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Tri-n-butyltin Fluoride. A Novel Coordination Polymer in Solution

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SUMMARY

Tri-n-butyltin fluoride dissolves in nonpolar organic solvents to give viscous solutions which are believed to contain polymeric aggregates of the organotin compound. Certain organic compounds when added to these viscous solutions can cause marked changes in viscosity. These changes have been studied to gain an insight into the structure of the aggregates.

INTRODUCTION

It is now generally accepted that in the solid state tin(IV) may form five-coordinate complexes when bound to suitable ligands. Much of this work has recently been reviewed by Davies [1] while Janssen and others [2] showed that tri-n-butyltin imidazole exists as a linear polymeric chain in solution, in toluene, as well as in the crystalline state.

The structure of crystalline trimethyltin fluoride has been shown [3] in an x-ray study, to consist of a polymeric chain of penta-coordinate tin atoms, linked by bridging fluorine atoms. Several inorganic compounds, such as molybdenum oxyfluoride [4] and rhenium oxyfluoride [5] have recently been shown to have crystal structures involving bridging fluorine atoms.

The present study resulted from the observation that tri-n-butyltin

fluoride, although insoluble in most organic solvents, would dissolve in some to give very viscous solutions. The work presented is believed to be the first evidence for the existence of bridging fluorine atoms in solution and is provided by nonspectroscopic means, in contrast to most recent studies on similar systems.

The work is presented in the same way as the earlier paper by Janssen and others [2] to enable a comparison to be made between the two systems. In the first section, a model for the structure of solutions of tri-*n*-butyltin fluoride is presented which rationalizes all the results obtained in this study. The second section deals with the effect of a wide variety of additives on the viscosity of solutions of tri-*n*-butyltin fluoride in an effort to elucidate the type of bonding occurring in these solutions.

EXPERIMENTAL

Tri-*n*-butyltin fluoride was prepared by the reaction of ammonium fluoride on bis(tri-*n*-butyltin) oxide as previously reported [6] crystallized from methanol, and carefully dried before use. All solvents were fractionated. Viscosity determinations were made at 37° in a suspended level viscometer incorporating a sintered-glass filter disk [7]. This temperature was chosen as being near to 100°F (37.7°C) used in much standard viscometric work, and was found to be a suitable compromise between the higher viscosities on the one hand or solvent evaporation on the other encountered at lower and higher temperatures, respectively.

The kinematic viscosity (ν) was calculated from the usual equation:

$$\nu = \frac{\eta}{\rho} = At - \frac{B}{t}$$

where the constants A and B were determined from measurements on liquids of known viscosity, and t was the measured time of flow. The viscosity is expressed throughout in centistokes (cSt).

The effect of certain additives on solution viscosity was investigated by shaking measured amounts of the additive in stoppered tubes with 10 ml of a solution (2 g/liter, 0.0064 mole/liter) of tri-*n*-butyltin fluoride in *n*-hexane. Solution viscosity was measured at 37° and a graph plotted of solution viscosity vs additive concentration.

RESULTS AND DISCUSSION

A. Tri-*n*-butyltin Fluoride Solutions

Tri-*n*-butyltin fluoride is insoluble in many organic solvents, but dissolves to the extent of about 2% in methanol to give nonviscous solutions. In contrast, it dissolves slowly to the same extent in carbon tetrachloride or in *n*-hexane to give very viscous solutions. The increase in viscosity with concentration for these two solvents is shown in Fig. 1.

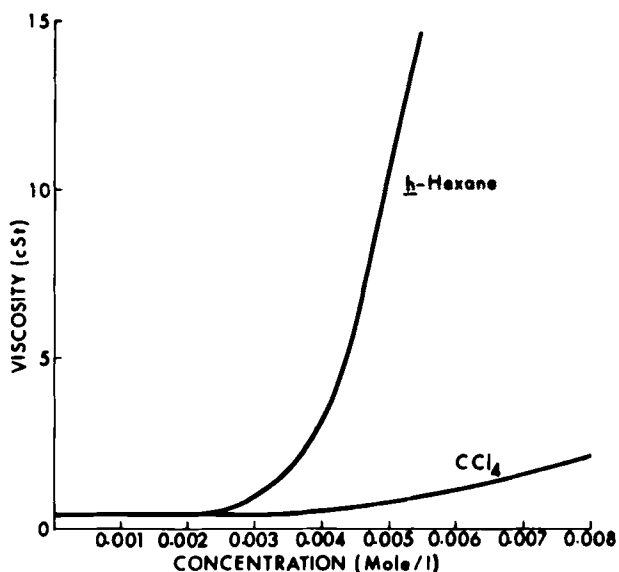


Fig. 1. Effect of concentration on the viscosity of solutions of tri-*n*-butyltin fluoride in *n*-hexane and carbon tetrachloride at 37°.

