CHEMISTRY LETTERS, pp. 1015-1018, 1976. Published by the Chemical Society of Japan

THE ASSOCIATION OF i-BUTYRATE AND TRIMETHYLACETATE IONS IN WATER

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The electric conductivities of sodium i-butyrate and trimethylacetate were measured in water at 25°C. It was shown that the molar conductivities of both solutions reach a maximum at a concentration of about 1 mol m^{-3} (McBain effect), and that the hydrophobic interaction of i-butyrate and trimethylacetate ions is so strong that these ions form a dimer.

Many investigations have been made on the hydrophobic interaction between organic ions or molecules in aqueous solution, because hydrophobic interaction contributes significantly to their behavior in aqueous solution. One of the important findings is that the reversible association of long apolar chain molecules or ions, such as those of surfactants, depends mainly on hydrophobic interaction.

Franks and Smith1) suggested that in aqueous solution of isomeric butanols long-range hydrophobic interaction persists even when the solution is very dilute. Recently, Dashevsky and Sarkisov2) showed that hydrophobic interaction operates between two methane molecules even if they are greatly apart. Therefore, association by hydrophobic interaction is expected to occur even in organic ions that have a small molecular weight. In the present study we estimated the association of the sodium salts of i-butyric and trimethylacetic acids (Nai-BuA and NaTMA) in aqueous solutions at 25°C by measuring their electric conductivity, for changes in the association of organic ions in a very dilute solution are reflected sensitively in electric conductivity.

Trimethylacetic and i-butyric acids were neutralized with NaOH (Merck, G.R.).

These salts were recrystallized five times from ethanol. Deionized and distilled water was used; its electrolytic conductivity was approximately 1 x 10^{-6} Ω^{-1} cm^{-1} at 25°C. All the solutions were prepared by weighing, all weights corrected to those in vacuum. The molar concontrations of the solutions were calculated from the densities, which were measured with a densimeter DMA 02C (Anton Paar Co.) at 25 ± 0.001°C. The conductivities were measured at 25 ± 0.001°C in an oil-bath. The measuring equipment consisted of an RC 433 oscillator (Kikusui Co.), a Jones bridge (Leeds & Northrup Co.) and a 4403A amplifier (Yokogawa-Hewlett-Packard Co.). The null detector was a 310A oscilloscope (National Co.).

The relations between the molar conductivity and the concentration of the two salts at 25°C are given in Fig. 1. The molar conductivities of both salts reach a maximum at a concentration of about 1 mol m^{-3} and then decease linearly with the square root of the concentration. The linear parts of the two conductivity curves are parallel with each other. The maximum conductivity values of Nai-BuA and NaTMA are 80.2 and 77.7 Ω^{-1} cm^2 mol^{-1}, respectively. On the contrary, the molar conductivity[3)] of aqueous solution of potassium n-butyrate follows Shedlovsky's extension[4)] of Onsager's equation, and does not show a maximum.

