PREFERENTIAL SOLVATION OF L-ARABINOSE AND DL-MALIC ACID IN ETHANOL + WATER MIXTURES

SOLVATACIÓN PREFERENCIAL DE L-ARABINOSA Y ÁCIDO DL-MÁLICO EN MEZCLAS ETANOL + AGUA

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Abstract

By using the inverse Kirkwood-Buff integrals (IKBI) method, the differences between the local, around the solute and the bulk mole fractions of both solvents in saturated solutions of L-arabinose (compound 3) and DL-malic acid (compound 3) in ethanol (compound 1)+ water (compound 2) binary mixtures were derived from their thermodynamic properties. Accordingly, it is found that these compounds are sensitive to preferential solvation effects; in this way, the preferential solvation parameter ($\delta x_{1,3}$) for L-arabinose is slightly positive in water-rich mixtures but negative in those beyond 0.25 in ethanol mole fraction. In different way, the $\delta x_{1,3}$ values of DL-malic acid are negative in almost all the compositions. The highest solvation by ethanol observed in water-rich mixtures for L-arabinose could be due mainly to polarity effects. Otherwise, the preference of these compounds for water in ethanol-rich mixtures could be explained in terms of the higher acidic behavior of water interacting with hydrogen-acceptor hydroxyl groups in L-arabinose and DL-malic acid.

Keywords: L-arabinose, DL-malic acid, ethanol, solubility, IKBI, preferential solvation.

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Resumen

Utilizando algunas propiedades termodinámicas clásicas de disolución se calcularon los parámetros de solvatación preferencial ($\delta x_{1,3}$) de L-arabinosa y ácido DL-málico en mezclas etanol + agua mediante el método de las integrales inversas de Kirkwood-Buff (IKBI, por sus siglas en inglés); estos parámetros $\delta x_{1,3}$ corresponden a las diferencias entre las fracciones molares locales alrededor del soluto y en el grueso de la solución. Se observó que estos compuestos son sensibles a efectos específicos de solvatación según la composición de la mezcla cosolvente. Así, los valores de $\delta x_{1,3}$ para la L-arabinosa son positivos en mezclas ricas en agua pero negativos en composiciones desde 0,25 en fracción molar de etanol hasta el etanol puro. Sin embargo, en el caso del ácido DL-málico los valores de $\delta x_{1,3}$ son negativos en todas las composiciones cosolventes analizadas. En mezclas ricas en agua la mayor solvatación de la L-arabinosa por parte de las moléculas de etanol podría deberse principalmente a efectos de polaridad. De otro lado, la preferencia que manifiestan ambos compuestos por el agua en mezclas ricas en etanol, podría explicarse en términos de la mayor acidez del agua, la cual estaría interactuando con los grupos aceptores de hidrógeno presentes en los dos solutos.

Palabras clave: L-arabinosa, ácido DL-málico, etanol, solubilidad, IKBI, solvatación preferencial.

Introduction

L-Arabinose (also known as pectinose, $C_5H_{10}O_5$, molar mass 150.13 g mol^{-1}, CAS number 147-81-9, Fig. 1-B is a monosaccharide including an aldehyde functional group found in hemicelluloses and pectin [1]. DL-Malic acid (Hydroxybutanedioic acid, $C_4H_6O_5$, molar mass 134.09 g mol^{-1}, CAS number 617-48-1, Fig. 1-C) is a hydroxy-dicarboxylic organic acid present in several fruits and commonly used as food additive [1]. In the industrial manufacture of L-arabinose and DL-malic acid, these compounds are purified through crystallization from diluted or concentrated solutions as the final step. In this way, aqueous alcoholic mixtures are widely used with this purpose. Because the knowledge about the equilibrium solubility is a crucial factor for crystallization processes Jiang et al. [2] and Yuan et al. [3] studied, respectively, the solubility of L-arabinose and DL-malic acid in several ethanol + water mixtures at different temperatures.

