

CONDUCTOMETRIC EVALUATION OF INTERACTIONS OF ELECTROLYTES WITH D-GLUCITOL, D-GLUCOSE, GLYCEROL, D-MANNITOL, AND SUCROSE

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ABSTRACT

By measurement of the conductance of various electrolytes in solutions of D-glucitol, D-glucose, glycerol, D-mannitol, and sucrose, the hydration of the polyhydroxy compounds and their association with electrolytes have been examined. The results have been analyzed in the light of conductance equations; it was found that D-glucose and sucrose associate with electrolytes, glycerol and D-mannitol are practically inert, and D-glucitol is only rarely bound. The association constants are of the order of 10^{-1} to 10^{-2} . The results indicate that anions guide the process, with a free-energy change of $1.5-3.0 \text{ kcal.mole}^{-1}$, the order of the energy of hydrogen bonding. In the analysis of conductance data, neglect of association may introduce hydration numbers many times greater than are usual.

INTRODUCTION

Polyhydroxy compounds are known to interact with electrolytes in solution^{1,2}. Definite adducts of many carbohydrates with salts and hydrated oxides of alkali and alkaline-earth metals have been reported in recent years³⁻⁵. However, the efficiency of such interactions in solution has not been quantitatively evaluated, for lack of a suitable, experimental probe. In two recent papers^{6,7}, equations that can relate the conductance of nonhydrated and hydrated insulator-type bodies (including several proteins and polyhydroxy compounds) have been reported, and the alteration in conductance has been attributed to the obstruction of the electrical migration of ions by the environmental, nonelectrolyte entities. Significant changes in conductance of carbohydrate-electrolyte solutions were also reported in a very recent Note⁸.

In the present paper, the results of further measurements have been analyzed in the light of an extended, conductance theory. The (long-anticipated) carbohydrate-salt complexation in solution has been quantitatively estimated with the help of this theory. When the complexation is zero, the basic theory can evaluate the hydration numbers of the polyhydroxy compounds concerned.

THEORETICAL ASPECTS

Electrical migration of ions through a continuous medium may be altered either by placing therein (a) nonconducting (or weakly conducting) materials of comparatively larger dimensions as obstructants, or (b) nonconducting materials that can associate (or complex) with the ions. The obstructing effect has been identified with the increase in resistance of the solution caused by detours of the ions in the cell, thus making necessary a correction for the cell constant. By incorporating such a correction, it has been shown⁷ that:

$$k = k'(1 + m\phi + m'\phi^2 + m''\phi^3 + \dots), \quad (1)$$

where k and k' are the conductances of the medium and the solution respectively, ϕ is the volume fraction of the added obstructant, and m , m' , and m'' are appropriate constants. In earlier reports, low values of ϕ were used, and terms having powers higher than unity were neglected. In this report, terms having a power higher than 2 are neglected, and so:

$$k = k'(1 + m\phi + m'\phi^2). \quad (2)$$

Equation 2 was chosen for use in the region where the equations of Fricke⁹ and others^{10,11} are seldom trusted.

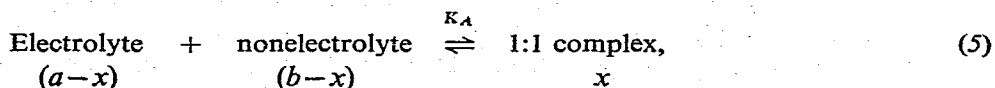
Equation 2 may be rearranged in the following forms:

$$(k - k')/k'\phi = m + m'\phi, \quad (3)$$

and

$$(k - k')/k' C = mV + m' V^2 C, \quad (4)$$

where V is the specific volume (in ml.g^{-1}) of the obstructant introduced and C is its concentration. Equation 4 may be modified on the basis of association between the ion and the nonelectrolyte. (Whether or not a definite compound actually exists in solution, inter-particle attraction at close proximity may be identified in essentially the same way as ions missing from the migration stream because of compound formation.)



