Flory–Huggins models, it is necessary to know the molar volumes of the sugars. In the open literature it is possible to find molar volume data for D-glucose, D-fructose, and sucrose at different temperatures [21–28]. However, there is a considerable difference between the values proposed by different authors and, therefore, in this work, the molar volumes of the above-mentioned sugars were measured at 25, 35, and 55 °C using a digital densimeter.

2. Experimental

Materials.—For the solubility measurements double-deionized water was used. For the density measurements double-distilled water was used. In all experiments the anhydrous D-glucose, D-fructose, and sucrose, supplied by Sigma Chemical Co., were dried under vacuum at 60 °C and used without further purification. The ethanol and methanol used for the preparation of the solvent mixtures were supplied by Merck, with a minimum purity of 99.8 vol%. No further purification was employed.

Table 1
Molar volumes (cm^3/mol) obtained in this work for D-glucose, D-fructose, and sucrose at 25, 35, and 55 °C

Sugar	MV (cm^3/mol)		
	25 °C	35 °C	55 °C
D-Glucose	111.82	112.94	114.37
D-Fructose	110.99	112.05	113.76
Sucrose	211.69	212.91	215.25

Density.—Densities were measured at 25, 35, and 55 °C with a vibrating tube digital densimeter (model DMA 55, Anton Paar). The thermal stability was better than ±0.01 °C. The densimeter was calibrated with water and air. Each molar volume presented in this work is calculated from the densities of eight diluted solutions (less than 5 wt%) prepared by weighting, on a 0.1-mg precision balance, the desired amount of water and sugar. For each solution, five experimental determinations were carried out. The molar volumes obtained at each temperature are presented in Table 1. The accuracy of the reported values for the molar volumes is ±0.01 cm^3/mol.

Figs. 1–3 show a comparison between the molar volumes obtained in this work with those available in the literature for D-glucose, D-fructose, and sucrose, respectively. From these figures it can be seen that the values measured in this work qualitatively agree with the majority of the literature values, although

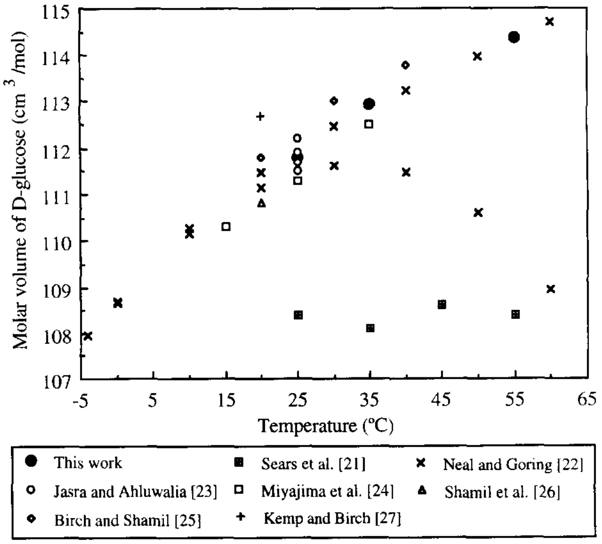

Fig. 1. Comparison between the molar volumes of D-glucose calculated in this work and the values published in the literature.

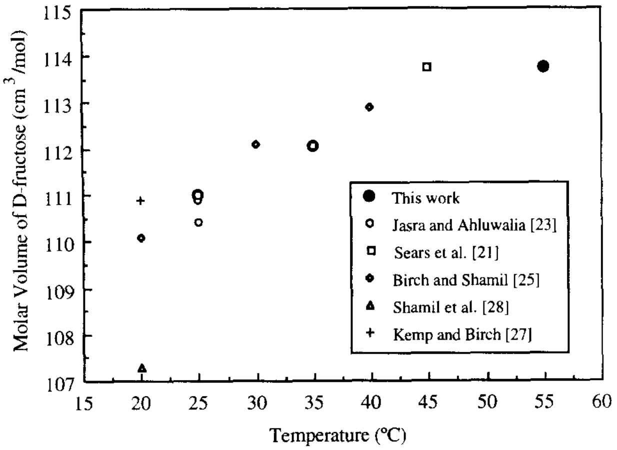

Fig. 2. Comparison between the molar volumes of D-fructose calculated in this work and the values published in the literature.

there is a significant discrepancy between some of the published values.

Solubility.—Apparatus and procedure. The solubility of sucrose in water–ethanol, water–methanol, and ethanol–methanol mixtures at 25, 40, and 60 °C was determined using the same isothermal method described in detail in a previous work [5].

Glass jacketed cells of about 80 – 100 cm^3 each were charged with different mixtures of the desired concentration of the mixed solvents and kept inside an insulated box. The temperature inside the box was controlled in order to maintain it constant. The temperature in each cell was controlled by circulating thermostatic water in the jacket and was considered to be accurate within ± 0.1 °C.

Dried sucrose was added to the solution until a small excess of sugar remained undissolved. The liquid and solid phases were stirred for at least 48 h and allowed to stand for about 24 h at a constant temperature to enable any finely dispersed solids to settle down.

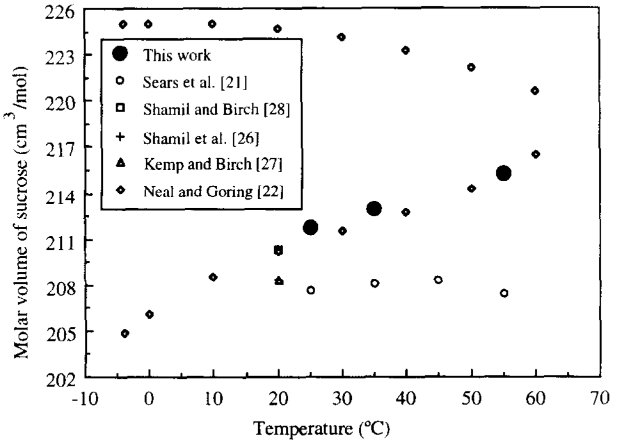

Fig. 3. Comparison between the molar volumes of sucrose calculated in this work and the values published in the literature.

From each equilibrium cell, samples of the clear supernatant liquid were carefully withdrawn using pipettes at a slightly higher temperature than the solution temperature in order to avoid any precipitation. The solubility was determined by slow evaporation of the solvent mixture from a previously weighted sample of saturated solution and by weighting the precipitated sugar regularly until a constant value was achieved. The drying procedure consisted of two steps: first, the sample was allowed to dry slowly at ambient temperature to avoid losing any solid, until the majority of the solvent mixture has been evaporated; and later, the remaining sample was dried in a vacuum oven at approximately 60 °C. Each experimental point was taken as an average of three different results that met one of the following criteria: (1) If the experimental solubility was less than 0.2 wt% than the maximum deviation allowed (from the average), must be less than 3%. (2) If the experimental solubility is between 0.2 and 10 wt%, then the standard deviation (σ) of the three measurements should be less than 0.005. (3) For solubilities higher than 10 wt%, the 2σ/solubility should be less than 0.001 [29].

Solubility data. The experimental data obtained for the systems sucrose–water–ethanol, sucrose–water–methanol, and sucrose–ethanol–methanol at 25, 40, and 60 °C are given in Tables 2–4, respectively.

3. Model development

In this work, a search for a reliable UNIQUAC-based activity coefficient model that, together with enthalpy and temperature of fusion data for the sugars, could describe satisfactorily several thermodynamic properties of aqueous and non-aqueous sugar solutions, was carried out.

The performance of three UNIQUAC-based models to describe the osmotic coefficient, water activity, vapor pressure, and solubility of one or more sugars in water, and the solubility of one sugar in mixed solvent systems was evaluated and compared. The models investigated are the modified UNIQUAC model, the entropic free-volume model (Entropic-FV), and the original Flory–Huggins model (original FH).

