EFFECTS OF HYDROPHOBIC INTERACTION IN 
n-ALKANECARBOXYLATE HYDRATE MELT

Shigehito DEKI, Hiroshi NAKAHARA, Junji KONDO, and Akihiko KAJINAMI

Department of Chemical Science & Engineering, 
Faculty of Engineering, Kobe University 
Rokkodai-cho, Nada-ku, Kobe 657, Japan

Ultrasonic velocity, $u$, and adiabatic compressibility, $\beta$, were measured for sodium $n$-alkanecarboxylate hydrate, $C_nH_{2n+1}COONa$, melts ($n=0$-$4$). The maximal value of $u$ and minimal value of $\beta$ were observed in a systems except that of sodium formate hydrate at the composition range of $R=[H_2O]/[salt]=4$-$20$. The linear relationships were obtained between these values and the alkyl chain length, $n$. Because these maximal or minimal values were not observed for the systems containing the salts without hydrophobic groups, this composition dependence seems to be related to the hydrophobic hydration in hydrate melts. The several systems containing alkali metal $n$-alkanecarboxylate hydrate melts were measured. However, the differences of values of $u$ and $\beta$ caused by the difference of cation species were smaller than those by anion. Consequently, the hydrophobic effect caused by $n$-alkyl chain was dominant for the interactions among the dissolved species in these systems.

INTRODUCTION

A large amount of research has been done on hydrophobic interaction among nonpolar molecules or nonelectrolyte molecules with comparatively simple structure (1). Those hydrophobic effects in monohydric-alcohol solutions lead to a large negative excess entropy of mixing, a positive heat capacity of solution, and a negative excess partial molar volume of alcohol. These results suggested that hydrophobic groups form the voluminous cage structure with hydrogen bonding effect, which causes the anomalous properties of water at higher temperature range. Organic molten salts show most distinctive physicochemical properties, in case that the ratio of ionic charge to the total number of atoms in the ion is fairly high. In this case, strong primary electrostatic forces among the ionic species are not highly shielded by the organic part in the ion. Ionic interactions in these systems have some influence on the hydration. However, few kinds of electrolyte solution have been investigated sufficiently.

Electrochemical Society Proceedings Volume 96-7

28
Aqueous alkali metal n-alkanecarboxylate systems can cover wide composition range from aqueous solution to hydrate melt. The system keeps a stable liquid state in the relatively low water content range such as hydrate melt and even at the temperature below the melting point as a supercooled liquid. Therefore, these systems are suitable for the investigation of properties in the boundary region between the molten salt and the aqueous solution. Additionally, the n-alkanecarboxylate anion which is one of the components in these systems is different from inorganic anions in the nature, because both a hydrophilic carboxyl and a hydrophobic alkyl groups are included in their molecular structures.

We have been focusing on alkali metal n-alkanecarboxylate /water systems, which can cover widely composition range in aqueous solution and hydrate melt. Various physical properties (2) and structural analysis by X-ray diffraction (3) have been reported for the system containing alkali metal acetate and water in a wide concentration range between dilute aqueous solution and hydrate melt. Formate, acetate, propionate, butyrate, and valerate ions were chosen as anions in order to discuss hydrophobic interactions in the highly concentrated solution and the hydrate melt. Changing the alkyl chain length in n-alkanecarboxylate anions gives some information regarding the effect of the hydrophobic interaction in the system.

For these systems, the ultrasonic velocity were measured and the adiabatic compressibility was calculated in the wide composition range. The effect of the anionic hydration condition is discussed for several kinds of n-alkanecarboxylate ions.

**EXPERIMENTAL**

**Preparation of Samples**

Several kinds of sodium n-alkanecarboxylate hydrate melt were prepared. Component table of cation and anion is shown in Table 1. Double distilled water was used for dissolving and diluting. As a reference, aqueous sodium chloride solution was prepared. These samples were filtered with a sintered glass filter through a hot funnel in order to eliminate precipitations and solid impurities. The concentration was determined by the gravimetry. Concentration of each solution was represented by the molar ratio; \( R = \frac{[\text{H}_2\text{O}]}{[\text{salt}]} \). Though the concentration ranges depend on the solubilities, it was concentrated enough to discuss in this study. The values of \( R \) ranged from ca. 2 to 50 for most of the system containing hydrate.