where a , b , and x are the concentrations of electrolyte, nonelectrolyte, and the presumed complex, respectively. A 1:1 complex is anticipated on the basis of our recent findings^{4,5}. For dilute solutions of electrolytes, conductance may be taken to be linearly proportional to concentration:

$$k' = \bar{C}a, \quad (6)$$

and

$$k'' = \bar{C}(a-x), \quad (7)$$

where \bar{C} is the proportionality constant, and k' and k'' are the conductances for the two situations. From equations 6 and 7,

$$x = (k' - k'')/\bar{C}. \quad (8)$$

Now, according to equation 5, the formation constant (K_A) is:

$$K_A = [x]/[a-x][b-x]. \quad (9)$$

Hence, from equations 6-9,

$$K_A = (k' - k'')/k''[b-x]. \quad (10)$$

For conditions in which $b \gg x$,

$$K_A = (k' - k'')/k''b, \quad (11)$$

or,

$$k' = k''(1 + K_A b). \quad (12)$$

Combination of 2 and 12 gives

$$k = k''(1 + K_A b)(1 + m\phi + m'\phi^2). \quad (13)$$

On expressing concentrations in g.ml^{-1} , equation 13 becomes:

$$k = k''[1 + (1000 K_A C)/M](1 + mVC + m'V^2 C^2), \quad (14)$$

where M is the molecular weight of the nonelectrolyte. On simplifying and rearranging, and neglecting terms having a power higher than 2,

$$k = k''[1 + [mV + 1000 K_A/M]C + [m'V^2 + 1000 K_A mV/M]C^2]. \quad (15)$$

The subsequent linear form is,

$$(k - k'')/k''C = [mV + 1000 K_A/M] + [m'V^2 + 1000 K_A mV/M]C. \quad (16)$$

This linear equation can be used directly. In the absence of any association between the ions and the nonelectrolyte, it is reduced to equation 4.

EXPERIMENTAL

The materials used were either of pro Analyti (E. Merck) or AnalaR (BDH) grades. Resistance measurements were made with a Philips Conductivity Bridge PR 9500, operated in the most sensitive range, the solutions being placed in a water bath thermostatically controlled at $30 \pm 0.2^\circ$. The reliability of readings obtained with the bridge was checked with standard resistances. A maximum error of 2% was observed in the range of 1-100 k Ω .

Before the experiments were performed, equivalent conductances at infinite dilution of NaCl and KCl were determined with the apparatus, and compared with the literature data (NaCl: lit. value, 142.0; found, 141.7; KCl: lit. value, 165.5;

found, 164.8). In all the experiments, 2mM solutions of the electrolyte were used. This low concentration, in effect, lessened the contribution of interionic attractions to the conductance.

A sample of a polyhydroxy compound was placed in a volumetric flask and accurately weighed, and the volume was made to the mark with double-distilled, conductivity water (specific conductance, $k = 1.0 \mu\text{mho.cm}^{-1}$) and the electrolyte solution. The final concentration of the electrolyte solution was 2mM. This solution (20 ml) was introduced into a wide test-tube, into which a dip-type conductivity cell (cell constant 1.30) was placed. The test tube was well immersed in the constant-temperature bath, and sufficient time was allowed for the contents to attain the temperature of the bath. The initial resistance was measured; then, the solution was successively diluted with 2mM electrolyte solution taken from a container kept in the bath, and the resistance was measured after each dilution. The conductance of the 2mM electrolyte solution at several concentrations of the polyhydroxy compound was thus obtained. In final processing, the data were expressed as conductance ratios, thereby presumably minimizing the inherent errors of measurement.

RESULTS

Fig. 1 depicts the dependence of conductance on the concentration of the polyhydroxy compounds; representative examples for only a few electrolytes are given. For the D-glucose-electrolyte system, the concentration of electrolytes used was 10mM. An apparent order of differences among electrolytes used in the presence of a single nonelectrolyte, and of differences among nonelectrolytes for a single electrolyte, were apparent from these results.