The activity coefficient of a component can be expressed as the combination of two contributions: the combinatorial term that takes into account the differences in size and shape between the molecules,

Table 2
Solid–liquid equilibrium data for sucrose–water–ethanol at 25, 40, and 60 °C

25 °C			40 °C			60 °C		
w'_{water} [a]	Sucrose (wt%)	σ [b]	w'_{water} [a]	Sucrose (wt%)	σ [b]	w'_{water} [a]	Sucrose (wt%)	σ [b]
0.000	0.0501	–	0.000	0.0816	–	0.000	0.1874	–
9.995	0.6794	0.002	9.992	1.0418	0.001	10.056	2.0512	0.004
19.894	4.2244	0.003	20.028	6.5890	0.003	20.032	11.2242	0.005
29.896	14.4279	0.005	29.884	19.0122	0.008	30.021	28.9266	0.011
39.758	26.7090	0.007	40.010	34.3119	0.012	39.730	45.4875	0.019
50.004	38.9091	0.011	50.006	45.4830	0.019	50.067	55.8653	0.023
59.924	48.2336	0.016	59.076	53.4487	0.022	59.836	61.8534	0.029
70.025	55.6056	0.022	70.524	60.4991	0.028	79.850	69.8577	0.033
79.987	60.3325	0.029	80.112	64.4311	0.031	100.000	74.3711	0.035
100.000	67.4623	0.031	100.000	70.1888	0.034			

[a] w'_{water} is the water mass percentage in the sugar-free solvent mixture.
[b] σ is the standard deviation of the experimentally measured sucrose weight percentage.

Table 3
Solid–liquid equilibrium data for sucrose–water–methanol at 25, 40, and 60 °C

25 °C			40 °C			60 °C		
w'_{water} [a]	Sucrose (wt%)	σ [b]	w'_{water} [a]	Sucrose (wt%)	σ [b]	w'_{water} [a]	Sucrose (wt%)	σ [b]
0.000	0.6627	0.002	0.000	0.9962	0.003	0.000	1.8309	0.003
9.905	2.2217	0.002	10.098	3.2821	0.003	9.997	6.7843	0.004
19.979	6.3312	0.004	19.989	9.7585	0.005	19.895	18.4980	0.009
29.944	15.7410	0.007	29.218	21.6473	0.009	29.902	36.0736	0.017
39.758	28.9476	0.010	39.732	37.9694	0.013	39.787	50.0608	0.023
49.977	41.1992	0.017	50.082	49.7914	0.022	49.762	58.7036	0.028
59.936	49.8836	0.021	59.832	56.1027	0.027	59.951	64.4322	0.032
70.032	56.8490	0.026	69.990	61.4483	0.030	80.077	70.7825	0.033
79.970	61.0928	0.029	80.005	64.9330	0.031	100.000	74.3780	0.035
100.000	67.4623	0.031	100.000	70.1888	0.034			

[a] w'_{water} is the water mass percentage in the sugar-free solvent mixture.
[b] σ is the standard deviation of the experimentally measured sucrose weight percentage.

Table 4
Solid–liquid equilibrium data for sucrose–ethanol–methanol at 25, 40, and 60 °C

25 °C			40 °C			60 °C		
w'_{ethanol} [a]	Sucrose (wt%)	σ [b]	w'_{ethanol} [a]	Sucrose (wt%)	σ [b]	w'_{ethanol} [a]	Sucrose (wt%)	σ [b]
0.000	0.6627	0.002	0.000	0.9962	0.003	0.000	1.8309	0.003
10.020	0.5300	0.003	10.085	0.8025	0.005	10.012	1.5147	0.004
19.623	0.4380	0.001	19.984	0.6436	0.005	19.971	1.2560	0.0002
29.961	0.3475	0.003	30.056	0.5142	0.002	29.911	1.0120	0.001
40.116	0.2637	0.0004	39.915	0.4066	0.003	39.961	0.8025	0.001
50.646	0.1980	–	49.872	0.3249	0.001	49.876	0.6445	0.005
59.989	0.1518	–	59.960	0.2443	–	60.327	0.4967	0.002
70.060	0.1157	–	70.034	0.1855	–	69.867	0.4012	0.001
80.004	0.0871	–	80.104	0.1430	–	79.848	0.3132	0.003
100.000	0.0501	–	100.000	0.0816	–	100.000	0.1874	–

[a] w'_{ethanol} is the ethanol mass percentage in the sugar-free solvent mixture.
[b] σ is the standard deviation of the experimentally measured sucrose weight percentage.

and the residual term due to the energetic interactions between the molecules.

The combinatorial contribution of the three models investigated in this work can be expressed by the expression of the combinatorial term of the molar excess Gibbs free energy proposed by Larsen et al. [13]:

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

where φ_i is the molecular volume fraction of component i defined as:

$$\varphi_i=\frac{x_i Z_i}{\sum_j x_j Z_j} \tag{2}$$

The three models studied have different definitions of the parameter Z_i:

(i) Modified UNIQUAC model,

$$Z_i=(R_i)^{2/3} \tag{3}$$

(ii) Entropic-FV model,

$$Z_i=\mathrm{MV}_i-\mathrm{MV}_{\mathrm{w}i} \tag{4}$$

(iii) Original FH model,

$$Z_i=\mathrm{MV}_i \tag{5}$$

where R_i is the applied volume parameter of the component i, MV_i is the molar volume, and $\mathrm{MV}_{\mathrm{w}i}$ is the van der Waals molar volume.

For the residual contribution, the original UNIQUAC equation (Abrams and Prausnitz [30]), with the same linear temperature dependency for the interaction parameters, proposed by Hansen et al. [14], was used for the binary interaction parameters in accordance to:

$$\ln(\gamma_i^R)=Q_i\left[1-\ln\left(\sum_j \theta_j\tau_{ji}\right)-\sum_j\frac{\theta_j\tau_{ij}}{\sum_k \theta_k\tau_{kj}}\right] \tag{6}$$

where θ_i is the molecular area fraction of component i defined as:

$$\theta_i=\frac{x_i Q_i}{\sum_j x_j Q_j}, \tag{7}$$

Q_i is the surface area of component i, and τ_{ij} is a parameter given by the following expression:

$$\tau_{ij}=\exp\left(-\frac{a_{ij}}{T}\right) \tag{8}$$

where

$$a_{ij}=a_{ij}^{\mathrm{o}}+a_{ij}^{\mathrm{t}}(T-T^{\mathrm{o}}) \tag{9}$$

where 'a' represents the UNIQUAC interaction parameters, T is the mixture temperature, T^{o} is an arbitrary reference temperature which was, in this work, set equal to 298.15 K, and i and j refer to the molecules present in solution.

In this work, the interaction parameters for the sugar–water pairs are temperature-dependent, and those for the sugar–alcohol and the solvent–solvent pairs are temperature independent (a_{ij}^{t} equal to zero).

The applied volume (R_i) and surface area (Q_i) parameters of D-glucose, D-fructose, sucrose, ethanol, methanol, and water needed for the equations were calculated from the size parameters of the groups involved in the molecules. These size parameters were taken from the UNIFAC Parameter Tables [14, 31–35], and are given in Table 5. This table also gives the van der Waals molar volumes of the above-mentioned components that were taken from Bondi [36].

Table 5
Structural parameters (R_i and Q_i) and van der Waals molar volumes for D-glucose, D-fructose, sucrose, ethanol, methanol, and water

	R_i	Q_i	$\mathrm{MV}_{\mathrm{w}i}$ (cm^3/mol)
D-Glucose	8.1528	7.920	88.03
D-Fructose	8.1529	8.004	88.03
Sucrose	14.5496	13.764	160.35
Ethanol	2.5755	2.588	31.94
Methanol	1.9011	2.048	21.71
Water	0.9200	1.400	11.49

In this work, two kinds of equilibria calculations have been performed: vapor pressure of aqueous sugar solutions at a known temperature, and solubility of one or more sugars in water and of one sugar in mixed solvent mixtures.

