Activity Coefficients of Dimethyl-β-cyclodextrin in Aqueous Solutions

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Synopsis. The activity coefficients of aqueous solutions of dimethyl-β-cyclodextrin were measured by vapor pressure osmometry at 25, 35, and 45±0.1 °C. The activity coefficient decreased with increase of concentration at each temperature. Both the excess enthalpy and the excess entropy were positive. The negative excess free energy originates from the large excess entropy term, indicating that dimethyl-β-cyclodextrin is a hydrophobic solute.

In a previous paper,[1] we determined the activity coefficients of α- and γ-cyclodextrins in aqueous solutions at 25 °C. In contrast with the concentration dependence of activity coefficients of aqueous solutions of D-glucose,[2] the activity coefficients of these cyclodextrins decreased with increase of concentration, implying that these solutes either associate or break the water structure.

Dimethyl-β-cyclodextrin(DM-β-CD) is heptakis(2,6-di-*O*-methyl)-β-cyclodextrin. The solubility of DM-β-CD in water is about ten times larger than that of β-CD and is soluble in organic solvents.[3] The complex formation and the properties of complexes are now being extensively studied.

From these points of view, we determined the temperature dependence of the activity coefficients of DM-β-CD in aqueous solutions to elucidate the solution property.

Experimental

Materials. DM-β-CD supplied from Toshin Chemicals was recrystallized from water. The purity was confirmed by HPLC and ^{1}H NMR. The compound was dried in vacuo at room temperature for several days before use. The melting point was 96 °C. Reagent grade sodium chloride obtained from Nakarai Chemical Co. Ltd. was used after drying in vacuo at 100 °C for 2 d. Aqueous solutions of these compounds were prepared with water purified by distillation and deionization.

Method. Vapor pressure over aqueous solution was measured at 25, 35, and 45±0.1 °C with an osmometer model 117 manufactured by Corona Electric Co. Ltd. To obtain the accurate results, osmotic pressures of DM-β-CD solution and NaCl solution (reference) of corresponding concentration were measured consecutively in every set of measurement. The experimental determination of osmotic coefficient was precise to ±0.02.

Results

The relations between the osmotic coefficients ϕ and the concentration m in mol^{-1}kg at 25, 35, and 45 °C are shown in Fig. 1. The values of ϕ decrease with increase of concentration at each temperature. By the least-square fitting, the values of ϕ at the respective temperatures are expressed in terms of m as

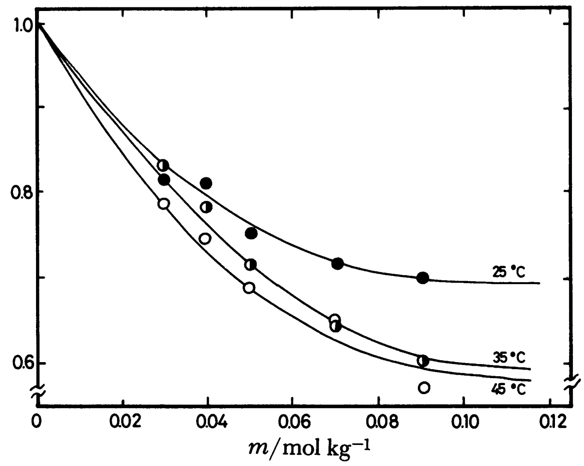

Fig. 1. Relation between osmotic coefficient and concentration for DM-β-CD at various temperatures. ●: 25 °C, ◑: 35 °C, ○: 45 °C.

$$\phi_{25} = 1 - 6.73\,\mathrm{m} + 37.4\,\mathrm{m}^2,$$

$$\phi_{35} = 1 - 7.07\,\mathrm{m} + 28.0\,\mathrm{m}^2, \tag{1}$$

and

$$\phi_{45} = 1 - 8.49\,\mathrm{m} + 44.4\,\mathrm{m}^2.$$

The activity coefficient is calculated from Eq. 2.

$$\ln\gamma = (\phi - 1) + \int_0^m \frac{\phi - 1}{m}\mathrm{d}m \tag{2}$$

Introducing Eq. 1 into Eq. 2 and integrating, we obtain

$$\ln\gamma_{25} = -\ 13.5\,m + 56.6\,m^2,$$

$$\ln\gamma_{35} = -\ 14.1\,m + 42.0\,m^2, \tag{3}$$

and

$$\ln\gamma_{45} = -\ 17.0\,m + 66.6\,m^2.$$

The activity coefficient vs. m curves are shown in Fig. 2.

