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ASSOCIATIVE ORGANOTIN POLYMERS. 2. SOLUTION PROPERTIES OF SYMMETRIC TRIALKYLTIN FLUORIDES

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ABSTRACT

The solubilities and viscosities of four novel symmetric tri-*n*-alkyltin fluorides in various organic solvents were studied. It is shown that these compounds do behave as transient polymers. Increasing the length of the *n*-alkyl chain beyond *n*-butyl imparts considerable solubility to this class of associative polymers and offers no steric hindrance to polymer chain formation. The effects of concentration, solvent type, temperature, and brine on the solution viscosities were also studied. These associative polymers effectively viscosify compressed gases (having liquid-like densities), such as propane and *n*-butane. They can therefore be used in enhanced oil recovery operations as well as in fracturing of oil wells.

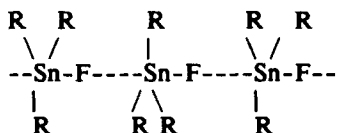
INTRODUCTION

The efficiency of enhanced oil recovery (EOR) by dense carbon dioxide (CO₂) and liquified petroleum gases (LPG) is often marred by an unfavorable mobility ratio. Mobility, in petroleum engineering practice, is defined as the

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ratio of effective permeability of a fluid in porous rock to the viscosity of that fluid. Thus, a mobility ratio greater than unity, involving the displacement of a viscous fluid by a less viscous one, is unfavorable since the frontal instability usually results in the growth of "viscous fingers" and early breakthrough of the displacing fluid. Thus, to increase the viscosity of displacing fluids, such as CO₂ and LPG, a novel approach was undertaken and is the subject of this paper.

Dunn and Oldfield [1] reported that tri-*n*-butyltin fluoride (Bu₃SnF) increases the viscosity of nonpolar solvents such as *n*-hexane and carbon tetrachloride. According to these authors, Bu₃SnF forms linear polymeric chains of infinite length by intermolecular associations. This can be represented as follows:



Since tri-*n*-alkyltin fluorides (R₃SnF) with alkyl chains lower than *n*-butyl are known [2] to be insoluble in most organic solvents, and since literature on R₃SnF compounds with alkyl chains higher than *n*-butyl is scarce, we have synthesized several novel organotin fluorides. The synthesis and characterization of four symmetric tri-*n*-alkyltin fluorides, namely triamyl, trihexyl, trioctyl, and tridecyl, were described previously [3]. This paper describes solution properties of these four symmetric R₃SnF compounds, with special emphasis on those properties important to EOR.

EXPERIMENTAL

Viscosity Measurements

The flow times for all solutions were measured in Cannon-Fenske viscometers, the dimensions of which are given in Table 1. The approximate shear rate at the wall for individual viscosity measurements was calculated by the formula

$$\gamma_w = \frac{4V}{\pi R^3 t}$$

TABLE 1. Dimensions of Cannon-Fenske Viscometers Used to Measure Viscosities

Viscometer size	Capillary diameter, mm	Bulb volume, mL	Shear-rate constant ^a
25	0.0155	1.6	547 060
50	0.022	3.15	376 662
100	0.0315	3.15	128 318
150	0.038	3.15	67 612
200	0.051	3.15	30 235
300	0.63	3.15	16 039
350	0.076	3.15	9 136
450	0.1175	3.15	2 471

^a $4V/\pi R^3$. To obtain shear rate at the wall (S_w) for individual viscosity measurements, simply divide the shear rate constant for a given viscometer by the efflux time in seconds.

where γ_w is the shear rate at the wall, V is the volume of the viscometer bulb, R is the capillary radius, and t is the efflux time. Efforts were made to use appropriate viscometers to keep the efflux time, in most cases, between 150 and 600 s.

Procedure for Studying the Effect of H₂O and Brine on R₃SnF Solutions

A 1.5% *n*-hexane (w/v) solution of R₃SnF compound was prepared in a 50-mL volumetric flask. The viscosity at 45°C was measured with a Cannon-Fenske viscometer. A 20-mL portion of this solution was transferred by pipette into a bottle with a tight-fitting cap. An equal volume of aqueous phase, either distilled water or 1% NaCl brine, was added to the bottle. The mixture was shaken vigorously by hand for 10 min and then left undisturbed for 24 h. The phase separation, however, did not require more than a few minutes, and no precipitation of solid was noticed. Most of the *n*-hexane phase was removed by pipette, and 2-mL aliquots were transferred to three

preweighed Petri dishes. The concentration of solute (presumably R_3SnF with no NaCl) in each dish was obtained after evaporation of *n*-hexane, and the mean of these readings was taken as the average concentration of R_3SnF compound in the *n*-hexane phase after treatment with the aqueous phase. The remaining amounts of R_3SnF from the three Petri dishes were combined and redissolved in *n*-hexane, giving a solution with a concentration of about 0.5%. The viscosity of this solution at 45°C was measured.

