Determination and correlation of the solubility of L-arabinose and D-galactose in binary solvent mixtures from 278.15 to 333.15 K

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Abstract−L-arabinose and D-galactose could be released during the hydrolysis process of Arabic gum. The development of a crystallization process of L-arabinose is highly dependent on the knowledge of the solubility of both saccharides. In this work, the solubility of L-arabinose and D-galactose in binary mixtures of methanol-water or ethanol-water (mole fraction of water ≤0.5816) was determined at temperatures between 278.15 and 333.15 K by a static equilibrium method. The experimental data correlated well with the modified Apelblat equation, the simplified polynomial empirical equation, NRTL model and UNIQUAC model. Additionally, the thermodynamic properties including the dissolution enthalpy and entropy were obtained from the experimental data. Within the studied temperature range, the dissolution is endothermic and the dissolution process is non-spontaneous.

Keywords: Solubility, L-arabinose, D-galactose, Methanol-water, Ethanol-water

INTRODUCTION

Crystallization is normally the preferred method for purification of either final chemical substances or intermediates in the synthesis process of pharmaceutical and agricultural chemical industries [1]. Solvent selection is a critical task during development of a crystallization process. It directly determines crystallization yield and manufacturability [2]. Solubility plays a prominent role in solvent selection because crystallization is always preferable at relatively low temperature and/or with the addition of anti-solvent [3]. To date, some chemicals are still short of solubility data; thus solvent selection is largely dictated by researchers' preference or laborious trial-and-error experiments.

L-arabinose ($C_5H_{10}O_5$, CAS No. 87-72-9, MW 150.13, Fig. 1) is a useful starting material for the chemical synthesis of L-pentoses and derivatives thereof [4,5]. As investigated by researchers, L-arabinose might assist with weight loss and control of diabetes by inhibiting sugar absorption noncompetitively, so it has received growing interest [6]. L-arabinose can be readily prepared by the hydrolysis of Arabic gum [7]. During the hydrolysis process, both L-arabinose and D-galactose were released from the polysaccharides in the form of a free sugar. Indeed, D-galactose ($C_6H_{12}O_6$, CAS No. 59-23-4, MW 180.16, Fig. 1) is a stubborn impurity in the industrial production of L-arabinose owing to their very similar structures and properties. Crystallization is generally the first choice for the purification of L-arabinose. Consequently, it is very necessary to obtain the solubility data in the related solvents for the crystallization process, and it is desirable to calculate the solubility using validated thermodynamic models. However, the evaluation of solvation behavior based on modeling is not easy because of neighboring hydroxyl groups in their molecular skeletons, resulting in complicated intra-molecular interactions [8]. Therefore, to study and optimize such predictive tool as modeling technology, a considerable amount of experimental phase equilibrium data are highly desired [9].

To the best of our knowledge, the reports on the solubility of both saccharides are scarce [10-12]. In this work, we attempted to measure the solubility data of L-arabinose and D-galactose in binary mixed solvents containing ethanol/methanol and water from 278.18 K and 333.15 K. Especially, the results at the low temperatures will play an important role in the design and operation of a cooling crystallizer. The experimental data were further correlated with the modified Apelblat equation, polynomial empirical equation, non-random two liquid (NTRL) model and universal quasi-chemical (UNIQUAC) model. The deviation of the different models was calculated to analyze the reliability of prediction of these models. Additionally, the dissolution thermodynamic properties of L-arabinose and D-galactose were also calculated based on the experimental data and van't Hoff equation.
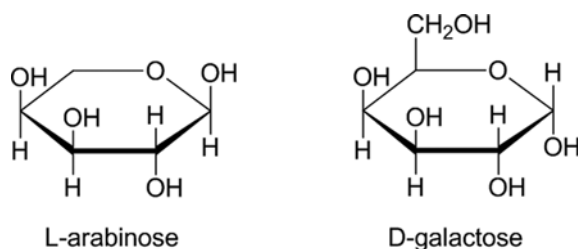

Fig. 1. Chemical structures of L-arabinose and D-galactose.

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Table 1. Purities and sources of chemicals

Name	Mass fraction purity	Supplier	Purity analysis method
L-arabinose	0.99	Alfa Aesar.	Stated by supplier
D-galactose	0.99	Alfa Aesar.	Stated by supplier
Methanol	0.999	Merck Co., Germany	Stated by supplier
Ethanol	0.999	Merck Co., Germany	Stated by supplier
Acetonitrile	0.999	Merck Co., Germany	Stated by supplier
NaCl	0.9999	Alfa Aesar.	Stated by supplier
Deionized water	Electrical conductivity≤10 μs/cm	Prepared by Reverse-osmosis	None

EXPERIMENTAL

1. Materials

L-arabinose ($C_5H_{10}O_5$, 99%) and D-galactose ($C_6H_{12}O_6$, 99%) were purchased from Alfa Aesar and used without further purification. Methanol, ethanol and acetonitrile used in the experiment were commercially available and of analytical purity grade without further treatment. Distilled deionized water was used for all experiments with its purity verified by pH and electrical conductivity. The details of the materials used in this work are listed in Table 1.

