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The Separation of the Oxidation States of Some Elements with the Use of Tri-n-butyl Orthophosphate

Madhukar L. Thakur[a]
[a] MEDICAL RESEARCH COUNCIL CYCLOTRON UNIT HAMMERSMITH HOSPITAL, LONDON, ENGLAND

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NOTE

The Separation of the Oxidation States of Some Elements with the Use of Tri-*n*-butyl Orthophosphate

MADHUKAR L. THAKUR
MEDICAL RESEARCH COUNCIL
CYCLOTRON UNIT
HAMMERSMITH HOSPITAL
LONDON W.12, ENGLAND

Summary

The tri-*n*-butyl orthophosphate:acetic acid:acetone solvent system has been studied for the paper chromatographic separation of the oxidation states of 16 elements. The separation of As^{3+}, As^{5+}; Cr^{3+}, Cr^{6+}; Fe^{2+}, Fe^{3+}; Hg^{+}, Hg^{2+}; Mn^{2+}, Mn^{3+}, and Mn^{7+}; Sb^{3+}, Sb^{5+}; Tl^{+}, Tl^{3+}; Cl^{-}, ClO_3^{-}; Br^{-}, BrO_3^{-}; I^{-}, IO_3^{-}; $P_2O_7^{4-}$ PO_4^{3-}, and PO_3^{-} has been achieved. Multiple zones obtained with Fe^{3+} and Tl^{3+} species are discussed.

INTRODUCTION

Many times it is essential to know the oxidation states of elements in solutions. Though solvent extraction and ion exchange methods can be used for such a purpose, paper chromatographic methods are preferred since they require only small samples and are usually simple to perform.

Many workers (*1–7*) have made valuable contributions in the paper chromatographic field by means of which the separation of valency states of elements could be carried out; but for the separation of the oxidation state of each element either a different solvent or a different condition has been used.

Tri-*n*-butyl orthophosphate (TBP), a basic nonelectrolyte, has been found by Irving (*8*), Ishimori (*9*), and Morris (*10–17*) to be an efficient solvent for extracting inorganic species of various valency states from their aqueous solutions. Of those, Ishimori et al. (*9*) have reported different distribution coefficients for Se^{4+}, Se^{6+}; Tl^{+}, Tl^{3+}; Te^{4+},

Te^{6+}; and for Np^{4+}, Np^{5+}, and Np^{6+} from 1 to 12 M hydrochloric acid into TBP. These studies indicated that TBP might be a useful solvent for the paper chromatographic separation of the oxidation states of some elements.

In the work reported here, TBP mixed in a certain proportion with acetic acid and acetone has been used as a single solvent for the paper chromatographic separation of the oxidation states of several elements. The solvent system is simpler than those used by the previous workers, and no special precautions are needed to carry out the separations.

EXPERIMENTAL

Solvents

(a) Tri-*n*-butyl orthophosphate (G.P.R.) grade without purification.

(b) 5 M acetic acid (50 ml, Analar glacial acetic acid diluted to 175 ml with deionized water).

(c) Acetone-Analar.

When the above reagents were mixed in the proportion of 1:1:3 respectively, a homogeneous solution of pH 3 was obtained.

Chromatographic Paper

5 × 20 cm and 10 × 20 cm sheets of Whatman No. 1 chromatographic paper were used.

Apparatus

Commercially available developing jars, spraying units, and microcapillaries for spotting were used.

Solutions

Analar grade compounds were weighed and dissolved either in acid or in water and were stabilized at essential pH conditions. Sb_2O_3 and $SbCl_5$ (oxidized with H_2O_2) were dissolved in 2% tartaric acid. About 10 μg of the elements were spotted on the paper in about 5 μl of the solutions.

Detection

Suitable reagents were sprayed for detection of zones.

R_F Values

All the spotted solutions were air dried and the solvent front was allowed to ascend 15 cm at room temperature (19 to 22°C). This took about 2 hr. To evaluate the R_F values, the distance between the point of application and the center of the colored zones was measured. The R_F values of some of the elements were checked by radioactive tracer methods. The reported values are the average values of at least three results.

RESULTS AND DISCUSSION

The work was initiated to study the feasibility of using TBP as a paper chromatographic solvent for the separation of valency states of antimony. Acetic acid was added to decrease the pH and acetone was used to increase the solubility of the acid in TBP. The mixture thus obtained is a homogeneous solution of pH 3. By the use of this solvent, Sb^{3+} and Sb^{5+}, which were in 2% tartaric acid, were separated with the R_F values of 0.0 and 0.5, respectively. The work was then continued for the separation of valency states of the other elements.

In general the zones obtained are compact and the separation is unambiguous. Although the R_F values for Cr^{3+} and Cr^{6+} and for As^{3+} and As^{5+} are relatively close, even these species may be separated satisfactorily.

The basis on which ions of different valency states can be resolved is that the metals form ionic or covalent complexes depending upon their oxidation states and that the ionic complexes associate with polar solvents and covalent complexes with nonpolar ones. The solvent is nonpolar, and it is clear from Table 1 that higher valency states exhibit increased migration. This may be attributed to the formation of their covalent complexes. Such a type of complex formation has been found by Irving and Edgington (*8*), particularly in the HCl–TBP system. The multiple spot formation phenomenon of Hg^{+} and Sb^{5+} (*7*) is not observed here, except for a little streaking in the Hg^{+} zone.

