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Technical Note

Calcium Chloride Complex Formation of Glucose Syrups and Their Fractions

ABSTRACT

Glucose syrups react with calcium salts in aqueous solution to form complexes. As a consequence, the specific rotation, viscosity, electrical conductivity and osmotic pressure of the syrups differ from those of untreated glucose syrups. Complex formation depends on calcium ion concentration, and interaction of the glucose syrup with the calcium salt affects, in turn, the activity of the calcium ions.

INTRODUCTION

Carbohydrates form the major portion of a normal diet and vary in form from simple compounds such as glucose to complex molecules such as starch. The interaction of the cation of metallic compounds with carbohydrates has nutritional significance. Sugar chelates of iron facilitate the transport of this metal across biological membranes and it has been proposed that sugar chelates play an important rôle in the nutritional utilisation of other trace metals in the diet (Charley & Saltman, 1963). Interaction of calcium ions with carbohydrates has been implicated in such biological processes as the stimulation of calcium absorption from rat gut (Wasserman & Comar, 1959), calcium transport (Charley & Saltman, 1963; Moore, 1971), cell–cell adhesion (Hays *et al*, 1965; Mannery, 1966), calcification (Bowness, 1968; Smith *et al*, 1971) and binding of glycoproteins to cell surfaces (Pricer & Ashwell, 1971). It has been proposed (Hood & O'Shea, 1977) that interaction between metal cations and carbohydrates could also influence metal-requiring chemical and biochemical reactions in foods.

At relatively high concentrations, salts lower the gelatinization temperature of starch granules. Minerals also affect the chemical behaviour of pectins and alginic acid as ion exchangers and gel formers. Both latter polysaccharides have industrial importance.

The presence of minerals in a glucose syrup can have a significant effect upon the syrup's physical properties. Deionisation decreases hygroscopicity (Kearsley, 1975), which in turn may affect the shelf life of some foods (Duck & Cross, 1957) and increase both optical rotation and average molecular weight.

To provide proof of the existence of the carbohydrate–salt complex, solubility curves, stability studies, phase studies and infra-red studies of adducts have been carried out (Helderman, 1920; Nishizawa & Hachihama, 1929; Tipson & Isbell, 1960). Published information on the complexes formed by carbohydrates and metal ions has often been difficult to interpret, mainly because ions of these metals do not form stable complexes in aqueous solutions and study of such weak interactions is beset with many analytical difficulties.

The ability of a dissolved salt to change the specific rotation of many sugars and sugar derivatives is now generally believed to be due to complex formation (Rendleman, 1966). It has been shown that the optical rotation of sucrose depends upon the concentration of the sugar but is also affected by the presence of otherwise optically inactive salts (Varineez, 1962). The optical rotations of sucrose and D-fructose in 4M solutions of alkali metal salts were dependent upon the cation and the anion (Ramaiah & Vishnu, 1959). Salts of alkaline-earth metals do not generally differ from salts of alkali metals in their effect upon the specific rotation of carbohydrate. However, it has been demonstrated that calcium ions complex with both uncharged and anionic (Rendleman, 1966) carbohydrates in aqueous solutions, but little is known about either the factors involved in calcium–carbohydrate interactions or the stoichiometry of the resultant complexes. The variations in the rotations of the oligosaccharides reported by various workers may result in part from the presence of salts that are effective in depressing the rotation. This suggests that the minerals interact with the carbohydrates to form some sort of a complex in which the usual solution molecular conformation is distorted (Kearsley & Birch, 1975; Kearsley & Birch, 1977*a*).

Viscosity is a function of chain expansion and should decrease with decreasing charge density of the macromolecule. The lower the negative charge density, the lower the interionic repulsion responsible for polymer expansion. The increase in the viscosity of sucrose by the addition of salts has been studied (Naffa & Frégé, 1959). Also, the addition of potassium chloride to an alkaline solution of amylase (Banks *et al*, 1971) has been studied and iodine and 1-butanol in neutral solution have been shown to decrease the viscosity of starch (Banks & Greenwood, 1971). It has been reported that the viscosity of a carrageenan dispersion is relatively unaffected by salts of monovalent cations but that calcium ions reduce the viscosity (Stoloff, 1959). Amylographic viscosity measurements of potato starch with, bi- and trivalent ions have indicated that the viscosity of the potato starch pastes was changed (due to the presence of its esterified phosphate groups) (Rüggeberg, 1953). The viscosity of a glucose syrup is of great importance in the food industry and is also important in intestinal transport (Kearsley & Birch, 1977*b*).