2. Apparatus and Procedure

All experiments were performed at atmospheric pressure using a static equilibrium method [13-15]. The measurements were carried out by means of a jacketed glass vessel (50 mL) with magnetic stirring. A constant temperature was controlled by circulating fluid through the outer jacket of the glass vessel from a thermostatic bath, and the actual temperature was measured by a thermometer (±0.1 K). A condenser was connected with the vessel to prevent the solvent from evaporating. An excess amount of solute powder was added to the aqueous solution of ethanol (or methanol), and was stirred for at least 12 h, which had been examined to be an adequate length of time for the system to reach solid-liquid equilibrium. The resulting mixture was then held still for about 2 h at a constant temperature to enable any finely dispersed solids to settle. The sample of the clear supernatant part of the mixture was withdrawn using a preheated glass syringe with a syringe filter (PTFE, hydrophobic, 0.25 μm) at a slightly higher temperature than the solution temperature in order to avoid any precipitation, and transferred to a flask and then appropriately diluted to the desired volume. The diluted sample was finally analyzed by HPLC. Each experiment at a given condition was repeated five times and an average value was provided. No degradation of both monosaccharides was found during the entire experiments at the range of temperatures studied. The reported expanded uncertainty has a level of confidence of approximately 95% and is based on the standard uncertainty multiplied by a coverage factor k=2. The standard solutions for constructing calibration curve were separately prepared by dissolving an accurate amount of solute weighed with an analytical balance (Mettler Toledo AB204-N, Switzerland, ±0.0001 g) in deionized water.

3. Sample Analysis

A high-performance liquid chromatography (HPLC) system (Dionex, US) equipped with a corona charges aerosol detector (CAD) was used to monitor the concentration of L-arabinose and D-galactose. All chromatographic analyses were carried out at 30 °C using a Grace Prevail Carbohydrate ES (250 mm×4.6 mm, 5 μm) with a mobile phase of acetonitrile: water (75 : 25, v/v) at a flow rate of 1 mL·min^{-1} with an injection volume of 5 μL. Calibration curves were constructed by using the standard solutions in the following concentration ranges: L-arabinose, 0.5 to 4.0 mg·mL^{-1}; D-galactose, 0.1 to 1 mg·mL^{-1}.

4. DSC Measurement

The melting point (T_m) and fusion enthalpy ($\Delta_{fus}H$) of L-arabinose and D-galactose were measured using differential scanning calorimetry (DSC Q200, TA Co., American) under a nitrogen atmosphere with constant flow rate of 50 mL·min^{-1}. About 6 to 8 mg of samples were placed in sealed aluminum pans, and the samples were scanned from room temperature to 473.15 K with a heating rate of 10 K·min^{-1}. The melting point (T_m) and the molar enthalpy change ($\Delta_{fus}H$) are important thermodynamic properties that are

Table 2. Solubility of glucose in ethanol/water mixtures containing 20 wt% water at the temperature T^a range of (273.15 to 293.15) K at temperature and ambient pressure p=0.1 MPa^b

T/K	x/g·g^{-1}		^{c}Relative deviation/%	^{d}Expanded uncertainty
	Literature values [12]	Experimental values		
273.15	0.01520	0.01516	0.26137	0.02465
283.15	0.03170	0.03184	0.42614	0.00606
293.15	0.04670	0.04680	0.21468	0.00970

^{a,b}The standard uncertainty u are u(T)=0.1 K, u$_r$(p)=0.1

^{c}The relative deviation is calculated as $\left|\dfrac{x_{literature}-x_{experiment}}{x_{literature}}\right|\times 100\%$

^{d}The expanded uncertainty (±) has a level of confidence of approximately 95%

Table 3. The experimental mole fraction solubility (x_1) of L-arabinose and D-galactose in methanol-water mixtures at temperature T and ambient pressure p=0.1 MPa[a], and the methanol mole fraction in solute-free solvent, x_2

Saccharide	T/K	[b]x_1 (Methanol [c]x_2)		
		0.5093	0.6402	0.8001
L-arabinose	278.15	0.00682	0.00317	0.00184
	288.15	0.01426	0.00589	0.00304
	298.15	0.02246	0.01064	0.00520
	303.15	0.02759	0.01451	0.00689
	313.15	0.04045	0.02159	0.01225
	323.15		0.03135	0.02075
	333.15		0.04980	0.02949
D-galactose	278.15	0.00171	0.00084	0.00046
	288.15	0.00285	0.00151	0.00081
	298.15	0.00535	0.00273	0.00145
	303.15	0.00734	0.00374	0.00202
	313.15	0.01201	0.00618	0.00345
	323.15	0.02050	0.01003	0.00545
	333.15		0.01832	0.00987

[a,c]The standard uncertainty u are u(T)=0.1 K, u_r(p)=0.1, u_r(x_2)= 0.01
[b]The relative standard uncertainty of the solubility measurement is u_r(x_1)=0.03

Table 4. The experimental mole fraction solubility (x_1) of L-arabinose and D-galactose in ethanol-water mixtures at temperature T and ambient pressure p=0.1 MPa[a], and the ethanol mole fraction in solute-free solvent, x_2

Saccharide	T/K	[b]x_1 (Ethanol [c]x_2)		
		0.4184	0.5522	0.7351
L-arabinose	278.15	0.00670	0.00284	0.00148
	288.15	0.01208	0.00608	0.00251
	298.15	0.01834	0.01088	0.00370
	303.15	0.02231	0.01429	0.00417
	313.15	0.03045	0.02043	0.00661
	323.15	0.03723	0.02812	0.00968
	333.15		0.03693	0.01864
D-galactose	278.15	0.00107	0.00067	0.00027
	288.15	0.00271	0.00119	0.00058
	298.15	0.00528	0.00230	0.00092
	303.15	0.00660	0.00291	0.00120
	313.15	0.01095	0.00487	0.00179
	323.15	0.01559	0.00789	0.00272
	333.15		0.01172	0.00517

[a,c]The standard uncertainties u are u(T)=0.1 K, u_r(p)=0.1, u_r(x_2)= 0.01
[b]The relative standard uncertainty of the solubility measurement is u_r(x_1)=0.03

also necessary information for the local thermodynamic model.

RESULTS AND DISCUSSION

1. Solubility Data of L-arabinose and D-galactose

To validate the method of solubility measurement, the solubility of glucose in the studied binary systems of ethanol-water mixtures containing 20 wt% water at the temperature range from 273.15 to 293.15 K was repeated three times to check the reproducibility and uncertainty, and also was compared to the literature [16]. It was found that the relative deviation between the experimental and the previously reported data was less than 0.5% (Table 2), indicating it was in good agreement with that reported in the literature. This further confirmed the experimental data obtained by this method are repeatable and credible.

