

Calorimetric Studies on Molecular Inclusion. III. Gibbs Energies and Entropies of Inclusion of 1-Propanol and 1-Pentanol into Cyclohexaamylose and Cycloheptaamylose in Aqueous Solutions at 298.15 K.

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(Received Jan. 28, 1983)

For the molecular inclusion equilibrium between cyclohexaamylose and 1-propanol or 1-pentanol with a 1:1 inclusion complex in dilute aqueous solution: $(\text{CyD})_{\text{aq}} + (\text{ROH})_{\text{aq}} \rightleftharpoons (\text{CyD}\cdot\text{ROH})_{\text{aq}}$, the equilibrium constant K and the limiting molar ratio y_{max} of the alcohol included have been refined by the improved version of procedures which were proposed by the present authors [original, *Nippon Kagaku Kaishi*, 1983, 188; the improved version, *Netsusokutei*, 10, 43 (1983)]. The most probable values refined for $\log_{10} K$ and y_{max} are 3.124 and 0.495 for $\text{C}_3\text{H}_7\text{OH}$, and 4.265 and 0.785 for $\text{C}_5\text{H}_{11}\text{OH}$, respectively.

From these results and those for cycloheptaamylose and the same alcohols reported earlier by the present authors, the enthalpies, Gibbs energies, and entropies of inclusion have been evaluated. The entropy changes are positive in all systems, showing that common "driving-force" is the increase of the entropy. The enthalpy changes are, however, exothermic for the inclusion into the rather small cavities of cyclohexaamylose, but are endothermic for the inclusion into the larger cavities of cycloheptaamylose in aqueous solutions.

1. Introduction

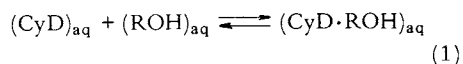
The enthalpies of inclusion of 1-propanol and 1-pentanol with cyclohexaamylose¹⁾ and cycloheptaamylose²⁾ in aqueous solutions at 298.15 K were determined previously from the results of experimental enthalpies of transfer of the alcohols from aqueous to aqueous cycloamylose solutions. In the course of these calculations the equilibrium constants K 's of the formation of 1:1 clathrates were obtained for the alcohol + cycloamylose systems as well as the limiting molar ratios y_{max} 's of the alcohols included, by use of merely the calorimetric results obtained at one temperature, 298.15 K.

In this report we evaluate the Gibbs energies and the entropies of inclusion of the above alcohols with the cycloamyloses mentioned above and compare the effects of difference in diameters of

the cavities between those cycloamyloses. Prior to calculating the thermodynamic functions, however, the refinements of the procedures of finding the best values of K 's and y_{max} 's are described in detail for the cases of cyclohexaamylose.

2. Refinement of Mathematical Procedures

A new method for obtaining an equilibrium constant K from merely the calorimetric measurement at only one fixed temperature was proposed by the present authors, to find the equilibrium constant of the formation of a 1:1 complex in a solvent.^{1,2)} An example of it is formation of a 1:1 inclusion complex in an aqueous solution as shown in Eq. (1).



The equilibrium constant K for this case is given by Eq. (2) and it can be obtained approximately through Eq. (3) for very dilute solutions.

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$$K = \frac{a_4}{a_2 \cdot a_3} \quad (2)$$

$$= \frac{\left(\frac{n_4}{n_1+n_2+n_3-n_4}\right)}{\left(\frac{n_2-n_4}{n_1+n_2+n_3-n_4}\right)\left(\frac{n_3-n_4}{n_1+n_2+n_3-n_4}\right)} \quad (3)$$

where a means the (relative) activity, n the amount of substance, and subscript figures, 1 to 4 represent water, cycloamylose, alcohol, and the 1:1 complex, respectively.

