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POLAROGRAPHIC STUDIES OF SOME ORGANO-TIN COMPOUNDS IN ANHYDROUS (N,N)-DIMETHYLFORMAMIDE

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POLAROGRAPHIC STUDIES OF SOME ORGANO-TIN COMPOUNDS IN
ANHYDROUS N,N'-DIMETHYLFORMAMIDE

BY

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This dissertation has been examined and approved.

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INTRODUCTION

The purpose of this investigation was to study the polarographic behavior of some organo-tin compounds and to extend the investigation of nonaqueous polarography.

The first recorded polarographic reduction of an organo-tin compound was that of diethyltin dichloride $(C_2H_5)_2SnCl_2$ by L. Riccoboni and P. Popoff.(1) It was reduced in 1N potassium chloride with a half-wave potential of -0.574 vs. (S.C.E.), and involves a two electron change. The product was diethyltin, $(C_2H_5)_2Sn$, and was considered stable under these conditions.

Giacomo Costa(2) studied $Et_3SnCl(Br,I,F), Pr_3SnCl$ and Bu_3SnCl in 30% isopropyl alcohol and obtained three reduction waves which were usually distinguishable and separable. Coulometric analysis of the first two reduction waves at -1.1 and -1.5v., corresponded to the discharge of one and two electrons respectively. The first was postulated to be the formation of hexaalkylditin. The second step was reported to be the reduction of the tetravalent tin to the divalent tin. No analysis was made concerning the third reduction.

V. F. Toropova and M. K. Saikina(3) studied similar compounds in 40% aqueous ethyl alcohol solutions of varying pH. One and two waves were observed. The presence

and absence of maxima in the waves appeared to depend on the concentration and pH. The ease of reduction was dependent upon the radicals in the order ethyl > propyl > butyl. The position of the methyl compounds varied with conditions. Increasing the number of radicals in the molecule made the potential more negative. R_4Sn compounds were not reducible.

More recently Saikina(4), using an oscillographic polarograph, obtained data on the reversibility of the above organo-tin compounds in acidic and basic media. In all cases the reductions were irreversible, ranging from 91.3% for Et_2SnCl_2 in 0.1N NaOH to 73% for Et_3SnCl at a pH of 1.

Because of the decreasing solubility of the organo-tin compounds with increasing size of the organic radicals and the reaction of these compounds with water, a nonaqueous solvent was required.

Anhydrous ethyl acetate and N,N'-dimethylform-amide, hereafter called DMF, were both tried but due to low solubility of supporting electrolytes and consequently a high (11,000 ohms) resistance, ethyl acetate was not used. The use of DMF as a polarographic solvent has become quite common.(5-10) It has a high dielectric constant(36.7 at 25°), a convienient liquid range (freez-ing point -63°, boiling point 153°), a relatively low

viscosity (0.802 cp at 25°) and a low vapor pressure
(3.7mm at 25°),all of which are good properties for a
polarographic solvent. The physiological properties are
such that certain precautions should be taken for its
use.(11)

EXPERIMENTAL

Instrumentation. All polarograms were obtained with a Sargent Model XXI Polarograph. The electromotive force recorded by the instrument was checked with a Leeds and Northrup K-2 potentiometer. The half-wave potentials, $E_{\frac{1}{2}}$, were calculated directly from the polarograms by the method described by Willard, Merritt, and Dean.(12) A second determination of $E_{\frac{1}{2}}$ was made on some polarograms by making the log $1/(i_d-1)$ vs. E plot. The resistance of the cell containing 0.1M tetra n-butyl ammonium perchlorate in DMF, as measured with an Industrial Instruments Inc. conductivity bridge Model RC-16B1, at 1000 cps, was a maximum of 500 ohms. In order to have continuity of results all runs were made with a 1000-ohms resistor inserted in the galvanometer circuit, i.e. dampening position #2 on the polarograph. The total resistance in the current measuring circuit had a maximum value of 1500 ohms. Because of this resistance, corrections were made for iR drop when the current became greater than 1×10^{-6} amps. or 1 microamp.(ua)

All diffusion currents were corrected for the residual current. At potentials more negative than -1.5v. the residual current became sufficiently large to alter the wave form. The cathode was a dropping mercury electrode and the anode a quiet mercury pool. The half-

wave potentials were measured against the mercury pool as the nonpolarized electrode.

Maxima in the polarograms were frequently observed, especially at higher concentrations of reducible ions. Polarograms could be obtained for all compounds at sufficiently low concentrations where no maxima were observed. No maxima suppressors were used because of previous experimental work which indicated them to be ineffective.

The dropping mercury electrode was a Sargent 2-5 second capillary, 14.1cm. long, operated at 56.5 cm. of mercury, with a drop time of 4.1 seconds (open circuit) in 0.1M tetra n-butyl ammonium perchlorate. The $m^{2/3}t^{1/6}$ value was 1.596 $mg^{2/3}sec.^{-1/2}$.

Four different cells were used in this study; (a) Sargent electrolysis vessel 30 mm, 5 ml, Number S-29370, (b) Sargent electrolysis vessel, "H" type, Number S-29400, (c) Sargent microelectrolysis vessel, Number S-29376 and (d) Sargent electrolysis vessel, 2 section, Number S-29385. Cells (a) and (b) were used to study the reference electrode, i.e, the mercury pool. Cell (c) was initially used for the concentration experiments but due to the large mercury flow, which quickly covered the nitrogen inlet tube, this cell could not be used. Cell(d) was used for all concentration experiments. This cell also had the advantage of being all glass and

prevented outside contamination of the solutions. The disadvantage of the cell was that it required a minimum of 3cc. of solution be used in order that the nitrogen inlet tube be below the surface of the solution. Because of the glass top to the cell it was not possible to use a sintered glass dispersion tube for oxygen removal which shortens deaerating time to 3-4 minutes.

Oxygen was removed from all solutions by bubbling tank nitrogen, obtained from the Olin Matheson Company, first through a Sargent deoxygenator, Number S-36517, and then through a gas saturating bottle containing DMF, before entering the cell for a minimum of 10 minutes. A three way stopcock was inserted after the presaturator so that the nitrogen could be passed over the electrolysis solution during a run. All tubing used in the nitrogen train was tygon. The tygon tubing used with the DMF was cleaned with live steam for 30 minutes and dried in a vacuum oven for 30 minutes at $60^{\circ}C$ and 27mm of mercury.

It has been found(9) that the temperature coefficient of the diffusion current in DMF is quite large and consequently temperature control is necessary for reproducibility. In the present work however the temperature was controlled to only $1^{\circ}C$ since the experimental error is about 5% due to surface activities which will be discussed later.

Materials. Dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, dibutyltin oxide, dibutyltin sulfide, tetrabutyltin, tetraphenyltin, tributyltin acetate, tributyltin oxide, dimethyltin dichloride, tributyltin chloride, trimethyltin chloride, triphenyltin chloride, phenyltin trichloride and dibutyltin dichloride were obtained from the Metal and Thermit Corporation and used without further purification.

Diphenyltin dichloride, dibutyltin, hexaphenylditin, diphenyltin, 5,5-dichloro-10,11-dihydrodibenzo-(b,f)stanniepin, and tetraphenylditin dichloride were prepared by Oscar F. Beumel of this department. The stannic chloride was C.P. Baker's Analyzed Anhydrous.

Two supporting electrolytes were tried, tetra n-butyl ammonium iodide and tetra n-butyl ammonium perchlorate. The tetra n-butyl ammonium iodide was obtained from Eastman Organic Chemicals Company and was purified by recrystallization from anhydrous ethyl acetate according to the directions of Laitinen and Wawzonek(13). It was dried at 60°C in a vacuum oven at 27mm pressure. Tetra n-butyl ammonium perchlorate was prepared by the reaction of tetra n-butyl ammonium iodide and silver perchlorate, from Fischer Scientific Company, in 95% ethanol. Silver iodide is insoluble in ethanol but a colloidal precipitate is formed so the solution was allowed to stand for 24 hours. Silver iodide was filtered off and the

ethanol was removed at room temperature. The tetra
n-butyl ammonium perchlorate obtained was recrystallized
from anhydrous ethyl acetate.(14) The crystals obtained
were usually light brown due to impurities. The crystals
were then redissolved in ethyl acetate and heated to boil-
ing with about one and one-half times their weight of
Norite. The hot solution was filtered and the Norite
washed twice with ethyl acetate. The crystals were again
recrystallized from ethyl acetate, collected on a sinter-
ed glass filter, and washed three times with ice cold
ethyl acetate. The resulting tetra n-butyl ammonium per-
chlorate was polarographically pure.

Ethyl acetate and DMF were used as solvents in
this study. Ethyl acetate, from Olin Matheson Company,
was used without further purification. DMF, from
Matheson Company and DuPont, was further purified despite
reports that the commercial product could be satisfactor-
ily used. Findies and DeVries(9) reported that no
measurable difference was noted between polarograms obtain-
ed with solvent which was dried by distallation over cal-
cium hydride and the technical grade solvent. Thomas and
Rochow(15),however,in their conductance studies of organo-
metallic chlorides of Group IV B in DMF, report that DMF
is very difficult to purify. Trace amounts of proton-
releasing impurities have a profound effect on the

observed conductimetric and polarographic behavior of any solute which yields a hydrogen halide as a solvolysis product. Curve A in Polarogram #1 shows the technical grade DMF and curve B shows the purified DMF. Impurities of importance in this respect include water, alcohols and primary and secondary amines. The DMF used in the present study was first treated with anhydrous potassium carbonate, which had been dried at 110° for 24 hours, for 4-5 days. The dried DMF was then distilled under nitrogen at atmospheric pressure through a 5 foot jacketed column packed with stainless steel helices. About a 50% reflux was maintained. For the best fraction only the 153°C fraction was retained. The volume collected was only about 40% of the total distillate. The DMF was stored under nitrogen in a bottle fitted with a water bottle head. All transfers were made under nitrogen until added to the cell. Further purification on one sample was tried by passing it through an ion-exchange column containing Amberlite MB-1 resin, obtained from the Fischer Scientific Company. The DMF obtained was slightly improved. A possible disadvantage is the release of hydrogen and hydroxyl ions from the resin.

