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Solubility of Vitamin C in Water, Ethanol, Propan-1-ol, Water + Ethanol, and Water + Propan-1-ol at (298.15 and 308.15) K

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Solubility data of vitamin C are essential to fields such as medicine, food, and biochemistry. Regarding recent publications, for hydrotropism studies, it is shown that the knowledge of the solubility of vitamin C in different solvents is very important. In the present paper, solubility data of vitamin C in water, ethanol, propan-1-ol, water + ethanol, and water + propan-1-ol were measured by a gravimetric method at (298.15 and 308.15) K at an atmospheric pressure of 0.0920 MPa. The solubility data were correlated against the mass fraction of water. The solubility of vitamin C in water, ethanol, and water + ethanol was high compared to that with propan-1-ol and water + propan-1-ol.

Introduction

New technologies for separating acid from water solutions may significantly lower the cost of producing and purifying some organic acids. To study this and to perform design calculations of each process, experimental data for liquid–liquid (LLE) and solid–liquid (SLE) equilibrium need to be known.¹

Solubility data of acid compounds have a broad application and importance in the pharmaceutical industry.^{2–4} A variety of pure solvents, including water and solvent mixtures, can usually be employed in a particular crystallization process during the manufacturing of pharmaceuticals.^{3,4} Measurements of acid solubilities in water and aqueous solutions have been receiving a growing interest.^{1,4–7} Although there are some experimental phase equilibrium data in aqueous solutions of acid compounds,^{1,4–7} very little are available for those with no aqueous media.

Ascorbic acid is a sugar acid with antioxidant properties. Its appearance is white to light-yellow crystals or powder, and it is water-soluble. The L-enantiomer of ascorbic acid is commonly known as vitamin C. In industry, L-(+)-ascorbic acid is produced from D-glucose by a Reichstein procedure via several complex chemical and biotechnological stages. The obtained solid ascorbic acid has a mass fraction purity in the range from (96 to 98) %, which is achieved by several recrystallization stages from water.^{8–13}

The solubility of L-(+)-ascorbic acid in water, ethanol, methanol, propan-2-ol, acetone, acetonitrile, ethyl acetate, and tetrahydrofuran from (293 to 323) K using a gravimetric method has been studied previously by Shalmashi and Eliassi.¹³ The solubility data were correlated against temperature, and the solubility of L-(+)-ascorbic acid in water and methanol was high compared with that of other solvents. Research involving the addition of methanol, ethanol, and propan-2-ol as cosolvents to the main solvent, water, in the nucleation process of ascorbic acid has been reported previously.^{14,15} Finally, solubilities of L-(+)-ascorbic acid in four-component (L-(+)-ascorbic acid + methanol + ethanol + water) solutions have also been investigated.^{16,17}

Table 1. Suppliers and Purities of the Chemicals

substance	certified purity	supplier
L-(+)-ascorbic acid	99.0 %	Labsynth
ethanol	99.5 %	Proquimicos
propan-1-ol	99.5 %	Vetec
water		distilled and deionized

In this work, the solubility of L-(+)-ascorbic acid in water, ethanol, propan-1-ol, water + ethanol, and water + propan-1-ol was measured by a gravimetric method at (298.15 and 308.15) K, and the solubility data were correlated against the mass fraction of water present in the initial mixture of solvents at free basis of vitamin C. When it was possible and data available, the experimental results were compared with literature data.¹³

Experimental Section

Chemicals. All chemicals used in the experimental part are listed in Table 1. The compounds were used without further purification. Deionized (E. J. Krieger & Cia. Ltd., model Permution) and distilled (Quimis, model G.341.25) water was used in all cases.

Apparatus and Procedures. The solubility of L-(+)-ascorbic acid was measured using an equilibrium cell similar to that described in the literature.¹⁸ More details about the equipment, such as dimensions, have been published elsewhere.¹⁹ The experiments were carried out in a magnetically stirred, jacketed equilibrium cell with a volume of approximately 50 mL. To prevent solvent evaporation, the equilibrium cell was sealed by a Teflon plug, and its temperature was controlled by circulating water from a thermostatic bath within ± 0.05 K. The sample mass was determined by an electronic balance (AX 200, Shimadzu, Brazil) with uncertainty of ± 0.1 mg.

