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Separation of Tin and Thallium Valences by Paper Chromatography

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Summary

Separation of tin and thallium valences has been sucessfully carried out by the technique of paper chromatography. Tin valences, which have been reported difficult to separate, have been resolved via their addition compounds with oxygen-containing solvents such as esters. Separation of thallium valences was comparatively simple, because thallic ion evinced greater propensity toward complexation in solvents like propanol and butanol. Precipitation chromatography using hydrochloric acid was also found effective in this separation.

There is a great void in the literature concerning the mechanism of separation of the same metallic ions in different valence states. There has been some work in the separation of the valence states of trace elements (*1,2*) in the biological field. There have also been a few attempts in the inorganic field to resolve the metals in different valence states, such as iron (*3–11*), uranium (*5,10,12*), arsenic (*13*), antimony (*13–16*), chromium (*3,15*), mercury (*13,14*), plutonium (*17*), and platinum (*13*).

These attempts made in the past were more or less of an empirical nature. The present paper is a study of the mechanism of separation of tin and thallium valences leading to an explanation of their differential behavior in different oxidation states.

THEORETICAL CONSIDERATIONS

Chromatographic migration of an ion is largely dependent on the solubilization of the ion in its particular state of valence. Solubilization depends on the following factors: (1) the coordination number of the metal ion and the probable stereo configuration of the metallic complex, (2) the polarizability of the metal ion (*18*) or that of the coordinating ligands, and (3) the steric effect of the entering ligands besides the dielectric constant of the solvents. The metal ions in different valence states are expected to show varying degrees of electronegativity, according to which the complexes formed by them will differ in their degree of ionic and covalent nature. The cellulose substratum of chromatographic paper is an amphoteric complex and the migration of metallic ions on it will be greatly influenced by the ionic or covalent nature of the metallic complex. Following the adage "like dissolves the like," it may be stated that the ionic complexes migrate faster in ionic solvents, whereas the covalent complexes do so in the nonpolar solvents. This is the fundamental basis that operates in the separation of metals in their different valence states.

Coordinate covalent linkages are effected through a hybridization of the orbitals. In the case of tin and thallium, which are *p*-valenced elements, hybridization is possible between *ns*, *np*, and *nd* orbitals. When a metal exhibits a coordination number of 4, the complex can assume a tetrahedral or square planar structure through sp^3 or dsp^2 hybridization, respectively. Similarly, when the coordination number is 6, the most probable spatial arrangement is octahedral with a d^2sp^3 hybridization. During chromatographic migration, a complex will, more often than not, change from one stereo form into another, according to the number of solvent ligands it imbibes. The transformation of a tetrahedral into an octahedral structure would convert a more covalent structure into a more ionic one. Generally, solvents that are more polar favor the formation of ionic structures and, conversely, the less polar solvents the covalent structures. Separation of the two valence states will then become possible for the following reasons: (1) one of the valence states prefers to give a more ionic structure than the other by virtue of differences in coordination numbers; or (2) one of the valences shows facility to form both the covalent and the ionic structures, thereby getting solvated both in the polar and nonpolar solvents.

SEPARATION OF TIN VALENCES 2 AND 4

Stereochemistry of Tin

Stannous tin shows coordination numbers of 3 and 4 in acid medium, the corresponding anions being $(SnCl_3)^-$ and $(SnCl_4)^{2-}$.

The configuration of these complexes can be pyramidal with P^3 and tetrahedral with sp^3 hybridizations, respectively. A planar configuration suggested for the latter from X-ray studies (*19*) was found incompatible with other observations. The highly ionic nature of stannous tin makes one doubt the tetrahedral configuration. In analogy with $SnCl_2 \cdot 2H_2O$, a pyramidal structure with sp^3 hybridization as suggested by Cotton and Wilkinson (*20*) is more suitable and this structure is more ionic than covalent.

Stannic tin exhibits coordination numbers of 5 and 6, giving complexes of the types $(SnCl_5)^-$ and $(SnCl_6)^{2-}$. The possible electronic configurations are sp^3d and sp^3d^2, with trigonal bipyramidal and octahedral structures, respectively. Both these structures are more ionic than covalent.

Experimental

Preparation of Solutions. *Stannous chloride.* Stannous solution was prepared by dissolving AnalaR tin in a deficiency of hydrochloric acid medium, the stannous ion $(SnCl_3)^-$ is highly reducing in An aliquot was then suitably made up with concentrated hydrochloric acid to get a 0.2 *M* solution. Extremely unstable, the solution must be prepared fresh every day. One μliter of 0.2 *M* solution is equivalent to 23.74 μg of tin.

Stannic chloride. A 0.2 *M* solution was prepared by dissolving AnalaR hydrated stannic chloride ($SnCl_4 \cdot 5H_2O$) in concentrated hydrochloric acid. One μliter of this solution is equivalent to 23.74 μg of tin.

Stability of the Ions. Being a *p*-valenced element, one would expect Sn^{2+} to oxidize only slowly because its 5*s* electrons are inert. This is true only in the anhydrous condition. In the aqueous acid medium, the stannous ion $(SnCl_3)^-$ is highly reducing in character (*21*) and a slight oxidation is always observed in the chromatograms.