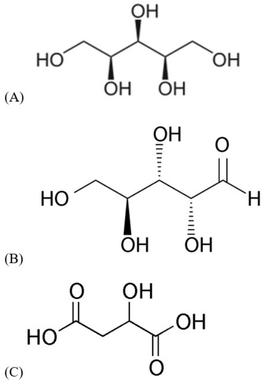

FIGURE 1. *Molecular structure of xylitol (A), L-arabinose (B), and DL-malic acid (C).*

Considering that the cosolvency or solvent blending has been employed for a long time to increase or decrease the solubility of organic compounds [4, 5], which is a desired effect to optimize the crystallization processes of solutes, a deep physical-chemical approach of the mechanisms involved in solubilization and/or desolubilization processes, including preferential solvation [6, 7], regains significance.

Regarding thermodynamic studies, some recent researches have been published based on the enthalpic and entropic contributions to the Gibbs energy of solution of these organic hydroxyl-compounds [3, 4]. Nevertheless, the preferential solvation, i.e. the cosolvent specific composition around L-arabinose and DL-malic acid molecules has not been studied. Therefore, the main goal of this research is to evaluate the preferential solvation of these compounds in ethanol + water cosolvent mixtures, based on some classical thermodynamic definitions [8, 9]. L-Arabinose and DL-malic acid were chosen as model solutes for this research owing their multiple pharmaceutical and chemical applications. Thus, this work is very similar to that presented previously in the literature for the preferential solvation of the sweetening agent xylitol (Fig. 1-A) in similar cosolvent mixtures [10].

Theoretical Background

The Kirkwood-Buff integrals (KBIs, $G_{i,S}$) are given by the following expression:

$$G_{i,S} = \int_0^{r_{cor}} (g_{i,S} - 1) 4\pi r^2 dr \qquad (1)$$

Here $g_{i,S}$ is the pair correlation function for the molecules of the solvent i in cosolvent mixtures around the solute (S), r the distance between the centers of the molecules of solute and solvent components, and r_{cor} is a correlation distance for which $g_{i,S}(r > r_{cor}) \approx 1$. The results are expressed in terms of the preferential solvation parameter $\delta x_{i,S}$ for the solute in the saturated solutions by the component solvents, i.e. ethanol and water [11]. For solvation of L-arabinose (component 3) or DL-malic acid (component 3), this parameter is defined for ethanol (component 1) as:

$$\delta x_{1,3} = x_{1,3}^L - x_1 = -\delta x_{2,3} \qquad (2)$$

Where x_1 is the mole fraction of ethanol in the bulk solvent mixture and $x_{1,3}^L$ is the local mole fraction of ethanol in the environment near to the solute. If $\delta x_{1,3} > 0$ the solute is preferentially solvated by ethanol; on the contrary, if it is < 0 the solute is preferentially solvated by water, within the correlation volume ($V_{cor} = (4\pi/3) r_{cor}^3$) and the bulk mole fraction of ethanol, x_1. Values of $\delta x_{1,3}$ are calculable from those of $G_{1,3}$ and $G_{2,3}$, which are obtained from thermodynamic data of the cosolvent mixtures with and without the solute dissolved on them [8].

Mathematical manipulation of the basic expressions reported by Newman [11] leads to practical expressions for the Kirkwood-Buff integrals (expressed in $\mathrm{cm^3\ mol^{-1}}$) for the individual solvent components as shown in equations 3 and 4 [6, 7]:

$$G_{1,3} = RT\kappa_T - V_3 + x_2 V_2 D/Q \qquad (3)$$

$$G_{2,3} = RT\kappa_T - V_3 + x_1 V_1 D/Q \qquad (4)$$

Here κ_T is the isothermal compressibility of the ethanol + water solvent mixtures (expressed in GPa^{-1}), V_1 and V_2 are the partial molar volumes of the solvents in the mixtures (expressed in cm^3 mol^{-1}), and similarly, V_3 is the partial molar volume of the solute L-arabinose or DL-malic acid in these cosolvent mixtures (expressed in cm^3 mol^{-1}). The function D is the derivative of the standard molar Gibbs energies of transfer of the solute from neat water to ethanol + water mixtures regarding to the ethanol proportion in the mixtures (expressed in kJ mol^{-1}, as also is RT). The function Q involves the second derivative of the excess molar Gibbs energy of mixing of both solvents (G_{1+2}^{Exc}) in function of the water proportion in the mixtures (also expressed in kJ mol^{-1}) [6, 7]. Thus, functions D and Q are defined as:

$$D = \left(\frac{\partial \Delta_{tr} G^{\circ}_{3,2\to 1+2}}{\partial x_1} \right)_{T,p} \tag{5}$$

$$Q = RT + x_1 x_2 \left(\frac{\partial^2 G_{1+2}^{Exc}}{\partial x_2^2} \right)_{T,p} \tag{6}$$

