

**REVERSED-PHASE CHROMATOGRAPHY
OF AMINES, PHENOLS, AND METAL CATIONS
ON SILICA LAYERS
IMPREGNATED WITH TRIBUTYL PHOSPHATE,
USING SURFACTANT-MEDIATED MOBILE PHASES**

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SUMMARY

The analytical potential of tri-*n*-butyl phosphate (TBP) as impregnant in the thin-layer chromatographic separation of mixtures of amines, phenols, or metal ions has been investigated. Silica gel impregnated with 0.001 M TBP as stationary phase and an aqueous micellar solution (0.01 M) of CTAB, a cationic surfactant, as mobile phase was found to be the best chromatographic system for achieving important separations of metal cations (e.g. Cr³⁺ from Cr⁶⁺, Fe³⁺ from Mn²⁺ and Cr⁶⁺, VO²⁺ from Mn²⁺ and Cr⁶⁺) and phenols (e.g. *o*-cresol from *m*-cresol, *m*-aminophenol from *o*-aminophenol) from their mixtures. An aqueous solution (8.3×10^{-6} M) of the non-ionic surfactant, Brij-35 proved suitable for achieving good separations of amines (e.g. *p*-dimethylaminobenzaldehyde from L-tryptophan, *p*-dimethylaminobenzaldehyde from indole) on silica layers impregnated with 0.001 M TBP. The effect of metal cations on the separation of amines and phenols was examined, as was the effect of amines and phenols on the separation of metal ions. The effect of foreign substances on the separation of analytes was marginal.

INTRODUCTION

Amongst methods available for the analysis of inorganic ions, thin layer chromatography (TLC) is the most useful technique because of (i) low cost, (ii) minimal sample clean up, (iii) wide choice of mobile phases, (iv) flexibility in sample detection, (v) high sample-loading capacity, and (vi) ease of handling. In 1985, Winchester [1] first combined the favourable features of high-molecular weight extractants with a chromatographic

technique and separated several rare earth elements by using di 2-ethyl-hexyl phosphoric acid on alumina as stationary phase and dilute HCl as mobile phase. Since then the technique of reversed-phase chromatography (or reversed-phase extraction chromatography) has become very popular. Several papers have been published on reversed-phase thin-layer chromatography (RPTLC) of metal ions using long-chain aliphatic amines, substituted quaternary ammonium salts, heterocyclic amines, and neutral organophosphorus compounds as stationary phase impregnants [2–6]. Solutions of strong monobasic acids or their alkali metal salts are generally selected as the mobile phase.

Tri-*n*-butyl phosphate (TBP), one of the most versatile extractants has received considerable attention in analytical separation chemistry, because, under suitable conditions, it can be used to extract most elements of the period table. Since its first use to separate Th and V from impurities [7], TBP has been used extensively as extractant to accomplish analytical scale separations of actinides, lanthanides, and Pt-group elements. Its use for separation of transition metals has, however, been limited. According to the literature, layers of silica gel, poly(vinyl chloride), and cellulose impregnated with TBP have been used to separate a variety of metal ions [8–10]. Our work was aimed at using the analytical potential of TBP as impregnant for qualitative analysis of metal ions, phenols, and amines. Separation and identification of amines and phenols by TLC have received considerable attention in recent years, because of the toxicological, pharmaceutical, and industrial importance of the compounds. Several adsorbents have been used including alumina, cellulose, polyacrylonitrile, silica gel, NH₂-modified silica gel, and silica gel impregnated with metal salts and organic nitro compounds [11–16]. A few studies have also been performed on the TLC separation of amines by charge-transfer complexation with nitro compounds [17,18]. Studies on the separation of phenols by use of a variety of mobile phases [19–26] have also been reported.

Surfactants are amphiphilic materials containing both non polar (hydrophobic) and polar (hydrophilic) groups. This dual character leads to self-association or formation of surfactant micelles in water or similar solvents. Micellar solutions are transparent, non-volatile, inexpensive, and relatively non-toxic. Although micelle structures have been extensively studied by physical chemists and biochemists, it is only recently that analytical chemists have realized that micellar systems can be used to advantage in chemical analysis [27]. The apparent advantages of using surfactant solutions as the mobile phase in liquid chromatography include:

(i) their ability to solublize hydrophobic compounds; (ii) highly selective partitioning of many solutes into micelles; (iii) low cost; and (iv) the ability to change the polarity of the micellar mobile phase simply by changing the concentration of surfactant in solution. The unique possibilities of separating structurally similar solutes with a micellar mobile phase arise because the micelles solublize and bind a variety of solute molecules via hydrophobic, electrostatic, and hydrogen-bonding interactions.

We recently started a systematic study of the use of surfactant-mediated mobile phases in the TLC separation of organic [28,29] and inorganic [30,31] substances. The current study was undertaken to determine the feasibility, effectiveness, and advantages of using aqueous surfactants as mobile phases to obtain optimum conditions for identification and separation of amines and phenols (organic pollutants) and metal ions (inorganic pollutants) on TBP-impregnated silica layers. Studies reported so far include only the use of TBP-impregnated layers for analysis of either inorganic or organic substances separately, i.e. none of the studies investigated the use of TBP-impregnated layers for analysis of both organic and inorganic compounds by use of the same mobile phase. The current study deviates from TLC methods reported earlier, because it involves the use of TBP-impregnated layers in combination with cationic, anionic, or non-ionic surfactant-containing mobile phases for mutual separation of organic and inorganic compounds. The findings of our study might facilitate the removal of inorganic impurities from organic compounds and the removal of organic impurities from inorganic (or metallic) compounds.

EXPERIMENTAL

Chemicals and Reagents

Tributyl phosphate (Indian Drugs and Pharmaceuticals), sodium dodecyl sulphate (SDS; BDH, India), *N,N,N*-cetyltrimethyl ammonium bromide, and CTAB (Central Drug House, India) were analytical reagent grade. *iso*-Octylphenoxypolyethoxy ethanol, Triton X-100 (denoted TX-100) and Brij-35 (polyoxyethylene dodecyl ether) were both obtained from Loba Chemical (India) and used without further purification.

