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Concentration dependence of the distribution coefficient of maltooligosaccharides on a cation-exchange resin

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Abstract

The distribution coefficients of glucose, maltose and maltotriose on a cation-exchange resin in the sodium form at 60°C depended on the solute concentration, being larger at higher concentration. The dependence of the coefficient on concentration decreased in the order maltotriose > maltose > glucose. The dependence was explainable by considering the swelling pressure of the resin, which decreased at higher solute concentrations.

1. Introduction

Cation-exchange resins are widely used to separate mono- and oligosaccharides [1–4]. The adsorption of a solute on a resin is characterized by a distribution coefficient, which is defined as the ratio of the solute concentration in the resin phase to that in the external phase. The distribution coefficient is usually obtained at a low solute concentration, and has been considered as an intrinsic value for a combination of the solute and the resin at a constant temperature, and to be independent of the solute concentration. However, dense solutes are often used as samples in practical separation processes on an industrial scale. Ito et al. [5] reported that the distribution coefficient of nistose (fructotriosylglucoside) on a cation-exchange resin in the Na^+ form depended on its concentration, and increased with increase in concentration. However, they did not explain why the coefficient depended on the solute concentration.

In this work, the distribution coefficients of glucose, maltose and maltotriose on a cation-exchange resin in the Na^+ form and containing 4% of divinylbenzene content were obtained at various concentrations. It was found that the swelling pressure of the resin plays an important role in the dependence of the distribution coefficient on the solute concentration.

2. Experimental

2.1. Materials

We used a cation-exchange resin (Dowex) with sulphonate groups and a divinylbenzene content of 4%. The resin was converted into the alkali metal form (Li^+, Na^+ or K^+) or the hydrogen form according to standard procedures [6].

Glucose, maltose, maltotriose and maltotetra-

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ose were products of Hayashibara (Okayama, Japan). The bed voidage of the column packed with the resin was determined using pullulan (Hayashibara) or soluble starch (Nacalai Tesque, Kyoto, Japan). Other chemicals were of analytical-reagent grade.

2.2. Distribution coefficient

The cation-exchange resin was converted into the Na^+ form. The distribution coefficients of glucose, maltose and maltotriose on the resin were determined at 60°C, to prevent microbial growth and owing to the low viscosity at that temperature. Practical separations on an industrial scale have also been carried out at such a temperature. The resin was separated on a sintered-glass filter. The wet resin (about 5.3 g) was placed in a vial, glucose, maltose or maltotriose solutions of a known concentration C_0 were added and kept at 60°C for 30 min, then the external solution was decanted. This was repeated at least three times to attain equilibrium. Finally, the resin was separated on the sintered-glass filter and excess solution on the resin surface was removed with filter-paper. The solute concentration in the filtrate was determined by high-performance liquid chromatography to confirm that the equilibrium concentration was C_0. The wet resin was used to measure the amount adsorbed and to evaluate the apparent density of the resin, ρ_p, by pycnometry.

The filtered resin was weighed (W_R) in an Erlenmeyer flask, then distilled water of volume V_d (usually 50 ml) was added. The flask was gently shaken to desorb the solute for at least 1 h, then the solute concentration in the external solution, C_d, was determined. The distribution coefficient, K, of the solute was evaluated using the following equation:

$$K = \frac{C_d V_d / (W_R / \rho_p)}{C_0} \quad (1)$$

2.3. Determination of the molar volume of a solute

A solute of mass W_S was placed in a volumetric flask of volume V (about 10 ml), which was precisely determined using distilled water. The solute was dissolved in distilled water, which was further added to dilute to the mark at 60°C. The mass of water added, W_W, was precisely measured. The concentrations of the solute, C_S, and water, C_W, were evaluated using the equations

$$C_S = W_S / (M_S V) \quad (2a)$$

$$C_W = W_W / (M_W V) \quad (2b)$$

where M_S and M_W are the molecular masses of the solute and water, respectively.