Quantities Spotted. Twenty μliters of the solution was spotted in each case, using "Agla" micrometer syringe whose least count was 0.2 μliter.

Chromatographic Paper. Circles of Whatman No. 1 paper 15 cm in diameter were used.

Spraying Reagent. A 5% aqueous solution of phosphomolybdic acid was used to detect Sn^{2+} (blue color); the sensitivity of the reagent was 0.03 μg of tin. A 5% alcoholic solution of 8-hydroxyquinoline was used to reveal Sn^{4+}. This gave a yellow color in acid medium and it is sensitive to 1 μg of tin.

Measurement of R_F Values. R_F values were evaluated by measuring the distance between the center of the spot applied and the outer boundary of the chromatographic bands. Whenever the bands were irregular, measurements were taken at several points on the band and the average struck.

Radial Paper Chromatography. Radial chromatography (22) was adopted for its well-known advantages over the other techniques: (1) a better band sharpness due to progressive dilution of the solute during radial migration; (2) more than one sample can be simultaneously chromatographed by the Kawerau modification of the technique; and (3) the facility to work with more than one developer by cutting out sectors from the completed chromatograms and treating them separately. For convenience in comparing the R_F values of the ions, the Kawerau modification of the Rutter technique was adopted in the present work. The filter paper was demarcated into three segments by cutting slots. One each of these segments was used for the two individual ions and the third for the mixture. Although slight variation in R_F values in the same system is a common experience in chromatography, there is an additional possibility of error due to variations in the physical contact between the paper and the irrigating wick. To allow for this error, the method adopted in this laboratory was to compare R_F values for fixed-distance runs of the solvent front, i.e., the solvent was allowed to run to a preset distance from the center, irrespective of time.

Polarographic Estimation of Tin. The chromatographically resolved ions were estimated polarographically using a Radiometer Polariter PO3. The supporting electrolyte used in this laboratory was a 1:1 mixture of 4 M NH_4Cl and M HCl. Only a single well-defined step was observed with a half-wave potential at −0.52 V vs. SCE, which corresponded to the reduction of $Sn^{2+} \rightarrow Sn$. This is also corroborated by the work of Lingane and Nishida (23).

Working Graph. Quantities ranging from 60 to 360 μg were spotted on Whatman No. 1 paper. The filter paper in each case was dried and the spotted area punched out and extracted with hydrochloric acid. The excess acid was removed by boiling and the solution made up to 10 ml with 1:1 mixture of M HCl and 4 M NH_4Cl. The solution was deaerated with purified H_2 and the polarograms

TABLE 1

Polarographic Data[a]

Item no.	Vol. of soln., spotted, ml	Quantity in the spot, μg		Height of wave, cm	
		Sn	Tl	Sn	Tl
1	0.01	—	423.8	—	1.9
2	0.02	63.2	847.6	0.9	4.0
3	0.03	—	1271.4	—	6.1
4	0.04	126.4	1695.2	1.8	8.0
5	0.06	189.6	—	2.6	
6	0.09	284.4	—	3.7	
7	0.12	379.2	—	4.7	

[a] Molarity of spotted solution: Sn, 0.0266; Tl, 0.2074.

of the different concentrations were recorded for the preparation of the working graph (see Table 1).

Phosphomolybdic acid spraying reagent would interfere with polarographic estimations of tin and was therefore avoided on chromatograms used for polarographic estimations. From a knowledge of pilot experiments, the areas of Sn^{2+} and Sn^{4+} were marked out on the chromatograms. The punched-out regions were given the same treatment as under working graph. Wave heights of the unknown were then referred to the working graph.

Discussion

Previous Work. Separation of tin valences has hitherto received little attention. Elbeih et al. (*24*) have studied the migrations of tin in its two valences in different solvent systems and their chart reveals very close R_F values for both ions. The work of Anderson and Martin (*25*) and Lederer (*26*) reveals close R_F values for the two ions—so much so, it should have been difficult to resolve the two ions satisfactorily.

Present Work. In acid solutions the Sn^{2+} with a pyramidal structure and the Sn^{4+} with a bipyramidal or octahedral structure will both be ionic and their migration is expected to be similar, as testified to by previous workers (*24–26*), as well as by the close R_F values of Sn^{2+} and Sn^{4+} obtained in this laboratory in chromato-

TABLE 2

Resolution of Sn^{2+} and Sn^{4+a}

Item no.	Chromatogram no.	Solvent[b]			R_F[c]		Resolution factor, ratio of R_F values[d]	Estimated weight, μg[e]		% error on total Sn	Redox ratio after chromatography[f]
					Sn^{2+}	Sn^{4+}		Sn^{2+}	Sn^{4+}		
1	1	MeOH 100	Conc. HCl 1		1.0	1.0	1.0	—	—	—	—
2	2	MeOH 100	Glac. HAc 100	H_2O 100	0.95	0.95	1.0	—	—	—	—
3	3	BuOH 100	Glac. HAc 50	Ethyl acetate 50	0.80	0.85	1.06	—	—	—	—
4	4	Ethyl acetate 100	Glac. HAc 100		0.80	0.85	1.06	—	—	—	—
5	5	20% NaOH			0.80	0.90	1.12	—	—	—	—
6	6	Acetone			1.0	1.0	1.0	—	—	—	—
7	7	Ethyl acetate			0.65	1.0	1.54	201	294	4.26	59.39
8	8	Ethyl acetate 100	Glac. HAc 1		0.62	1.0	1.61	201	300	5.52	59.88
9	—	Ethyl acetate 100	98% Formic acid 1		0.62	1.0	1.61	207	240	−5.86	53.69
10	9	Ethyl acetate 1	Methyl salicylate 1		0.31	0.97	3.13	213	249	−2.70	53.91