Ben-Naim [12] demonstrated that the preferential solvation parameter can be calculated from the Kirkwood-Buff integrals as follows:

$$\delta x_{1,3} = \frac{x_1 x_2 (G_{1,3} - G_{2,3})}{x_1 G_{1,3} + x_2 G_{2,3} + V_{cor}} \tag{7}$$

The correlation volume (V_{cor}) is commonly obtained by means of the following expression [6, 7]:

$$V_{cor} = 2522.5 \left(r_3 + 0.1363 (x_{1,3}^L V_1 + x_{2,3}^L V_2)^{1/3} - 0.085 \right)^3 \tag{8}$$

Here r_3 is the molecular radius of the solute (expressed in nm) and may be calculated from the molar volume by using the Avogadro number (N_{Av}) as:

$$r_3 = \left(\frac{3 \times 10^{21} V_3}{4\pi N_{Av}} \right)^{1/3} \tag{9}$$

However, the definitive correlation volume requires iteration because it depends on the local mole fractions. This iteration is performed by replacing $\delta x_{1,3}$ in the equation 2 to calculate $x_{1,3}^L$ until a non-variant value of V_{cor} is obtained.

Results and Discussion

Standard molar Gibbs energy of transfer of these organic compounds from neat water to ethanol + water mixtures was calculated and correlated to regular third degree polynomials from the drug solubility data taken from [2, 3] by using equation 10. Table 1 and Fig. 2 show the Gibbs energy of transfer behavior at all the temperatures studied. Temperatures from 293.15 to 313.15 K were considered owing the thermodynamic quantities required for IKBI calculations have been reported in this range [10, 13]. The respective polynomial coefficients are shown in Table 2.

$$\Delta_{tr}G^{\circ}_{3,2\rightarrow 1+2} = RT\ln\left(\frac{x_{3,2}}{x_{3,1+2}}\right) = a + bx_1 + cx_1^2 + dx_1^3 \tag{10}$$

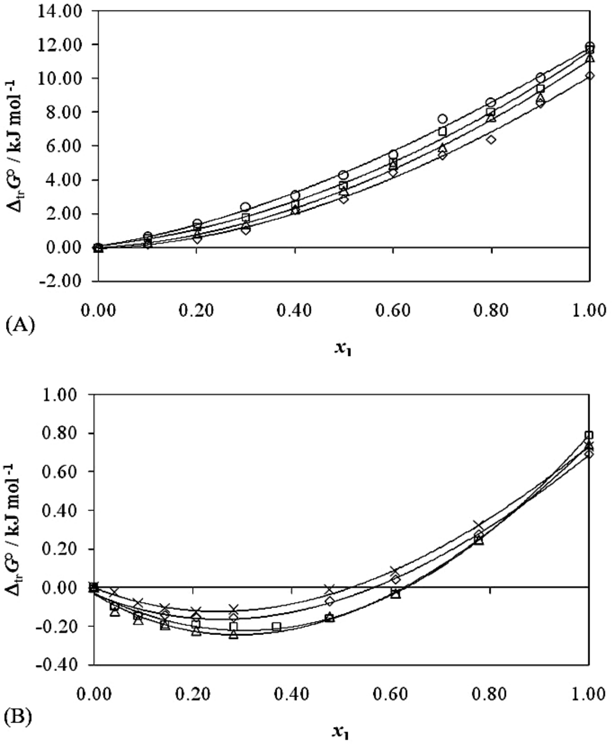

FIGURE 2. *Gibbs energy of transfer of L-arabinose (A) and DL-malic acid (B) from neat water (2) to ethanol (1) + water (2) mixtures at several temperatures. ○: 293.15 K, □: 298.15 K, △: 303.15 K, ◊: 308.15 K, ×: 313.15 K.*