Electrical conductance measurements are effective in determining the proportion of free cations in solution and the proportion of cations bound by a carbohydrate. The conductivities of a wide range of salts in both the presence and absence of sucrose have been determined and an increase in the carbohydrate concentration caused a decrease in conductivity (Selix, 1950). The low degree of carbohydrate–salt interaction in aqueous solution is appropriately illustrated by the virtual inability of locust-bean gum to affect the conductivities of different ions (Barry & Halsey, 1963).

No published data were found regarding the effect of a salt on the osmotic pressure of a carbohydrate. Since the osmotic pressure of sugars is important in the preservation of certain foods and in the fractionation of glucose syrups by reverse osmosis (Kearsley, 1976), this phenomenon has thus been examined in this present work.

A large number of salts are used, either directly or indirectly, in the food industry and reasons for their use vary considerably. Calcium salts are largely used in carbohydrate containing foods such as jelly (Cakebread, 1974) to control gel strength, as an enzyme stabilizer (Allen & Spradlin, 1974) and for the hardening of canned vegetables (Powers *et al*, 1950).

This paper details effects produced by increasing concentrations of calcium chloride added to glucose syrups. These include changes of optical rotation, osmotic pressure, viscosity and conductivity in glucose syrups of different dextrose equivalents (DE).

MATERIALS AND METHODS

Materials

Commercial glucose syrups were provided by Corn Products Ltd, Manchester, Great Britain.

Glucose syrup fractions were produced by a reverse osmosis technique (Birch & Kearsley, 1974). (Carbohydrate composition of commercial glucose syrups and glucose syrup fractions is given in Table 1.)

Calcium chloride (AnalaR grade) was obtained from Fisons Scientific Apparatus, Loughborough, Leicestershire, Great Britain.

Methods

Specific rotation

This is calculated from the optical rotation produced by a 1 % solution of the syrup at 22 °C using the sodium D-line. Optical rotation is measured on a Bendix NPL automatic polarimeter type 1430 using a 10 mm cell and sucrose as a standard.

Electrical conductivity

Conductivities were measured using a Type MCL (Mark III) conductivity measuring Bridge (Electronic Switchgear Ltd, London), the difference in conductivity between pure $CaCl_2$ solutions and experimental solutions

TABLE 1

Carbohydrate Composition (%) of Commercial Glucose Syrups and Glucose Syrup Fractions

Carbohydrate	*Dextrose equivalent*					
	15F	*18C*	*20F*	*25C*	*43C*	*70F*
Glucose	0	3	6	8	19	45
Maltose	1	7	6	8	14	22
Maltotriose	2	5	6	7	12	11
Maltotetraose	8	5	6	7	10	7
Higher	89	80	76	70	45	15

F = Glucose syrup fraction.
C = Commercial glucose syrup.

($CaCl_2$ + glucose syrup) being used to calculate the percentage depression of conductivity.

Density determinations

Previously calibrated 10 ml densitometric flasks were used at ambient temperature. The apparent density of each solution was determined by weighing known volumes of the solutions in these flasks in air.

Viscosity estimations

An Oswalt viscometer was used for the determinations. This was suspended in a temperature controlled water-bath at 25 °C and exactly 10 ml of solution added. Duplicate measurements were made for each sample and the average calculated.

Osmotic pressure determinations

All measurements were made with 0·25 ml of sample using an Advanced Clinical Osmometer, Model 3A Eurolab Scientific NV Holland.

Sample preparation

Each glucose syrup was dried at 65 °C under vacuum to constant weight (0 % moisture) and weighed accurately into a volumetric flask to which was added calcium chloride to give salt:carbohydrate ratios of

0·1:1(0·1 g $CaCl_2$ + 1 g CHO per 100 ml deionised water)
0·2:1(0·2 g $CaCl_2$ + 1g CHO per 100 ml deionised water)
0·3:1(0·3 g $CaCl_2$ + 1 g CHO per 100 ml deionised water)

All measurements were carried out 5 h after adding salt to carbohydrate to ensure that no shift in mutarotational equilibrium would affect the results.

