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EXPERIMENTAL STUDY AND THERMODYNAMIC MODELING OF XYLITOL AND SORBITOL SOLUBILITY IN MIXTURES OF METHANOL AND ETHANOL AT DIFFERENT TEMPERATURES

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ABSTRACT

The development of techniques related to biomass conversion into chemical products needs additional study and advances. It is necessary to perform experimental investigations and modeling in order to produce information about mixtures that could be used as reaction media or in separation processes. Research on phase equilibrium is fundamental for the achievement of valuable knowledge. Therefore, this research aims to perform a study of xylitol and sorbitol solubility in methanol-ethanol mixtures throughout the molar composition range and at temperatures ranging from 293.15 K to 323.15 K, under atmospheric conditions. The Jouyban-Acree, NRTL and UNIQUAC models were fitted to experimental data. The parameters of the models were explicitly obtained as temperature dependents.

1. INTRODUCTION

Global energy demand and the exploitation of renewable resources is expected to increase significantly in the coming decades as human society grows. Knowledge about carbon sources able to be converted into energy, fuel, and chemical products would be very convenient and useful. This type of technology is endorsed by the biorefining concept based on the use of biomass-derived substrates as feedstock for chemical transformations allowing the production of energy or high value-added products [1].

Biomass, such as wood, wood wastes, agricultural crops, animal wastes, and waste from food processing [2] are primarily composed of cellulose, hemicellulose, and lignin [3]. This biomass has the potential to be an abundant source of renewable energy as well as a source of chemical building blocks [4].

Chemical building blocks are molecules with multiple functional groups with the potential to be converted into secondary chemicals used as plasticizers, pH control agents, resins, solvents and many other applications [5]. In order to obtain these molecules, processes such as hydrolysis [6, 7] and depolymerization [8] are used to break the bigger molecules into small saccharides that can be converted into compounds of interest. Considering that carbohydrates are the most abundant chemicals on planet [1], sugars and some of their derivatives like sugar alcohols are a prominent alternative to be considered.

Also known as polyols, sugar alcohols are a group of carbohydrates used in food products as sugar replacers. In addition, they can be used as ingredients in sugar-free and sugar-reduced products providing taste and texture [9]. Different chemical routes and processes [10, 11] are used to obtain sugar alcohols from bigger carbohydrates molecules.

Sorbitol and xylitol, shown in Figure 1(a) and Figure 1(b), respectively, are among the most prominent sugar alcohols and have a wide range of applicability in nutrition, cosmetic and medicine, and also as potential building blocks. In addition, they have been considered two of the

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top twelve building blocks with higher potential to yield high-value bio-based chemicals or materials [12].

These building blocks have several barriers to their production. Yields need to be increased and cost-efficient separation and purification methods need to be developed. Part of these challenges can be addressed by studies of solid-liquid equilibrium, which provides fundamental experimental information and leads to modeling of the distribution of the desired product under multiple conditions.

This work presents an experimental evaluation of xylitol and sorbitol solubility in methanol-ethanol binary mixtures, for the temperatures of 293.15 K, 303.15 K, 313.15 K, and 323.15 K. For the polyols studied, the experiment was conducted under atmospheric pressure and over the complete composition range of the binary mixture. The Jouyban-Acree model was used to correlate the experimental solubility data. The solid-liquid equilibrium was modeled by means of the excess Gibbs free energy models NRTL and UNIQUAC.

2. EXPERIMENTAL STUDY

The solubility of xylitol and sorbitol in the binary solutions formed by ethanol and methanol was determined by gravimetric method, similar to one previously published [13]. The liquid reagents used in this experiment were not submitted to any further purification and their purities were checked by measuring the refractive index at 298.15 K in a digital refractometer (Atago, model RX-5000i, accuracy ± 0.00004). The solids were previously dried in an electrical furnace for 1 hour under the temperature of 353 K before the beginning of the experiment and kept in a desiccator until their use. Table 1 presents the source and purity of the materials used and Table 2 compares the refractive index of the liquids with literature data.

