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Enthalpic characteristics of interactions occurring between an ascorbic acid and some saccharides in aqueous solutions

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Abstract

The enthalpies of solution of mono- and disaccharides were measured in water and aqueous ascorbic acid solutions at 298.15 K using a calorimeter of solution. Enthalpies of transfer of saccharides from water to aqueous ascorbic acid solutions were derived, and enthalpic coefficients of pair interaction h_{xy} were calculated according to MacMillan–Mayer theory. Interactions of ascorbic acid with D-fructose and sucrose are energetically favorable and characterized by negative h_{xy} coefficients while h_{xy} for the interactions occurring between ascorbic acid and α-D glucose, D-galactose and maltose are positive. The obtained results are interpreted in terms of the influence of structure and solvation of solutes on the thermodynamic parameters of their interaction in solutions.

Keywords: Ascorbic acid; Saccharides; Aqueous solutions; Enthalpic virial coefficients; Enthalpy of solution

1. Introduction

It is well known that an ascorbic acid (or Vitamin C) provides normal course of biochemical and physiological processes. However, it is easily oxidized to an inactive form [1]. With the purpose of protection of biological activity of an ascorbic acid during processing and storage different stabilizing materials are used [2–8]. For example, ascorbate-glucose [2] and ethylcellulose-coated ascorbic acid [3] as well as the derivatives of Vitamin C (L-ascorbyl-2-monophosphate [4] L-ascorbate-2-sulfate [5] and L-ascorbyl-6-palmitate [6]) were found to be more stable. It is supposed that the mechanism of protection consists in the participation of ascorbic acid OH-groups in complexation with stabilizing substances. Similar effects were found out for complex formation of Vitamin C with a boric acid [7]. It also was noticed, that saccharides are able to protect biomolecules such as proteins due to their ability to form hydrogen bonds with the polar groups of protein molecules [8,9].

The aim of the present work, which is the first stage of the research of Vitamin C encapsulation by oligosaccharides, consisted in the revealing of the features of interactions occurring between ascorbic acid and mono- and disaccharides in aqueous solutions by means of calorimetry of solution. In this case the enthalpy of transfer can be considered as a main thermodynamic parameter to study the interactions between two different solute molecules in solution [10,11]. In this paper the enthalpies of transfer of D-fructose, α-D-glucose, D-galactose, sucrose and maltose from the water to aqueous solutions of ascorbic acid at 298.15 K have been reported.

2. Experimental

D-Fructose, D-galactose, sucrose and maltose (monohydrate) were purchased from "ICN Pharmaceuticals" and were >98% pure. An ascorbic acid and α-D-glucose were additionally purified by recrystallization from water–ethanol mixtures. All reactants were dried under vacuum at 333 K for 4 days before use. All solutions were prepared by weight on the basis of twice distilled water.

Solution enthalpies were measured at 298.15 K using a calorimeter. The calorimetric installation consists of a calorimetric cell, a system for measuring the temperature in the

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cell and systems of air and liquid thermostatting for maintaining the isothermal regime of the work. The calorimeter has high temperature-control accuracy of ±0.001 K. Calorimetric cell contains a vessel (17 ml), a temperature gage, a heater, an ampule holder, a mercury seal to prevent heat losses.

To estimate the accuracy and reliability of the operation of the calorimeter, we carried out a 10 measurements of the enthalpy of dissolution of KCl in water at 298.15 K. The ΔH^{∞} value for KCl was 17,232 ± 56 J mol^{-1}, which agrees with the published data, 17,225 J mol^{-1} [12]. Therefore, the measurements can be considered reliable.

The enthalpies of solution of solid saccharides were measured in water and aqueous ascorbic acid solutions (V = 16 ml). The concentration of the sugars was constant (≈2.5 × 10^{-3} mol kg^{-1}), the concentration of ascorbic acid ranged from 0.05 to 0.30 mol kg^{-1}. The solution process takes several seconds. Since the concentration of saccharides was very low, the average value of enthalpy of solution was treated as the enthalpy of solution at infinite dilution. All experiments were performed at least twice and were reproducible within 0.8%. As was confirmed by Jastra and Ahluwalia [13], the corrections due to mutarotation are negligible and within experimental error.

3. Results

The process of solution of sugars in water and aqueous solutions of ascorbic acid is endothermic. Experimentally determined enthalpies of solution of saccharides in pure water are presented in Table 1. Our results are in well agreement with the literature data [13–17].