L-arabinose [a]					DL-Malic acid [b]				
x_1 [c]	293.15 K	298.15 K	303.15 K	308.15 K	x_1	298.15 K	303.15 K	308.15 K	313.15 K
0.000	7.36	7.32	7.27	7.29	0.000	4.70	4.60	4.42	4.24
0.042	8.03	7.87	7.58	7.46	0.100	4.61	4.48	4.32	4.22
0.089	8.78	8.53	8.07	7.78	0.200	4.56	4.44	4.28	4.16
0.144	9.75	9.11	8.64	8.32	0.300	4.51	4.41	4.28	4.14
0.207	10.39	9.88	9.51	9.51	0.400	4.51	4.38	4.27	4.11
0.281	11.64	11.01	10.65	10.15	0.500	4.50	4.36	4.27	4.13
0.370	12.79	12.31	12.15	11.74	0.600	4.50	4.50	4.37	4.23
0.477	14.98	14.15	13.20	12.73	0.700	4.54	4.45	4.35	4.23
0.610	15.95	15.34	14.98	13.68	0.800	4.67	4.57	4.47	4.32
0.779	17.36	16.74	16.16	15.79	0.900	4.95	4.85	4.70	4.57
1.000	19.21	19.05	18.52	17.44	1.000	5.49	5.34	5.11	4.97

[a] Calculated from solubility values reported by Jiang et al. [2].

[b] Calculated from solubility values reported by Yuan et al. [3].

[c] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

Table 1. *Gibbs energy of transfer (kJ mol^{-1}) of L-arabinose (3) and DL-malic acid (3) from neat water (2) to ethanol (1) + water (2) mixtures at several temperatures.*

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	4.41	3.26	1.72	1.18	-1.27	-1.52	-1.05	-1.00
0.100	6.28	4.95	3.85	3.25	-0.85	-0.96	-0.62	-0.59
0.200	8.00	6.63	5.88	5.21	-0.43	-0.44	-0.22	-0.19
0.300	9.58	8.30	7.83	7.09	-0.02	0.05	0.16	0.18
0.400	11.02	9.95	9.69	8.86	0.40	0.51	0.51	0.52
0.500	12.32	11.59	11.45	10.54	0.82	0.92	0.83	0.83
0.600	13.48	13.22	13.13	12.13	1.24	1.30	1.13	1.13
0.700	14.49	14.83	14.71	13.62	1.65	1.65	1.40	1.39
0.800	15.37	16.43	16.20	15.02	2.07	1.96	1.64	1.63
0.900	16.10	18.01	17.60	16.32	2.49	2.23	1.86	1.85
1.000	16.69	19.58	18.92	17.52	2.91	2.46	2.05	2.04

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

Table 2. *Coefficients of the Equation [16] (kJ mol^{-1}) applied to Gibbs energy of transfer of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures at several temperatures.*

D values were calculated from the first derivative of polynomial models solved according to the cosolvent mixtures composition. This procedure was performed varying by 0.05 in mole fraction of ethanol but in the following tables the respective values are reported varying only by 0.10 to save space in the article. D values are reported in Table 3.

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	4.41	3.26	1.72	1.18	-1.27	-1.52	-1.05	-1.00
0.100	6.28	4.95	3.85	3.25	-0.85	-0.96	-0.62	-0.59
0.200	8.00	6.63	5.88	5.21	-0.43	-0.44	-0.22	-0.19
0.300	9.58	8.30	7.83	7.09	-0.02	0.05	0.16	0.18
0.400	11.02	9.95	9.69	8.86	0.40	0.51	0.51	0.52
0.500	12.32	11.59	11.45	10.54	0.82	0.92	0.83	0.83
0.600	13.48	13.22	13.13	12.13	1.24	1.30	1.13	1.13
0.700	14.49	14.83	14.71	13.62	1.65	1.65	1.40	1.39
0.800	15.37	16.43	16.20	15.02	2.07	1.96	1.64	1.63
0.900	16.10	18.01	17.60	16.32	2.49	2.23	1.86	1.85
1.000	16.69	19.58	18.92	17.52	2.91	2.46	2.05	2.04