Binary solutions, were prepared for each molar fraction by using a balance (uncertainty ± 0.001g). An excess of solid was transferred along with the binary solution into a jacketed glass cell,

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also known as an equilibrium cell, connected to a thermostatic bath (uncertainty ± 0.1 K). The temperature of the mixture inside the equilibrium cell was monitored using a bulb thermometer (uncertainty ± 0.5 K). To ensure contact of the liquid solution and the solid during the dissolution process, a magnetic stirrer was used. The assays were conducted under atmospheric pressure for the isotherms of 293.15 K, 303.15 K, 313.15 K and 323.15 K.

After loading the equilibrium cell with the binary mixtures and an excess of solid, the stirring speed and the thermostatic bath temperature were adjusted. Subsequently, the circulation system of the heating fluid was activated. The system remained under intense agitation for 3 hours to guarantee the contact among the components and provide mass transfer. After the agitation period, the system was kept under no agitation for 5 hours, to allow for the solid-liquid phase separation.

A sampling system was prepared using a plastic syringe connected to a stainless steel catheter which was connected to the lid of the equilibrium cell. Aliquots of 10 ml were taken out in triplicates, and placed into flat-bottom flasks of known weights, covered with glass lids. The samples were kept in a desiccator until their temperature equilibrated, then their masses were determined. The glass vessels with the samples were placed into an electrical furnace at 353 K, in order to allow the solvent to evaporate. They were weighted in 12 hours intervals to follow the mass reduction. After sampling, a new aliquot of solid and solution were put into the equilibrium cell and a new temperature was set, starting the experiment again. The solubility of each polyol, determined by the average of the triplicates, was expressed by means of mass fraction and mole fraction.

3. THERMODYNAMIC MODELING

The experimental solubility data at each temperature T were fitted by the Jouyban-Acree model [20-22] represented by Equation (1). The solubility expressed as mole fraction is denoted by x_s. The mole fraction of components 1 and 2 in the binary mixture are represented by x_1 and x_2.

Finally, x_1^0 and x_2^0 symbolise the solubility in the pure components 1 and 2 and J_i are the adjustable parameters.

$$\ln x_s = x_1 \ln x_1^0 + x_2 \ln x_2^0 + x_1 x_2 \sum_{i=0}^{2} \frac{J_i}{T}(x_1 - x_2)^i \tag{1}$$

The coefficients J_i are calculated as a function of temperature and the linear system is solved by the application of least square optimization. The average relative deviation (*ARD*) between calculated solubility $x_{s,i}^{calc}$ and experimental solubility $x_{s,i}$ is calculated by Equation (2) in which N_p represents the number of data points.

$$ARD = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{x_{s,i} - x_{s,i}^{calc}}{x_{s,i}} \right| \tag{2}$$

In accordance with a criterion of phase equilibrium, the fugacity of a solid dissolved in a liquid $\left(f_s^l\right)$ must be equal to the fugacity of the solid in the phase containing just solid (f_s^s) as shown by Equation (3).

$$f_s^l(T, P, x_s) = f_s^s(T, P) \tag{3}$$

Under equilibrium, the fugacity of the dissolved solid may be expressed by the activity coefficient of the solute in the liquid phase γ_s.

$$x_s \gamma_s(T, P, x_s) f_s^l(T, P) = f_s^s(T, P) \tag{4}$$

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When describing the fugacity of the pure solid in the liquid phase and in the solid phase, Equation (4) assumes the rigorous format as presented by Equation (5) [23] wherein $\Delta_{\text{Fus}}H_s$ represents the enthalpy of fusion, T_{m_s} is the melting temperature, R is the universal gas constant, T is the experimental temperature and ΔC_{p_s} is the difference between the molar heat capacity of the melting and solid states of the solute.