[a] Paper: Whatman No. 1. Spotted: Sn^{2+} and Sn^{4+}, 237.4 μg each (20 μl *M*/10 with respect to each). Redox ratio: $Sn^{4+}/(Sn^{2+} + Sn^{4+}) = 50\%$.

[b] Solvent ratio is by volume.

[c] R_F values are average of at least three chromatograms.

[d] Resolution factor is the ratio between the R_F of the faster moving species with the R_F of the slower species. A resolution factor of 1.0 would therefore mean that there is no separation and values of higher than 1 would indicate resolution.

[e] Polarography.

[f] Redox ratio percentages are a quantitative index of the separation of the two valences. The number 50 indicates 100% separation without oxidation or reduction. A number lower or higher than 50 indicates reduction or oxidation, respectively, having taken place during chromatography.

grams 1–5 (see Fig. 1 and Table 2). Attempts were made to separate the two ions using ester-type eluents.

Sn^{2+} and Sn^{4+} have been reported to give coordination complexes and addition compounds with oxygen-containing organic solvents (*27–33*). For instance, the solubility of Sn^{2+} and Sn^{4+} in acetone is high. But in the absence of acids, acetone-solubilized stannous tin seems to be unstable (undergoing oxidation instantaneously)—so much so that only a feeble band corresponding to stannous tin is seen, whereas the stannic band is predominant and masks the stannous band (see Fig. 2). The poor stability of stannous ion is greatly responsible for the difficulty of resolution of stannous from stannic, especially in polar solvents and acidic media. Nonpolar, nonacidic media do not bring about migration. The only solvent by which a certain amount of resolution is achieved is ethyl acetate, in which the stannous has an R_F of 0.65 and the stannic 1.00 (see Fig. 3). A certain amount of tailing was observed in the case of Sn^{2+} which was considerably reduced when methyl salicylate or formic acid or acetic acid was included in the eluent (see Figs. 4 and 5). The resolution was appreciable when methyl salicylate was used.

Resolution of Sn^{2+} from Sn^{4+} using ethyl acetate as eluent is explained as follows: Sn^{2+} gives a complex $(SnCl_3\text{–ethyl acetate})^-$ by the replacement of the loosely held fourth chlorine atom in the pyramidal $(SnCl_4)^{2-}$ ion. Under the same circumstances the stannic ion yields an octahedral configuration ($SnCl_4$–2 ethyl acetate) by the replacement of two chlorine atoms of $(SnCl_6)^{2-}$ by the solvent molecules. It will be seen that stannic ion imbibes more solvent molecules into its coordination shell than the stannous ion and this would account for its greater solubilization and migration.

Addition of organic acids such as formic, acetic, and butyric acids to ethyl acetate did not appreciably improve the resolution; however, increasing the acidity reduced the tailing. A mixture of methyl salicylate and ethyl acetate very much improved the resolution (see Fig. 5). Sn^{4+} ion forms a 5-covalent chelate with methyl salicylate (*33*). The Sn^{2+} ion, on the other hand, does not give a corresponding complex. It would therefore appear that stannic tin is solubilized by both components of the mixture, whereas stannous tin is solubilized only by ethyl acetate. This would account for the greater R_F of the former (see Fig. 6).

In conclusion it may be stated that the resolution of Sn^{2+} from Sn^{4+} is made difficult, if not impossible, because of (1) the insta-