The first-degree, conductance equation reported in our previous paper⁷ was found to hold for concentrations of $\sim 0.1 \text{ g.ml}^{-1}$. The earlier analysis afforded 1.93 as the value for the first-degree constant m . The results for protein solutions were all well within 0.1 g.ml^{-1} , and use of a second-degree equation was unnecessary. The experimental results reported here are mostly above 0.1 g.ml^{-1} , and this invites use of equations 3 and 4. To check the working domain of these equations, data on glass¹⁶, sand particles⁹, and dog blood-cells⁹ were plotted according to equation 4 (see Fig. 2), from which it may be seen that the intercepts consistently converge on the value of 1.80 (the earlier average value was 1.93). The linearity of the lines for all of the systems was maintained up to $\sim 0.35 \text{ g.ml}^{-1}$. The value of m was therefore modified to 1.80, and equations 3, 4, and 16 are believed to be true up to at least the concentration limit of 0.30 g.ml^{-1} .

Having thus established the value of m and the concentration limit for equations 4 and 16, the results for the various systems in the presence of different electrolytes were plotted (see Figs. 3-6). For all of the systems, linearity is maintained up to at least 0.30 g.ml^{-1} , as anticipated. The extensive collection of data thus establishes with certainty the applicability of equations 4 and 16. To calculate K_A , use was made of the hydration numbers of the polyhydroxy compounds; these

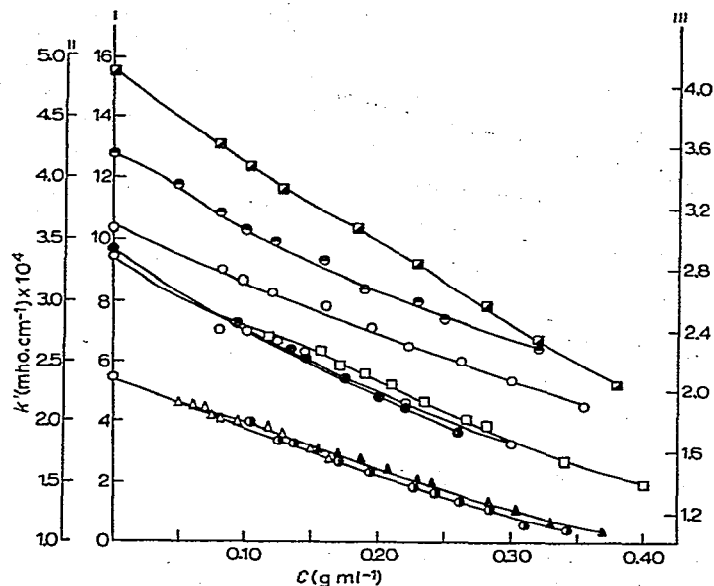


Fig. 1. Specific conductance of electrolytes in the presence of polyhydroxy compounds. [Key: \square , 10mM HCl in D-glucose solution (Scale III-I); \bullet , 10mM NaCl in D-glucose solution (Scale I-I); \circ , 10mM CaCl₂ in D-glucose solution (Scale I-I); \square , \circ , and \bullet , 2mM KCl in solutions of glycerol, sucrose, and D-glucose, respectively (Scale II-I); Δ , \triangle , and \bullet , 2mM CaCl₂ in solutions of glycerol, D-mannitol, and sucrose, respectively (Scale II-I).]

