

Selective Hydrophobic Interactions of Monosaccharides with Planar Compounds

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In order to study the hydrophobic interaction between monosaccharides and the hydrophobic solutes, the solubility of hydrophobic model compounds was measured in the aqueous solutions of D-glucose, D-mannose, D-galactose, D-arabinose, D-xylose and D-ribose. These sugars appreciably increased the solubility of planar model compounds such as $[\text{Cu}(\text{acac}_2\text{en})]$ and $[\text{Cu}\{\text{sal}(\text{acac})(\text{en})\}]$. On the other hand, the solubility of the bulky model compound, $[\text{Co}(\text{acac})_3]$, decreased with increasing the concentration of the sugars studied. These results indicate that the selective hydrophobic interaction occurs between the hydrophobic surface formed by CH and CH_2 groups of the sugars and the planar aromatic or pseudo-aromatic parts of the metal chelates.

Key words: Monosaccharide, Hydrophobic Interaction, Solubility, Metal Chelates

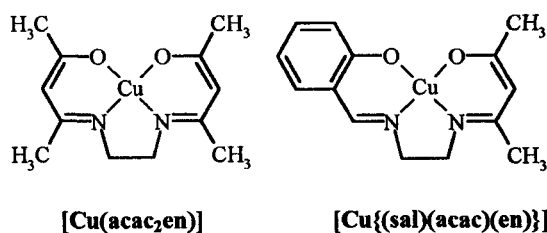
1. INTRODUCTION

Pyranose and furanose sugars have two kinds of the conflicting properties to water. One is the hydrophilic property due to OH groups and another is the hydrophobic property due to CH and CH_2 groups.

In the case of polysaccharides such as cyclodextrins and the helical-segment of amylose, the hydrophobic sites of the constituent units are favorably aligned so as to produce a large hydrophobic region and the hydrophobic property becomes more and more conspicuous. On the other hand, monosaccharides, which are the main constituents of such polysaccharides, do not have such clear hydrophobic regions and have been thought to be hydrophilic in nature. However, Janado *et al.* have shown that the solubility of 1-octanol is decreased with increasing concentration of the pentoses and hexoses, however, the solubility of planar hydrocarbons such as naphthalene and biphenyl is increased appreciably with increasing concentration of these sugars [1,2]. They concluded that the increasing in solubility of planar aromatic compounds in aqueous sugar solutions are due to the nonpolar sugar-aromatic hydrocarbon interactions[2]. Shigematsu has also showed the hydrophobic characteristics of monosaccharides by fluorescence of pyrene [3]. According to these results, it is presumed that such hydrophobic interactions of monosaccharides may be specifically observed in the interactions with planar compounds and that such interactions may occur between the hydrophobic planar parts of the compound and hydrophobic sites of the monosaccharides.

In the present study, we chose three different metal chelates in shape as model compounds in order to study the interactive mode with the monosaccharides. Tris(2,4-pentanedionato)cobalt(III) ($[\text{Co}(\text{acac})_3]$) was chosen as an aliphatic and nearly spherical model compound, and N,N'-bis(1-methyl-3-oxobutylidene)-ethylenediaminatocopper(II) ($[\text{Cu}(\text{acac}_2\text{en})]$) and N-(salicylidene)-N'-(1-methyl-3-oxobutylidene)-

ethylenediaminatocopper(II) ($[\text{Cu}\{\text{sal}(\text{acac})(\text{en})\}]$) were chosen as pseudo-aromatic and planar model compounds. Their solubility in water and in aqueous monosaccharide solutions was determined at 25 °C. The structures of $[\text{Cu}(\text{acac}_2\text{en})]$ and $[\text{Cu}\{\text{sal}(\text{acac})(\text{en})\}]$ are shown below.



2. EXPERIMENTAL

All the monosaccharides were analytical reagent grade and used as received. The metal complexes, $[\text{Co}(\text{acac})_3]$, $[\text{Cu}(\text{acac}_2\text{en})]$ and $[\text{Cu}\{\text{sal}(\text{acac})(\text{en})\}]$, were prepared and purified according to the literatures [4-6].