The solubility of L-(+)-ascorbic acid in three pure solvents (water, ethanol, and propan-1-ol) and in their mixtures (water + ethanol and water + propan-1-ol) has been determined gravimetrically at (298.15 and 308.15) K. The suitable time for the equilibrium was 2 h. This time was chosen on the basis of past investigations.¹³ For each experiment, an excess of mass of L-(+)-ascorbic acid was added to a known mass of solvent or solvent mixture. This methodology allowed obtaining a

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Table 2. Fitted Parameters of Equation 1 for the Systems Studied

system	<i>T/K</i>	parameters of eq 1			
		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
L-(+)-ascorbic acid (3) + water (1) + ethanol (2)	298.15	0.11367	0.26235	2.97987	−1.78952
L-(+)-ascorbic acid (3) + water (1) + ethanol (2)	308.15	0.19392	3.69346	−1.22463	−0.09908
L-(+)-ascorbic acid (3) + water (1) + propan-1-ol (2)	298.15	0.04154	1.30588	2.24721	−2.06686
L-(+)-ascorbic acid (3) + water (1) + propan-1-ol (2)	308.15	0.04633	2.59770	1.50499	−1.59444

Table 3. Experimental and Correlated Data of the Ternary System L-(+)-Ascorbic Acid (3) in Water (1) + Ethanol (2) at 298.15 K

<i>w</i> _{1,12}	<i>m</i> ₃ mol·kg ^{−1}	<i>m</i> ₃ ¹¹ mol·kg ^{−1}	10 ¹ <i>σ</i> ₁	<i>m</i> ₃ correlated mol·kg ^{−1}	10 ¹ <i>σ</i> ₂
0.0000	0.0817 ± 0.0022	0.0591	0.1598	0.1136	0.2256
0.2024	0.3606 ± 0.0047			0.2740	0.6124
0.4002	0.4283 ± 0.0049			0.5812	1.0812
0.6007	0.8286 ± 0.0030			0.9586	0.9192
0.8002	1.4558 ± 0.0180			1.3147	0.9977
1.0000	1.5230 ± 0.0101	1.4237	0.7022	1.5663	0.3062

supersaturated system after a period of stirring and decanting or repose. The equilibrium cell was heated to the required temperature with continuous stirring. After 2 h, the stirring was stopped, and the solution was kept decanting for around 2 h. Then, an excess of solid was observed in the lower part of the cell.

The samples were withdrawn carefully through sealed sample ports using a glass syringe of 10 mL. The samples were dried in an oven at 333.15 K, and they were weighted every 24 h in a total period of 72 h. Thus, the vitamin C molalities of the sample were determined. An average value was taken from three measurements for each temperature.

The temperature system was determined using a calibrated thermocouple, manufactured by a full gauge, model TIC-17 RGT, which was inserted in the body of the equilibrium cell. A standard mercury thermometer manufactured by Incoterm, model 5097, with a scale from (263.2 to 373.2) K with a decimal variation of 0.1 K and a temperature measurement uncertainty of 0.05 K was used for the calibration work. This methodology was used by Malagoni and Franco, Jr.²⁰

The molalities of the solute were calculated and reported with the standard deviation. The uncertainties of the determined molalities were ± 0.0001 mol·kg^{−1}.

Results and Discussion

Ascorbic acid is a polar organic molecule that has many hydroxyl groups in its structure. For that reason, it is believed that smaller molecules such as water compared to ethanol and propan-1-ol achieve equilibrium more easily because the hydroxyl groups exist on vitamin C to establish hydrogen bonds, favoring the increase of its solubility.

For the systems L-(+)-ascorbic acid (3) + water (1) + ethanol (2) and L-(+)-ascorbic acid (3) + water (1) + propan-1-ol (2), eq 1²¹ was modified being used with four parameters to adjust the experimental results. The model used in this work is defined as

$$m_3/\text{mol}\cdot\text{kg}^{-1} = a + b\cdot w_{1,12} + c\cdot w_{1,12}^2 + d\cdot w_{1,12}^3 \quad (1)$$

where *m*₃ is the molality and *w*_{1,12} is the mass fraction of water in the vitamin-free solution. The dimensionless parameters *a*, *b*, *c*, and *d* are listed in Table 2.