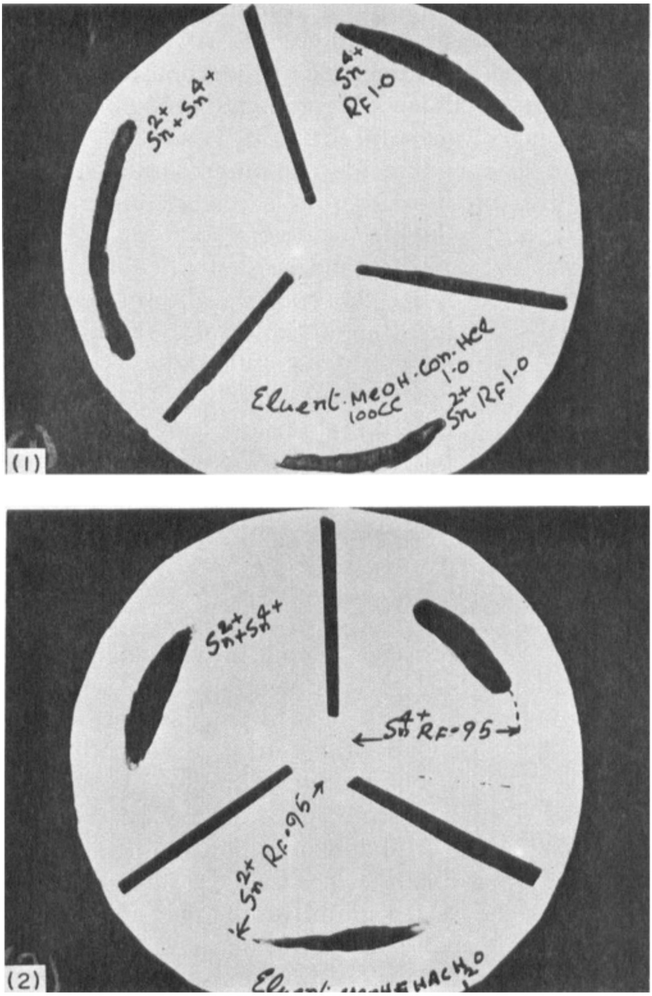

FIG. 1. Chromatograms 1 to 5. Chromatographic migration of Sn^{2+} and Sn^{4+} ions in different solvents. Note the close R_F values of the ions.

bility of the Sn^{2+} ion and (2) the similarity of the ionic nature of the solvo complexes formed by the two ions. However, a satisfactory resolution has been achieved by making use of a mixture of ethyl acetate and methyl salicylate as eluent.

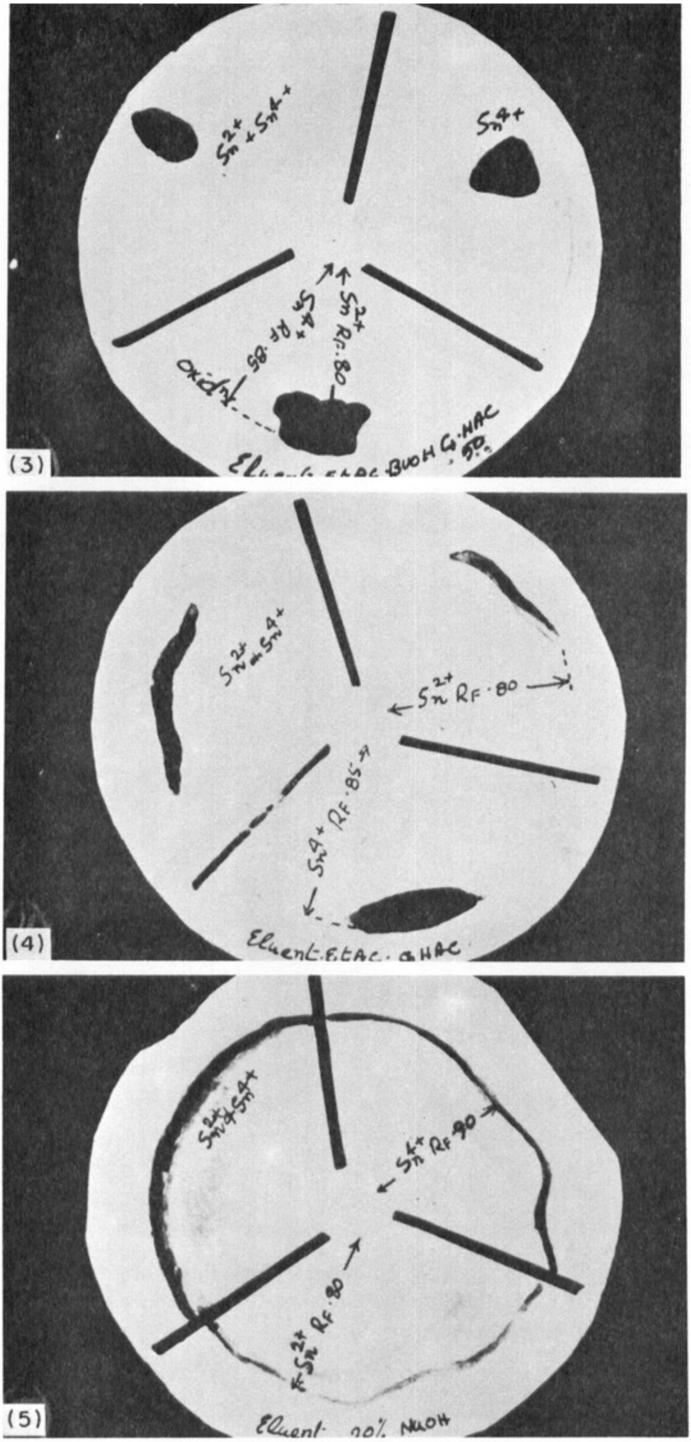

FIG. 1 *(continued)*

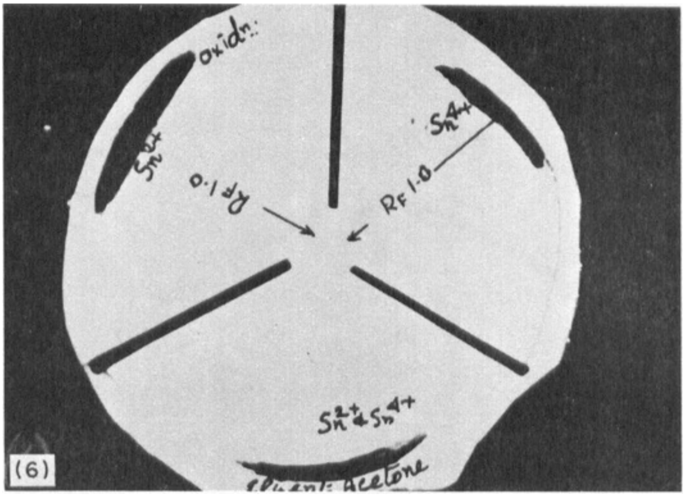

FIG. 2. Chromatogram 6, showing considerable oxidation of stannous tin in acetone.