Under the assumptions that the volumes of a solute and water are independent and that additivity holds, the following equation is obtained:

$$C_W = \frac{1}{v_W} - \frac{v_S}{v_W} \cdot C_S \quad (3)$$

where v_S and v_W are the molar volumes of the solute and water, respectively. Since the v_W value at 60°C can be calculated from the density [7], the v_S value can be calculated if the plot of C_W versus C_S gives a straight line.

2.4. Determination of the equivalent volume of a resin

The equivalent volume, V_e, is defined as the volume of resin per unit equivalent of fixed ions. The V_e values of the resins in the H^+, Li^+, Na^+ and K^+ forms were determined as described [8]. The bed voidage was measured by means of the pulse response, using pullulan as the solute.

2.5. Determination of the swelling pressure of the resin

The resin in the Li^+, Na^+ or K^+ form was packed into a column of 1.52 cm I.D. with a jacket. The bed height was about 44 cm, which was precisely measured in each experiment. Pulse response experiments were performed at 60°C, using 1% (w/v) glucose, maltose and

maltotriose as the samples. Maltotetraose [1% (w/v)] was also used for the resin in the Na^+ form. The eluent was distilled water. The bed voidage was determined from the pulse response curves of pullulan [1% (w/v)]. The pulse response experiments were carried out at three or four different flow-rates for each solute and the elution profiles were monitored using a YRU-883 refractometer (Shimamura Seisakusho, Tokyo, Japan) and recorded on an R-11 strip-chart recorder (Rikadenki, Tokyo, Japan). The elution curves were analysed according to Nakanishi et al. [9] to evaluate the distribution coefficient, K, of each solute. These methods are based on moment analysis of the elution curves.

We have proposed an equation which relates the K value with the swelling pressure of the resin, II [8]. Assuming that v_S is independent of pressure, the chemical potentials of the solute in the external solution and resin phases, μ_1 and μ_2 are given by the following equations:

$$\mu_1 = \mu(P^0) + RT \ln a_1 + (P_1 - P^0)v_S \quad (4a)$$

$$\mu_2 = \mu(P^0) + RT \ln a_2 + (P_2 - P^0)v_S \quad (4b)$$

where P is the pressure, R is the gas constant, T is the absolute temperature, a is the activity, P^0 is the standard pressure and the subscripts 1 and 2 denote the external solution and resin phases, respectively. Since μ_1 is equal to μ_2 at equilibrium, we can obtain the following equation:

$$\frac{a_2}{a_1} = \exp\left(-\frac{\Pi}{RT} \cdot v_S\right) \quad (5)$$

where $\Pi = P_2 - P_1$ and is the swelling pressure of the resin. The distribution coefficient K is defined as the ratio of the solute concentration in the resin phase to that in the external solution phase. Therefore, the distribution coefficient can be expressed by

$$K = \gamma_0 \exp\left(-\frac{\Pi}{RT} \cdot v_S\right) \quad (6a)$$

where γ_0 is a parameter related to the ratio of the activity coefficient of the solute in the external solution phase to that in the resin phase. Taking the logarithms of both sides of Eq. 6a,

$$\ln K = -\frac{\Pi}{RT} \cdot v_S + \ln \gamma_0 \quad (6b)$$

If Eq. 6b is applicable to the present system, the II value can be calculated from the slope of the line obtained from the plots of ln K versus v_S.

2.6. Bed shrinkage by dense solute solutions

The resin in the Na^+ form was packed into a column with a water-jacket. The I.D. of the column was 1.52 cm and the bed height was about 44 cm, which was precisely measured in each experiment. The bed was kept at 60°C by circulating thermostated water through the jacket.

A 20% (w/v) solution of glucose, maltose or maltotriose was continuously applied to the bed at a flow-rate of 1.7 ml/min until there was no further bed shrinkage. Usually the volume of the applied solute was about 1.5 times that of the bed. The bed shrinkage was monitored using a video camera. After bed shrinkage had ceased, pulse response studies using soluble starch [1% (w/v)] in the solute solution were performed using the solute as the eluent, to determine the bed voidage when glucose and maltose were used as the solute. The effluent was fractionated using a Type 2112 fractionator (LKB, Bromma, Sweden) and the concentration of soluble starch in each was determined. These experiments were also repeated at solute concentrations of 40 and 60% (w/v).

