Thermodynamics of Ternary Mixtures Containing Sugars. SLE of d-Fructose in Pure and Mixed Solvents. Comparison between Modified UNIQUAC and Modified UNIFAC

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Thermodynamics of Ternary Mixtures Containing Sugars. SLE of D-Fructose in Pure and Mixed Solvents. Comparison between Modified UNIQUAC and Modified UNIFAC

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New experimental data on the solubilities of D-fructose in the mixed solvents water/ethanol, water/methanol, and ethanol/methanol at 25, 40, and 60 °C are presented. These data were obtained using a standard, simple, and accurate experimental technique. Therefore, the database generated in our laboratory throughout a 4-year project now contains 205 solubility data points for systems with D-glucose, sucrose, and D-fructose in pure water, ethanol, and methanol and their mixtures. All of these data were correlated using the modified UNIQUAC, the entropic free-volume, and the original Flory–Huggins models, and the new parameters are given. The modified UNIQUAC model is the more accurate for the representation of the data. At the same time, predictions obtained with two different UNIFAC methods are compared.

1. Introduction

Carbohydrate solutions play an important role in our modern industrial society, being the basis of important industries, namely, those related to sugar manufacture, paper, textiles, plastics, foods, pharmaceuticals, and, in general, chemicals. As mentioned in previous papers,[1–3] in contrast to the case of the thermodynamic properties for aqueous sugar solutions, the data available for mixed-solvent systems were very scarce and inconsistent[4–7] in the recent past.

Among sugars, D-glucose, D-fructose, and sucrose are especially important in biological systems and in the food industry. These sugars are the major constituents of food products such as juices (e.g., apple, grape) and honey. On the other hand, water/alcohol and alcohol/alcohol solvents are used in the isolation, by precipitation, of expensive sugars that appear in nature together with other sugars. For the study and development of industrial processes related to this kind of system, the availability of both reliable experimental data over a wide range of conditions and flexible thermodynamic models for interpolation and prediction is required.

Therefore, as a long-term project, it was decided to establish a reliable, extensive database for solubilities of these three sugars in water/alcohol and alcohol/alcohol solvent mixtures. To accomplish this objective, extensive experimental measurements were carried out and reported in a series of previous publications[1–3] for systems containing D-glucose and sucrose. Regarding the thermodynamic modeling, a sustained effort to improve the description of this kind of system was also set as a general goal for this project.[3,8–10]

The purpose of the present work is multifold. First, the database is extended with new experimental data on the solubilities of D-fructose in the mixed solvents water/ethanol, water/methanol, and ethanol/methanol at 25, 40, and 60 °C, which were obtained using a standard experimental technique. These data, together with those reported in previous publications,[1–3] are used to complete the evaluation of available thermodynamic models. The modified UNIQUAC,[8] the entropic free-volume,[11] and the original Flory–Huggins[12–15] equations are considered. The first model proved to be able to describe this kind of system well.[1–3,8] The other two models were chosen to evaluate the importance of the free volume contribution, which, for other solutions such as polymers, is too important to be neglected.[11–16] Simultaneously, predictions obtained with the modified UNIFAC method proposed in another work[9] and the UNIFAC approach suggested by Gabas and Laguérie[17–19] are compared.

2. Experimental Section

2.1. Materials. For the solubility measurements, twice-deionized water was used. In all experiments, anhydrous D-fructose, supplied by Sigma Chemical Co. with a minimum purity of 99.95%, was dried under vacuum at 55 °C and used without further purification. The ethanol and methanol used for the preparation of the solvent mixtures were supplied by Merck with minimum purities of 99.8 vol %. No further purification was employed.

2.2. Solubility Apparatus and Procedure. The solubilities of D-fructose in water/ethanol, water/methanol, and ethanol/methanol mixtures at 25, 40, and 60 °C were determined using the isothermal method described in detail in previous works.[1–3,20]

The accuracy of the temperature measurements was ±0.1 °C.

As was already explained in previous papers,[1–3,20] each experimental point is an average of three different results obeying one of the following criteria: (i) If the experimental solubility is less than 0.2 wt %, then the maximum deviation allowed (from the average) must be less than 3%. (ii) 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. (iii) For solubilities higher than 10 wt %, then 2σ/solubility should be less than 0.001.[21,22]

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Table 1. Experimental Solubilities of D-Fructose in Water/Ethanol Mixtures at 25, 40, and 60 °C

W_{water}^a	solubility at 25 °C (wt %)	σ	W_{water}^a	solubility at 40 °C (wt %)	σ	W_{water}^a	solubility at 60 °C (wt %)	σ
0.000	1.702	0.001	0.000	3.008	0.001	0.000	6.501	0.001
10.024	10.207	0.004	5.025	7.602	0.001	4.914	20.204	0.004
19.971	31.332	0.006	10.039	18.147	0.001	9.859	58.828	0.010
29.983	50.278	0.010	20.099	48.874	0.009	19.850	74.307	0.015
39.891	60.243	0.018	29.885	61.902	0.017	30.046	81.596	0.019
49.951	66.641	0.019	39.911	69.224	0.017	40.153	84.825	0.024
59.817	70.991	0.020	49.936	74.436	0.019	49.789	86.719	0.026
80.241	76.960	0.025	59.905	77.870	0.025	60.795	88.978	0.026
100.000	80.104	0.028	79.428	81.964	0.025	81.736	91.247	0.030
			100.000	84.365	0.027	100.000	92.449	0.032

[a] W_{water} is the water mass percentage in the sugar-free solvent mixture.

