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Butyl acetate solubility in unsaturated solutions of glucose, sucrose and fructose at low temperatures

Flavio C.Silva¹, Maria A.Barros^{2*}, Moilton R.Franco Jr.²

¹IFTM – Instituto Federal do Triângulo Mineiro – Av. Belarmino Vilela Junqueira s/n°, Bairro Novo Tempo 2, CEP: 38.305-200, Ituiutaba-MG, (BRASIL)

²Chemical Eng. Faculty, Federal University of Uberlândia, Av. João Naves de Ávila 2121, 38408-100, Uberlândia-MG, (BRASIL)
E-mail : moilton@ufu.br

ABSTRACT

Interactions between water and flavour molecules have been widely studied and are characterized by the hydrophobicity and volatility. The influence of different types of sugar should be known in case of they are part from the material. Flavour release from complex food matrices is difficult to predict and solubility data would be helpful. Thus, interactions between flavour molecules and other compounds are often investigated in binary and ternary model systems (e.g., water, flavour compounds, carbohydrates) to characterize specific release mechanisms.

In this paper, the solubility of butyl acetate from pure water and various low-viscosity aqueous solutions (D-Sucrose, D-Glucose, D-Fructose), at 10-30 gL⁻¹, was investigated. Static isothermal method was used and concentrations of the aroma or flavour compound at thermodynamic equilibrium were monitored by analyzing liquid samples using gaseous chromatography. Experiments were carried out at temperature range of 278.2 - 298.2 K. Flavour solubility from mixtures decreased with increasing temperature and decreased with molecular superficial area of the sugar compound. The flavour compound was retained more extensively in the presence of glucose agent, compared to in pure water, while an increase in the solubility was observed in presence of sucrose and fructose. All aqueous solutions had similar behavior as sugar concentration was increased, although it was expected that sugar molecular weight tended to have influences in the equilibrium concentration. A correlation between temperature or sugar concentration and butyl acetate solubility in the low-viscosity solutions was evident. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Butyl acetate;
Sugars;
Solubility;
Unsaturated.

INTRODUCTION

Esters, alcohols and ketones are considered important with respect to fruit and synthetic drinks flavours.

Furanones and esters have been described as the most important aroma-active constituents in sweets and juices^[1]. Among esters, ethyl and butyl acetate are included. The largest group of flavour compounds in wines

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consists of esters of the aliphatic monocarboxylic acids. Butyl acetate and many of the long-chain esters in wine are formed by yeast principally by enzyme reactions during fermentation and not in chemical reactions between ethanol and corresponding acids^[2,3]. It is known that 29% of compounds detected in nature fruit are esters. Also, they had a higher number of identified compounds, and the sweet fruity notes of acerola or cupuaçu aroma, for example, were attributed by their presence. Aliphatic esters comprised the largest class (31%) of the total volatiles compounds found in the sweet fruity juice. The extract obtained from different fruit samples from Brazil presents a pleasant fruity sweet aroma, having higher proportions of sweet high-boiling compounds^[3].

The commercial interest in volatiles, such as butyl acetate, stems from their aromatic and flavour qualities. Several of them, have significant antimicrobial and anti-neoplastic activity. Volatiles are obtained from plants by distillation at or by extraction with organic solvents (ethanol, chloroform, hexane, benzene and so on)^[4].

The exact compositions of many alcoholic beverages are trade secrets; however, there is extensive literature on the aroma components which are usually present at low levels, more than 1300 of which have been identified^[3]. Information about nonaroma compounds is less extensive. An interesting example is Chinese liquor^[5] which has strong fruit, pineapple and banana-like aromas. Sixty-eight volatile components, including alcohols, esters, acids, acetals, ketones, aldehydes and heterocyclic compounds, have been identified in Chinese liquors^[5]. Very few studies report on aroma compounds in them. It would be very important the knowing of equilibrium concentration data to the aroma of Chinese aroma-type liquor, based on the calculated odour activity value. Up to now, no studies have reported on the contribution of aroma compounds to the characteristic bouquet of this liquor^[5].

