Thermogravimetric Measurement of the Distribution Coefficients of Maltooligosaccharides upon a Cation-exchange Resin

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Thermogravimetry under nitrogen atmosphere was applied to measure the distribution coefficients of maltooligosaccharides upon a cation-exchange resin. Thermal degradation of the solute occurred at about 200°C and its weight decreased gradually with increases in temperature, while that of the resin occurred above 350°C. The solute distributed in the resin also degraded at that temperature. Thus, it was demonstrated that thermogravimetry was applicable to measurement of the distribution coefficient. The coefficients determined by this method coincided well with those determined by the conventional method. Because the amount of solute distributed in the resin became large when the bulk concentration of solute was high, the thermogravimetric determination of the amount was more accurate. Thus, this technique was useful for the measurement of the coefficient at higher bulk concentrations of solute.

Keywords: distribution coefficient, thermogravimetry, maltooligosaccharide

The distribution coefficient of a solute upon a resin is an important parameter to predict the elution behavior of the solute on chromatography. The coefficient is usually evaluated from the peak position of the elution curve when a solute loaded as a pulse input into a packed-bed of the resin is eluted with an appropriate eluent (Takeuchi & Mori, 1972). To evaluate the coefficient more precisely, moment analysis of the elution curve is adopted (Kucera, 1965; Nakanishi et al., 1977). Although this pulse response method is useful to evaluate the coefficient in a dilute solution system, it is difficult due to large consumption of the solute to use this method for evaluation of the coefficient when the equilibrium concentration of the solute in the bulk phase is high. For such a case, a batchwise method is used. That is, the resin is equilibrated with a solute solution and then separated from the solution by filtration after equilibrium is reached. The solute distributed upon the resin is desorbed with a large volume of solvent and is determined. The solute concentration in the resin phase is estimated from the amount of solute desorbed and the apparent density of the resin (Adachi et al., 1995). This batchwise method, however, is tedious and time-consuming.

When the solute concentration is dense and the distribution coefficient is supposed to be not extremely small, a certain amount of the solute is distributed upon the resin phase. We supposed that the amount of the solute distributed upon the resin phase could be determined by thermogravimetry if the solute is liable to degradation at a lower temperature than the resin. Thermogravimetry would be a convenient method to monitor the weight change of a sample under arbitrary temperature conditions. In this context, we examined the applicability of thermogravimetry to estimate the distribution coefficients of maltooligosaccharides upon a cation-exchange resin.

Materials and Methods

Materials   Glucose was purchased from Wako Pure Chemicals, Osaka, Japan. Maltose and maltotriose were products of Hayashibara Biochemicals, Okayama, Japan. The cation-exchange resin (Dow Chemicals) used was a styrene-type possessing a sulfonate group as an exchange group and its content of divinylbenzene was 4 %. The resin was conditioned in Na^+ form according to the standard procedure (Kakihana & Mori, 1969).

Thermal degradation of solutes and resin   To estimate the temperatures at which thermal degradation of the solutes and the resin occurred, their thermogravimetric curves were observed under a nitrogen atmosphere in constant increments of 5°C/min from room temperature to 500 or 600 °C using a thermogravimeter (TGA-50H, Shimadzu Seisaku-sho, Kyoto, Japan). The rate of nitrogen flow was 20 ml/min. About 10 mg of a solid solute or wet resin, measured precisely in each experiment, was put into an aluminum cell (6 mm in diameter and 2.5 mm in depth).