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

TABLE 3. *D values (kJ mol^{-1}) of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures at several temperatures.*

Q and $RT\kappa_T$ values of the binary aqueous-ethanol mixtures at all temperatures, as well as the partial molar volumes of ethanol and water were taken from those reported in previous studies with other solutes [10, 13, 14]. Otherwise, in a first approach the molar volume of these compounds were considered here as independent of the cosolvent composition and temperature, and also as equivalent to those presented in solid state. Thus, these values were calculated by considering the density values reported in the literature (1.585 g cm^{-3} for L-arabinose and 1.601 g cm^{-3} for DL-malic acid) [15]. In this way, the molar volume values of 83.75 and 94.72 cm^3 mol^{-1} were obtained, respectively. Furthermore, from these values the molecular radiuses (r_3) of both compounds were calculated by using the equation 9 as 0.335 nm for L-arabinose and 0.321 nm for DL-malic acid.

Table 4 shows that all the $G_{1,3}$ values of both compounds are negative with the maximum values in neat ethanol for L-arabinose and neat water for DL-malic acid. In different way, Table 5 shows that $G_{2,3}$ values of L-arabinose are negative in water-rich mixtures but positive beyond in the mixture with x_1 ≥0.30 reaching maximum value in the mixture with x_1 =0.80. Otherwise, $G_{2,3}$

values of DL-malic acid are negative in almost all mixtures with the exception of x_1 =0.80 at all temperatures and x_1 =0.90 at 298.15 K and 303.15 K. These results could be interpreted as the preference of both solutes by water molecules in ethanol-rich mixtures.

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	-60.9	-69.8	-81.2	-85.2	-91.9	-93.5	-90.0	-89.6
0.100	-44.6	-54.1	-62.2	-66.5	-89.2	-90.2	-87.5	-87.3
0.200	-32.0	-41.2	-45.9	-50.1	-85.7	-85.8	-84.0	-83.8
0.300	-23.0	-32.0	-34.8	-39.8	-82.2	-81.7	-80.9	-80.7
0.400	-15.8	-24.5	-27.2	-33.6	-79.2	-78.5	-78.5	-78.4
0.500	-9.0	-17.1	-20.5	-28.4	-76.4	-75.9	-76.6	-76.7
0.600	-4.2	-10.3	-14.5	-23.5	-73.9	-73.8	-75.1	-75.3
0.700	-10.7	-12.1	-15.5	-23.8	-72.5	-72.8	-74.3	-74.5
0.800	-40.1	-36.9	-38.1	-42.7	-74.3	-74.7	-75.8	-75.8
0.900	-74.2	-72.0	-72.4	-74.0	-78.3	-78.5	-78.9	-78.9
1.000	-91.9	-91.9	-91.8	-91.8	-80.9	-80.8	-80.8	-80.7

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

TABLE 4. *$G_{1,3}$ values (cm^3 mol^{-1}) of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures at several temperatures.*

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	-93.6	-93.6	-93.6	-93.5	-82.6	-82.6	-82.6	-82.6
0.100	-77.1	-80.2	-82.8	-84.2	-84.7	-85.1	-84.2	-84.1
0.200	-45.5	-52.5	-56.0	-59.2	-84.9	-85.0	-83.6	-83.5
0.300	3.9	-8.0	-11.8	-18.7	-82.3	-81.5	-80.4	-80.2
0.400	79.3	60.7	54.7	40.4	-75.7	-74.2	-74.2	-74.1
0.500	197.9	171.1	159.0	131.3	-63.1	-61.5	-64.0	-64.5
0.600	382.9	351.9	329.0	280.2	-40.0	-39.7	-46.9	-48.2
0.700	612.1	601.9	571.7	501.5	-4.0	-7.0	-20.4	-22.5
0.800	698.8	747.1	729.2	663.5	24.6	17.9	1.4	0.6
0.900	527.0	603.2	590.0	542.7	15.1	5.3	-8.7	-8.7
1.000	307.5	371.4	350.7	313.8	-12.1	-23.2	-33.4	-34.0

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

TABLE 5. *$G_{2,3}$ values (cm^3 mol^{-1}) of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures at several temperatures.*

As was already mentioned, to use the IKBI method, the correlation volume of both compounds was iterated three times by using the equations 2, 7 and 8) to obtain the values reported in Table 6. It is noteworthy that these values are almost independent on temperature in water-rich mixtures but they increases slightly in ethanol-rich mixtures. This could be a consequence of the higher thermal expansibility of ethanol compared with water [16].