Juices were already characterized by sugar, amino acid, carboxylic acid and ash pseudocomponents in aqueous solution^[6]. To correlate interaction parameters of traditional or new equations, it is important to obtain experimental data for the systems involved. To study the distillation as well as extraction processes, will be necessary to obtain thermodynamic equilibrium data for the liquid-liquid equilibrium^[7-11] so as to determine the

compositions and their possible industrial uses.

A viable candidate for use as an aroma is butyl acetate. However, it has not been possible to find in the literature^[12] a comprehensive experimental study of its isobaric solubility in unsaturated mixtures of the water-glucose, water-fructose and water-sucrose systems at atmospheric pressure. Usually, the equilibrium data for this system, which are necessary for the design and simulation of the extraction and distillation process, have been obtained from predictions by means of thermodynamic models with parameters based on the correlation of binary VLE and LLE data.

In this work, solubility of butyl acetate in both pure water and several unsaturated aqueous solutions of some monosaccharide, D-(+)-Glucose, D-(-)-Fructose, D-(+)-Sucrose, has been measured at temperature range from 278.2 - 298.2 K. using an isothermal method. Also, this paper has presented the discussion of the influence of the temperature and sugar concentration with respect to these systems. Also, the knowledge of butyl acetate solubility, in fruits and drinks media at low temperatures will allow a better understanding of the physic-chemical interactions of volatile molecules in food and drinks at this range of temperatures.

MATERIALS AND METHODS

Experimental

Chemicals

The sugar compounds (D-Glucose (>99.8%), D-fructose (>99.0%) and D-sucrose (>99.9%)) used in the study were all supplied by VETEC Química (Rio de Janeiro - Brazil). Butyl Acetate (>99.8%) was purchased from ISOFAR. Distilled and deionized water was produced using an academic compact water purification system (Quimis- Brazil). All materials were used as received without any further purification.

Apparatus and procedure

The solubility measurements were performed using an isothermal technique based on the research group experience on solid-liquid and liquid-liquid equilibrium^[7-11].

Jacketed glass cells of about 40 cm³ each were loaded with the appropriate amount of compounds, sugar and water, to perform the desired concentration

10.0-30.0 gL⁻¹. Each solution of different composition was prepared by weighting the desired amount of each compound in a ± 0.0001 g precision balance. Butyl acetate was added to the solution rapidly in a slight excess of over the expected solubility, to a specified liquid sugar solution. Preliminary experiments were made to estimate the amounts to be added of this component. The internal temperature of the cell was controlled by circulating thermostatic liquid in the jacket with a low-temperature thermostat bath (Nova Ética - Brazil) and was also measured with a calibrated thermometer. The thermostatic liquid was a mixture of water and glycerol. The temperature can be considered to be accurate within ± 0.1 K. Mixtures were magnetically stirred at constant temperature for at least 2.0 h, the time considered to be sufficient to reach the equilibrium, based on some preliminary tests and according to the experience of the team^[10,11]. Once the solution was saturated, the stirring was stopped and the excess aroma gradually supernatant in the surface, resulting in a clear bottom liquid phase. The mixture then was allowed to settle for at least 24 h at a constant temperature. In intervals of three or more hours, sampling was carefully made in triplicate, using 2 mL syringes equipped with filter. The solubility of butyl acetate or aroma was determined using a high performance gas chromatography (Focus CG SSI/FID - Thermon Eletron S.p.A) coupled with a FID detector with a OV-5 fused silica capillary column (30m x 0.25mm x 0.25 μ m, 5% phenyl-methylpolysiloxane). The temperature of the column was 513.2 K and the flow rates of gases were: N₂ 30.0 L·min⁻¹, Synthetic air 280 L·min⁻¹ and H₂ 30.0 L·min⁻¹. All samples were withdrawn in triplicates. The average standard deviation on the measurements was approximately 0.002 g·L⁻¹.

RESULTS

It is well known that sugars have very high affinity for water^[14], and considering few concentrations used in trials, so all sugars aqueous solutions had completely dissolution. Relatively few data are available in the literature for sugar mixtures and flavors^[15] compounds.