RESULTS AND DISCUSSION

Solubility

The solubility behavior of Bu_3SnF reported by Dunn and Oldfield [1] is intriguing. This compound is reported to be soluble, among *n*-alkanes, in *n*-hexane only and not in the other alkanes. The reason offered is that the molecular size of the solvent is responsible for the slow permeation into the solid, thus producing the viscous solutions by a slow swelling process. Dunn and Oldfield [1] also argued that chloroform and carbon tetrachloride are solvents for Bu_3SnF by virtue of their molecular size. On reexamination, we indeed found the solubility of Bu_3SnF in *n*-heptane to be negligible. However, it dissolved in *n*-pentane and increased its viscosity to an extent comparable to that of *n*-hexane solutions at the same concentrations. This indicated that the upper limit for the solubility of Bu_3SnF in the *n*-alkane series was C_6 and prompted us to examine its solubility in lower *n*-alkanes. We found [4] that the solubility of Bu_3SnF in *n*-butane and propane at 8.3 MPa and 25°C was in excess of 0.5%. It was, however, only sparingly soluble in ethane under similar conditions. Thus, the range of solubility for Bu_3SnF in this homologous series is from C_3 to C_6 .

Solubility data for several symmetric R_3SnF compounds in various organic solvents are listed in Table 2. The solubilities of most R_3SnF compounds were measured above the threshold concentration, which we have loosely defined as the concentration at which the viscosity vs concentration curve rises sharply. For the R_3SnF series, the threshold concentration was between 0.2 and 0.4%. It is evident from Table 2 that the solubility of R_3SnF in *n*-alkanes increases as the number of carbon atoms in the R group increases and vice versa. For example, R_3SnF compounds with chain lengths greater than *n*-butyl were soluble in normal alkanes higher than *n*-hexane as well as in many more solvents in which Bu_3SnF was insoluble. These higher R_3SnF compounds were also soluble in chloro- and bromobenzene (20%), chloroform (>10%), and amyl alcohol (<1%). These results also

show that solvation of R_3SnF does not depend on the size of the solvent molecules, as suggested by Dunn and Oldfield [1], but rather on the structure of the R group. It has been shown [3] that an increase in the chain length of the R group increases the "amorphousness" of R_3SnF . The observed solubility behavior of R_3SnF illustrates how an increase in "amorphousness" enhances the solubility in this class of compounds.

In most solvents the solubility of R_3SnF with an alkyl chain length higher than C_4 was in excess of 0.5%. However, as shown in Table 2, the solubility of these compounds in CO_2 did not exceed 0.17%, whereas a solubility of 0.3 to 0.5% would probably be needed to obtain a more than tenfold increase in the viscosity. Unlike the structure-solubility behavior observed for these compounds in other organic solvents, no such relationship was observed for CO_2 .

Viscosity

It has been known for some time that organotin fluorides of the structure R_3SnF exist in the form of pentacoordinated species, with R being independently an alkyl, alkylaryl, or aryl group. It has been suggested that such compounds, when dissolved in nonpolar solvents with negligible dipole moment, form linear, high-molecular-weight polymer chains by transient associations (weak dipole-dipole interactions) between adjacent molecules [1, 7]. The dipole moment found for these molecules has been ascribed to the difference between the electronegativity of tin and that of fluorine atoms.

Even at low concentrations, these transient polymer chains increase the viscosity of a nonpolar solvent by several times. For example [1], at a concentration of 10 g/L and at $37^\circ C$, Bu_3SnF increases the viscosity of *n*-hexane from 0.4 to 300 cSt, while that of tetrachloroethylene is increased from 0.5 to 190 cSt. The viscosity of solvents having dipole moments, however, remains relatively unaffected, irrespective of the Bu_3SnF concentration. For example [1], under the concentrations listed above, the viscosity of chloroform (dipole moment 1.0) remains at 0.3 cSt, while that of trichloroethylene (dipole moment 0.8) is only increased from 0.3 to 0.7 cSt. The reason for the lack of viscosity increase in a solvent with a dipole moment is given by Dunn and Oldfield [1] as follows. The dipole-dipole interactions between solvent molecules and tributyltin fluoride molecules deny opportunities for the solute molecules to become pentacoordinated with each other, thus preventing the formation of long polymer chains.