Vapor – liquid equilibria.—Assuming the vapor phase behavior as ideal gas, and since it does not contain sugar molecules, the vapor pressure of an aqueous sugar solution (P) at a constant temperature can be calculated directly using the following relationship:

$$P=\gamma_{\mathrm{w}}x_{\mathrm{w}}P_{\mathrm{w}}^{\mathrm{o}} \tag{10}$$

where P is the total pressure of the system or the vapor pressure, γ_{w} is the symmetric mole fraction activity coefficient of water, x_{w} is the mole fraction of water, and $P_{\mathrm{w}}^{\mathrm{o}}$ is the vapor pressure of pure water calculated using the Antoine equation with the constants taken from Gmehling and Onken [37].

Osmotic coefficient.—The osmotic coefficient of the aqueous sugar solutions was calculated using the following equation:

$$\phi = -\frac{1000}{M_w m}\ln(a_w) \quad (11)$$

where ϕ is the osmotic coefficient, M_w is the molecular weight of the solvent (water), m is the molality of the solution, and a_w is the solvent activity (water activity).

Solid–liquid equilibria.—In order to calculate the solubility of the anhydrous solid form of a sugar in water or in mixed solvent mixtures, an equation based on the symmetric convention for the calculation of the activity coefficients was used. This equation was derived assuming that the difference between the heat capacities of the pure liquid and the pure solid sugars (ΔC_p) is a linear function of temperature in the temperature range T (temperature of the mixture) and T_m (melting point of the sugar):

$$\Delta C_p = \Delta A + \Delta B(T - T^o) \quad (12)$$

where ΔA and ΔB are two parameters to be estimated.

The following equation can be obtained:

$$\ln(\gamma_{sug} x_{sug}) = \left[-\frac{\Delta H_f}{R} + \frac{\Delta A - \Delta B T^o}{R} T_m + \frac{\Delta B}{2R} T_m^2\right] \times \left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{\Delta A - \Delta B T^o}{R}\ln\left(\frac{T}{T_m}\right) + \frac{\Delta B}{2R}(T - T_m) \quad (13)$$

where the solubility of the sugar in the solvent(s) is related to some thermodynamic properties of the sugar such as the melting temperature (T_m) and the enthalpy of fusion (ΔH_f) at T_m, published in the literature [38–40].

Sugar(s) – water systems.—Modified UNIQUAC model. Previous works [10,12] show that the modified UNIQUAC model is able to describe the vapor–liquid and the solid–liquid equilibria of aqueous systems containing D-glucose, D-fructose, or sucrose: water activity, osmotic coefficient, vapor pressure, boiling temperature, freezing point, and solubility data. These works also show that the UNIQUAC model can predict successfully the vapor–liquid and solid–liquid equilibrium data for ternary and quaternary mixtures of D-glucose, D-fructose, sucrose, and water. In this work, only the Peres and Macedo [12] approach is used, since it allows a straightforward extension to systems of more than one solvent. The sugar–water UNIQUAC interaction parameters, and the ΔA and ΔB parameters of Eq. (12) for each sugar are taken from the literature [12].

Entropic free-volume and original Flory–Huggins models. Both the Entropic-FV and the original FH models have been widely used in the description of solvent activities in polymer solutions [15,20]. The major difference between the Entropic-FV model and the original FH model is that the combinatorial term of the latter does not take into account the free-volume differences between the sugar and solvent molecules. Both these models require the knowledge of the dependency of the molar volume of each component with the temperature. For the sugars studied (D-glucose, D-fructose, and sucrose), only the calculated values obtained in this work (Table 1) were used and thus a linear dependency of the molar volume with the temperature was established between 25 and 55 °C:

D-Glucose:

$$\text{MV}\,(\text{cm}^3/\text{mol}) = 109.86 + 0.0830T\,(^\circ\text{C}) \quad (14)$$

D-Fructose:

$$\text{MV}\,(\text{cm}^3/\text{mol}) = 108.76 + 0.0914T\,(^\circ\text{C}) \quad (15)$$

Sucrose:

$$\text{MV}\,(\text{cm}^3/\text{mol}) = 208.74 + 0.1184T\,(^\circ\text{C}) \quad (16)$$

For the solvents the molar volumes were calculated from the densities of the pure solvents. These are evaluated from the DIPPR Tables [41].

The performances of the Entropic-FV and the original FH models to represent thermodynamic properties of aqueous sugar solutions (water activity, osmotic coefficient, vapor pressure, and solubility) were studied using a similar approach to the one used for the modified UNIQUAC model: the new sugar–water Entropic-FV and original FH UNIQUAC interaction parameters together with the ΔA and ΔB parameters were estimated using the thermodynamic properties of aqueous sugar solutions and the prediction capabilities tested with the solid–liquid equilibria data of aqueous solutions containing two sugars. However, since the molar volumes were measured at temperatures between 25 and 55 °C, some thermodynamic properties used to estimate the sugar–water interaction parameters for the modified UNIQUAC model cannot be used: boiling temperatures and freezing points (less than 0 °C and higher than 100 °C).

Four kinds of experimental data (water activity, osmotic coefficient, vapor pressure, and solubility data) [9,42–60], available in the literature, were used as the database to estimate new UNIQUAC interaction parameters for the D-glucose–water, D-fructose–water, and sucrose–water systems for the Entropic-FV and for the original FH models. Table 6 presents detailed information concerning the experimental data, collected from the literature and used in this work. As can be seen from the table, these data cover large temperature and concentration ranges: from 0 to 100 °C, and from diluted solutions until saturation. It should be noticed that the osmotic coefficient data were, whenever possible, recalculated from the initial isopiestic experimental ratios data using the data published recently for the osmotic coefficients of electrolytes used as the standard solutions [61,62]. The ΔA and ΔB parameters of Eq. (12) were estimated simultaneously with the UNIQUAC parameters using the aqueous solubility data available for each sugar.

New temperature-dependent UNIQUAC interaction parameters were estimated. For each binary system six parameters are estimated simultaneously from all the data: four temperature-dependent interaction parameters, $(a^{o}_{sug/w};\ a^{t}_{sug/w})$ and $(a^{o}_{w/sug};\ a^{t}_{w/sug})$; and two temperature-independent coefficients, ΔA and ΔB of Eq. (12). These parameters were estimated using a IMSL routine, that uses a finite difference Levenberg – Marquardt algorithm to minimize the following objective function:

$$F_{obj} = \sum_{i} \frac{\sum_{n} \left(\frac{V_n^{exp} - V_n^{calc}}{V_n^{exp}} \right)_i^2}{NDE_i} \qquad (17)$$

where V and i represent the thermodynamic properties, the superscripts calc and exp mean calculated values according to the model and experimental data, respectively, and NDE is the number of data points for the property i.

The estimated temperature-dependent interaction parameters obtained are listed in Tables 7 and 8.

Table 9 presents the thermodynamic data needed for the calculation of the solubility of D-glucose, D-fructose, and sucrose in water (Eq. (13)) and the selected values used (values in bold), for each sugar and model studied, in the present work. The selected fusion values, for each sugar studied, are the ones

Table 6
Number of data points (first row), experimental temperature (second row), and concentration ranges (third row) used to estimate the sugar–water interaction parameters and the ΔA and ΔB parameters of Eq. (12) for the Entropic-FV and original FH models

	Water–D-glucose	Water–D-fructose	Water–sucrose
Water activity	22 [a] 25 °C 1.24–7.24 mol/kg	37 [b] 25 °C 0.62–22.20 mol/kg	33 [c] 25 °C 0.20–5.86 mol/kg
Osmotic coefficient	54 [d] 25, 37, and 60 °C 0.34–10.32 mol/kg	n.a.	110 [e] 25 °C 0.15–5.73 mol/kg
Vapor pressure	33 [f] 25, 35, 45, 55, and 65 °C 0.66–13.61 mol/kg	n.a.	n.a.
Solubility	17 [g] 10-90.8 °C 5.53–31.21 mol/kg	19 [h] 0-70 °C 15.55–70.49 mol/kg	98 [i] 10–100 °C 5.24–14.22 mol/kg
Total data	126 10-90.8 °C 0.34–31.21 mol/kg	56 0-70 °C 0.62–70.49 mol/kg	241 10–100 °C 0.15–14.22 mol/kg

n.a. not available.