Some experiments were carried out by monitoring the liquid phase. It was done withdrawing an aliquot of the glucose solution in different intervals of time. Figure 1 is an example of the obtained result. It can be seen

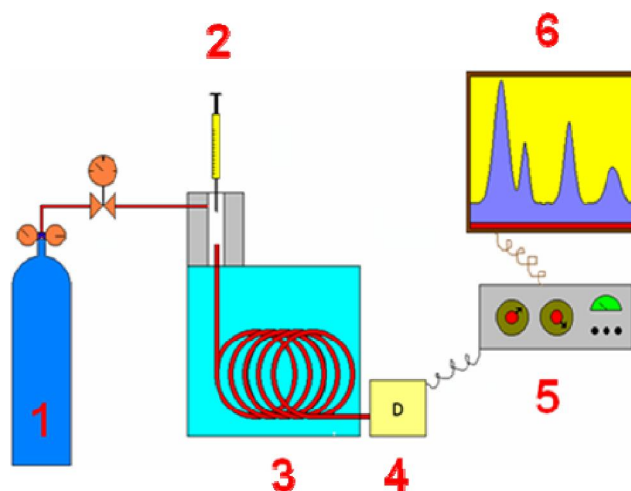


Figure 1 : Equipment used for sample analysis - 1. Gas container and flow control valve; 2. Seringue 3. Column and oven; 4. F. I. Detector; 5. Signal amplifier; 6. Register.

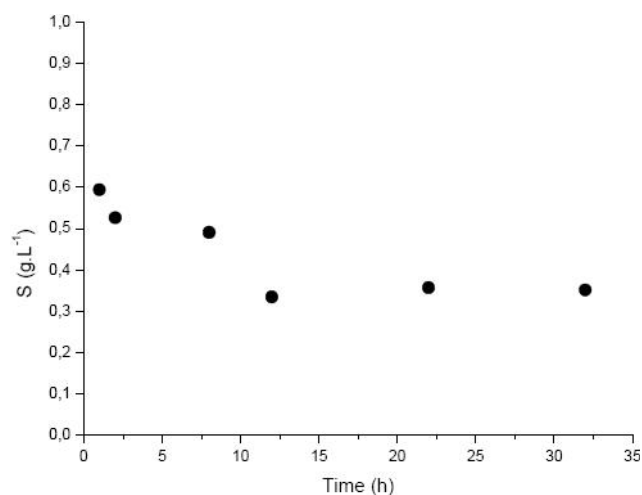


Figure 2 : Solubility as a function of time (h) for butyl acetate in glucose solution. (10 g L⁻¹)

that after 22 hours the ester concentration is constant and then, the phases reached equilibrium.

The isothermal method was used to determine solubility of butyl acetate in pure water. The results obtained by the application of this method to the acetate are presented in TABLE 1, where the solubilities are expressed in terms of grams of ester per 100 grams of solution. The solubility of the flavour compound in water presented in TABLE 1 are compared with the literature and showed good agreement for 298.2 K.

In TABLE 2, experimental results for solubility of butyl acetate in water/sugar systems at 288.2 K shows the influence of sugar concentration on ester solubility. For solution of water/glucose and water/fructose, solubility of butyl acetate decreased while sugar concentra-

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TABLE 1 : Solubility of butyl acetate ($\text{g}\cdot 100\text{g}^{-1}$) in pure water at different temperatures

Reference	T (K)				
	278.2	283.2	288.2	293.2	298.2
This work	1.08514	0.7748	0.7327	0.6630	0.5917
Literature 1*	-	-	-	-	0.5928
Literature 2 **	-	-	-	-	0.6573

* Smith and Bonner (1950); ** Krupatkin and Glagoleva (1970)

TABLE 2 : Solubility of butyl acetate in water/sugar systems at 288.2K

Ester/sugar	Sugar concentration ($\text{g}\cdot\text{L}^{-1}$)		
	10.0	20.0	30.0
	Ester solubility ($\text{g}\cdot\text{L}^{-1}$)		
Butyl acetate/sucrose	0.2984	0.3812	0.3107
Butyl acetate/glucose	0.4608	0.4165	0.4132
Butyl acetate/fructose	0.8244	0.5590	0.2718

tion increased. Furthermore, this behavior was not observed in water/sucrose.