Having synthesized four symmetric R_3SnF derivatives, we studied the effects of solvent type, temperature, and contact with water and brine on their solution viscosities.

TABLE 2. Solubilities of R_3SnF Compounds in Various Solvents at 25°C^a

	Solubility parameter, cal/cm ³	Dipole moment, ^c D	Dielectric constant, ^c ϵ	Solvent viscosity, cSt
Carbon dioxide ^b	6.0	0		0.07
Ethane	6.0	0		0.16 ^e
Propane	6.4	0		0.22 ^e
Decane	6.6	0	1.99	1.26
Butane	6.8	0		0.27 (38°) ^e
Pentane	7.0	0	1.84	0.4
Hexane	7.3	0.08	1.89	0.4
Heptane	7.4	0	1.92 (20°)	0.6
Methylcyclohexane	7.8	0	2.02	
Cyclohexane	8.2	0	2.02	1.3 (17°)
Carbon tetrachloride	8.6	0	2.24	0.5
Cyclopentane	8.7	0	1.96	0.65 (13.5°)
Toluene	8.9	0.36	2.38	0.6 (30°)
Benzene	9.2	0	2.275	0.7
Trichloroethylene	9.2	0.9	3.42 (16°)	0.3
Tetrachloroethylene	9.3	0	2.30	0.5
Chloroform	9.3	1.0		0.3

^a0, Insoluble; X, solubility at least 0.2%; X⁺, solubility \gg 0.4%. Numbers in parentheses indicate temperatures other than 25°C.

^bThe solubility in CO₂ is expressed in g/L.

^cFrom Ref. 5.

^dFrom Ref. 1.

^eFrom Ref. 6.

Pr_3SnF	Bu_3SnF	Am_3SnF	Hx_3SnF	Dec_3SnF	Oct_3SnF
0.77	0.94	0.80	1.33	1.72	1.26
	X ⁺	X ⁺	X ⁺	X ⁺	X ⁺
	0		X ⁺	X ⁺	X ⁺
0	X ⁺	X ⁺	X ⁺	X ⁺	X ⁺
0	X ⁺	X ⁺	X ⁺	X ⁺	X ⁺
	X ^{+d}	X ⁺	X ⁺	X ⁺	X ⁺
0	0 ^d	X ⁺	X ⁺	X ⁺	X ⁺
0	0	X ⁺	X ⁺	X ⁺	X ⁺
X ⁺	0	X ⁺	X ⁺	X ⁺	X ⁺
X	X ^{+d}	X ⁺	X ⁺	X ⁺	X ⁺
0	0	X ⁺	X ⁺	X ⁺	X ⁺
0		X ⁺	X ⁺	X ⁺	X ⁺
	0				
	X ^{+d}	X ⁺	X ⁺	X ⁺	X ⁺
	X ⁺	X ⁺	X ⁺	X ⁺	X ⁺
	X ^{+d}	X ⁺	X ⁺	X ⁺	X ⁺

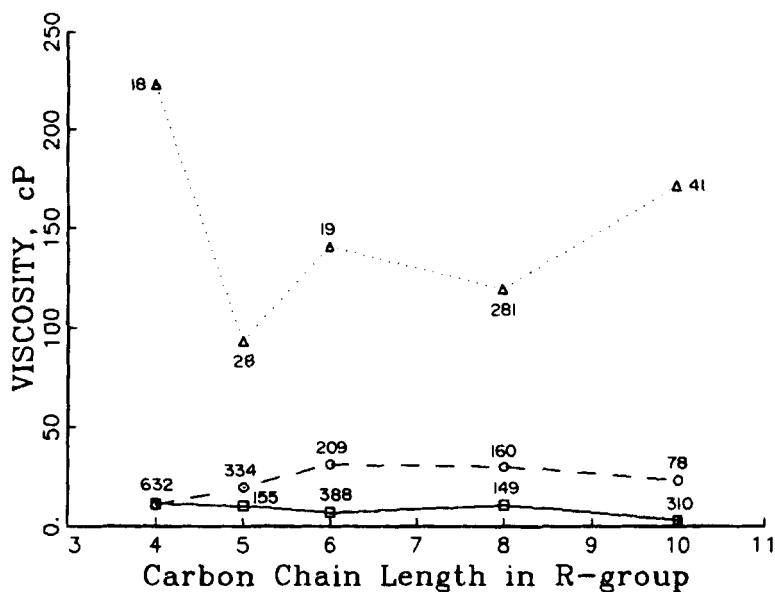


FIG. 1. Effect of carbon chain length in R group of tri-*n*-alkyltin fluorides on viscosity in different solvents. Concentration of R_3SnF 12 mmol/L; temperature 25°C. The numbers near each data point indicate the approximate shear rate at the wall. (□) Toluene, (○) carbon tetrachloride, (Δ) *n*-hexane.