RESULTS AND DISCUSSION

Triplicate measurements of specific rotation were made for each glucose syrup fraction and each commercial glucose syrup in the presence of increasing concentrations of calcium chloride. The results are shown in Table 2 along with the results of a statistical analysis used to determine the best fit regression line for specific rotation measurements. The addition of calcium chloride to glucose syrups can be seen to cause a reduction in

TABLE 2

Specific Rotations of Glucose Syrups in the Presence of Calcium Chloride

DE of glucose syrup	*Salt: Carbohydrate ratio*				*Regression line data*		
	0:1	*0·1:1*	*0·2:1*	*0·3:1*	*Slope*	*Intercept*	*Correlation coefficient*
15 F	182·0	173·7	173·0	172·1	−30·40	179·8	0·857
18 C	178·5	173·2	173·2	173·2	−15·90	176·9	0·775
20 F	171·5	166·0	165·6	162·9	−26·20	170·4	0·938
25 C	164·3	157·5	155·3	154·2	−32·50	162·7	0·926
43 C	144·8	139·3	139·8	136·8	−23·50	143·7	0·905
70 F	95·9	94·9	94·9	94·9	−4·00	96·0	0·894

F, Glucose syrup fraction.
C, Commercial glucose syrup.

specific rotation at all DEs. The reduction in specific rotation is seen to be greatest in the lower DE syrups because, in these syrups, the higher oligomers tend to form a helical conformation and the inorganic ions are thought to enter the helix and form a complex. Obviously, as the DE increases, the average DP decreases and fewer helical sites for complex formation are then present in the solution. The observed changes in physical properties in the presence of minerals are always more marked with the high molecular weight fractions of glucose syrups (Kearsley &

TABLE 3

Osmotic Pressure (m Osm × 10^{-2}) of Glucose Syrups in the Presence of Calcium Chloride

DE of glucose syrups	*Salt: Carbohydrate ratio*				*Regression line data*		
	0:1	*0·1:1*	*0·2:1*	*0·3:1*	*Slope*	*Intercept*	*Correlation coefficient*
15 F	0·73	0·60	0·44	0·40	−1·150	0·715	−0·977
18 C	0·80	0·71	0·66	0·56	−0·770	0·798	−0·993
20 F	0·92	0·80	0·74	0·68	−0·780	0·902	−0·983
25 C	1·58	1·44	1·38	1·26	−1·020	1·568	−0·989
43 C	2·24	2·20	2·10	2·05	−0·670	2·248	−0·986
70 F	3·41	3·20	3·00	2·92	−1·670	3·383	−0·983

F, Glucose syrup fraction.
C, Commercial glucose syrup.

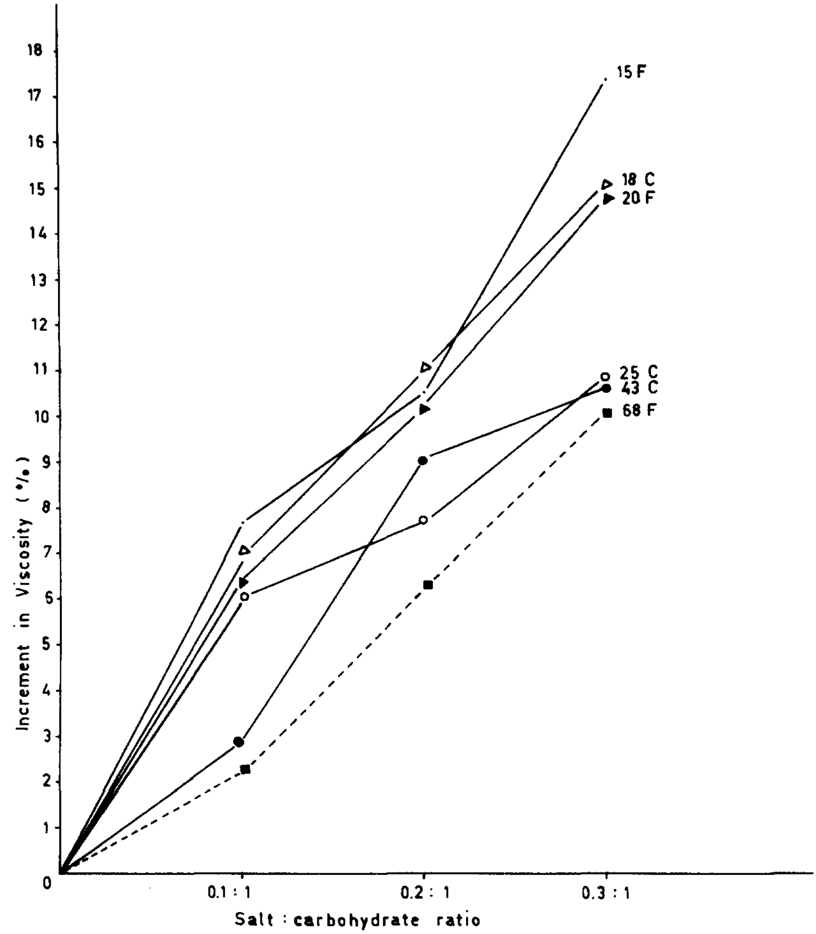

Fig. 1. Increment in viscosity (%) of glucose syrups in the presence of calcium chloride.