The solubility of L-arabinose and D-galactose in the studied binary systems of methanol-water mixtures or ethanol-water mixtures (volume percentage of water ranged from 10% to 30%) at temperatures in the range of 278.15-333.15 K are summarized in Tables 3 and 4 and depicted in Figs. 4 and 5. Overall, L-arabinose had significantly better solubility than D-galactose, although D-galactose molecule had one more hydroxyl group. This suggests hydrogen bond is a key factor, but not the only factor, to determine the solubility. Other properties such as chain length, melting properties and viscosity also contribute to the process of dissolution. A stronger overall solute-solvent interaction gives a higher solubility of monosaccharide in the selected media.

According to thermal analysis shown in Figs. S1 and S2 of Supporting Information, L-arabinose and D-galactose displayed only

one clear peak. The melting point and the fusion enthalpy change were 433.05 K (Δ_{fus}H=255.1 J/g or 38.30 kJ/mol) and 443.35 K (Δ_{fus}H=259.7 J/g or 46.79 kJ/mol) for L-arabinose and D-galactose, respectively. For ideal solution, the solubility can be calculated through the following equation [17,18]:

$$\ln x = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{1}$$

At a certain temperature,

$$\ln x_{arabinose} - \ln x_{galactose} = \frac{38.3 \times 10^3}{8.314}\left(\frac{1}{433.05} - \frac{1}{T}\right)$$
$$- \frac{46.8 \times 10^3}{8.314}\left(\frac{1}{443.35} - \frac{1}{T}\right) = \frac{1022}{T} - 2.06 \tag{2}$$

At temperature from 278.15 to 333.15 K:

$$\ln x_{arabinose} - \ln x_{galactose} > 0 \tag{3}$$

So, connecting to melting properties, the solubility of L-arabinose is higher than that of D-galactose within the temperature range in this work.

As seen from Table 3 and Table 4, the solubility of both monosaccharides in the binary mixtures of alcohol-water is expected to increase not only as equilibrium temperature increases, but also with the increased water volume fraction in saccharide-free solution. It is easy for us to understand that both saccharides are quite soluble in the studied aqueous alcohol solutions because of the strong hydrogen bonding interaction between carbohydrate and water. Compared to ethanol, methanol is a more favorable solvent media for enhancing both saccharides' solvation because of its

higher polarity. According to the empirical rule "like dissolves like," the dissolution is easier if the solute and solvent have similar polarity. Accordingly, the higher polarity of methanol is beneficial to forming stronger hydrogen bonding interaction between solvent and saccharides, leading to a higher solubility than that in ethanol.

Furthermore, the measured solubility was compared with literature values. The solubility data of D-galactose in the mixture of ethanol-water at 273.2, 288.2 and 303.2 K, have been reported by Zhang et al. [10], and Jiang et al. [11] reported the solubility of L-arabinose in ethanol-water ranging from 283.15 to 308.15 K. These values were compared to the experimental results and shown in Fig. 4 and Fig. 5, from which it can be found that the solubility data in references show slightly different from those determined in this work. The deviation between the reported data in the references and that in this work may be attributed to the different measurement procedure and analysis method.

2. Correlation of the Experimental Data

Since solid-liquid equilibrium data are not readily available, especially in mixed solvents, correlation and prediction of solubility are frequently employed. First, we used two empirical fitting equations including the modified Apelblat model and polynomial equation to correlate the obtained solubility of L-arabinose and D-galactose. The Apelblat equation is an empirical fitting equation, which was extensively used to correlate the solute concentration in saturated aqueous organic acids by Apelblat and Manzurola [19,20]. Besides, we adopted another empirical fitting equation: the polynomial empirical equation [21].

The solubility as a function of temperature fit by the modified Apelblat equation and the simplified polynomial empirical equation are shown as follows, respectively:

$$\ln x_1 = A' + \frac{B'}{T} + C' \ln T \tag{4}$$

$$x_1 = A + BT + CT^2 + DT^3 \tag{5}$$

where x_1 is the mole fraction solubility of monosaccharides, T is the absolute temperature (K), and A′, B′, C′, A, B, C and D are dimensionless coefficients determined by least square analysis and

Table 5. Parameters for correlation Eq. (4) in binary solvents of alcohols and water at 278.15 K to 333.15 K together with the root-mean-square deviation RMSD, and alcohols mole fraction in solute-free solvent, x_2

Saccharide	Solvent (x_2)	A′	B′	C′	[a]10^2RMSD
L-arabinose	Methanol (0.5093)	391.1	−21032	−56.93	0.051
	Methanol (0.6402)	−26.6	−2670	5.44	0.087
	Methanol (0.8001)	332.6	−19847	−47.61	0.044
	Ethanol (0.4184)	464	−23823	−68.12	0.091
	Ethanol (0.5522)	388.6	−21267	−56.48	0.032
	Ethanol (0.7351)	−650.75	25972	97.92	0.043
D-galactose	Methanol (0.5093)	−74.9	−1152	12.91	0.025
	Methanol (0.6402)	−324.9	10302	49.92	0.020
	Methanol (0.8001)	−270.8	7784	41.81	0.029
	Ethanol (0.4184)	487.4	−26318	−70.98	0.018
	Ethanol (0.5522)	199.8	−13573	−28.15	0.010
	Ethanol (0.7351)	−502.3	18818	75.85	0.015

[a]RMSD is the root-mean-square deviation calculated by Eq. (8)

Table 6. Parameters for correlation Eq. (5) in binary solvents of alcohols and water at 278.15 K to 333.15 K together with the root-mean-square deviation RMSD, and alcohols mole fraction in solute-free solvent, x_2

