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Transportation of Monosaccharides by Electrodialysis with Ion-Exchange Membranes. I

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The effects of voltage, electrolytes, monosaccharides, and pH on the transportation of monosaccharides by electrodialysis were investigated. Transportation was strongly affected by the formation of monosaccharide-borate esters. It was possible to separate saccharides using an electrodialysis technique.

Formaldehyde is one the C_1-type compounds which are both inexpensive and obtainable in large quantities. On the basis of elemental composition, it was assumed that carbohydrates, such as D-glucose and D-fructose, could be regarded as the condensates of formaldehyde, CH_2O. From this point of view, many investigations concerning the self-condensation of formaldehyde catalyzed by a base have been undertaken since Butlerow(1) first studied the condensation reaction in 1861. This type of reaction is called a "formose reaction"; "formose" is the generic name for a product which is a mixture of carbohydrates and their analogues. There are two big problems concerning the effective utilization of formose. One is its complex nature, since it comprises a large number of products (often over 30); another is the difficulty to separate the products. Though some reaction conditions yield a selective formation of products,(2—6) highly efficient separation methods of formose are still awaited. Until now, column and thin-layer chromatography, gas chromatography, and high-performance liquid chromatography have been tried for the separation of formose. Although these methods were suitable for the analysis of formose, they couldn't be applied to the preparative separation of a large quantity of the mixture.

Interest in establishing a new procedure for separating mixtures of sugars and their analogues motivated the present authors to carry out the research described in this paper.

Electrodialysis with ion-exchange membranes has been applied to the desalting of sugar solutions,(7) the preferential separation of fructose from a mixture of glucose and fructose,(8) and so on. In our previous research,(9) Ca^{2+} was removed from a sugar solution by electrodialysis using ion-exchange membranes under various conditions. In the present study, the same technique was applied to the transportation of typical monosaccharides such as D-glucose, D-fructose, and so on through an anion-exchange membrane in the presence of borates which form borate complexes(10) with sugars.

Experimental

Materials. The ion-exchange membranes (Selemion CMV, 2.0 mequiv g^{-1} and an experimental material, Selemion AMV-N, 2.1 mequiv g^{-1}) were supplied by Asahi Glass Co., Ltd. In order to regenerate these ion-exchange membranes, used membranes were soaked in 3.0 M** aq NaCl for more than one day, and then washed with distilled H_2O.

Extra-pure reagents (unless otherwise noted) were purchased from Nakarai Tesque, Inc. or Wako Pure Chemical Industries, Ltd., and were used without further purification.

Apparatus and Procedures. The apparatus for electrodialysis comprised three compartments. An anodic cell (Part A) and a cathodic cell (Part C) were separated from the sample cell (Part O) by an anion-exchange membrane (Selemion AMV-N) and a cation-exchange membrane (Selemion CMV), respectively. The effective area of the ion-exchange membrane was 12.5 cm^2. Both the anode and cathode were platinum plate electrodes with apparent surface areas of 3 cm^2. The distance between the two membranes was 5.5 cm and the distance between the membrane and the electrode was 3 cm. In the experiment 100 mls of a sugar solution, aqueous KOH, and aqueous HCl were added to Part O, A, and C, respectively; these solutions were not stirred during electrodialysis. The potential between the electrodes was regulated by a Metronix Model 411-125 constant power supply. The rise in the temperatures of the solutions with the passage of a current was negligible.

Typical electrodialysis was carried out under the following conditions: 8.0 V, free current, room temperature, [KOH] of Part A=0.10 M, [HCl] of part C=0.10 M; the sugar solution of Part O containing 0.02 M of D-fructose and 0.04 M of boric acid was adjusted to the prescribed pH with aqueous KOH. Before electrodialysis, 5 ml solutions were sampled from Part O, Part A, and Part C, respectively. The amounts of the sugars were determined by a phenol-sulfuric acid method;(11) except that the optical density was measured at 485 nm, or by gas chromatography of the pertrimethylsilylated sugars using *O*-tetrakis(trimethylsilyl)pentaerythritol as an internal standard. The sugars were trimethylsilylated in the usual manner(12) and extracted with chloroform. A Shimadzu GC-4CMPF chromatograph equipped with a hydrogen-frame ionization detector was used under the following conditions: coiled glass column of 3 m by 3 mm i.d., 5% silicon gum SE-30 on 60—80 mesh chromosorb-W; nitrogen flow rate,

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** 1 M=1 mol dm^{-3}.