Birch, 1975). Also, glucose residues do not themselves easily chelate with ions (Rendleman, 1966; Angyal & Pickles, 1972).

Osmotic pressure determinations of glucose syrups in the presence of calcium chloride are shown in Table 3. The results obtained showed that the presence of calcium chloride lowers the osmotic pressure in all cases. The osmotic pressure of glucose syrups in the presence of increasing salt: carbohydrate ratios, (0·1 : 1, 0·2 : 1 and 0·3 : 1) showed a significant increase for all samples tested.

Figure 1 shows the results of (%) incremental rise in viscosity versus salt: carbohydrate ratio for glucose syrups. The greatest increment is seen to be at the lowest (15) DE glucose syrup where presumably more salt is

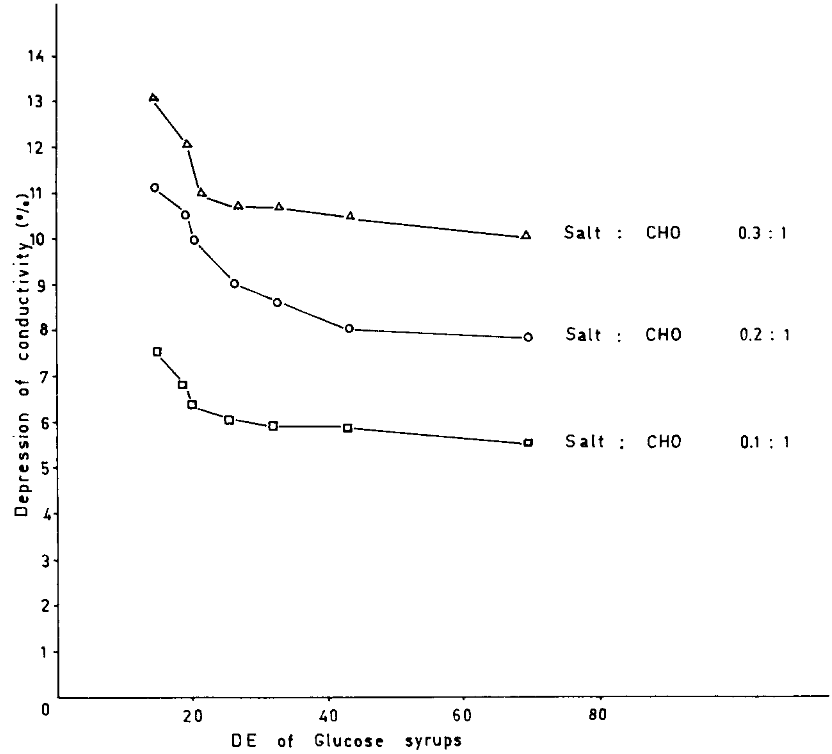

Fig. 2. Depression of conductivity (%) of glucose syrups in the presence of calcium chloride.

chelated. The lowest increment is shown by the highest (68) DE glucose syrup. In all cases an increment in viscosity was observed with increasing salt:carbohydrate ratios (0·1:1, 0·2:1 and 0·3:1).

The electrical conductivities of different DE glucose syrups at different salt:carbohydrate ratios were determined. Figure 2 shows the results of (%) depression of electrical conductivity versus DE of glucose syrups. The greatest depression is seen to be at the lower DE of glucose syrup. For all salt:carbohydrate ratios, again, the lowest depression is observed in the higher DE glucose syrup. It is interesting to note that the changes which occur due to the presence of calcium chloride depend largely on the salt:carbohydrate ratios in the case of osmotic pressure and viscosity as well as electrical conductivity determinations. However, the specific rotation measurements for the highest DE (68) glucose syrups did not show any significant change in relation to the salt:carbohydrate ratios.

All the above results are consistent with complex formation between the calcium chloride and the components of glucose syrups, particularly those of higher molecular weight. They underline some of the previous suggestions from this laboratory and help to explain many of the interactions of carbohydrates and related molecules in food systems.

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