$$\ln x_s = -\ln \gamma_s + \frac{\Delta_{\text{Fus}}H_s}{R}\left(\frac{1}{T_{m_s}} - \frac{1}{T}\right) - \frac{1}{RT}\int_{T_{m_s}}^{T} \Delta C_{p_s}\,dT + \frac{1}{R}\int_{T_{m_s}}^{T}\frac{\Delta C_{p_s}}{T}\,dT \tag{5}$$

Neglecting the terms containing ΔC_{p_s}, the following simplified equation allows the calculation of solid solubility depending mainly on the melting properties of the solid and the activity coefficient of the solid solubilized.

$$\ln x_s = \frac{\Delta_{\text{Fus}}H_s}{R}\left(\frac{1}{T_{m_s}} - \frac{1}{T}\right) - \ln \gamma_s \tag{6}$$

Table 3 shows the values of enthalpy of fusion, entropy of fusion, molar mass (M) and melting temperature of the solids studied in this work [24-26].

In order to calculate the activity coefficient as a function of temperature and mixture composition, local composition models such as NRTL (Non-Random Two-Liquids) and UNIQUAC (Universal Quasi Chemical) were applied to correlate the experimental solubility data. A comprehensive explanation of the semi-empirical models and their equations is presented in the literature [23, 27]. The UNIQUAC structural parameters, r and q, for each component calculated in accordance with literature [28] are presented in Table 4.

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The binary interaction parameters, considered as dependents of the temperature for both UNIQUAC and NRTL, were obtained by the minimization of the objective function represented by Equation (7), in which 1 represents the solute solubilized, 2 represents the ethanol and x is the mole fraction in liquid phase.
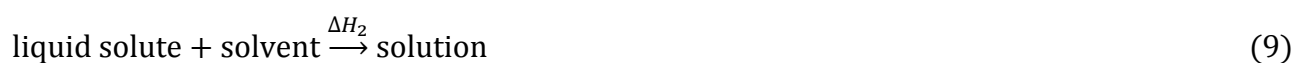
$$OF = \frac{100}{N_p} \sum_{i=1}^{N_p} \left[\frac{\left| x_{1,i}^{\exp} - x_{1,i}^{\text{calc}} \right|}{x_{1,i}^{\exp}} + \frac{\left| x_{2,i}^{\exp} - x_{2,i}^{\text{calc}} \right|}{x_{2,i}^{\exp}} \right] \tag{7}$$

The average relative deviation (*ARD*) represented by Equation (2) was also applied in order to check the ability of the models to fit the solubility data.

4. RESULTS AND DISCUSSION

The experimental solubility expressed as molar fractions (x_s) and mass fractions (w_s) are presented in Table 5 for all studied temperatures, in which 1 represents methanol and 2 represents ethanol. Figure 2 shows the solubility expressed in mole fraction as a function of molar composition of the binary mixture fitted by the Jouyban-Acree equation.

Analyzing the data, it was observed that the solubility increases as the temperature increases for all solids studied. This phenomenon can be interpreted if considered that two steps accomplish the dissolution process; first, the solid melts (Equation (8)) and second the two liquids mix with each other (Equation (9)).

$$\text{solid solute} \xrightarrow{\Delta H_1} \text{liquid solute} \tag{8}$$

$$\text{liquid solute} + \text{solvent} \xrightarrow{\Delta H_2} \text{solution} \tag{9}$$

The dissolution of a solid in an ideal solution ($\Delta H_2 = 0$) results that the solubility is governed by the enthalpy of fusion (ΔH_1). For a real process of dissolution, ΔH_2 is positive or negative depending on the amount of solid solubilized (interaction of solute and solvent) [29], formation of ions, hydration [30] or specific effects, although in general the magnitude of the effect is not high. For xylitol and sorbitol in the studied mixtures and range of temperature, the enthalpy of solution ($\Delta H_1 + \Delta H_2$) seems to be positive due to the increase of solubility with temperature. The fusion of both components is accompanied by an endothermic process ($\Delta H_1 > 0$) thus the dependence of solubility with temperature seems to be mainly due to the fusion process.

