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Thermochimica Acta 444 (2006) 13–15
thermochimica acta
www.elsevier.com/locate/tca

Thermochemical behavior of 18-crown-6 in aqueous solutions of some monosaccharides

N.L. Volkova, V.P. Barannikov, E.V. Parfenyuk *

Institute of Solution Chemistry of Russian Academy of Sciences, 1 Akademicheskaya Str., Ivanovo 153045, Russia

Received 26 December 2005; received in revised form 6 February 2006; accepted 7 February 2006
Available online 23 March 2006

Abstract

Enthalpies of solution of 18-crown-6 in water–monosaccharide mixtures have been measured at 298.15 K. The values of standard enthalpies of solution of the crown ether are negative for all studied systems but the shape of the solution enthalpy curves differs from one mixed solvent to another. Measurements performed in this work demonstrate the influence of the stereochemical structure of the monosaccharides and their hydration on the enthalpies solution of the crown ether.

Keywords: Monosaccharides; Crown ether; Enthalpy of solution; Solvation

1. Introduction

Studies of selective interactions of saccharides with macrocyclic ligands in solution have intensified in recent years [1–7]. The increased interest is connected with a search for new synthetic saccharide receptors and their practical applications [3–6] as well as elucidation of pharmacological activity of drugs [7].

Studies of interactions of mono- and disaccharides with 18-crown-6 in dilute aqueous solutions have demonstrated that some saccharides form molecular complexes with the macrocycle [8–10]. Selectivity of the interaction is determined by two factors, hydration of the saccharide molecule and the presence of appropriate centers for binding. The present work reports a study of the heat effects of solution of 18-crown-6- in monosaccharide–water mixed solvents in order to get more information about an influence of the hydration on the saccharide–macrocycle interactions.

2. Experimental

18-Crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane) (MP Biomedicals), D-glucose, D-galactose, β-D-fructose and L-arabinose (Fluka, >99% pure) were used without further purification. All chemicals were dried in vacuum at 323 K (crown ether) and 343 K (monosaccharides) during several days before use. Solutions were prepared by weight in doubly distilled deionized water.

Enthalpies of solution of 18-crown-6 in different monosaccharide–water mixtures were measured with an isoperibol calorimeter [11] at 298.15. The amount of 18-crown-6 in glass ampoule was ≅0.02 g. The ampoule breaking-heat effect was negligible. The uncertainty in the measured enthalpies was estimated to be ±0.6%. The solute molality in all cases was estimated to be $\cong 1 \times 10^{-3}$ mol kg^{-1}, which can be considered as infinitely dilute, and the measured enthalpies of solution were regarded as standard enthalpies of solution ($\Delta_{sol}H^{\circ}_{cr}$). The obtained value of the standard solution enthalpy of 18-crown-6 in water (-21.49 ± 0.12 kJ mol^{-1}) is in a good agreement with literature data (-21.54 ± 0.05 kJ mol^{-1}) [12].

3. Discussion

The enthalpies of solution of 18-crown-6 in water and mixtures of water with D-galactose, D-glucose, β-D-fructose and L-arabinose are plotted in Fig. 1 as a function of the molality of the monosaccharides. Because we discuss the dissolution process of the same solute in different solvents, interactions

* Corresponding author. Fax: +7 4932 33 62 37.
E-mail address: evp@isc-ras.ru (E.V. Parfenyuk).

0040-6031/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.tca.2006.02.011

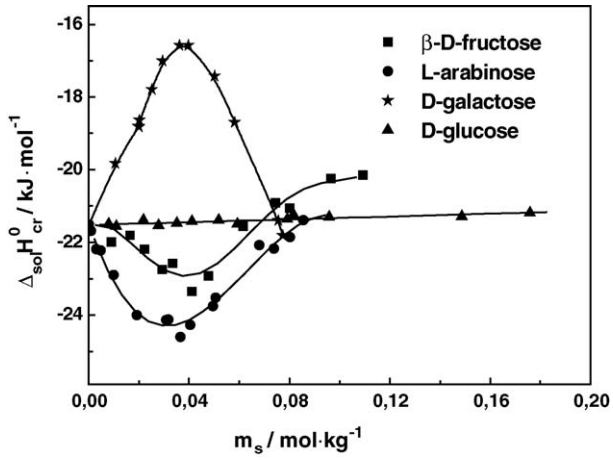

Fig. 1. Standard enthalpies of solution of 18-crown-6 in mixtures of water with monosaccharides as function of the solvent composition at 298.15 K.

of the solute molecules in the pure solid are constant. Consequently, the enthalpies of solution characterize the solute solvation. Fig. 1 shows that $\Delta_{sol}H^{\circ}_{cr}$ values are negative for all systems studied but the shape of the solution enthalpy curves differs from one solvent to anther. The order of the curves at low monosaccharide concentrations shows that the exothermicity of the solvation of the crown ether increases: D-galactose < D-glucose < β-D-fructose < L-arabinose.

