

Calorimetric Study of Interactions of Sodium, Calcium and Lanthanum Ions with Methyl Glycofuranosides in Aqueous Solutions

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Interactions of sodium, calcium and lanthanum ions with some methyl glycofuranosides has been studied by a microcalorimetric technique. The stoichiometry of the complexes formed is discussed on the basis of the calorimetric data. A comparison with previous equilibrium data for these systems has been made.

It is known that certain polyols of low molecular weight form in acidic and neutral aqueous solutions relatively stable complexes with alkaline earth metal cations.¹ The most extensive investigations concern the structures of the complexes of cyclic polyols having six-membered rings, ¹H NMR shift measurements being the experimental technique generally applied.^{2–8} In contrast, exact equilibrium and thermodynamic data on the subject are limited.^{7,9,10} We have reported previously on the interactions between methyl glycosides with five-membered rings and sodium, calcium and lanthanum ions in aqueous and methanolic solutions.^{11,12} To further the understanding of these weak interactions, particularly from a thermodynamic point of view, and to confirm the previous conclusions concerning the steric requirements of the complex formation, we now report on a calorimetric study of complexing of methyl glycofuranosides with sodium, calcium and lanthanum ions in aqueous solution.

EXPERIMENTAL

Materials. Methyl glycofuranosides used in calorimetric measurements were prepared as described earlier^{13–15} and dried over concentrated

sulfuric acid. The salts employed were commercial reagents of analytical grade. Solutions were made in distilled and degassed water.

Calorimetric measurements. The apparatus used in calorimetric experiments was an LKB 10700-2 Batch Microcalorimeter. The compartments of the reaction cell were loaded with aqueous solutions of appropriate salt and glycoside, and those of the reference cell with distilled water. Solutions were added with an automatic pipette giving a volume of 1.75 cm³ in each compartment. When the enthalpies of dilution were determined, the salt or glycoside solution was replaced by distilled water. The enthalpies of interaction of cations with methyl glycofuranosides were obtained by subtracting the enthalpies of dilution for the salt and glycoside solutions from the enthalpy of mixing of the same solutions.

RESULTS AND DISCUSSION

A possible way to study the stoichiometry of a complex in solution is to apply the so-called method of continuous variation.¹⁶ Here a series of solutions is prepared in which the sum of the total concentrations of the cation and ligand remains constant, whereas their proportions vary continuously. If any property of the solution, which depends linearly on the concentration of the complex, is plotted against the proportion of one of the reaction components, the abscissa of the maximum reveals the composition of the complex formed. Table 1 summarizes the calorimetric data for the interactions of sodium, calcium and lanthanum ions with various methyl glycofuranosides. When the method described

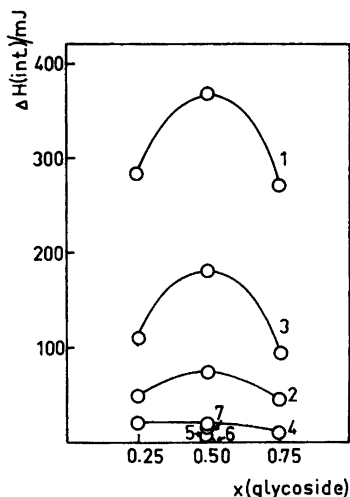


Fig. 1. Enthalpies of interaction, $\Delta H(\text{int.})$, of methyl glycofuranosides with calcium ions plotted against the proportion of the glycoside, $x(\text{glycoside})$, in the mixtures. For enumeration see Table 1.

above is applied to the data of calcium ion, the plots presented in Fig. 1 are obtained. Symmetry of the curves with respect to the proportion of 0.5 for calcium ion strongly suggests that complexes between calcium ion and methyl glycofuranosides are of the type 1:1, as comparable amounts of cation

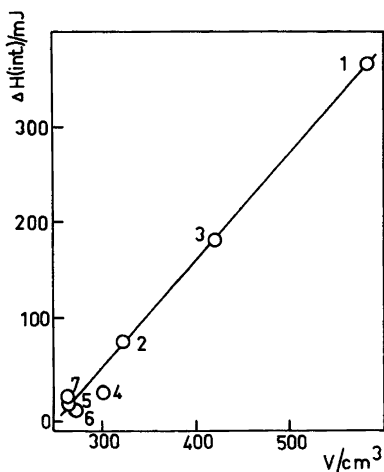


Fig. 2. Enthalpies of interaction, $\Delta H(\text{int.})$, of methyl glycofuranosides with calcium ions plotted against the retention volumes, V , of methyl glycofuranosides on a strong cation exchange resin loaded with calcium ions. For enumeration see Table 1.

and ligand are present. The result is expected on the basis of previous observations,^{7,10} and lends support for the assumptions made in our preceding treatments.^{11,12}

The enthalpies of interactions between methyl glycofuranosides and calcium ion correlate excellently with the previous results on the complexing efficiencies of various glycofuranosides.¹¹ For example, the maximum enthalpies from Fig. 1 are linearly related to the retention volumes that methyl glycofuranosides exhibit on a strong cation exchange resin loaded with calcium ions (Fig. 2).¹¹ The latter quantities have been shown¹¹ to reflect quite sensitively the stabilities of the Ca^{2+} -glycoside complexes in solution. The calorimetric measurements thus give further evidence for the usefulness of the chromatographic technique in the study of weak complexes.

