Calorimetric study of the interactions of disaccharides with crown ethers in water

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10.1070/MC2001v011n05ABEH001455

In aqueous solutions, D-maltose and especially sucrose can form specific intermolecular interactions with 18-crown-6; this is in contrast to their behaviour with 15-crown-5.

This work is part of an extensive systematic study of the ability of saccharides to selectively interact with non-electrolytes having varying nature and structure in water and non-aqueous media. As is known, compounds with carbohydrate moieties are receptors for bonding hormones, toxic and pharmacologically active substances *etc.*, in living organisms.[1] Of particular interest are the interactions between saccharides and macrocyclic compounds because the latter are often considered as models for studying cyclic antibiotics and enzymes.[2]

The enthalpies of solution of 15-crown-5 and 18-crown-6 in aqueous D-maltose and sucrose† at 298±0.005 K were measured using an isothermal calorimeter. The error in the heat effect measurements was not greater than 0.05 J.

The sampels of 15-crown-5 and 18-crown-6 were dissolved in aqueous D-maltose and sucrose solutions of different concentrations (0.00–0.06 mol kg^{-1}) in order to obtain the limiting enthalpies of interactions ΔH^0_{sol} for calculating the enthalpic coefficients of pair interactions according to refs. 3, 4. The values of enthalpic coefficients (h_{xy}) of pair interactions between the disaccharides and the crown ethers are collected in Table 1.

As can be seen in Table 1, the coefficient h_{xy} characterising the interactions of the disaccharide with 18-crown-6 is negative, whereas it is positive for 15-crown-5. The value of h_{xy} is lower for sucrose as compared to D-maltose, especially for the systems containing 18-crown-6.

Several OH groups in disaccharide molecules are available for hydrogen bonding. Besides, the disaccharide molecules are flexible because of the glycoside bond between monosaccharide moieties.[5]

It is well known that crown ether molecules have hydrophobic outer surfaces and hydrophilic cavities. The diameter of the cavity of 15-crown-5 and that of 18-crown-6 are 1.7–2.2 and 2.6–3.2 Å, respectively. Crown ethers are able to form complexes with various species.[2]

The large negative h_{xy} coefficient for sucrose–18-crown-6 in water can be explained by strong specific interactions of the crown ether with the disaccharide leading possibly to the formation of an intermolecular complex. In contrast to sucrose, D-maltose is not able to interact strongly with 18-crown-6. It may be owing to differences in their structures (the D-maltose molecule consists of two glucose moieties whereas the sucrose molecule consists of the moieties of glucose and fructose in its furanose form[6]), and also in the conformational state in solution.

It should be noted that the size of the crown ether cavity (or molecule) influences the interactions between disaccharides and crown ethers. Steric hindrances may prevent D-maltose and sucrose molecules from specific interactions with 15-crown-5.

Table 1 Enthalpic coefficients of pair interactions between disaccharides (x) and crown ethers (y) in water at 298.15 K.

$x + y$	h_{xy}/kJ kg mol^{-1}
15-Crown-5 + D-maltose	39.33 (0.28)[a]
15-Crown-5 + sucrose	30.35 (0.24)
18-Crown-6 + D-maltose	–10.70 (0.13)
18-Crown-6 + sucrose	–98.40 (0.27)

[a]The 95% confidence range is presented in parentheses.

† 15-Crown-5 (Sigma) was treated with 0.3 nm molecular sieves and used without further purification. 18-Crown-6 (Sigma) was dried in a vacuum at 308 K over several days before use. D-Maltose monohydrate (pure) was purified by recrystallization from water. The amount of water was determined by thermogravimetry and the molality of the solutions was corrected taking account of the water content of the sample. Sucrose (pure) was purified by recrystallization from methanol and dried in a vacuum at 350 K. Solutions were prepared by weight using double-distilled and degassed water.

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Received: 28th March 2001; Com. 01/1781