Effect of Solvent Type

The viscosities of several R_3SnF compounds in three solvents are shown in Fig. 1. The viscosities of all compounds were highest in *n*-hexane and lowest in toluene, which has a dipole moment of 0.35 Debye units. However, the viscosity in toluene at the concentration used was at least ten times that of the solvent. Since different shear rates are involved in capillary viscometry, the comparison of the effectiveness of various R_3SnF species in increasing viscosity of a given solvent is only qualitative.

The viscosities of R_3SnF compounds were also tested at various concentrations in *n*-butane and propane (Figs. 2 and 3). Here "drop time of the bar" is a measure of the viscosity of the medium. The experimental procedure for the measurement of drop time [8] and the extensive mathematical treatment to calculate viscosity from the drop time [9] can be found in previous reports. The adequate solubility (and hence, viscosity) of R_3SnF in these dense gases

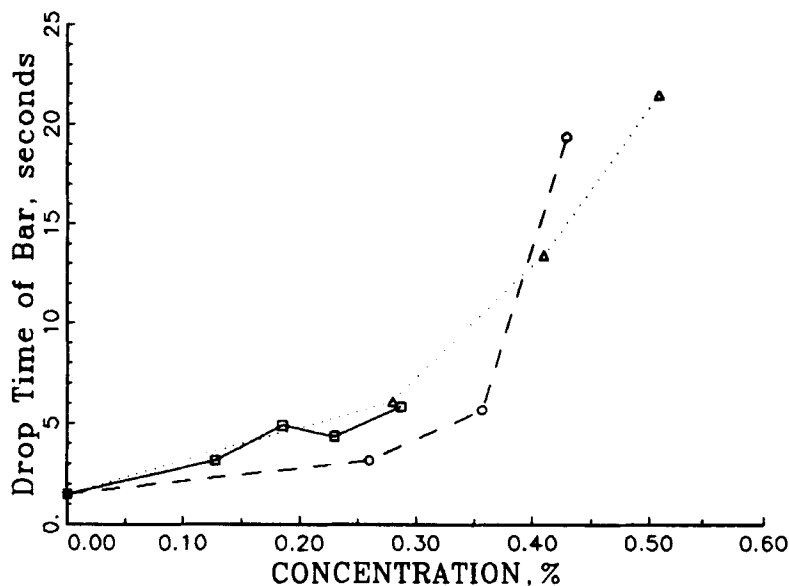


FIG. 2. Viscosity of tri-*n*-alkyltin fluorides in *n*-butane (8.3 MPa, 25°C) as a function of concentration. (□) Tributyltin fluoride, (○) triamyltin fluoride, (△) trihexyltin fluoride.

may provide applications for these associative polymers in enhanced oil recovery with LPG as well as in oil- and gas-well fracturing operations [3].

Effect of Temperature

The temperature dependence of the viscosity in hexane solutions of R_3SnF is shown in Fig. 4. At a given concentration the viscosity decreases with increasing temperature. These results concur with the well-known viscosity-temperature relationship in pure solvents as well as solutions of covalently bonded polymers.

Effect of Water and Brine

In the application of any EOR agent, a question is often raised about the agent's behavior on contact with water and brine. To answer this question with respect to R_3SnF , a series of experiments, identical except that one

