

Reverse Phase Partition Chromatographic Studies of Trisoxalatocobalt(III) with Polyvinyl Chloride Powder Impregnated with Long-chain Amines

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Reverse phase partition chromatographic behaviour of the anionic complex, trisoxalatocobalt(III) dissolved in perchloric acid on polyvinyl chloride (PVC) powder impregnated with long-chain amines has been investigated. The results are comparable to those obtained in solvent extraction. The effect of irradiation on impregnated PVC with gamma rays from ^{60}Co has also been studied. Gamma irradiation of PVC is found to increase the partition due to the *in situ* production of HCl.

IN continuation of the work on solvent extraction of trisoxalatocobalt(III) anion by long-chain amines from dilute acid solutions^{1,2}, the results of reverse phase partition chromatographic studies of this complex on polyvinyl chloride (PVC) powder impregnated with these amines are reported in this note.

The amines employed were Primene JMT, Amberlite LA-2, tri-*n*-hexylamine (THA) and triisooctylamine (TIOA). Potassium trisoxalatocobalt(III) tagged with ^{60}Co was prepared and purified as described earlier¹. The concentration of the complex was kept at $1 \times 10^{-3}M$. Calculated amounts of the amines were dissolved in chloroform into which a weighed quantity of PVC powder was added. The mixture was dried at room temperature with occasional stirring. The dry powder, crushed and thoroughly mixed, served as the solid phase. The solid sample (1 g each) was equilibrated for 2 hr with the complex solution (5 ml each) in perchloric acid of appropriate strength, with the help of a mechanical shaker. After equilibration, the solutions were centrifuged and 2-3 ml portions were pipetted from the supernatant (taking special care to see that not a single particle of the solid phase comes in) and counted in a well-type gamma scintillation assembly. An equal volume of the reference solution was also counted under similar conditions. The partition coefficient of the complex was calculated from the data. If A was the activity (cpm) of the aqueous solution before equilibration and B after equilibration, the partition coefficient P is given by $(A-B)/B$.

The mechanism of partition of $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ on PVC impregnated with amines is the same as that for liquid-liquid extraction^{1,2}. Thus at constant [perchloric acid], a plot of $\log P$ against $\log [\text{amine}]$ should be linear with a slope equal to 3 and at constant [amine] a plot of $\log P$ against $\log [\text{acid}]$ should also give a slope of 3.

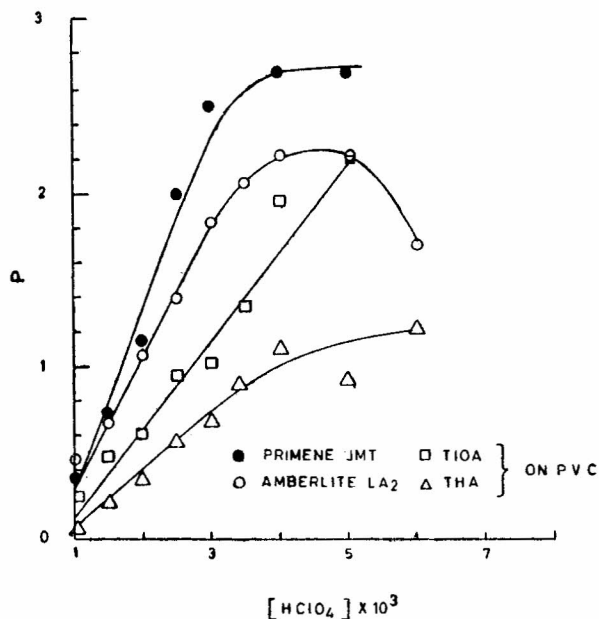


Fig. 1 — Plots of partition coefficient (p) versus $\log [\text{HClO}_4]$ for the partition of trisoxalatocobalt(III) ion on PVC impregnated with various amines

The partition of the complex was studied on PVC impregnated with amines (10%, v/w) from different concentrations of HClO_4 . The plots of P against [perchloric acid] are shown in Fig. 1. As in the case of solvent extraction¹, PVC-Primene JMT system showed the maximum uptake of the complex followed by PVC-LA-2 and then by PVC-TIOA and THA. It may be recalled that in the case of solvent extraction of this complex, TIOA and THA plots could be superposed on each other, while in these studies, PVC-TIOA has a distinctly higher partition than PVC-THA. This difference may be due to the fact that TIOA with eight carbon atoms is more basic than THA with six carbon atoms. In solvent extraction, this higher basicity of TIOA was offset by the steric hindrance offered by the branched chain whereas in view of the decreased mobility of the reactive amine molecules when adsorbed on to a solid surface such as PVC, the effect of steric hindrance might be of less significance in contrast to a liquid-liquid extraction system³. On examining the plots of $\log P$ against $\log [\text{HClO}_4]$ (not included for brevity), the slopes were always less than 3. This may be due to the competition offered by ClO_4^- ion for partition.

Dependence of [amine] on partition coefficient was studied from a $5 \times 10^{-3}M$ perchloric acid solution. The plots of $\log P$ against $\log (\% \text{ amine})$ gave slopes of 2-2.5 for all the amines. It may be recalled that in the solvent extraction experiments with perchloric acid, plots of $\log E$ against $\log (\% \text{ amine})$ gave a slope of 3 for Primene JMT and of 6 for other amines. The aggregation of amines which was present in xylene was absent when the extractant was doped on a solid support.