The solubility of $[\text{Co}(\text{acac})_3]$, $[\text{Cu}(\text{acac}_2\text{en})]$ and $[\text{Cu}\{\text{sal}(\text{acac})(\text{en})\}]$ were measured in the solutions of D-glucose, D-mannose, D-galactose, D-xylose, D-fructose, D-arabinose and D-ribose in the concentration range 0-40 % except for D-galactose (0-30%). The solubilities of the metal complexes in pure water and the monosaccharide solutions were measured as follows.

Sufficient amount of the metal complex, about 10 cm³ of pure water or the monosaccharide solution and a magnetic stirring bar were placed in a small vial. The vial was tightly closed with an inner rubber cap and a screw cap. The mixture was stirred with a magnetic stirrer in a water bath maintained at 25.0 ± 0.05 °C for 48-72h. The saturated solution was separated from the

mixture by the filtration through a membrane filter with a pore size of 0.2 μm . The saturated solution was diluted with water to give a suitable absorbance for the spectroscopic measurement.

The absorbance was measured at 592 nm for $[\text{Co}(\text{acac})_3]$, 301 nm for $[\text{Cu}(\text{acac}_2\text{en})]$ and 314 nm for $[\text{Cu}(\text{sal})(\text{acac})(\text{en})]$, respectively. The solubility of $[\text{Co}(\text{acac})_3]$, $[\text{Cu}(\text{acac}_2\text{en})]$ and $[\text{Cu}(\text{sal})(\text{acac})(\text{en})]$ in pure water was 4.04×10^{-3} , 8.77×10^{-4} and 3.63×10^{-4} mol dm^{-3} , respectively.

For convenience, the solubility of the metal chelate in aqueous monosaccharide solutions is expressed as the relative solubility (A_s / A_w), in which A_s is the absorbance of the saturated solution of the metal chelate in the monosaccharide solution and A_w is that of the metal chelate in pure water.

3. RESULTS AND DISCUSSION

Fig. 1 shows relative solubility of $[\text{Co}(\text{acac})_3]$ in pentose and hexose solutions. The solubility of $[\text{Co}(\text{acac})_3]$ smoothly decreases with increasing the concentration of all monosaccharides used and the coexist monosaccharides show large solubility decreasing-effect to this nearly spherical model compound. For example, in 40 % monosaccharide solutions, the solubility of $[\text{Co}(\text{acac})_3]$ is only 20 %, compared with the solubility in pure water. The similar phenomenon has been observed in the solubility of the aliphatic alcohols. Janado *et al.* showed that the solubility of 1-octanol in aqueous monosaccharide solutions decreases as the sugar concentration increases up to 40% sugar concentration [1,2].

In $[\text{Co}(\text{acac})_3]$, Co(III) ion is octahedrally coordinated by three 2,4-pentanedionate anions. Since six methyl groups are situated on the periphery of the chelate rings, $[\text{Co}(\text{acac})_3]$ exhibits a hydrophobic characteristic [7,8]. The large solubility-decreasing effect by sugars may be similar to the salting out effect of the hydrophobic solute by the hydrophilic salt. Since the hydrophobic parts of this metal chelate accessible to the sugar consist of the methyl groups, the large solubility-decreasing effect results from the interactions with sugars by the aliphatic methyl groups.

In Fig. 2, the relative solubility of $[\text{Cu}(\text{acac}_2\text{en})]$ in pentose and hexose solutions is shown. Unlike the solubility of $[\text{Co}(\text{acac})_3]$, the solubility increases with increasing the sugar concentration especially in the solutions of D-ribose, D-xylose and D-mannose.

In this metal chelate, two 2,4-pentanedionate residues are joined with a ethylenediamine and two co-planar pseudo-aromatic rings are made of 2,4-pentanedionate residues and Cu(II) ion. This metal chelate is able to interact with sugars by the upper and lower sides of two pseudo-aromatic rings as well as the methyl groups of 2,4-pentanedionate residues and the ethyl group of the ethylenediamine residue. The interactions with sugars by the aliphatic groups would bring about unfavorable solubility-decreasing effect as the case of $[\text{Co}(\text{acac})_3]$. Therefore, the increase in the solubility with increasing the sugar concentration may be attributed to the interaction with the parts of co-planar pseudo-aromatic rings of this metal chelate. Similar phenomena were observed for the solubility of