The solubility is also affected by the concentration of the binary liquid mixture. For all the solids studied, it was observed that the solubility is higher in methanol than in ethanol. It was observed that the addition of ethanol in the mixture leads to a reduction of solubility due to the change in the dielectric constant of the mixture. All the solids studied in this work are polar molecules, with a higher affinity by methanol, due to its higher dielectric constant than that of ethanol at the same temperature.

The size and spatial arrangement of a molecule also affect solid solubility. Xylitol is a linear molecule, composed of five hydroxyl groups, each one bound to a carbon atom. On the other hand, sorbitol is composed of six atoms of carbon and six hydroxyl groups. The higher solubility observed for xylitol is due to its size. As xylitol molecule is smaller than sorbitol, it makes more stable bounds with the components present in the binary mixture.

The Jouyban-Acree equation is able to correlate the data using three adjustable parameters. Table 6 presents the values obtained for the parameters along with the average relative deviations. It was observed that the best and worst fits resulted in a deviation of 1.2% and 4.1%, respectively.

Local compositions models, UNIQUAC and NRTL, were shown to be adequate for data correlation of xylitol and sorbitol in mixtures formed by ethanol and methanol. Thermodynamic

modeling of the solid-liquid phase equilibrium is performed in terms of mole fraction composition of the ternary mixture.

The adjustable parameters of both models were linearly correlated with the inverse of temperature, allowing the generation of liquid composition for the temperature ranging from 293.15 K to 323.15 K or even for temperatures slightly above or below the range investigated. Tables 7, 8, and 9 present the dependence of each parameter with temperature. It is important to note that the non-randomness parameter for the NRTL model, α, can be considered as being constant and equal to 0.3, just as proposed in the theoretical studies of the model by other research groups [23, 31-32].

The supplementary data file of this article presents Table 1S containing the composition of the liquid phase calculated by the NRTL and UNIQUAC models. In order to illustrate the behavior of the models, Figure 3(a) and (b) present plots of the mole fraction of the solid solubilized in the ternary mixture against the ratio of the ethanol mole fraction (2) and methanol mole fraction (3), x_2/x_3, for both experimental points and modeling.

Table 10 presents the average relative deviation for the mole composition of xylitol and sorbitol in ethanol/methanol mixtures obtained with the use of UNIQUAC and NRTL models. The *ARD* for the modeling with semi-empirical models indicate that for all mixtures studied, the NRTL model performs better than UNIQUAC model. In general it is observed that the models, with exception of the temperature of 323.15 K, provide a better fit to the data of mixtures involving sorbitol.

5. CONCLUSION

The solubility of xylitol and sorbitol in mixtures of methanol-ethanol depends on the temperature and composition of the binary liquid solution. For all the solids studied, the solubility increases as the temperature increases and as the composition of methanol increases due to changes in dielectric constant of the liquid mixture. The empirical Jouyban-Acree model shows the

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capability to correlate the data, although the adjustable parameters do not show dependence on temperature. The semi-empirical models NRTL and UNIQUAC are able to correlate the solubility data and the binary interaction parameters are dependent on temperature for the mixtures investigated.

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Table 1 Source and purity of the chemicals used in this work

Component	Source	Mass fraction	Analysis method	Purification method
methanol	Biotec - Brazil	0.999	refractive index	none
ethanol	Biotec - Brazil	0.995	refractive index	none
xylitol	ChemCruz - USA	0.990	none	drying
sorbitol	Sigma - USA	0.980	none	drying

Table 2 Experimental refractive indexes (n_D^{Exp}) and literature values (n_D^{Lit}) at 298.15 K and 0.1 MPa

Component	n_D^{Exp}	n_D^{Lit}
methanol	1.32655	1.32629 [14], 1.32645 [16], 1.32661 [18]
ethanol	1.35947	1.35922 [15], 1.3591 [17], 1.35972 [19]

Standard uncertainties u are $u(T) = 0.03$ K, $u(p) = 0.01$ MPa and $u(n_D) = 2 \cdot 10^{-5}$

Table 3 Values of enthalpy of fusion (ΔH_f), entropy of fusion (ΔS_f), molar mass (M), and melting temperature (T_m) of the solids studied.