Table 2. Experimental Solubilities of D-Fructose in Water/Methanol Mixtures at 25, 40, and 60 °C

W_{water}^a	solubility at 25 °C (wt %)	σ	W_{water}^a	solubility at 40 °C (wt %)	σ	W_{water}^a	solubility at 60 °C (wt %)	σ
0.000	12.107	0.002	0.000	22.534	0.007	0.000	62.978	0.022
9.986	30.011	0.001	4.979	36.389	0.008	5.012	70.492	0.022
20.000	48.221	0.018	9.994	50.025	0.015	10.387	75.447	0.026
30.015	59.378	0.023	19.930	63.255	0.017	19.923	81.582	0.024
39.941	65.922	0.024	30.106	71.147	0.020	30.050	85.793	0.023
50.083	70.826	0.025	39.970	75.330	0.020	40.068	88.154	0.023
59.829	73.692	0.026	50.116	77.967	0.026	49.960	89.109	0.025
78.640	77.356	0.029	58.732	79.659	0.027	59.606	89.866	0.024
100.000	80.104	0.028	80.462	82.602	0.028	79.197	91.387	0.027
			100.000	84.365	0.027	100.000	92.449	0.032

[a] W_{water} is the water mass percentage in the sugar-free solvent mixture

3. Modeling

3.1. Phase Equilibria. In this work only solid−liquid equilibrium (SLE) is considered.

The equation needed to describe the SLE is the same as used before[3,20]

$$\ln(\gamma_{sug}x_{sug}) = \left[-\frac{\Delta H_f}{R} + \frac{\Delta A - \Delta BT^0}{R}T_m + \frac{\Delta B}{2R}T_m^2\right] \times$$
$$\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{\Delta A - \Delta BT^0}{R}\ln\left(\frac{T}{T_m}\right) + \frac{\Delta B}{2R}(T - T_m) \quad (1)$$

where γ_{sug} and x_{sug} are, respectively, the sugar activity coefficient and mole fraction; R is the universal gas constant; T is the mixture temperature; ΔA and ΔB are two temperature-independent parameters to be estimated; T^0 is the reference temperature, which, in this work, was set equal to 298.15 K; T_m is the melting temperature; and ΔH_f is the enthalpy of fusion at T_m, which is published in the literature.[19,23,24]

In eq 1, the key variable is the sugar activity coefficient. In this context, an accurate model should be chosen to describe the activity coefficient.

3.2. Models for Activity Coefficients. *3.2.1. Molecular Models.* The molecular models adopted for the representation of the solubilities of the three sugars were those studied previously for sucrose and D-glucose in the same mixed solvents: the modified UNIQUAC,[8] entropic free-volume,[11] and original Flory−Huggins[12−15] models. The linear temperature dependence used for the residual terms of the three models is that proposed by Hansen et al.[25] 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.

3.2.2. Group-Contribution Models. The modified UNIFAC method proposed by Peres and Macedo[9,10] was used in this work to predict the D-fructose solubility in the different solvent mixtures. The combinatorial term is

that suggested by Larsen et al.[26] According to the definition of groups for this model, the D-fructose molecule is composed of one FUR 1 group, two CH_2 groups, and five OH $_{ring}$ groups.[9] The residual term is the original one proposed by Fredenslund et al.[27] All UNIFAC parameters used for the calculations presented here are those of Peres and Macedo.[9]

For comparison purposes, following the study carried out for sucrose and D-glucose, the UNIFAC method proposed by Gabas and Laguérie[17−19] was also used. For this method, the authors used the combinatorial and residual expressions from the original UNIFAC model.[28] The calculations with this model were performed using the same groups, UNIFAC interaction parameters, volume and surface area parameters, and enthalpies and temperatures of fusion defined and/or estimated by those authors.[17−19] Thus, D-fructose is built up with the groups "F" and "OH" introduced in their work.

The other UNIFAC approach presented recently in the literature by Spiliotis et al.[29] was not used in this work, as it uses ternary data (one sugar, two solvents) to estimate the interaction parameters. The main goal of using a group-contribution method here is to evaluate the predictive capabilities for multicomponent mixtures containing sugar(s) with solvent(s), with interaction parameters estimated using only binary data (one sugar, one solvent).

4. Results

4.1. Solubility Data. The experimental data obtained for the systems D-fructose/water/ethanol, D-fructose/water/methanol, and D-fructose/ethanol/methanol at 25, 40, and 60 °C are given in Tables 1−3, respectively. The corresponding standard deviations (σ) are also presented.

It can be seen that the solubility increases monotonically with temperature and water concentration. For the mixed solvent ethanol/methanol, the solubility decreases when the content of ethanol increases.