In our theoretical treatment the molar ratio of the alcohol included is expressed by Eq. (4), which is equivalent to the Eq. (21) written in the reference 1.

$$y = \frac{1}{2} + \frac{1-f}{2f} + \frac{(1-f)z}{2f(1+K)} - \sqrt{\left\{\frac{1}{2} + \frac{1-f}{2f} + \frac{(1-f)z}{2f(1+K)}\right\}^2 - \frac{(1-f)K}{f(1+K)}} \quad (4)$$

where

$$y = n_4/n_3, \quad z = n_1/n_2, \quad \text{and} \quad f = n_3/(n_2+n_3). \quad (5)$$

Since the molar enthalpy of transfer of the alcohol $\Delta_{tr}H_m$ from aqueous to aqueous cycloamylose solutions is proportional to the molar ratio of the alcohol included when it is transferred into the aqueous cycloamylose solution, the function Y defined by Eq. (6)

$$Y(K, z, f) \stackrel{\text{def}}{=} \frac{100}{y_{\max}} y, \quad (6)$$

and $(100/\Delta_{tr}H_m^\infty)\Delta_{tr}H_m(z, f)$ are equivalent, where

$$y_{\max} \stackrel{\text{def}}{=} \lim_{f \rightarrow 0} y = \frac{K}{1+z+K}, \quad (7)$$

and $\Delta_{tr}H_m^\infty = \lim_{f \rightarrow 0} \Delta_{tr}H_m$.

As the value of z was kept to be nearly constant in each particular system during the measurement with various values of f , the best value of K was determined by comparison of the theoretical function Y with the experimental $(100/\Delta_{tr}H_m^\infty)\Delta_{tr}H_m$.

In the first paper¹⁾ of this series concerning the two systems of 1-propanol and 1-pentanol with cyclohexaamylose, the comparison was carried out at only one mole fraction, namely $f = 0.55$, and furthermore the value of $\Delta_{tr}H_m^\infty$ was separately estimated by the least-squares analysis of the

experimental results through an empirical formula shown by Eq. (8).

$$\Delta_{tr}H_m = \Delta_{tr}H_m^\infty + mf^n, \quad (8)^3$$

In the second paper,²⁾ however, determination of the best-fit values of K and $\Delta_{tr}H_m^\infty$ was done in more elegant manner. Both of them were obtained simultaneously by the least-squares calculation to get the minimum value of r in Eq. (9).

$$r = \sum_i \left[(100/\Delta_{tr}H_m^\infty)\Delta_{tr}H_m(z_i, f_i) - Y(K, z_i, f_i) \right]^2, \quad (9)$$

Thus, the reported values for the systems of cycloheptaamylose in the paper II are the most probable ones. For the systems of 1-propanol + cyclohexaamylose and 1-pentanol + cyclohexaamylose, we have determined the best-fit values in this time by the latter procedure. The new refined values for these systems are shown in Table 1. The detailed procedures used are quite the same as those described in the paper II.²⁾ The improvement in the degree of fitting of the smoothed curves obtained by the least-squares method to the experimental results are illustrated in Figs. (3) and (4). On the other hand, Figs. (1) and (2) show the results obtained in the paper I. For the case of 1-propanol + cyclohexaamylose, the theoretical values of $Y = 100y/y_{\max}$ which were determined by the original procedures¹⁾ do not coincide well with the experimental values as shown in Fig. (1), where a dotted curve represents the smoothed values of the experimental $100\Delta_{tr}H_m/\Delta_{tr}H_m^\infty$ calculated by Eq. (8). Comparing Fig. (1) and Fig. (3), we can find that the excellent improvement has been achieved by the improved procedures for the system 1-propanol + cyclohexa-

Table 1 Refined values of the equilibrium constants for the formation of 1:1 inclusion complexes and the limiting molar enthalpies of transfer of alcohols at 298.15 K.

	$\log_{10} K$	$\frac{\Delta_{tr}H_m^\infty}{\text{kJ}\cdot\text{mol}^{-1}}$	s^a
1-C ₃ H ₇ OH + α -CyD ^b	3.124	-3.29	0.08
1-C ₅ H ₁₁ OH + α -CyD	4.265	-10.9	0.4

^a Standard deviations, see Eq. (8) of the reference 2.