High molecular weight compounds dissolve in organic solvents to produce viscous solutions, and the viscosity increase of the solution over that of the solvent can be related to the molecular weight of the solute. This effect usually becomes apparent when the molecular weight of the solute is above several thousand [8]. We believe that the viscosity increase observed with solutions of tri-*n*-butyltin fluoride is due to the presence of polymeric aggregates of the compound in the solution. However, the increase in viscosity with concentration was so rapid that no reliable estimate of the molecular weight could be made from the solution viscosity.

The viscous solutions appear to be produced by swelling and dissolution of the organotin compound over the course of a few days. The increase in viscosity of the solution becomes apparent at a solute concentration of only 0.003 mole/liter, suggesting that even in very dilute solution the organotin fluoride is present as polymeric chains of sufficient length to significantly increase the viscosity of the solvent. Table 1 lists the properties of some solutions of tri-*n*-butyltin fluoride, of tri-*n*-butyltin imidazole and, for comparison, of polystyrene. The efficiency of tri-*n*-butyltin fluoride in producing these viscous solutions, as compared to that of tri-*n*-butyltin imidazole or of polystyrene, is evident.

The behavior of the organotin compound in solution can be explained by considering that a single isolated tri-*n*-butyltin fluoride molecule will possess a dipole moment due to the electronegativity difference between tin and fluorine. This could lead to a weak dipole-dipole type interaction between adjacent molecules, resulting in the tin atoms becoming penta-coordinate and linked through fluorine bridges in the type of structure already reported [3] for crystalline compounds such as trimethyltin fluoride. As all the organotin molecules in solution possess this dipole moment, an infinitely long, linear, polymer chain could be formed.

Solid tri-*n*-butyltin fluoride might be considered as being analogous to a two-dimensional ionic crystal lattice, but with dipole-dipole rather than ionic forces holding the molecules together in the solid state. Solvent molecules of a suitable molecular size and zero dipole moment will slowly permeate the solid to produce a viscous solution by a slow swelling process as is observed in practice. Solvents which do this are carbon tetrachloride and *n*-hexane. Other alkanes will not dissolve the compound. The structure is represented diagrammatically in Fig. 2.

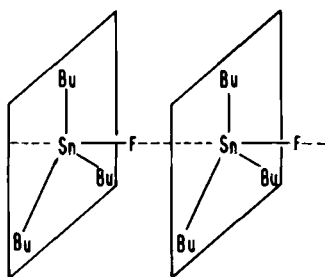


Fig. 2. Diagrammatic representation of long chains of tri-*n*-butyltin fluoride in nonpolar solvents.

Table 1. Solution Properties of Some Organotin Compounds and of Polystyrene at 37°

Compound	Solvent	Solvent dipole moment (D) [9]	Solvent viscosity (cSt)	Solution viscosity ^a (cSt)
Tri- <i>n</i> -butyltin fluoride	n-Hexane	0	0.4	300
	Carbon tetrachloride	0	0.5	200
	Tetrachloroethylene	0	0.5	190
	Trichloroethylene	0.8	0.3	0.7
	Chloroform	1.0	0.3	0.3
	1, 1, 1-Trichloroethane	1.8	0.5	2.8
Tri- <i>n</i> -butyltin imidazole	n-Hexane	0	0.4	2.4
Polystyrene	Toluene	—	0.6 ^b	1.0

^aConcentration of all solutions, 10 g/liter.^bAt 30°.

The molecular size of chloroform is similar to that of carbon tetrachloride, and it can also penetrate solid tri-*n*-butyltin fluoride to form a solution. Because it has a dipole moment it interacts with the organotin molecules to give monomers with the tin atom coordinated to the solvent rather than to another tri-*n*-butyltin fluoride molecule. The polymeric nature of the solute is thus destroyed, and the viscosity of the solution is similar to that of the pure solvent.

An intermediate form of interaction producing solvated oligomers would lead to a partial reduction in the solution viscosity. This situation exists with tetrachloroethylene and with trichloroethylene (Table 1). The former compound, which has no dipole moment, gives viscous solutions with tri-*n*-butyltin fluoride, indicating that it has a suitable molecular size, whereas trichloroethylene with a similar size, but having a dipole moment, gives a nonviscous solution with the same concentration of organotin compound.

Thus polar solvents can compete successfully with the organotin molecules for the fifth coordination position of the tin atom, as is shown in Fig. 3.

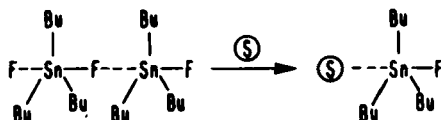


Fig. 3. Diagrammatic representation of the effect of polar solvents on the properties of tri-*n*-butyltin fluoride molecules in solution.