Thermogravimetric measurement of the distribution coefficient   Wet resin in Na^+ form (about 1 g) was put into a vial, into which was then poured 10 ml of a solute solution of a given concentration. The vial was kept at room temperature for a few minutes, and then the solution was discarded by decantation. Ten ml of the solute solution was then added into the vial, and this procedure was repeated three times. At the last addition of solute solution, the vial was kept at 60°C for at least 60 minutes with occasional shaking to attain equilibrium, after which the resin was separated from the solution by filtration through a sintered glass filter of G2. Excess solution on the resin surface was removed by a filter paper, and the resin was subjected to thermogravimetric measurement. The equilibrium concentration of the solute in the bulk phase was also determined using the filtrate by
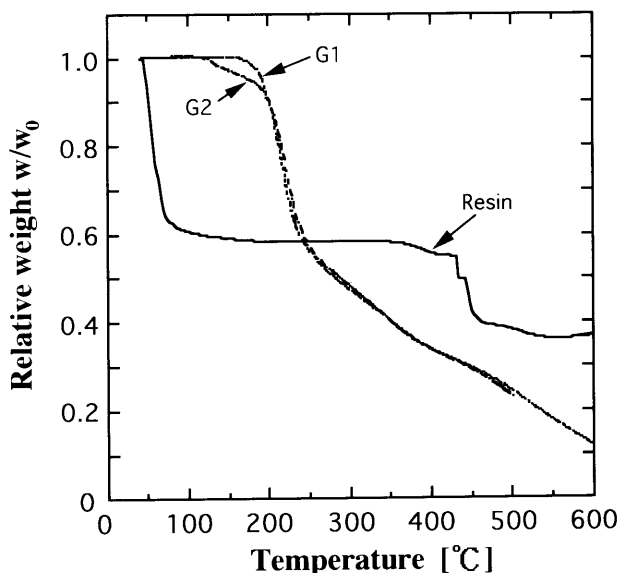
thermogravimetry.

Based on the findings from the experiments described above, thermogravimetric measurements were conducted under a nitrogen atmosphere with the following temperature program consisting of five steps. The temperature was raised from room temperature to 105°C in increments of 5°C/min (step 1) and then maintained at 105°C for 20 minutes (step 2). Subsequently, it was again raised to 350°C in increments of 5 °C/min (step 3) and then kept at 350°C for 60 minutes (step 4). Finally, the temperature was raised to 600°C in increments of 5°C/min (step 5). The initial weights of samples were in the range of 5 to 20 mg.

Density of the dry resin The resin in Na$^+$ form was dried under vacuum and its density was measured pycnometrically at 60°C using water as the solvent (Sugawara *et al.*, 1990).

Results and Discussion

Thermal degradation of solutes and resin Figure 1 shows the thermogravimetric curves of dry glucose and maltose and that of wet ion-exchange resin in Na$^+$ form observed under a nitrogen atmosphere with temperature increments of 5°C/min. The curves were normalized by the initial sample weights. Thermal degradation of glucose and maltose occurred at about 150°C, and their weights decreased gradually with increasing temperature. Evaporation of water in the wet resin was completed at about 150°C, and the dry resin retained its weight up to 350°C. As the temperature was raised beyond this value, the weight of the resin decreased. The curves indicated that the ion-exchange resin was more stable toward thermal degradation than the solutes. Therefore, it seemed that thermogravimetry was applicable to measure the amount of a solute distributed upon the resin and that such measurement would enable us to estimate the distribution coefficient.
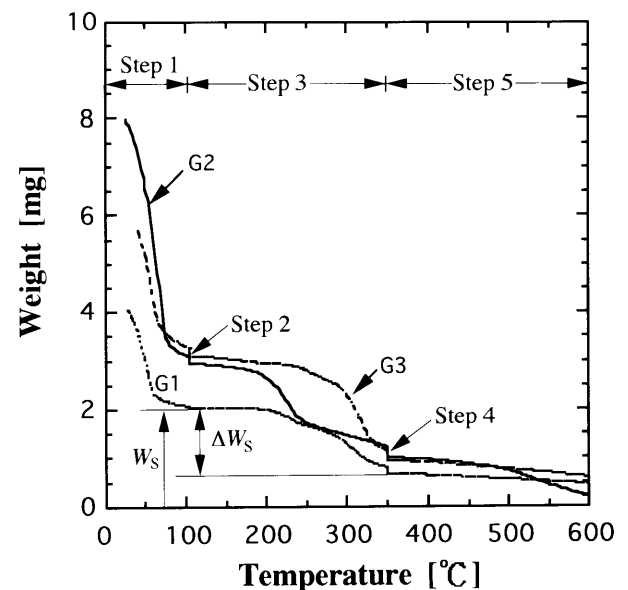
Relationship between weight loss of solutes and their initial weights Based on the thermogravimetric curves shown in Fig. 1, a temperature-increase program to measure the amount of solute distributed upon the resin was determined as described above. The thermogravimetric curves of solute solutions of various concentrations were plotted according to this temperature-increase program. Some of the curves are shown in Fig. 2. The dry mass of a solute W_S was estimated from the weight at the end of step 2. The weight loss during steps 3 and 4 was denoted as ΔW_S. The relationship between ΔW_S and W_S for glucose, maltose and maltotriose is shown in Fig. 3. For all the solutes, ΔW_S values were linearly related to the W_S values as follows:

$$\Delta W_S = 0.673 \cdot W_S \qquad (1)$$

Measurement of the distribution coefficient The thermogravimetric curve of the wet resin upon which a solute was distributed was observed according to the temperature-increase program described above. The thermogravimetric curve of the bulk solution was also observed. These measurements were carried out for glucose, maltose and maltotriose at various bulk-phase concentrations. Figure 4 shows the curves in cases where the ion-exchange resin was equilibrated with about 40%(w/v) maltose solution at 60°C. The weights of water included in the wet resin W_{WR} and the bulk solution W_{WB} were estimated from the weight loss during steps 1 and 2. The weight of the solute in the bulk solution W_{SB} was given by the weight at the end of step 2. Under the assumption that the volumes of water and the solute are independent and that additivity holds between them, the volume of the bulk solution applied to the thermogravimetric measurement, V_B,

Fig. 1. Thermogravimetric curves of glucose, maltose and ion-exchange resin in Na$^+$ form. Glucose and maltose used were in the solid state, while the resin was wet. The curves were obtained under a nitrogen atmosphere with temperature increments of 5°C/min. The sample weight W was normalized by the initial weight W_0. G1 and G2 indicate glucose and maltose, respectively.

Fig. 2. Thermogravimetric curves of glucose, maltose and maltotriose solutions. The curves were obtained under a nitrogen atmosphere. The temperature was raised from room temperature to 105°C in increments of 5°C/min (step 1), held at 105°C for 20 min (step 2), raised to 350°C in the same increments (step 3), held at 350°C for 60 min (step 4), and then raised to 600°C in the same increments (step 5). W_S is the sample weight at the end of step 2, and ΔW_S is the weight loss during steps 3 and 4. G1, G2 and G3 indicate glucose, maltose and maltotriose, respectively.
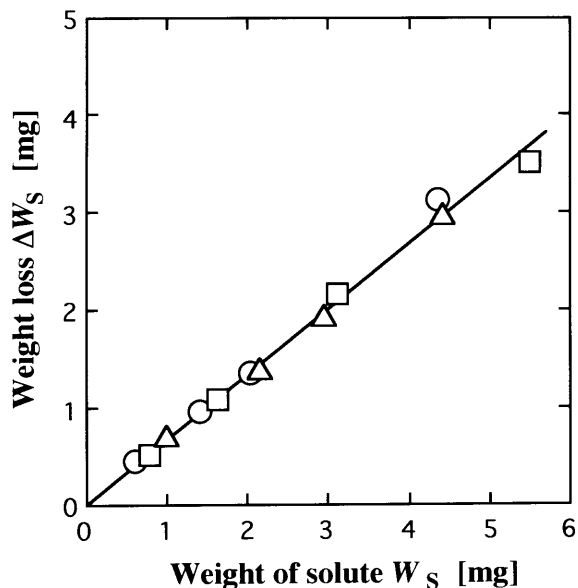
Fig. 3. Relationship between the weights of solutes, W_S, and the weight losses during steps 3 and 4, ΔW_S. The symbols, ○, △ and □, represent glucose, maltose and maltotriose, respectively.