[a] Rüegg and Blanc [57]; [b] Rüegg and Blanc [57], Correa et al. [60], and Lerici et al. [59]; [c] Chuang and Toledo [56], Rüegg and Blanc [57], and Lerici et al. [59]; [d] Bonner and Breazeale [52], Stokes and Robinson [53], and Miyajima et al. [58]; [e] Robinson and Sinclair [43], Scatchard et al. [44], Robinson et al. [45], and Robinson and Stokes [50]; [f] Taylor and Rowlinson [48]; [g] Young [49], Stephen and Stephen [51], Mullin [55], and Abed et al. [9]; [h] Jackson et al. [42], Young et al. [47], Vasátko and Smelík [54], and Abed et al. [9]; [i] Young and Jones [46], Stephen and Stephen [51], and Mullin [55].

Table 7
New UNIQUAC interaction parameters for the Entropic-FV model: first row $a_{ij}^{\,0}$; second row $a_{ij}^{\,t}$ (K)

$i\backslash j$	D-Glucose	D-Fructose	Sucrose	Water
D-Glucose	0	0 [a]	0 [a]	−132.6968 [b]
	0	0 [a]	0 [a]	0.9957 [b]
D-Fructose	0 [a]	0	0 [a]	81.6247 [b]
	0 [a]	0	0 [a]	2.0656 [b]
Sucrose	0 [a]	0 [a]	0	6.5575 [b]
	0 [a]	0 [a]	0	1.6412 [b]
Water	170.1197 [b]	−80.8178 [b]	34.3515 [b]	0
	−1.1090 [b]	−3.8082 [b]	−0.4773 [b]	0

[a] Set in this work equal to zero.
[b] Estimated parameters.

Table 8
New UNIQUAC interaction parameters for the original FH model: first row, $a_{ij}^{\,0}$; second row, $a_{ij}^{\,t}$ (K)

$i\backslash j$	D-Glucose	D-Fructose	Sucrose	Water
D-Glucose	0	0 [a]	0 [a]	23.7553 [b]
	0	0 [a]	0 [a]	2.2624 [b]
D-Fructose	0 [a]	0	0 [a]	54.5525 [b]
	0 [a]	0	0 [a]	0.9753 [b]
Sucrose	0 [a]	0 [a]	0	61.4502 [b]
	0 [a]	0 [a]	0	1.7338 [b]
Water	52.8654 [b]	19.4720 [b]	61.3339 [b]	0
	−1.2636 [b]	−4.6088 [b]	−0.6402 [b]	0

[a] Set in this work equal to zero.
[b] Estimated parameters.

Table 9
Thermodynamic data used for the calculation of the solubility of D-glucose, D-fructose, and sucrose in water

	D-Glucose		D-Fructose		Sucrose	
Melting temperature (K)		416.15 [a]		381.15 [a]		463.15 [a]
	423.15 [b]			**378.15** [b]		458.15 [b]
		419.15 [c]		377.15 [c]		**459.15** [c]
Fusion enthalpy (J mol^{-1})		32248 [a]		30447 [a]		40391 [a]
	32432 [b]			**32428** [b]		41076 [b]
		31432 [c]		36030 [c]		**46187** [c]
	Entropic-FV	Original FH	Entropic-FV	Original FH	Entropic-FV	Original FH
ΔA (J mol^{-1} K^{-1})	145.7410 [d]	70.8357 [d]	323.3455 [d]	314.6937 [d]	193.0197 [d]	193.2997 [d]
ΔB (J mol^{-1} K^{-2})	0 [d]	0.5986 [d]	0 [d]	0 [d]	0 [d]	0 [d]

[a] Roos [40].
[b] Raemy and Schweizer [38].
[c] Gabas and Laguérie [39].
[d] Parameters estimated in this work.

Table 10
Comparison between the RMSD (first row) and AAD (second row) values calculated with the Entropic-FV and original FH models, and those obtained by Peres and Macedo [12] for the modified UNIQUAC model, for the database used in this work

System	Model	Water activity	Osmotic coefficient	Vapor pressure	Solubility data	Total data
D-Glucose–water	Modified UNIQUAC (Peres and Macedo [12])	0.32%	0.48%	0.77%	0.42%	0.54%
		0.28%	0.40%	0.71%	0.27%	0.44%
	Entropic-FV (this work)	0.34%	0.37%	0.65%	0.43%	0.47%
		0.29%	0.28%	0.62%	0.29%	0.37%
	Original FH (this work)	0.35%	0.40%	0.64%	0.45%	0.47%
		0.30%	0.33%	0.60%	0.33%	0.39%
D-Fructose–water	Modified UNIQUAC (Peres and Macedo [12])	0.60%	–	–	0.52%	0.58%
		0.44%	–	–	0.38%	0.42%
	Entropic-FV (this work)	0.61%	–	–	0.28%	0.53%
		0.47%	–	–	0.20%	0.38%
	Original FH (this work)	0.59%	–	–	0.28%	0.51%
		0.44%	–	–	0.20%	0.36%
Sucrose–water	Modified UNIQUAC (Peres and Macedo [12])	0.41%	0.52%	–	0.72%	0.60%
		0.31%	0.43%	–	0.61%	0.49%
	Entropic-FV (this work)	0.42%	0.38%	–	0.40%	0.39%
		0.31%	0.31%	–	0.32%	0.31%
	Original FH (this work)	0.42%	0.38%	–	0.38%	0.39%
		0.31%	0.31%	–	0.31%	0.31%

that allow a better agreement between model calculated values and the literature data. Table 9 also gives the estimated values of the temperature-independent coefficients of Eq. (12), ΔA and ΔB, which were estimated simultaneously with the interaction parameters.

The Entropic - FV and original FH models can describe quite satisfactorily the experimental osmotic coefficient, water activity, vapor pressure, and solubility data for the binary systems studied: D-glucose–water, D-fructose–water, and sucrose–water.

In Table 10 a comparison between the RMSD and AAD values calculated in this work for the Entropic-FV and original FH models, and those obtained by Peres and Macedo [12] for the modified UNIQUAC model, for the experimental database used here, is given. The RMSD and AAD values were calculated using the following equations:

$$\mathrm{RMSD}=\sqrt{\frac{\sum_{n}\left|\frac{V_n^{\mathrm{exp}}-V_n^{\mathrm{calc}}}{V_n^{\mathrm{exp}}}\right|^2}{\mathrm{NDE}}}\times 100 \qquad (18)$$

$$\mathrm{AAD}=\frac{\sum_{n}\left|\frac{V_n^{\mathrm{exp}}-V_n^{\mathrm{calc}}}{V_n^{\mathrm{exp}}}\right|}{\mathrm{NDE}}\times 100 \qquad (19)$$

The Entropic-FV and the original FH models give a slightly better result than the modified UNIQUAC model. Nevertheless, all the three models are able to describe the experimental data with similar accuracy, which turns out to be an advantage for the modified UNIQUAC model due to its wider range of applicability: boiling temperatures and freezing points of sugar solutions.