The solvation process of a solute is affected by at least of two contributions: the structure and properties of the mixed solvent and the interactions of the solute with its environment. According to a classification [13], saccharides are hydrophilic structure makers that promote structuring of the solvent for the increased solute–solvent hydrogen bonds. Table 1 represents literature data on different properties of aqueous solutions of the monosaccharides characterizing their interactions with water. As seen in Table 1, the strength of the interaction between the monosaccharides and water increases in the order which is opposite to the mentioned above (except D-galactose): L-arabinose < D-galactose < β-D-fructose < D-glucose. Hence, in general, the weakening hydration of the monosaccharides promotes the dissolution of 18-crown-6.

It is interesting to note quit different changes of the enthalpy of solution of 18-crown-6 in aqueous solutions of two epimers D-glucose and D-galactose. The $\Delta_{sol}H^{\circ}_{cr} = f(m_s)$ curve for the crown ether in aqueous D-galactose exhibits a pronounced decrease in the exothermic effect reaching a maximum value at low monosaccharide content. In contrast, additions of D-glucose induce a small nearly linear decrease of negative $\Delta_{sol}H^{\circ}_{cr}$ values. Saccharides are amphiphilic compounds. According to literature data [17], D-glucose molecule as whole is more hydrophobic than D-galactose one. However, due to a definite steric orientation of OH groups, D-galactose molecule has a larger hydrophobic patch on its surface which can be a target for hydrophobic interactions [18,19]. It should be noted that crown ether molecules are also amphiphilic and have hydrophilic cavity and hydrophobic outer part. Probably, these interactions make the solvation of 18-crown-6 more thermochemically unfavorable upon addition of small amounts of D-galactose in comparison with D-glucose. This result is in agreement with our previous data [8]. In more concentrated D-galactose solutions a deficit of water leads to weakening the hydrophobic effect.

As can be seen from Fig. 1, the enthalpies of solution of 18-crown-6 become more negative upon addition of small amounts of L-arabinose or β-D-fructose up to definite concentrations of the monosaccharides. It means that the solvation of the crown ether in the mixed solvents becomes enthalpically more favorable than that in pure water. The observed effect may be explained by prevailing hydrophilic interactions (dipole–dipole or hydrogen bonding) of 18-crown-6 molecules with their environment in these systems. Complexes of the crown ether with L-arabinose or β-D-fructose probably are formed. The shape of the $\Delta_{sol}H^{\circ}_{cr} = f(m_s)$ curves may be associated with a competition of the above mentioned specific interactions and probably changes in the saccharide hydration due to reducing amount of water. The presence of high concentration of the monosaccharides provokes attenuation of hydrophilic interactions [12].

It should be noted that the $\Delta_{sol}H^{\circ}_{cr} = f(m_s)$ functions exhibit extrema in the aqueous solutions of the monosaccharides that have an axial OH-group at the fourth (C4) carbon atom. The importance of the axial configuration of the hydroxyl group at the C4 position of the sugar for binding has been stressed earlier in literature [19–22]. Complementarity of the interacting molecules can play a decisive role. Also note that L-arabinose and β-D-fructose have 1C conformation of their pyranose form in solution in contrast to C1 conformation for D-glucose and D-galactose [23].

Table 1
Properties of some monosaccharide–water mixed solvents at 298.15 K

Monosaccharide	*B*-coefficient (308.15 K)[a]	$\bar{v}_2^0 \times 10^{22}$ (cm^3 molecule^{-1})[b]	h_{ii} (J mol^{-1})(mol kg^{-1})[c]
D-Glucose	0.4428	1.858 ± 0.001	343 ± 10
β-D-Fructose	0.4370	1.844 ± 0.001	264 ± 18
D-Galactose	0.3935	1.831 ± 0.001	133 ± 8
L-Arabinose	0.3665	1.551 ± 0.001[d]	178 ± 9

B-coefficient is the viscosity coefficient in Jones–Dole equation; $\bar{v}_2^0$ is the partial molecular volume at infinite dilution; h_{ii} is the pair-wise enthalpic interaction coefficient.

[a] Ref. [14].
[b] Ref. [15].
[c] Ref. [16].
[d] D-Arabinose.

4. Conclusions

Measurements performed in this work demonstrate the influence of the stereochemical structure of the monosaccharides and their hydration on the enthalpies of solution of the crown ether.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.02.011.

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