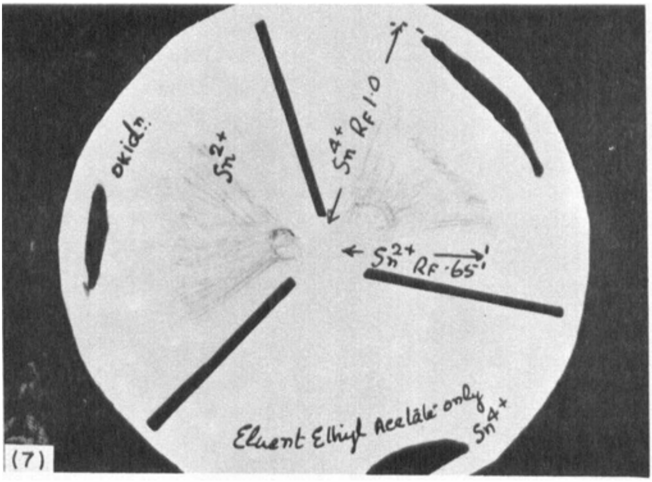

FIG. 3. Chromatogram 7, showing fair degree of resolution of Sn^{2+} from Sn^{4+} ions in ethyl acetate. Note the diffusion due to absence of acid.

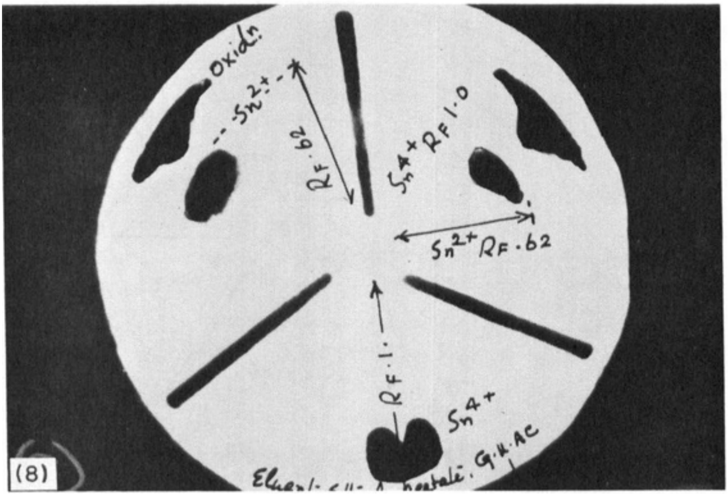

FIG. 4. Chromatogram 8, showing the resolution of Sn^{2+} from Sn^{4+} in ethyl acetate and glacial acetic acid.

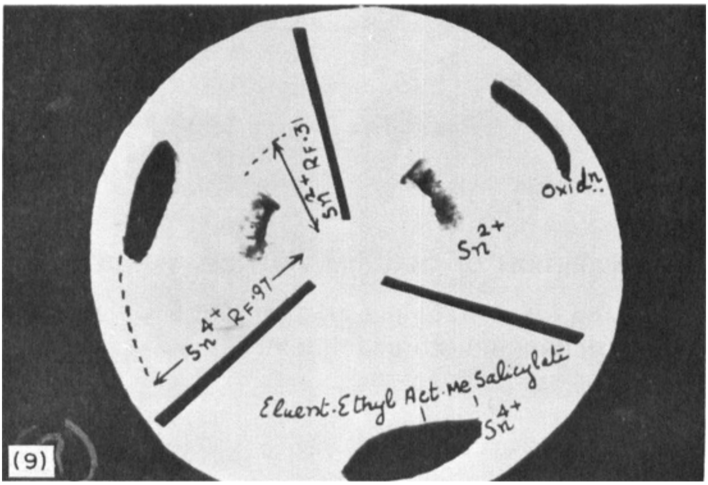

FIG. 5. Chromatogram 9, showing improved resolution when methyl salicylate is added to ethyl acetate.