The behavior of tri-*n*-butyltin fluoride both in the solid and in viscous and nonviscous solutions is consistent with the reversible nature of the type of interaction suggested. It also illustrates the weakness of the bonding, whether to solvent molecules or to other molecules of tri-*n*-butyltin fluoride. The relative insolubility of the fluoride in most organic solvents is probably due to the inability of these solvents to penetrate the crystal lattice.

Although several instances have been reported where fluorine acts as a bridging atom in organometallic or inorganic compounds in the solid, this is the first time such an effect has been noted in solution. An x-ray diffraction study of tri-*n*-butyltin fluoride in the solid state, and as a viscous solution in carbon tetrachloride, has confirmed the same general polymeric structure in both states.

The interaction of organotin fluoride molecules in solution, being only

electrostatic in nature, can be easily disrupted by the addition of certain compounds, and this effect has been further investigated.

B. Effect of Additives on Solution Viscosity

When small amounts of certain compounds are added to viscous solutions of tri-*n*-butyltin fluoride in *n*-hexane (0.2%, w/v solution), a marked reduction in the viscosity of the solution can occur. By comparing the reduction in viscosity of solutions at the same molar concentration of additive, an indication of the relative complexing ability of the additive can be obtained. Complexing may take the form of the dipolar solvation noted with the halogenated solvents or the form of a specific interaction between the additive and the tin atom to give a new penta-coordinate species. Previous work [1, 6] has shown that trialkyltin halides form stable 1:1 complexes with nitrogen bases, and these complexes can, under favorable conditions, be isolated. This is the type of interaction expected to occur with tri-*n*-butyltin fluoride.

The effect of adding various compounds to viscous solutions of tri-*n*-butyltin fluoride in *n*-hexane is shown in Fig. 4. For subsequent comparisons, the viscosities of the solutions in the presence of 0.1 mole/liter of additive

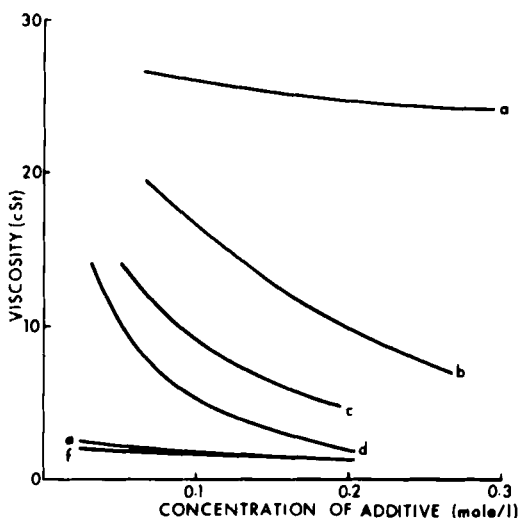


Fig. 4. Graph showing the effect of various additives on a solution (0.2% w/v) of tri-*n*-butyltin fluoride in *n*-hexane at 37°. The additives are: (a) toluene, (b) chloroform, (c) acetophenone, (d) methanol, (e) triethylamine, and (f) *N,N*-dimethyl-formamide.

were determined from graphs plotted for each additive. The viscosities of the solution without additives and of the pure solvent were 27 and 0.4 cSt, respectively.

The nitrogen-containing bases are the most effective of the additives studied in reducing the solution viscosity to that of the pure solvent. This implies that these compounds coordinate most strongly with the organotin fluoride. By comparison, other compounds such as toluene interact only very weakly with the organotin compound in solution, if at all. As the solution contains 0.0064 mole/liter of organotin fluoride, there is about a sixteenfold molar excess of the additive when used at a concentration of 0.1 mole/liter. The most effective additives, however, reduced the solution viscosity to that of the solvent at concentrations much below this, and in the case of piperidine the concentration was 0.03 mole/liter, or roughly a fivefold excess.

The effect of a range of nitrogen-containing additives on the solution viscosity of tri-*n*-butyltin fluoride in *n*-hexane is given in Table 2.

Table 2. Effect of Amine-Type Additives on Solutions of Tri-*n*-butyltin Fluoride in *n*-Hexane

Additive ^a	Solution viscosity (cSt) ^b
Solvent, <i>n</i> -hexane	0.4
Solution, no additive	27.0
<i>N,N</i> -Diethylaniline	19.5
Aniline	6.2
Triethylamine	1.0
Diethylamine	0.6
1,2-Diaminopropane	0.5
Dimethyl formamide	0.5
<i>N</i> -Ethyl formamide	0.4
Piperidine	0.4

^aConcentration of additive, 0.1 mole/liter.

^bConcentration of tri-*n*-butyltin fluoride, 2 g/liter 0.0064 mole/liter, at 37°.

