Carbohydrate Research, 115 (1983) 231–233
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Lithium chloride–2-methoxyethanol as a solvent system for carbohydrates

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(Received April 3rd, 1982; accepted for publication, July 22nd, 1982)

The solubility of carbohydrates in non-aqueous solvents has been reviewed in some detail[1], but the better solvents, for instance morpholine and *N*,*N*-dimethylformamide, are unsuitable for large-scale use. Suitable solvents are those that do not contain any reactive functional groups and do not have any health restrictions. Alcohols and ethers fit this description and contain the hydrogen-bond acceptor and donor functions considered necessary for good solvent character. Ethylene glycol derivatives have health-related restrictions but were used for the initial study, rather than the safe propylene glycol derivatives, because of their ready availability.

The solubility of carbohydrates in alkoxyethanols is fairly low, except a temperatures too high for industrial sugar processing because of undesirable side reactions. The character of the solvent may be changed by adding a second component that increases the polarity of the solvent. Alkali-metal halides have this property and have been used to diminish the solubility of non-polar compounds in methanol[2] and to increase the solubility of polar compounds in amide solvents[3], including the dissolution of cellulose in *N*,*N*-dimethylacetamide[4].

Lithium halides are the alkali-metal salts most soluble in organic solvents, and the solvent system lithium chloride–2-methoxyethanol was chosen for the initial investigation because of the high solubility of lithium chloride in this solvent (28%). Greatly enhanced solubilities of several mono- and di-saccharides were found in the presence of this salt.

Solutions containing 0, 5, 10, 15, and 20% (w/w) lithium chloride in 2-methoxyethanol were shaken at 20° and at 60° with an excess of each crystalline sugar until no further dissolution occurred. The concentration of carbohydrate was determined by diluting the filtered or centrifuged solution into water and measuring the optical rotation. It had been previously established that neither the solvent nor the salt has any effect on the rotation, although increased rates of mutarotation, for D-glucose and D-fructose, were observed in the presence of lithium chloride. For sucrose, no decomposition or loss occurred in these solutions, as determined by high-pressure liquid chromatography on Aminex Q150S under standard conditions.

0008-6215/83/$ 03.00

TABLE I

SOLUBILITY OF CARBOHYDRATES IN LITHIUM CHLORIDE–2-METHOXYETHANOL

Percent of lithium chloride (w/w) *in 2-methoxyethanol*	*Solubility* (%)[a]					
	Sucrose		D-*Glucose*		D-*Fructose*	
	20	*60*	*20*	*60*	*20*	*60*
0	0.4	1.0	2.3	4.2	6.0	18.8
5	5.0	10.3	6.6	7.8	22.7	15.9
10	19.2	23.0	6.2	7.8	5.4	25.0
15	7.6	10.9	12.6	13.8		
20	11.2	11.7	12.1	15.1		

[a]Expressed as w/w in total solution

TABLE II

SOLUBILITY OF CARBOHYDRATES IN LITHIUM CHLORIDE–2-METHOXYETHANOL

Percent of lithium chloride (w/w) in 2-methoxyethanol	*Solubility* (%)[a] *at 20*			
	Cellobiose	*Maltose hydrate*	*α-Lactose hydrate*	*α,α-Trehalose dihydrate*
0	0.1	5.9	0.1	0.2
5	0.1	10.4	0.4	0.2
10	0.5	15.1	2.6	0.4
15	2.0	33.7	12.8	22.3
20	3.8	29.0	14.3	24.7

[a]Expressed as w/w in total solution.

The increases in solubility for sucrose, D-glucose and D-fructose are listed (Table I). Sucrose shows maximum solubility at a lithium chloride concentration of 10%, with an almost 50-fold increase at 20°. These solutions become very viscous and it is possible that they are not saturated. Glucose shows a similar increase in solubility, but solutions of D-fructose become too viscous to handle at high concentrations of lithium chloride. Precipitation of a D-fructose–lithium chloride complex occurred when these solutions were kept. The formation of such complexes is well established[5] and accounts for the decrease in the solubility of sucrose and D-glucose at higher concentrations of lithium chloride.

The solubilities of four disaccharides were measured at 20° with various concentrations of lithium chloride (Table II). Cellobiose is essentially insoluble in 2-methoxyethanol and is moderately soluble in 20% lithium chloride–2-methoxyethanol. The other three disaccharides, maltose, α-lactose, and α,α-trehalose, all showed a considerable increase in solubility, over 100-fold for trehalose. However, it

should be noted that these disaccharides are hydrated in the crystalline form and the solution formed could be described as being a mixed aqueous system. Preliminary results show increased solubility of such polysaccharides as starch and dextran in these solvent systems.

Other combinations of hydroxyethers and alkali-metal halides are being investigated as solvent systems for carbohydrates to establish whether such systems could be useful in synthetic studies and as means of extracting carbohydrates from mixtures containing non-carbohydrates.

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