Saccharide	Solvent (x_2)	A	B	C	D	[a]10^2RMSD
L-arabinose	Methanol (0.5093)	−6.979	0.072542	−0.000253	2.98×10^{-7}	0.067
	Methanol (0.6402)	−5.799	0.060163	−0.000209	2.44×10^{-7}	0.070
	Methanol (0.8001)	0.544	−0.00321	2.20×10^{-6}	8.42×10^{-9}	0.059
	Ethanol (0.4184)	4.611	−0.04641	0.0001538	-1.67×10^{-7}	0.039
	Ethanol (0.5522)	0.890	−0.00809	0.0000228	-1.85×10^{-8}	0.018
	Ethanol (0.7351)	−5.510	0.05595	0.00019	2.15×10^{-7}	0.039
D-galactose	Methanol (0.5093)	−2.97	0.031918	0.0001147	1.38×10^{-7}	0.017
	Methanol (0.6402)	−3.79	0.039076	0.000134	1.55×10^{-7}	0.028
	Methanol (0.8001)	−1.84	0.019072	0.000066	7.61×10^{-8}	0.015
	Ethanol (0.4184)	0.55	−0.004698	0.000012	-8.13×10^{-9}	0.013
	Ethanol (0.5522)	−0.40	0.004705	0.0000185	2.43×10^{-8}	0.038
	Ethanol (0.7351)	−1.45	0.014811	0.0000502	5.69×10^{-8}	0.024

[a]RMSD is the root-mean-square deviation calculated by Eq. (8)
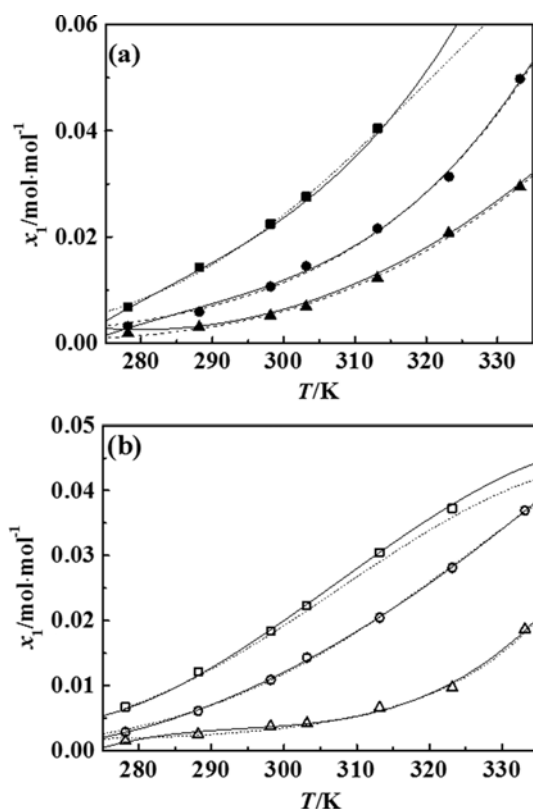
Fig. 2. The mole fraction solubility of L-arabinose in the aqueous solutions of methanol (a) and in mixed solvents of ethanol-water (b) from 278.15 K to 333.15 K: ■, water-0.5816 (mole fraction); ●, water-0.4478; ▲, water-0.2649: Symbols represent the measured results of this work, and the dash lines indicate the values calculated from Eq. (4), the continuous lines indicate the values calculated from Eq. (5).
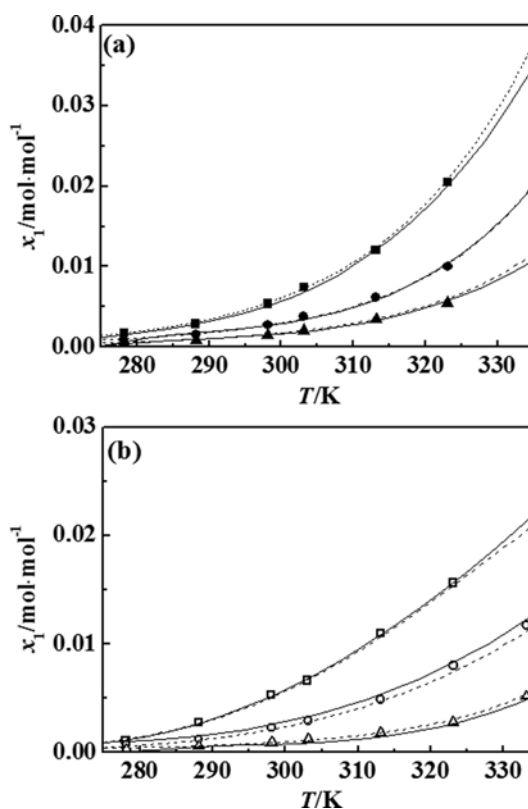

Fig. 3. The mole fraction solubility of D-galactose in the aqueous solutions of methanol (a) and in mixed solvents of ethanol-water (b) from 278.15 K to 333.15 K: ■, water-0.5816 (mole fraction); ●, water-0.4478; ▲, water-0.2649: Symbols represent the measured results of this work, and the dash lines indicate the values calculated from Eq. (4), the continuous lines indicate the values calculated from Eq. (5).

are presented in Tables 5 and 6 and shown in Fig. 2-3. x_1 is calculated based on Eq. (6). And the solvent composition x_2 could be calculated by Eq. (7).

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{6}$$

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{7}$$

where m_1, M_1: quality and relative molecular weight of solute (g, g·mol^{-1}), m_2, M_2 and m_3, M_3: quality and relative molecular weight of alcohol and water (g, g·mol^{-1}).