Table 3. Experimental Solubilities of D-Fructose in Ethanol/Methanol Mixtures at 25, 40, and 60 °C

W'_{water}[a]	solubility at 25 °C (wt %)	σ	W'_{water}[a]	solubility at 40 °C (wt %)	σ	W'_{water}[a]	solubility at 60 °C (wt %)	σ
0.000	12.107	0.002	0.000	22.534	0.007	0.000	62.978	0.022
10.015	10.021	0.002	9.934	18.297	0.005	9.909	54.121	0.010
20.044	8.113	0.004	20.017	15.037	0.005	19.948	45.674	0.008
29.992	6.790	0.004	29.888	12.248	0.004	30.457	36.467	0.005
40.128	5.602	0.003	39.932	10.002	0.004	40.145	28.554	0.003
49.211	4.652	0.002	49.819	8.286	0.002	50.217	22.457	0.004
59.934	3.746	0.002	60.030	6.734	0.001	60.081	17.401	0.004
79.980	2.492	0.002	69.953	5.505	0.001	70.135	12.997	0.003
100.000	1.702	0.001	80.116	4.454	0.002	79.918	10.204	0.002
			90.119	3.602	0.002	90.131	8.179	0.003
			94.990	3.235	0.003	100.000	6.501	0.001
			100.000	3.008	0.001			

[a] $W'_{ethanol}$ is the ethanol mass percentage in the sugar-free solvent mixture

Table 4. Structural Parameters (R_i and Q_i) and van der Waals Molar Volumes (MV$_{wi}$) for D-Glucose, D-Fructose, Sucrose, Ethanol, Methanol, and Water

	R_i	Q_i	MV$_{wi}$ (cm³/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

4.2. Modeling Results. *4.2.1. UNIQUAC-Based Models.* The performance of the modified UNIQUAC, entropic free-volume, and original Flory–Huggins models is evaluated. The strategy adopted previously is implemented. Accordingly, new D-fructose/alcohol interaction parameters are estimated, and the D-glucose/alcohol, sucrose/alcohol, and solvent/solvent interaction parameters given by Peres and Macedo[1–3] are re-estimated using all of the experimental solubility information available for D-glucose, D-fructose, and sucrose in mixed-solvents—a total of 205 data points. The few data published by other authors[4,6–7] for these ternary mixtures of sugar/mixed solvents were not included in the database as none of the above-mentioned reproducibility criteria (section 2.2), recommended and used here were obeyed.

For each model, the sugar/water UNIQUAC interaction parameters and the ΔA and ΔB parameters of eq 1, as well as the enthalpy and temperature of fusion of each sugar, are taken from Peres and Macedo.[3,8] Thus, 18 new temperature-independent interaction parameters are estimated simultaneously for each model studied: D-glucose/ethanol, D-glucose/methanol, D-fructose/ethanol, D-fructose/methanol, sucrose/ethanol, sucrose/methanol, water/ethanol, water/methanol, and ethanol/methanol.

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[25,28,30–33] and are given in Table 4. This table also shows the van der Waals molar volumes of the above-mentioned components, which were taken from Bondi.[34]

For the entropic free-volume and original Flory–Huggins models, the molar volumes of the sugars considered here were obtained from ref 3. For the solvents, the molar volumes were calculated from the pure-solvent densities. These were evaluated from the DIPPR Tables.[35]

The regressed UNIQUAC interaction parameters are listed in Tables 5–7. These parameters were used in the calculations of the solubilities of D-glucose, D-fructose, and sucrose in water/ethanol, water/methanol, and ethanol/methanol mixtures with eq 1.

Table 5. New Interaction Parameters (a_{ij}^o) for the Modified UNIQUAC Model

$i \backslash j$	interaction parameters (K)					
	D-glucose	D-fructose	sucrose	water	ethanol	methanol
D-glucose	0.0000	0.0000[a]	0.0000[a]	b	9.1123	113.54
D-fructose	0.0000[a]	0.0000	0.0000[a]	b	40.292	131.58
sucrose	0.0000[a]	0.0000[a]	0.0000	b	−48.437	147.00
water	b	b	b	0.0000	−132.51	85.696
ethanol	178.83	122.76	197.58	249.06	0.0000	155.07
methanol	43.726	12.452	−8.4134	13.026	−140.35	0.0000

[a] Parameters set equal to zero. [b] From Peres and Macedo.[8]

Table 6. New Interaction Parameters (a_{ij}^o) for the Entropic–FV Model

$i \backslash j$	interaction parameters (K)					
	D-glucose	D-fructose	sucrose	water	ethanol	methanol
D-glucose	0.0000[a]	0.0000[a]	0.0000[a]	b	−114.57	−81.536
D-fructose	0.0000[a]	0.0000[a]	0.0000[a]	b	19.156	5.2335
sucrose	0.0000[a]	0.0000[a]	0.0000[a]	b	−99.706	−99.871
water	b	b	b	0.0000[a]	357.82	53.672
ethanol	309.67	125.50	244.95	−152.02	0.0000[a]	85.275
methanol	213.38	93.804	209.67	12.570	−85.104	0.0000

[a] Parameters set equal to zero. [b] From Peres and Macedo.[3]