Although reverse phase partition chromatography using long-chain amines was used for separation chemistry^{4,5}, the effect of ionizing radiation on the solid support was never studied before. Radiation

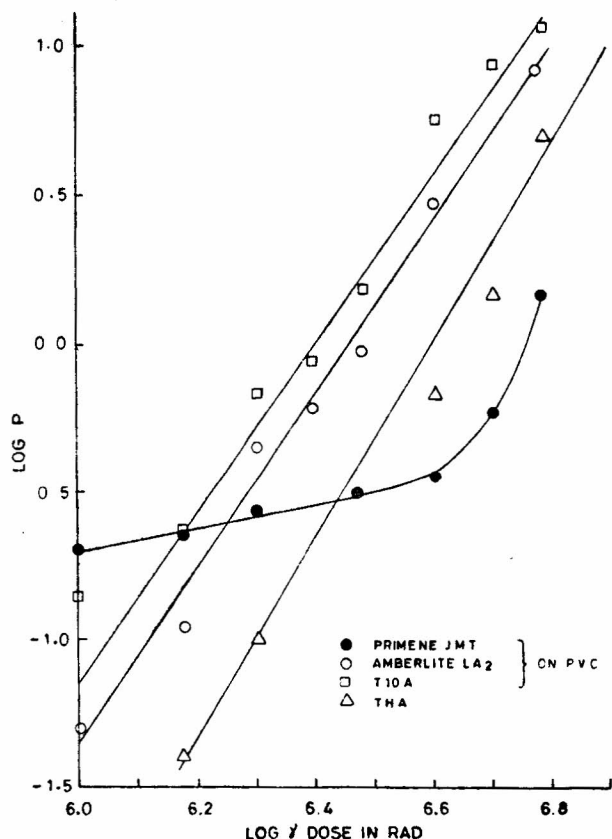


Fig. 2—Plots of $\log p$ versus \log (dose) for trisoxalato-cobalt(III) on PVC impregnated with various amines and irradiated to varying doses from ^{60}Co gamma radiation

is known to produce HCl ⁶ in PVC and this may help the partition of the complex. PVC impregnated with amines was irradiated to varying doses from ^{60}Co gamma radiation. The gamma irradiated PVC was equilibrated with water. The supernate on mixing with silver nitrate solution gave a precipitate which was identified to be silver chloride. Plots of $\log P$ against \log (dose) are shown in Fig. 2 (to check the assumption that the HCl produced during irradiation was giving rise to the amine hydrochloride, which in its turn will take up the anionic complex from neutral solution). The slopes for Amberlite LA-2 and T10A are slightly < 3 and that for THA is slightly > 3 . For Primene JMT the plot was of a special nature. The initial portion of the plot had a small slope, which became high afterwards. For the same dose, partition decreased in the order of T10A $>$ Amberlite LA-2 $>$ Primene JMT $>$ THA.

If we assume that partition on irradiated PVC is only due to the production of hydrochloric acid, then plots in Fig. 2 should be similar to plots of $\log E$ against $\log [\text{HCl}]$ in liquid-liquid extraction. The slopes in Fig. 2 for different amines do correspond with the slopes obtained in liquid-liquid extraction from HCl solution². In liquid-liquid extraction the order of selectivity was Amberlite LA-2 $>$ T10A $>$ Primene JMT $>$ THA. The inversion of selectivity in the case of Amberlite LA-2 and T10A might suggest a radiation effect on the secondary amines.

Ishihara has reported that the extraction of thorium into LA-2 in kerosene decreases when irradiated to gamma rays whereas that into TOA—a tertiary amine—remains unaffected⁷.

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Spectrophotometric Determination of Aromatic Nitro Compounds

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A rapid and simple method for the micro-determination of aromatic nitro compounds has been developed. The aromatic nitro compound is converted into aryhydroxylamine using zinc, in the presence of ammonium chloride, as the reducing agent. The resultant aryhydroxylamine forms a violet complex with Fe(III) and acetyl chloride. The method is applicable for the determination of 50 μg –10 mg of the compound and has an accuracy of $\pm 1.17\%$.

THE determination of aromatic nitro compounds depends mainly upon their reduction by suitable reagents. Very few spectrophotometric methods have been reported in the literature for the determination of nitro compounds^{1,2}. Colorimetric method for the determination of aliphatic and aromatic nitro compounds by oxidation of Fe(II) to Fe(III) reported by Bartos³ is long and tedious. Tiwari *et al.*⁴ reported a method for the determination of aromatic *m*-poly-nitro compounds using sodium borohydride but it cannot be applied for all types of nitro compounds. We report here a new method for the determination of aromatic nitro compounds based on reduction of the aromatic nitro compounds to hydroxylamine which gives a violet complex with ferric nitrate in the presence of acetyl chloride, the complex is determined spectrophotometrically.

Bausch & Lomb Spectronic-20 (USA) spectrophotometer was used for the spectrophotometric work. Elico $p\text{H}$ meter model L1-10 was employed for $p\text{H}$ measurements. All the reagents were of AR grade.