Brown and Al-Urfali(10) reported that solutions of tetra n-butyl ammonium iodide in DMF decomposed slowly on standing. The impurity current, or residual current,

Polarogram #1

A-DuPont Technical Grade DMF

B-153°C Distillation Fraction

Wave Height (mm)

E (v)
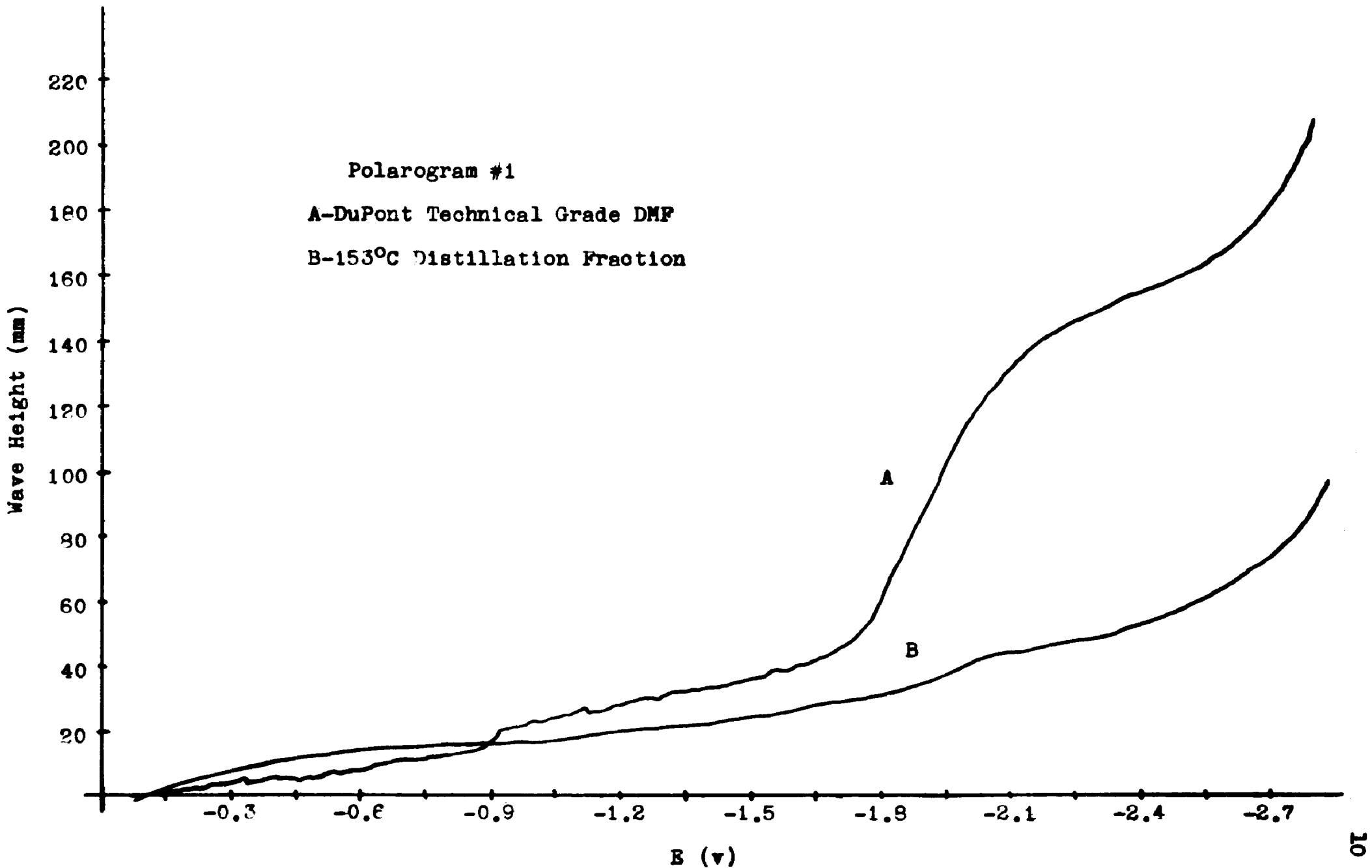
became appreciable after several weeks. It was found in the present work that tetra n-butyl ammonium perchlorate solutions were only good for about one week before the residual current took on a definite wave form. Polarogram #2 shows a freshly prepared solution of tetra n-butyl ammonium perchlorate and a similar solution ten days old. Because of this, stock solutions of 0.1M tetra n-butyl ammonium perchlorate were made up in small volumes and made up fresh weekly. The decomposition voltage of a 0.1M solution of tetra n-butyl ammonium iodide in DMF at $25^{\circ}C$ was -0.6 to -2.4v. vs. a quiet mercury pool. For tetra n-butyl ammonium perchlorate the range was -0.2 to -2.8v. vs. a quiet mercury pool. Because some of the organo-tin compounds are reduced at potentials near the oxidation potential of the iodide, perchlorate was used in the final concentration experiments.

Procedures. The concentration experiments were made by making succesive additions of a stock solution of the reducible substance to a quantity of 0.1M tetra n-butyl ammonium perchlorate. When the tin compounds were solid they were weighed out directly into a volumetric flask along with sufficient tetra n-butyl ammonium perchlorate to make a 0.1M solution when brought to volume with DMF. The normal concentrations used were $1x10^{-3}M$. In the case

Polarogram #2

A   Fresh 0.1M Tetra n-Butyl Ammonium Perchlorate Solution

B   10 Day Old 0.1M Tetra n-Butyl Ammonium Perchlorate Solution
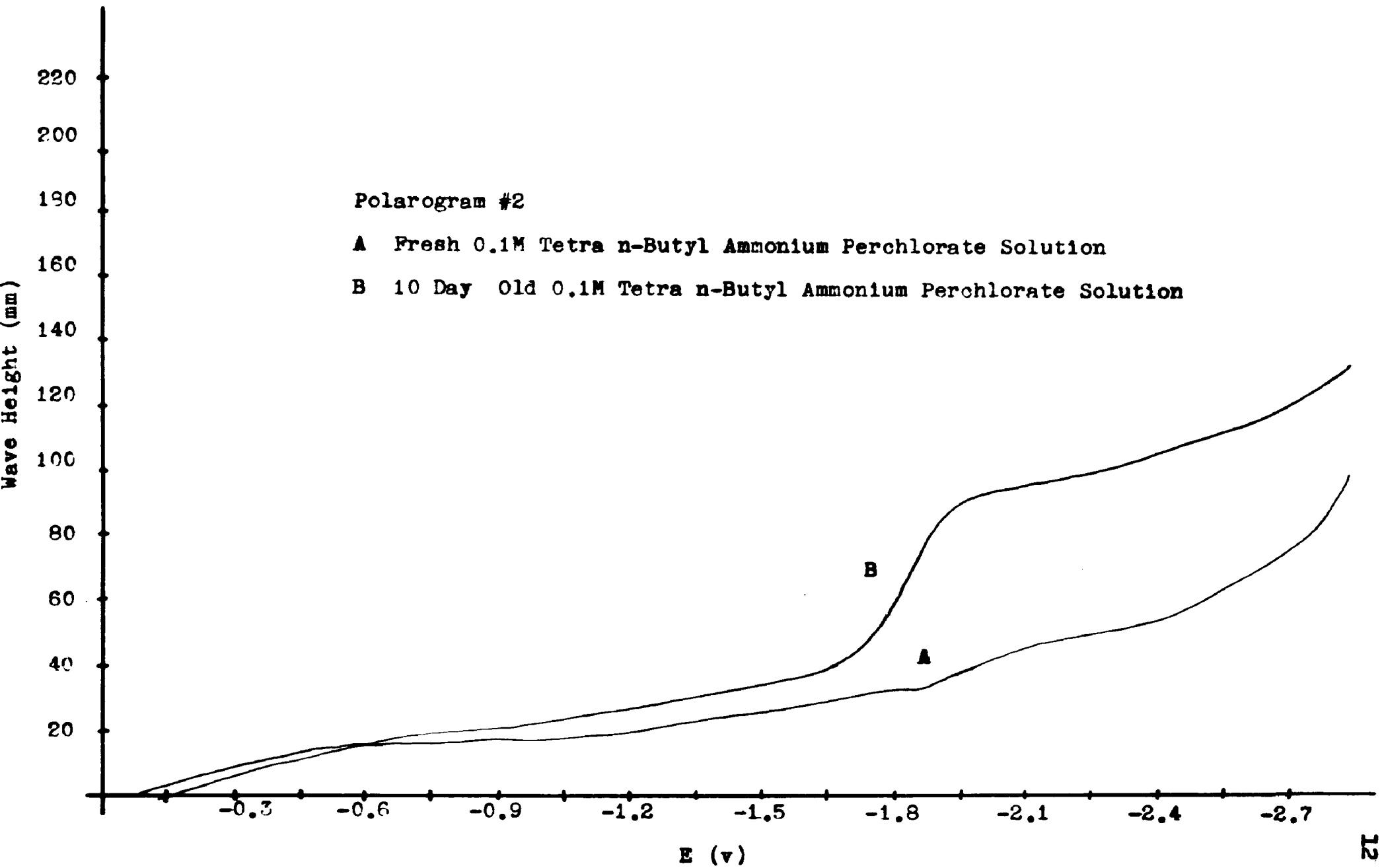
of liquid tin compounds an ultramicroburet was used to introduce the compounds directly into the cell without making up stock solutions. Difficulty in this method was encountered when dibutyltin sulfide and phenyltin trichloride reacted with the mercury in the buret.

It was found early in the work that DMF dissolved sufficient impurities from rubber and cork to give two or three waves in the normal working range. As a consequence rubber and cork stoppers could not be used on the electrolysis cells because the degassing process caused the DMF to splash up on the stoppers and contaminate the solutions. To prevent this, the rubber stoppers were first wrapped in aluminum foil, but later were replaced with a solid piece of Teflon which was turned down to fit the cell opening. The final concentration experiments were carried out in all glass cells.

DATA

The following table lists the half-wave potentials of the organo-tin compounds at concentrations where the waves are well defined and the half-wave potentials are constant.

Table I

Best half-wave potentials of organo-tin compounds

Compound		Concentration m/l	$E_{\frac{1}{2}}$ corr.
Tributyltin chloride		1.46×10^{-4}	-1.310
Trimethyltin chloride		1.74×10^{-4}	-1.192
Triphenyltin chloride	1st	2.22×10^{-4}	-1.061
	2nd	2.22×10^{-4}	-2.282
Dibutyltin dichloride		6.25×10^{-4}	-0.786
Dimethyltin dichloride	1st	6.51×10^{-4}	-0.834
	2nd	6.51×10^{-4}	-1.000
Diphenyltin dichloride		7.61×10^{-4}	-0.539
Tetraphenylditin dichloride		- - -	-0.820
5,5-dichloro-10,11-dihydro-dibenzo(b,f)stanniepin	1st	1.99×10^{-4}	-0.526
	2nd	1.99×10^{-4}	-1.040
Phenyltin trichloride		1.34×10^{-3}	-0.353
Tetraphenyltin		3.64×10^{-4}	-2.574
Tetrabutyltin		5.94×10^{-3}	-1.283
Dibutyltin diacetate		4.35×10^{-3}	-1.195
Dibutyltin dilaurate		3.22×10^{-3}	-1.757
Dibutyltin maleate		1.89×10^{-4}	-0.825
Dibutyltin sulfide		1.35×10^{-3}	-1.268
Tributyltin oxide		1.38×10^{-2}	-1.243
Tributyltin acetate		1.9×10^{-4}	-1.478

RESULTS

Reference Electrode. Initially the polarograms were obtained using a standard "H" cell (type b) with a saturated calomel electrode (S.C.E.) as the reference cell. An agar-agar plug saturated with potassium chloride was used to separate the reference cell from the working cell. Even though the potassium chloride is relatively insoluble in DMF, sufficient amounts of potassium ions and water diffused through the plug to give a large reduction wave for potassium and cause the reduction potential of the supporting electrolyte to shift to a less negative potential. Because of this the use of the S.C.E. was abandoned in favor of the quiet mercury pool.

