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Thermodynamics of intermolecular interactions between saccharides and 18-crown-6 in water

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The intermolecular complexes of D-galactose, D-maltose, sucrose and raffinose with 18-crown-6 were found to be entropy stabilised.

Crown ethers are analogues of enzymes and cyclic antibiotics.[1] The carbohydrate components of cell membranes are the receptors of biologically active compounds (enzymes, drugs, *etc*.).[2] Therefore, the interactions between crown ethers and carbohydrates are of particular interest.

We used 18-crown-6 and saccharides (D-galactose, D-maltose, sucrose and raffinose)[†] as model compounds.

The heats of interactions were measured on an automatic titration differential calorimeter[3] at 298.15 K. An aqueous solution of the crown ether [(2–7)×10^{-3} mol dm^{-3}] was titrated with aqueous saccharide solutions (~0.2 mol dm^{-3}). Corrections for the heats of dilution of the crown ether were made. The stoichiometry of complexes was determined from titration curves. The stability constant K and the enthalpy change ΔH were calculated on a computer by varying K_i and ΔH_i to minimise $U(H_i, K_i) = \sum(Q_{\rm expt} - Q_{\rm calc})$.[2] Assuming the 1:1 complex stoichiometry, the U value was minimised to give an optimised set of K and ΔH for 1:1 complexation.

Table 1 summarises the stability constants and the thermodynamic parameters of interactions between the saccharides and 18-crown-6.

It can be seen that the intermolecular complexes are stable in water. The complex of D-galactose with 18-crown-6 is most stable complex. The complex of sucrose with 18-crown-6 exhibited the lowest stability. The interactions between the saccharides and the crown ether are accompanied by exothermic effects. However, the entropy changes mainly contributed to the ΔG values. The saccharide and crown ether molecules are strongly hydrated in aqueous solutions. The hydration shells of saccharide molecules are formed by the interactions of OH groups with water and by hydrophobic hydration. D-Maltose molecules have stronger and more compact hydration shells than those of sucrose molecules.[4] Therefore, the interactions between D-maltose and 18-crown-6 are accompanied by much greater entropy changes and become less favourable in terms of enthalpy as compared with sucrose. Moreover, the disaccharide and crown ether molecules are conformationally flexible.[1,5,6] This factor may contribute to ΔS and ΔH values, especially in the case of raffinose.

Thus, the studied complexes are entropy stabilised. The contribution from the entropy of dehydration processes is the major factor affecting intermolecular interactions in the test systems.

Table 1 Stability constants and thermodynamic parameters of interactions between the saccharides and 18-crown-6 in water at 298.15 K.

Saccharide	log K	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	$T\Delta S$/kJ mol^{-1}
D-Galactose	3.60±0.12	–20.55	–1.45±0.05	19.08
D-Maltose	3.35±0.45	–19.12	–0.87±0.11	18.25
Sucrose	2.53±0.06	–14.45	–4.85±0.04	9.60
Raffinose	2.77±0.06	–15.82	–2.26±0.05	13.66

[†] 18-Crown-6 (Sigma) and D-galactose (Sigma) were dried in a vacuum at 308 and 353 K, respectively. D-Maltose (monohydrate) and raffinose (pentahydrate) (Serva, analytical reagent grade) were used without further purification. Sucrose (pure) was recrystallised from ethanol and dried in a vacuum at 353 K. Solutions were prepared using double-distilled degassed water.

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