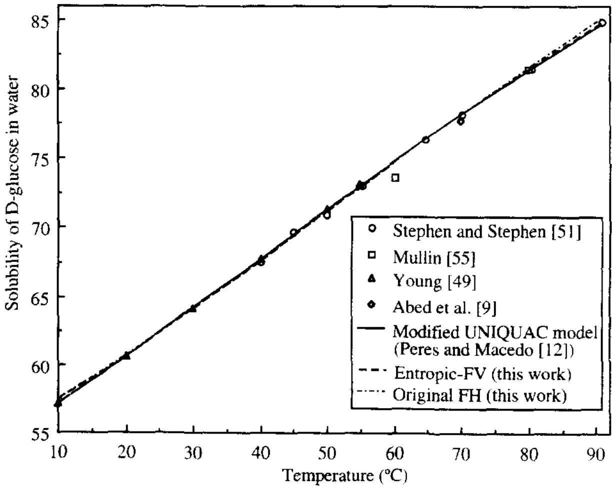

Fig. 4. Solubility of D-glucose in water: comparison between experimental data and the model curves.

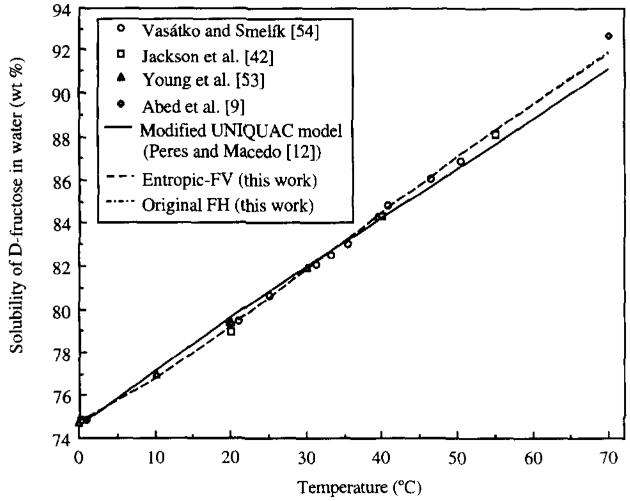

Fig. 5. Solubility of D-fructose in water: comparison between experimental data and the model curves.

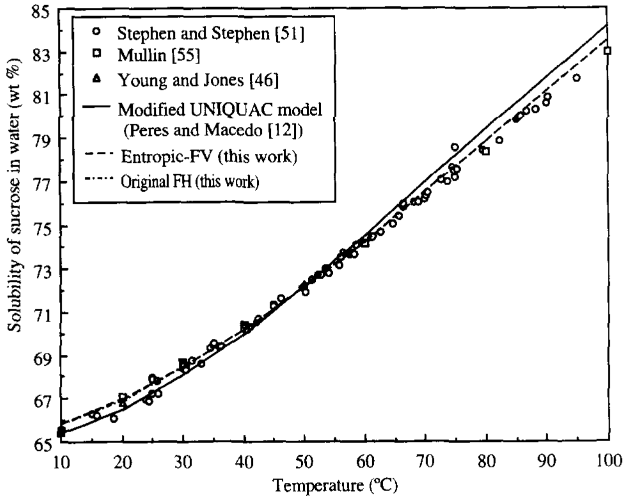

Fig. 6. Solubility of sucrose in water: comparison between experimental data and the model curves.

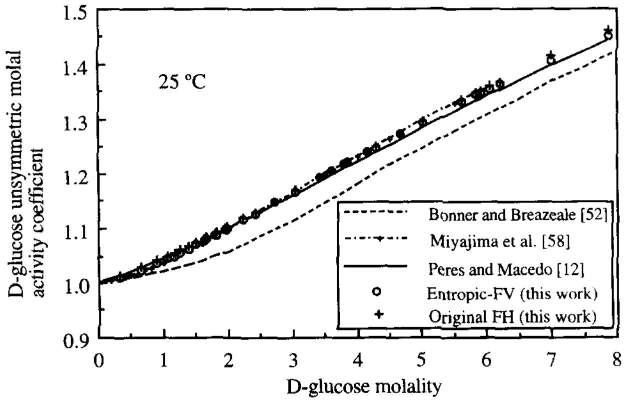

Fig. 7. Literature and calculated activity coefficients of D-glucose in water at 25°C.

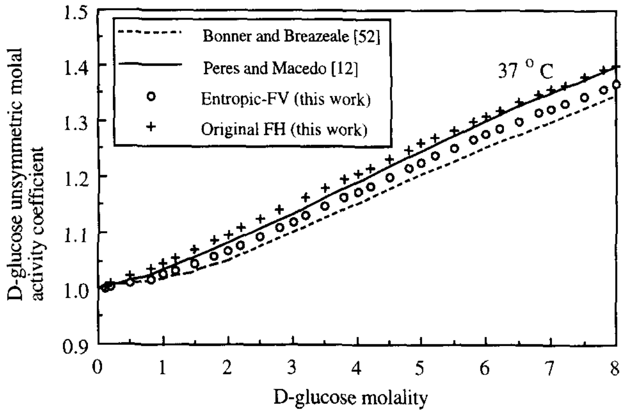

Fig. 8. Literature and calculated activity coefficients of D-glucose in water at 37 °C.

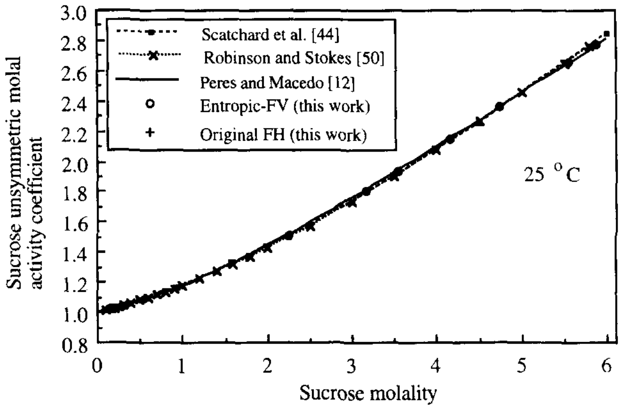

Fig. 9. Literature and calculated activity coefficients of sucrose in water at 25 °C.

Figs. 4 – 6 present a comparison between the experimental solubility data, the correlation results obtained with the three models for D-glucose, D-fructose, and sucrose, respectively. These figures show that the two new models investigated in this work can describe more accurately the experimental data than the modified UNIQUAC model, especially for D-fructose and sucrose.

A comparison between the unsymmetric molal activity coefficients calculated by the three models and the ones published in the literature at the same temperatures is shown in Figs. 7–9, for the D-glucose–water system at 25 and 37 °C, and for the sucrose–water system at 25 °C, respectively. The literature unsymmetric molal activity coefficients were calculated from the osmotic coefficient experimental data at the same temperatures, using the following equation:

$$\ln \gamma_{\mathrm{sug}}^{*} = \phi - 1 + \int_0^m \frac{\phi - 1}{m}\,\mathrm{d}m \qquad (20)$$

Table 11
Comparison between experimental [63] and predicted values of water activities and osmotic coefficients for the system D-glucose–sucrose–water at 25 °C

Sucrose molality	Glucose molality	Osmotic coefficient				Water activity			
		Exptl value	Predicted values			Exptl value	Predicted values		
			This work		Peres and Macedo [12]		This work		Peres and Macedo [12]
			Entropic-FV	Original FH			Entropic-FV	Original FH	
2.8039	0.5542	1.271	1.2647	1.2753	1.2800	0.9260	0.92634	0.92575	0.92549
2.3504	1.0996	1.237	1.2203	1.2384	1.2444	0.9260	0.92696	0.92592	0.92557
1.2166	2.4489	1.165	1.1399	1.1625	1.1674	0.9260	0.92749	0.92610	0.92581
1.7391	1.8737	1.197	1.1725	1.1955	1.2016	0.9251	0.92653	0.92514	0.92477
0.8286	2.9503	1.144	1.1244	1.1427	1.1457	0.9251	0.92631	0.92516	0.92497
0.3648	3.4947	1.120	1.1119	1.1209	1.1208	0.9251	0.92560	0.92502	0.92503

where γ_{sug}^{*} is the unsymmetric molal activity coefficient of the sugar in the aqueous solution, ϕ is the osmotic coefficient, and m is the molality of the solution. Figs. 7–9 show a satisfactory agreement between the two kinds of calculated properties for both models.