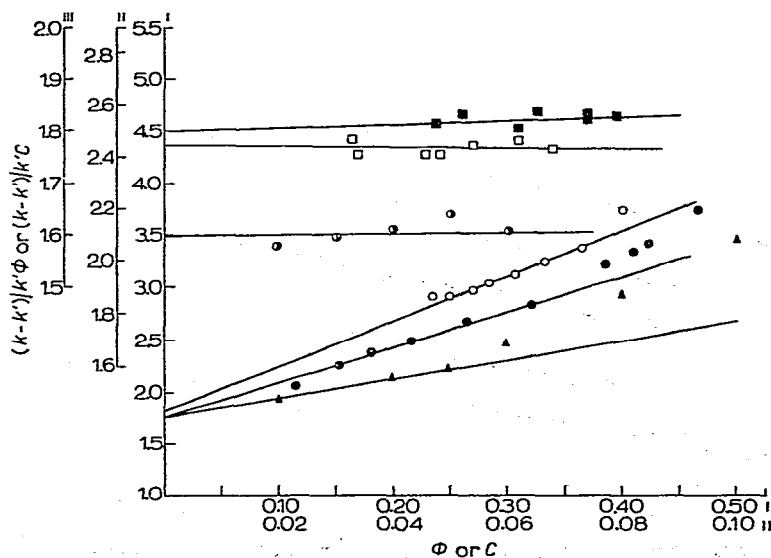


Fig. 2. Plots of $(\kappa - \kappa')/\kappa'\phi$ or $(\kappa - \kappa')/\kappa'C$ versus ϕ or C for various systems. [Key: Δ , Sand particles⁹ II (Scale I-I); \bullet , dog blood-cells⁹ (Scale I-I); \circ , sand particles⁹ I (Scale I-I); \circ , myoglobin¹⁶ (Scale II-II); and \square , \blacksquare , glass particles¹⁶ (Scale III-II).]

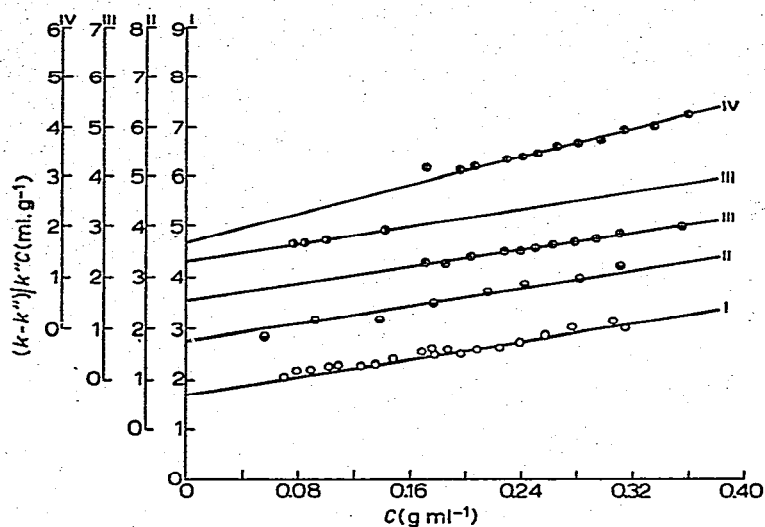


Fig. 3. Plots of $(k-k'')/k''C$ versus C for various systems. [Key: \odot , \ominus , \oplus , 2mM CuCl_2 in solutions of sucrose, D-glucose, and glycerol, respectively; \bullet , 2mM KBr in D-mannitol solution; and \otimes , 2mM SrCl_2 in D-glucitol solution.]