The Amines, Phenols and Metal Ions Studied

The aliphatic and aromatic amines used in this study were aniline (AL), *o*-chloroaniline (*o*-CAL), *m*-chloroaniline (*m*-CAL), *p*-chloroaniline

(*p*-CAL), *m*-toluidine (*m*-TLD), *p*-toluidine (*p*-TLD), diphenylamine (DPA), indole (ID), *p*-dimethylaminobenzaldehyde (*p*-DAB), L-tryptophan (L-TRYP), methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), tributylamine (TBA), diethylamine (DEA), and triethylamine (TEA). The phenolic derivatives used were resorcinol (Rol), pyrogallol (Pol), phloroglucinol (PgL), *o*-cresol (*o*-Crol), *m*-cresol (*m*-Crol), *p*-cresol (*p*-Crol), *m*-nitrophenol (*m*-NPh), *p*-nitrophenol (*p*-NPh), *o*-nitrophenol (*o*-NPh), *o*-aminophenol (*o*-Aph), *m*-aminophenol (*m*-Aph), *p*-aminophenol (*p*-Aph), orcinol (Ool), and pyrocatechol (*p*-Col). The metal ions studied were Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, VO²⁺, UO₂²⁺, Zn²⁺, Cd²⁺, Ag⁺, Pb²⁺, Tl⁺, Bi³⁺, Hg²⁺, Mo⁶⁺, Cr⁶⁺, Cr³⁺, and Ti⁴⁺.

Test solutions (1%) of the amines and phenols were prepared in methanol. Solutions (1%) of metal ions as their chloride, nitrate, or sulphate salts were prepared in double-distilled water with addition of few drops of corresponding acids to prevent hydrolysis.

Chromatography

The stationary phases used were silica gel G (E. Merck, India) and silica gel G impregnated with 0.001 M TBP in acetone. The mobile phases investigated are listed in Table I.

Preparation of TLC Plates

Plain Silica Gel Plates

TLC plates were prepared by mixing silica gel G with demineralized water (DMW) in a 1:3 ratio. The resulting slurry was shaken mechanically for 5 min then coated on to 7.5 cm × 2.5 cm glass plates as 0.25 mm layers by means of a Toshniwal (India) TLC applicator. The plates were dried in air at room temperature then activated by heating at 100°C for 1 h. After activation the plates were kept in air-tight chamber until used.

TBP-Impregnated Plates

Two methods were adopted for preparation of impregnated silica gel plates:

(i) *Precoating method*. A solution of the impregnant (TBP) in acetone was substituted for DMW in the slurry used to coat the plates. For example, the slurry was made by mixing a solution of 0.001 M TBP (in acetone) with silica gel in the ratio of 3:1 and TLC plates were prepared by use of the resulting slurry under the same experimental conditions as cited above for plain silica gel plates, including activation at 100°C for 1 h.

Table I

The mobile phases investigated.

Code	Composition
M ₁	Distilled water
M ₂	0.1 M SDS
M ₃	0.01 M SDS
M ₄	0.0064 M SDS
M ₅	0.00067 M SDS
M ₆	0.01 M CTAB
M ₇	0.001 M CTAB
M ₈	0.00075 M CTAB
M ₉	0.000075 M CTAB
M ₁₀	0.03 M TX-100
M ₁₁	0.003 M TX-100
M ₁₂	0.002 M TX-100
M ₁₃	0.0002 M TX-100
M ₁₄	0.0012 M Brij-35
M ₁₅	0.00012 M Brij-35
M ₁₆	0.000083 M Brij-35
M ₁₇	0.00000832 M Brij-35

(ii) *Post-coating method.* The activated silica gel plates were impregnated with the desired concentration of TBP (0.001, 0.01, 0.1, 0.5, 1.0, or 2.0 M) in acetone by dipping them into a solution of the impregnant for a specific time then drying at room temperature (30°C). The post coating method was found to be suitable for preparation of high quality silica gel plates.

Procedure

Thin layer chromatography was performed on TLC plates coated with unimpregnated and TBP impregnated silica gel layers in 10 cm × 4 cm glass jars. Approximately 10 µL of the standard test solutions were spotted separately 2 cm from the lower edges of the plates by means of micropipettes. The spots were left to dry and the plates were then developed to a distance of 10 cm from the point of application, by the ascending technique, in the desired mobile phase, at room temperature. After development, the plates were dried in air at room temperature and the positions of amine or phenol spots were located by exposing the plates to iodine vapour for 10 min. Metal ions were detected by spraying with the appropriate

chromogenic reagent (Table II). R_F values were determined by use of the formula $R_F = (R_L + R_T)/2$ where R_L is the R_F of the leading front of the spot and R_T is the R_F of the trailing front.

Table II

The reagents used to detect the metal cations

Cations	Chromogenic reagent
Cu^{2+} , UO_2^{2+} , VO^{2+} , and Fe^{3+}	1% Aqueous solution of potassium ferrocyanide
Ni^{2+} and Co^{2+}	0.2% Alcoholic, alkaline solution of dimethylglyoxime
Cd^{2+} , Zn^{2+} , Ag^+ , Tl^+ , Bi^{3+} , Pb^{2+} , and Hg^{2+}	0.5% Solution of dithizone in carbon tetrachloride
Cr^{6+}	Saturated alcoholic solution of AgNO_3
Cr^{3+}	1% Methanolic solution of alizarin red 's'
Al^{3+}	1% Aqueous solution of aluminon
Mn^{2+}	1:1 (v/v) mixture of 2.0 M NaOH and 30% H_2O_2
Mo^{6+}	1% Ferric chloride solution

Separations

Test solutions (approx. 10 μL) containing two or more analytes (amine, phenol or metal ion) to be separated were spotted on TLC plates and chromatography was performed using different mobile phases. The resolved spots were visualized by spraying with suitable chromogenic reagents or by exposing the plates to iodine vapour for 10 min. The R_F values of the resolved spots were then determined.