^b cyclohexaamylose

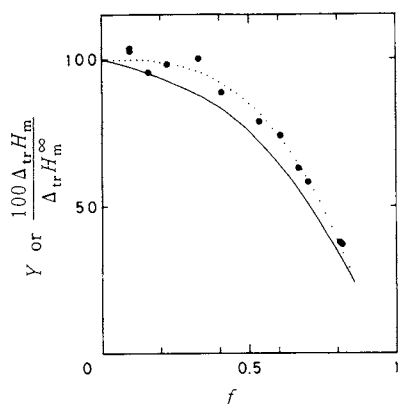


Fig. 1 Comparison of the dependencies upon f of the theoretical function Y which was obtained by the original procedures¹⁾ and the experimental molar enthalpies of transfer of 1-propanol from aqueous to aqueous cyclohexaamylose solution at 298.15 K. The solid curve represents $Y = 100y/y_{\max}$ where y and y_{\max} are defined by Eqs. (4), (5), and (7),⁴⁾ the circle (●) the experimental value of $100\Delta_{\text{tr}}H_m/\Delta_{\text{tr}}H_m^{\infty}$,¹⁾ and the dotted curve by Eq. (8).⁵⁾

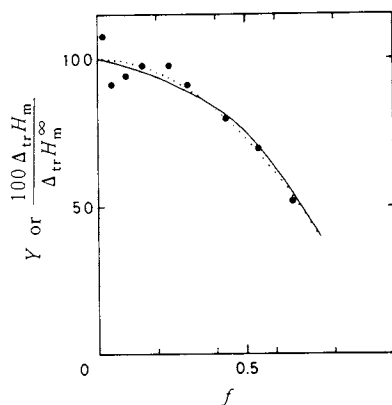


Fig. 2 Comparison of the dependencies upon f of the theoretical function Y which was obtained by the original procedures¹⁾ and the experimental molar enthalpies of transfer of 1-pentanol from aqueous to aqueous cyclohexaamylose solution at 298.15 K. The solid curve represents $Y = 100y/y_{\max}$ where y and y_{\max} are defined by Eqs. (4), (5), and (7),⁴⁾ the circle (●) the experimental value of $100\Delta_{\text{tr}}H_m/\Delta_{\text{tr}}H_m^{\infty}$,¹⁾ and the dotted curve the smoothed values of the latter calculated by Eq. (8).⁵⁾

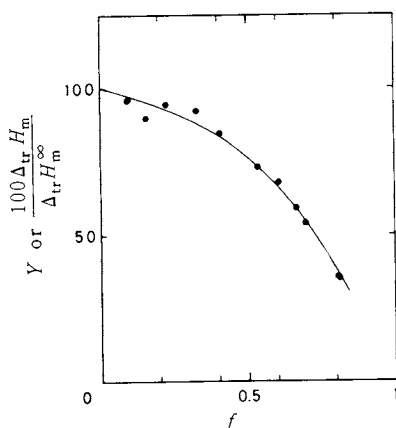


Fig. 3 Comparison of the theoretical function Y which have been obtained by use of the refined procedures²⁾ with the experimental results¹⁾ for 1-propanol + cyclohexaamylose at 298.15 K: ●, the experimental values of $100\Delta_{\text{tr}}H_m/\Delta_{\text{tr}}H_m^{\infty}$; —, $Y = 100y/y_{\max}$ where $z_{\text{mean}} = 1356$ and $\log_{10}K = 3.124$.

