

Some Further Results on the Concentration Dependence of Tin(IV) Isomershifts in Ice

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Sn(IV) isomeric shift in ice have been studied as a function of 1) concentration of added KF, 2) concentration of added HCl and extra IN HF, and 3) fraction of the concentrations of KCl and HCl while their overall Cl⁻ concentration is kept constant. The results show that the isomer shifts will be affected by the type and the concentration of anions but not depend on the presence of different cations.

SIGNIFICANT concentration dependence of Sn(IV) isomer shift in the ice has been observed by us⁽¹⁾. The observed results show that the isomershift will continuously changes when the anion concentration in the tin solution is changed. The amount and the direction of the change in the isomer shift due to the change of the anion concentration depends on the type of anion as well as its stability to form tinhalied complex. This result has triggered a series of questions on the factor of the change in the isomershift such as a presence of different cations (other than Sn (IV)) as well as a. different combinations of anions in the solution.

Here we report our experimental result as a part of answers to those questions. The experimental method were standard as reported in the previous paper⁽¹⁾. The various combinations of solvent in the tin solution beeing tested in this work are summarized in Table I. and Fig. 1. Those measurements could be divided into three groups :

The first one has only one extra solvent KF in 0.22M SnCl₄·5H₂O solution and the concentration of KF is changed from 0.5N to 2N. The results shows monotonic decrease in the isomershift. In the Fig. 1 the changes of the isomershift with respect. to the concentration of various solvents are shown. And the figure is essentially a supperposotion of the Fig. 2 in the previous paper") and the present results. Previous results are shown in thin curves labeled [HBr], [HCl], [Sn Cl₄] and [HF], whereas present results are drawn by medinm and heavy lines with experimental points labeled [KF], and IN HF+[HCl]. From curves [HF] and

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Table I. Isomershift of various freezing solutions

0.22M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution plus	Isomershift (mm/sec) (Ca_2SnO_4 as the host crystal of the source)
0.5N KF	-0.11
1.0N KF	-0.13
1.5N KF	-0.22
2.0N KF	-0.33
2N KCl	-1.69
1N KCl-1N HCl	-1.62
0.5N KCl-1.5N HCl	-1.63
1N HF+ 2N HCl	-0.11
1N HF+ 4N HCl	-0.08
1N HF + 6N HCl	+0.23
1N HF + 12N HCl	+0.42

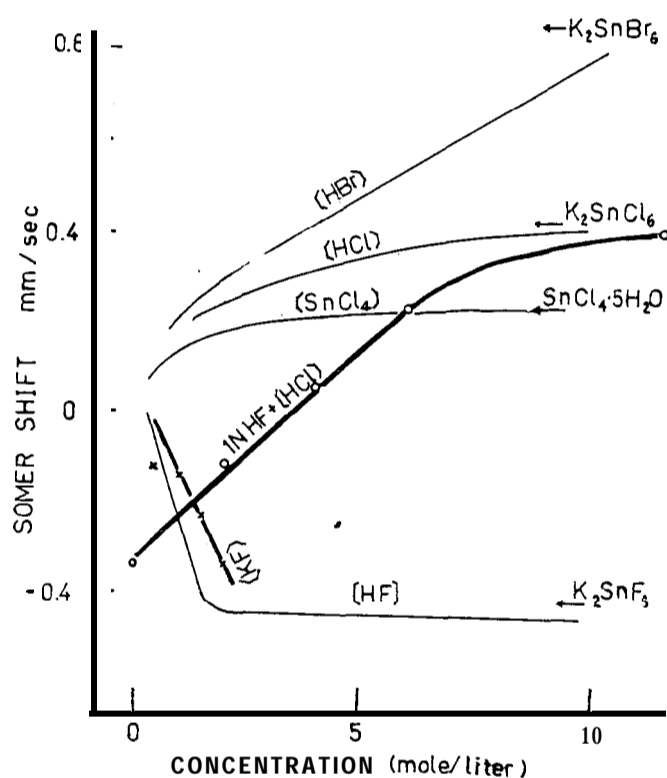


Fig 1. Curves showing the variation of the isomer shifts as a function of the concentrations of the indicated solvents. The label IN + [HCl] indicate that the isomer shift was measured with 0.2% molar SnCl_4 mixed one normal HF plus increasing amount of HCl solvent in the solution. The labels [KF], [HF], [HCl], and [HBr] are the curves indicating the variations of the isomer shift of 0.22 molar SnCl_4 and added different concentrations of indicated solvents. [SnCl_4] was obtained by varying the concentration of SnCl_4 in pure water. Arrows give isomer shifts of those indicated chemicals for comparison.

curves [KF] we see that the change due to the variation of KF concentration resembles to that of HF.

The second series of the experiment consists of three measurements. Here, we use HCl and KCl as two extra solvent in the 0.22 M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution, and with keeping Cl^- concentration constant, the ratio of KCl and HCl concentrations is varied. The isomershifts of those experiments are almost the same. Those results shows that the presence of different kinds of cations do very small (if there is any) influence on the isomershift on Sn cation.

In the third experiment we have changed HCl concentration in the 1N HF plus 0.22M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution. From the Table I and the Fig. 1 we see again continuous variation of the isomershift against HCl concentration. Moreover, the isomershift reaches to negative side and indicates that Sn(IV) cation experiences strong influence from the F^- anion even when the Cl^- concentration is four time greater than that of F^- . The fact agrees with the argument that the stability of the formation of SnF_6 is much higher than that of SnCl_6 .

From those experiments we could concluded that:

- (1) the presence of different kind of cation do not give influence on the isomershift of the freezing solution.
- (2) the isomershift changes continuously against the change on the anion concentration.
- (3) And the amount of the change in the isomershift depend not only on the concentration and their ratio of the concentrations of different kind of anions, but also on the chemical properties of those anions.

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