RESULTS

The results of this study have been summarized in Tables III–VII and Figs 1–3. To find the optimum concentration of TBP impregnant, analytes (metal ions, amines and phenols) were chromatographed on silica layers impregnated with different concentrations from 0.001 to 2.0 M using distilled water (M_1) as mobile phase. As the concentration of TBP was increased the R_F values of the amines decreased substantially, as is apparent from the representative plots depicted in Figs 1a–c. This decrease in the R_F values of the amines (i.e. reduction in mobility) can be attributed to strong partitioning of the amines in the TBP. Similar trends,

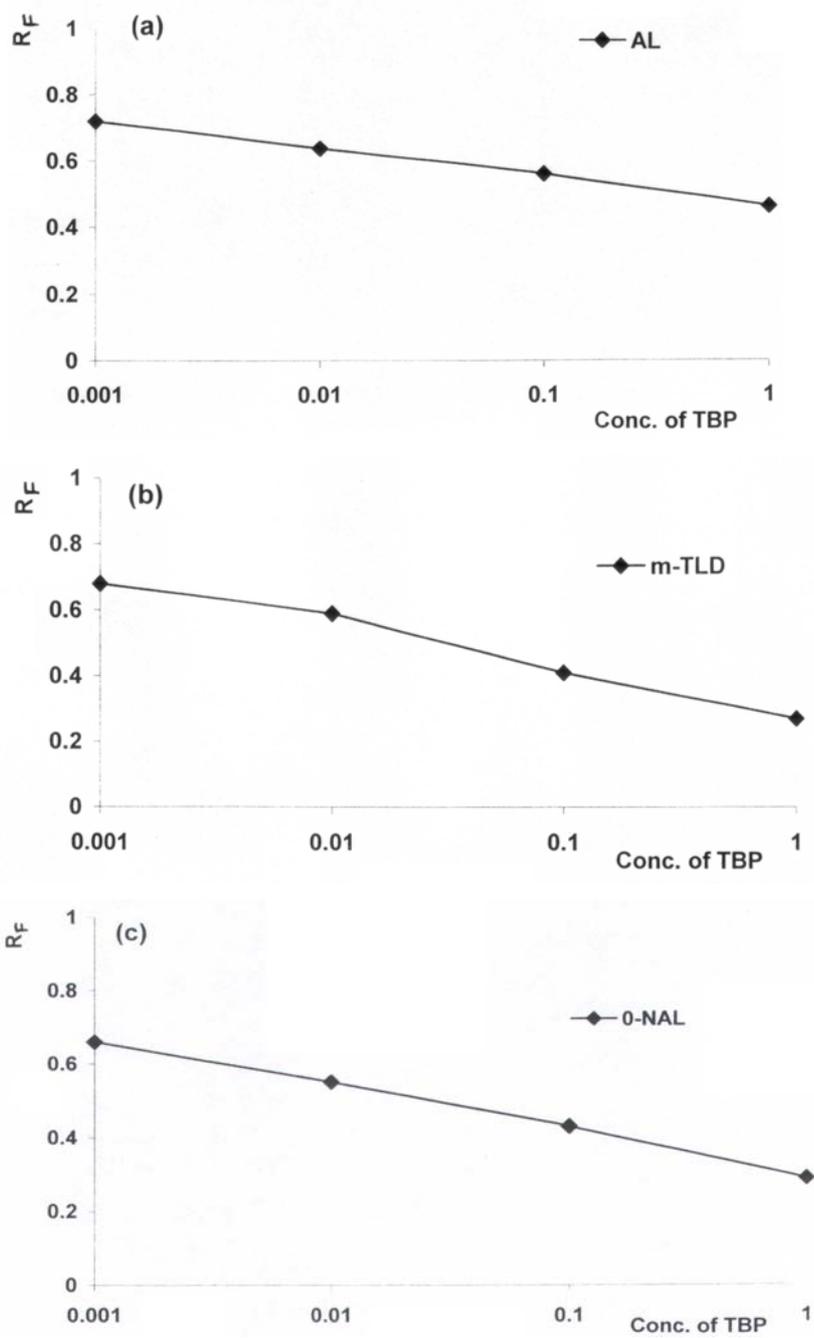


Fig. 1

Plots of R_F of (a) AL, (b) m-TLD, and (c) o-NAL against concentration of TBP

i.e. decreasing R_F values with increasing impregnant concentration, were observed for metal ions and phenols, with the highest concentrations of TBP (>0.5 M) leading to tailing spots for some of the metal ions and phenols. Chromatography on silica plates impregnated with high levels of TBP suffered from several disadvantages including prolonged development time, poor detection, less compact spots, difficulty in drying the plates, poor adhesion of the modified silica to glass surface, etc. A TBP concentration of 0.001 M was therefore chosen for plate impregnation owing to the advantages of shorter development times, detection clarity, formation of compact spots, and better durability of TLC plates.

The mobility of the amines, phenols and metal ions was also examined on unimpregnated silica gel plates with DMW as mobile phase. Plots of ΔR_F (where $\Delta R_F = R_F$ on unimpregnated layers $- R_F$ on impregnated layers) are shown in Figs 2a–c. The positive ΔR_F values obtained for the amines AL, o-CAL, p-TLD, p-NAL, MA, TMA, TEA, and DPA, for m-APh, and for all the metal ions are indicative of greater selectivity of the TBP-impregnated silica layer towards these analytes. In contrast, the negative ΔR_F values obtained for the amines m-CAL, p-CAL, m-TLD, o-NAL, ID, p-DAB, L-TRYP, DMA, TBA, and DEA, and for most of the phenols are indicative of higher selectivity of plain (i.e. unimpregnated) silica layers towards these analytes. Better chromatographic performance, in respect of clarity of detection, compactness of spots, and improved separations was, however, observed on TBP-impregnated plates. For example, binary separation of p-DAB from ID or TRYP, of Cd^{2+} from Zn^{2+} or Pb^{2+} , and of m-APh from m-NPh could be achieved on TBP-impregnated layers only.