The root-mean-square deviation (RMSD) shown in both tables is defined as:

$$RMSD = \left[\frac{1}{n}\sum_{i=1}^{n}(x_{i,cal} - x_{i,exp})^2\right]^{1/2} \tag{8}$$

where n is the number of experimental points, $x_{i,cal}$ and $x_{i,exp}$ represent the experimental and calculated solubility of monosaccharide in solvent i.

A parity plot of experimental versus calculated lines is shown in Figs. 2 and 3, and parameters of the models are listed in Tables 5 and 6 along with the RMSD. In most cases, the correlated results for
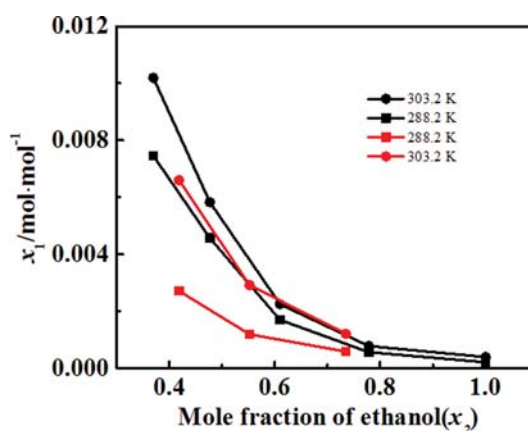

Fig. 4. Comparison of mole fraction solubility (x_1) of D-galactose in the mixed solvents of ethanol-water at 288.2 K (■) and 303.2 K (●): red, this work; black, literature [10].

L-arabinose and D-galactose solubility of the modified Apelblat equation and polynomial empirical equation both show consistent trends. The calculated solubility data are very close to the measured solubility, indicating that both models fit the data well (RMSD^2<0.1%). Both models can be used to describe the solubility and to obtain

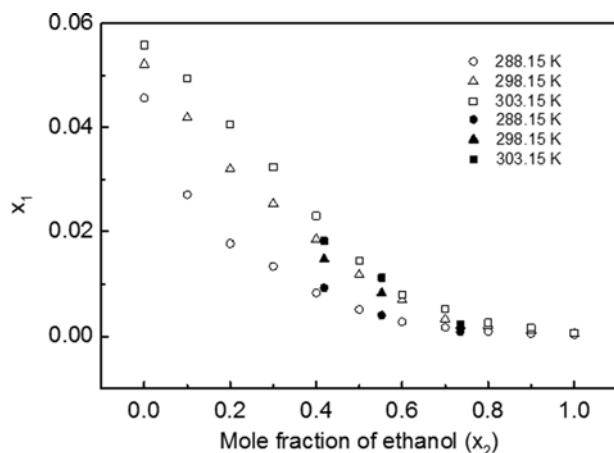**Fig. 5. Mole fraction solubility (x_1) of L-arabinose in mixed solvents of ethanol-water at different temperatures (T) in this work (solid) and literature (hollow) [11].**

solubility data by interpolation within the studied temperatures for the alcohol-water mixtures at a given volume fraction of water.

Apart from empirical model, the local thermodynamic models such as NRTL and UNIQUAC equation are suitable to correlate the solubility data changing with both temperature and composition of mixed solvent. Based on the theory of solid-liquid equilibrium, the solubility of solute in the solution can be described by the following equation [22,23]:

$$\ln x_1 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) - \frac{\Delta C_P}{R}\left(\ln\frac{T}{T_m} - \frac{T}{T_m} + 1\right) - \ln\gamma_i \quad (9)$$

where T_m, $\Delta_{fus}H$ and ΔC_p represent the melting point, the enthalpy of fusion and the difference between the molar heat capacity of the melting and solid states of the solute, respectively. γ_i represents the activity coefficient of the solute. The melting temperature and the fusion enthalpy are easily available by means of DSC experiment. ΔC_p is assumed negligible and considered to be zero. So the

Eq. (9) can be simplified as follows:

$$\ln x_1 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) - \ln\gamma_i \quad (10)$$

The activity coefficient of solute was expressed by the NRTL and UNIQUAC equation in this study. The NRTL model for the activity coefficient in the binary solvent is given by the following equations [24,25]:

$$\ln\gamma_i = \frac{(G_{ij}x_j + G_{ki}x_k)(\tau_{ji}G_{ji}x_j + \tau_{ki}G_{ki}x_k)}{(x_i + x_jG_{ji} + x_kG_{ki})^2}$$
$$+ \frac{[\tau_{ij}G_{ij}x_j^2 + G_{ij}G_{kj}x_jx_k(\tau_{ij} - \tau_{kj})]}{(x_i + x_jG_{ji} + x_kG_{ki})^2}$$
$$+ \frac{[\tau_{ik}G_{ik}x_k^2 + G_{ik}G_{jk}x_jx_k(\tau_{ik} - \tau_{jk})]}{(x_k + x_iG_{ik} + x_jG_{jk})^2} \quad (11)$$

where G_{ij}, G_{ik}, G_{ji}, G_{jk}, G_{ki}, G_{kj}, τ_{ij}, τ_{ik}, τ_{ji}, τ_{jk}, τ_{ki}, and τ_{kj} are parameters of this model. The definition of these terms is:

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (12)$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \quad (13)$$

where τ refers to a constant related to the non-randomness of the solution, g represents the Gibbs energy of intermolecular interaction, and α is an adjustable empirical constant between 0 to 1. In this study, α was set to 0.3, so the NRTL equation has six adjustable parameters.