Arthur and Lyons(16) report that in nonaqueous polarography the solution must be degassed before the mercury pool is added and subjected to a final minute of degassing to remove oxygen inadvertently admitted during the addition of the pool. Spurious waves were noted when the pool was added to the sample before degassing the system. Findles and DeVries(9) reported no such waves in their work in DMF. In this work however it was found that a wave appeared at about -0.3v., the size of which depended upon the time of the addition of the mercury pool and the length of time the pool remained in contact with the solution.

Because this wave occurs near the reduction potential of some organo-tin compounds it was studied in order to determine whether it could be eliminated or if its presence had any adverse effect on the organo-tin waves. In working with a quiet mercury pool in cell (a) the possibility existed that the mercurous ions formed at the anode during an electrolysis run were diffusing to the cathode and boihg reduced. The height of this wave appeared to be dependent upon the amount of current which had been passed through the cell. Since mercurous ions were formed at the anode during electrolysis it would follow that the wave would increase after each run. In order to eliminate this diffusion of mercurous ions to the dropping mercury electrode, an "H" type cell was used. The first cell replaced the sintered disc with a stopcock which was only opened during a run. Each side was degassed separately so that there was no transfer of ions between sides of the cell. The quiet mercury pool on one side was connected to the polaro-graph through a platinum point electrode. The mercury from the dropping mercury electrode in the other side collected at the bottom of the cell and did not alter the quiet pool in any way. This procedure decreased the height of the wave but diffusion of ions still occured. The second cell tried was a standard "H" cell with the

sintered disc separating the compartments. This cell slowed the diffusion of ions between the two compartments. Having isolated the pool and dropping mercury electrode, additions of mercurous ions to the cathode compartment allowed their controlled study. For concentrations of mercurous ions added, the diffusion currents were; 5×10^{-4}M, $i_d = 0.794$ua; 9.6×10^{-4}, $i_d = 1.554$ua; and 1.4×10^{-3}, $i_d = 2.246$ua; which was a linear relationship. Although this experiment indicated the mercurous ions were responsible for the unknown wave, the use of the "H" cell could not be used since it was found that a junction potential was established at the sintered disc. This potential varied with the concentration of ions present and with different ions. A shift in the potential of the mercury pool was also discovered when the concentration of the potential determining species was varied over a large range. When mercurous iodide was added to the cathode compartment, a negligible shift in the potential of the system was observed. However, when slightly larger additions were made to the anode compartment, a shift of 0.15 volts was observed. The shift in potential can be accounted for by the change in activity of the mercurous iodide. The potential determining reaction being $2Hg \rightarrow Hg_2^{++} + 2e$, in the presence of iodide ions.

In a system containing tetra n-butyl ammonium perchlorate, addition of sodium perchlorate to the anode compartment caused a shift of 0.553 volts in the negative direction. In order to obtain a shift of 0.553 volts the activity of the mercurous ion would have had to change by a factor of 10^{18}. Because this is highly unlikely it appeared that the cell reaction had altered. In this case it was probable that the large amount of perchlorate present had caused the solubility product constant of mercurous perchlorate to be attained and consequently mercurous perchlorate was now the reaction product, i.e. $2Hg + 2ClO_4^- \longrightarrow Hg_2(ClO_4)_2 + 2e$. This reaction was similar to the potential change in going from mercury-mercurous ion to mercury-mercurous chloride in the aqueous system. The potential change being 0.521 volts.

Even though it has been shown that the potential of the quiet mercury pool will shift with large changes in concentration of anions present, this shift also depends upon the formation of mercurous ions at the anode. In a series of experiments the number of mercurous ions formed will depend upon the total amount of current flowing through the cell, i.e. it will obey Faraday's law. In the normal polarographic run, with small current flow, the number of mercurous ions formed would be insufficient to cause a shift in the reference pool's potential.

The reason for the formation of the wave when the solution is degassed with the mercury pool in place is still not clear.

Organo-tin Reductions. In order to study the
relative reduction potentials of the organo-tin com-
pounds, the compounds have been classified in two groups:
One, compounds with different organic radicals and two,
compounds with different anions. Within each class
there was usually a definite shift in half-wave potent-
ial and frequently an apparent change in reduction
mechanism. A comparison of the diffusion currents, the
diffusion coefficients of the reducible substances, the
electron change and the apparent reversibility or irre-
versibility of the reactions was also made.

R_3SnCl Compounds. Triphenyltin chloride, tri-
methyltin chloride, tributyltin chloride were the
compounds in this group. Table II lists the concen-
tration range, the half-wave potentials, electron change
and diffusion currents for these compounds.

Table II

Compound	Concentration range	Half-wave potential	Electron change	Diffusion current
Tributyltin chloride	1.77×10^{-5} to 3.09×10^{-4}	-1.408 to -1.294	0.478	0.272 to 1.772
Trimethyltin chloride	8.93×10^{-5} to 3.33×10^{-4}	-1.190 to -1.210	0.806	0.520 to 6.956
Triphenyltin chloride	1.78×10^{-4} to 5.15×10^{-4}	1)-1.068 to -1.094	0.558	0.761 to 2.433
		2)-2.28 to -2.292		0.478 to 1.183

The reduction of the monochloride compounds,
listed with decreasing ease of reduction is phenyl,
methyl, butyl. Because the order does not follow the
increase or decrease in size of the organic radical it
may be assumed that steric hinderance is not a prominent
factor in the reduction process.

The half-wave potential of the first wave of
triphenyltin chloride was constant at -1.065 v. until
the maximum began to form. (Polarogram #3) As the con-
centration increased the half-wave potential shifted to
more negative potentials. The half-wave potential for
trimethyltin chloride was relatively constant at -1.195v.,
even at concentrations where the maximum more than
tripled the wave height.

The upper half of the tributyltin chloride waves
varied from run to run making analysis uncertain. In
some runs there was a very small rounded "maximum" and
on others in the same concentration range, there was
quite a sharp break at the top of the wave. Above a
concentration of 2×10^{-4} M the potential became relatively
constant at about -1.31v. It has been postulated that
the first step was the reduction to a ditin compound.(2,3)
In the above three compounds the products would be hexa-
phenylditin, hexamethylditin, and hexabutylditin. Since
there is only one wave with the methyl and butyl compounds

Polarogram #3

Triphenyltin Chloride

A 1st Reduction Wave

B 2nd Reduction Wave

C Impurity Wave
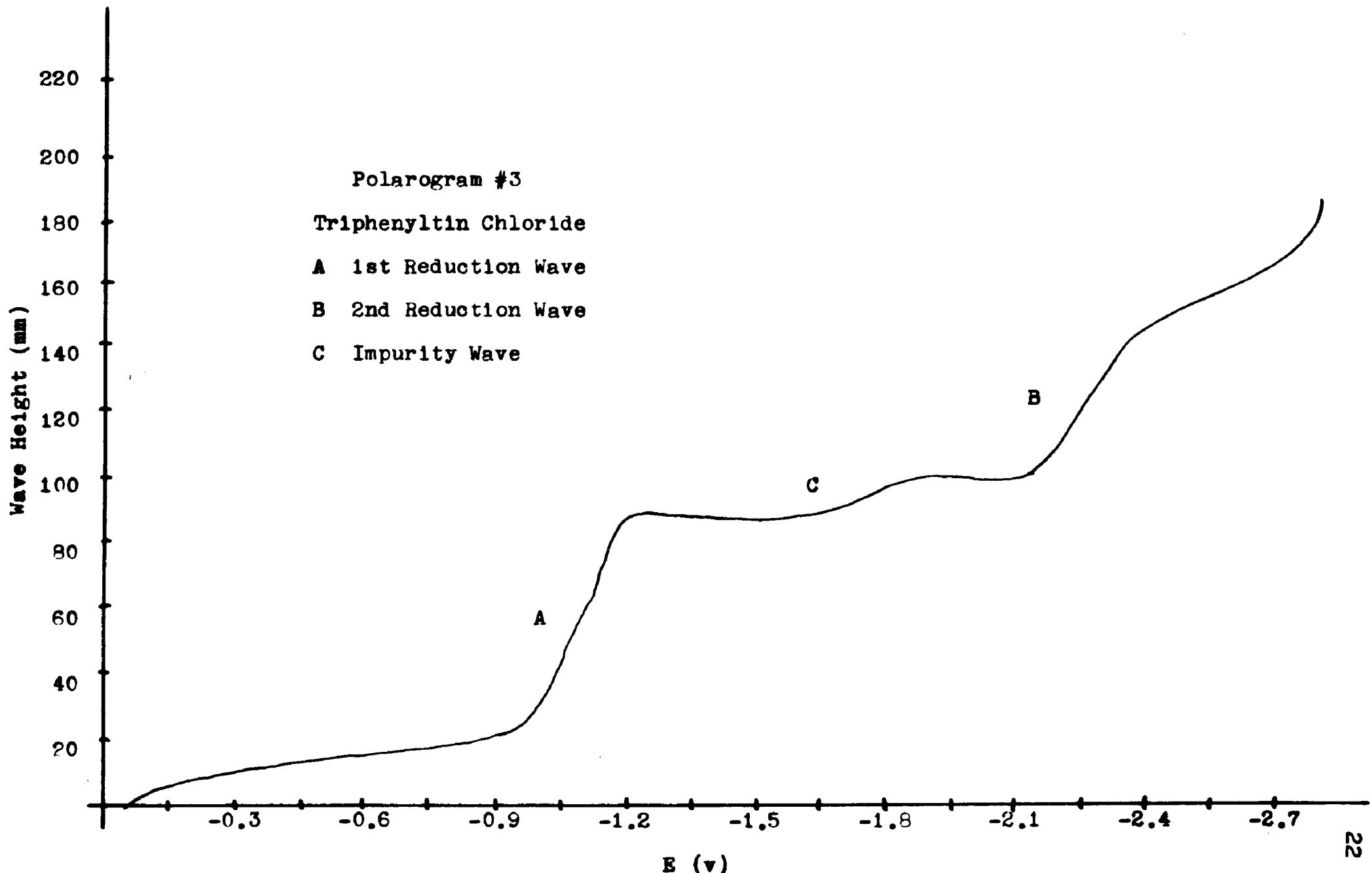
it must be assumed that these compounds are not further reducible in the present system.