All the additives capable of reducing the solution viscosity to less than 1 cSt are, within experimental error, considered to be equally effective. Substitution on the nitrogen atom in the additives by alkyl groups has little effect on the complexing ability of the compound, and this suggests that the basicity of the nitrogen is the determining factor. In aniline and diethylaniline the aromatic ring could be reducing this basicity by electron withdrawal from the nitrogen towards the aromatic ring. Amines and amides appear to be of comparable effectiveness, indicating that the extent of coordination of tri-*n*-butyltin fluoride with both these types of additives is similar.

The incorporation of the nitrogen into a heterocyclic ring system also effects the activity of the additive and the results for four such compounds are given in Table 3(A).

Pyridine is a weaker ligand than its saturated analog piperidine, whereas pyrrole occupies an intermediate position between these compounds. A comparison of the activity of pyrrole with that of furan and thiophene is shown in Table 3(B). Likewise a comparison of pyrrole with pyrrolidine and furan with tetrahydrofuran also shows that the saturated analog has the greater complexing ability. As shown in Table 3(C), amides are more effective complexing agents for tri-*n*-butyltin fluoride than ketones.

The effect of a number of halogenated compounds in reducing the viscosity of solutions of tri-*n*-butyltin fluoride in *n*-hexane has also been investigated. The results are given in Table 4, together with some reported values for dipole moments.

Additives with a large dipole moment interact with the organotin fluoride to reduce the viscosity of the solutions, whereas additives with no dipole moment, such as carbon tetrachloride and tetrachloroethylene, have little or no effect.

Within a particular series of additives an approximate correlation exists between the dipole moment and the extent to which the solution viscosity is reduced by the additive, that is, the extent to which the polymeric chains are disrupted. Carbon tetrachloride, with no dipole moment, has negligible effect, fluorotrichloromethane (dipole moment, 0.45 D) reduces the viscosity to 25 cSt, while chloroform (dipole moment, 1.02 D) reduces the viscosity even further to a value of 14 cSt.

Replacing a given atom in an additive by one of greater atomic weight gives compounds with greater effectiveness in reducing the viscosity of organotin fluoride solutions. Thus deuteriochloroform is more effective than chloroform, and tetrabromoethane is more effective than tetrachloroethane.

Table 3. Effect of Additives on Solutions of Tri-n-butyltin Fluoride in n-Hexane

A		B		C	
Additive ^a	Solution ^b viscosity (cSt)	Additive ^a	Solution ^b viscosity (cSt)	Additive ^a	Solution ^b viscosity (cSt)
Aniline	6.2	Furan	24.0	Acetone	9.3
Pyridine	2.3	Thiophene	21.0	Acetophenone	7.8
Pyrrole	1.4	Tetrahydrofuran	8.4	N,N-Dimethylformamide	0.8
		Pyrrole	1.4		
Piperidine	0.5	Pyrrolidine	0.4	N-Ethylformamide	0.5

^aConcentration of additive, 0.1 mole/liter.

^bConcentration of tri-n-butyltin fluoride, 2 g/liter, 0.0064 mole/liter, at 37°.

Table 4. Effect of Halogenated Compounds on Solutions of Tri-*n*-butyltin Fluoride in *n*-Hexane

Additive ^a	Dipole moment [9] of additive (D)	Solution ^b viscosity (cSt)
Carbon tetrachloride	0	27
Fluorotrichloromethane	0.45	25
Chloroform	1.02	14
Deuteriochloroform	c	12
Tetrachloroethylene	0	27
Trichloroethylene	0.8	24
sym-Tetrachloroethane	1.3	9
sym-Tetrabromoethane	1.7	7
1,1,1-Trichloroethane	1.8	22
1-Chlorobutane	2.1	22

^aConcentration of additive, 0.1 mole/liter.

^bConcentration of tri-*n*-butyltin fluoride, 2 g/liter, 0.0064 mole/liter, at 37°.

^cNot available.

The effects noted earlier (Section A) of the polar halogenated solvents on solution viscosity appear to be the same as when these same compounds are used as additives to reduce the viscosity of solutions of tri-*n*-butyltin fluoride in *n*-hexane. This suggests that the *n*-hexane fits into the spaces around the polymeric chain in the solid without disrupting the dipole-dipole forces that cause aggregates of the organotin fluoride to form. The addition of polar solvents to the viscous solutions disrupts the forces holding the polymeric chains together, thus splitting the chains, and this results in a reduction in solution viscosity.

The greater activity of the nitrogen-containing bases, especially those with an unhindered nitrogen atom, indicates a specific interaction in this case between the lone pair and the tin atom. The polymeric tri-*n*-butyltin fluoride in solution is broken down to a type of complexed monomer, comprising a penta-coordinated tin atom bonded to a molecule of the base, three *n*-butyl groups, and a fluorine atom.

The effect of additives on the solution properties of tri-n-butyltin fluoride dissolved in n-hexane supports the proposed polymeric structure of the compound in solution.

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