The predictive capabilities of the Entropic-FV and original FH models were studied based on the available literature data on water activity, osmotic coefficient, and solubility data for ternary aqueous systems containing D-glucose, D-fructose, and/or sucrose, and compared with those of the modified UNIQUAC model [12]. For the prediction calculations of ternary systems, the UNIQUAC interaction parameters between two sugars were fixed and set equal to zero as it was done in previous works [8,12,63].

The three models are able to satisfactorily predict the water activities and the osmotic coefficients of the ternary D-glucose–sucrose–water system at 25 °C [64]. However, only the original FH model gives a more satisfactory description than the modified UNIQUAC model, as can be seen in Table 11.

Figs. 10 and 11 show a comparison between the predicted values calculated using the Entropic-FV and the original Flory–Huggins models, the predicted values calculated using the modified UNIQUAC model [12], and the experimental data available in the literature [9] for the solid–liquid phase equilibrium compositions of D-glucose–sucrose–water and D-fructose–sucrose–water mixtures at 70 °C, respectively. They also present a comparison with the predicted values calculated by Gabas and Laguérie [8]

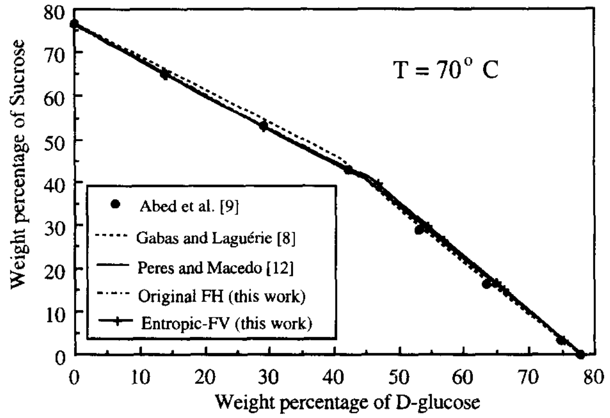

Fig. 10. Comparison between predicted and experimental data for the solid–liquid phase equilibrium compositions of D-glucose–sucrose–water mixture at 70 °C.

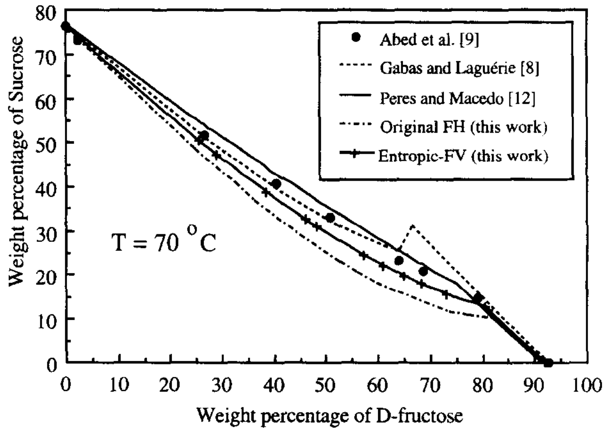

Fig. 11. Comparison between predicted and experimental data for the solid–liquid phase equilibrium compositions of D-fructose–sucrose–water mixture at 70 °C.

using the UNIFAC model proposed by Abed et al. [9]. From Figs. 10 and 11 it is clear that the two new models investigated here fail to represent the SLE of D-fructose and sucrose in water at 70 °C, although they are able to describe, with success, the other ternary system at 70 °C, with similar accuracies as the models used by Gabas and Laguérie [8] and by Peres and Macedo [12].

Results and discussion. The results obtained with the two models studied in this work, concerning the description of some aqueous sugar properties—osmotic coefficient, water activity, vapor pressure and solubility—show that, in general, a slightly improvement can be achieved using either the Entropic-FV or the original FH models instead of the modified UNIQUAC model. The original FH model shows a better predictive performance than the Entropic-FV and the modified UNIQUAC models, except for the D-fructose–sucrose–water system at 70 °C. From these results it seems that, for this kind of solutions, the free-volume contribution is not so important as in other systems, such as polymers, and that only a slight improvement is reached with the original FH model when compared with the global performance of the modified UNIQUAC model. Although the comparison between the performances of these three models indicates that the original FH model is, generally, better than the Entropic-FV and modified UNIQUAC models, this comparison is unfair for the latter model, since the database used to estimate the new Entropic-FV and original FH UNIQUAC interaction parameters and the respective ΔA and ΔB parameters of Eq. (12) does not include boiling temperature and freezing point data.

Sugar–solvent(s) systems.—Modified UNIQUAC model. The modified UNIQUAC model [12] was successfully extended to the description of the solubilities of D-glucose in water–ethanol, water–methanol, and ethanol–methanol mixtures at 40 and 60 °C [5,6]. In this work, the performance of this model to simultaneously describe the solid–liquid equilibria of D-glucose and sucrose in mixed solvent mixtures at different temperatures is evaluated and compared with the results of the other two models studied. New sucrose–alcohol UNIQUAC interaction parameters are estimated and the D-glucose–alcohol and solvent–solvent interaction parameters given by Peres and Macedo [5,6] are re-estimated using all the experimental solubility information available for the sucrose and D-glucose in mixed solvent mixtures. The sugar–water UNIQUAC interaction parameters, and the ΔA and ΔB parameters of Eq. (12) are taken from Peres and Macedo [12]. Therefore, a total of 14 new interaction parameters are estimated.

Entropic free-volume and original Flory–Huggins models. The D-glucose–water and sucrose–water interaction parameters, and the ΔA and ΔB parameters of Eq. (12) are those estimated in this work (Tables 7–9). Therefore, as for the modified UNIQUAC model, 14 new interaction parameters (sugar–alcohol and solvent–solvent) are estimated using the solubility data of D-glucose and sucrose in mixed solvent mixtures.

Estimation of the new interaction parameters. Concerning the modeling of the solid–liquid equilibrium data, the ability of the modified UNIQUAC model, the Entropic-FV model, and the original FH model to describe the SLE experimental data was evaluated based on the correlation of the solubility of D-glucose in water–ethanol, water–methanol, and ethanol–methanol systems at 40 and 60 °C and of sucrose in the same three mixed solvent systems at 25, 40, and 60 °C. Unfortunately, the performances of the three models cannot be tested using SLE data of D-fructose in mixed solvents since until recently no experimental data were reported in the literature. A total of 127 experimental data points were used: 16 from Peres and Macedo [5], 35 from Peres and Macedo [6], and 76 presented in this work. The data measured by Bockstanz et al. [4] for D-glucose–water–ethanol at 35 °C were not included in the database since neither of the above-mentioned reproducibility criteria, recommended and used here, are obeyed.

In order to describe the solid–liquid equilibrium of D-glucose and sucrose in mixed solvent mixtures, 14 new temperature-independent interaction parameters were estimated simultaneously (a^{t}_{ij} set equal to zero) for each model studied: D-glucose–ethanol, D-glucose–methanol, sucrose–ethanol, sucrose–methanol, water–ethanol, water–methanol, and ethanol–methanol, using the same IMSL routine used before, to minimize the following objective function:

$$F_{\mathrm{obj}} = \sum_{n} \left(\frac{S^{\mathrm{exp}}_{\mathrm{sug}} - S^{\mathrm{calc}}_{\mathrm{sug}}}{S^{\mathrm{exp}}_{\mathrm{sug}}} \right)^2_n \tag{21}$$

where n is the number of experimental data points and S represents the solubility of the sugar in the mixed solvent mixtures. For the modified UNIQUAC model, the D-glucose–water and sucrose–water interaction parameters and the ΔA and ΔB parameters of Eq. (12) are taken from Peres and Macedo [12]. For the Entropic-FV and original FH models, the UNIQUAC interaction parameters used are presented in Tables 7 and 8, respectively. The ΔA and ΔB parameters used for these latter two models are given in Table 9.