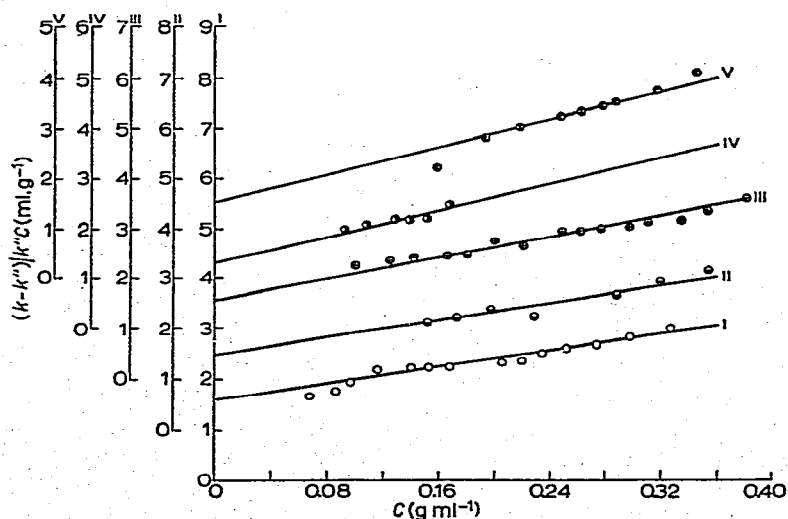


Fig. 4. Plots of $(k-k'')/k''C$ versus C for various systems. [Key: \odot , \ominus , \oplus , \bullet , \otimes , 2mM BaCl_2 in solutions of sucrose, D-glucose, glycerol, D-mannitol, and D-glucitol, respectively.]

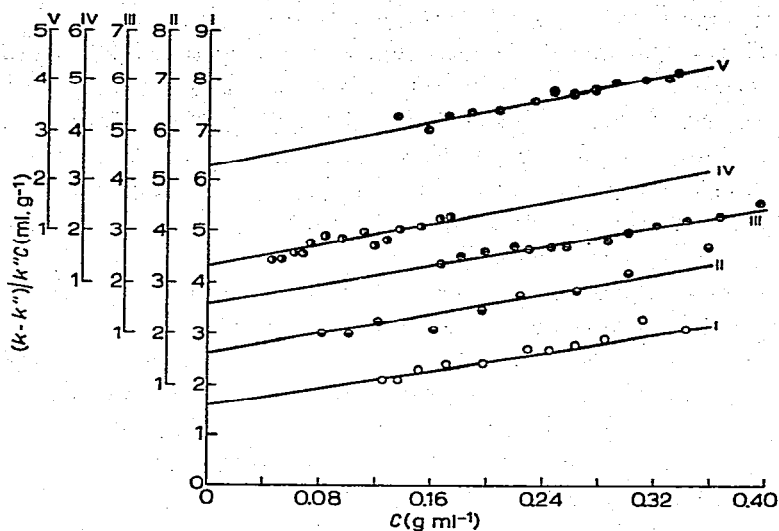


Fig. 5. Plots of $(k - k'')/k''C$ versus C for various systems. [Key: \odot , \ominus , \oplus , \otimes , \circ , 2mM CaCl_2 in solutions of sucrose, D-glucose, glycerol, D-mannitol, and D-glucitol, respectively.]

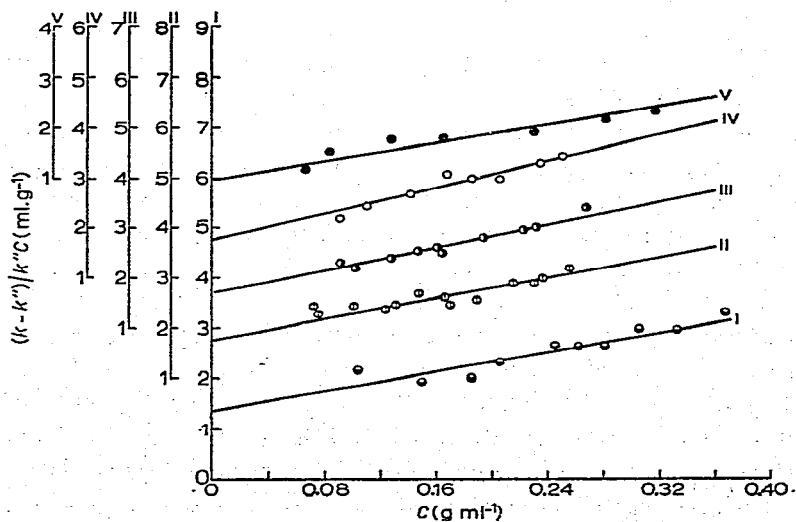


Fig. 6. Plots of $(k - k'')/k''C$ versus C for various systems. [Key: \ominus , \odot , 2mM KI in sucrose and D-glucose solutions; \oplus , 2mM K_2SO_4 in D-glucose solution; \circ , 2mM potassium hydrogen phthalate in D-glucose solution; and \bullet , 2mM HCl in D-glucose solution.]

