THE EFFECT OF CARBOXYLATE ANIONS ON THE FORMATION OF CLATHRATE HYDRATES OF TETRABUTYLAMMONIUM CARBOXYLATES

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ABSTRACT. The solid-liquid phase diagrams of binary mixtures of water with tetrabutylammonium carboxylate having an unsaturated alkyl group in the carboxylate anion ((n-C₄H₉)₄NOOCR; R=C₂H₃-C₉H₁₇) were examined in order to confirm the formation of clathrate-like hydrates. The results are summarized as follows: (1) the formation of a clathrate-like hydrate is newly confirmed for all the 13 carboxylates examined; (2) these hydrates are classified into three groups I, II, and III on the basis of the hydration numbers; (3) the group I hydrates, which are formed by the carboxylates with R=C₂ and R=C₃, have hydration numbers around 30 and are the most stable hydrates among those examined in this study; (4) the group II hydrates, with hydration numbers around 39, are formed by all the carboxylates with R=C₄ and C₅ including sorbate and are less stable than the group I hydrates; (5) the group III hydrates, with hydration numbers around 30 like the group I hydrates, are formed by carboxylates with long alkyl chains such as 2-octenoate and 2-decenoate and are generally unstable.

1. INTRODUCTION

In a previous paper¹) the formation of a clathrate-like hydrate by a series of tetrabutylammonium carboxylates ((n-C₄H₉)₄NOOCR) with a saturated alkyl group in the carboxylate anion was confirmed from the solid-liquid phase diagrams and these hydrates were classified into three groups, I, II, and III, on the basis of the hydration numbers. The main characteristics for these three groups of hydrates are summarized as follows:

(1) The group I hydrates include the hydrates formed by the carboxylates with R=H, CH₃, C₂H₅, n-C₃H₇, i-C₃H₇, and t-C₄H₉. These hydrates are fairly stable. From the fact that the hydration number is around 30 the crystal structure of the hydrate seems to be isomorphous with that of a well-known tetrabutylammonium fluoride hydrate. Since high stability of the group I hydrates cannot be explained by a simple distortion effect of the anion on the hydrogen-bonded water framework within the hydrate, as discussed in the previous paper;¹ ²) it has been
concluded that such alkyl groups as CH₃, C₂H₅, and C₃H₇ are located in a vacant pentagonal dodecahedron. Similar consideration has also been proposed by Dyadin et al. on the basis of X-ray diffraction characteristics.

(2) The group II hydrates are formed exclusively by all the carboxylates with R=C₄H₉ and C₅H₁₁ except for t-C₄H₉, and have hydration numbers around 39. The crystal structure of these hydrates seems to be essentially the same as that of the tetrabutylammonium benzoate hydrate, which has an ideal composition of \((n\text{-C}_4\text{H}_9)_4\text{NOOCC}_6\text{H}_5\cdot39.5\text{H}_2\text{O}\) in which the benzoate anion is surrounded by one large water cage. From the relationship between the melting points of the hydrates and the shape of an alkyl group in the carboxylate anion, it has been concluded that the methyl group attached to the carbon atom of 2-position causes a considerable distortion in the hydrogen-bonded water framework.

(3) The formation of a clathrate-like hydrate for the tetrabutylammonium carboxylates with long alkyl chains ranging from n-C₅H₁₃ to n-C₁₀H₂₁ is clearly confirmed from the phase diagrams. These hydrates are classified as the group III hydrates. The hydration number is around 30, just as in the group I hydrates, and the melting points are very low. From the fact that the hydration number is around 30, the possible crystal structure of these hydrates will be that they are isomorphous with \((n\text{-C}_4\text{H}_9)_4\text{NF}\) hydrate and the long alkyl chain in the carboxylate anion penetrates into two (or three) pentagonal dodecahedra which are face-sharing with each other.

In this paper new results for a similar type of investigation about unsaturated carboxylates are presented and discussed from a similar point of view. The main objectives of this investigation are (1) new confirmation of the formation of a clathrate-like hydrate of tetrabutylammonium unsaturated carboxylates and (2) an examination of the influence of the presence of a double bond in the alkyl group of the carboxylate anion (such as the change in chain length, the decrease in chain flexibility, and the decrease in the number of hydrogen atoms) upon the stability of the hydrate in comparison with the case of the saturated carboxylates briefly summarized above.

2. MATERIALS AND METHODS

An aqueous solution of tetrabutylammonium unsaturated carboxylates was prepared by a reaction between tetrabutylammonium iodide and silver carboxylate in water, followed by filtration of AgI precipitate. Tetrabutylammonium iodide was synthesized by reacting tributylamine with butyl iodide in ethyl acetate and was purified by recrystallization from ethyl acetate-acetone mixture. Since the solubilities of the silver carboxylates used in water are fairly low (for example, at 25°C, 1.30wt% for CH₂CHCOOAg, 0.29wt% for CH₃CHCHCOOAg, and 0.021wt% for CH₃-(CH₂)₆CHCHCOOAg), these silver salts can be obtained as a precipitate by mixing silver nitrate solution with an aqueous solution of sodium carboxylate, which was prepared beforehand by neutralization of the corresponding carboxylic acid with sodium hydroxide, followed by repeated washing with water to remove the resultant sodium nitrate.