Carbohydrate Research, 29 (1973) 509–512

Note

Influence of reducing and nonreducing carbohydrates on the conductance of aqueous solutions of electrolytes

SATYA P. MOULIK AND ASOKA K. MITRA
Carbohydrate Research Unit, Department of Food Technology & Biochemical Engineering, Jadavpur University, Calcutta-32 (India)
(Received January 22nd, 1973; accepted January 31st, 1973)

Many carbohydrates are known to have the capability of combining with metal ions, especially with those of the alkali and alkaline-earth metal groups[1]. Formation of adducts between D-glucose (and maltose) and the hydroxides of alkaline-earth metals has been reported from this laboratory[2–5]. However, such interactions at the molecular level, in solution, have seldom been studied.

One way of working on this problem is to measure the conductance of salt solutions in the presence and absence of carbohydrates. Stokes *et al.*[6] reported only the limiting, equivalent conductances and transference numbers of a number of electrolytes in aqueous solutions of sucrose, D-mannitol, or glycerol. In elaborating this study, as well as to gain understanding of the probability of association of carbohydrates with metal ions, measurements of the conductance of solutions in different electrolytes were undertaken, employing, as the solute, D-glucose and sucrose as representative carbohydrates, and glycerol and D-mannitol as typical alditols.

EXPERIMENTAL

Materials. — *Pro analysi* grade (E. Merck) $BaCl_2$, $CaCl_2$, $CoCl_2$, HCl, KCl, $MgCl_2$, NH_4Cl, $NiCl_2$, and $SrCl_2$, were used. Solutions were made in double-distilled water (sp. cond. 2 μmho$\cdot$cm^{-1}), and standardized by estimating the chloride by titration against standard $AgNO_3$, employing dibromofluorescein as the indicator.

The D-glucose and sucrose were of Analar grade (BDH), and the glycerol was of *pro analysi* grade (E. Merck). Pure grade D-mannitol (S. Merck, India) was recrystallized before use. All of the solutions of the polyhydroxy compounds were tested conductimetrically and found to have negligible conductance in comparison with the conductance of 1mM salt solutions. All of the measurements were performed at 35 $\pm$0.5° in a constant-temperature water-bath. The conductance instrument was a Philips PR 9500 bridge, operated at its most sensitive range. The selection of cell dimension was so made that results were obtained in the range of minimum error of the bridge. Still unavoidable errors were largely nullified by always presenting the data as conductance ratios.

RESULTS

As had been anticipated, the conductance of electrolyte solutions was found to decrease with increasing concentration of a polyhydroxy compound as the solute. However, the rate of decrease was found not to be identical for different electrolytes. In Tables I–IV, the ratio (*R*) of the specific conductance in the presence of a polyhydroxy compound (*k'*) to that in its absence (*k*) is listed, along with the percentage composition of the solution.

TABLE I

D-GLUCOSE–ELECTROLYTE SYSTEM AT 35°

D-*Glucose* (%)	R (=k'/k)						
	*2-Amino-2-deoxy-*D-*glucose hydrochloride*	NH_4Cl	$BaCl_2$	$SrCl_2$	$MgCl_2$	$CoCl_2$	$NiCl_2$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
6	0.92	0.91	0.89	0.79	0.90	0.94	—
7.8	0.88	0.85	0.83	0.76	0.81	0.91	0.85
12	0.83	0.79	0.73	0.70	0.73	0.84	0.75
13.8	0.81	0.70	0.67	0.62	0.70	0.82	0.69
18	0.73	0.65	0.61	0.58	0.62	0.77	0.63
25.8	0.65	0.63	0.48	0.46	0.52	0.63	0.60

TABLE II

SUCROSE–ELECTROLYTE SYSTEM AT 35°

Sucrose (%)	R (=k'/k)							
	HCl	*2-Amino-2-deoxy-*D-*glucose hydrochloride*	*KCl*	$CaCl_2$	$BaCl_2$	$SrCl_2$	NH_4Cl	$CoCl_2$
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
5	0.96	0.89	0.86	0.86	0.87	0.86	0.92	0.86
10	0.90	0.82	0.82	0.76	0.79	0.78	0.79	0.76
20	0.79	0.67	0.69	0.64	0.64	0.65	0.68	0.64
25	0.73	0.60	0.63	—	0.57	0.61	0.60	—
30	0.68	0.53	0.57	—	0.51	0.52	0.52	0.45
35	0.65	0.49	—	—	0.45	0.47	0.47	0.40

DISCUSSION

The results can be studied either by the obstruction theory of Fricke[7], or by use of the concept of effect of dielectric constant, due to Rayleigh and others[8]. In the work of Stokes *et al.*[6], only a preliminary exploration of the obstruction possibility was made.