We have reported previously the stability constants for the complexes of various glycofuranosides with calcium ion in neutral aqueous solution.¹¹ These values enable the estimation of the concentrations of the complexes formed in calorimetric experiments. Consequently, the approximate reaction enthalpies and entropies for the complex formation can be calculated. For example, the calcium complex of methyl α -D-ribofuranoside exhibits the values of -10 kJ mol^{-1} and $-30 \text{ J K}^{-1} \text{ mol}^{-1}$ for ΔH and ΔS under the experimental conditions. For methyl α -D-lyxofuranoside values of the same order are obtained, while complexing of other glycofuranosides is too weak to allow any reliable conclusions concerning the thermodynamics of the complex formation to be drawn.

Table 1 also includes the enthalpies of interaction of methyl glycofuranosides with sodium and lanthanum ions. These data appear to be consistent with the stability constants estimated on the basis of the influences that metal ions exert on the acid-catalyzed methanolysis of methyl glycofuranosides.¹² For example, the enthalpy of interaction of lanthanum ion with α -lyxoside is greater than that of lanthanum ion with α -riboside, although the situation is the reverse with calcium ion. The stability constants obtained in methanol vary similarly. The reason for this change in complexing abilities of glycofuranosides on going from Ca^{2+} to La^{3+} is difficult to explain,¹² but it seems to be real. It should also be noted that the enthalpies of interaction of glycofuranosides with

Table 1. Enthalpies of interaction, $\Delta H(\text{int.})$, of methyl glycofuranosides with Na^+ , Ca^{2+} and La^{3+} ions in aqueous solution, and the enthalpies of dilution, $\Delta H(\text{dil.})$, for the salt and glycoside solutions at 298.2 K.

Methyl glycofuranoside	$n/10^{-4}$ mol ^a	$-\Delta H(\text{dil.})/$ mJ	Salt	$n/10^{-4}$ mol ^a	$-\Delta H(\text{dil.})/$ mJ	$-\Delta H(\text{int.})/$ mJ
1. Methyl α -D-ribofuranoside	1.75	6	CaCl_2	5.25	267 ^b	280
	3.50	38	CaCl_2	3.50	163 ^b	370
	5.25	87	CaCl_2	1.75	73 ^b	270
	3.50		$\text{La}(\text{NO}_3)_2$	3.50	117 ^c	110
	3.50		NaCl	3.50	5 ^d	40
2. Methyl β -D-ribofuranoside	1.75	9	CaCl_2	5.25		50
	3.50	29	CaCl_2	3.50		80
	5.25	86	CaCl_2	1.75		50
3. Methyl α -D-lyxofuranoside	1.75	10	CaCl_2	5.25		110
	3.50	40	CaCl_2	3.50		180
	5.25	99	CaCl_2	1.75		100
	3.50		$\text{La}(\text{NO}_3)_2$	3.50		225
	3.50		NaCl	3.50		8
4. Methyl α -D-xylofuranoside	1.75	10	CaCl_2	5.25		20
	3.50	42	CaCl_2	3.50		20
	5.25	85	CaCl_2	1.75		10
5. Methyl β -D-xylofuranoside	3.50	34	CaCl_2	3.50		10
6. Methyl α -D-arabinofuranoside	3.50	38	CaCl_2	3.50		0
7. Methyl β -D-arabinofuranoside	3.50	37	CaCl_2	3.50		16

^a Initially in 1.75 cm³ of water. ^b From Ref. 18: 273, 158 and 66 mJ, respectively. ^c From. Ref. 19: 130 mJ. ^d From. Ref. 20: 26 mJ.

lanthanum ion are smaller than those of the interaction with calcium ion, although several lines of evidence^{3,7,12} suggest that the lanthanum complexes are more stable. These two findings together indicate that ΔS^\ominus for the formation of lanthanum complexes is more positive than the respective values for calcium complexes. In other words, the more favorable entropy change in the formation reaction gives rise to higher stabilities of lanthanum complexes, despite the fact that reaction enthalpies remain less negative than in the case of calcium ion. A possible explanation for this entropy gain might be a greater loss of solvent molecules in the solvation sphere of the La^{3+} ion than in that of the Ca^{2+} ion. On the other hand, it is a common trend that ΔS^\ominus increases with increasing electrostatic interaction between the cation and ligand.¹⁷

As seen in Table 1, the interaction of methyl α -ribose with sodium ion also exhibits a small enthalpy value, whereas in the case of α -lyxoside no heat effect can be observed. These findings agree

well with the previous equilibrium data obtained in methanol.¹² Possibly, the ionic charge of sodium ion is too small to cause the conformational changes in α -lyxoside required for complex formation. In contrast, calcium and lanthanum ions, being of approximately the same size as sodium ion, with their greater ionic charges can change the conformation of this compound suitably for complexing. Consequently, the calcium and lanthanum complexes of α -lyxoside can be understood to be nearly as stable as those of α -ribose, although this is not the case with the sodium complexes.

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