**Ultrasonic Measurement**

A send-receive type ultrasonic cell equipped with an x-cut quartz crystal as a transducer was used for the measurement of ultrasonic velocity in the sample liquid. The schematic drawings of block diagram are shown in Fig.1. Model UAC-77-S ultrasonic attenuation comparator (Teitsu Denshi Kenkyusho Co. Ltd.), model UAC-77-012 synchronous divider (Teitsu Denshi Kenkyusho Co. Ltd.), and DL2120 digital oscilloscope (Yokogawa Denki Co. Ltd.) were assembled for the measurement of the ultrasonic velocity. The path-length of the ultrasonic wave was adjusted with a micrometer. In order to prevent contamination caused by cell components, most of parts contacted with liquid were made of glass and polytetrafluoroethylene. Ultrasonic velocity was directly obtained from the delay time.
required for the propagation of the pulsed ultrasonic wave with the variation of the path-length. All measurements were carried out at a frequency of 10 MHz and in the temperature range between 30 and 65°C. The temperature of the sample was controlled within ±0.1°C of each designated temperature by immersion of the ultrasonic cell in a water bath.

Calculation of Adiabatic Compressibility

Adiabatic compressibility, $\beta$, is given by the Eq. [1].

$$\beta = \frac{1}{d} \frac{dt}{v^2}$$  [1]

where, $d$ is the density of the hydrate. In order to calculate $\beta$, the density of the hydrate melt should have been measured. The density was measured by the Archimedean method weighing a ceramic sinker with an electronic balance.

RESULTS AND DISCUSSION

Ultrasonic Velocity

Composition dependence of the ultrasonic velocity was observed for the ultrasonic velocity in sodium $n$-alkanecarboxylate hydrate as shown in Fig.2. For the system containing sodium formate only, the ultrasonic velocity increased as the water content decreased simply, as well as the dependence for the system of aqueous NaCl solution. For the other systems, $\text{C}_3\text{H}_6\text{COONa-H}_2\text{O}$, $\text{C}_2\text{H}_5\text{COONa-H}_2\text{O}$ and $\text{n-C}_3\text{H}_9\text{COONa-H}_2\text{O}$, which have hydrophobic parts in themselves, each composition dependence of ultrasonic velocity showed a maximal value. In the composition range of $R$>25, those four systems having a hydrophobic parts showed nearly similar values at the same water content. In the range of $R$<25, the longer the $n$-alkyl chain length was, the more gently the curve rose toward the maximal. Ultrasonic velocities for the systems having hydrophobic parts were larger than that of the system without hydrophobic group in the composition range at $R$>25, where water molecules are considered to exist enough to form the hydration structure.

Adiabatic Compressibility

Calculated adiabatic compressibility, $\beta$, are shown in Fig.2. As well as the results of the ultrasonic velocity, these composition dependences were classified in two groups based on the structural difference of ions. The compressibility decreased simply as the water content decreased for the system containing sodium formate. Based on the hydrate structure of formate acid, formate anion forms hydration structure with six water molecules (4). In dilute concentration range of sodium formate solution, this bulky cluster may lead to larger adiabatic compressibility in HCOONa-H$_2$O than that in the other sodium n-alkanecarboxylates. For the system containing the anion having hydrophobic groups, the minimal values of the compressibility were observed and increased as the alkyl chain length increased.

We also measured the temperature dependence of the adiabatic compressibility. In the higher concentration range of $R$ (dilute range), the value of $\beta$ has a minimal point around 40°C. However the linear relationship between the compressibility and temperature was observed at a range lower than $R$ at which the compressibility has the minimal value. This
results also suggested that the hydration structure changed at this concentration range.