numbers are known¹² to be 2, 4, 2, 2, and 5 for D-glucitol, D-glucose, glycerol, D-mannitol, and sucrose. The specific, hydrated volumes were then calculated from the densities of the anhydrous materials and the volume contributions of appropriate water molecules attached. The V values (hydrated) thus became 0.869, 0.750, 0.851, 0.726, and 0.710 for D-glucitol, D-glucose, glycerol, D-mannitol, and sucrose, respectively. Now, from a knowledge of m and V , the value of K_A could be obtained from the intercept, $[mV + 1000K_A/M]$. From this value of K_A , the second virial constant (m') was calculated. These results are given in Table I.

From Table I, it is apparent that K_A is small, and of the order of 10^{-1} to 10^{-2} . The significance of such a small value for the association constant is revealed if the specific volumes (and, hence, the hydration numbers) are to be calculated by omitting the K_A term from the intercept. On dividing the intercept of equation 4 by m (i.e., 1.80), these hydration numbers are obtained (see Table II). For D-glucose and sucrose, the enormous effect of a small value of K_A on the hydration number is observed. For D-glucitol, glycerol, and D-mannitol (except with CaCl_2 and SrCl_2), the hydration numbers are low and of the order expected¹².

DISCUSSION

The K_A values reveal that both D-glucose and sucrose complex with electrolytes. D-Glucitol, glycerol, and D-mannitol are all inert towards complexation (except for SrCl_2 and CaCl_2). It was observed that the divalent cations Ca^{2+} , Ba^{2+} , Sr^{2+} , and Cu^{2+} behave differently from the monovalent cations. Again, for the same cation, such anions as Br^- , Cl^- , I^- , NO_3^- , SO_4^{2-} , and phthalate²⁻ yield different K_A values. It should be mentioned that the K_A values recorded in Table I are not truly thermodynamic quantities, as activity terms were not used in the calculation. Because the solutions of electrolytes used in this work were all very dilute (2mM) and the activities of the nonelectrolytes do not greatly deviate from unity¹³, the results tabulated are not far from thermodynamic values. For the D-glucose system, use of HCl did not reveal any association; actually, the intercept is less than the value predicted if there is no association. This seems to be due to the special type of conduction of hydrogen ions in water by the proton-jump mechanism¹³. In this context, mention may be made of the work of Stokes *et al.*¹⁴, who observed ionic mobility to decrease in the presence of several polyhydroxy compounds, as in our recent investigation⁸.

As regards the center of attack of electrolytes, it is probable that, as in carbohydrate-amine interaction¹⁵, the anions may be weakly linked with the acidic hydrogen atom at O-1 of D-glucose. This would lead to a hydrogen-bonded type of entity that could lessen the mobility of the attached ion. The order of the change in free energy also accords with a hydrogen-bonded type of association. It is probable that bivalent, cationic salts hold the acidic hydrogen atom more strongly than monovalent salts. More inert molecules, such as glycerol and D-mannitol (and, perhaps, D-glucitol) are thus not prone to association; they can only obstruct the ions, and the hydration numbers can be obtained from the intercepts⁷ by following

TABLE I

THE ASSOCIATION CONSTANT, K_A , AND THE SECOND VIRIAL COEFFICIENT, m'