The UNIQUAC model for the activity coefficient in binary solvent is given by [26]

$$\ln\gamma_i = \ln\frac{\phi_i}{x_i} + \left(\frac{z}{2}\right)q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{3}x_jl$$
$$+ q_i - q_i\ln\left(\sum_{j=1}^{3}\theta_j\tau_{ij}\right) - q_i\sum_{j=1}^{3}\frac{\theta_j\tau_{ij}}{\Sigma_{k=1}^{3}\theta_k\tau_{kj}} \quad (14)$$

Table 7. Parameters of the NRTL and UNIQUAC models for L-arabinose and D-galactose in binary solvent

	J·mol^{-1}	L-arabinose		D-galactose	
		Methanol+Water	Ethanol+Water	Methanol+Water	Ethanol+Water
NRTL	Δg_{12}	−5671	−3410	−6139	−4791
	Δg_{13}	20045	20655	28688	16282
	Δg_{21}	35383	26891	23960	86765
	Δg_{23}	12597	11776	14566	11181
	Δg_{31}	42693	26091	33339	34435
	Δg_{32}	24539	9737	24626	19318
	10^4RMSD	1.88	4.91	0.36	0.20
UNIQUAC	Δu_{12}	3467	1160	−2844	−17344
	Δu_{13}	−7953	35257	−1127	−788
	Δu_{21}	−773	769	9521	−1205
	Δu_{23}	−8701	−34892	−3208	−1029
	Δu_{31}	804	−2486	−1245	−31
	Δu_{32}	594	660	−3615	−29416
	10^4RMSD	0.77	3.74	0.048	1.02

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{3} r_j x_j}, \quad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{3} q_j x_j} \tag{15}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - q) \tag{16}$$

$$\tau_{ij} = \exp\left(\frac{u_{ij} - u_{jj}}{RT}\right) = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) \tag{17}$$

where z represents the coordination number to be set as 10. r_i and q_i are defined as the structural parameters of solute or solvent, and were taken from reference [26-28]. The adjustable parameters Δu_{ij} are related to interaction energy between solvent and solute.

Model parameters can be obtained by least-squares regression. The parameters along with the RMSD of both models are summarized in Table 7. The RSMD for both models was less than 0.05%. It can be concluded that as a function of both temperature and the mole fraction of lower alcohols, the NRTL and the UNIQUAC model can still give good correlation results with satisfactory accuracy.

3. Thermodynamic Properties of Solution

In this work, the apparent molar enthalpies of solution could be described as the van't Hoff equation. First, another quantity called the standard molar dissolution enthalpy ($\Delta_{sol}H_m^0$) should be defined and the description of the model and equations can be found elsewhere [29-31]:

$$\Delta_{sol}H_m^0 = -R \times \left(\frac{\partial \ln x_1}{\partial(1/T)}\right) \tag{18}$$

where x_1 is mole fraction solubility of L-arabinose or D-galactose, R is the gas constant, T is the absolute temperature. Over a limited temperature interval, the standard molar dissolution enthalpy could also be valid for the mean temperature; thus the equation can be rewritten as:

$$\Delta_{sol}H_m^0 = -R \times \left(\frac{\partial \ln x_1}{\partial(1/T - 1/T_{mean})}\right) \tag{19}$$

where T_{mean} represents the mean temperature of the temperature range.

Because of the lack of activity coefficients, in this work the Gibbs free energy of solution can be determined as an apparent value. Thus, the equation of the molar dissolution Gibbs free energy is given as [21,32]:

$$\Delta_{sol}G_m^0 = -RT_{mean} \times \text{intercept} \tag{20}$$

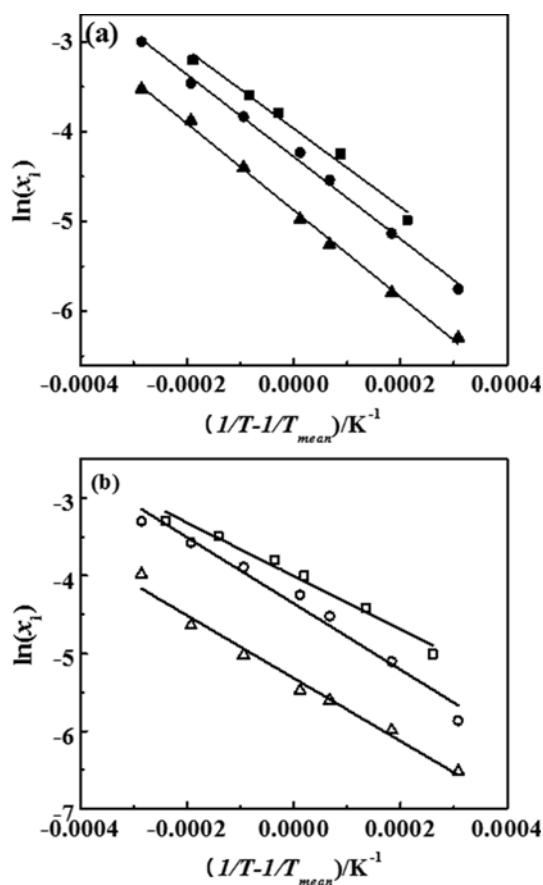in which the intercept is determined in plots of $\ln x_1$ versus ($1/T -$