2.7. Analysis

The concentrations of glucose, maltose and maltotriose were determined using an LC-6A high-performance liquid chromatograph (Shimadzu, Kyoto, Japan) with an St/6DVB-15(N) separation column (Japan Organo, Tokyo, Japan) and a YRU-880 refractometer (Shimamura). Distilled water was used as the eluent. The concentration of soluble starch was measured by the KI–I_2 method [10].

3. Results and discussion

3.1. Distribution coefficients at various solute concentrations

Fig. 1 shows the distribution coefficients at 60°C of glucose, maltose and maltotriose on a resin in the Na^+ form at various equilibrium concentrations. The open symbols represent single-component systems. The closed symbols represent a binary component system which consisted of maltose and maltotriose and where the concentration of maltotriose was fixed at 5.0% (w/v). The distribution coefficients of maltose and maltotriose in the binary system are plotted against their total concentrations. The distribution coefficients of all the solutes depended on their concentrations, and the extent of the dependence was in the order maltotriose > maltose > glucose.

Eq. 6a suggests the reason for this. If the swelling pressure Π is lower at higher solute concentrations, the distribution coefficient might increase. The dependence of the swelling pressure on the solute concentration was studied, and the molar volumes of the solutes were determined as shown below.

3.2. Molar volumes of the solutes

The water concentrations at different solute concentrations were plotted against the solute concentrations and are shown in Fig. 2. The plots gave a straight line for each solute. The molar volume of water at 60°C was 0.0183 l/mol [7]. According to Eq. 3, the molar volumes of glucose, maltose and maltotriose were calculated from the slopes of the respective lines as 0.116, 0.216 and 0.313 l/mol, respectively. The molar volume of maltotetraose, which will be necessary in Fig. 3, was calculated to be 0.416 l/mol by extrapolating the relationship between the molar volume and the molecular mass for the above three solutes.

3.3. Relationship between equivalent volume and swelling pressure

The equivalent volume of the resin was considered as a parameter that related the swelling pressure with the bed shrinkage. The resin in the H^+ form was packed into a column, and the bed voidage of the bed, ε_H, was determined from the pulse response experiments using pullulan as the solute. The equivalent volume of the resin in the H^+ form was calculated to be 0.470 l/equiv.

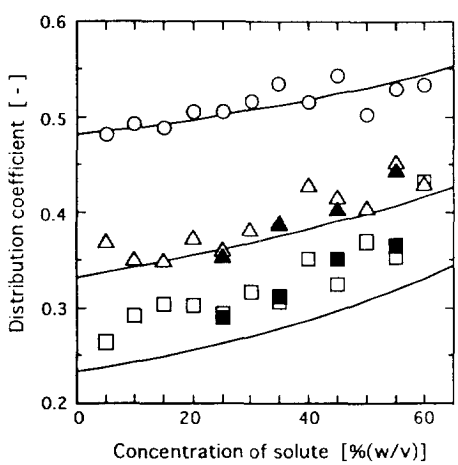

Fig. 1. Distribution coefficients of (○) glucose, (△) maltose and (□) maltotriose at 60°C on a cation-exchange resin in the sodium form. The solid curves are calculated.

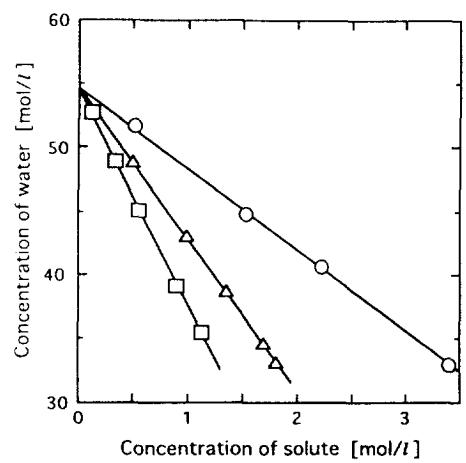

Fig. 2. Concentrations of water in (○) glucose, (△) maltose and (□) maltotriose solutions at 60°C.