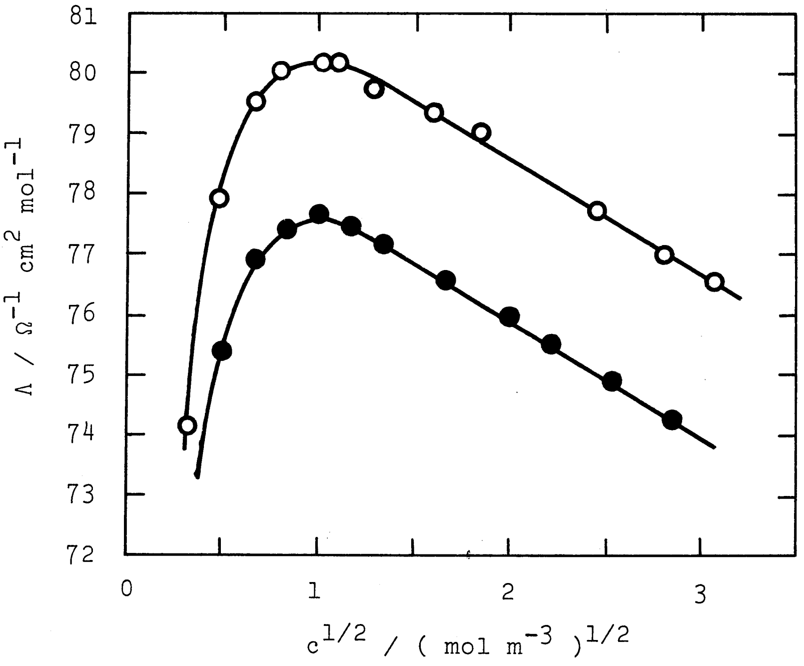

Fig. 1. Electric conductivities of sodium i-butyrate and sodium trimethylacetate in water at 25°C.
○ : sodium i-butyrate, ● : sodium trimethylacetate.

Since the mobility of an ion is proportional to z/r, where z is the charge and r the radius of the ion, it follows that Nai-BuA and NaTMA, which exist as sigle ions in very dilute solutions, associate to some extent in relatively concentrated solutions as is seen in the curves in Fig. 1, where the conductivity rises with increasing concentration. This phenomenon, which is called the McBain effect, is commonly observed in aqueous solutions of dyes,[5,6] although it has not been known in such small electrolytes. According to Robinson,[5] the increase in conductivity before the maximum is reached can only be explained by the formation of micelles that have a higher conductivity than single ions. No hydrogen bond contributes to the micelle formation of i-BuA$^-$ and TMA$^-$ ions, since both salts dissociate perfectly in aqueous solution. Furthermore, if i-BuA$^-$ or TMA$^-$ ions form a micelle by a hydrogen bond, the molar conductivity should decrease without presenting the McBain effect. As it is, hydrophobic interaction must be the primary cause of the association.

An estimate can be made of the degree of association of i-BuA$^-$ and TMA$^-$ ions at a given concentration, if the mobility at infinite dilution is available. Since it is not, there is no choice but to assume that the limiting mobility is equal to the value at the lowest concentration. Thus, the limiting mobolity of i-BuA$^-$ and TMA$^-$ ions was regarded as 24 and 23 Ω^{-1} cm^2 mol^{-1}, respectively, since that of the sodium ion is 50.1 Ω^{-1} cm^2 mol^{-1}.[7]

The molar conductivity of the sodium ion Λ (Na$^+$) at 25°C is expressed by[7],

$$\Lambda\ (\mathrm{Na}^+) = \Lambda_0(\mathrm{Na}^+) - 1.3\sqrt{c} \qquad (1)$$

where Λ_0(Na$^+$) is the limiting mobility of the sodium ion. From this, the values of molar conductivity of i-BuA$^-$ and TMA$^-$ ions at the concentration of 1 mol m^{-3} are calculated as 31.4 and 28.9 Ω^{-1} cm^2 mol^{-1}, respectively.

According to Robinson and Garrett[8], the molar conductivity of a micelle Λ (m) is expressed approximately by,

$$\Lambda\ (\mathrm{m}) = \Lambda_0\ n^{2/3} \qquad (2)$$

where Λ_0 is the limiting mobility of the single anion and n the association number. The values for the association number for i-BuA$^-$ and TMA$^-$ ions are 1.5 and 1.4, respectively. However, since the limiting mobility has been assumed, the true association number for i-BuA$^-$ and TMA$^-$ ions is thought to be two.

The limiting mobility of the n-butyrate ion[3] is 32.6 Ω^{-1} cm^2 mol^{-1}, and is larger than that of the i-BuA$^-$ ion, although the two ions are nearly equal in volume. Therefore, the microviscosity of water around the i-BuA$^-$ ion is larger than that around the n-butyrate ion9). This means that the terminal methyl groups in the i-BuA$^-$ ion contribute greatly to the very strong hydrophobic hydration as in isomeric butanols1).

We wish to thank Dr. Hatsuho Uedaira for her helpful discussion.

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(Received June 21, 1976)