The excess thermodynamic quantities are calculated from Eqs. 4, 5, and 6

$$G^{\mathrm{ex}} = mRT(1 - \phi + \ln\gamma), \tag{4}$$

$$S^{\mathrm{ex}} = -\left(\frac{\partial G^{\mathrm{ex}}}{\partial T}\right)_{\mathrm{p}} \tag{5}$$

and

$$H^{\mathrm{ex}} = G^{\mathrm{ex}} + TS^{\mathrm{ex}}, \tag{6}$$

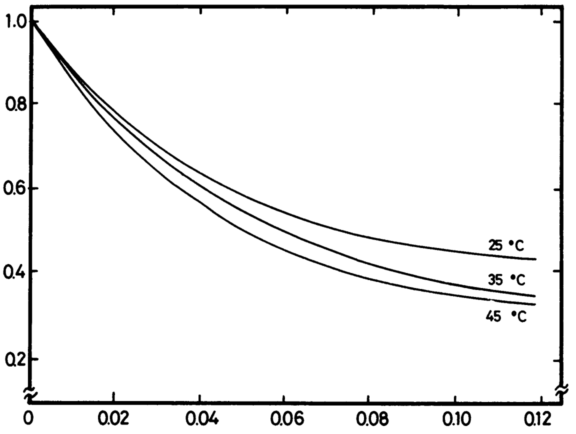

Fig. 2. Relation between activity coefficient and concentration at various temperatures.

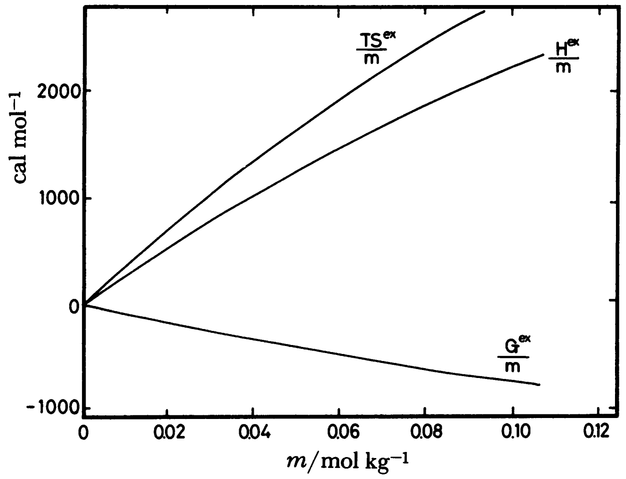

Fig. 3. Molar excess thermodynamic quantities vs. concentration curves at 35 °C. (1 cal=4.184 J)

where R and T are of usual meanings. The molar excess thermodynamic quantities are shown in Fig. 3 as a function of m.

Discussion

As shown in Figs. 1 and 2, the values of ϕ and γ decrease with increase of m. Similar trends were observed in aqueous solutions of α- and γ-CDs. But the decreasing tendency of activity coefficient with increase of m for DM-β-CD is more significant than those of α- and γ-CDs. In general, the decrease in activity coefficient with increase of m is interpreted in terms of two different effects, i.e. structure breaking effect and the association of the solutes. However, such a large decrease of activity coefficient in low concentration is more likely to take place as a results of the solute-solute interaction rather than the solute-solvent interaction. In contrast with the case of aqueous α-CD solution, the negative excess free energy of aqueous DM-β-CD solution originates from the predominance of positive entropy term over positive enthalpy as seen in Fig. 3, indicating that DM-β-CD is a hydrophobic solute like tetrabutylammonium salts.[5] The self salting-in effect based on the hydrophobic interaction among DM-β-CD molecules increase with concentration, resulting in the increase of excess entropy by the destruction of ice-berg around DM-β-CD molecules. Positive enthalpy also increases with concentration because of the melting of iceberg. But the values of TS^{ex} is larger than that of H^{ex} for the hydrophobic solute. The hydrophobic nature of DM-β-CD should be attributed to the methyl groups which locate on the outer surface of the molecule.

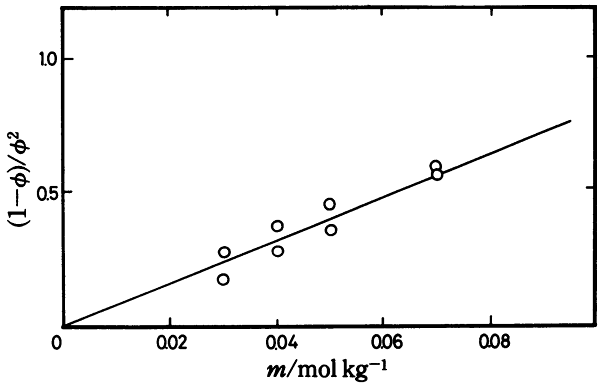

Fig. 4. $(1-\phi)/\phi^2$ vs. concentration curve at 25 °C.

By assuming that the large decrease of activity coefficient with increase of m is based on the dimer formation through hydrophobic interaction, we calculated the formation constant(K) at each temperature with Eq. 7.[6]

$$K = (1-\phi)/m\phi^2 \tag{7}$$

The relation between $(1-\phi)/\phi^2$ and m at 25 °C is shown in Fig. 4. From the slope of curve, 8.1, 11.4, and 12.5 mol^{-1}kg were obtained as the K values at 25, 35, and 45 °C. The increase of K with temperature is consistent with the theoretical results of hydrophobic interaction between leucine and isoleucine in water.[7]

In conclusion, DM-β-CD is a hydrophobic solute in contrast with α- and γ-CDs which are hydrophilic.[1]

References

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