Table 7. New Interaction Parameters (a_{ij}^o) for the Original FH Model

	interaction parameters (K)					
$i \backslash j$	D-glucose	D-fructose	sucrose	water	ethanol	methanol
D-glucose	0.0000[a]	0.0000[a]	0.0000[a]	b	12.311	152.36
D-fructose	0.0000[a]	0.0000[a]	0.0000[a]	b	93.334	94.295
sucrose	0.0000[a]	0.0000[a]	0.0000[a]	b	−66.209	185.20
water	b	b	b	0.0000	−61.966	59.545
ethanol	172.09	75.064	225.06	324.42	0.0000	185.23
methanol	21.389	42.337	−8.6221	109.60	−151.78	0.0000

[a] Parameters set equal to zero. [b] From Peres and Macedo.[3]

Table 8. SLE for Sugar/Mixed Solvent Mixtures: AAD Values from Different Models

			model (AAD value, %)		
system	T (°C)	NDE	modified UNIQUAC	entropic FV	original FH
D-glucose/	40	8	3.1	6.4	3.9
water/ethanol	60	8	1.9	5.5	2.3
D-glucose/	40	9	1.6	2.9	1.0
water/methanol	60	9	1.2	3.1	1.6
D-glucose/	40	8	1.2	4.0	2.0
ethanol/methanol	60	9	2.2	1.4	3.0
D-fructose/	25	8	3.0	7.0	2.4
water/ethanol	40	9	1.7	2.5	6.0
	60	9	3.6	8.6	6.7
D-fructose/	25	8	2.9	2.9	7.4
water/methanol	40	9	1.4	3.3	5.6
	60	9	3.8	4.8	2.9
D-fructose/	25	7	5.4	11.0	12.7
ethanol/methanol	40	10	1.7	3.9	3.9
	60	9	5.6	9.7	11.9
sucrose/	25	9	2.8	8.1	8.0
water/ethanol	40	9	2.6	6.9	7.3
	60	8	2.2	9.6	9.4
sucrose/	25	9	2.9	5.2	3.8
water/methanol	40	9	1.6	4.9	3.4
	60	8	3.9	9.5	7.1
sucrose/	25	8	3.4	5.6	8.4
ethanol/methanol	40	8	1.6	2.1	3.1
	60	8	2.5	2.7	6.4
total	25, 40, 60	205	2.6	5.4	5.4

Table 8 provides a comparison between the AAD values calculated per temperature and per system studied for the modified UNIQUAC-based models. As can be observed from the results obtained, the modified UNIQUAC model can describe the data with an AAD of 2.6%, versus 5.4% for the other two models. It should be emphasized that the solubilities calculated using the modified UNIQUAC model usually show relative deviations smaller than 7%, except for 10 of the 205 data points, where the deviations can be up to 10%. In
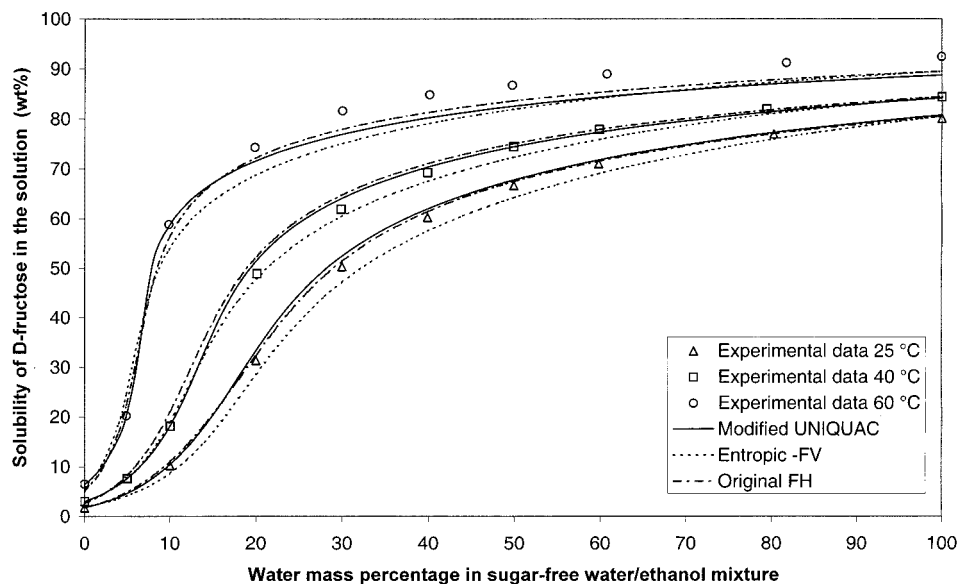
Figure 1. Correlated and experimental results for D-fructose/water/ethanol at 25, 40, and 60 °C.
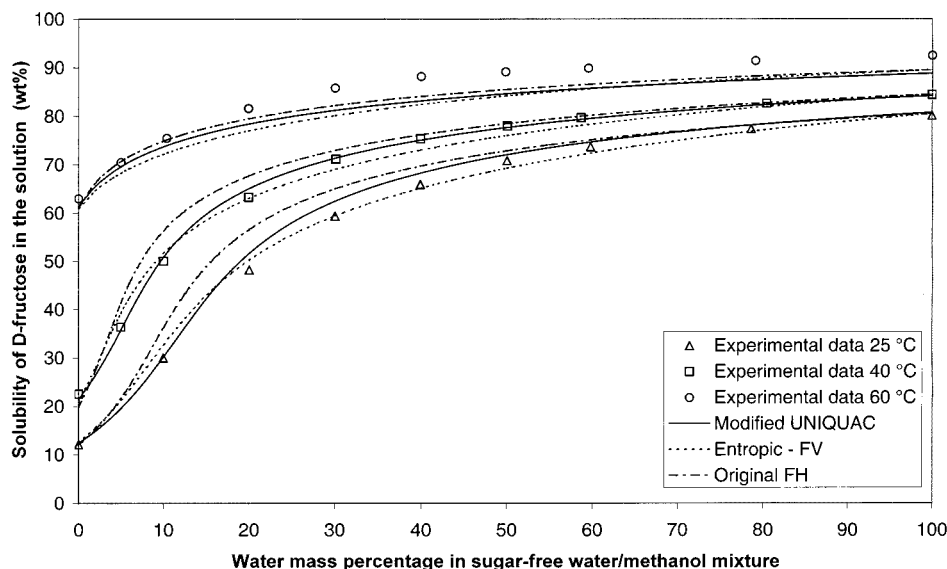
Figure 2. Correlated and experimental results for D-fructose/water/methanol at 25, 40, and 60 °C.
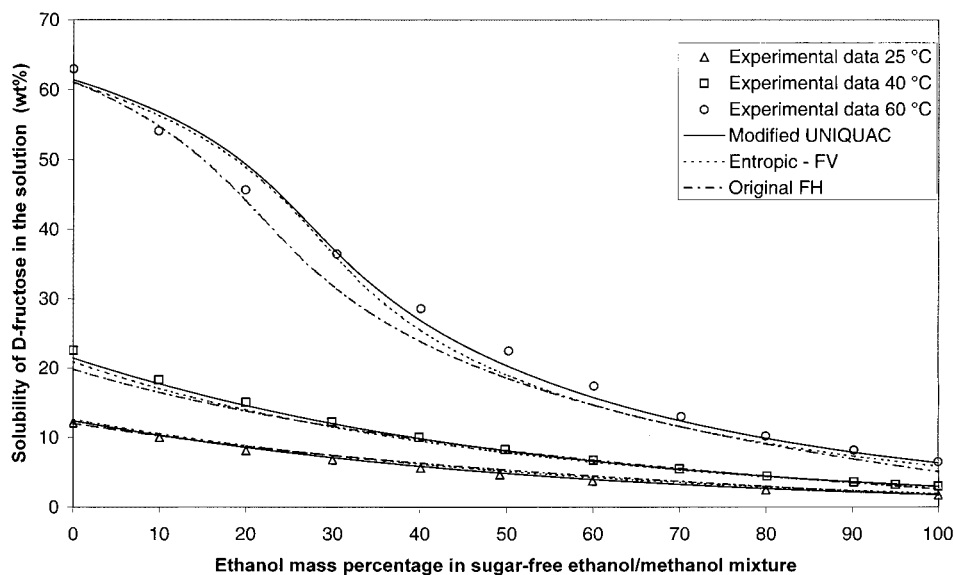

