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ELECTRON SPIN RESONANCE STUDY OF SPIN PROBES IN FROZEN AQUEOUS SOLUTIONS. II(1). ICE STRUCTURE BREAKING EFFECTS OF ALKALI HYDROXIDES

Eiji SATO, Shogo UEMATSU, and Yukio AKAHORI
Shizuoka College of Pharmacy
Oshika 2-2-1, Shizuoka 422

The ESR spectra of 12-nitroxide stearic acid (12-NS) in frozen aqueous solutions of LiOH, KOH, and CsOH with temperature are composed of a sharp triplet and a broad singlet, as the case of frozen aqueous solutions of NaOH. As radius of alkali metal ion becomes larger, the strength of breaking ice structure increases at frozen state. The ice-structure-breaking effects of alkali ions are $Cs^+ > K^+ > Na^+ > Li^+$ in frozen aqueous solutions.

It has been reported that some amounts of 12-nitroxide stearic acid (12-NS) move rapidly in frozen aqueous solutions of NaOH and the values of ΔH of the transformation from the broad singlet to the sharp triplet were calculated.1) The overlaped ESR spectra of the singlet and the triplet have been also observed in frozen aqueous solutions of LiOH, KOH, and CsOH. It has been well known that the sharp triplet is due to rapid isotropic moving of probes and the broad singlet indicates association of the probes.

The preparation of all samples and the measurements of ESR spectra were performed as before.1)

Ionic solutes exert an influence on equilibrium between the ice-like and non-ice-like forms which are present in room-temperature water.2) In this experiment alkali ions influence the equilibrium between free rotating and associated 12-NS probes in frozen aqueous solutions. Alkali hydroxides are somehow breaking frozen structure because some amounts of 12-NS molecules move rapidly in ice just the same way in aqueous solutions. Figure 1 shows plots of the ΔH versus normality of the solutions of alkali hydroxides. The values of ΔH are calculated from the intensity ratio between the sharp triplet and the broad singlet at equilibrium in ice.1) The temperature region of the overlaping of the spectra is the widest in the case of CsOH at the same concentration of alkali hydroxides in the range from 1 to 0.01N. The sharp triplet appears on the broad singlet at the lowest temperature in the case of CsOH at the same concentration of alkali hydroxides. The values of ΔH are LiOH > NaOH > KOH > CsOH at the same concentration generally. For example, the calculated values are 250, 190, 140, and 130 kcal/mol for the 0.02N solutions of LiOH,NaOH,KOH, and CsOH, respectively. Ice structure is obviously destroyed by further addition of alkali hydroxide. The temperature region becomes wider with further addition of these hydroxides and increasing radii of alkali metal ions, which means larger ice-structure-breaking effects. The values of ΔH decrease with increasing of temperature region. Therefore it is concluded that smaller values of ΔH indicate stronger ice-structure-breaking effects. As radius of alkali metal ion becomes larger, the strength of breaking ice structure

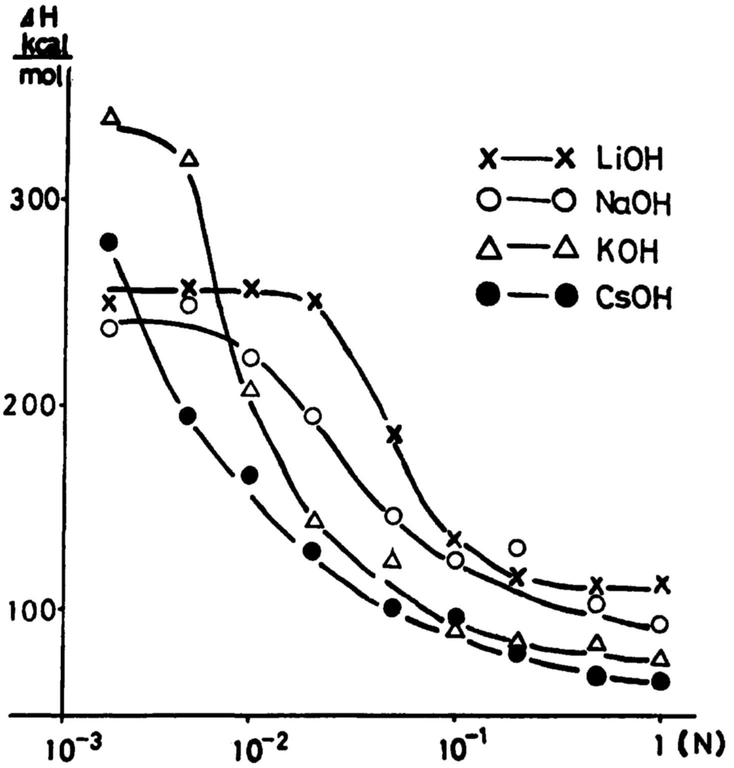

Fig.1. Plots of the ΔH vs. normality of the solutions of alkali hydroxides.

increases. The ice- structure-breaking effects of alkali ions are $Cs^+ > K^+ > Na^+ > Li^+$ at real frozen state. This tendency is concerned with size of alkali ions. This behavior has been attributed to the ability of these ions to destroy ice structure in their vicinity. The effects are analogous to the structure-breaking effects in aqueous solutions.2) Nemethy and Scheraga proposed a model for the structure of ice-like liquid water and most of all experiments were undertaken in aqueous solutions.3) But in our case the mobile molecules are observed in real frozen state of the aqueous solutions so that it is a paradoxical experimental condition at a glance. It exhibits a co-operative nature in ice. If one 12-NS molecule is able to move rapidly concerned with many water molecules in frozen aqueous solutions, it may be not so queer that large values of ΔH(70∽330 kcal/mol) calculated with such a co-operative phenomenon. The experimental errors are large at the lower concentrations of alkali hydroxide(0.005∽0.002N), because the variation of ESR spectra occurs in narrow temperature range of about 0.5°C just below the melting point. The cause of the inversion of the values of ΔH between the case of LiOH or NaOH and that of KOH or CsOH at the lowest concentration of alkali hydoxide is not cleared. This spin-probe study is a new approach to an interaction between microscopic-water-region and ice structure in frozen aqueous solutions.

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