The phenyl compound on the other hand had a second reduction step. The half-wave potential of the second wave was constant over the entire concentration range at -2.285v.. The waves were well formed and no maxima were observed. The second step for organo-tin compounds was reported to be the reduction of the tetravalent tin to the divalent tin compound. The second reduction for the triphenyltin chloride would be to diphenyltin. This reduction should occur at the potential. of the proposed product of the first step, i.e. hexaphenylditin. The reduction of hexaphenylditin occured at a potential of -2.69v. vs. the quiet mercury pool, which was about 0.4v. more negative than the second step in the triphenyltin chloride reduction.

A maximum was observed with the first wave with all three compounds, the concentrations at which it was observed however, differ. Concentrations, of the methyl compound above 8.9×10^{-5}M, of the butyl compound above 1.6×10^{-4}M and of the phenyl compound above 1.7×10^{-4}M showed a maximum. The second wave of the phenyl compound did not show a maximum up to a concentration of 6.0×10^{-4}M.

The diffusion current, i_d, for tributyltin

chloride is linear over the lower range of concentrations
studied. (Graph #1, curve A) If the peak of the maximum
was used as the diffusion plateau for the determination
of the diffusion current, it too gave a linear plot at
higher concentrations. Both waves for triphenyltin
chloride gave linear plots of i_d vs. concentration,
and increased at the same rate as did the tributyltin
chloride, if the maximum peak of the first wave was
used. (Graph #1, curve B) The trimethyltin chloride,
however, did not give a linear plot but increased quite
rapidly with increasing concentration. (Graph #1, curve C)
This was the more normal situation when a maximum was
taken as the diffusion current.

The number of electrons consumed in the reduction
can be computed from the slope of the log $1/i_d-i$ vs. E
plot, where i_d is the diffusion current, i is the current
at the potential E, and E is the potential of the dropping
mercury electrode. It can also be calculated from the
equation $E_{3/4} - E_{1/4} = -0.0564/n$, where n is the number
of electrons consumed and $E_{1/4}$ and $E_{3/4}$ are the potent-
ials at 1/4 and 3/4 of the reduction wave respectively.(17)
The "n" value for tributyltin chloride was 0.26, for tri-
phenyltin chloride the "n" value for the first wave was
0.56, and for trimethyltin chloride "n" was 0.81, at
concentrations of 1.39×10^{-4}M, 1.78×10^{-4}M and 1.18×10^{-4}M

Graph #1

A Tributyltin Chloride

B Triphenyltin Chloride, 1st Wave

C Trimethyltin Chloride

Diffusion Current (ua)

Concentration x 10^5
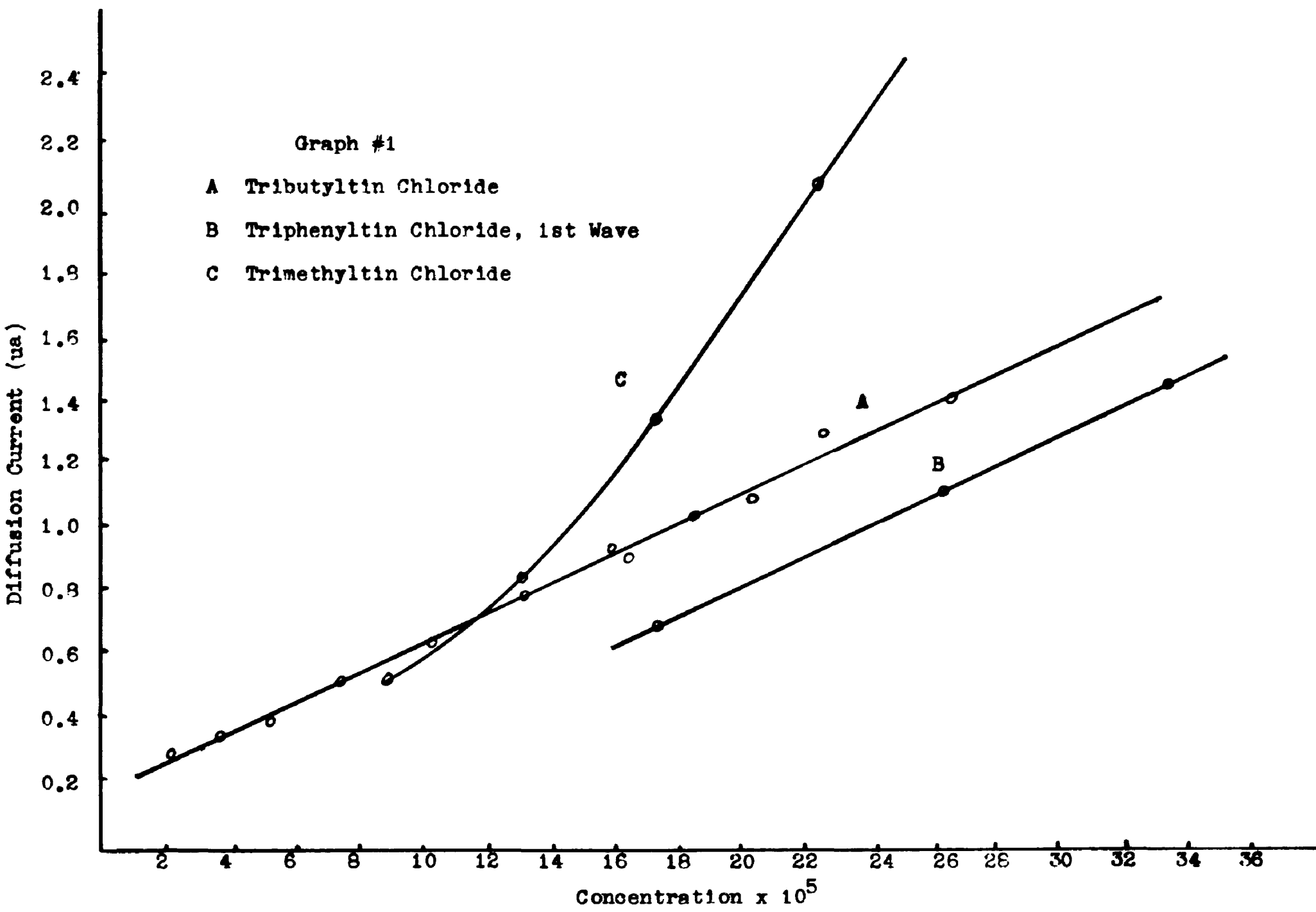
for the butyl, phenyl and methyl compounds respectively. Since the first reduction wave involved a one electron change it was obvious that all three reactions were irreversible, the butyl chloride the most and the methyl chloride the least. The second triphenyltin chloride wave had an "n" value of 0.77 which again was far different from the proposed two electron change for the second wave. It was, therefore, assumed that the second wave was highly irreversible.

Diffusion coefficients are normally calculated from the Ilkovic equation (18), $i_d = 607 n D^{1/2} C_m^{2/3} t^{1/6}$, where i_d is the diffusion current, n is the electron change per molecule, C is millimoles per liter, D is the diffusion coefficient, m is the mass of mercury flowing per second and t is the drop time in seconds. In this case it was not possible to evaluate the diffusion coefficient because of the irreversibility of the reactions and consequently the incorrect value of "n".

R_2SnCl_2 Compounds. Dimethyltin dichloride, dibutyltin dichloride, diphenyltin dichloride, tetra-phenylditin dichloride, and 5,5-dichloro-10,11-dihydro-dibenzo(b,f)stanniepin were the compounds studied in this group. Table III lists the concentration range, the half-wave potentials, electron change and diffusion currents

Table III

R_2SnCl_2 Compounds

Compound	Concentration range	Half-wave potential	Electron change	Diffusion current
Dimethyltin dichloride	9.97×10^{-5} to 1.24×10^{-3}	1)-0.867 to -0.832	0.762	0.254 to 2.328
		2)-0.985 to -1.020	- -	0.549 to 1.524
Dibutyltin dichloride	3.26×10^{-4} to 3.48×10^{-3}	-0.778 to -0.789	0.570	0.252 to 3.169
Diphenyltin dichloride	7.61×10^{-4} to 2.14×10^{-3}	-0.539 to -0.541	1.04	0.590 to 1.662
Tetraphenyl-ditin dichloride	- - -	-0.534	0.895	0.16
5,5-dichloro-10,11-dihydro-dibenzo(b,f)-stanniepin	3.05×10^{-5} to 2.19×10^{-4}	-0.538 to -0.491	0.626	0.133 to 0.189

for these compounds. The compounds are listed with in-
creasing ease of reduction. The last three compounds
had approximately the same reduction potential. Again
the apparently sterically hindered molecules had the
lowest reduction potential. With the addition of the
second chloride atom to the tin molecule the reactivity
of the compound was increased. Rochow(19) reported
dimethyltin dichloride ionizes to give doubly charged
dimethyltin and chloride ions. In pure water the extent
of the ionization of dimethyltin dichloride was 10.5%.
In anhydrous DMF, organo-metallic chlorides of Group
IV B compounds do not dissociate into organo-metallic
cations and chloride ions. Since DMF is difficult to
purify, appreciable amounts of water may remain in the
DMF after purification. Dimethyltin dichloride was found
to be slightly dissociated even when the DMF used had
been purified to the greatest possible extent, indicating
a small amount of water remaining. If water was present
and dissociation did take place, the possibility existed
that two reducible species were present in the system.

If the dissociation rate was rapid compared to
the reaction rate at the dropping mercury electrode, then
only one wave would have been observed. If the disso-
ciated cation was reduced at a lower potential than the
undissociated molecule then only the wave for the

dissociated cation would have been observed. The undisso-
ciated molecule would not have been reduced since it was
dissociated immediately upon approaching the dropping
mercury electrode. If on the other hand the dissocia-
tion rate was much lower than the reaction rate at the
electrode, then two waves would have been observed, the
heights being proportional to the concentration of the
two species in the bulk of the solution. If the disso-
ciation rate was intermediate between these two extremes
then dissociation would have occured at the potentials on
the plateau of the dissociated wave. If the concentra-
tion of the dissociated specie in the bulk of the sol-
ution was small, the observed current at the potential
at which the dissociated specie alone was reduced would
have been entirely kinetic in nature.

In this study dimethyltin dichloride, dibutyltin
dichloride and tetraphenyltin dichloride all exhibited a
prewave, which indicated that some water still remained
in the DMF. Addition of water to the system increased
the wave height of the prewave linearly and there was a
corresponding decrease in the height of the main wave.
The total wave height was not exactly constant but this
can be attributed to the change in diffusing specie and
small changes in the solvent system itself.