TABLE III

D-MANNITOL–ELECTROLYTE SYSTEM AT 35°

D-*Mannitol* (%)	R (= k′/k)					
	HCl	*2-Amino-2-deoxy-D-glucose hydrochloride*	*$CaCl_2$*	*$MgCl_2$*	*$NiCl_2$*	*$CoCl_2$*
0	1.00	1.00	1.00	1.00	1.00	1.00
3	0.975	0.85	0.96	0.98	0.95	0.94
6	0.92	0.82	0.92	0.94	0.91	0.88
9	0.87	0.80	0.88	0.89	0.86	0.85
12	0.83	0.76	0.82	—	0.82	0.78
15	0.76	0.73	0.79	0.84	0.72	0.75
18	0.72	0.69	0.77	0.80	0.70	0.71
20	0.69	0.67	0.74	0.76	0.66	0.70
22	0.675	0.65	—	0.74	—	0.65

TABLE IV

GLYCEROL–ELECTROLYTE SYSTEM AT 35°

Glycerol (%)	R (= k′/k)							
	HCl	*2-Amino-2-deoxy-D-glucose hydrochloride*	*KCl*	*$CaCl_2$*	*$BaCl_2$*	*$SrCl_2$*	*$MgCl_2$*	*NH_4Cl*
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.96	0.97	0.97	0.96	0.97	0.97	0.99	0.97
4	0.92	0.91	0.93	0.93	0.93	0.93	0.94	0.95
6	0.90	0.90	0.90	0.91	0.90	0.90	0.91	0.91
8	0.86	0.86	0.86	0.86	0.87	0.85	0.86	0.87
10	0.82	0.85	0.84	0.84	0.84	0.82	0.84	0.86
12	0.79	—	0.80	0.81	0.81	0.81	0.81	0.82
16	0.74	0.77	0.75	0.74	0.74	0.73	0.78	0.76
20	0.70	0.71	0.70	0.69	0.69	0.69	0.71	0.70
25	0.66	0.69	0.64	0.63	0.56	0.61	0.66	0.64

In judging the present data in the light of Fricke's theory[7], the polyhydroxy compounds would be regarded as obstructing the electrical migration of the ions of the electrolytes between the electrodes of the conductivity cell; this would evidently increase the resistance and thus decrease the conductance. However, the decrease observed has been found to be much more than that demanded by this theory. This unexpectedly large hindrance presumably arises from association of the ions with the polyhydroxy compounds, because Fricke's theory holds for many macromolecular systems and can, therefore, be assumed to hold for the present systems, even though the polyhydroxy compounds employed in our study have small molecules and, consequently, should not afford much obstruction to the small ions. Were this the only effect operative, a decrease in conductance less than that demanded by Fricke's theory would be expected, whereas, it was larger; this supports the concept of association (interaction) of the polyhydroxy compounds with the various electrolytes.

Of the four polyhydroxy compounds studied, the order of interaction seems to be D-glucose > sucrose > glycerol = D-mannitol. As all of the salts used have the chloride ion as a common constituent, any difference in behavior (as between two salts) is the property of the particular cation constituting the complete electrolyte; the results indicate that salts of the alkaline-earth metals are more prone to interaction. Because the hydroxides of those metal ions are more given to association[1–3], dilute aqueous solutions (1mM) of the hydroxides of barium, calcium, and strontium were also subjected to conductometric study (see Table V). The decrease in conductance was found to be even greater, thus providing conductometric evidence of association in solution, especially of the hydroxides of the alkaline-earth metals with D-glucose. Glycerol, on the other hand, does not markedly decrease the conductance of calcium hydroxide solution. Quantitative calculation of the association constant is, at present, infeasible.

TABLE V

CARBOHYDRATE–HYDROXIDE SYSTEMS AT 35°

Carbohydrate (%)	R (= k′/k)			
	$Ca(OH)_2$		*$Ba(OH)_2$–D-glucose*	*$Sr(OH)_2$–D-glucose*
	D-*Glucose*	*Glycerol*		
0	1.00	1.00	1.00	1.00
1	—	—	0.69	—
2	0.70	0.94	0.57	0.64
3	—	—	0.54	—
4	0.65	0.93	0.53	0.62
5	—	—	0.50	—
6	0.60	0.86	0.49	0.57
7	—	—	0.47	—
8	0.58	0.78	0.46	0.56
10	0.54	0.76	—	0.51
12	0.52	0.72	—	0.50
14	—	0.68	—	—
15	0.48	—	—	0.46
16	—	0.66	—	—
20	0.45	0.51	—	0.44
25	0.40	—	—	0.41

REFERENCES

1 J. A. RENDLEMAN, JR., *Advan. Carbohyd. Chem.*, 21 (1966) 264.
2 N. ROY AND A. K. MITRA, *Carbohyd. Res.*, 24 (1972) 175.
3 N. ROY AND A. K. MITRA, *Carbohyd. Res.*, 24 (1972) 180.
4 S. P. MOULIK AND A. K. MITRA, *J. Indian Chem. Soc.*, 48 (1971) 905.
5 C. R. SAHU AND A. K. MITRA, *J. Indian Chem. Soc.*, 48, (1971) 796.
6 B. J. STEEL, J. M. STOKES, AND R. H. STOKES, *J. Phys. Chem.*, 62 (1958) 1514.
7 H. FRICKE, *Phys. Rev.*, 24 (1924) 575.
8 R. A. ROBINSON AND R. H. STOKES, *Electrolyte Solutions*, 2nd edn., Butterworths, London, 1965.