Solid	M (g·mol^{-1})	T_m (K)	ΔH_f (kJ·mol^{-1})	ΔS_f (J·mol^{-1}·K^{-1})
Xylitol	152.15	367.52	33.68	91.64
Sorbitol	182.17	372.39	30.66	82.34

Table 4 Structural parameters for the UNIQUAC model

Component	r	q
ethanol	1.4311	1.9721

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methanol	2.1054	1.4323
sorbitol	9.7107	8.0284
xylitol	7.8953	6.7450

Table 5 Solubility of xylitol and sorbitol expressed as molar compositions (x_s) and mass compositions (w_s) for the different temperatures studied.

	293.2 K		303.2 K		313.2 K		323.2 K	
x_2	w_s	x_s	w_s	x_s	w_s	x_s	w_s	x_s

Xylitol

1.0000	0.00564	0.00171	0.00984	0.00300	0.01709	0.00524	0.03056	0.00945
0.8999	0.00636	0.00188	0.01103	0.00326	0.01931	0.00575	0.03433	0.01033
0.7993	0.00718	0.00205	0.01239	0.00355	0.02163	0.00625	0.03842	0.01123
0.6991	0.00824	0.00228	0.01417	0.00394	0.02460	0.00689	0.04372	0.01242
0.5980	0.01035	0.00277	0.01792	0.00482	0.03114	0.00847	0.05630	0.01561
0.4993	0.01205	0.00312	0.02071	0.00540	0.03592	0.00947	0.06473	0.01745
0.3999	0.01361	0.00340	0.02319	0.00584	0.04213	0.01077	0.07391	0.01937
0.3000	0.01792	0.00433	0.03056	0.00745	0.05298	0.01315	0.10186	0.02631
0.2050	0.02169	0.00506	0.03669	0.00866	0.06355	0.01533	0.12305	0.03119
0.1000	0.02370	0.00531	0.03945	0.00895	0.07541	0.01761	0.14074	0.03475
0.0000	0.02828	0.00609	0.04815	0.01054	0.08627	0.01949	0.15769	0.03793

Sorbitol

1.0000	0.00521	0.00132	0.00642	0.00163	0.01051	0.00268	0.01795	0.00460
0.8998	0.00563	0.00139	0.00799	0.00197	0.01258	0.00311	0.02137	0.00533
0.7991	0.00606	0.00144	0.00838	0.00200	0.01356	0.00325	0.02366	0.00572
0.6961	0.00665	0.00153	0.00954	0.00220	0.01547	0.00359	0.02710	0.00635
0.5990	0.00769	0.00172	0.01111	0.00249	0.01802	0.00406	0.03138	0.00714
0.4962	0.01069	0.00231	0.01394	0.00302	0.02190	0.00477	0.03743	0.00826
0.3998	0.01189	0.00248	0.01602	0.00335	0.02537	0.00535	0.04384	0.00939
0.3028	0.01407	0.00284	0.01916	0.00388	0.03020	0.00617	0.05246	0.01091
0.1998	0.01624	0.00315	0.02241	0.00436	0.03640	0.00717	0.06304	0.01271
0.1000	0.01820	0.00339	0.02687	0.00504	0.04399	0.00838	0.07907	0.01552
0.0000	0.02661	0.00479	0.04003	0.00728	0.06421	0.01192	0.11413	0.02216

x_2 is the mole fraction of ethanol in the {methanol (1) + ethanol (2)} mixtures free of solute

Table 6 Coefficients J_i and average relative deviations (*ARD*) for the fitting of Jouyban-Acree model

