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# Separation and Determination of Some Amines by Ion-Exchange Chromatography

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## Abstract

Papers impregnated with stannic molybdate have been used to chromatograph various amine hydrochlorides in varying concentrations of aqueous sodium nitrate and hydrochloric acid solutions. Various important separations are listed. The theoretical behavior of the movement of amine hydrochlorides on these papers is discussed with the help of plots of pH vs $R_M$.

## INTRODUCTION

Paper chromatography has recently been used for the specific detection of aromatic *o*-diamines (*1*). Primary mono- and diamines have been determined spectrophotometrically after elution from a cation-exchange resin (*2*). Ion-exchange chromatography of primary amines has also been studied (*3*). Undissociated diphenylamines have little interaction with the resin in the column. In the past studies, amines have been taken directly for chromatographic investigations. However, if the salts of amines were prepared, then the ion-exchange would have played the primary role for such separations. Therefore, the present study was undertaken to study the chromatography of amine ions (formed as amine hydrochloride) on papers impregnated with stannic molybdate, an inorganic ion exchanger, on the basis of differences in $R_F$ values. The amine ions were separated on these papers and on columns of the stannic molybdate ion exchanger.

After separation, the amine ions, eluted successively from an exchanger column, were spectrophotometrically determined using our earlier method (*4*).

## EXPERIMENTAL

### Apparatus

Chromatography was performed on impregnated Whatman No. 3 paper strips 15 × 2.5 cm using 20 × 5 cm glass jars.

### Reagents

Chemicals and solvents were of analytical grade.



### Preparation of Ion Exchange Papers

Whatman No. 3 paper strips of the required size were cut and impregnated with stannic molybdate as before (*5*).

### Preparation of Amine Hydrochlorides

Amine hydrochlorides were prepared by dropping hydrochloric acid into sulfuric acid. The dry HCl gas evolved was passed into amine solutions in ether. The amine hydrochlorides formed were obtained in solid or liquid form immiscible with ether. One percent solution of amine hydrochlorides was prepared in water.

### Detectors

For the detection of various amine hydrochlorides, ninhydrin and *p*-dimethyl aminobenzaldehyde were used. Ninhydrin detector was prepared by dissolving 0.2 g. of ninhydrin in 100 ml of *n*-butanol saturated with water. This detector was used to detect the hydrochlorides of the following amines: ethylamine, dimethylamine, piperidine, 1, 2-diaminoethane, ethanolamine, and amylamine. One percent *p*-dimethylamino benzaldehyde in ethanol + hydrochloric acid (95: 5) was used to detect the hydrochlorides of α-naphthylamine, β-naphthylamine, diphenylamine, *p*-toluidine, pyridine, *N*-phenyl-1-naphthylamine, aniline, and dichlorohexylamine.

## PROCEDURE

One or two spots of amine hydrochloride solution were placed with the help of a fine glass capillary on the impregnated strip. The strip (11 cm in all cases) was allowed 15 min for conditioning and then the solvent was allowed to ascend. The $R_F$ values were calculated as usual.

### Synthesis of Stannic Molybdate

Stannic molybdate was prepared as before (*6*). This was converted to the $H^+$ form and used for column operation.

### Separations

A 30 × 0.39 $cm^2$ glass burette was used for separation studies. Stannic molybdate (2.0 g) was placed in the burette with a glass wool support forming the ion exchanger column. The flow rate of the effluent was 8 to 9 drops/min. The effiuent was collected in 10 ml fractions and was analyzed spectrophotometrically (*4*).



TABLE 1

$R_F$ Values of Amine Hydrochlorides on Stannic Molybdate Papers with Varying Concentrations of Sodium Nitrate

| Amine hydrochlorides | Concentrations (*M*) | | | |
|---|---|---|---|---|
| | 0.001 | 0.01 | 0.1 | 1.0 |
| Aniline | 0.80 | 0.85 | 0.90 | 0.90 |
| Amylamine | 0.45 | 0.50 | 0.62 | 0.85 |
| Ethanolamine | 0.44 | 0.60 | 0.65 | 0.85 |
| Dichlorohexylamine | 0.75 | 0.80 | 0.84 | 0.90 |
| Pyridine | 0.42 | 0.45 | 0.65 | 0.85 |
| *p*-Toluidine | 0.70 | 0.80 | 0.85 | 0.95 |
| 1,2-Diaminoethane | 0.20 | 0.35 | 0.35 | 0.45 |
| Piperidine | 0.50 | 0.60 | 0.77 | 0.83 |
| Dimethylamine | 0.45 | 0.50 | 0.62 | 0.62 |
| Ethylamine | 0.35 | 0.57 | 0.70 | 0.90 |
| β-Naphthylamine | 0.35 | 0.35 | 0.45 | 0.50 |
| α-Naphthylamine | 0.45 | 0.45 | 0.55 | 0.58 |
| Diphenylamine | 0.00 | 0.00 | 0.00 | 0.00 |
| Isoquinoline | 0.00 | 0.00 | 0.00 | 0.00 |
| *N*-Phenyl-1-naphthylamine | 0.00 | 0.00 | 0.00 | 0.00 |