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	565	566	566	566	529	529	530	530
0.100	632	632	633	634	590	591	592	593
0.200	694	695	697	699	651	653	655	656
0.300	751	753	755	758	713	715	717	719
0.400	801	805	808	812	773	775	778	780
0.500	847	852	856	862	832	835	837	841
0.600	888	894	899	907	890	893	896	900
0.700	933	937	943	952	946	950	954	959
0.800	1002	1003	1008	1016	1006	1010	1015	1019
0.900	1099	1100	1104	1110	1070	1074	1079	1084
1.000	1190	1194	1199	1203	1134	1138	1142	1147

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

TABLE 6. *Correlation volume (cm^3 mol^{-1}) of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures at several temperatures.*

The values of $\delta x_{1,3}$ vary non-linearly with the ethanol proportion in these aqueous mixtures at all the temperatures studied (Table 7 and Fig. 3). In water-rich mixtures, the addition of ethanol to water makes positive the $\delta x_{1,3}$ values of L-arabinose from pure water to the mixture with $x_1 = 0.20$ reaching a maximum of 4.2×10^{-3} in the mixtures with $x_1 = 0.10$ at 298.15 K. This maximum diminishes with the temperature arising. On the contrary, the $\delta x_{1,3}$ values of DL-malic acid are slightly negative in water-rich mixtures, except in $x_1 = 0.30$ at 298.15 K, where a really low positive value is observed. Nevertheless, it is not easy to assign these $\delta x_{1,3}$ values to preferential solvation effects because they are lower than 0.01 and could be owing to uncertainties propagation in the IKBI calculations [12, 17].

Otherwise, from these ethanol proportions up to neat ethanol, the $\delta x_{1,3}$ values are significantly negative, and hence, L-arabinose and DL-malic acid are preferentially solvated by water in ethanol-rich

x_1 [a]	L-arabinose				DL-Malic acid			
	293.15 K	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.000	0.00	0.00	0.00	0.00	0.000	0.000	0.000	0.000
0.100	0.52	0.42	0.34	0.29	-0.080	-0.092	-0.060	-0.058
0.200	0.33	0.28	0.25	0.23	-0.021	-0.021	-0.011	-0.009
0.300	-0.76	-0.68	-0.66	-0.61	0.002	-0.005	-0.016	-0.018
0.400	-2.71	-2.46	-2.37	-2.16	-0.118	-0.147	-0.145	-0.146
0.500	-5.50	-5.06	-4.85	-4.37	-0.436	-0.472	-0.410	-0.399
0.600	-8.95	-8.45	-8.06	-7.25	-0.980	-0.983	-0.814	-0.779
0.700	-11.80	-11.63	-11.17	-10.16	-1.608	-1.540	-1.263	-1.215
0.800	-10.65	-11.17	-10.93	-10.14	-1.663	-1.554	-1.294	-1.274
0.900	-4.99	-5.55	-5.43	-5.05	-0.839	-0.751	-0.628	-0.625
1.000	0.00	0.00	0.00	0.00	0.000	0.000	0.000	0.000

[a] x_1 is the mole fraction of ethanol (1) in ethanol (1) + water (2) mixtures free of solute.

TABLE 7. *100 $\delta x_{1,3}$ (cm^3 mol^{-1}) of L-arabinose (3) and DL-malic acid (3) in ethanol (1) + water (2) mixtures according to IKBI method at several temperatures.*

mixtures. Both compounds act as Lewis acids in solution owing the hydrogen atoms in their -OH groups (Fig. 1) to establish hydrogen bonds with proton-acceptor functional groups in the solvents (oxygen atoms in -OH groups). Additionally, these compounds could act as Lewis bases due to the free electron pairs in the oxygen atoms of their hydroxyl and carbonyl groups (Fig. 1) to interact with the acidic hydrogen atoms in both solvents.