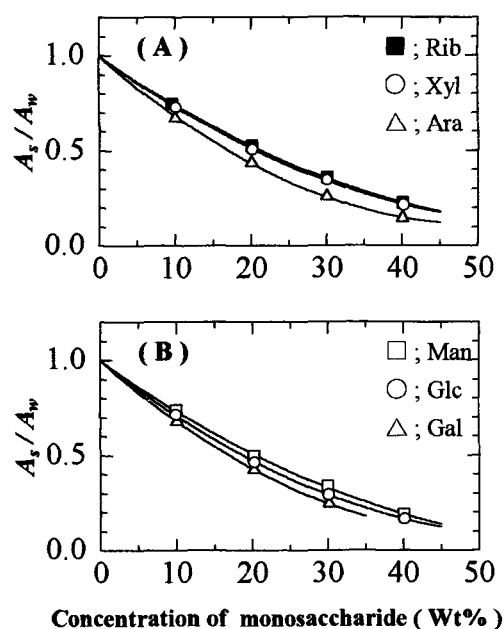


Fig. 1 Relative solubility of $[\text{Co}(\text{acac})_3]$ in aqueous monosaccharide solutions at 25 °C. (A) : in the pentose solutions, (B) : in the hexose solutions .

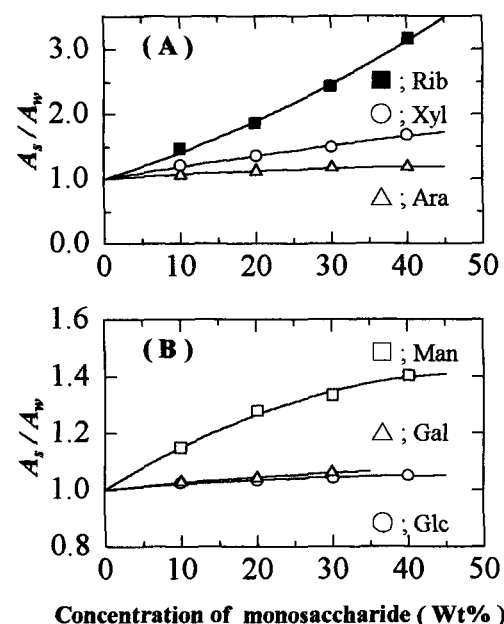


Fig. 2 Relative solubility of $[\text{Cu}(\text{acac}_2\text{en})]$ in aqueous monosaccharide solutions at 25 °C. (A) : in the pentose solutions, (B) : in the hexose solutions .

naphthalene [2], biphenyl [2] and pyrene [3]. Janado *et al.* have reported that the increases in solubility in monosaccharide solutions are brought about by the interactions with aromatic hydrocarbons that occur at the hydrophobic surfaces of the sugar molecules [2].

Fig. 3 shows the relative solubility of [Cu(sal)(acac)(en)] in the same monosaccharide solutions. In this metal chelate, one 2,4-pentanedionate residue is replaced by one salicylaldehyde residue. In the absence of the methyl group the salicylaldehyde residue is less sterically hindered. It would be expected to facilitate the interactions with sugars from the upper and lower sides of the aromatic ring. The solubility of this metal chelate is, in fact, markedly increased with increasing the sugar concentration. The solubility of [Cu(sal)(acac)(en)] is increased by sugars in the order, arabinose < xylose < ribose for pentoses and glucose \cong galactose < mannose for hexoses. These orders may be compared with the hydrophobic indexes for monosaccharides proposed by Miyajima *et al.* They showed that the ratio of its total hydrophobic surface area to its total hydrophilic surface area accessible to water is a good measure of the hydrophobicity of the sugar and that the larger the index is the stronger the hydrophobicity. According to these indexes proposed by Miyajima *et al.*, the hydrophobic strength lies in the order, xylose (44.1) < arabinose (48.1) < ribose (51.9) and glucose (38.7) < galactose (40.6) < mannose (42.0), where hydrophobic indexes (Index A) are shown in parentheses [9]. Although the reversing of the order is observed at the xylose and arabinose as compared with that of the increase in solubility of planar solutes, above facts suggests that such a hydrophobic surface plays an important role in the interaction of monosaccharides and hydrophobic solutes.