TABLE 2

$R_F$ Values of Amine Hydrochlorides on Stannic Molybdate Papers at Different pH Values

| Amine hydrochlorides | pH | | | | |
|---|---|---|---|---|---|
| | 0.0 | 1 | 1.3 | 2 | 3 |
| Aniline | 0.83 | 0.75 | 0.71 | 0.66 | 0.52 |
| Amylamine | 0.80 | 0.77 | 0.75 | 0.71 | 0.67 |
| Ethanolamine | 0.94 | 0.90 | 0.86 | 0.74 | 0.67 |
| Dichlorohexylamine | 0.65 | 0.55 | 0.52 | 0.45 | 0.38 |
| Pyridine | 0.85 | 0.81 | 0.80 | 0.75 | 0.69 |
| *p*-Toluidine | 0.77 | 0.68 | 0.67 | 0.57 | 0.49 |
| 1,2-Diaminoethane | 0.95 | 0.92 | 0.90 | 0.88 | 0.83 |
| Piperidine | 0.85 | 0.82 | 0.77 | 0.73 | 0.62 |
| Dimethylamine | 0.92 | 0.87 | 0.85 | 0.74 | 0.66 |
| Ethylamine | 0.90 | 0.86 | 0.84 | 0.77 | 0.72 |
| β-Naphthylamine | 0.48 | 0.44 | 0.31 | 0.30 | 0.14 |
| α-Naphthylamine | 0.59 | 0.50 | 0.45 | 0.39 | 0.31 |
| Diphenylamine | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Isoquinoline | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *N*-Phenyl-1-naphthylamine | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |



TABLE 4

Some Separations on Stannic

| No. | Separation | Order and eluents[a] | Volume of effluent (ml) |
|---|---|---|---|
| 1 | Aniline—diphenylamine | Aniline—D.M.W. | 40 |
| | | Diphenylamine—1% $Fe(NO_3)_3$ | 50 |
| 2 | Aniline—α-naphthylamine | Aniline—D.M.W. | 40 |
| | | α-Naphthylamine—1% $Fe(NO_3)_3$ | 50 |
| 3 | Aniline—β-naphthylamine | Aniline—D.M.W. | 40 |
| | | β-Naphthylamine—1% $Fe(NO_3)_3$ | 40 |
| 4 | Pyridine—isoquinoline | Pyridine—D.M.W. | 40 |
| | | Isoquinoline—1% $Fe(NO_3)_3$ | 30 |
| 5 | *p*-Toluidine—*N*-phenyl-1-naphthylamine | *p*-Toluidine—D.M.W. | 40 |
| | | *N*-Phenyl-1-naphthylamine—1% $Fe(NO_3)_3$ | 60 |
| 6 | Piperidine—isoquinoline | Piperdine—D.M.W. | 30 |
| | | Isoquinoline—1% $Fe(NO_3)_3$ | 30 |

[a] D.M.W. = demineralized water.

## RESULTS

The $R_F$ values in various concentrations of aqueous sodium nitrate solution (0.001 to 1.0 *M*) are presented in Table 1. Aqueous hydrochloric acid systems have also been used to observe the effect of pH on the movement of amine ions. The $R_F$ values in such systems with pH values of 0.0 to 3.0 are given in Table 2.