The mobility of amines, phenols and metal ions was also studied using aqueous surfactant (anionic, cationic, or non-ionic) solutions as mobile phases; surfactant concentrations were approximately twelve or 1.2 times higher or lower than their critical micellar concentrations (CMC). The CMC values of SDS, CTAB, TX-100, and Brij-35 in water are 0.008, 0.0009, 0.0028, and 0.0001 M, respectively. The mobility trends of amines, phenols and metal ions observed on (0.001 M) TBP-impregnated silica layers developed with different concentrations of anionic, cationic or non-ionic surfactants are discussed below.

Chromatography with SDS

The mobility of amines, phenols, and metal ions was examined with aqueous solution of anionic SDS surfactant as mobile phases. Although

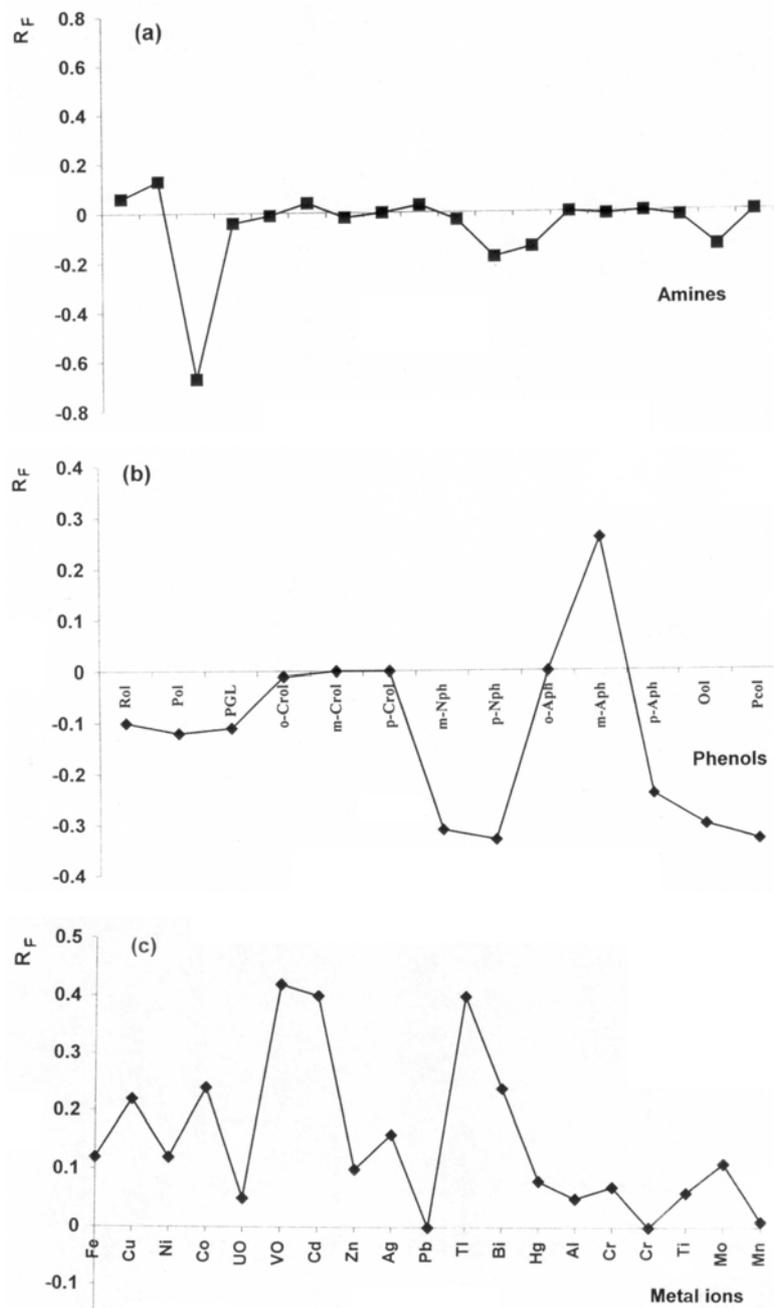


Fig. 2

Variation of ΔR_F (R_F on unimpregnated layers – R_F on impregnated layers) for (a) amines, (b) phenols, and (c) metal ions

mobilities were high for some of the amines (AL, m-CAL, p-CAL, m-TLD or p-TLD), phenols (RoI, Pol, PGL, m-NPh, p-NPh, Ool or p-Col), and metal ions (Ni^{2+} , Cd^{2+} , Mo^{6+} or Mn^{2+}), because of the absence of differential migration or the appearance of elongated spots good separation of mixtures of metal ions, amines, or phenols could not be achieved with aqueous SDS mobile phases (M_2 – M_5).

Chromatography with CTAB

The results obtained by use of CTAB are listed in Table III. From these data several mobility trends are apparent.

Amines: Compact spots were obtained for p-DAB by use of mobile phases M_8 or M_9 (R_F values 0.56 and 0.62, respectively) but use of mobile phases M_6 or M_7 resulted in elongated spots. Compact spots were obtained for all the other amines, irrespective of the concentration of CTAB (M_6 – M_9). o-CAL was not detected, p-CAL gave tailing spots and DPA either remained near the point of application ($R_F = 0.02$ – 0.07) or gave a tailing spot irrespective of whether the CTAB concentration (M_6 – M_9) was above or below its CMC.

Phenols: For all phenols except m-Crol, p-Crol, and o-APh ($R_F = 0.00$) mobility was high and more or less constant ($R_F = 0.70$ – 0.95) irrespective of whether the concentration of cationic surfactant was above or below the CMC.