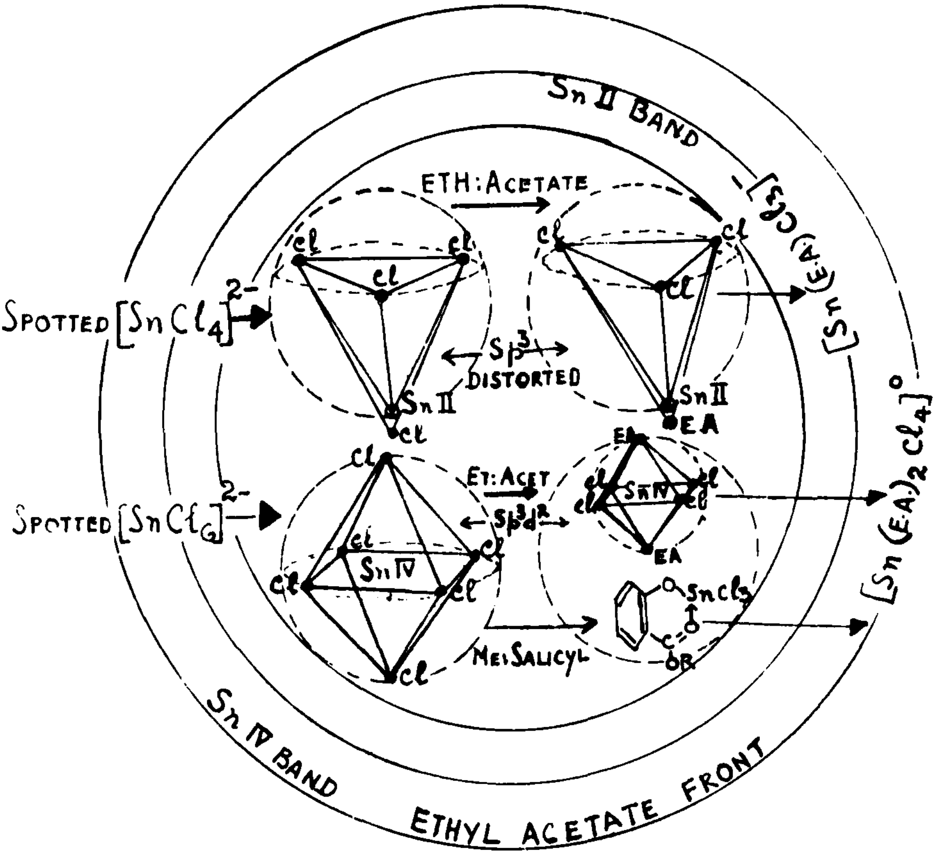

FIG. 6. Schematic representation of the resolution of stannous from stannic tin.

SEPARATION OF THALLIUM VALENCES 1 AND 2

Anderson and Martin (25) and Lederer (26) have attempted the separation of thallium ions from other metals and in their different valence states.

Stability of Thallium Ions

In the case of thallium, the "inert-pair" effect is most predominant, so much so that the group valence 3 is unstable and the monovalent thallium is the stabler of the two. Even mild reducing agents can reduce Tl^{3+} to Tl^{+} whereas strong oxidizing agents are needed for the reverse process. Because thallous chloride is sparingly soluble and thallic chloride is unstable, it was found necessary to use the nitrates of the element for spotting purposes. However, the stability of the thallic nitrate was found to be poor in the presence of moisture and therefore thallic ion must be spotted in the form of a bromocomplex, $H(TlBr_4)$ (*34*).

Experimental

Preparation of Solutions. *Thallous nitrate.* Thallous ion was spotted at its nitrate. A 0.2 *M* solution was prepared by dissolving thallous nitrate $TlNO_3$ in AnalaR 4 *N* nitric acid. One μliter of this solution contained 40.88 μg of thallium.

Thallic salt solution. Thallic ion was spotted as its stable complex bromide $H(TlBr_4)$. A 0.2 *M* solution of the complex was prepared by boiling thallous nitrate in acid medium with excess bromine water and boiling off the excess bromine (1 μliter = 40.88 μg).

Spraying Reagent. Ten per cent aqueous solution of KI (iodine-free) was used to detect both Tl^+ and Tl^{3+}. The former gave an intense yellow color, whereas the latter gave a reddish-brown color fading to yellow after a couple of hours. The reagent is sensitive to 0.6 μg of Tl^+ and 0.2 μg of Tl^{3+}.

Other details of chromatographic technique are as given for tin.

Polarographic Estimation of Thallium. As is the case with *p*-valenced elements, the polarographic wave corresponding to the first step of reduction of $Tl^{3+} \rightarrow Tl^+$ is not well defined. However, the second step of reduction of $Tl^+ \rightarrow Tl$ yields a well-defined wave with an $E_{1/2}$ of 0.5 V vs. SCE. The half-wave potential of this wave is not altered, and it remains more or less the same in molar solutions of different electrolytes (*35–37*). This is due to the fact that the thallous ion seldom forms complexes.

The supporting electrolyte used for this work was *M* HNO_3, and the preparation of the working graph is similar to that already discussed for tin (see Table 3). Concentrations in the range of 400–1700 μg of thallium were used in the preparation of the working graph. Refer to the data in Table 1.