60 ml min^{-1}; temperature, 100—250 °C, rising at the rate of 4 °C min^{-1}.

Results and Discussion

Effect of the Applied Voltage on the Movement of Monosaccharides. We first examined the effects of the applied voltage, which was the driving force in the movement of monosaccharides from Part O to Part A.

As shown in Fig. 1, the amount of D-fructose that moved from Part O to Part A increased with an increase in the applied voltage, becoming constant (ca. 80%) above 16.0 V. The amounts of D-fructose that moved at zero applied voltage and at 8.0 V were about 3 and 55%, respectively. On the other hand, the effects of the applied voltage on the movement of D-glucose were similar to those in the case of D-fructose, though the amount of D-glucose that moved from Part O to Part A was less than that of D-fructose. The amounts of D-glucose that moved at zero applied voltage, 8.0 V, and 16.0 V were ca. 1, 45, and 55%, respectively. At 16.0 V, the amount of D-glucose that moved in the presence of 0.015 M of $K_2B_4O_7$ was ca. 70%. The effects of $K_2B_4O_7$ on the movement of monosaccharides will be reported following this report. It seemed that D-fructose-borate esters could be formed more easily than D-glucose-borate esters,[13] and that D-glucose might require more boric acid to form D-glucose-borate esters than D-fructose.

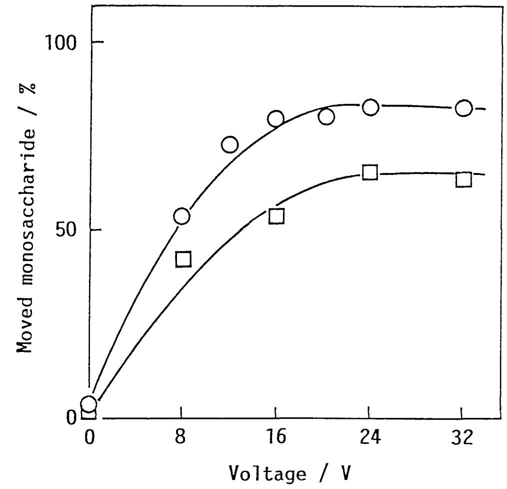

Fig. 1. Relationship between the applied voltage and the amount of moved monosaccharides by electrodialysis. Part A: [KOH]=0.1 M; Part C: [HCl]=0.1 M; Part O: [monosaccharide]=0.02 M, [$K_2B_4O_7 \cdot 4H_2O$]=0.01 M; r.t.; time, 180 min. ○, D-Fructose; □, D-glucose.

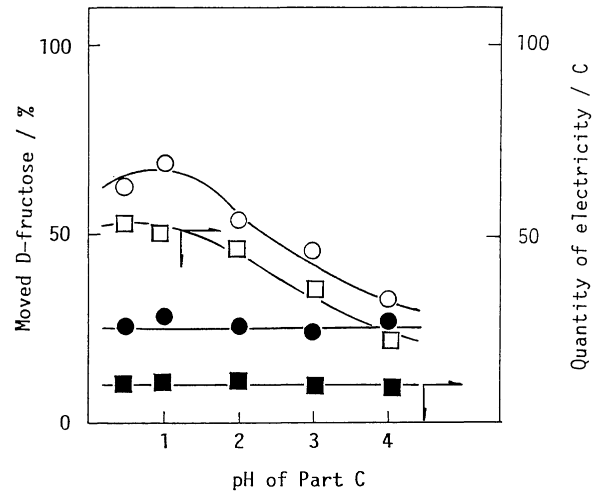

Fig. 2. Effect of the pH of Part C on the amount of moved D-fructose and quantity of electricity. Part A: [KOH]=0.1 M; Part C: the pH of Part C was adjusted by 1.0 M HCl: Part O: [D-fructose]=0.02 M, [H_3BO_3]=0.04 M; r.t.; time, 180 min; applied voltage, 8 V. ○, □: The pH of Part O was adjusted to 7.0 with 1.0 M KOH. ●, ■: The pH of Part O was not adjusted.

In this study, electrodialysis was carried out at an applied voltage of 8.0 V, causing ca. 50% of the movement of D-fructose from Part O to Part A.

Effect of pH and Electrolyte of Part C. Figure 2 shows the relationship between the pH of Part C and the amount of D-fructose moved. The pH of Part C was adjusted by adding 1.0 M HCl.