Figure 3. Correlated and experimental results for D-fructose/ethanol/methanol at 25, 40, and 60 °C.

contrast, the other two models frequently give deviations from 7 up to 25% (for 64 and 57 of the 205 data points using the entropic FV and the original FH models, respectively). Therefore, the modified UNIQUAC model is the only one that can be applied with success to the simultaneous description of the solubilities of D-glucose, D-fructose, and sucrose in the above-mentioned mixed solvents and temperature range.

This analysis was not extended to the model suggested by Catté et al.,[36] because the theoretical background used by those authors for the solubility representation (based on dilution data) does not allow for a direct extrapolation to this kind of system because of the lack of data concerning the enthalpies and heat capacities at infinite dilution for the mixed solvents of interest.

Figures 1–3 present a comparison between the experimental data and the correlation results obtained with the three UNIQUAC-based models for D-fructose.

It is clearly shown that, except for the D-fructose/ethanol/methanol system at 60 °C, all three models

under study (modified UNIQUAC, entropic FV, and original FH), and especially the modified UNIQUAC, are able to describe the solubility curve shapes.

It can be also stated that, for these systems, the differences in size and shape of the molecules are better described by the structural area and volume parameters (Q_i, R_i). Indeed, it seems that the free-volume effect is not very important for the sugar solutions studied: the free-volume based models (entropic free-volume and original Flory–Huggins) provide worse descriptions of the solid–liquid equibria data. However, taking into account that the present work deals only with mono- and disaccharides, some precautions should be made when trying to extend these conclusions to other sugar mixtures, especially for higher oligosaccharides or polysaccharides. It is expected that, because of the size of these molecules, the importance of the free-volume effect, and therefore of the corresponding model, will increase.