T/K	J_0	J_1	J_2	*ARD*	J_0	J_1	J_2	*ARD*
			Xylitol				**Sorbitol**	
293.2	-50.4992	-154.3975	56.0120	2.3088	-181.6737	-34.4696	-431.5511	4.0856

303.2	-58.1333	-146.7528	-10.3376	2.5693	-200.1679	203.3896	-216.1091	3.2571
313.2	-86.6887	-168.2785	83.3306	1.1897	-236.8917	194.4767	-200.4971	2.1767
323.2	-114.4228	-271.1155	229.7975	2.3325	-271.8976	244.7705	-177.3708	1.5751

Table 7 Binary interaction parameters, a_{ij} (K), for the UNIQUAC model

i/j	xylitol	sorbitol	ethanol	methanol
xylitol	0.00	0.00	$13270.23 - 98.05/T$	$35109.96 + 39.74/T$
sorbitol	0.00	0.00	$-23175.87 + 16.24/T$	$-18851.47 + 226.74/T$
ethanol	$15236.36 + 144.35/T$	$2367.67 + 204.20/T$	0.00	$6217.01 + 136.95/T$

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methanol	3848.99 – 25.91/T	-1823.86 – 12.04/T	-46317.01 + 22.08/T	0.00

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Table 8 Binary interaction parameters, τ_{ij}, for the NRTL model

i/j	xylitol	sorbitol	ethanol	methanol
xylitol	0.00	0.00	-1061.70 + 1.15/T	922.67 – 4.70/T
sorbitol	0.00	0.00	811.73 – 5.47/T	-1070.29 + 1.99/T
ethanol	-1612.74 + 8.38/T	-1002.36 + 6.56/T	0.00	1137.31 – 2.31/T
methanol	-1279.94 + 6.52/T	-559.13 + 3.94/T	744.85 – 0.09/T	0.00

Table 9 Parameter α for the NRTL model obtained for the ternary mixtures investigated

xylitol + ethanol + methanol	sorbitol + ethanol + methanol
$0.3379 - 15.4080/T$	$0.3281 - 9.8639/T$

Table 10 Average relative deviations for the solubilities of xylitol and sorbitol in mixtures of ethanol/methanol calculated by the NRTL and UNIQUAC models