The pH of Part O, to which 0.02 M of D-fructose and 0.04 M of boric acid were added, was ca. 4.5; it changed to 5.6—6.0 at the completion of electrodialysis. In these cases, without any adjustment of the pH of Part O (Fig. 2), the movement of D-fructose from Part O to Part A was not affected by the pH of Part C, due to the low pH (4.5—6.0) of Part O, since the movement of D-fructose is governed by the concentration of D-fructose-borate esters, which are not formed at acidic pH values.[14]

When the pH of Part O was adjusted to 7.0 by adding 1.0 M KOH, the amount of D-fructose that moved from Part O to Part A increased with a decrease in the pH of Part C. Furthermore, the electric current increased with an increase in the amount of D-fructose moved. These results indicate that the concentration of the electrolyte of Part C is one of the dominant factors in the electrolysis of monosaccharides. This assumption was supported by the following experiment.

The concentration of Cl$^-$ in Part C was adjusted to 0.1 M with HCl and KCl in order to maintain the concentration of the electrolyte under various pHs of Part C; the other electrodialysis conditions were the same as those shown in Fig. 2. In this case, the amount of D-fructose that moved from Part O to Part A was roughly constant (50—60%), regardless of the pH of Part C.

Effect of the pH and Electrolyte of Part A on the Movement of D-Fructose. Figure 3 shows the effect of the pH of Part A on the movement of D-fructose by electrodialysis. Below pH 11.0 in Part A, the amount

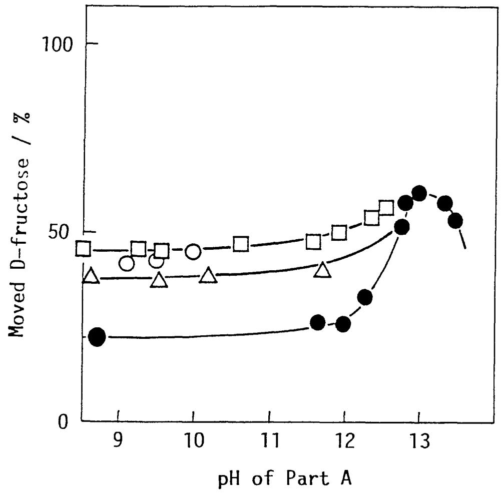

Fig. 3. Relationship between the pH of Part A and the amount of moved D-fructose. Part A: the pH of Part A was adjusted with KOH and KHCO$_3$: △, [K$^+$]=0.05 M; □, [K$^+$]=0.1 M; ○, [K$^+$]=0.15 M; ●, the pH of Part A was adjusted with KOH only; Part C: [HCl]=0.1 M; Part O: [D-fructose]=0.02 M, [H$_3$BO$_3$]=0.04 M, the pH of Part O was adjusted to 8.5 with 1.0 M KOH; r.t.; time, 180 min; applied voltage, 8 V.

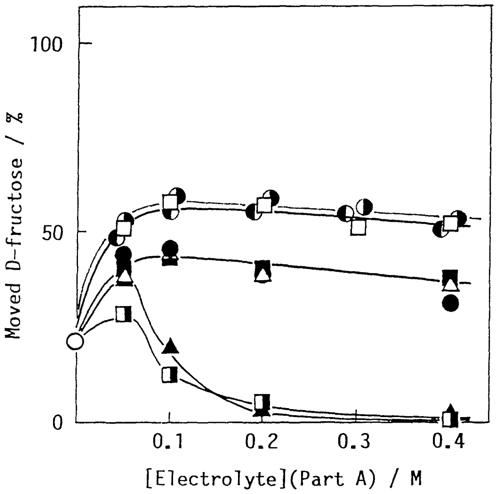

Fig. 4. Relationship between the concentration of electrolytes of Part A and the amount of moved D-fructose. Part A: □, KOH; ◐, NaOH; ◑, LiOH; ●, KCl; △, KHCO$_3$; ■, HCOOK; ▲, HCl; ◧, HCOOH; Part C: [HCl]=0.1 M; Part O: [D-fructose]=0.02 M, [H$_3$BO$_3$]=0.04 M, the pH of Part O was adjusted to 8.5 with 1.0 M KOH; r.t.; time, 180 min; applied voltage, 8 V.

of D-fructose that moved from Part O to Part A was constant. It increased with an increase in the pH of Part A in the pH range 11.5—13.0. Above pH 13.0 in Part A, the amount of D-fructose that moved from Part O to Part A decreased with an increase in pH. Below pH 11.0 in Part A, the amount of D-fructose moved from Part O to Part A increased with an increase in the concentration of the electrolytes in Part A, and reached a maximum when the concentration was 0.1 M. These phenomena suggest that the concentration of D-fructose-borate esters should increase with an increase in pH, as described by S. A. Barker et al.[14] However, the amount of electrolytes, such as KOH and KCl, moved from Part A to Part O, which compete with D-fructose regarding movement from Part O to Part A, increased with an increase in the concentration of the electrolytes of Part A. This is because the electrolytes pass through the anion-exchange membrane, due to the high electrolyte concentration of Part A.