The enthalpy of transfer $\Delta H_{tr}(w \rightarrow w + y)$ is the difference between the enthalpy of solution of saccharide in ascorbic acid solutions $\Delta H_{sol}(w + y)$, and the enthalpy of solution of saccharide in pure water $\Delta H_{sol}(w)$:

$$\Delta H_{tr}(w \rightarrow w + y) = \Delta H_{sol}(w + y) - \Delta H_{sol}(w) \quad (1)$$

The $\Delta H_{tr}(w \rightarrow w + y)$ values for all studied systems are listed in Table 2.

On the basis of the experimental results the enthalpic virial coefficients were calculated according to MacMillan–Mayer theory formalism [18]:

$$\frac{\Delta H_{tr}(w \rightarrow w + y)}{m_y} = 2h_{xy} + 3h_{xyy}m_y + 3h_{xxy}m_x + \cdots \quad (2)$$

where m_x and m_y are the molalities of the saccharide and ascorbic acid, respectively; h_{xy}, h_{xxy}, h_{xyy} the enthalpic coefficients of pair and triplet interactions; $\Delta H_{tr}(w \rightarrow w + y)$ the enthalpy of transfer of saccharide from water to aqueous solutions of ascorbic acid.

Since we used dilute solutions and the concentration of saccharides was constant and very small, the last term in Eq. (2) can be neglected. The h_{xy} and h_{xyy} coefficients were

Table 1
Experimental enthalpies of solution of saccharides in water at 298.15 K ($m_{saccharide}$ ≈ 2.5 × 10^{-3} mol kg^{-1}) in combination with the literature data

Saccharide	$\Delta H_{sol}(w)$ (kJ mol^{-1})	Literature data (kJ mol^{-1})
D-Fructose	9.95 (±0.04)	10.08 [14]
α-D-Glucose	11.01 (±0.07)	11.028 [16], 11.01 [15]
D-Galactose	17.11 (±0.04)	17.10 [15], 17.20 [13]
Maltose (×H_2O)	9.71 (±0.05)	9.56 [17]
Sucrose	5.85 (±0.03)	5.76 [17]

Table 2
Enthalpies of transfer of saccharides from water to aqueous solutions of ascorbic acid at 298.15 K ($m_{saccharide}$ ≈ 2.5 × 10^{-3} mol kg^{-1})

$m_{ascorbic\ acid}$ (mol kg^{-1})	ΔH_s (J mol^{-1})	$\Delta H_{tr}(w \rightarrow w + y)$ (J mol^{-1})
D-Fructose		
0.0498	9 809 (±48)	−141
0.0769	9 709 (±58)	−241
0.1018	9 609 (±43)	−341
0.1244	9 485 (±56)	−465
0.1505	9 337 (±39)	−613
0.1736	9 191 (±46)	−759
0.2102	8 932 (±27)	−1017
0.2467	8 641 (±38)	−1309
α-D-Glucose		
0.0714	11 160 (±53)	148
0.0984	11 245 (±49)	233
0.1274	11 321 (±59)	309
0.1528	11 398 (±57)	386
0.1713	11 473 (±86)	461
0.2122	11 628 (±60)	616
0.2352	11 758 (±69)	746
Sucrose		
0.0956	5 747 (±45)	−106
0.1279	5 663 (±36)	−190
0.1729	5 533 (±50)	−320
0.2191	5 349 (±43)	−504
0.2511	5 200 (±54)	−653
0.2866	4 980 (±50)	−873
0.3098	4 869 (±53)	−984
D-Galactose		
0.0625	17 232 (±37)	119
0.0707	17 271 (±46)	158
0.0981	17 324 (±80)	211
0.1517	17 558 (±71)	445
0.1999	17 688 (±55)	575
0.2164	17 764 (±99)	651
0.2624	17 989 (±79)	876
Maltose		
0.1002	9 805 (±47)	93
0.1254	9 832 (±40)	120
0.1507	9 875 (±55)	163
0.1786	9 952 (±50)	240
0.2219	10 031 (±50)	319
0.2441	10 091 (±64)	379
0.2945	10 292 (±59)	580

Table 3
Enthalpic virial coefficients for the interactions of ascorbic acid with saccharides in water at 298.15 K

System $x + y$	h_{xy} (J kg mol^{-2})	h_{xyy} (J kg^2 mol^{-3})
D-Fructose + ascorbic acid	−1074 (±36)	−4266 (±93)
α-D-Glucose + ascorbic acid	834 (±39)	2023 (±164)
D-Galactose + ascorbic acid	820 (±75)	2186 (±307)
Maltose + ascorbic acid	166 (±44)	1763 (±149)
Sucrose + ascorbic acid	−99 (±25)	−3233 (±76)

calculated by the linear least-squares method on the basis of Eq. (2). The results of calculations are summarized in Table 3.