Fig. 5. Distribution coefficients of maltooligosaccharides at various bulk concentrations upon the ion-exchange resin in Na⁺ form. The distribution coefficients were obtained at 60°C. The closed and open symbols represent the distribution coefficients evaluated by the present and by the conventional method, respectively. The solutes are glucose (●, ○), maltose (▲, △) and maltotriose (■, □). The solid curves were calculated by the model proposed in our previous study (Adachi et al., 1995). G1, G2 and G3 indicate glucose, maltose and maltotriose, respectively.
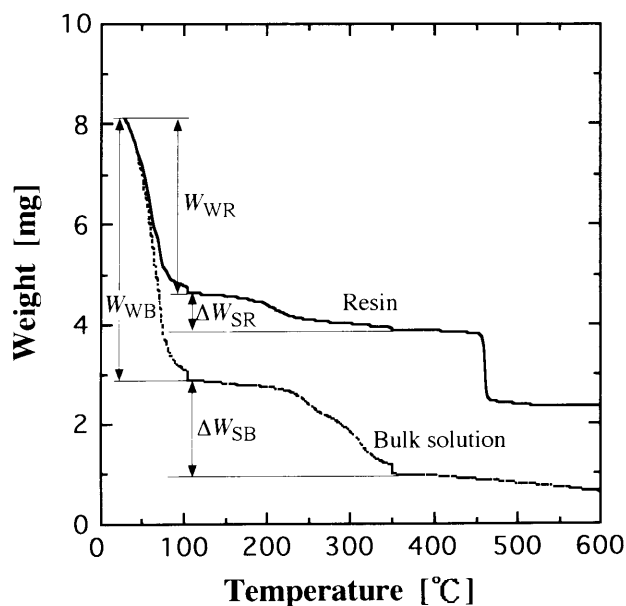

Fig. 4. Thermogravimetric curves of the ion-exchange resin upon which maltose was distributed and of the bulk solution. The resin was equilibrated with 40%(w/v) maltose at 60°C. The curves were obtained under the same conditions as in Fig. 2. W_{WR} and W_{WB} are the weight losses during steps 1 and 2, and ΔW_{SR} and ΔW_{SB} are the weight losses during steps 3 and 4.

Fig. 6. Distribution coefficient of water upon the ion-exchange resin in Na⁺ form at various saccharide bulk concentrations. Details are the same as those in the legend of Fig. 5.

is given as:

$$V_B = \frac{W_{WB}}{M_w/v_w} + \frac{W_{SB}}{M_S/v_S}, \quad (2)$$

where v is the molar volume, M is the molar mass, and the subscripts, W and S, represent water and the solute, respectively. The v_w value at 60°C was calculated from the density at that temperature to be 0.0183 l/mol(Weast, 1988). The v_S values of glucose, maltose and maltotriose were 0.116, 0.216 and 0.313 l/mol, respectively (Adachi et al., 1995). The
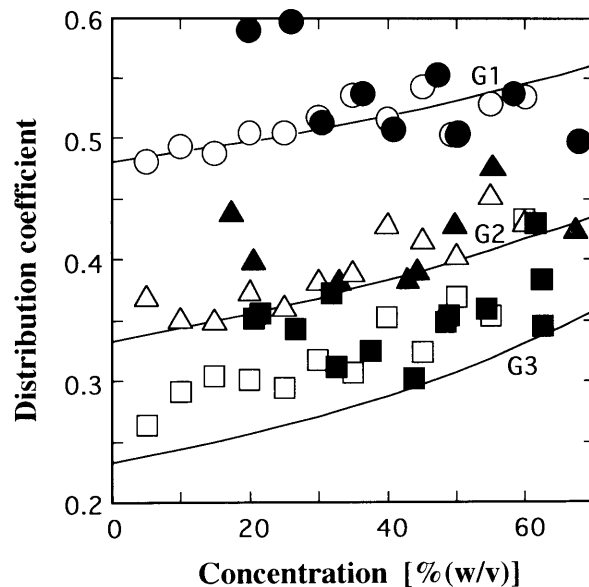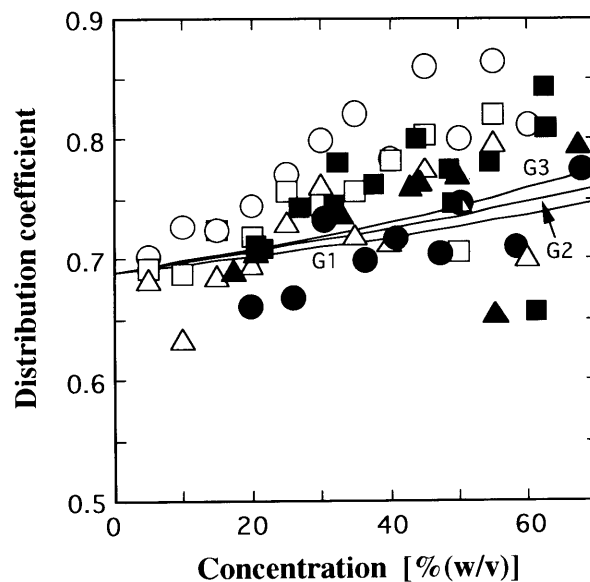
solute concentration of the bulk solution C_{SB} was calculated from