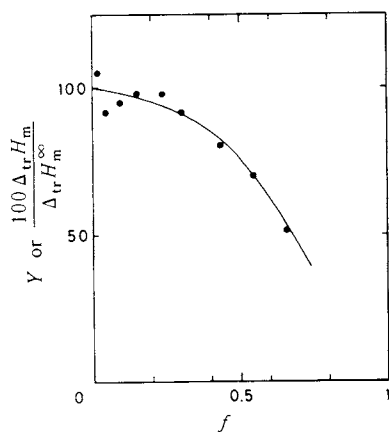


Fig. 4 Comparison of the theoretical function Y which have been obtained by use of the refined procedures²⁾ with the experimental results¹⁾ for 1-pentanol + cyclohexaamylose at 298.15 K: ●, the experimental values of $100\Delta_{\text{tr}}H_m/\Delta_{\text{tr}}H_m^{\infty}$; —, $Y = 100y/y_{\max}$ where $z_{\text{mean}} = 5048$ and $\log_{10}K = 4.265$.

amylose. For the case of 1-pentanol + cyclohexaamylose, although the fitting of the theoretical curve obtained in the paper I is good as shown in Fig. (2), the fitting is more satisfactory when the results were obtained by the improved procedures

as shown in Fig. (4). Thus, we can safely conclude that the excellent improvement in the mathematical procedures are obtainable by use of the latter method.

The new values of y_{\max} have been calculated

through Eq. (7) by use of the refined values of K , given in Table 1, and the experimental values of z_{mean} .¹⁾ Then, the most probable values of molar enthalpies of inclusion $\Delta_{\text{inc}}H_m$ of 1-propanol and 1-pentanol into cyclohexaamylose have been evaluated as $\Delta_{\text{tr}}H_m^\infty/y_{\text{max}}$. These values are summarized in Table 2 together with those for the systems with cycloheptaamylose.²⁾

3. Evaluation of the Gibbs energies and the entropies of inclusion

As the best-fit values of $\log_{10}K$ and $\Delta_{\text{inc}}H_m$ are obtained for all the systems, the molar Gibbs energies and the molar entropies of inclusion of the alcohols at 298.15 K were evaluated through Eqs. (10) and (11). They are listed in Table 2 as well as the molar enthalpies of inclusion.

$$\Delta_{\text{inc}}G_m = -RT \ln K \quad (10)$$

$$\Delta_{\text{inc}}S_m = \frac{\Delta_{\text{inc}}H_m - \Delta_{\text{inc}}G_m}{T} \quad (11)$$

4. Discussions

Validities of the assumptions involved

The assumptions used in our above procedures are following.

- (1) The inclusion complexes present in the solutions are only of 1:1 type.
- (2) All the activity coefficients are unity.

The assumption (1) may hold true in all the systems measured, because the mole fractions of cycloamylose in our systems are smaller than 0.0007, namely those are $x_2 = 7 \times 10^{-4}$ for the 1-propanol + cyclohexaamylose system and $x_2 = 2 \times 10^{-4}$ for all other systems, and those of the alcohols are the same order of magnitude of those

of the cycloamyloses.

As for the assumption (2), this approximation is thought not to introduce significant errors into the determination of the equilibrium constants and y_{max} given Eq. (7), since the mole fractions of the cycloamyloses in the solutions are very small and constant for each solution, and those of the alcohol used are similar to those of the cycloamyloses.

Thermodynamic behaviors of the alcohols in the systems

The earlier values¹⁾ of the molar ratio of the alcohol included at $f \approx 0$ and the molar enthalpy of inclusion of alcohol at 298.15 K, i.e., $y_{\text{max}} = 0.60$ and 0.67 and $\Delta_{\text{inc}}H_m/\text{kJ}\cdot\text{mol}^{-1} = -5.14$ and -16.2 for 1-propanol +, and 1-pentanol + cyclohexaamylose respectively, have been refined to the new values shown in Table 2. The changes in these values, however, do not cause any modification in the discussions given in paper I.