The estimation method used to determine the equation parameters was Levenberg–Marquardt. Additionally, the correlation coefficient obtained in the adjustment was equal to

Table 4. Experimental and Correlated Data of the Ternary System L-(+)-Ascorbic Acid (3) in Water (1) + Ethanol (2) at 308.15 K

<i>w</i> _{1,12}	<i>m</i> ₃ mol·kg ^{−1}	<i>m</i> ₃ ¹¹ mol·kg ^{−1}	10 ¹ <i>σ</i> ₁	<i>m</i> ₃ correlated mol·kg ^{−1}	10 ¹ <i>σ</i> ₂
0.0000	0.1761 ± 0.0031	0.0828	0.6597	0.1939	0.1259
0.1999	0.9373 ± 0.1009			0.8825	0.3875
0.3993	1.4264 ± 0.0076			1.4671	0.2878
0.6005	1.9207 ± 0.0287			1.9487	0.1980
0.7995	2.3618 ± 0.0037			2.3134	0.3422
1.0000	2.5472 ± 0.0070	2.8014	1.7975	2.5636	0.1160

Table 5. Experimental and Correlated Data of the Ternary System L-(+)-Ascorbic Acid (3) in Water (1) + Propan-1-ol (2) at 298.15 K

<i>w</i> _{1,12}	<i>m</i> ₃ mol·kg ^{−1}	<i>m</i> ₃ correlated mol·kg ^{−1}	10 ¹ <i>σ</i> ₂
0.0000	0.0364 ± 0.0041	0.0415	0.0361
0.2014	0.3948 ± 0.0059	0.3788	0.1130
0.3995	0.7781 ± 0.0192	0.7901	0.0849
0.5996	1.1789 ± 0.0114	1.1869	0.0566
0.7998	1.4800 ± 0.0157	1.4660	0.0990
1.0000	1.5230 ± 0.0101	1.5277	0.0332

Table 6. Experimental and Correlated Data of the Ternary System L-(+)-Ascorbic Acid (3) in Water (1) + Propan-1-ol (2) at 308.15 K

<i>w</i> _{1,12}	<i>m</i> ₃ mol·kg ^{−1}	<i>m</i> ₃ correlated mol·kg ^{−1}	10 ¹ <i>σ</i> ₂
0.0000	0.0616 ± 0.0051	0.0463	0.1082
0.1996	0.5740 ± 0.0026	0.6121	0.2694
0.3996	1.2226 ± 0.0026	1.2229	0.0021
0.5976	1.8722 ± 0.0189	1.7959	0.5395
0.7980	2.1919 ± 0.0047	2.2674	0.5339
1.0000	2.5770 ± 0.0050	2.5545	0.1591

0.99301. The average molality value of all samples was calculated for the corresponding range of confidence on the 95 % level.

Tables 3, 4, 5, and 6 give the experimental results of molality as a function of the mass fraction of water in the vitamin-free solution with the standard deviations at two temperatures for the each studied system. Published results for water and ethanol were found in previous papers and included for comparison. The root-mean-square deviation (*σ*₁) is defined as

$$\sigma_1 = \left[\frac{\sum_{i=1}^n (m_{3\text{literature}}/\text{mol}\cdot\text{kg}^{-1} - m_3/\text{mol}\cdot\text{kg}^{-1})^2}{n - 1} \right]^{1/2} \quad (2)$$

where *m*_{3literature} and *m*₃ are literature and experimental molalities, respectively, and *n* is the number of experimental points. The root-mean-square deviations of the literature molalities with respect to the experimental molalities are reported in Tables 3 and 4. Also, the experimental results for all systems were compared with correlated data. The root-mean-square deviation (*σ*₂) was calculated by the same eq 2, changing the *m*_{3literature} with *m*_{3correlated}. The root-mean-square deviations of the correlated molalities with respect to the experimental molalities are reported in Tables 5 and 6.