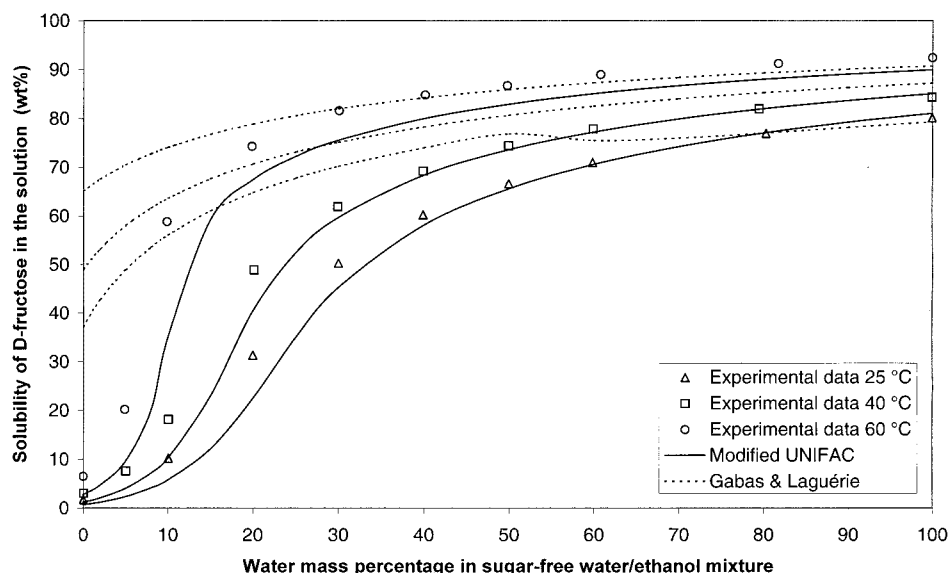*4.2.2. UNIFAC-Based Models.* In this study, two UNIFAC approaches were also investigated: the modi-

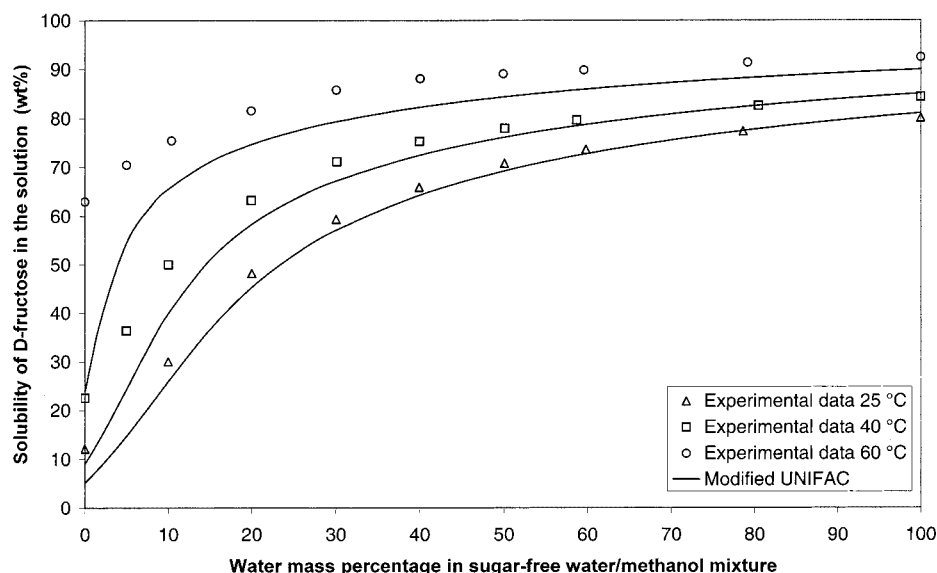**Figure 4.** Predicted and experimental results for D-fructose/water/ethanol at 25, 40, and 60 °C.

Figure 5. Predicted and experimental results for D-fructose/water/methanol at 25, 40, and 60 °C.

fied UNIFAC model of Peres and Macedo[9] and the UNIFAC method suggested by Gabas and Laguérie.[17−19]

The predictions obtained from the modified UNIFAC method proposed in an earlier paper are shown here only for D-fructose ternary mixtures (Figures 4−6) because, for both D-glucose and sucrose in mixed water/alcohol and alcohol/alcohol solvents, they were reported in an earlier publication.[9]

The figures show that the modified UNIFAC method satisfactorily predicts the solubilities of D-fructose in water/ethanol at 25, 40, and 60 °C (AADs smaller than 16.6, 17.3, and 19.0%, respectively) and in water/methanol at the same temperatures (AADs smaller than 9.8, 13.5, and 13.5%, respectively). It should be stated that these AAD values are mostly due to the deviations obtained in the alcohol-rich zone. In fact, the model is able to predict the solubilities of this sugar in the mixed solvents with water weight percentages higher than 15−20% with relative deviations smaller than 9%, generally between 1 and 5%. However, the model is unable to

predict the solubilities of D-fructose in ethanol/methanol solutions at the three temperatures studied.

The UNIFAC model of Gabas and Laguérie[17−19] fails to predict the solubility data of D-fructose in water/ethanol at the three temperatures of interest. Indeed, the model is not able to represent the SLE even qualitatively, predicting solubilities of this sugar in pure ethanol that are 14−47 times higher than the experimental values. For the systems containing methanol, this approach was not used, as no UNIFAC parameters are available for the methanol molecule and it cannot be considered to be built from −CH₃− and −OH− groups.

From the above remarks it is clear that, of the two UNIFAC-based methods studied here, only the modified UNIFAC model proposed by these authors can be used to predict satisfactorily the solubilities of different sugars in mixed solvents.