From preliminary experiments of the partition coefficients of [Co(acac)₃] and [Cu(acac)₂(en)] between heptane and aqueous monosaccharide solutions at 15, 25 and 35°C, the signs of thermodynamic parameters for the transfer of [Co(acac)₃] and [Cu(acac)₂(en)] from water to the monosaccharide solutions could be estimated. For examples, thermodynamic parameters for the transfer of [Co(acac)₃] from water to the 40% xylose solution at 25°C were $\Delta G_{tr}^\circ > 0$, $\Delta H_{tr}^\circ > 0$, $\Delta S_{tr}^\circ > 0$ and those for [Cu(acac)₂(en)] were $\Delta G_{tr}^\circ < 0$, $\Delta H_{tr}^\circ > 0$, $\Delta S_{tr}^\circ > 0$, respectively. Therefore, the decrease in the solubility of [Co(acac)₃] in monosaccharide solutions results from the unfavorable increase in enthalpy. On the other hand, the increase in the solubility of [Cu(acac)₂(en)] originates from the favorable increase in entropy. According to the interaction models of Desnoyers *et al.* [10], the former is the indication of the hydrophobic-hydrophilic interaction and the latter is that of the hydrophobic-hydrophobic interaction. Therefore, the hydrophobic-hydrophilic interaction occurs between the hydrophobic methyl groups of [Co(acac)₃] and the hydrophilic parts of xylose. On the other hand, the hydrophobic-hydrophobic interaction occurs between the hydrophobic pseudo-aromatic rings of [Cu(acac)₂(en)] and the hydrophobic parts of xylose.

At the present, we cannot clearly show which parts of the individual monosaccharide exhibit the hydrophobic property. However, the alternating arrangement of three

axial CH groups and the adjacent arrangement of three axial-equatorial-axial CH groups can be found in monosaccharide and it is probable that respective three CH groups form the hydrophobic plane. It is presumed that such a hydrophobic plane stacks well with a planar part of the hydrophobic solute, and that monosaccharides can interact selectively with planar compounds.

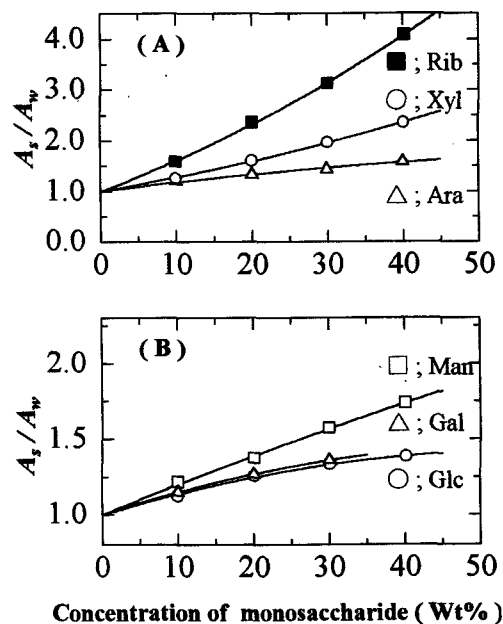


Fig. 3 Relative solubility of [Cu(sal)(acac)(en)] in aqueous monosaccharide solutions at 25 °C. (A) : in the pentose solutions, (B) : in the hexose solutions .

4. References

- [1] M. Janado and T. Nishida, *J. Solution Chem.*, **10**, 489 (1981).
- [2] M. Janado and Y. Yano, *Bull. Chem. Soc. Jpn.*, **58**, 1913 (1985).
- [3] M. Shigematsu, *Carbohydr. Res.*, **292**, 165 (1996).
- [4] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).
- [5] P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).
- [6] M. Yamamoto, *J. Phys. Chem.*, **88**, 3356 (1984).
- [7] Y. Yoshimura, N. Sato, and M. Kikuchi, *Bull. Chem. Soc. Jpn.*, **59**, 2135 (1986).
- [8] K. Miyajima, K. Machida, and M. Nakagaki, *Bull. Chem. Soc. Jpn.*, **58**, 2595 (1985).
- [9] J. E. Desnoyers, M. Arel, G. Perron, and J. Jolicoeur, *J. Phys. Chem.*, **73**, 3346 (1969).

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