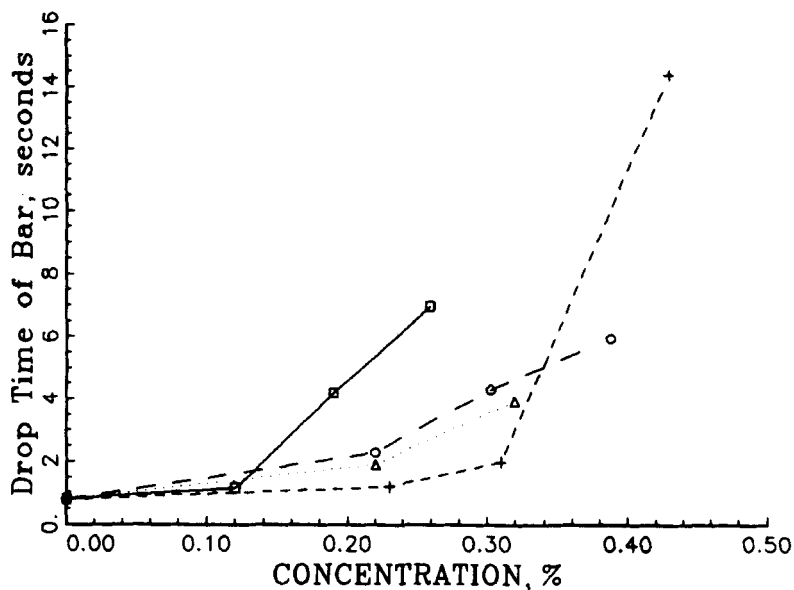


FIG. 3. Viscosity of tri-*n*-alkyltin fluorides in propane (8.3 MPa, 25°C) as a function of concentration. (□) Tributyltin fluoride, (○) triamyltin fluoride, (△) trioctyltin fluoride, (+) tridecyltin fluoride.

series involved Bu_3SnF and the other tri-*n*-octyltin fluoride (Oct_3SnF), was carried out. These two compounds were chosen as they differ substantially in the chain length of the R groups. The experimental results are condensed in Fig. 5, and the procedural details are given in the Experimental Section.

A generalized interpretation of Fig. 5 is as follows: A solution of a R_3SnF compound in a nonpolar solvent retains most of its viscosity after contact with distilled water or low-concentration brine. However, it loses much of its viscosity on vigorous mixing with a high-concentration brine. However, despite a considerable loss in viscosity on mixing with brine, the R_3SnF solution still retained a substantial viscosity (which is 10-20 times higher than that of the solvent). Also, redissolution of the precipitated R_3SnF by a fresh solvent slug should result in the enhancement of solvent viscosity. The results of these experiments offer some qualitative answers to the problems that may be encountered in the field application of R_3SnF compounds as EOR agents.

Based on the limited experimental data obtained, the following mechanism is proposed for the observed loss of R_3SnF solution viscosity on contact with