Metal Ions: The mobility of Ni^{2+} was high (R_F value 0.72–0.82) irrespective of CTAB concentration (M_6 – M_9). Tailing spots were, however, obtained for Ni^{2+} when an aqueous non-micellar solution of CTAB (concentration one twelfth its CMC), M_9 , was used as mobile phase. Co^{2+} or Mn^{2+} moved near the middle of the plate ($R_F = 0.47$ – 0.6) whereas the mobility of Cr^{6+} and Mo^{6+} was high ($R_F = 0.78$ – 0.97) irrespective of the mobile phase used (M_6 – M_9). The mobility of Cd^{2+} was low ($R_F = 0.25$ – 0.32) and tailing spots were obtained for Hg^{2+} , Ag^+ , Bi^{3+} or Ti^{4+} irrespective of CTAB concentration (M_6 – M_9).

Aqueous micellar CTAB was found to be best means of achieving good separations of metal ions and phenols. For example, Cr^{3+} from Cr^{6+} , Fe^{3+} from Co^{2+} and Cr^{6+} , VO^{2+} from Mn^{2+} and Mo^{6+} , o-Crol from m-Crol, and m-APh from o-APh. These separations could not be achieved with anionic surfactant SDS because well resolved spots could not be obtained by use of aqueous micellar/non micellar solutions of SDS as mobile phase (M_2 – M_5). Thus, CTAB is better mobile-phase component than SDS for achieving separations of metal ions and phenols, because it induces diffe-

Table III

R_F values of amines, phenols, and metal ions on TBP (0.001 M)-impregnated silica layers developed with aqueous solutions of the cationic surfactant CTAB (mobile phases M_6 – M_9)

M_6						M_7					
Amines	R_F value	Phenols	R_F value	Metal ions	R_F value	Amines	R_F value	Phenols	R_F value	Metal ions	R_F value
AL	0.84	Rol	0.88	Ni^{2+}	0.72	AL	0.71	Rol	0.81	Ni^{2+}	0.72
m-CAL	0.75	Pol	0.96	Co^{2+}	0.55	m-CAL	0.75	Pol	0.95	Co^{2+}	0.55
p-CAL	0.76	PGL	0.87	Cd^{2+}	0.28	p-CAL	0.72	PGL	0.79	Cd^{2+}	0.32
m-TLD	0.77	o-Crol	0.78	Ag^+	0.15T ^a	m-TLD	0.74	o-Crol	0.79	Ag^+	0.15T
p-TLD	0.72	m-NPh	0.86	Ti^+	0.17T	p-TLD	0.71	m-NPh	0.83	Ti^+	0.15T
o-NAL	0.70	p-NPh	0.81	Bi^{3+}	0.16T	o-NAL	0.57	p-NPh	0.88	Bi^{3+}	0.17T
p-NAL	0.40T	m-APh	0.72	Hg^{2+}	0.36T	p-NAL	0.44T	m-APh	0.80	Hg^{2+}	0.20T
DPA	0.02	p-APh	0.88	Cr^{6+}	0.97	DPA	0.07	p-APh	0.88	Cr^{6+}	0.97
ID	0.57	Ool	0.83	Mo^{6+}	0.85	ID	0.60	Ool	0.79	Mo^{6+}	0.92
p-DAB	0.26T	p-Col	0.76	Mn^{2+}	0.48	p-DAB	0.27T	p-Col	0.75	Mn^{2+}	0.49
L-TRYP	0.77					L-TRYP	0.84				
M_8						M_9					
Amines ^b	R_F value	Phenols ^c	R_F value	Metal ions ^d	R_F value	Amines	R_F value	Phenols	R_F value	Metal ions	R_F value
AL	0.86	Rol	0.90	Ni^{2+}	0.82	AL	0.82	Rol	0.92	Ni^{2+}	0.71T ^d
m-CAL	0.90	Pol	0.80	Co^{2+}	0.60	m-CAL	0.91	Pol	0.91	Co^{2+}	0.48
p-CAL	0.72	PGL	0.85	Cd^{2+}	0.30	p-CAL	0.81	PGL	0.88	Cd^{2+}	0.25
m-TLD	0.73	o-Crol	0.89	Ag^+	0.16T	m-TLD	0.75	o-Crol	0.84	Ag^+	0.15T
p-TLD	0.80	m-NPh	0.89	Ti^+	0.17T	p-TLD	0.82	m-NPh	0.83	Ti^+	0.15T
o-NAL	0.63	p-NPh	0.88	Bi^{3+}	0.15T	o-NAL	0.61	p-NPh	0.86	Bi^{3+}	0.18T
p-NAL	0.37T	m-APh	0.70	Hg^{2+}	0.55T	p-NAL	0.45T	m-APh	0.84	Hg^{2+}	0.62T
DPA	0.25T	p-APh	0.90	Cr^{6+}	0.96	DPA	0.25T	p-APh	0.92	Cr^{6+}	0.78
ID	0.67	Ool	0.82	Mo^{6+}	0.91	ID	0.91	Ool	0.78	Mo^{6+}	0.89
p-DAB	0.56	p-Col	0.70	Mn^{2+}	0.47	p-DAB	0.62	p-Col	0.78	Mn^{2+}	0.51
L-TRYP	0.84					L-TRYP	0.91				

^aT denotes tailed spot ($R_L - R_T > 0.30$)

^bo-CAL was not detected; MA, DMA, TMA, DEA, and TEA (aliphatic amines) remained near the point of application ($R_F = 0.02$ – 0.11)

^cm-Crol, p-Crol and o-APh remained at the point of application ($R_F = 0.00$)

^d Fe^{3+} , Cu^{2+} , UO_2^{2+} , VO_2^{2+} , Zn^{2+} , Pb^{2+} , Al^{3+} , Cr^{3+} , and Ti^{4+} remained near the point of application ($R_F = 0.02$ – 0.06)

rential migration, and yields more compact spots and superior detection clarity. This result is in consonance with our earlier studies on the TLC of metal ions [32].