The results listed in Table 2 tell us that the entropy changes on inclusion of the alcohols into the cavities of the cycloamyloses in aqueous solution are always positive in the present cases. Thus, the increase of entropy seems to be the "driving-force" in the processes of molecular inclusion in the present systems. For the cases of inclusion of 1-propanol and 1-pentanol into the cavities of cyclohexaamylose, both systems become energetically more stable presumably by the enhancement of intermolecular interactions due to the van der Waals forces between the hydrophobic parts of the alcohol molecules and the inner walls of the cavities. For the inclusion by cyclohexaamylose of the linear alcohols studied, both changes of enthalpy and entropy contribute to

Table 2 The mean value of z^a , the molar ratio of alcohol included at $f \approx 0$, and the changes of thermodynamic functions on the formation of the 1:1 inclusion complex at 298.15 K.

	z_{mean}	y_{max}	$\frac{\Delta_{\text{inc}}H_m}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{inc}}G_m}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-T\Delta_{\text{inc}}S_m}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{inc}}S_m}{\text{J}\cdot(\text{K}\cdot\text{mol})^{-1}}$
1-C ₃ H ₇ OH + α -CyD ^b	1356 ¹⁾	0.4950	-6.6	-17.8	-11.2	37.5
1-C ₅ H ₁₁ OH + α -CyD	5048 ¹⁾	0.7847	-13.9	-24.4	-10.4	34.9
1-C ₃ H ₇ OH + β -CyD ^c	5090 ²⁾	0.1837 ²⁾	1.9 ²⁾	-17.5	-19.4	65.0
1-C ₅ H ₁₁ OH + β -CyD	5205 ²⁾	0.6388 ²⁾	2.2 ²⁾	-22.6	-24.8	83.2

^a $z = n_1/n_2$

^b cyclohexaamylose

^c cycloheptaamylose

promote the formation of 1:1 complexes. On the other hand, for the inclusion by cycloheptaamylose having a larger diameter of cavities, the same alcohols show the enthalpic unstabilization presumably owing to the insufficient stabilization in the cavities to compensate the enthalpy required for the preceding dehydration, because of the presence of vacant spaces between the alcohol molecules and the inner walls of the cavities. This

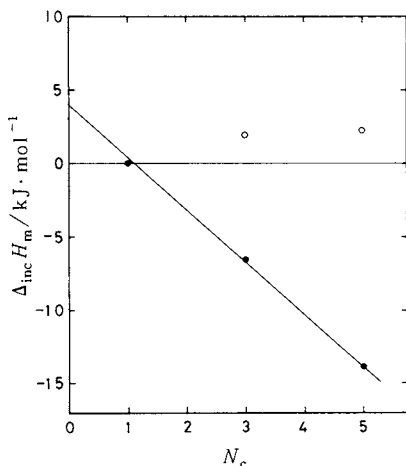


Fig. 5 Dependency of the enthalpy of inclusion into the cycloamylose upon the number N_c of carbon atoms in a molecule of alcohols: ●, $\Delta_{\text{inc}} H_m$ for cyclohexaamylose; ○, for cycloheptaamylose. The open circle for methanol is superposed on the filled circle.

situation can be understood easily by the famous illustration given by Lennard-Jones and Devonshire.⁶⁾ In this case only the increase of entropy contributes to the formation of the inclusion complexes. These are the most important results obtained by this study about the effect of the difference in diameter of the cavities between cyclohexaamylose and cycloheptaamylose.

To illustrate quantitatively, the enthalpies of inclusion are plotted in Fig. 5 against the number of carbon atoms of alcohol molecule. The straight line through the values of 1-propanol and 1-pentanol reproduces the athermal inclusion of methanol¹⁾ into cyclohexaamylose. Further discussions would be given in the following paper with the results of other alcohols.

References

- 1) Mune Maeda and Sadao Takagi, *Nippon Kagaku Kaishi*, **1983**, 188.
- 2) Mune Maeda and Sadao Takagi, *Netsusokutei*, **10**, 43 (1983).
- 3) Eq. (10) of the reference 1. Here, the notations of the quantities are slightly modified.
- 4) $z_{\text{mean}} = 1356$ and $\log_{10} K = 3.3_1$ for 1-propanol + cyclohexaamylose; $z_{\text{mean}} = 5048$ and $\log_{10} K = 4.0_2$ for 1-pentanol + cyclohexaamylose.¹⁾
- 5) Parameters used are shown in Fig. 2 of the reference 1.
- 6) J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc., London*, **A163**, 53 (1937).