T (K)	Xylitol		Sorbitol	
	UNIQUAC	NRTL	UNIQUAC	NRTL
293.2	6.4	4.3	2.1	1.4
303.2	4.9	4.1	4.2	1.8
313.2	6.5	4.5	5.6	3.5
323.2	6.4	3.4	8.4	4.0
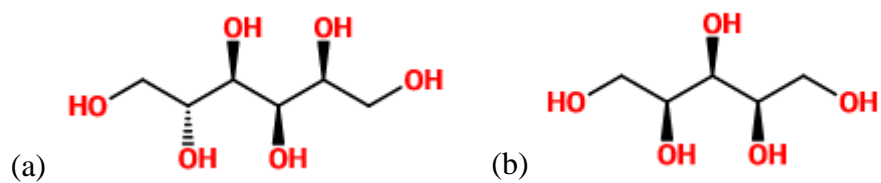
Fig. 1. Chemical structures of (a) sorbitol and (b) xylitol
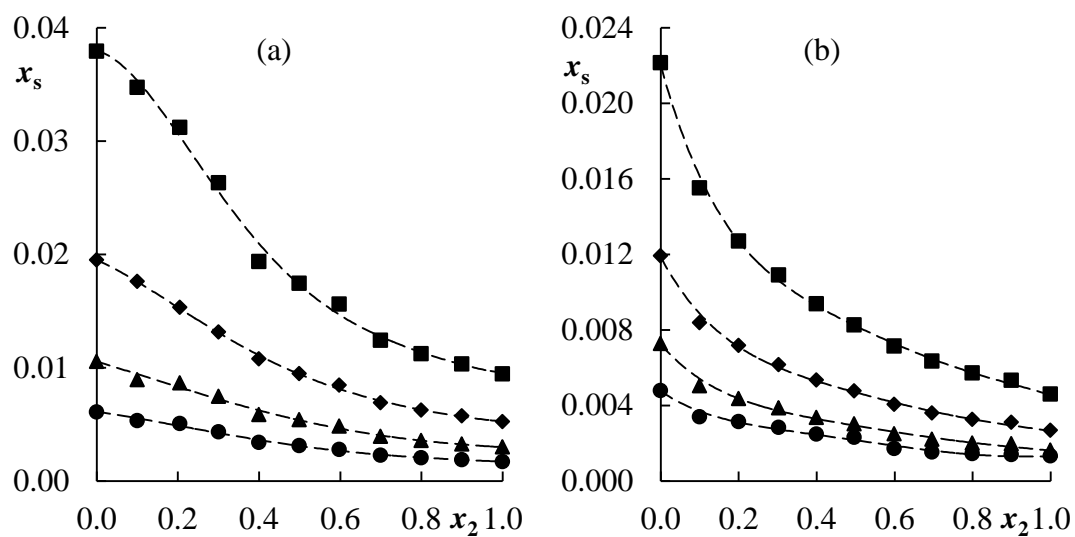
Fig. 2. Solubilities of xylitol (a) and sorbitol (b) as functions of mole fraction: ● 293 K; ▲ 303 K; ♦
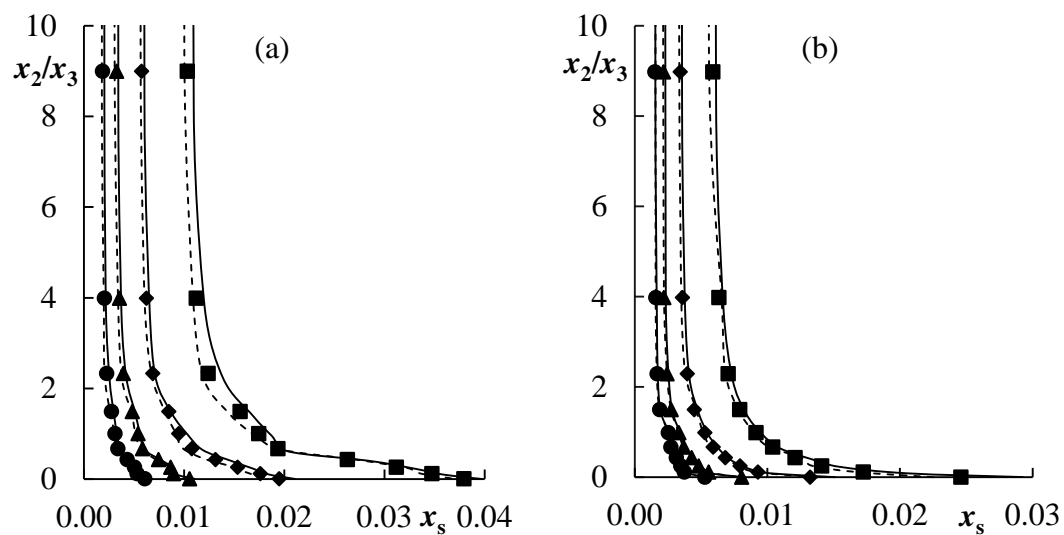
313 K; ■ 323 K; ---- Jouyban-Acree equation

Fig. 3. Behavior of the models ---- NRTL and — UNIQUAC against experimental points for the

mixtures involving xylitol (a) and sorbitol (b): ● 293 K; ▲ 303 K; ♦ 313 K; ■ 323 K

Highlights

- Solubility of xylitol and sorbitol in binary liquid mixtures of methanol/ethanol were determined.

- The experimental data were correlated by the Jouyban-Acree model.

- Solid-liquid equilibrium was modeled by NRTL and UNIQUAC