Chromatography with TX-100

With different concentrations of the non-ionic surfactant TX-100 in the mobile phase (M_{10} – M_{13}) some of the amines (AL, m-CAL, p-CAL, m-TLD, p-TLD, o-NAL or ID), phenols (Rol, Pol, PGL, m-NPh, p-NPh, m-APh, p-APh, Ool or p-Col) and metal ions (Cr^{6+} , Mo^{6+} , Ni^{2+} , or Co^{2+}), moved near the solvent front ($R_F = 0.70$ – 0.92) but, because of the appearance of elongated spots and lack of differential migration, separations could not be achieved experimentally. Interestingly, however, some important ternary separations of amines and phenols, e.g. o-APh from m-APh and p-APh, DPA from p-DAB and L-TRYP, and DPA from ID and L-TRYP, seemed possible with M_{12} ; aqueous solutions of TX-100 (M_{12}) with some modification might, therefore, prove useful for achieving important separations of amines or phenols.

Chromatography with Brij-35

Results obtained with Brij-containing mobile phases (M_{14} – M_{17}) have been encapsulated in Table IV. From these data several conclusions about mobility trends of amines, phenols and metal ions can be drawn.

Amines: AL, m-CAL, p-CAL, m-TLD, p-TLD, o-NAL, ID, and L-TRYP were highly mobile ($R_F = 0.60$ – 0.89) and p-DAB moved near the middle of the plate ($R_F = 0.45$ – 0.56) at all concentration levels of Brij-35 (M_{14} – M_{17}) DPA remained near the point of application ($R_F = 0.02$) producing a very compact spot. It gave tailing spots with M_{15} – M_{17} , however.

Phenols: Rol, Pol, PGL, m-NPh, m-APh, p-APh, Ool, and p-Col were very mobile ($R_F = 0.73$ – 0.97) at all concentration levels of Brij-35 (M_{14} – M_{17}). With aqueous micellar solutions of Brij-35 (M_{14} or M_{15}) high R_F values, 0.82 and 0.80 respectively, were obtained for o-Crol. The compound remained near the point of application, however, when non-micellar aqueous solutions of Brij-35 (M_{16} or M_{17}) were used. Thus, the mobility of o-Crol is strongly determined by the concentration of Brij in the aqueous phase. o-APh remained at the point of application ($R_F = 0.00$) for all concentrations of Brij-35, with the exception of mobile phase M_{15} which led to a tailed spot.

Metal Ions: Ni^{2+} , Co^{2+} , Cr^{6+} or Mo^{6+} were very mobile ($R_F = 0.68$ – 0.97) at all concentration levels of Brij-35 (M_{14} – M_{17}). Cd^{2+} R_F values were 0.72 and 0.74 when mobile phases M_{14} and M_{17} , respectively, were used. When M_{15} or M_{16} were used, however, the mobility of Cd^{2+} was less – R_F values were 0.47 and 0.34, respectively. Tl^+ , Bi^{3+} , and Hg^{2+} gave tailed spots and Zn^{2+} remained near the point of application ($R_F = 0.07$ – 0.10) at

all concentration levels of Brij-35, with the exception of mobile phase M14, which led to a tailed spot.

Table IV

R_F values of amines, phenols, and metal ions on TBP (0.001 M)-impregnated silica layers developed with aqueous solutions of Brij-35 (mobile phases M₁₄–M₁₇)

M ₁₄						M ₁₅					
Amines	R_F value	Phenols	R_F value	Metal ions	R_F value	Amines	R_F value	Phenols	R_F value	Metal ions	R_F value
AL	0.85	RoI	0.94	Ni ²⁺	0.86	AL	0.82	RoI	0.92	Ni ²⁺	0.73
m-CAL	0.69	Pol	0.95	Co ²⁺	0.85	m-CAL	0.62	Pol	0.94	Co ²⁺	0.82
p-CAL	0.65	PGL	0.97	Cd ²⁺	0.72	p-CAL	0.60	PGL	0.96	Cd ²⁺	0.47
m-TLD	0.75	o-Crol	0.82	Zn ²⁺	0.16T ^a	m-TLD	0.65	o-Crol	0.80	Zn ²⁺	0.07
p-TLD	0.72	m-NPh	0.82	Tl ⁺	0.20T	p-TLD	0.62	m-NPh	0.82	Tl ⁺	0.17T
o-NAL	0.67	p-NPh	0.89	Bi ³⁺	0.15T	o-NAL	0.60	p-NPh	0.80	Bi ³⁺	0.17T
p-NAL	0.40T	o-APh	0.00	Hg ²⁺	0.70T	p-NAL	0.35T	o-APh	0.30T	Hg ²⁺	0.60T
DPA	0.02	m-APh	0.83	Cr ⁶⁺	0.95	DPA	0.27T	m-APh	0.72	Cr ⁶⁺	0.97
ID	0.83	p-APh	0.75	Mo ⁶⁺	0.94	ID	0.81	p-APh	0.81	Mo ⁶⁺	0.97
p-DAB	0.52	Ool	0.81	Mn ²⁺	0.88	p-DAB	0.56	Ool	0.84	Mn ²⁺	0.72
L-TRYP	0.89	p-Col	0.85			L-TRYP	0.84	p-Col	0.90		
M ₁₆						M ₁₇					
Amines ^b	R_F value	Phenols ^c	R_F value	Metal ions ^d	R_F value	Amines	R_F value	Phenols	R_F value	Metal ions	R_F value
AL	0.79	RoI	0.92	Ni ²⁺	0.82	AL	0.82	RoI	0.92	Ni ²⁺	0.92
m-CAL	0.72	Pol	0.90	Co ²⁺	0.68	m-CAL	0.75	Pol	0.95	Co ²⁺	0.92
p-CAL	0.70	PGL	0.97	Cd ²⁺	0.34	p-CAL	0.76	PGL	0.94	Cd ²⁺	0.74
m-TLD	0.79	o-Crol	0.00	Zn ²⁺	0.07	m-TLD	0.69	o-Crol	0.02	Zn ²⁺	0.10
p-TLD	0.82	m-NPh	0.79	Tl ⁺	0.16T	p-TLD	0.72	m-NPh	0.80	Tl ⁺	0.16T
o-NAL	0.69	p-NPh	0.86	Bi ³⁺	0.17T	o-NAL	0.65	p-NPh	0.87	Bi ³⁺	0.18T
p-NAL	0.52T	o-APh	0.00	Hg ²⁺	0.17T	p-NAL	0.41T	m-APh	0.00	Hg ²⁺	0.36T
DPA	0.17T	m-APh	0.73	Cr ⁶⁺	0.92	DPA	0.25T	p-APh	0.82	Cr ⁶⁺	0.97
ID	0.75	p-APh	0.85	Mo ⁶⁺	0.90	ID	0.75	p-APh	0.84	Mo ⁶⁺	0.94
p-DAB	0.45	Ool	0.83	Mn ²⁺	0.65	p-DAB	0.48	Ool	0.80	Mn ²⁺	0.60
L-TRYP	0.84	p-Col	0.94			L-TRYP	0.89	p-Col	0.95		