The polarograms of the dichloride compounds were

further complicated by the appearance of two or three waves which could be attributed to the presence of hydrogen chloride in the system. (Polarogram #4) Whether these waves were due to hydrogen chloride itself or to some reaction product, was not determined. In order to obtain the reduction potentials of the compounds under study, the waves which occurred at the potential of the hydrogen chloride were not included. Dimethyltin dichloride had two reduction waves, -0.83 and -1.01v., which could not be attributed to hydrogen chloride. Dibutyltin and diphenyltin dichlorides exhibited only one reduction wave at -0.79 and -0.54v. respectively. The first step has been postulated by Saikina(4) to be the reduction to a ditin similar to that postulated in the monochlorides. The products would be tetramethylditin dichloride, tetrabutylditin dichloride and tetraphenyl-ditin dichloride.

The second reduction step for the dimethyltin dichloride in 40% aqueous ethanol was observed only in acid and slightly basic solutions as the first and second waves merged in more basic solutions. The second wave corresponded to the reduction to dimethyltin. Riccobone and Poppff(1) however, have reported that diethyltin dichloride has only one reduction wave. It was concluded that the primary reaction product was the radical diethyltin, a two electron change.

Polarogram #4

A Diphenyltin Dichloride

B Hydrogen Chloride-DMF
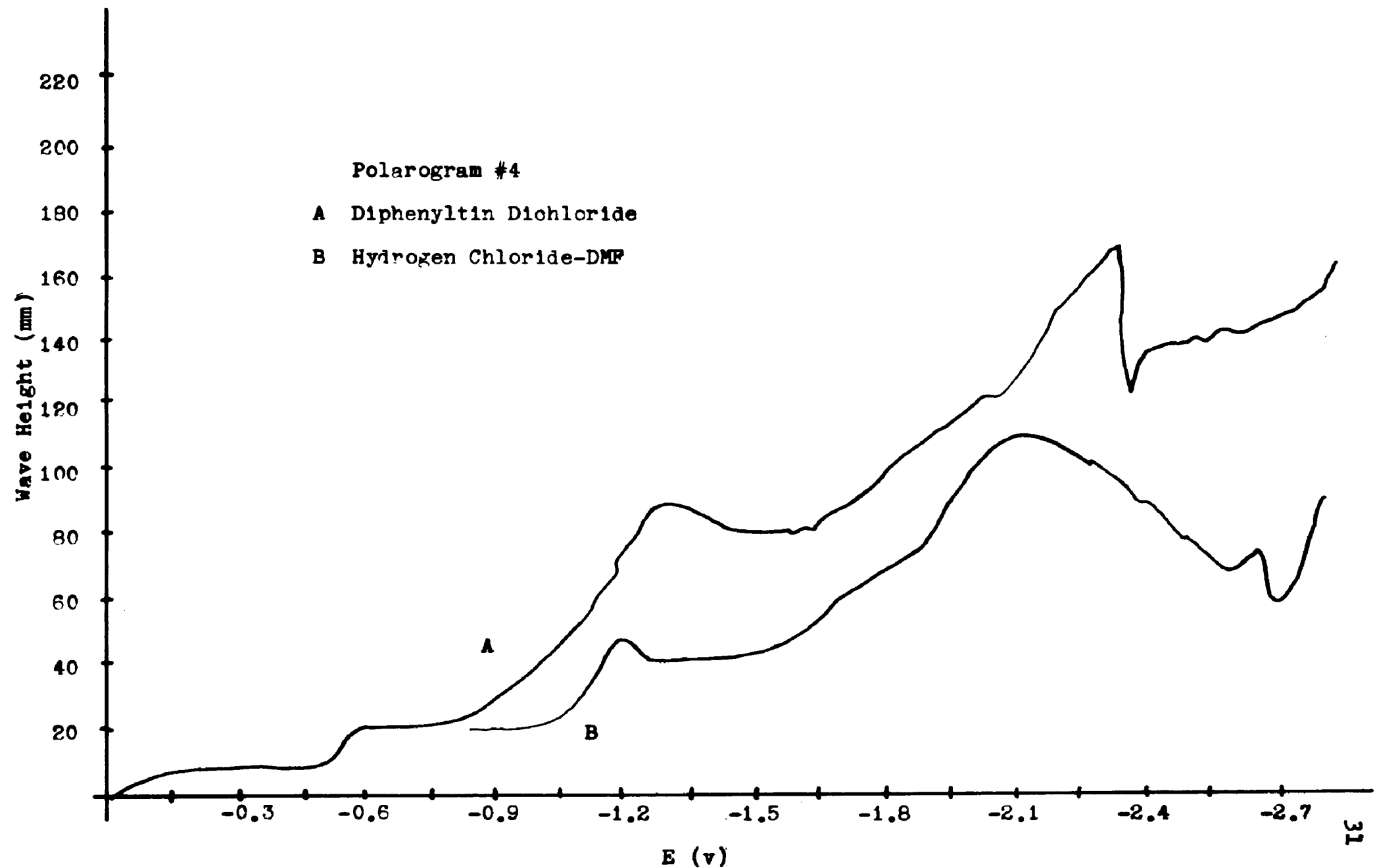
Because of the hydrogen chloride waves it was not possible to determine whether the diphenyltin dichloride and dibutyltin dichloride had a second reduction wave. Since the electrode reactions were irreversible, the electron change in the reaction gave no true indication of the actual reaction taking place at the electrode.

The 5,5-dichloro-10,11-dihydrodibenzo(b,f)-stanniepin had two reduction waves, the first at -0.51 and the second at -2.81v. Tetraphenylditin dichloride had two waves, -0.534 and -0.820v., the first wave however, was shown to be a dissociation, or hydrolysis product. As the concentration of water was increased in the solution the hydrogen chloride obscured the second wave completely. Since the tetraphenylditin dichloride has been postulated to be the reaction product of the first reduction step of diphenyltin dichloride, it should have had a wave corresponding to the second wave for diphenyltin dichloride. Since diphenyltin dichloride had only one observed wave it must be assumed that the hydrogen chloride discharge obscured this wave or that due to the uncertainty of the purity of the tetraphenylditin dichloride this wave was due to an impurity.

The reaction product of the 5,5-dichloro-10,11-dihydrodibenzo(b,f)stanniepin if postulated to be a similar ditin compound would be sterically hindered due

to the two large fixed ring radicals.

The diffusion currents for dimethyltin dichloride were linear over the concentration range studied. (Graph #2, curve A) The first wave, which was well defined in all cases, had no maximum as long as the water in the system was at a minimum. As soon as water was introduced and the prewave became well defined, however, a maximum was observed on the first wave. Dilution of the solution with water caused a decrease in wave height of the first wave by a factor of 0.5 for a change in concentration from $1.24x10^{-3}$ to $1.16x10^{-3}M$. A corresponding increase in the prewave was noted, both changes being linear with concentration.

The second dimethyltin dichloride wave did not become well defined until a concentration of $5x10^{-4}M$ whereas the first wave was quite well defined at $1x10^{-4}M$. The diffusion plateau above $1x10^{-3}M$ became obscure due to a maximum following the second wave. Upon addition of water the second wave increased in height initially, then decreased rapidly.

The diphenyltin dichloride diffusion current was measured over a small concentration range due to the maximum which formed at concentrations greater than $7x10^{-4}M$. (Graph #2, curve B) The plot of diffusion current vs. concentration is linear if the top of the

Graph #2

A Dimethyltin Dichloride, 1st Wave

B Diphenyltin Dichloride

C Dibutyltin Dichloride
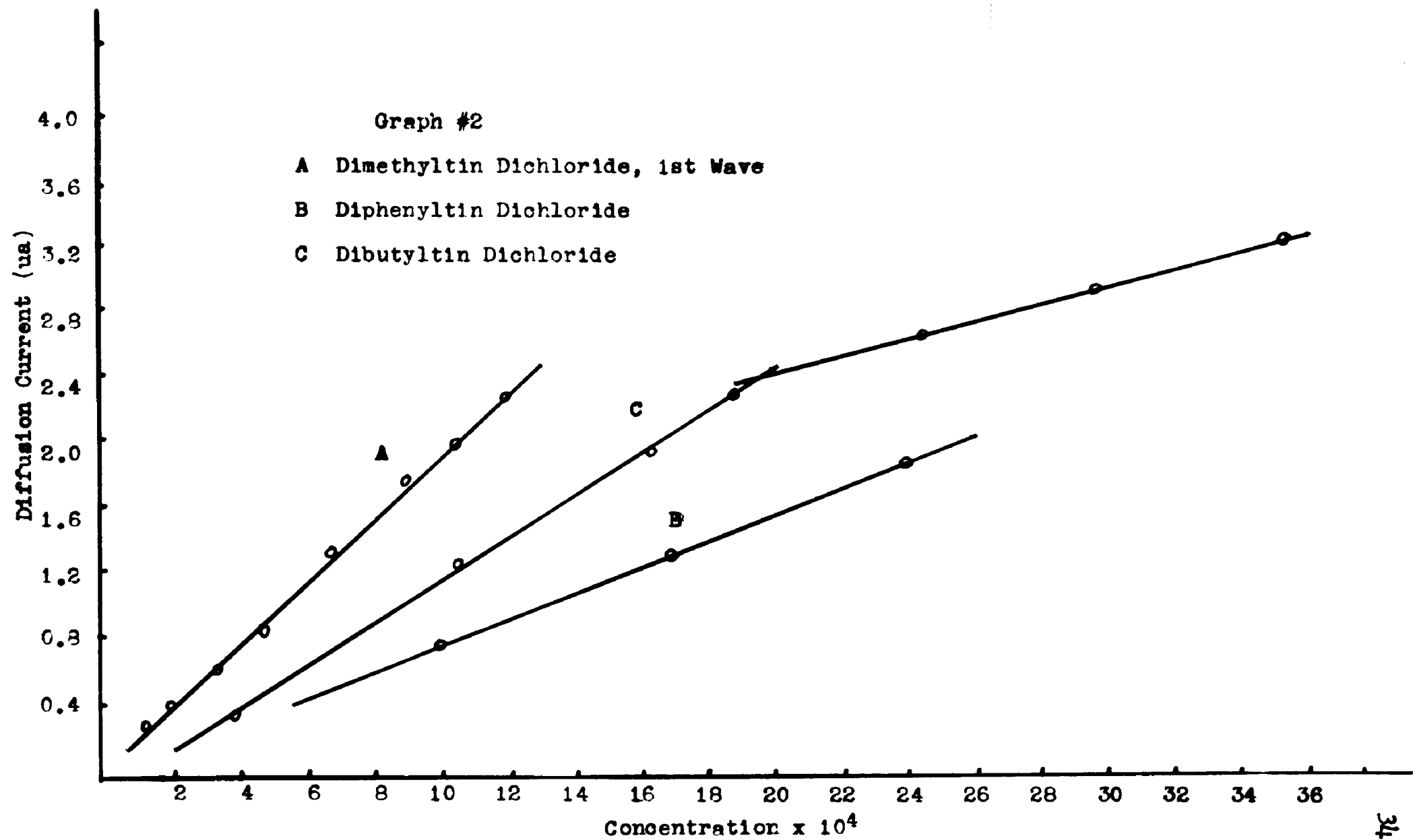
maximum was used. The slope of the plot was less than that of either the first or second dimethyltin dichloride wave. Addition of water to diphenyltin dichloride at a concentration sufficiently low to prevent a maximum, caused a maximum to form on the wave, which increased with increased addition of water.