In the systems with pure ethanol, there was a small amount of vitamin C in sampled solutions, for which reason the

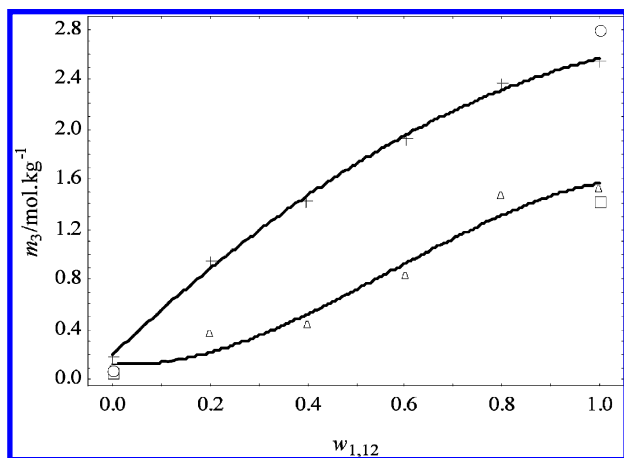


Figure 1. Solubility of L-(+)-ascorbic acid (3) as a function of the mass fraction of water in the water (1) + ethanol (2) initial solution without vitamin C at two temperatures: Δ , $T = 298.15 \text{ K}$; $+$, $T = 308.15 \text{ K}$; solid line, eq 1; \square , literature molality at 298.15 K; \circ , literature molality at 308.15 K.

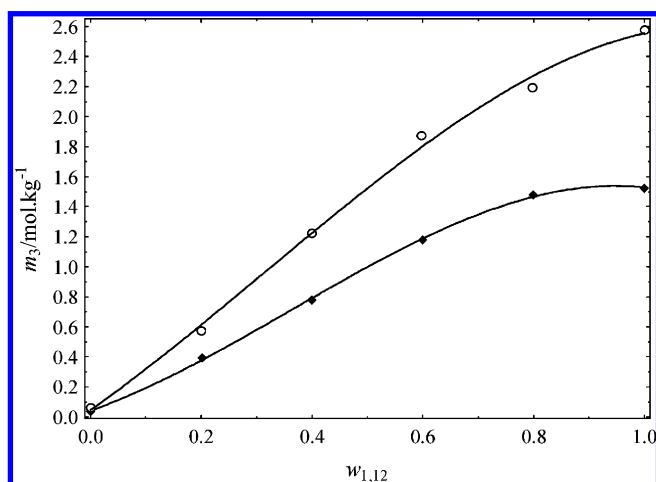


Figure 2. Solubility of L-(+)-ascorbic acid (3) as a function of the mass fraction of water in the water (1) + propan-1-ol (2) initial solution without vitamin C at two temperatures: \blacklozenge , $T = 298.15 \text{ K}$; \circ , $T = 308.15 \text{ K}$; solid line, eq 1.

quantification of the mass present on samples was difficult. Therefore, the root-mean-square deviations σ_1 were more pronounced in this case. The root-mean-square deviations σ_2 were lower for the studied cases.

The solubility of L-(+)-ascorbic acid (3) increases as a function of the mass fraction of water presents in the initial mixture of water (1) + ethanol (2) on free basis of vitamin C at (298.15 and 308.15) K. It was also noted that the solubility of ascorbic acid increases as the temperature rises.

The ascorbic acid is a cyclic polar molecule, and its solubility increases in the solvent of high polarity. The solubility of L-(+)-ascorbic acid in water showed a higher value than those in the other alcoholic solvents. Thus, water may be a better solvent to separate and purify L-(+)-ascorbic acid from solutions as can be seen in Tables 3 through 6.

The solubility of L-(+)-ascorbic acid increases with the temperature. This can be confirmed by observing Figures 1 and 2. Both show that the measurements for the experimental solubilities at 308.15 K are higher than the experimental solubilities at 298.15 K.