The 14 new UNIQUAC interaction parameters estimated in this work for each model are listed in Tables 12 – 14. These parameters were used in the calculations of the solubility of D-glucose or sucrose in water – ethanol, water – methanol and ethanol – methanol mixtures with Eq. (13).

Table 15 gives a comparison between the AAD and RMSD values calculated per temperature and per system studied for the modified UNIQUAC, Entropic-FV, and original FH models. The results obtained clearly show that the Entropic-FV and the original FH models do not give acceptable results and that they are not able to describe the solid–liquid equilibria of D-glucose and sucrose in the mixed solvent mixtures and temperatures studied, although these two models describe very satisfactorily some thermodynamic properties of one or more sugars in water as mentioned before.

Figs. 12 – 17 show a comparison between the experimental data and the correlation results obtained with the modified UNIQUAC model.

The above - mentioned figures together with the results given in Table 15 show that only the modified UNIQUAC model is able to describe satisfactorily and simultaneously the 'S' shape curves of the solu-

Table 12
Modified UNIQUAC model temperature-independent interaction parameters estimated in this work (Kelvin). Sugar–water parameters are linear temperature-dependent values

$i \backslash j$	D-Glucose	Sucrose	Water	Ethanol	Methanol
D-Glucose	0	0	−68.6157 [a] −0.0690 [a]	53.5398	121.0846
Sucrose	0	0	−89.3391 [a] 0.3280 [a]	17.5323	146.7731
Water	96.5267 [a] 0.2770 [a]	42.3676 [a] −2.2511 [a]	0	−78.5272	93.6153
Ethanol	136.2574	128.1468	207.4055	0	25.6195
Methanol	37.3725	−8.3068	9.1172	−47.4326	0

[a] Peres and Macedo [12].

Table 13
Entropic-FV temperature-independent interaction parameters estimated in this work (K)

$i \backslash j$	D-Glucose	Sucrose	Water	Ethanol	Methanol
D-Glucose	0	0	[a]	−116.3906	−31.7765
Sucrose	0	0	[a]	−99.6765	22.3418
Water	[a]	[a]	0	386.8807	623.4648
Ethanol	310.8935	244.9484	−173.7386	0	31.8238
Methanol	150.0501	68.7644	−225.1710	−58.0703	0

[a] Estimated in this work (Table 7).

Table 14
Original FH temperature-independent interaction parameters estimated in this work (K)

$i \backslash j$	D-Glucose	Sucrose	Water	Ethanol	Methanol
D-Glucose	0	0	[a]	110.5295	187.4291
Sucrose	0	0	[a]	62.0273	211.6467
Water	[a]	[a]	0	16.8224	119.0270
Ethanol	89.4822	95.6237	305.0788	0	8.1691
Methanol	−0.9787	−22.3078	85.1450	−26.4637	0

[a] Estimated in this work (Table 8).

Table 15
Comparison between the AAD and RMSD values calculated for the three models studied in this work: modified UNIQUAC, Entropic-FV, and original FH models

System	T (°C)	NDE	Modified UNIQUAC		Entropic-FV		Original FH	
			AAD (%)	RMSD (%)	AAD (%)	RMSD (%)	AAD (%)	RMSD (%)
D-Glucose–water–ethanol	40	8	2.0	2.6	6.4	7.5	4.1	6.4
	60	8	1.3	1.4	5.5	6.2	2.2	3.2
D-Glucose–water–methanol	40	9	1.0	1.3	2.0	2.5	2.0	2.3
	60	9	1.2	1.5	2.8	3.0	1.9	2.6
D-Glucose–ethanol–methanol	40	8	1.2	1.4	3.0	3.6	0.84	0.98
	60	9	0.96	1.2	1.1	1.3	1.0	1.2
Sucrose–water–ethanol	25	9	3.0	3.8	8.0	10.2	7.6	9.2
	40	9	1.9	2.9	7.3	8.0	5.8	7.4
	60	8	1.8	2.9	9.7	11.1	6.6	10.2
Sucrose–water–methanol	25	9	2.9	3.7	5.7	7.4	5.5	6.2
	40	9	1.4	1.7	2.6	3.0	2.6	3.1
	60	8	3.7	5.2	5.4	7.4	6.2	9.0
Sucrose–ethanol–methanol	25	8	2.5	3.4	6.8	8.0	5.4	5.9
	40	8	1.5	1.9	2.6	3.4	2.6	3.2
	60	8	1.4	1.8	3.8	5.2	3.4	3.6
Total	25;40;60	127	1.8	2.7	4.8	6.5	3.8	5.7

bilities of D-glucose or sucrose in water–ethanol or methanol mixtures, as well as the monotonous decreasing behavior of the solubility of these sugars in the mixed ethanol–methanol solvents at 25 °C and/or 40 and 60 °C. The main feature is that for the sugar mixtures studied in this work, the differences in size and shape between the molecules present in solution are better represented by the structural parameters (R_i and Q_i). The results obtained for the description of the solid–liquid equilibrium of the sugars in mixed solvent mixtures show that the free-volume approach gives the worse description of the experimental SLE data, and, therefore, it can be said that for the molecules and mixtures studied in this work it is not important.

Unfortunately, since the database is limited to six sugar – mixed solvent systems at temperatures between 25 and 60 °C and to only two sugars, the generalization of the conclusions drawn about the

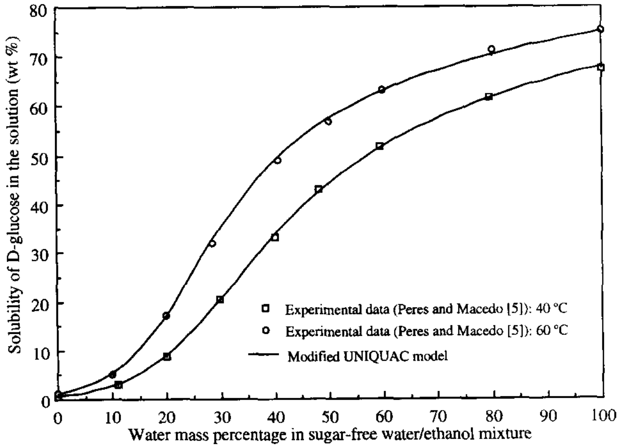

Fig. 12. Correlated and experimental results for D-glucose–water–ethanol at 40 and 60 °C.

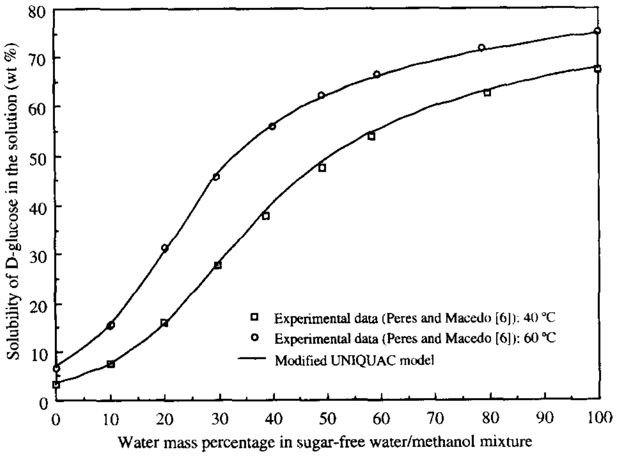

Fig. 13. Correlated and experimental results for D-glucose–water–methanol at 40 and 60 °C.