Discussion

Monovalent thallium resembles the alkali salts in several respects (*38*). It seldom forms complexes. Because of the small de-

TABLE 3

Resolution of Tl^+ and Tl^{3+}

Item no.	Chromatogram no.	Solvents[b]			R_F[c]		Resolution factor, ratio of R_F values[d]	Estimated weight, μg[e]		% error on total Tl	Redox ratio after chromatography[f]
					Tl^+	Tl^{3+}		Tl^+	Tl^{3+}		
1	10	MeOH 100	Conc. HNO_3 1		0.45	1.0	2.22	560	480	1.76	46.15
2	11	EtCH 100	Conc. HNO_3 1		0.22	1.0	4.54	580	480	3.72	46.2
3	—	PrOH 100	Conc. HNO_3 1		0	1.0	∞	500	460	−6.07	47.92
4	12	BuOH 100	Conc. HNO_3 1		0	1.0	∞	580	480	3.72	45.28
5	13	MeOH 50	Ethyl acetate 50	Conc. HNO_3 1	0.25	1.0	4.0	560	500	3.72	47.18
6	14	MeOH 100	Conc. HCl 1		0	1.0	∞	580	500	3.72	47.18
7	—	MeOH 100	98% Formic acid 1		0.45	1.0	2.22	560	480	1.76	46.15
8	—	EtOH 100	98% Formic acid 1		0.23	1.0	4.34	560	500	3.72	47.18
9	—	PrOH 100	98% Formic acid 1		0	1.0	∞	520	460	−4.11	46.95
10	—	BuOH 100	98% Formic acid 1		0	1.0	∞	500	480	−4.11	48.98

[a] Paper: Whatman No. 1. Spotted: Tl^+ and Tl^{3+}, 511 μg each (25 μl $M/10$ with respect to each). Redox ratio: $Tl^{3+}/(Tl^+ + Tl^{3+}) = 50\%$.

[b] Solvent ratio is by volume.

[c] Values given in the table are averages of at least three chromatograms.

[d] Resolution factor is the ratio between R_F values of the faster moving species with R_F of the slower species. A resolution factor of 1.0 would therefore mean that there is no separation. Values higher than 1 would indicate resolution.

[e] Polarography.

[f] Redox ratio percentages are a quantitative index of the separation of the two valences. The number 50 indicates 100% separation without oxidation or reduction. A number lower or higher than 50 indicates reduction or oxidation, respectively, having taken place during chromatography.

formability of the oxygen atom, thallous nitrate is completely ionized, similar to the alkali metals. Also, the atomic size of thallium does not permit any strong hydration and so there is little chance of Tl^+ forming solvo complexes. Under these circumstances thallous thallium migrates on paper through ion association, rather than coordination with the solvent. The work in this laboratory reveals that the migration of Tl^+ is poor in many solvents and the R_F markedly decreases from 0.45 to zero as the eluent is changed from the more polar methanol to the less polar butanol (see Fig. 7). Its ion association is closely linked with the dielectric constant of the solvent, as shown by the fact that its R_F of 0.45 in methanol is reduced to 0.25 when a 50:50 mixture of methanol and ethyl acetate was used as eluent (see Fig. 8 and item 5 in Table 3). The nonimprovement of resolution on the inclusion of organic acids such as formic acid, acetic acid, etc., in the solvent indicates that no complex is formed by these acids with the thallous ion.

With thallous hydroxide in anhydrous alcohol, acetyl acetone has been known to give a bidentate chelate which is soluble in benzene (*39–41*). Since Tl^+ was spotted as $TlNO_3$ in aqueous acid medium, no chelate was formed and the attempt to separate thallium valences using acetyl acetone in benzene was not successful as there was no migration of both ions.

Thallic ion readily forms coordination complexes with several solvents (*38,42*). Tl^{3+} is spotted as the anionic complex $(TlBr_4)^-$, which splits up under the effect of the solvent molecules yielding $(TlBr_3{\cdot}sol)$. The resultant solvo complex enables the Tl^{3+} ion to migrate with greater facility than the Tl^+, which does not form similar complexes. This, therefore, affords an easy means for the separation of Tl^+ from Tl^{3+} Tl^{3+} is found to migrate almost with the solvent front, with R_F values of about 1; whereas the Tl^+ either does not migrate or migrates poorly, with R_F values not exceeding 0.45.

Inclusion of hydrochloric acid in the eluent brought about a precipitation of thallous chloride at the spot of application (*26*) (see Fig. 9), whereas Tl^{3+} moved as usual. This is very similar to the precipitation technique used for the separation of mercurous from mercuric ions (*14*). It may be remarked that the instability of thallic ion is so marked that its partial reduction to the thallous can hardly be prevented.