However, Fe^{3+} indicated its presence in two bands with R_F values of 0.56 and 0.7. It was thought that this may be due to the incorporation of NH_4^{+} or SO_4^{2-} species (from ferric ammonium sulfate) into the covalent complex of Fe^{3+}–TBP. To avoid this possibility, Fe^{3+} as ferric chloride was used; but the R_F values (and also the shapes) of

TABLE 1

Ions with Separable Valency States

Ion	R_F value
As^{3+}	0.42
As^{5+}	0.57
Cr^{3+}	0.1
Cr^{6+}	0.26
Fe^{2+}	0.0
Fe^{3+}	0.56, 0.7
Hg^{+}	0.0[a]
Hg^{2+}	0.92
Mn^{2+}	0.18
Mn^{3+}	0.0
Mn^{7+}	0.0
Tl^{+}	0.05
Tl^{3+}	0.3
Sb^{3+}	0.0
Sb^{5+}	0.5
$P_2O_7^{4-}$	0.0
PO_4^{3-}	0.37
PO_3^{-}	0.07
F^{-}	0.0
Cl^{-}	0.13
ClO_3^{-}	0.32
Br^{-}	0.2
BrO_3^{-}	0.13
I^{-}	0.28
IO_3^{-}	0.0

[a] Streaking observed.

the zones obtained from ferric ammonium sulfate in 2 and 8 *M* HCl and from ferric chloride in 2 and 8 *M* HCl are identical (Fig. 1). Doubts of the incorporation of NH_4^+ or SO_4^{2-} ions into the complex are removed because the different complexes are unlikely to have the same R_F values. At the same time, because Fe^{3+} does not form an anion of the type $FeCl_4^-$ in 2 *M* HCl but still shows the same type of multiple zones as is shown in 8 *M* HCl, the possibility of $FeCl_4$–TBP type of complex may be ruled out. Tl^+ and Tl^{3+} are separated at R_F values of 0.05 and 0.3, respectively, but Tl^{3+} in an excess of hydrochloric acid, where it is known to form chloro complexes, is resolved into 3 zones at R_F values of 0.3, 0.55, and 0.9. The influence of acetic acid

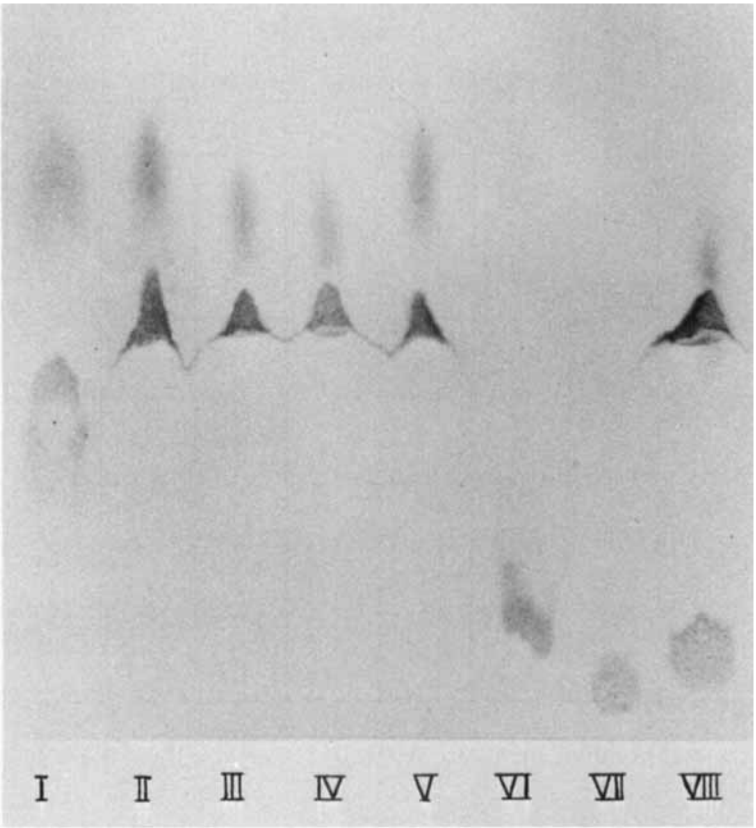

FIG. 1. Quantity of Fe^{2+} or Fe^{3+} spotted = 10 μg. I: $FeCl_3$ in 0.1 *M* HCl. II: $FeCl_3$ in 2.0 *M* HCl. III: $FeCl_3$ in 8.0 *M* HCl. IV: $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 8 *M* HCl. V: $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 2.0 *M* HCl. VI: $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 0.1 *M* HCl. VII: $FeSO_4 \cdot 7H_2O$ in 0.5 *N* H_2SO_4. VIII: Solution IV + VII.

and acetone in the solvent on such types of complex formation is not yet understood. Further work in this connection is under progress.

Of the transition elements studied, Fe^{2+}, Fe^{3+} and Cr^{3+}, Cr^{6+} were separated but Ti^{3+} and Ti^{4+} remained at the point of application. This may be attributed to the formation of their insoluble phosphates. The same may be true for Ce^{3+} and Ce^{4+} (Table 2).

Se^{4+} and Se^{6+} migrated to the same extent. The results could not be improved by washing the chromatographic paper with 2 *M* HNO_3 to avoid the reduction of Se^{6+} to Se^{4+}.

Acid washed paper (*1*), a CO_2 atmosphere in the developing jar

TABLE 2

Ion with Nonseparable Valency States

Ion	R_F value
Ce^{3+}	0.0
Ce^{4+}	0.0
Cu^{+}	0.0[a]
Cu^{2+}	0.0[a]
Se^{4+}	0.33
Se^{6+}	0.33
Ti^{3+}	0.0
Ti^{4+}	0.0

[a] Streaking observed.

(*3*), or a combination of both did not succeed in separating Cu^{+} and Cu^{2+}.

The R_F values obtained for the halogens are close, but as the zones are very compact, their detection is not difficult.

The solvent can also be used for the separation of ink pigments, indicators, and various constituents of some dyes.

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