Figures 2-4 show curves that gives the evolution of the magnitudes, $S(\text{g}\cdot 100\text{g}^{-1}$, solubility), as a function of temperature for each sugar used. These Figures shows the experimental results and is possible to observe the influence of sugar concentration on butyl acetate solubility. The low retention of butyl acetate in sugars solution, compared with pure water, is really linked to molecular weight of sugars samples involving interactions with macromolecules.

According to the Figure 3, in mixtures at $20\text{ g}\cdot\text{L}^{-1}$, solubility of butyl acetate in fructose solution was big-

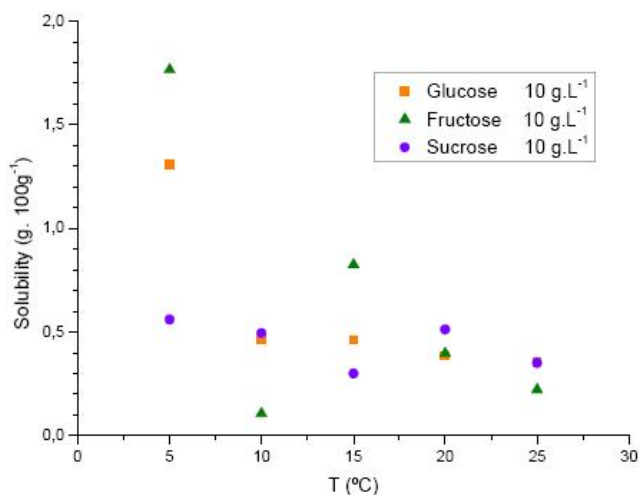


Figure 3 : Solubility of butyl acetate as a function of temperature in aqueous solutions ($10\text{ g}\cdot\text{L}^{-1}$) (■ Glucose ▲ Fructose ● Sucrose)

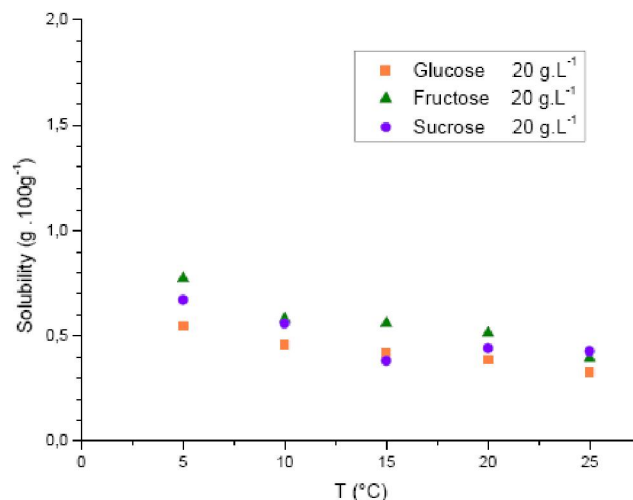


Figure 4 : Solubility of butyl acetate as a function of temperature in aqueous solutions ($20\text{ g}\cdot\text{L}^{-1}$)

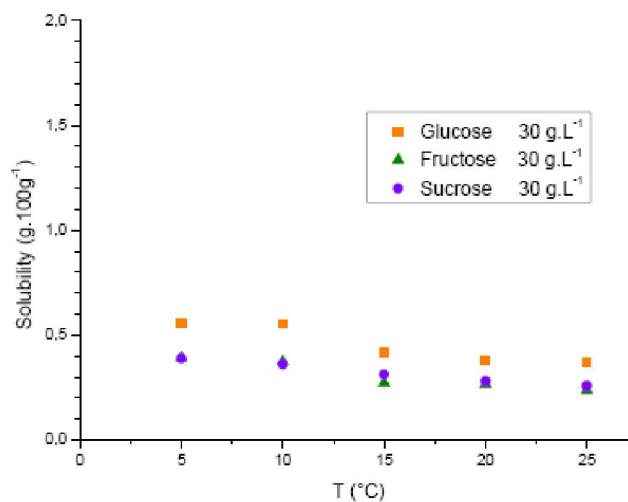


Figure 5 : Solubility of butyl acetate as a function of temperature in aqueous solutions ($30\text{ g}\cdot\text{L}^{-1}$)