Mass fractions of L-(+)-ascorbic acid (3) as a function of the mass fraction of alcohol in the water (1) + alcohol (2) initial solution without vitamin C at studied temperatures were plotted

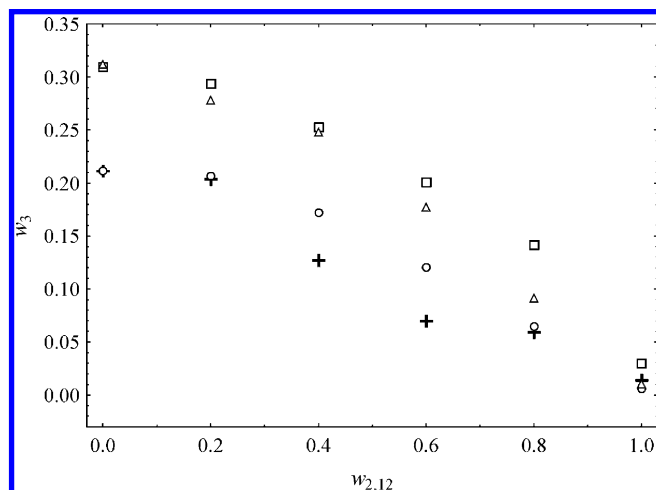


Figure 3. Mass fraction of L-(+)-ascorbic acid (3) as a function of mass fraction of alcohol (2) in the water (1) + alcohol (2) initial solution free of vitamin C. $+$, water + ethanol at 298.15 K; \square , water + ethanol at 308.15 K; \circ , water + propan-1-ol at 298.15 K; Δ , water + propan-1-ol at 308.15 K. (2) alcohol: ethanol or propan-1-ol.

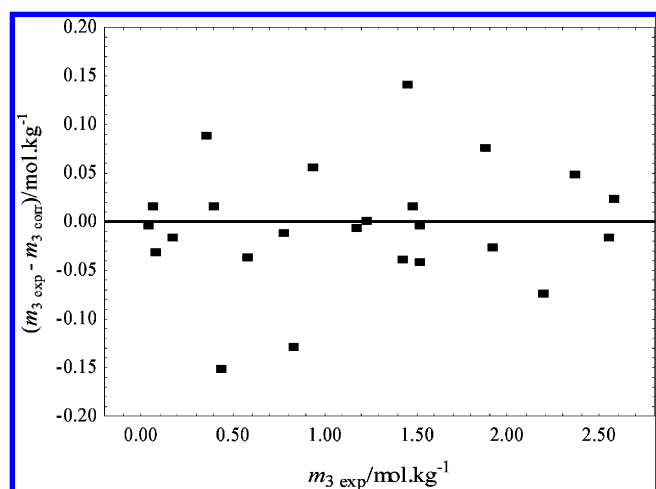


Figure 4. Absolute deviation distribution of the experimental molalities $m_{3\text{exp}}$ of vitamin C from values $m_{3\text{corr}}$ obtained with the eq 1 as a function of molality m_3 . \blacksquare , experimental points of this work.

in the Figure 3. From this figure, it can be seen that neither temperature nor the kind of alcoholic solvent hardly influence the mass fraction of L-(+)-ascorbic acid, especially for the low moisture—water content region or when $w_{2,12}$ is higher than 0.9. In contrast, at lower alcohol concentrations, the dependence on temperature has been observed and is more pronounced.

The absolute residual distribution was determined by comparing the experimental molality obtained in this work with the correlated molality adjusted. The absolute deviation ($m_{3\text{experimental}} - m_{3\text{correlated}}$) was plotted as a function of the experimental molality as shown in Figure 4.

Conclusions

The simple apparatus designed for the measurement of L-(+)-ascorbic acid solubilities in alcoholic mixtures using an analytical method showed efficiency in carrying out the experiments. When found and available, published results were compared to our results, which was possible only for L-(+)-ascorbic acid in pure water and ethanol, as can be seen in Tables 3 and 4. As can be noticed, there is a satisfactory agreement between our solubilities of L-(+)-ascorbic acid in water and ethanol and those reported in the literature. In addition, the equation used for

correlating the data is reliable and will suffice unambiguously for engineering purposes.

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