$$C_{SB} = W_{SB}/V_B. \quad (3)$$

The weight of the solute distributed upon the resin, W_{SR}, was evaluated from the weight loss during steps 3 and 4, ΔW_{SR}, using Eq. (1). The weight of the dry resin W_{RR} was calculated as follows:

$$W_{RR} = W_0 - W_{WR} - W_{SR}, \quad (4)$$

where W_0 is the initial weight of the wet resin. Assuming additivity among the volumes of water, the solute and the resin for the resin phase, the volume of the wet resin V_R is given by the following equation:

$$V_R = \frac{W_{WR}}{M_W/\nu_W} + \frac{W_{SR}}{M_S/\nu_S} + \frac{W_{RR}}{\rho_R}, \quad (5)$$

where ρ_R is the density of the dry resin and was estimated pycnometrically as 1588 g/l. The solute concentration of the resin phase C_{SR} can be calculated by

$$C_{SR} = W_{SR}/V_R. \quad (6)$$

Because the distribution coefficient of the solute K_S is defined as the ratio of the solute concentration of the resin phase to that of the bulk phase, it was evaluated as follows:

$$K_S = C_{SR}/C_{SB}. \quad (7)$$

Similary, we can evaluate the distribution coefficient of water upon the resin K_W. By replacing W_{SB} and W_{SR} by W_{WB} and W_{WR} in Eqs. (3) and (6), respectively, the concentrations of water in the bulk phase C_{WB} and in the resin phase C_{WR} can be estimated. The K_W value is then given by

$$K_W = C_{WR}/C_{WB}. \quad (8)$$

Dependence of the distribution coefficients on the solute concentrations   The distribution coefficients of the solutes and water estimated by the above thermogravimetric method are plotted against the solute concentrations in Figs. 5 and 6, respectively. In these figures, the closed symbols represent the distribution coefficients evaluated by the thermogravimetric method, and the open symbols represent the coefficients determined by the conventional method (Adachi *et al.*, 1995). The distribution coefficients evaluated by the thermo-gravimetric method coincided fairly well with those evaluated by the conventional method. The distribution coefficients of water were scattered compared with those of the solutes. The reason for the scattering is not clear. At the lower solute concentrations (20%(w/v) or less), the thermogravimetric method seemed to lack accuracy in evaluation of the co-efficient. This may be because of the smaller amount of solute distributed at lower bulk concentrations. We have previously determined that the distribution coefficients of the malto-oligosaccharides used here upon the ion-exchange resin in Na^+ form depended on the bulk concentrations of the solutes and proposed a model to explain this dependence (Adachi *et al.*, 1995). The distribution is related to the swelling pressure of the resin by the model and becomes large as the pressure decreases. At the higher solute concentrations, the resin shrinks, that is, the swelling pressure of the resin becomes lower. So, the low swelling pressure enlarges the distribution coefficient. The model is also applicable to predict the dependence of the distribution coefficient of water on the bulk concentration of solute. The solid curves in Figs. 5 and 6 were drawn according to the model.

As shown here, thermogravimetry was applicable to measurement of the distribution coefficient of a solute upon the ion-exchange resin. The method described here does not require any chemicals for determination of a solute and is simple if only a thermogravimeter is available.

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