^aT denotes tailed spot ($R_L - R_T > 0.30$)

^bo-CAL was not detected; MA, DMA, TMA, DEA, and TEA (aliphatic amines) remained near the point of application ($R_F = 0.02-0.12$)

^cm-Crol and p-Crol remained at the point of application ($R_F = 0.00$)

^dFe³⁺, Cu²⁺, VO₂²⁺, Ag⁺, Pb²⁺, Al³⁺, Cr³⁺, and Ti⁴⁺ remained near the point of application ($R_F = 0.02-0.11$)

DISCUSSION

Among ion-ionic surfactants, Brij-35 proved to be a better mobile phase component for achieving important binary separations of amines, owing to the differential migration of p-DAB, of ID, and L-TRYP. These separations could not be achieved when Brij-35 was substituted with TX-100, because of the formation of elongated spots.

Some important separations of amines, phenols, and metal ions achieved experimentally have been listed in Table V. From this table it is

Table V

Some important separations of amines, phenols, or metal ions on TBP (0.001 M)-impregnated silica layers with mobile phases M₆ or M₁₇

Analyte	Mobile phase	Separations (R_F)
Amines	M ₁₇	p-DAB (0.47) from ID (0.71) ^a , p-DAB (0.48) from p-TLD (0.69), p-DAB (0.45) from m-CAL (0.72), p-DAB (0.44) from p-CAL (0.75), p-DAB (0.46) from L-TRYP (0.77) ^a , o-NAL (0.63) from AL (0.80)
Phenols	M ₆	o-Crol (0.75) from m-Crol (0.00) ^a , o-Crol (0.76) from p-Crol (0.00), m-APh (0.72) from o-APh (0.00), p-APh (0.85) from o-APh (0.00), m-APh (0.70) from m-Crol (0.00), o-Crol (0.74) from o-APh (0.00), p-APh (0.84) from p-Crol (0.00), Rol (0.85) from m-Crol (0.00) or p-Crol (0.00) or o-APh (0.00), Pol (0.93) from p-Crol (0.00) or m-Crol (0.00) or o-APh (0.00), PGL (0.86) from m-Crol (0.00) or p-Crol (0.00) or o-APh (0.00)
Metal ions	M ₆	Cr ⁶⁺ (0.96) from Cr ³⁺ (0.03), VO ²⁺ (0.2) from Mn ²⁺ (0.45) and Cr ⁶⁺ (0.96) ^a , Fe ³⁺ (0.03) from Co ²⁺ (0.51) and Cr ⁶⁺ (0.96), Fe ³⁺ (0.02) from Mn ²⁺ (0.41) and Cr ⁶⁺ (0.97) ^a , VO ²⁺ (0.02) from Mn ²⁺ (0.49) and Mo ⁶⁺ (0.92)

^aTracings of the chromatograms have been provided for clear illustration of the separations achieved (Fig. 3)

apparent that the best TLC system for separation of amines is silica layers impregnated with TBP (0.001 M) as stationary phase and an aqueous solution of Brij-35 (M₁₇) as mobile phase. With this system p-DAB ($R_F = 0.47$), was successfully separated from binary mixtures with ID ($R_F = 0.71$) or L-TRYP ($R_F = 0.77$). Separation of p-DAB from indole is particularly important because p-DAB forms coloured products with ID in solution [33]. Furthermore p-DAB and ID react with 2,4 dinitrotoluene (DNT) in the