On the basis of the difference in $R_F$ values, some analytically important

TABLE 3

Separations Achieved Experimentally on Stannic Molybdate Papers (25 min)

| No. | Separations achieved | Solvent |
|---|---|---|
| 1 | Diphenylamine (0.0)—aniline (0.82–0.97) | 1.0 *M* HCl |
| 2 | α-Naphthylamine (0.0–0.2)—aniline (0.82–0.96) | 0.001 *M* $NaNO_3$ |
| 3 | *β-Naphthylamine (0.08–0.30)—aniline (0.80–0.92)* | *0.001 M* $NaNO_3$ |
| 4 | Isoquinoline (0.0)—pyridine (0.90–0.95) | 1.0 *M* HCl |
| 5 | Isoquinoline (0.0)—piperidine (0.74–0.85) | 1.0 *M* HCl |
| 6 | *N*-Phenyl-1-naphthylamine (0.0)—*p*-toluidine (0.78–0.87) | 1.0 *M* HCl |
| 7 | Diphenylamine (0.0) from other amines | 1.0 *M* HCl |
| 8 | Isoquinoline (0.0) from other amines | 1.0 *M* HCl |
| 9 | *N*-Phenyl-1-naphthylamine from other amines | 1.0 *M* HCl |

Molybdate Columns

| Amounts of amine hydrochlorides loaded (μg) | Amounts of amine hydrochlorides recovered (μg) | Amount of exchanger in the column (g) | % Error |
|---|---|---|---|
| 5,000 | 4,985 | 2.0 | −0.30 |
| 2,500 | 2,500 | | 0.0 |
| 5,000 | 4,980 | 2.0 | −0.20 |
| 2,300 | 2,310 | | +0.42 |
| 4,250 | 4,200 | 2.0 | −1.20 |
| 3,200 | 3,200 | | 0.0 |
| 2,000 | 1,981 | 2.0 | −1.0 |
| 4,000 | 4,010 | | +0.25 |
| 5,900 | 5,920 | 2.0 | +0.31 |
| 11,500 | 11,470 | | −0.20 |
| 1,400 | 1,375 | 2.0 | −1.7 |
| 4,000 | 4,000 | | 0.0 |

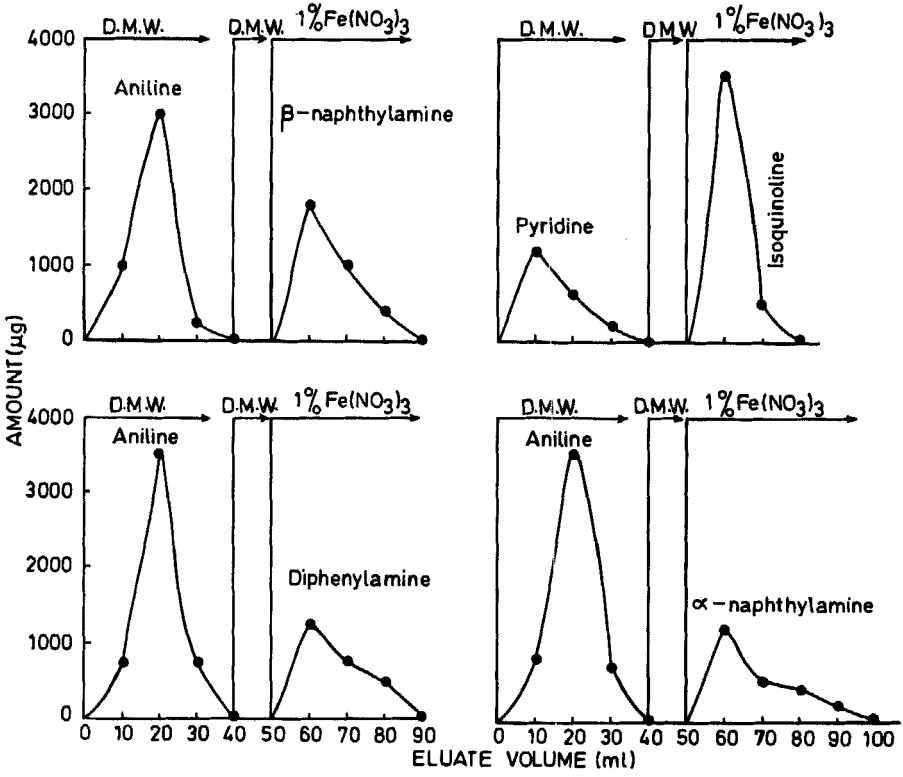


FIG. 1A. Separation of aniline from diphenylamine, α-naphthylamine, and β-naphthylamine, and of isoquinoline from pyridine on stannic molybdate.

separations were tried. Those achieved on the papers are summarized in Table 3.

Some of these separations were tried on columns of stannic molybdate exchanger. The results of these separations are given in Figs. 1A and 1B, and the quantitative limits are given in Table 4.