The diffusion current of dibutyltin dichloride was not linear over the entire concentration range. (Graph #2, curve C) Two straight line portions were observed, the first from 3.3×10^{-4}M to 1.9×10^{-3}M, and the second from 1.9×10^{-3}M to 3.5×10^{-3}M. The slope at the lower concentrations laid intermediate between the dimethyl and diphenyltin dichlorides. The slope of the higher concentrations was less than the diphenyltin dichloride. A maximum was formed when the concentration was greater than 2.3×10^{-4}M. As noted earlier a prewave was noted with all waves, and became quite large but not completely resolved at higher concentrations. Addition of water to the dibutyltin dichloride caused the prewave to increase and obscure the normal wave. The height of the prewave in excess water was slightly higher than the normal wave, probably due to an increase in diffusion rate of the dissociated ions.

Concentration runs were not made with tetraphenyl-
ditin dichloride or 5,5-dichloro-10,11-dihydrodibenzo(b,f)-
stanniepin because of limited supply and questionable
purity.

The electron changes for dimethyltin and dibutyl-
tin dichlorides were 0.762 and 0.570 for 1.24×10^{-3}M and
1.89×10^{-3}M solutions respectively. These two compounds
must then be assumed to be reduced irreversibly at the
dropping mercury electrode. The "n" value for the
diphenyltin dichloride however, had a value of 1.04 at
7.6×10^{-4}M, which agreed with the theoretical one electron
change. The accuracy of this value was slightly in
doubt since the addition of small amounts of water in-
creased the slope of the wave due to the maximum formed.

The first wave for tetraphenylditin dichloride
had an "n" value of 1.04. It was this value of "n", the
half-wave potential, and the increased wave height upon
addition of water, which caused the assumption to be made
that the first wave was due to impurities, hydrolysis
products, or reaction products; since all three factors
were in agreement with those of diphenyltin dichloride.
The second wave had an "n" value of 0.895, which indica-
ted an irreversible reaction.

The electron changes per molecule for the first
and second waves of 5,5-dichloro-10,11-dihydrodibenzo(b,f)-
stanniepin were 0.626 and 0.925 for 2.18×10^{-4}M and

3.05×10^{-5}M solutions respectively. Since these corresponded to the postulated 1 and 2 electron changes, the reactions were irreversible.

The diffusion coefficient for diphenyltin dichloride, calculated from the rearranged Ilkovic equation- $D^{1/2} = i_d/607nCm^{2/3}t^{1/6}$, was $2.93 \times 10^{-8} cm^2/sec..$ This value was low in comparison with diffusion coefficients in aqueous systems. Diffusion coefficients were not calculated for the other compounds because of the irreversibility of the reactions as indicated by the fractional "n" values.

RSnCl₃ Compounds. Phenyltin trichloride was the only compound available in this group. Table IV lists the concentration range, half-wave potentials, electron change and diffusion current range for this compound.

Table IV

Compound	Concentration range	Half-wave Potential	Electron change	Diffusion current
Phenyltin trichloride	1.34×10^{-3} to 2.64×10^{-3}	-0.353 to -0.376	0.868	1.44 to 3.22

Because of its reactivity with water some reaction took place immediately upon preparation of the solution. Since the nitrogen used to flush the cell was not dried, addition of moisture to the cell was possible. In order

to eliminate the preparation of stock solutions a micro-
buret was tried but a reaction between the mercury and
phenyltin trichloride prevented its use. Difficulty was
encountered in one run when the solution apparently
caused a partial blockage of the capillary.

Only one wave could be attributed to the phenyltin
trichloride because of the large hydrogen chloride waves
observed. The half-wave potential of the wave was -0.36v..
A very large maximum followed the wave and obscured the
diffusion plateau above $3x10^{-3}M$. Due to difficulties in
preparation of the stock solutions the concentration
range studied was $1x10^{-3}$ to $3x10^{-3}M$.. The diffusion
current appeared to be linear with concentration. The
electron change for the reaction was calculated to be
0.868. No diffusion coefficient was calculated.

$\underline{SnCl_4}$. Because of the reactivity of stannic
chloride no distinguishable waves could be observed. A
small wave was observed between the two hydrogen chloride
waves but was not sufficiently defined to allow analysis.

$\underline{R_4Sn\ Compounds}$. Saikina(4) has reported that R_4Sn
compounds were not reducible. Tetrabutyltin and tetra-
phenyltin were studied and both compounds gave reduction
waves. Table V lists the concentration range, half-wave
potentials, electron change and diffusion current range

for these compounds. The half-wave potential of the
tetrabutyltin was -1.285v. until the maximum began to
form and then the wave tended to shift to more negative
potentials. The reaction product can be postulated to
be hexabutylditin. Since only one wave was observed

Table V

Compound	Concentration range	Half-wave Potential	Electron change	Diffusion current
Tetra-phenyltin	1.90×10^{-4} to 1.78×10^{-3}	-2.508 to -2.752	0.437	0.778 to 9.288
Tetra-butyltin	1.78×10^{-3} to 2.13×10^{-2}	-1.281 to -1.318	0.564	0.129 to 1.401

the reduction to divalent tin did not occur in this
system. The half-wave potential for tetraphenyltin be-
came more negative as the concentration increased. The
potential changed from -2.507v. at a concentration of
1.9×10^{-4}M to -2.738v. at a concentration of 1.78×10^{-3}M.
The solution used was a stock solution made one day
before the concentration run was made. When small
amounts of solid tetraphenyltin were added to the sup-
porting electrolyte and DMF, no wave was immediately
observed. After five minutes however, a well formed
wave was observed, with a height of approximately 70 mm.
At the end of fifteen minutes the wave was 90 mm and
after eight hours the wave reached a maximum value of
105 mm. From this it was assumed that the wave is not

due to tetraphenyltin but to a reaction product with the
DMF or with the water in the DMF.

The diffusion current for tetrabutyltin was lin-
ear over the entire concentration range studied, i.e.
$1x10^{-3}$M. to $2x10^{-2}$M, if the maximum diffusion current
was used. At concentrations greater than $6x10^{-3}$M a
rounded maximum was formed. The diffusion current for
the reaction product of tetraphenyltin gave a linear plot.

Dibutyltin Compounds. Dibutyltin diacetate, di-
butyltin dilaurate, dibutyltin dichloride, dibutyltin
maleate, dibutyltin oxide and dibutyltin sulfide were
the compounds in this group. Table VI lists the concen-
tration range, half-wave potentials, electron change and
diffusion current range for these compounds.

Table VI

Compound	Concentration range	Half-wave potential	Electron change	Diffusion current
Dibutyltin diacetate	$7.24x10^{-4}$ to $8.67x10^{-3}$	-1.188 to -1.225	0.486	0.119 to 3.41
Dibutyltin dilaurate	$6.44x10^{-4}$ to $1.84x10^{-2}$	-1.706 to -1.865	0.359	0.772 to 33.60
Dibutyltin dichloride	$3.26x10^{-4}$ to $3.48x10^{-3}$	-0.778 to -0.797	0.570	0.252 to 3.196
Dibutyltin maleate	$3.22x10^{-5}$ to $2.86x10^{-4}$	-0.793 to -0.829	1.08	0.231 to 1.752
Dibutyltin sulfide	$6.76x10^{-4}$ to $3.38x10^{-3}$	-1.247 to -1.368	0.474	2.301 to 12.70

The apparent ease of reduction of the dibutyltin compounds was chloride, maleate, acetate, sulfide, and laurate in order of decreasing ease.

Dibutyltin oxide did not exhibit any reduction waves over the entire working range. This was probably due to the fact that dibutyltin oxide polymerized into long chains. The polymer is insoluble in most solvents, apparently including DMF, and therefore would not be reducible.

Because of the serious difficulties encountered in analyzing the polarograms in the presence of hydrogen chloride, a similar study was made on maleic acid and glacial acetic acid. Three waves were observed for maleic acid. The first wave, at -1.5v. was very small and presumably an impurity. The second wave began at -1.9v. and a maximum was noted on the wave. The third wave began at -2.4v. and continued to rise until the decomposition potential of the supporting electrolyte was reached. The wave could possibly have been the supporting electrolyte due to a shift in its decomposition potential caused by the presence of the maleic acid. The glacial acetic acid solution showed only one wave which began at -1.8v. No maximum was observed with acetic acid.

Dibutyltin dichloride showed only one wave when the hydrogen chloride waves had been subtracted. The half-wave potential was -0.79v.. (See R_2SnCl_2 compounds)

The dibutyltin maleate polarograms showed one
well defined wave at -0.82v. and was followed by a large
"hump". The nature of the "hump" was questionable in
that the current after passing through the maximum fell
back to the same value. With the normal maximum, the
current is usually much higher on the negative side than
on the positive side. The shape of the "hump" was sim-
ilar to that caused by the hydrogen chloride solutions.
The wave was shifted to more negative potentials as the
concentration increased. At higher concentrations of
dibutyltin maleate a small wave began to form just prior
to this "hump" indicating it was a rounded maximum for
a minor specie or possibly a second reduction wave. The
two waves at -2.4v. and -2.6v. are attributed to the
maleic acid solution.

Solutions of dibutyltin diacetate did not yield
good polarograms. Three small poorly defined waves were
observed, at -1.20v., -1.55v. to -1.59v. and -1.97v. to
-1.88v.. The first wave was the only one whose potential
remained constant over the concentration range studied.
At potentials greater than -1.2v. a large amount of sur-
face activity at the dropping mercury electrode took place.
This activity caused variations in the drop rate of the
mercury electrode. Since the current depends upon the
size of the mercury drop, any factor affecting the drop

rate affects the current. On the polarogram this shows up as a series of irregular peaks rather than the normal galvanometer fluctuations. Because of these peaks it was impossible to analyze small waves and tended to give inaccurate results on the larger waves. The second wave was quite small and therefore analysis was difficult. The apparent half-wave potential varied from -1.554v. to -1.586v. over the lower concentration range. At higher concentrations, $6x10^{-3}M$, the second and third wave merged. The third wave like the second varied with concentration, from -1.970v. to -1.878v.. About the same time the second and third waves merged, a maximum was formed on the third wave. At concentrations greater than $1x10^{-2}M$ the merged second and third waves became sufficiently large to obscure the diffusion plateau of the first wave.