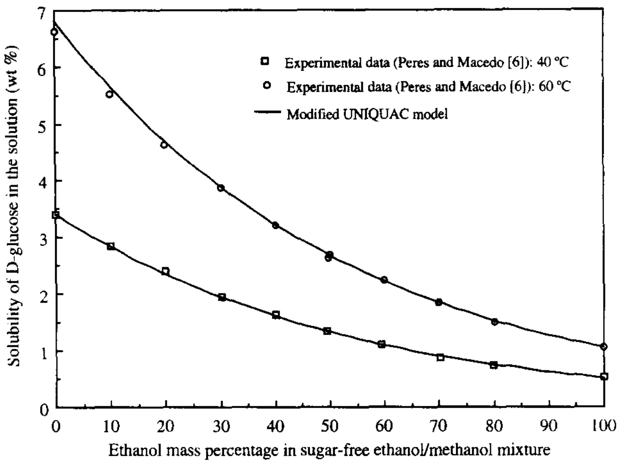

Fig. 14. Correlated and experimental results for D-glucose–ethanol–methanol at 40 and 60 °C.

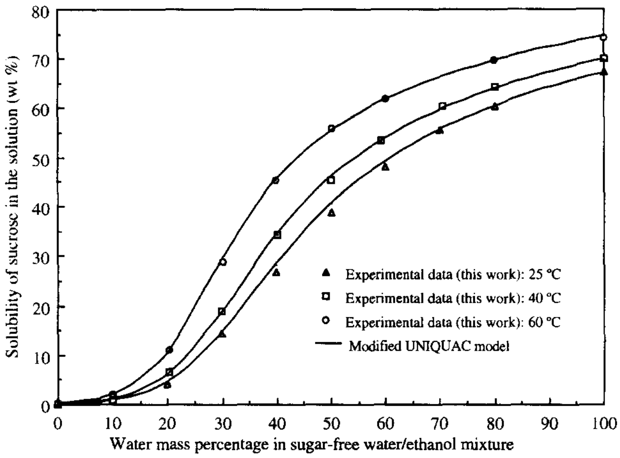

Fig. 15. Correlated and experimental results for sucrose–water–ethanol at 25, 40, and 60 °C.

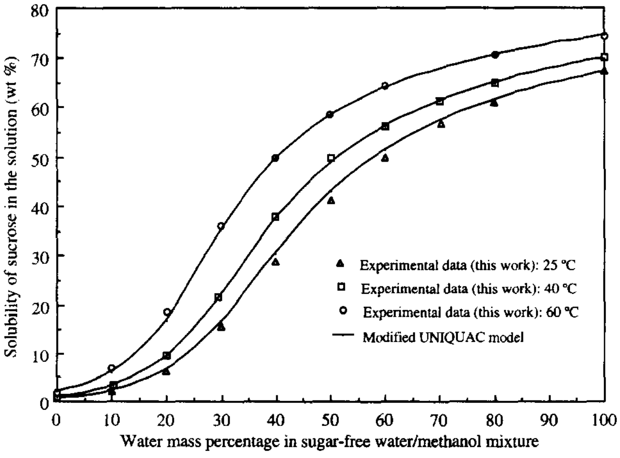

Fig. 16. Correlated and experimental results for sucrose–water–methanol at 25, 40, and 60 °C.

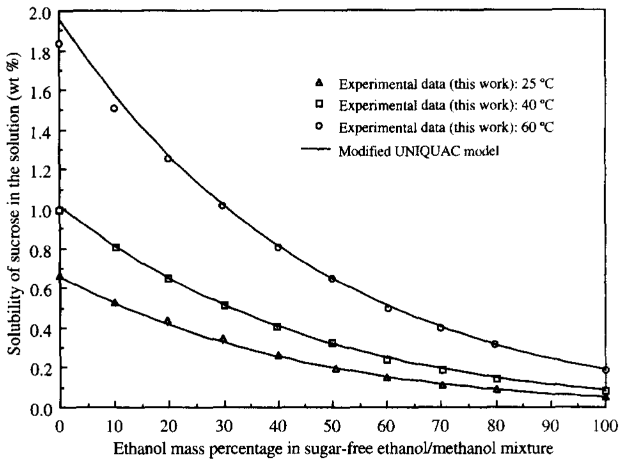

Fig. 17. Correlated and experimental results for sucrose–ethanol–methanol at 25, 40, and 60 °C.

better performance of the modified UNIQUAC model to other sugars or mixed solvents must be done with some precaution. Nevertheless, the results obtained remain a good indication about the performance of these models and can be extended to mixtures containing these sugars.

4. Conclusions

A comparison between three UNIQUAC-based activity coefficient models has been carried out taking into account their abilities to describe the vapor–liquid and the solid–liquid equilibria of aqueous solutions containing one or two sugars, as well as the solid–liquid equilibria of one sugar in mixed solvent mixtures at different temperatures. The results obtained clearly show that only the modified UNIQUAC model is able to give an accurate representation of all the above-mentioned equilibria. Although, the Entropic-FV and especially the original FH models show a slightly better performance than the modified UNIQUAC model concerning the description of aqueous sugar properties (osmotic coefficient, water activity, solubility, and vapor pressure data), these two models fail to predict the solid–liquid equilibria of D-fructose and sucrose in water or to correlate the solubilities of D-glucose and especially sucrose in the water–alcohol and alcohol–alcohol solvent mixtures at the temperatures studied. Therefore, it seems that for these kinds of sugar mixtures the free-volume contribution does not have a significative influence.

Despite the satisfactory and accurate results obtained with the modified UNIQUAC model concerning the description of the experimental solid–liquid equilibria of D-glucose and sucrose in water–ethanol, water–methanol, and ethanol–methanol mixtures at 25, 40, and 60 °C, calculations using the new UNIQUAC parameters and the thermodynamic constants estimated in this work must be made with precaution. This precaution is due to the scarcity of the experimental data on solubilities of sugars in mixed solvent mixtures. Nevertheless, the conclusions drawn throughout this work show that the modified UNIQUAC model can be used as an effective tool for preliminary design calculations of processes requiring the knowledge of solid–liquid equilibria data of sugar solutions

5. Nomenclature

a_{ij}, a_{ij}^{o}, a_{ij}^{t}	UNIQUAC interaction parameters, Eq. (9) (K)
AAD	average absolute deviation
F_{obj}	objective function
m	molality of the solution (mol/kg solvent)
MV	molar volume (cm^3/mol)
MV_{wi}	van der Waals molar volume (cm^3/mol)
n, NDE	number of data points
P	total pressure of the system or vapor pressure
P_{w}^{o}	vapor pressure of pure water
Q	group area parameter
R	group volume parameter, gas constant ($J\,mol^{-1}K^{-1}$)
RMSD	root mean square deviation
S	solubility of the sugar (wt%)
T	absolute temperature (K)
T_m	melting temperature (K)
T^{o}	arbitrary reference temperature, set equal to 298.15 K
V	thermodynamic property
x	mole fraction
Z	parameter in Eq. (2)

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γ	activity coefficient
ΔA	temperature-independent parameter ($J\,mol^{-1}K^{-1}$)
ΔB	temperature-independent parameter ($J\,mol^{-1}K^{-2}$)
ΔC_p	difference between the heat capacities of the pure liquid and the pure solid sugars ($J\,mol^{-1}K^{-1}$)
ΔH_f	enthalpy of fusion ($J\,mol^{-1}$)
θ	molecular area fraction
σ	standard deviation
τ	parameter in Eqs. (6) and (8)
φ	molecular volume fraction
ϕ	osmotic coefficient

Subscripts

i	thermodynamic property i, component i
j	component j
k	component k
n	data point n
sug	sugar
w	water

Superscripts

C	combinatorial
calc	calculated
exp	experimental
R	residual
*	unsymmetric convention
′	sugar-free solvent mixture.

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