ger than in glucose and sucrose, in the temperature range studied. In mixtures containing different sugars at concentrations of $30\text{ g}\cdot\text{L}^{-1}$ (Figure. 4), butyl acetate was retained more extensively in the presence of glucose agent, compared to in presence of sucrose and fructose.

As described in the literature, the molecular weight of polysaccharides is another parameter that can influence the compounds solubility^[4]. Comparing the results, Figure. 2-4, it is possible to observe the effect of substrate's nature and the concentration on butyl acetate solubility, when substrate concentration increased, solubility decreased and when the molecular weight of substrate is major, as sucrose, the solubility decreased. This both effect were detected by Covarrubias-

Cervantes et al^[15]. and they related that this last effect was more important in polyols than in carbohydrates solutions.

The result of increasing the temperature appears to be quite spectacular for butyl acetate, as is illustrated in Figure 2. For the water/butyl acetate system in the presence of sucrose the rise in temperature produces an insignificant increase in the solubility. In the presence of glucose and fructose, however, there is an important increase in solubility. Thus, it seems that the rise in temperature influences the solubility more than the sugar concentration. Likewise, one may note that the rise in temperature diminishes the solubility of this ester in pure water.

Figure 5 illustrates the influence of the sugar concentration in water-glucose mixtures. Differences between solubility values in any glucose solution were observed for butyl acetate. The effect of temperature for compound followed the same behavior in any aqueous solution as that observed for glucose solutions. Solubility decreased in the range from 298.2 down to 278.2 K.

According to our findings, it is clear that all sugars studied had a negative influence on butyl acetate solu-

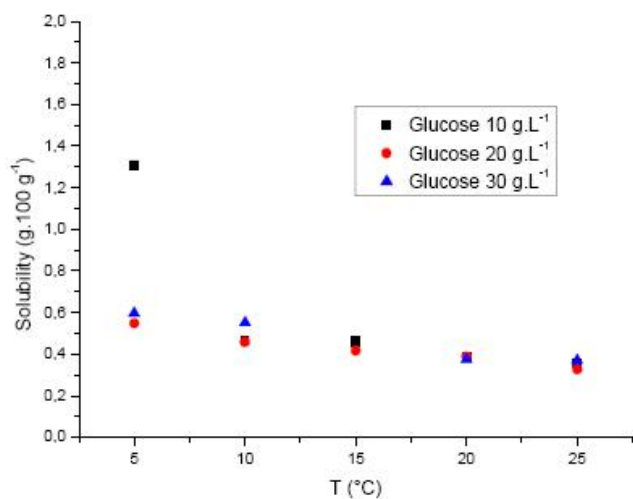


Figure 6 : Solubility of butyl acetate as a function of temperature in mixtures with different glucose concentration (■10, ●20 and ▲30 g. L⁻¹).

bility compared to in pure water. This result could be explained by the existence of interactions between intermolecular forces and molecules polarity of water, sugar and butyl acetate. Also, the data present in this paper indicate that the temperature (T) significantly affect aroma compounds, and overall quality, during the process and the storage of beverages.

Experimental data and adjustments of solubility

Literature^[7,8] has been recommending equations or models to correlate solubility data. We can cite the useful correlations proposed by Heidman et al., Yaws et al. and Wang et al. Similarly and following these authors, solubility (S, in g/L or X₂, in mole fraction) of butyl acetate in water and in sugar aqueous solutions was correlated by Eqs. (1), (2) and (3).

$$S = a + b \exp^{-T/c} \quad (1)$$

$$S = a' + b'T^{c'} \quad (2)$$

$$\ln X_2 = a''T^2 + b''T + c'' \quad (3)$$

where a, b, c; a', b', c'; and a'', b'', c'' are the set of parameters for each equation: Exponential, Power and Polynomial.