## DISCUSSION

The results of this study indicate that chromatography on papers impregnated with an inorganic ion exchanger can be used as an approach to predict the separations on columns of this ion exchanger. The results of

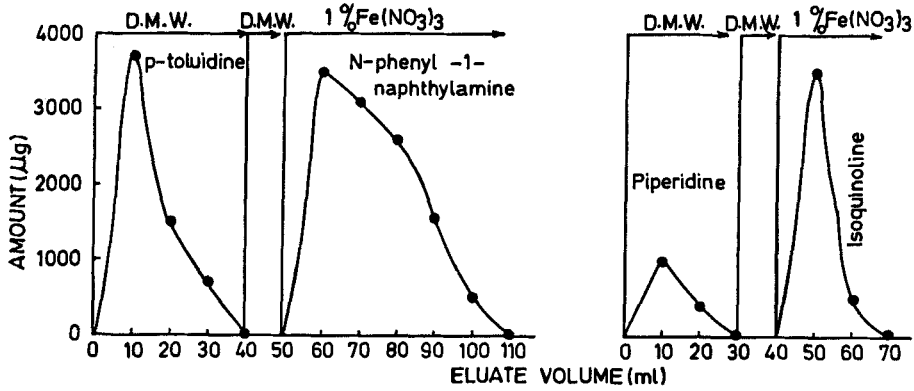


FIG. 1B. Separation of *N*-phenyl-1-naphthylamine from *p*-toluidine and of isoquinoline from piperidine on stannic molybdate.



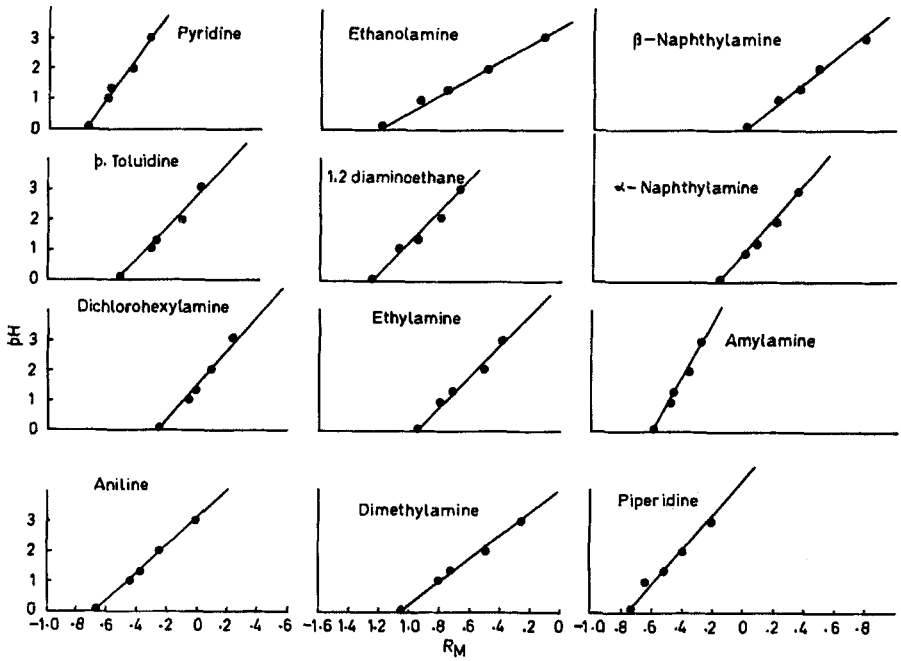


FIG. 2. Plot of pH vs $R_M$.

Table 3 and Figs. 1A and 1B reveal that most of the separations achieved on papers are also achieved on columns of ion exchanger. The amine ion which has a higher $R_F$ value (Table 1) is eluted first and that having a lower $R_F$ value is eluted later. This is because the ion having lower $R_F$ values has a higher affinity or selectivity toward the exchanger and hence elution will be later. This affinity sometimes is so much higher ($R_F = 0$) that the elution was not possible by the various salts applied. However, ferric nitrate gave positive results. The separations are distinct and quantitative (Table 4). These results are within the experimental error range.

The results of Table 2 seem to be in order of pH variation. Therefore, pH vs $R_M$ values [$R_M = \log \{(1/R_F) - 1\}$] plots were made (Fig. 2). These are straight lines. It is clear from this figure that there is a linear relationship between pH and the $R_M$ of amine ions on papers impregnated with stannic molybdate.



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