Finally, it should be stressed that all other available thermodynamic data for other sugars and derived products, such as fruit juices and honey, have been
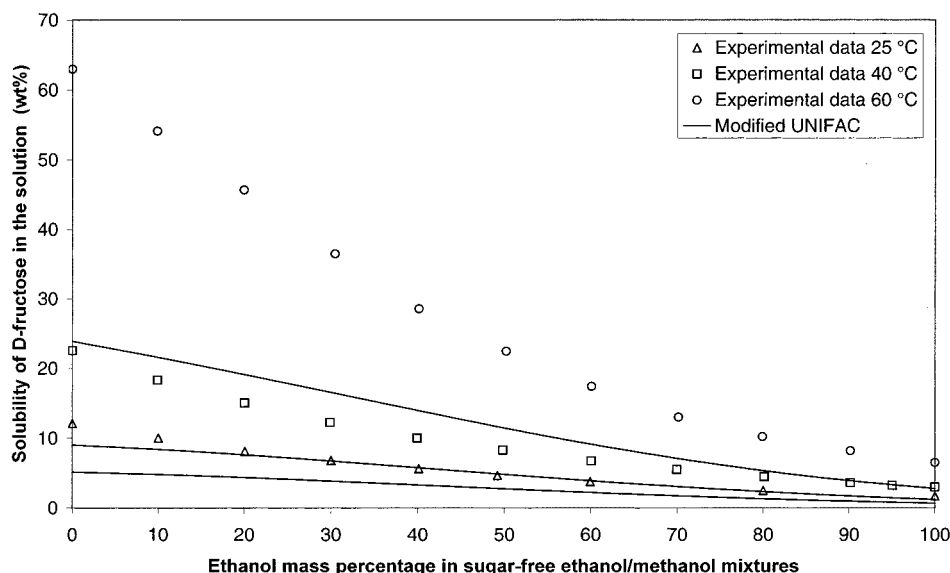
Figure 6. Predicted and experimental results for D-fructose/ethanol/methanol at 25, 40, and 60 °C.

studied with the same models by Peres and Macedo.[3,8−10,20]

5. Conclusions

A comparison of the performance between three UNIQUAC-based activity coefficient models has been carried out for solid−liquid equilibria data of D-glucose, D-fructose, and sucrose in mixed solvents at different temperatures. In total, 205 experimental data points were included in the database compiled for the calculations. The results obtained indicate that only the modified UNIQUAC model is able to describe all of the data accurately. 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.

Prediction results using two different group-contribution UNIFAC-based methods show that only the approach proposed by the authors in an earlier publication[9] produces fair results.

Nomenclature

a_{ij}, a_{ij}^o, a_{ij}^t = UNIQUAC interaction parameters (K)
AAD = average absolute deviation
MV_{wi} = van der Waals molar volume (cm³/mol)
NDE = number of data points
Q = group area parameter
R = group volume parameter; gas constant (J mol⁻¹ K⁻¹)
T = absolute temperature (K)
T_m = melting temperature (K)
T^b = arbitrary reference temperature, set equal to 298.15 K
x = mole fraction

Greek Letters

γ = activity coefficient
ΔA = temperature-independent parameter (J mol⁻¹ K⁻¹)
ΔB = temperature-independent parameter (J mol⁻¹ K⁻²)
ΔH_f = enthalpy of fusion (J mol⁻¹)
σ = standard deviation

Subscripts

i = component i

j = component j
sug = sugar
w = water

Superscripts

′ = sugar-free solvent mixture

Literature Cited

(1) Peres, A. M.; Macedo, E. A. Solid−Liquid Equilibrium of Sugars in Mixed Solvents. *Entropie* **1997**, *202/203*, 71−75.

(2) Peres, A. M.; Macedo, E. A. Measurement and Modeling of Solubilities of D-Glucose in Water/Alcohol and Alcohol/Alcohol Systems. *Ind. Eng. Chem. Res.* **1997**, *36*, 2816−2820.

(3) Peres, A. M.; Macedo, E. A. Phase Equilibria of D-Glucose and Sucrose in Mixed Solvent Mixtures: Comparison of UNIQUAC-Based Models. *Carbohydr. Res.* **1997**, *303*, 135−151.

(4) Stephen, H.; Stephen, T. *Solubility of Inorganic and Organic Compounds. Ternary Systems*; Pergamon Press: Oxford, U.K., 1963; Vol. II, Parts 1 and 2.

(5) Gabas, N.; Carillon, T.; Hiquily, N. Solubilities of D-Xylose and D-Mannose in Water−Ethanol Mixtures at 25 °C. *J. Chem. Eng. Data* **1988**, *33*, 128−130.

(6) Bockstanz, G. L.; Buffa, M.; Lira, C. T. Solubilities of α-Anhydrous Glucose in Ethanol/Water Mixtures. *J. Chem. Eng. Data* **1989**, *34*, 426−429.

(7) Flood, A. E.; Addai-Mensah, J.; Johns, M. R.; White, E. T. Refractive Index, Viscosity, Density, and Solubility in the System Fructose + Ethanol + Water at 30, 40, and 50 °C. *J. Chem. Eng. Data* **1996**, *41*, 418−421.

(8) Peres, A M.; Macedo, E. A. Thermodynamic Properties of Sugars in Aqueous Solutions: Correlation and Prediction Using a Modified UNIQUAC Model. *Fluid Phase Equilib.* **1996**, *123*, 71−95.