The most recent data for butyl acetate in water was presented by Daneshfar et al.^[12] and Yang and Wang^[11]. TABLE 1 presents their solubility data for comparison. Also, as can be seen in TABLE 2, our data are more closed to Yang and Wang data than the other authors. It can confirm the sentence written by Daneshfar et al.^[12] that the difference observed between their results and the results reported in literature is mostly due to the difference in methods of analysis or experimental error.

Correlating the butyl acetate solubility in mixtures

Eq. (3) was used to correlate the solubility data for each sugar concentration (x₂) as a function of temperature.

Results for solubility of butyl acetate in mixtures of sugar-water can be found in TABLE 2 including the ones for pure solvent. As can be seen, the standard

TABLE 3: Parameters from equations 1, 2 and 3 for systems butyl acetate in pure water.

Equation	A	b	c	R ²	R.M.S.D
$S = a + b \exp^{-T/c}$	6.065×10^1	1.1920×10^{20}	5.9218	0.9857	3.70
$S = a' + b'T^{c'}$	1.9525×10^2	-1.6164×10^2	3.27×10^{-2}	0.9188	6.88
$\ln X_2 = a''T^2 + b''T + c''$	2.173×10^{-3}	-1.2789	1.8322×10^2	0.9607	6.28

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TABLE 4 : Adjusted parameters using exponential equation for butyl acetate in sugar aqueous solutions.

Sugar	Concentration	S = a + b exp ^{-T/c}			R ²	R.M.S.D
		a	b	c		
Glucose	10 g L ⁻¹	3.598 x10 ¹	4.9940x10 ²⁶	4.502	0.9986	2.35
	20 g L ⁻¹	2.047 x10 ¹	1.6181 x 10 ⁵	2.1265 x10 ¹	0.9889	2.33
	30 g L ⁻¹	2.591 x10 ¹	2.5731x 10 ⁷	1.5359x10 ¹	0.9635	5.05
Fructose	10 g L ⁻¹	2.308 x10 ¹	6.6486x10 ¹²	9.364	0.9957	3.42
	20 g L ⁻¹	3.008 x10 ¹	3.0753x 10 ⁷	1.5432 10 ¹	0.9625	5.89
	30 g L ⁻¹	1.135 x10 ¹	5.6296104	2.283	0.9532	4.57
Sucrose	10 g L ⁻¹	2.703 x10 ¹	2.1369x10 ¹¹	1.0174x 10 ¹⁶	0.9752	5.02
	20 g L ⁻¹	4.051 x10 ¹	2.6120x10 ¹⁵	7.557	0.9947	1.57
	30 g L ⁻¹	-7.55x 10 ⁻³	1.5285x 10 ²	4.6786x10 ¹	0.9952	1.35

TABLE 5 : Adjusted parameters using power equation for butyl acetate in sugar aqueous solutions.

Solution	Concentration	S = a' + b'T ^{c'}			R ²	R.M.S.D
		a'	b'	c'		
Glucose	10 g L ⁻¹	-3.9421x10 ⁻¹	4.4470x10 ²⁵	-1.044x10 ²⁵	0.9238	16.06
	20 g L ⁻¹	5.3540 x 10 ¹	-3.878 x 10 ¹	5.5537x10 ⁻²	0.9823	2.66
	30 g L ⁻¹	1.2094 x 10 ³	-1.1886x10 ³	2.996 x10 ⁻³	0.9404	6.67
Fructose	10 g L ⁻¹	4.0728x 10 ³	-4.0139x10 ³	2.543x10 ³	0.9587	12.25
	20 g L ⁻¹	3.1249x 10 ²	-2.8616x10 ²	1.5228x10 ¹	0.9524	4.98
	30 g L ⁻¹	1.9377x 10 ³	-1.9238x10 ³	1.239 x10 ⁻³	0.9480	4.95
Sucrose	10 g L ⁻¹	1.1386x 10 ²	-9.5324x10 ¹	3.0744x10 ⁻²	0.9505	5.55
	20 g L ⁻¹	1.0529x 10 ⁴	-1.0509x10 ⁴	3.27x 10 ⁻²	0.9505	6.02
	30 g L ⁻¹	-2.1756x10 ¹	3.6893x 10 ¹	-9.068x 10 ⁻²	0.9936	1.62

TABLE 6 : Adjusted parameters using the nordstrom and rasmuson's equation for butyl acetate in sugar aqueous solutions.