Based on these preferential solvation results, it is probable that in water-rich mixtures, where the DL-malic acid is apparently preferentially solvated by ethanol molecules, this compound is slightly acting as Lewis acid with ethanol molecules because this cosolvent is more basic than water as described by their Kamlet-Taft hydrogen bond acceptor parameters, i.e. $\beta = 0.75$ and 0.47 for ethanol and water, respectively [18, 19]. On the other hand, in ethanol-rich mixtures, where both L-arabinose and DL-malic acid are preferentially solvated by water, these compounds could be acting mainly as Lewis bases in front of water because water is more acidic than ethanol as also described by their Kamlet-Taft hydrogen bond donor parameters, i.e. $\alpha = 1.17$ and 0.86 for water and ethanol, respectively [18, 20].

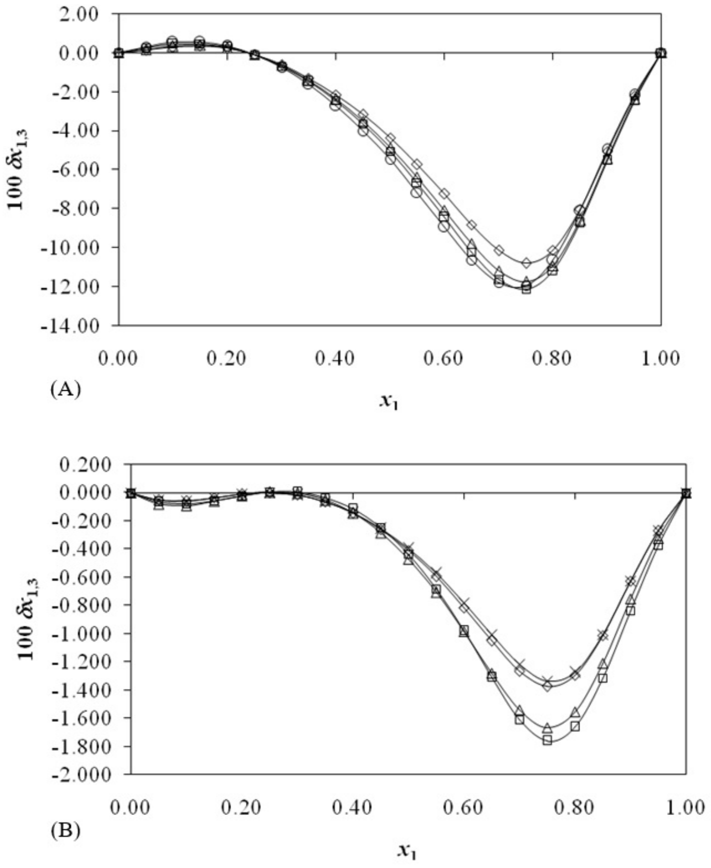

FIGURE 3. *$\delta x_{1,3}$ values of L-arabinose (A) and DL-malic acid (B) in ethanol (1) + water (2) mixtures according to the IKBI method at several temperatures. ○: 293.15 K, □: 298.15 K, △: 303.15 K, ◇: 308.15 K, ×: 313.15 K.*