(9) Peres, A. M.; Macedo, E. A. A Modified UNIFAC Model for the Calculation of Thermodynamic Properties of Aqueous and Non-Aqueous Solutions Containing Sugars. *Fluid Phase Equilib.* **1997**, *139*, 47−74.

(10) Peres, A. M.; Macedo, E. A. Prediction of Thermodynamic Properties using a Modified UNIFAC Model: Application to Sugar Industrial Systems. *Fluid Phase Equilib.* **1999**, *158−160*, 391−399.

(11) Elbro, H. S.; Fredenslund, Aa.; Rasmussen, P. A New Equation for the Prediction of Solvent Activities in Polymer Solutions. *Macromolecules* **1990**, *23*, 4707−4714.

(12) Flory, P. J. Thermodynamics of High Polymer Solutions. *J. Chem. Phys.* **1941**, *9*, 660.

(13) Flory, P. J. Thermodynamics of High Polymer Solutions. *J. Chem. Phys.* **1942**, *10*, 51.

(14) Huggins, M. L. Solutions of Long Chain Compounds. *J. Chem. Phys.* **1941**, *9*, 440.

(15) Huggins, M. L. Thermodynamic Properties of Solutions of High Polymers: The Empirical Constant in the Activity Equation. *Ann. N. Y. Acad. Sci.* **1942**, *1*, 431.

(16) Kontogeorgis, G. M.; Fredenslund, Aa.; Tassios, D. P. Simple Activity Coefficient Model for the Prediction of Solvent Activities in Polymer Solutions. *Ind. Eng. Chem. Res.* **1993**, *32*, 362−372.

(17) Abed, Y.; Gabas, N.; Delia, M. L.; Bounahmidi, T. Measurement of Liquid−Solid Phase Equilibrium in Ternary Systems of Water−Sucrose−Glucose and Water−Sucrose−Fructose, and Predictions with UNIFAC. *Fluid Phase Equilib.* **1992**, *73*, 175−184.

(18) Gabas, N.; Laguérie, C. Predictions with UNIFAC of Liquid−Solid Phase Diagrams: Application to Water−Sucrose−Glucose, Water−Sucrose−Fructose and Water−Xylose−Mannose. *J. Cryst. Growth* **1993**, *128*, 1245−1249.

(19) Gabas, N.; Laguérie, C. Modelling of Liquid−Solid Phase Equilibria with UNIFAC. Application to Sugar Systems. Presented at the European Symposium on Computer Aided Process Engineering−ESCAPE 2, Toulouse, France, Oct 5−7, 1992.

(20) Machado, J. J. B.; Coutinho, J. A. P.; Macedo, E. A. Solid−Liquid Equilibrium of α-Lactose in Ethanol/Water. *Fluid Phase Equilib.* **2000**, *173*, 121−134.

(21) Pinho, S. P.; Macedo, E. A. Representation of Salt Solubility in Mixed Solvents: A Comparison of Thermodynamic Models. *Fluid Phase Equilib.* **1996**, *116*, 209−216.

(22) Pinho, S. P. Phase Equilibria in Electrolyte Systems. Ph.D. Thesis, Faculdade de Engenharia da Universidade do Porto, Porto, Portugal, 2000.

(23) Raemy, A.; Schweizer, T. F. Thermal Behavior of Carbohydrates Studied by Heat Flow Calorimetry. *J. Therm. Anal.* **1983**, *28*, 95−108.

(24) Roos, Y. Melting and Glass Transitions of Low Molecular Weight Carbohydrates. *Carbohydr. Res.* **1993**, *238*, 39−48.

(25) Hansen, H. K.; Rasmussen, P.; Fredenslund, Aa.; Schiller, M.; Gmehling, J. Vapor−Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 5. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352−2355.

(26) Larsen, B. L.; Rasmussen, P.; Fredenslund, Aa. A Modified Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.

(27) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Non Ideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086−1099.

(28) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria using UNIFAC*; Elsevier: Amsterdam, 1977.

(29) Spiliotis, N.; Tassios, D. A UNIFAC Model for Phase Equilibrium Calculations in Aqueous and Nonaqueous Sugar Solutions. *Fluid Phase Equilib.* **2000**, *173* (1), 39−55.

(30) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapor−Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714−722.

(31) Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. Vapor−Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118−127.

(32) Macedo, E. A.; Weidlich, U.; Gmehling, J.; Rasmussen, P. Vapor−Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 3. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 676−678.

(33) Tiegs, D.; Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. Vapor−Liquid Equilibria by UNIFAC Group Contribution. 4. Revision and Extension 4. *Ind. Eng. Chem. Res.* **1987**, *26*, 159−161.

(34) Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; John Wiley & Sons: New York, 1968.

(35) *DIPPR Tables of Physical and Thermodynamic Properties of Pure Compounds*; AIChE: New York, 1984.

(36) Catté, M.; Dussap, C.-G.; Achard, C.; Gros, J.-B. Excess Properties and Solid−Liquid Equilibria for Aqueous Solutions of Sugars Using a UNIQUAC Model. *Fluid Phase Equilib.* **1994**, *96*, 33−50.