4. Discussion

Enthalpies of transfer are both positive and negative (Table 2). The negative values of $\Delta H_{tr}(w \rightarrow w+y)$ indicate that the transfer of saccharide from water to the ascorbic acid solution is energetically favorable process. A positive $\Delta H_{tr}(w \rightarrow w + y)$ means that it becomes less favorable. Virial coefficients h_{xy} represent enthalpic contributions to the corresponding coefficients of free energy and include change of energy in system originated from two types of interactions: solute–solute and solute–solvent. Coefficients h_{xy} provide information on a relationship between the solvation of molecules of the reactants and their ability to interact with each other [19]. Thus, enthalpic coefficients are the sum of the contributions from the following possible processes:

1. partial dehydration of solutes (endothermic effect);
2. hydrophobic interactions between nonpolar groups of ascorbic acid and saccharides (endothermic effect);
3. hydrophilic interactions between OH- and COOH groups of the solutes (exothermic effect).

The results in Table 3 indicate that interactions of ascorbic acid with glucose, galactose, and maltose are characterized by positive values of h_{xy}. Most likely, desolvation and hydrophobic interactions define the positive values of h_{xy}.

Molecules of glucose and galactose, which are epimers, differ structurally one another by orientation of OH-groups at $C_{(4)}$ carbon atom. In galactose molecule $OH_{(4)}$-group occupies an axial position, and in glucose it occupies an equatorial position. It turns out, that galactose is less hydrated [20]. Therefore the positive contribution from dehydration process should be smaller and the value of h_{xy} should be smaller for (galactose+ascorbic acid) system compared to (glucose + ascorbic acid). At the same time, the area of an apolar surface of a α-galactose molecule is larger, in comparison with α-glucose [21]. As consequence the positive contribution to h_{xy} from hydrophobic interactions should increase. These two contributions compensate each other, resulting in insignificant differences of h_{xy} coefficients for (ascorbic acid + glucose) and (ascorbic acid + galactose) systems.

It is seen from Table 3 that h_{xy} for maltose–ascorbic acid interaction accepts the smallest positive value. Ascorbic acid and saccharides possess potential sites for H-bonding. Disaccharides, being more flexible molecules due to rotation of monomers around glycosidic linkage [22], are capable to form the greater number of hydrogen bonds in comparison to its monomer units. Therefore, small positive value of h_{xy} reflects that the interaction of maltose with ascorbic acid is accompanied by H-bonding.

The results in Table 3 indicate that enthalpic coefficients for interactions of ascorbic acid with fructose and sucrose are negative. It suggests that in these systems the enthalpically favorable interactions dominate over endothermic effects of the solute dehydration. Molecules of saccharides and ascorbic acid having both hydrophilic and hydrophobic functional groups are considered as bifunctional compounds. Therefore, it is possible to attribute the exothermic effects in systems with fructose and sucrose to hydrogen bonding between OH-groups of saccharide and ascorbic acid. α-Fructose at dissolution in water is capable to pass in β-furanose and β-pyranose forms which maintenance in a solution is maximal (93% [23]). Process of mutarotation is also the fastest and finished for 20 min [24]. It supposes to assume that during calorimetric experiment β-anomers are present at a significant amount in solution. The area of hydrophilic surface of β-forms of sugars is larger compared to its α-forms [21]. Therefore, the negative contribution to h_{xy} from the interactions proceeding at the expense of hydrophilic groups of β-anomers increases. Fructose molecule in difference to glucose and galactose molecules contains the greater number of axial OH-groups, which are not capable to strong interaction with water molecules [20]. As consequence, fructose is less hydrated, and the contribution in h_{xy} value from desolvation process is decreased. We used these facts for explaining of negative values h_{xy} received for systems ascorbic acid + fructose and ascorbic acid + sucrose.

In conclusion, the structure and solvation state of considered solutes define the character of their interactions that is reflected in the thermodynamic parameters of intermolecular interactions.

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