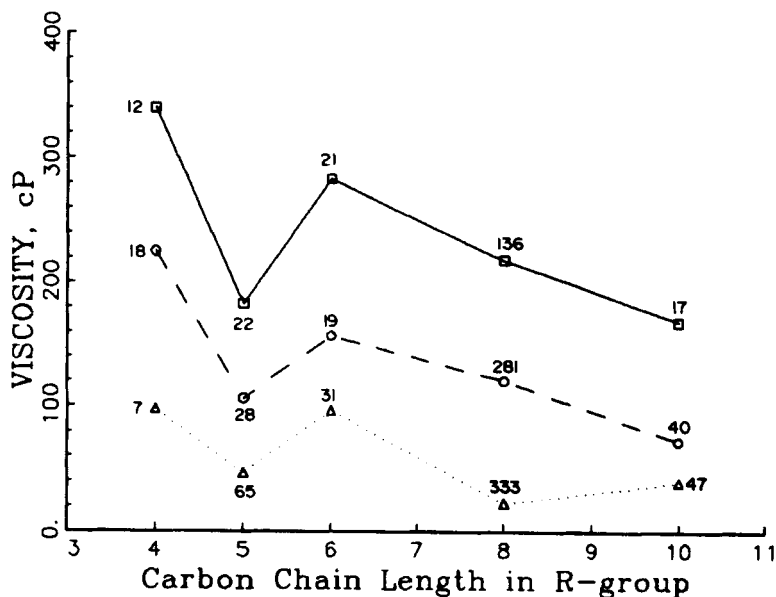
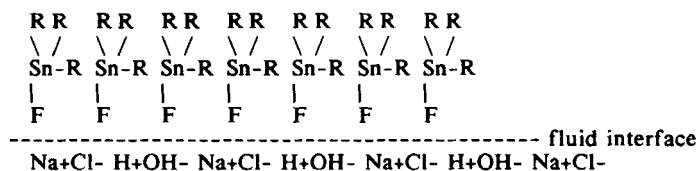
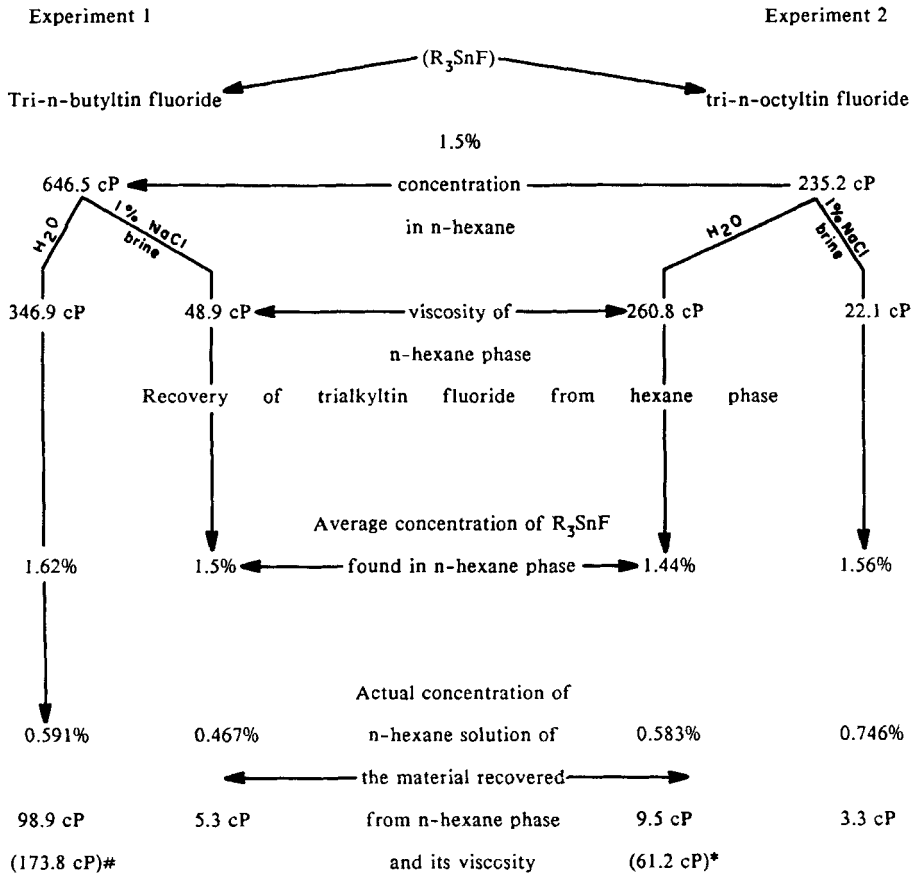


FIG. 4. Effect of temperature on viscosity of tri-*n*-alkyltin fluorides in hexane. Concentration of R_3SnF 12 mmol/L. The numbers near each data point indicate the approximate shear rate at the wall. (Δ) 35°C, (\circ) 25°C, (\square) 15°C.

brine. On mixing with brine, the polar fluorines are attracted to the polar side of the interface and thus are not available for associative bonding with neighboring Sn atoms. This can be represented schematically as



The realignment results in the reduction of the R_3SnF concentration in the bulk of the nonaqueous phase. However, the actual concentration in the nonaqueous phase remains unchanged. Several experimental observations support this argument. First, a translucent film formation (in the form of strands) was observed at the polar-nonpolar interface, especially when brine



Mixing experiments were carried out at room temperature.

All viscosities were measured at 45°C, and are expressed in cP.

Please see text for the detailed experimental procedure.

#Viscosity of untreated trialkyltin fluoride solution in *n*-hexane

*Viscosity at 35°C; the viscosity of untreated tri-*n*-octyltin fluoride at a concentration of 0.57% and 35°C is 53 cP.

FIG. 5. Plan of experiments to determine the influence of brine and water on tri-*n*-alkyltin fluorides.

was used. This is indicative of the migration of some R_3SnF molecules toward the interface. Second, in an identical but qualitative experiment performed on a highly concentrated solution (4.5%) of Bu_3SnF , some precipitation of the compound was seen at the nonaqueous brine interface.

CONCLUSIONS

The solubility of R_3SnF compounds in various organic solvents was increased considerably by increasing the chain length of the alkyl group. The work presented here has changed the long-standing concept that organotin fluorides, in general, are insoluble in most organic solvents due to their polymeric nature. It was found that these compounds effectively viscosify compressed gases such as *n*-butane and propane, which are the constituents of LPG. This effective viscosity may provide applications for R_3SnF compounds in EOR with LPG and in oil-well fracturing operations. None of the symmetrical R_3SnF compounds reported in this paper was soluble enough in dense CO_2 to increase viscosity by the amount required for use in EOR.

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