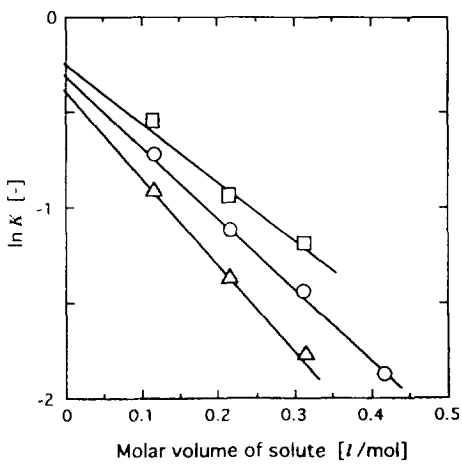

Fig. 3. Estimation of the swelling pressure of a cation-exchange resin in the (△) lithium, (○) sodium and (□) potassium forms. The distribution coefficients were observed at 60°C using distilled water as the eluent. The solutes were glucose, maltose, maltotriose and maltotetraose.

from its exchange capacity and apparent density. The resin was consecutively converted into the Li^+, Na^+ and K^+ forms by supplying LiCl, NaCl and KCl solutions, respectively, and by washing with distilled water. For the resin in each alkali metal form, the distribution coefficients, K, of the maltooligosaccharides and the bed voidage, ε, were measured using distilled water as the eluent. The equivalent volume, V_e, of the resin in each alkali metal form was calculated using the following equation:

$$V_e = \frac{V_{e,H} Z(1-\varepsilon)}{Z_H(1-\varepsilon_H)} \quad (7)$$

where Z and Z_H are the bed heights for the resins in alkali metal and H^+ forms, respectively, and $V_{e,H}$ is the equivalent volume of the resin in the H^+ form.

The swelling pressure of the resin in each alkali metal form was calculated using Eq. 6b. The distribution coefficients of the malto-oligosaccharides were plotted against their molar volumes on a semi-logarithmic scale (Fig. 3). The plots gave a straight line for the resin in each form. The swelling pressure Π and the γ_0 value were evaluated from the slope and the intercept of the line, respectively.

Gregor [11] has proposed a model in which the matrix of an ion-exchange resin is a network of elastic springs, and the equivalent volume of the resin is a linear function of the swelling pressure:

$$V_e = a\Pi + b \quad (8)$$

where the empirical constants, a and b, are characteristic of the resin and independent of the ionic form. Constant b is the equivalent volume of the unstrained resin. It has been reported that this model is applicable for styrene-type [11,12] and dextran gel-type [13] ion exchangers. Since the resin was a styrene type, the model should be applicable. As shown in Fig. 4, the equivalent volume of the resin was linearly related to the swelling pressure, indicating that the model was valid for the resin. The values of constants a and b were calculated to be 1.06×10^{-3} l/equiv. · atm and 0.334 l/equiv., respectively.

The parameter γ_0 was also a linear function of the swelling pressure (atm):

$$\gamma_0 = 1 - 2.60 \times 10^{-3}\Pi \quad (9)$$

This relationship was obtained empirically. Since the activity coefficients in the external solution

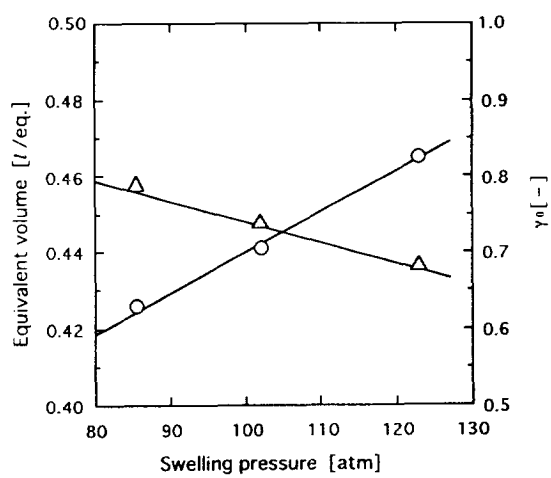

Fig. 4. Experimental relationships (○) between an equivalent volume of resin and the swelling pressure of the resin and (△) between the parameter γ_0 and the pressure.

and resin phases are the same when the swelling pressure is zero, the intercept on the axis should be 1.