Figure 4 shows the effect of various electrolytes and their concentrations in Part A on the movement of D-fructose. The best anolytes in Part A regarding the movement of D-fructose among the investigated electrolytes were KOH, NaOH, and LiOH. The amount of D-fructose moved was maximum in an electrolyte concentration range 0.05—0.1 M, and gradually decreased with an increase in the concentration of the electrolyte in Part A. In the case of an acid, such as HCl or HCOOH, the amount of D-fructose moved was below 5% for more than 0.2 M of the electrolyte concentration in Part A. Regardless of the kind of electrolyte, the quantity of electricity increased with an increase in the concentration of electrolyte in Part A.

As described above, the diffusion of the electrolyte from Part A to Part O at above 0.1 M of the electrolyte concentration caused a descrease in the D-fructose movement from Part O to Part A. On the other hand, above 0.2 M of the acid used as the electrolyte in Part A, the depressed D-fructose movement resulted from a dissociation of D-fructose-borate esters, owing to the low pH in ion-exchange membrane.

Effect of pH of Part O. Figure 5 shows the relationship between the pH of Part O and the amount of monosaccharides moved. In this case, the pH of Part O was adjusted to the prescribed value with 1.0 M KOH or 1.0 M HCl; the concentration of electrolyte was not kept constant. The pHs giving the maximum movement of D-fructose, D-glucose, and D-xylose from Part O to Part A were 7.0, 8.0, and 9.5, respectively. Furthermore, the quantity of electricity increased with an increase in the concentration of KOH or HCl added to Part O. The difference of pH giving maximum movement among the monosaccharides resulted from the character of the complex of monosaccharide with boric acid. S. A. Barker et al.[14] reported that, with phenylboronic acid, D-glucose was uncomplexed up to pH 6, and fully complexed beyond pH 9, whereas D-fructose began to form complexes near pH 5 and was 30% complexed before D-glucose began to react. Furthermore, it would be expected that monosaccharides could be separated by this technique.

In this case, it is also suggested that monosaccharide moved more from Part O to Part A with an increase in the concentration of monosaccharide-borate esters by increasing the pH; on the other hand, the movement of monosaccharide was depressed by a high concentration of electrolyte in Part O.

Electrodialyses under various pHs of Part O were carried out at the same concentration of total electrolytes in Part O. The concentration was adjusted to 0.025 M with HCl, KCl, and KOH. These results are shown in Fig. 6.

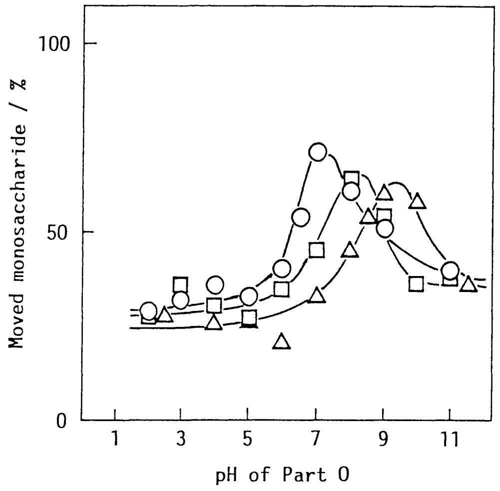

Fig. 5. Relationship between the pH of Part O and the amount of moved monosaccharides. Part A: [KOH]=0.1 M; Part C: [HCl]=0.1 M; Part O: [monosaccharide]=0.02 M, the pH of Part O was adjusted by 1.0 M KOH and 1.0 M HCl, $[H_3BO_3]$= 0.04 M; r.t.; time, 180 min; applied voltage, 8 V. ○, D-Fructose; □, D-glucose; △, D-xylose.