Solution	Concentration	ln X ₂ = a''T ² + b''T + c''			R ²	R.M.S.D
		a''	b''	c''		
Glucose	10 g L ⁻¹	3.740x10 ⁻³	-2.209	3.1986x10 ²	0.9957	4.66
	20 g L ⁻¹	2.480 x10 ⁻¹	-1.667 x 10 ⁻¹	2.1319x10 ¹	0.9884	2.29
	30 g L ⁻¹	6.0 x10 ⁻⁴	3.7275x10 ¹	5.1489x10 ¹	0.9641	4.86
Fructose	10 g L ⁻¹	2.6860x10 ⁻³	-1.6138	2.3532x10 ²	0.9935	5.89
	20 g L ⁻¹	4.050 x10 ⁻⁴	-2.6241x 10 ⁻¹	3.5422x10 ¹	0.9624	5.75
	30 g L ⁻¹	2.29x10 ⁻⁴	-1.5896x 10 ⁻¹	1.9651 x10 ¹	0.9559	4.55
Sucrose	10 g L ⁻¹	-1.0 x10 ²	3.3507x10 ⁻²	-7.9427	0.9801	3.09
	20 g L ⁻¹	1.287 x10 ⁻³	-7.6436x 10 ¹	1.0695 x10 ²	0.9970	1.09
	30 g L ⁻¹	2.0 x10 ⁻⁵	1.014 x10 ⁻²	-2.1936	0.9952	1.36

deviation (δ) presented low values in all cases. Differently from the butanedioic acid in ethanol-water mixtures^[19], citric acid has not shown maximum solubility value in any mixture. It was noted that solubility always increased for the studied temperature range. In addition, citric acid presented similar solubility in both alcohols and was more soluble in alcohol than in water contra-

dicting the results of Daneshfar et al. 2012.

In order to correlate the acid solubility in the ethanol-water mixtures, it was used the Eq. 5. For this equation, the fitted parameters are listed in TABLE 3. This TABLE shows the experimental and calculated results of solubility for citric acid in ethanol-water. The root-mean-square deviations results for the fitted curve are

also given in TABLE 3. In general, rmsd is found to be about 0.013 for all concentrations and, therefore, the equation predicts the experimental data reasonably well. The accuracy of the estimation of the equation parameters is satisfactory, as also presented in Oliveira^[10].

The parameters and the root-mean-square deviations (RMSD) for Eqs. 2-4 are shown in TABLE 3. The root-mean-square deviation is defined by Eq. (5).

$$\text{RMSD} = \left[\frac{1}{n-1} \sum_{i=1}^n (x_i^{\text{cal}} - x_i^{\text{exp}})^2 \right]^{1/2} \quad (5)$$

where n is the number of experimental points. Experimental (x^{exp}) and calculated (x_{c1} or x_{c2}) data for pure solvents are listed in TABLE 1. Also, TABLE 1 shows data from other researchers (x^{lit}) as well. It can be seen that the experimental data is reasonable correlated by both equations.

CONCLUSIONS

The various results presented here emphasize the relations between the molecular structure of sugars and their influence in the butyl acetate solubility in sugar solutions. The establishment of a hydrogen bond with oxygen of a carbonyl group seems to be the essential solubilization factor for the organic molecule. Concerning the effects of sugars, a specific interaction of the molecule with ester has been examined.

Further consideration should be given concerning the influences of the molecular structure of the sugar on ester solubility in the aqueous phase. Judging from the results obtained, it seems that in the higher sugar concentrations the interactions are very similar that the type of sugar has no influence in the measured solubility. Also, increasing the temperature disfavors ester solubility in the aqueous phase.

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