Furthermore, Fig. 4 compares the preferential solvation behavior of these compounds including xylitol at 298.15 K [10]. It is noteworthy that the behaviors exhibited by L-arabinose and xylitol are very similar, being both of them highly preferentially solvated by water in ethanol-rich mixtures, with maximum $\delta x_{1,3}$ values higher than -0.12 in the mixture with $x_1 = 0.75$; whereas, the preferential solvation of DL-malic acid by water is not so high as the other two compounds with a maximum $\delta x_{1,3}$ value of -1.76×10^{-2} in the mixture of $x_1 = 0.75$. These three hydroxyl-compounds present different functional groups as follows: xylitol is a polyhydroxy-alcohol, L-arabinose is a polyhydroxy-aldehyde, and DL-malic acid is a hydroxy-dicarboxylic acid. For this reason, as a polarity criterion [21], the Hildebrand solubility parameters (δ_3 expressed in MPa$^{1/2}$) were calculated for these compounds based on the Fedors method [22]. δ_3 values were calculated as $(\Delta U^\circ/V^\circ)^{1/2}$, with ΔU° (expressed in J mol^{-1}) as the molar internal energy and V° (expressed in cm^3 mol^{-1}) the molar volume [21]. Table 8 shows the respective ΔU° values for these compounds. In this way, δ_3 values are as follows: 36.0 MPa$^{1/2}$ for xylitol, 36.2 MPa$^{1/2}$ for L-arabinose, and 31.9 MPa$^{1/2}$ for DL-malic acid. It is noteworthy that solubility parameters of xylitol and L-arabinose are very similar as also are their preferential solvation behaviors. Thus, the δ_3 value is the lowest being the less polar compound and therefore, the DL-malic acid preferential solvation by water in ethanol-rich mixtures is significantly lower compared with xylitol and L-arabinose.

Finally, it is important to note that all these results about preferential solvation of these compounds are in good agreement with those described previously in the literature, which were based in more basic dissolution thermodynamic approaches [2, 3, 23].

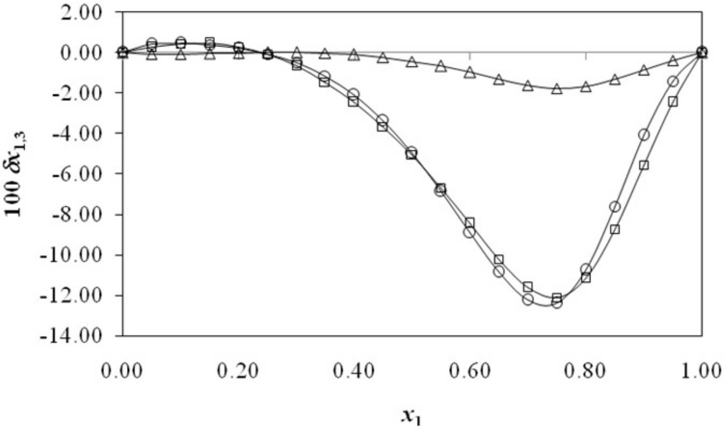

FIGURE 4. *$\delta x_{1,3}$ values of xylitol (○), L-arabinose (□) and DL-malic acid (△) in ethanol (1) + water (2) mixtures according to the IKBI method at 298.15 K.*

Group	Xylitol		L-arabinose		DL-Malic acid	
	Group number	$\Delta U°$/ kJ mol^{-1}	Group number	$\Delta U°$/ kJ mol^{-1}	Group number	$\Delta U°$/ kJ mol^{-1}
-CH2-	2	2 x 4.94 = 9.88	1	4.94	1	4.94
>CH-	3	3 x 3.43 = 10.29	3	3 x 3.43 = 10.29	1	3.43
-OH on adjacent C atoms	5	5 x 21.9 = 109.5	4	4 x 21.9 = 87.6	1	21.9
-CHO	-	-	1	21.4	-	-
-COOH	-	-	-	-	2	2 x 27.6 = 55.2
	Σ (Δ $U°$) = 129.67 kJ mol^{-1}		Σ (Δ $U°$) = 124.23 kJ mol^{-1}		Σ (Δ $U°$) = 85.47 kJ mol^{-1}	

TABLE 8. *Fedor's method applied to estimate the molar internal energy of xylitol (3), L-arabinose (3) and DL-malic acid (3).*

Conclusions

Quantitative values for the local mole fractions of ethanol and water around these compounds were derived based on the IKBI method applied to some literature equilibrium solubility values in ethanol + water mixtures at several temperatures. Thus, these compounds are preferentially solvated by water in mixtures beyond 0.20 or 0.25 in mole fraction of ethanol at all temperatures considered. It is noteworthy that these negative $\delta x_{1,3}$ values diminish as temperature arises for both compounds. It can also be concluded for these compounds that the less polar a compound is its $\delta x_{1,3}$ magnitude also is.

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