The values of $\beta$ were ranged at $2 \cdot 4 \times 10^{10}$ Pa$^{-1}$. These values were smaller that that of the adiabatic compressibility in aqueous media forming a hydrogen bonding network such as water ($4.2 \times 10^{10}$ Pa$^{-1}$ at 60°C) and acetic acid ($7.0 \times 10^{10}$ Pa$^{-1}$ at 60°C). This result indicates that the hydrophobic group influences the water-water interaction and forms the hydrophobic hydration.

The adiabatic compressibility decreased gradually as n-alkyl chain length increased from CH$_3$COONa-H$_2$O to C$_4$H$_9$COONa-H$_2$O in composition range of $R > 30$. Also, the values of adiabatic compressibility for these four systems were clearly smaller than those of NaCl-H$_2$O and HCOONa-H$_2$O systems which do not include the hydrophobic group. It is considered that an increase of the region of hydrophobic hydration lead to expansion with the alkyl chain length. An adiabatic compressibility showed the minimum value for each system containing the ion having hydrophobic part, such as C$_n$H$_{2n+1}$COONa (n=1-4). The composition range in which minimal values appeared increased as the alkyl chain length, as well as the variation for the ultrasonic velocity. In the following section, the effect of hydrophobic part of alkyl chain in the alkanecarboxylate ions are discussed.

Hydrophobic Effect

In the composition range of $R < 25$, different composition dependences appeared as shown in Fig.2 and 3. It is considered that the number of water molecule is not enough to make hydration structure and ion-water interactions and cation-anion interactions become dominant. In this composition range, at first, the number of water molecules which correlated to anion-water interactions decreases as water content decreased toward the minimal point of the adiabatic compressibility. An contribution of water-water interaction to ultrasonic velocity will be quite small due to a lack of water molecules in the solution. Considering the above results, the n-alkyl chain length may significantly influence the interactions among the dissolved species in a hydrate melt structure.

The minimal point of the adiabatic compressibility for each system appeared at higher water content with an increase of n-alkyl chain length in an anion as shown in Fig.4. These plots show a linear relationship of which gradient, $R/\text{C-atom}$, is ca. 4.7. This clear dependence suggests that this value is related to anion-water interaction, especially, between one-methylene group and water. The minimal points may appear at the composition at which the hydrophobic hydration of individual n-alkyl group-water interaction cannot be kept. The larger the n-alkyl chain length in the anion is, the more dominant the hydrophobic interactions may be in the melt, because the maximal ultrasonic velocity decreased in the increase of n-alkyl chain length. It is considered that an increase of the number of C-atoms caused that water molecules enter to the compressible part in the hydrate melt at the minimal point of adiabatic compressibility. Those water molecules in hydrate melt may form voluminous structure which have low energy of configurations such as the structure of ice (5). Consequently, it is concluded that the hydrophobic groups occupy large part of the hydrate melt and interactions in hydrate melt are related to the hydrophobic hydration of the alkyl groups.

In this composition range, in which hydrate melt exists, the ultrasonic velocity rapidly decreased as water content decreased. The size and chemical nature of the surfactant
hydrophobic n-alkyl chain have an important bearing on the magnitude of the critical micelle concentration, CMC. The values of CMC for this aqueous sodium n-alkanecarboxylate media represent that the hydrophobic and hydrophilic parts assemble the micelle structure. The values of CMC in the reference corresponded to the values of $R$ in which the maximal values of the ultrasonic velocity was obtained in this study (6). It is suggested that the micelle structure was formed and the phase separation between hydrophilic and hydrophobic parts occurred in these liquid media and related to the ultrasonic phenomena.