Dibutyltin sulfide had two reduction waves. The half-wave potential of the first reduction wave varied with concentration. At $7x10^{-4}M$ it was -1.250v. and at $4x10^{-3}M$ the value became 0.13 volts more negative to -1.387v.. As with the dibutyltin diacetate the surface activity at the dropping mercury electrode became sufficiently great beyond -1.2v. to hinder analysis. The shift in the half-wave potential however was much greater than can be accounted for by the analysis difficulties.

The wave form of the first wave was not ideal even at
the lowest concentrations studied. ($7x10^{-4}M$) The dif-
fusion current dropped off slowly from the top of the
curve to where the second wave began. The decrease in
current amounted to about 10% of the total wave height.
At a concentration of $2x10^{-3}M$ a definite rounded maximum
began to form.

The second reduction wave was quite well defined
if the sensitivity and the concentration were suffi-
ciently low. The half-wave potential of the second wave
was -2.23v. A sharp maximum began to form at a rela-
tively low concentration so the range of the second wave
analysis was limited.

As noted earlier a reaction took place in the
ultramicroburet between the dibutyltin sulfide and the
mercury in the buret. A black film, presumably mercur-
ous sulfide, was formed on the quiet mercury pool if the
dibutyltin sulfide solution remained in contact with it
for any length of time.

Dibutyltin dilaurate was the most difficult
compound of this group to reduce. Only one reduction
wave was observed. The diffusion plateau however, rose
quite rapidly after the wave and because of the increasing
recorder fluctuations at the more negative potentials, no
other wave could be found. The half-wave potential for

dibutyltin dilaurate was relatively constant at the
lower concentrations. The value was -1.751 ± 0.006v.
up to 6.0×10^{-3}M. Taking into account the surface ac-
tivity this was within the experimental error. Above
6.0×10^{-3}M however, the diffusion plateau tended to
level off and the half-wave potential became more neg-
ative. At a concentration of 2×10^{-2}M the corrected
half-wave potential was -1.865v. A correction for the
iR drop amounting to 0.05v. was required because of the
large current flowing at this concentration.

The diffusion currents of the dibutyltin com-
pounds varied to a much greater extent than did those
compounds which had the same anion. This would indicate
that the anion was the controlling factor in the dif-
fusion rates of the compounds.

The first wave of dibutyltin diacetate had the
smallest diffusion current of the compounds in this
group. (Graph #3, curve A) The plot of concentration
vs. diffusion current gave a linear relationship over
most of the concentration range studied. Below 1×10^{-3}M
the wave became too small for accurate analysis and
above 1×10^{-4}M the first and second waves were so close
together the diffusion plateau on the first wave was
distorted.

Graph #3

A   Dibutyltin Diacetate

B   Dibutyltin Dilaurate

C   Dibutyltin Maleate

Diffusion Current (ua)

Concentration x 10^4
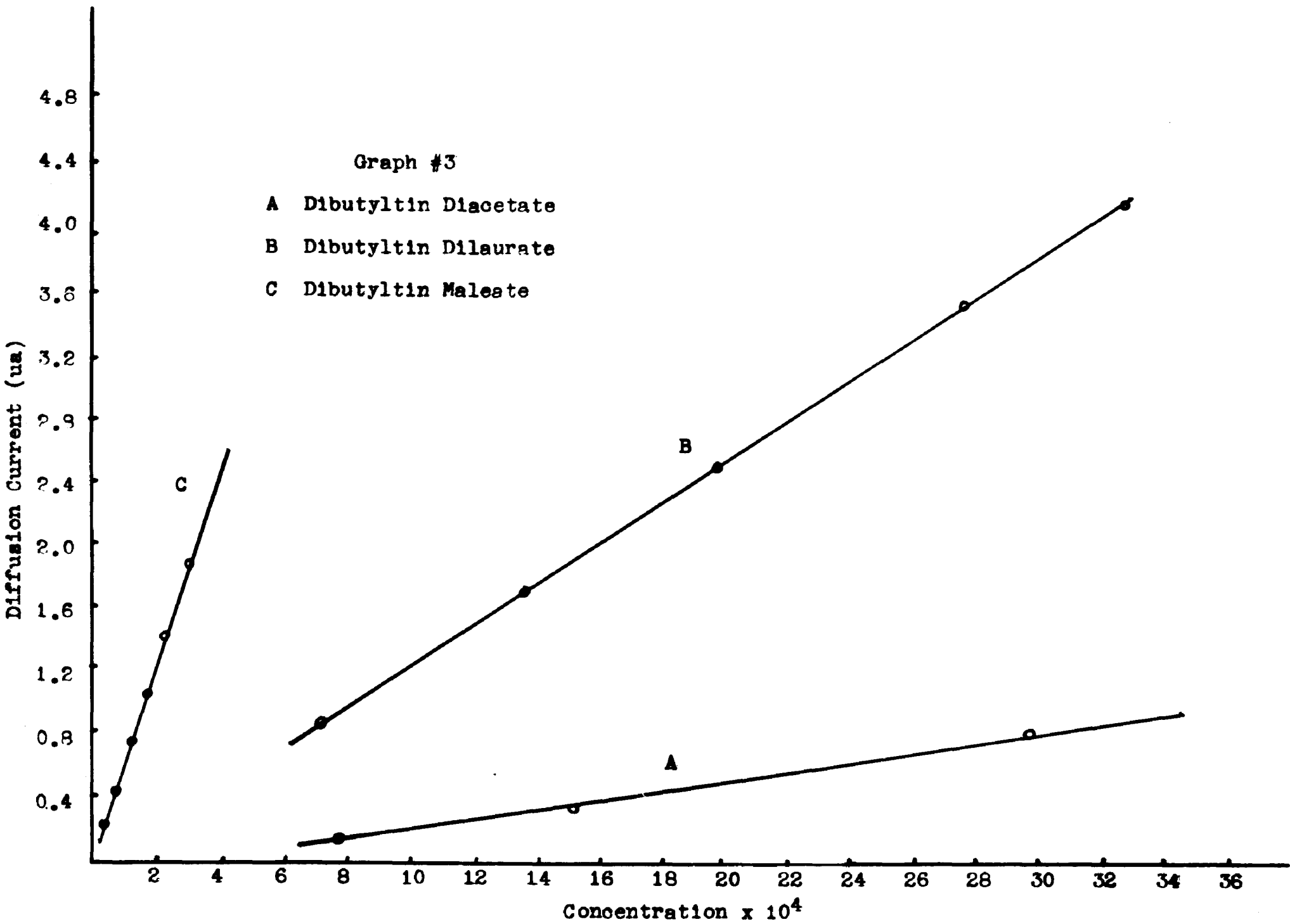
Measurements on the second wave were not made
because of the large surface activity in this region.

Dibutyltin dilaurate gave a relatively good
plot at the lower concentrations, i.e. 1.3×10^{-3}M to
7×10^{-3}M. (Graph #3, curve B) As the concentration
increased the diffusion current increased more rapidly
than did the concentration. Although there was no true
maximum formed at higher concentrations there was a
definite change in the diffusion plateau compared with
the lower concentrations.

The diffusion current of dibutyltin dichloride
and dibutyltin dilaurate were identical at the lower
concentrations. Above 2×10^{-3}M dibutyltin dichloride,
the diffusion current did not increase as rapidly and
the two plots diverged. The plot was again linear above
2×10^{-3}M to 4×10^{-3}M where the maximum became prominent.
The decrease in wave height was probably due to the
increase in height of the prewave which had been quite
small up to this concentration.

The diffusion current of dibutyltin sulfide was
by far the greatest of the compounds studied. Because
of the great amount of surface activity the calculations
of the diffusion current were not too accurate. With
this in mind the concentration vs. diffusion current
plot still gave a linear plot with a few points off the

curve. No plot was made of the second wave because of the sharp maximum.

Dibutyltin maleate waves were analyzed over a short concentration range, $3.2x10^{-5}$ to $2.9x10^{-4}$M because of maximum formation.(Graph #3,curve C) Except for the first two runs, which gave high results, the plot was linear throughout. This plot included three runs at the higher concentrations where the maximum had formed. The rate of increase of the wave height with increased concentration was much greater than that for dibutyltin sulfide. But since the concentration range was much lower, the sulfide had a larger current flow. The second wave was not plotted because the maximum had formed.

The electron changes for the dibutyltin compounds were as different as the diffusion currents. Because of measuring difficulties only the second wave for dibutyltin sulfide was measured. The smallest "n" value was found with dibutyltin dilaurate, 0.359, at a concentration of $6x10^{-3}$M. The first wave of dibutyltin sulfide had a value of 0.474 whereas the second wave had a value of 0.83. Both values were measured at a concentration of $7x10^{-4}$M.

Dibutyltin diacetate had an electron change of 0.486 at $2x10^{-3}$M. The "n" value for dibutyltin dichloride was 0.570 at a concentration of $2x10^{-3}$M.

From these values of "n" it was apparent that dibutyltin dilaurate, sulfide, diacetate and dichloride were irreversible; whether a one or two electron change was postulated for the first wave. Even the "n" value for the second wave of dibutyltin sulfide was too low to indicate a reversible one electron change.

The electron change for dibutyltin maleate on the other hand had a value of 1.08 at a concentration of 2×10^{-4} M which is just before the maximum forms. It was unfortunate that the remainder of the dibutyltin maleate polarogram had three large obscuring maxima since it could not be determined whether the first wave was a reversible one electron change or an irreversible two electron change.

Using the value of "n"= 1.08 and a concentration of 0.189, the diffusion coefficient for dibutyltin maleate was calculated to be 1.59×10^{-5} cm^2/sec.. The diffusion coefficients of the other compounds were not calculated because of the apparent irreversibility.

Tributyltin Compounds. Only three tributyltin compounds were available for this study; tributyltin oxide, tributyltin chloride and tributyltin acetate. The reduction of the compounds became more difficult in the order listed. Table VII lists the concentration range, the half-wave

potentials, electron change and diffusion currents for
these compounds.

Table VII

Compound	Concentration range	Half-wave potential	Electron change	Diffusion current
Tributyltin oxide	3.86×10^{-4} to 2.52×10^{-2}	-1.341 to -1.237	0.490	0.149 to 0.813
Tributyltin chloride	1.77×10^{-5} to 3.09×10^{-4}	-1.408 to -1.294	0.478	0.272 to 1.772
Tributyltin acetate	1.9×10^{-4} to 2.07×10^{-3}	-1.845 -1.734	0.600	0.092 to 1.962

Tributyltin oxide, unlike dibutyltin oxide does
not polymerize and is relatively soluble in DMF. Two
waves were observed for tributyltin oxide. The second
wave was small and did not increase in height as the
concentration increased. The first wave increased with
concentration and was the main wave. At lower concentra-
tions, 8×10^{-4}M, the two waves were combined into one
wave with a half-wave potential of -1.341v.. As the
concentration increased the half-wave potential became
more positive as the first wave became more prominent.
At a concentration of 1×10^{-2}M the first wave was the only
one which was measurable. The half-wave potential remain-
ed quite constant as the concentration increased to
2×10^{-2}M at -1.24v.. There was no maximum formed over the
entire concentration range studied.