3.4. Bed shrinkage by dense solute solutions

The resin in the Na^+ form was packed into a column. Glucose, maltose or maltotriose solutions of 20, 40 and 60% (w/v) were applied consecutively to the bed, and the bed height was read after no further shrinkage occurred. The bed voidage was also measured when glucose and maltose solutions were applied. The bed shrank with increasing solute concentration (Fig. 5). The relationship between the bed shrinkage and the solute concentration, C_S, was empirically expressed by a second-order function for each solute:

$$Z/Z_0 = 1 + cC_S + dC_S^2 \quad (10)$$

where Z and Z_0 are the bed heights at $C_S = C_S$ and $C_S = 0$, respectively, and C_S is in units of % (w/v). The values of the constants c and d were determined to be -4.83×10^{-4} and -6.25×10^{-6}, -6.86×10^{-4} and -5.21×10^{-6}, and -7.00×10^{-4} and -7.50×10^{-6} for glucose, maltose and maltotriose, respectively. The solid curves in Fig. 5 were drawn using these values of c and d.

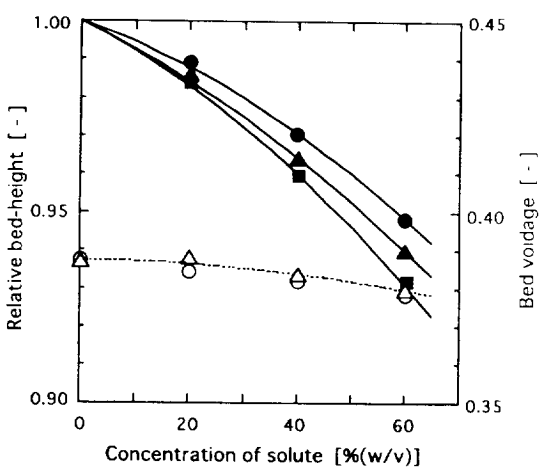

Fig. 5. Effects of the solute concentration on bed shrinkage and bed voidage. The closed and open symbols represent the relative bed height and bed voidage, respectively. ●, ○ = Glucose; ▲, △ = maltose; ■ = maltotriose.

The bed voidage also depended slightly on the solute concentration, as shown in Fig. 5. The bed voidage was not studied when maltotriose was applied, because the relationships between the bed voidage and C_S were similar for both glucose and maltose, and because maltotriose is much more expensive than the other solutes. The bed voidage could be empirically expressed by a second-order function of C_S:

$$\varepsilon = 0.387 - 2.00 \times 10^{-5} C_S - 1.87 \times 10^{-6} C_S^2 \quad (11)$$

where C_S is in units of % (w/v). The relationship of Eq. 11 is shown in Fig. 5 by the dotted curve.

3.5. Calculation of distribution coefficients at various solute concentrations

The bed shrinkage Z/Z_0 and the bed voidage ε at any solute concentration can be evaluated by Eqs. 10 and 11, respectively. The equivalent volume of the resin, V_e, at the concentration is given by

$$V_e = \frac{Z}{Z_0} \cdot \frac{1-\varepsilon}{1-\varepsilon_0} \cdot V_{e,0} \quad (12)$$

where the subscript zero represents the values at $C_S = 0$. The value of $V_{e,0}$ for the resin in the Na^+ form was 0.441 l/equiv. By substituting the V_e value into Eq. 8, the swelling pressure of the resin at the concentration was calculated. The γ_0 value corresponding to the swelling pressure was obtained from Eq. 9. Thus, all the values necessary to calculate the distribution coefficient K at the concentration using Eq. 6a were obtained.

The solid curves in Fig. 1 were drawn according to the procedures described above. The curves for glucose and maltose coincided well with the experimentally observed dependence of the distribution coefficients on solute concentration. For maltotriose, the calculated curve lies slightly below the symbols which represent the experimentally observed distribution coefficients. The reason for the discrepancy is not clear. However, the calculated curve showed a tendency for the distribution coefficient to be larger

at higher concentrations. The distribution coefficient of maltotriose depended most on the concentration among the solutes. This is ascribed to its large molar volume.

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