**Effect of Hydration of Cationic Species**

As mentioned above, the hydrophobic hydration effect of anion was dominant for the aqueous n-alkanecarboxylate. In order to support this result, we discuss the cation effect on the hydration phenomena in the viewpoint of ultrasonic properties. The variations of the ultrasonic velocities and the adiabatic compressibility with the composition ratio, $R$, are shown in Fig.5. Though values for the three kinds of hydrate melt are different at the same value of $R$, the minimal points of compressibility were close values among these systems. For the other systems containing the n-alkanecarboxylate, the same tendencies were observed. As described in previous section, the relationship between the values of $R$ at the minimal point of adiabatic compressibility and the number of C-atoms in the n-alkyl chain of carboxylate anion is shown in Fig.6. Linear relationships are observed for each kind of carboxylate. However, the difference among the cationic species are quite smaller than those of anions. Therefore, cationic species have a smaller effect in these systems than the anionic hydrophobic hydration in the alkali metal n-alkanecarboxylate hydrate.

**CONCLUSIONS**

The ultrasonic velocity and adiabatic compressibility were measured for the various kind of alkali metal n-alkanecarboxylate hydrates. The maximal value of the velocity and the minimal value of the compressibility were obtained for the system containing the anion having a hydrophobic part in itself. These results suggested that the phase separation related to molecular hydrophilicity occurred in the hydrate. The effect of hydrophobic hydration was larger than that of the cationic hydration in the alkali metal n-alkanecarboxylate hydrate melt.

**REFERENCES**

1) F. Franks and D. J. Ives, *Rev. Chem. Soc.*, **20**, 1 (1966).
2) S. Deki, T. Inuzuka, H. Nakahara, A. Kajinami, and Y. Kanaji, Proceedings of the Fourth Japan-China Bilateral Conference on Molten Salt Chemistry and Technology, p. 154, Kyoto (1992).
3) A. Kajinami, T. Otsuka, S. Deki, and Y. Kanaji, ibid, p. 142, Kyoto (1992).
4) R. P. Varma and A. Kumer, *Tenside Surf. Det.*, **29[5]**, 359 (1992).
5) A. Shi, J. V. Ford, S. Sei, and A. W. Castleman, Jr, *J. Chem. Phys.*, **99**, 8009 (1993).
6) I. J. Lin, *Soc. Mining Eng., AIME*, **250**, 225 (1971).
## Table I. Component table of cation and anion of prepared samples.

G.R.: anhydrous guaranteed reagent purchased. NTRL: neutralized from corresponding acid and hydroxide. All of reagents were guaranteed reagent.

| Cation | Anion | Formic | Acetic | Propionic | n-Butyric | n-Valeric |
|--------|-------|--------|--------|-----------|-----------|-----------|
| Li⁺    | —     | G.R.   | —      | NTRL      | NTRL      | —         |
| Na⁺    | G.R.  | G.R.   | G.R.   | NTRL      | NTRL      | —         |
| K⁺     | —     | G.R.   | NTRL   | NTRL      | —         | —         |

---

![Block diagram of the pulse method for measurement of ultrasonic velocity.](image-url)

**Fig. 1.** Block diagram of the pulse method for measurement of ultrasonic velocity.

![Composition dependence of the ultrasonic velocity for sodium n-alkanecarboxylate hydrate and sodium chloride systems at 60°C.](image-url)

**Fig. 2.** Composition dependence of the ultrasonic velocity for sodium n-alkanecarboxylate hydrate and sodium chloride systems at 60°C.
Fig. 5. Variations of (a) the ultrasonic velocities and (b) the adiabatic compressibilities with the compositions for the alkali metal acetate hydrate melt at 60°C.

Fig. 6. Relationships of $R$ at the minimal points of the adiabatic compressibilities with the number of C atoms in the alkyl chain of the carboxylate anion for the alkali metal $n$-alkanecarboxylate hydrate melt.
Fig. 3. Composition dependence of the adiabatic compressibility for sodium n-alkanecarboxylate hydrate and sodium chloride systems at 60°C.

Fig. 4. Relationship of $R$ at the minimal points of the adiabatic compressibility with the number of C-atoms in the n-alkyl group of carboxylate anion for $C_nH_{2n+1}COONa\cdot H_2O$ (n=1-4).