Fig. 6. van't Hoff plots of $\ln(x_1)$ versus $(1/T - 1/T_{mean})$ of L-arabinose in the aqueous solutions of methanol (a) and in mixed solvents of ethanol-water (b) from 278.15 K to 333.15 K: ■, water-0.5816 (mole fraction); ●, water-0.4478; ▲, water-0.2649.
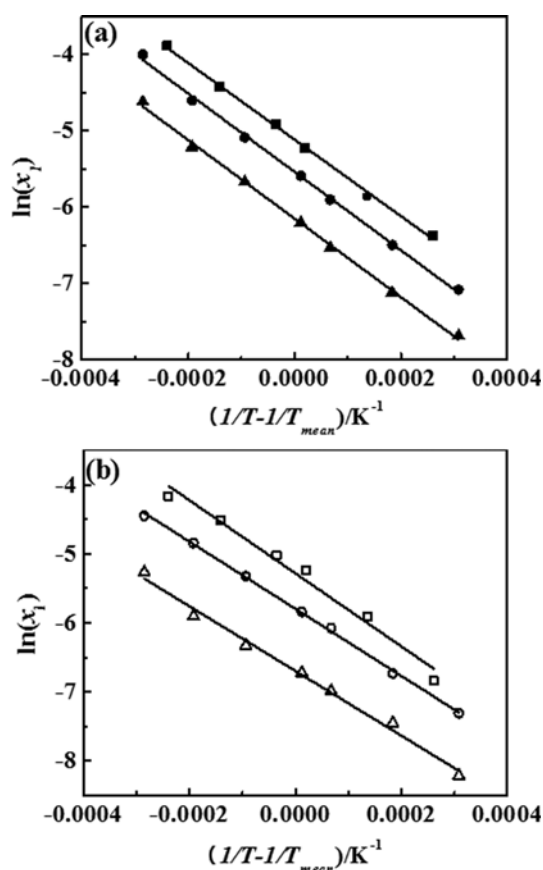

Fig. 7. van't Hoff plots of $\ln(x_1)$ versus $(1/T - 1/T_{mean})$ of D-galactose in the aqueous solutions of methanol (a) and in mixed solvents of ethanol-water (b) from 278.15 K to 333.15 K: ■, water-0.5816 (mole fraction); ●, water-0.4478; ▲, water-0.2649.

Table 8. Thermodynamic functions relative to solution process of monosaccharide binary solvents of alcohols and water at the mean temperature, and alcohols mole fraction in solute-free solvent, x_2

	Solvent (x_2)	$\Delta_{sol}H_m^0$ (kJ·mol^{-1})	$\Delta_{sol}G_m^0$ (kJ·mol^{-1})	$\Delta_{sol}S_m^0$ (J·mol^{-1}·K^{-1})
L-arabinose	Methanol (0.5093)	36.3382	9.74977	89.9310
	Methanol (0.6402)	38.0575	10.8271	89.5021
	Methanol (0.8001)	40.1105	12.3337	91.2980
	Ethanol (0.4184)	28.5040	9.9760	61.7792
	Ethanol (0.5522)	35.3576	11.0201	79.9935
	Ethanol (0.7351)	33.5992	13.4503	66.2264
D-galactose	Methanol (0.5093)	41.7043	12.7523	96.5367
	Methanol (0.6402)	42.7040	14.0055	94.3273
	Methanol (0.8001)	42.7568	15.5539	89.4114
	Ethanol (0.4184)	44.0593	13.1698	102.9969
	Ethanol (0.5522)	40.5376	14.6601	85.0551
	Ethanol (0.7351)	39.0209	16.9416	72.5710

$1/T_{mean}$) and then the molar dissolution entropy of solution ($\Delta_{sol}S_m^0$) is determined by:

$$\Delta_{sol}S_m^0 = \frac{\Delta_{sol}H_m^0 - \Delta_{sol}G_m^0}{T_{mean}} \tag{21}$$

The van't Hoff equation for real solutions relates the natural logarithm of the mole fraction solubility as a linear relationship with the reciprocal of the absolute temperature, as shown in Figs. 6 and 7. The values of $\Delta_{sol}H_m^0$, $\Delta_{sol}G_m^0$ and $\Delta_{sol}S_m^0$ of L-arabinose and D-galactose are summarized in Table 8. As found there, the standard enthalpy and entropy of dissolution for mixed solvents are positive, which demonstrates that the dissolution process of L-arabinose and D-galactose in the binary system was endothermic. For all cases in this work, the Gibbs free energy is positive, which demonstrates that the process is non-spontaneous.

CONCLUSIONS

The solubility of L-arabinose and D-galactose was measured in mixtures of alcohol (methanol or ethanol) and water at temperatures from 278.15 to 333.15 K, and the solubility of individual saccharide in aqueous alcohol mixtures decreased with decreasing temperature as well as water proportion. The calculated solubility regressed by the modified Apelblat equation, polynomial empirical equation, NRTL model and UNIQUAC model showed a good agreement with the experimental data. On the basis of obtained solubility data, the dissolving enthalpy and entropy in the binary solvent mixtures were calculated by the van't Hoff equation, and it indicated the process was endothermic and non-spontaneous. Overall, the solubility reported in this work might be helpful to develop a practical crystallization process for removing D-galactose from L-arabinose.

ACKNOWLEDGEMENTS

MOMENCLATURE

A', B', C' : parameters of the Apelblat equation
A, B, C, D : parameters of the simplified polynomial empirical equation
m_1 : mass of solute [g]
m_2 : mass of alcohol [g]
m_3 : mass of water [g]
n : number of data points
M_1 : relative molecular weight of solute [g·mol^{-1}]
M_2 : relative molecular weight of alcohol [g·mol^{-1}]
M_3 : relative molecular weight of water [g·mol^{-1}]
R : gas constant [8.314 J·mol^{-1}·K^{-1}]
RMSD : The root-mean-square deviation
T : temperature [K]
T_m : the melting point [K]
T_{mean} : the mean temperature [K]
x_1 : the mole fraction solubility of solute
x_2 : the mole fraction of alcohol in binary solvent
$x_{i,cal}$: regressed solubility value
$x_{i,exp}$: experimental solubility value
$\Delta_{fus}H$: the melting enthalpy [J·mol^{-1}]
$\Delta_{sol}H_m^0$: the molar dissolution enthalpy [kJ·mol^{-1}]
$\Delta_{sol}G_m^0$: the molar dissolution entropy [J·mol^{-1}·K^{-1}]
$\Delta_{sol}S_m^0$: the molar dissolution Gibbs free energy [kJ·mol^{-1}]
Δg_{ij} : adjustable parameters contained in the NRTL model [J·mol^{-1}]
Δu_{ij} : adjustable parameters contained in the UNIQUAC model [J·mol^{-1}]
γ : activity coefficient of the solute