Electrolyte	D-Glucose		Sucrose		Glycerol		D-Mannitol		D-Glucitol	
	K_A	m'	K_A	m'	K_A	m'	K_A	m'	K_A	m'
HCl	0	8.08	—	—	—	—	—	—	—	—
KCl	0.076	9.11	0.064	6.74	0	5.35	0	7.82	0	4.23
NaCl	0.082	8.38	—	—	0	5.17	—	—	0	5.00
KBr	0.012	8.56	0.074	6.24	0	5.74	0	8.22	—	—
KI	0.113	8.56	0.052	9.44	—	—	—	—	—	—
K H phthalate	0.078	11.18	—	—	—	—	—	—	—	—
K ₂ SO ₄	0.063	9.86	—	—	—	—	—	—	—	—
Na ₂ SO ₄	0.113	11.07	—	—	0	5.17	—	—	—	—
BaCl ₂	0.038	8.82	0.110	8.65	—	7.48	0	12.65	0	9.64
CaCl ₂	0.075	7.97	0.110	8.65	—	5.93	0	9.46	0.163	6.67
SrCl ₂	—	—	—	—	—	—	—	—	0.026	9.16
CuCl ₂	0.101	6.95	0.144	8.53	0	5.9	—	—	—	—

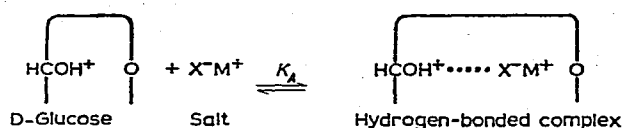
TABLE II
THE SPECIFIC VOLUME^a, V , AND THE HYDRATION NUMBERS^b, h

Electrolyte	D-Glucose		Sucrose		Glycerol		D-Mannitol		D-Glucitol	
	V	h	V	h	V	h	V	h	V	h
HCl	0.555	—	—	—	—	—	—	—	—	—
KCl	0.9166	31.97	0.8143	18.20	0.850	2.00	0.750	3.18	0.879	2.00
NaCl	0.9305	40.46	—	—	0.8333	1.953	0.7221	1.84	0.8143	—
KBr	0.778	6.03	0.8056	17.07	0.833	2.00	0.7221	1.85	—	—
KI	1.00 ^c	—	0.7776	12.50	—	—	—	—	—	—
K H phthalate	0.989	250	—	—	—	—	—	—	—	—
K ₂ SO ₄	0.9443	52.50	—	—	—	—	—	—	—	—
Na ₂ SO ₄	0.9443	52.84	—	—	0.833	1.953	—	—	—	—
BaCl ₂	0.8343	11.02	0.8888	43.81	0.8610	2.5	0.7221	1.85	0.8694	2.00
CaCl ₂	0.9166	31.96	0.8888	43.81	0.8610	2.5	0.7221	1.85	1.267 ^c	—
SrCl ₂	—	—	—	—	—	—	—	—	0.9445	19.4
CuCl ₂	0.9721	92.0	0.9445	106.7	0.8500	2.00	—	—	—	—

^aSpecific volumes of anhydrous D-glucitol, D-glucose, glycerol, D-mannitol, and sucrose are 0.869, 0.750, 0.851, 0.726, and 0.710, respectively. ^bTheir reported hydration numbers are 2, 4, 2, and 5, respectively.¹³ ^cThe values of V lead to absurd values of h , as a consequence of neglecting complexation.

equation 4. However, the activity of sucrose cannot be explained on the basis of the behavior of D-glucose; a different center of attack is necessary.

The hydrogen-bonded, acid-base type of binding¹⁵ has been also revealed by the surprising change in conductance of bases in the presence of carbohydrates⁸. From the scanty data available to us, a much greater extent of association is anticipated. Here, also, sucrose binds, but less strongly than D-glucose, as will be reported in a forthcoming paper. The following is a probable reaction scheme.



where M^+ is a metal ion, and X^- is its counter-ion.

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