In conclusion, the separation of thallous from thallic can be easily

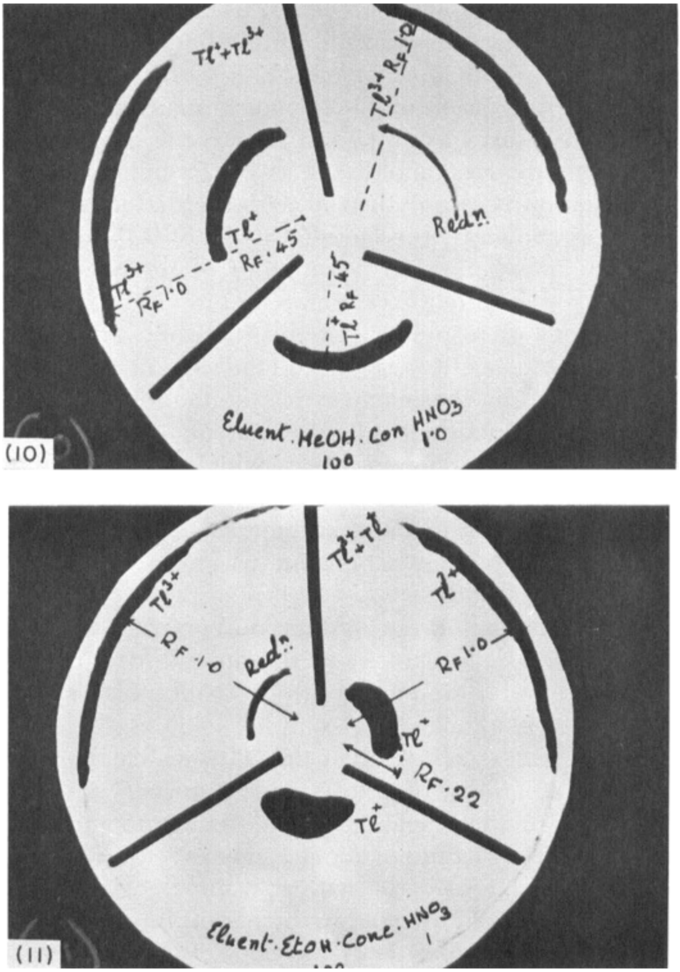

FIG. 7. Chromatograms 10 to 12. Chromatographic migration of Tl^{3+} and Tl^{+} in MeOH and BuOH (1% acid). Note the retardation of the R_F of Tl^{+} with decreasing polarity of the solvent.

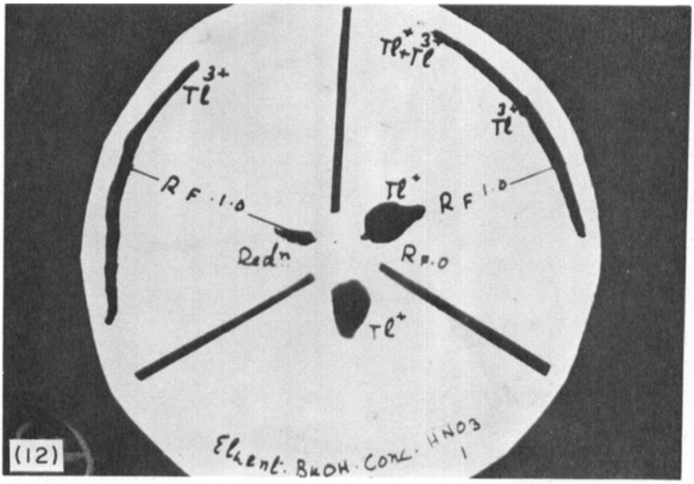

FIG. 7 (*continued*)

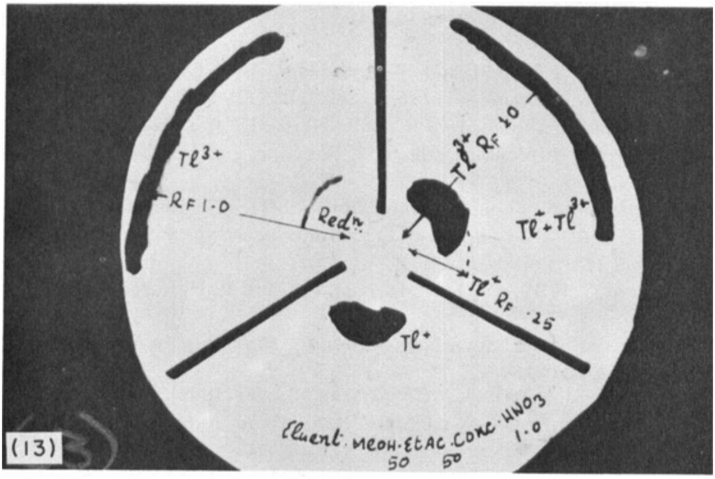

FIG. 8. Chromatogram 13, showing the influence of polarity of solvent on the R_F of Tl^+ and Tl^{3+}.

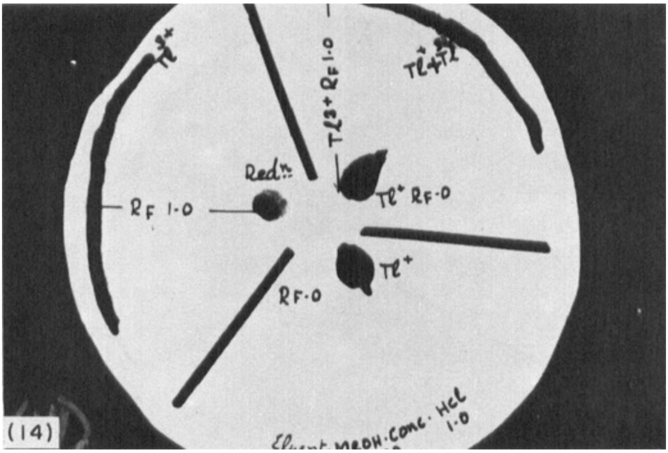

FIG. 9. Chromatogram 14. Precipitation chromatography of Tl^+ and Tl^{3+} using 0.1 *M* HCl as eluent.

carried out by the precipitation technique, using hydrochloric acid in the eluent or by using propanol or butanol containing 1% concentrated nitric acid as the eluent.

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