Tributyltin chloride had only one well defined wave. The diffusion plateau however, was not identical in each run as it varied between a rounded "maximum" and a sharp break which caused variations in the analysis. The half-wave potential varied from -1.40v. to -1.33v. as the concentration increased from $2x10^{-5}$M to $1x10^{-4}$M. Above $1x10^{-4}$M the half-wave potential was relatively constant about -1.32v..

Tributyltin acetate showed two reduction waves, the first was noted at low concentrations and the second at high concentrations. The half-wave potential of the first wave was not constant but tended to become more negative as the concentration increased. It was -1.452v. at $1x10^{-4}$M, and increased to -1.480v. at $5.4x10^{-4}$M. Above a concentration of $6x10^{-4}$M the diffusion plateau had the same slope as the wave so that the half-wave potential could not be obtained. The second wave did not become well formed until a concentration of $4x10^{-4}$M. The half-wave potential was relatively constant at -1.73v. until the maximum began to form. The accuracy of the half-wave potential measurements was very poor due to incompletely formed first wave and the maximum on the second wave.

The plot of diffusion current vs. concentration for tributyltin oxide did not give a linear relationship.

The diffusion current was quite constant at the lower concentrations and rose only slowly and irradically at higher concentrations. It would not be possible to determine concentration from the diffusion current plot.

The tributyltin acetate plot had a break at a concentration of $7x10^{-4}$M. A linear plot was obtained at the lower concentrations but the plot at higher concentrations had a number of large deviations. The plots were made using the diffusion plateau at the higher concentrations rather than the maximum. The deviations were much greater when the maximum was used.

Tributyltin chloride gave the only linear plot of the three compounds in the group. The maximum peak was used at higher concentrations in the plot. The tributyltin chloride had a rapid increase in diffusion current with concentration, being only slightly lower than dibutyltin maleate, the compound with the greatest change in diffusion current with concentration.

The electron change for tributyltin chloride was lowest for this group. It had a value of 0.478 at a concentration of $1.4x10^{-4}$M. At the relatively high concentration of $1.4x10^{-2}$M tributyltin oxide had an "n" value of 0.490. Tributyltin acetate had a slightly higher value of 0.60 at a concentration of $8.5x10^{-4}$M.

Again it was assumed that all three reactions are irreversible at the dropping mercury electrode.

No diffusion coefficients were calculated due to the irreversibility of the reactions.

Phenyltin Compounds. All the phenyl compounds have been covered under the preceeding groups but an interesting relationship exists between them. Table VIII lists the concentration range, the half-wave potentials, electron change and diffusion currents for the phenyltin compounds.

Table VIII

Compound	Concentration range	Half-wave potential	Electron change	Diffusion current
Tetra-phenyltin	1.90×10^{-4} to 1.78×10^{-3}	-2.508 to -2.752	0.437	0.778 to 9.288
Triphenyltin chloride	1.78×10^{-4} to 5.15×10^{-4}	1) -1.068 to -1.094	0.558	0.761 to 2.433
		2) -2.280 to -2.292	- -	0.478 to 1.183
Diphenyltin dichloride	7.61×10^{-4} to 2.14×10^{-3}	-0.539 to -0.541	1.04	0.590 to 1.662
Phenyltin trichloride	1.34×10^{-3} to 2.64×10^{-3}	-0.353 to -0.376	0.868	1.440 to 3.220

The half-wave potential of the reaction product of tetraphenyltin and DMF was approximately -2.7v.. Substitution of one chlorine atom for a phenyl group caused

the half-wave potential to shift to -1.06v. for the first wave and the formation of a second wave at -2.28v.

Substitution of a second chlorine atom caused a shift to more positive potentials and increased the reactivity of the molecule. The half-wave potential of the first wave was -0.54v.. Because of the reactivity of the molecule, it reacted with water or possibly DMF to give hydrogen chloride. The hydrogen chloride gave a large wave and a maximum which obscured the polarogram from -1.0v. to -2.8v.

Phenyltin trichloride was sufficiently active to react with mercury. Obtaining a polarogram presented difficulties because of the reactivity. The half-wave potential of the resulting wave was -0.36v. Again the hydrogen chloride present prevented observation of a second wave if it was present. Replacing all four phenyl groups, giving stannic chloride, produced a molecule which was evidently too reactive to be studied in DMF.

The diffusion currents for the phenyl compounds fell into two groups. At a concentration of 3×10^{-4}M the diffusion current for tetraphenyltin was 1.3ua and for the first wave of triphenyltin chloride it was 1.28 ua. The second wave had a diffusion current of 0.94 ua. The remaining two compounds, diphenyltin dichloride and phenyltin trichloride had diffusion currents of 0.23 and 0.24ua respectively.

The decrease in diffusion current of the diphenyltin dichloride and phenyltin trichloride was probably due to the reaction with water or DMF.

The electron changes were 0.437, 0.558, 1.04 and 0.864 for tetraphenyltin, triphenyltin chloride, diphenyltin dichloride and phenyltin trichloride, respectively, indicating the reactions became more reversible as the number of chloride atoms increased.

CONCLUSION

The use of DMF as a nonaqueous solvent for polarographic study of organo-tin compounds has the disadvantage of being difficult to purify. Because of the reaction between some of the organo-tin compounds and water, which is an impurity in DMF, it was not always possible to obtain complete polarograms. Tributyltin chloride, triphenyltin chloride and trimethyltin chloride were the only three compounds which gave well defined waves over the entire working range of the system. All the remaining compounds either gave poorly defined waves or had interfering impurity waves. It would not be possible to distinguish between two of these latter compounds in the same solution.

The ease of reduction of the compounds depended upon the organic radical and the anion. The dichloride compounds became easier to reduce as the size of the organic radical increased. The half-wave potential of dimethyltin dichloride was -0.825v. whereas 5,5-dichloro-10,11-dihydrodibenzo(b,f)stanniepin had a half-wave potential of -0.52v..

Increasing the number of organic radicals made the compounds more difficult to reduce as illustrated by phenyltin trichloride, and triphenyltin chloride. The half-wave potential of phenyltin trichloride was -0.36v.

and that of triphenyltin chloride was -1.07v.. Similarly the half-wave potentials of dimethyltin dichloride and trimethyltin chloride were -0.825v. and -1.20v. respectively. A change in half-wave potential was also noted as the anion was changed. Dibutyltin dichloride was the easiest dibutyltin compound to reduce with a half-wave potential of -0.790v.. The compounds became more difficult to reduce as the anion was changed in the order, maleate, acetate, sulfide and laurate. The half-wave potential of dibutyltin dilaurate was -1.8v..

For tributyltin compounds the order of reduction' ease was oxide, chloride and acetate. The half-wave potential of the oxide was the lowest at -1.3v. and the acetate was the highest at -1.46v..

It was not possible to compare the half-wave potentials of the organo-tin compounds in DMF and aqueous systems due to the different reference electrode and also due to the fact that the second wave in the aqueous system is pH dependent. It was noted, however, that the order of reduction and the dependence on the number of organic radicals in the compounds were the same in both systems.

From the Ilkovic equation, $i_d = 607nD^{1/2}C_m^{2/3}t^{1/6}$, it can be seen that the diffusion current, i_d, depends only upon the square root of the diffusion coefficient,

$D^{1/2}$, if the concentration of reducible ions and the electron changes are the same and if the same dropping mercury electrode is used. The diffusion currents listed in Table IX are for a concentration of 3×10^{-4} M. Extrapolation of some plots to this concentration were necessary.

Table IX

Compound	Diffusion current, ua.
Trimethyltin chloride	3.6 (max. current)
Dibutyltin maleate	1.8
Tributyltin chloride	1.5
Tetratphenyltin	1.3
Triphenyltin chloride (first wave)	1.3
Dibutyltin sulfide	0.95
Triphenyltin chloride (second wave)	0.90
Phenyltin trichloride	0.60
Dimethyltin dichloride	0.57
Dibutyltin dichloride	0.29
Dibutyltin dilaurate	0.29
Diphenyltin dichloride	0.24
Tributyltin acetate	0.17
Tributyltin oxide	0.17
Dibutyltin diacetate	0.06
Tetrabutyltin	0.00

As can be seen from this table, there was no definite relationship between the structure and the diffusion current. It follows then that there was no relationship between the diffusion coefficient and the structure.
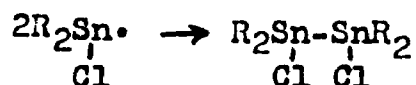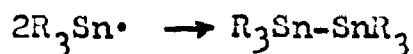
SUMMARY

1. N,N'dimethylformamide was found to be a poor solvent for most organo-tin compounds due to the small amount of water which remained in the dimethylformamide after distillation.

2. The potential of the quiet mercury pool was found to be constant if the total current flow through the cell was small.

3. Triphenyltin chloride, dimethyltin dichloride and 5,5-dichloro-10,11-dihydrodibenzo(b,f)stanniepin were the only three compounds which exhibited two distinguishable reduction waves.

4. The first reduction step has been postulated to be a one electron change. The electrode reactions being:

$$R_3SnCl + e \longrightarrow R_3Sn\cdot + Cl^-$$

$$2R_3Sn\cdot \longrightarrow R_3Sn\text{-}SnR_3$$

$$R_2SnCl_2 + e \longrightarrow R_2\underset{Cl}{Sn}\cdot + Cl^-$$

$$2R_2\underset{Cl}{Sn}\cdot \longrightarrow R_2\underset{Cl}{Sn}\text{-}\underset{Cl}{Sn}R_2$$

5. The second reduction step has been postulated to be a two electron change. The electrode reactions being:

$$R_3SnCl + 2e \longrightarrow R_2Sn + R\cdot + Cl^-$$

$$R_2SnCl_2 + 2e \longrightarrow R_2Sn + 2Cl^-$$
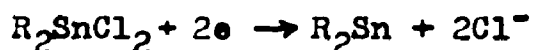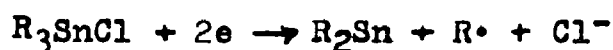
6. A reaction of the dichlorides, with the exception
of dimethyltin dichloride and the trichlorides, with the
residual water in the dimethylformamide produced hydro-
gen chloride which obscured any reduction wave in the
potential range -1.0 to -2.8v.

7. A similar reaction was noted with the acetates
and the maleate but the interfering waves were observed
at potentials of -1.9 and -2.0v. respectively.

8. All reduction waves gave electron changes of
less than one, except for diphenyltin dichloride and di-
butyltin maleate, which indicated the reactions to be
irreversible.

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