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Determination and correlation of the solubility of L-arabinose and D-galactose in binary solvent mixtures from 278.15 to 333.15 K

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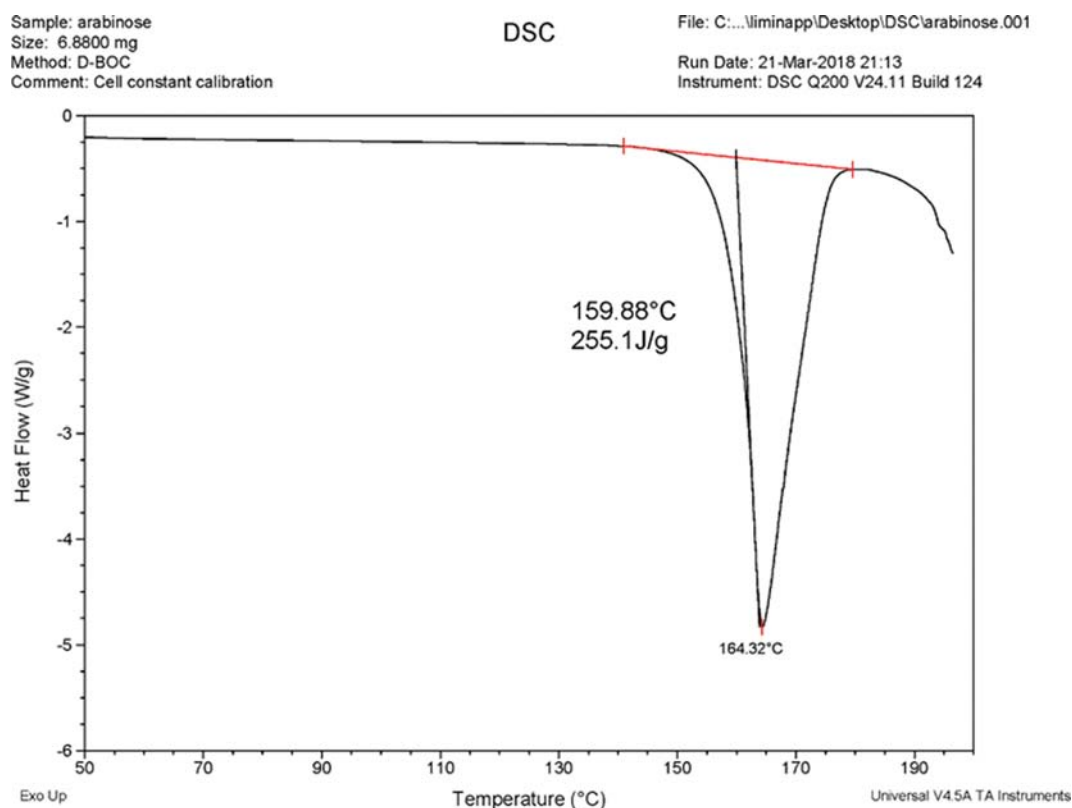
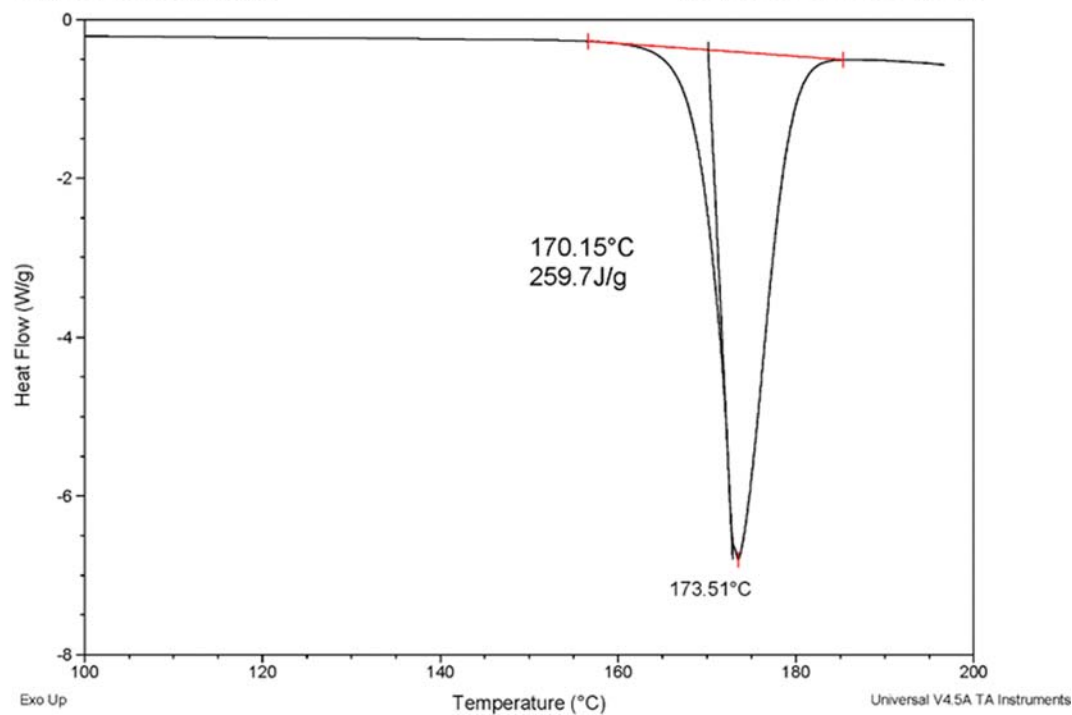Fig. S1. Differential scanning calorimetry (DSC) curves of L-arabinose.

Fig. S2. Differential scanning calorimetry (DSC) curves of D-galactose.