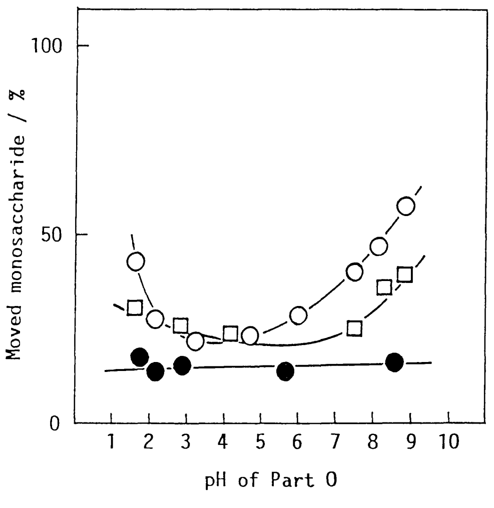

Fig. 6. Relationship between the pH of Part O and the amount of moved monosaccharides under the electrodialysis at the constant electrolyte concentration of Part O ([KOH]+[KCl]+[HCl]=0.025 M). Part A: [KOH]=0.1 M; Part C: [HCl]=0.1 M; Part O: [monosaccharide]=0.02 M, the pH of Part O was adjusted by 1.0 M KOH and 1.0 M HCl, $[H_3BO_3]$= 0.04 M; r.t.; time, 180 min; applied voltage, 8 V. ○, D-Fructose; □, D-glucose; ●, D-fructose: H_3BO_3 was not added.

In the absence of boric acid, the amount of moved D-fructose was about 15%, regardless pH of Part O. In the presence of boric acid, there was no pH value giving a maximum movement of D-fructose from Part O to Part A, as described above; below pH 3 of Part O, however, the amount of D-fructose that moved from Part O to Part A increased with decreasing pH in Part O. Although the amount of D-glucose moved was less than that of D-fructose, similar results were obtained in the electrodialysis of D-glucose (Fig. 6). In this case, the pH range giving a minimum movement of D-glucose was 4 to 6.

These results suggest that the formation of sugar-borate complexes,[7,8] not only in an alkaline solution but also in an acidic solution, might play an important role in moving monosaccharides from Part O to Part A during electrodialysis. However it has not been clarified in detail how or what interactions are formed between monosaccharide and boric acid at such pH in H_2O.

Furthermore, the amount of D-fructose moved from Part O to Part A increased when the electrolyte in Part O varied in the order KOH>HCl, H_2SO_4>CF_3SO_3H>KCl. Except for CF_3SO_3H, above 0.01 M of electrolytes in Part O the amount of D-fructose moved was constant. In the case of KCl, the amount of D-fructose moved was constant (about 20%), the same as that in the absence of an electrolyte in Part O.

Effect of Concentration of Monosaccharides. As shown in Fig. 7, the percentage of D-fructose moved was larger than that of D-xylose moved. Despite the concentration of the monosaccharides added to Part O, the percentage of monosaccharides that moved from

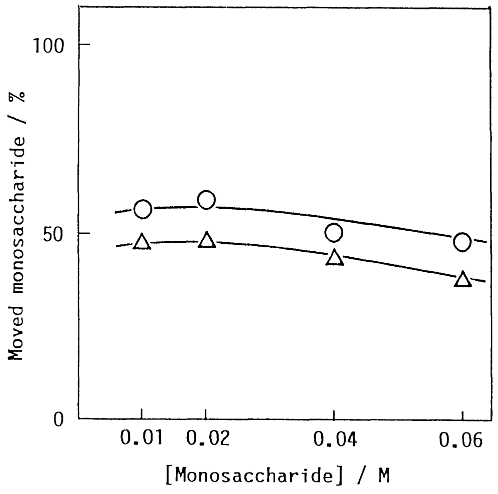

Fig. 7. Relationship between the concentration of monosaccharides and the amount of moved monosaccharides. Part A: [KOH]=0.1 M; Part C: [HCl]= 0.1 M; Part O: $[H_3BO_3]$/[monosaccharide]=2.0; time, 180 min; applied voltage, 8 V. ○, D-Fructose; △, D-xylose.

Part O to Part A was constant. The monosaccharide concentration of Part O was not an important factor in influencing the movement of monosaccharides from Part O to Part A by 180 min electrodialysis with ion-exchange membranes. Furthermore, the percentages of D-fructose and D-xylose that moved during 360 min were ca. 65—70 and 55—60%, respectively. These differences in the amount of monosaccharides moved can be attributable to differences in the formation of the monosaccharide-borate esters.

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