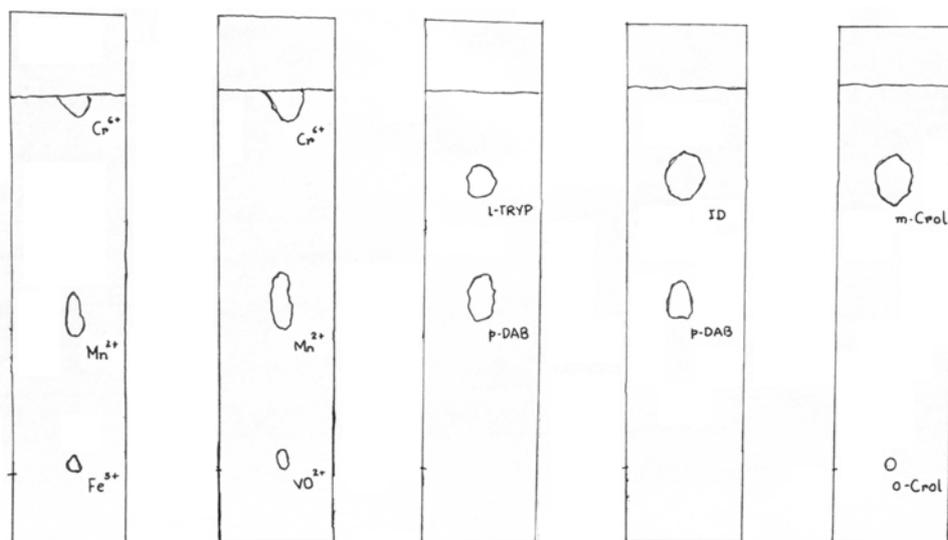


Fig. 3

Tracings of some important separations

solid state to produce yellow products [34], and hence the presence of p-DAB hampers detection of ID with DNT. Separation of p-DAB from ID is separation of a tertiary amine (p-DAB) from a secondary amine (ID). It is interesting to note from Table V that nitrogen compounds containing two aryl groups (ID and TRYP) move faster than p-DAB, which contains one aryl group.

TLC systems comprising TBP (0.001 M)-impregnated silica layers and aqueous micellar solutions of the cationic surfactant CTAB (M_6) are best for achieving good separations of mixtures of metal ions or phenols. Some important separations worth mentioning, achieved by use of these systems, include Cr^{3+} from Cr^{6+} , Fe^{3+} from Mn^{2+} and Cr^{6+} , VO^{2+} from Mn^{2+} and Cr^{6+} , o-Crol from m-Crol, and p-Aph from o-Aph. The ternary separation of Fe^{3+} or VO^{2+} from Mn^{2+} and Cr^{6+} is important, because these metal cations belong to the first transition series of the periodic table, and have similar physicochemical properties.

To widen the applicability of proposed TLC method, mutual separations of amines or phenols in the presence of metal cations and separations of metal cations in the presence of amines or phenols have been successfully achieved. The results obtained have been summarized in Tables VI and VII.

Table VI

Separation of metal ions, in the presence of amine or phenolic impurities, on TBP (0.001 M)-impregnated silica plates with mobile phase M_6

Impurities	Separations (R_F)
AL	Cr^{3+} (0.03) from Cr^{6+} (0.82), VO^{2+} (0.04) from Mn^{2+} (0.62) and Mo^{6+} (0.86), Fe^{3+} (0.02) from Mn^{2+} (0.60) and Cr^{6+} (0.82), Fe^{3+} (0.04) from Co^{2+} (0.49) and Cr^{6+} (0.83), VO^{2+} (0.02) from Mn^{2+} (0.45) and Cr^{6+} (0.80)
o-CAL	Cr^{3+} (0.02) from Cr^{6+} (0.81), VO^{2+} (0.02) from Mn^{2+} (0.59) and Mo^{6+} (0.85), Fe^{3+} (0.02) from Mn^{2+} (0.57) and Cr^{6+} (0.84), Fe^{3+} (0.02) from Co^{2+} (0.52) and Cr^{6+} (0.84), VO^{2+} (0.03) from Mn^{2+} (0.48) and Cr^{6+} (0.82)
m- CAL	Cr^{3+} (0.03) from Cr^{6+} (0.82), VO^{2+} (0.03) from Mn^{2+} (0.69) and Mo^{6+} (0.83), Fe^{3+} (0.03) from Mn^{2+} (0.55) and Cr^{6+} (0.83), Fe^{3+} (0.02) from Co^{2+} (0.50) and Cr^{6+} (0.85), VO^{2+} (0.02) from Mn^{2+} (0.46) and Cr^{6+} (0.83)
m-TLD	Cr^{3+} (0.04) from Cr^{6+} (0.87), VO^{2+} (0.02) from Mn^{2+} (0.58) and Mo^{6+} (0.84), Fe^{3+} (0.00) from Mn^{2+} (0.55) and Cr^{6+} (0.83), Fe^{3+} (0.02) from Co^{2+} (0.50) and Cr^{6+} (0.82), VO^{2+} (0.02) from Mn^{2+} (0.45) and Cr^{6+} (0.82)
p-NAL	Cr^{3+} (0.02) from Cr^{6+} (0.85), VO^{2+} (0.02) from Mn^{2+} (0.56) and Mo^{6+} (0.83), Fe^{3+} (0.04) from Mn^{2+} (0.52) and Cr^{6+} (0.82), Fe^{3+} (0.04) from Co^{2+} (0.40) and Cr^{6+} (0.75), VO^{2+} (0.02) from Mn^{2+} (0.42) and Cr^{6+} (0.76)
DMA	Cr^{3+} (0.02) from Cr^{6+} (0.81), VO^{2+} (0.03) from Mn^{2+} (0.82), Fe^{3+} (0.03) from Mn^{2+} (0.57) and Cr^{6+} (0.79), Fe^{3+} (0.00) from Co^{2+} (0.45) and Cr^{6+} (0.77), VO^{2+} (0.22) from Mn^{2+} (0.45) and Cr^{6+} (0.80)
p-Col	Cr^{3+} (0.05) from Cr^{6+} (0.89), VO^{2+} (0.03) from Mn^{2+} (0.50) and Mo^{6+} (0.85), Fe^{3+} (0.05) from Mn^{2+} (0.49) and Cr^{6+} (0.85), Fe^{3+} (0.05) from Co^{2+} (0.49) and Cr^{6+} (0.84), VO^{2+} (0.04) from Mn^{2+} (0.47) and Cr^{6+} (0.82).
PGL	Cr^{3+} (0.04) from Cr^{6+} (0.90), VO^{2+} (0.05) from Mn^{2+} (0.50) and Cr^{6+} (0.86), VO^{2+} (0.02) from Mn^{2+} (0.52) and Mo^{6+} (0.89), Fe^{3+} (0.04) from Mn^{2+} (0.54) and Cr^{6+} (0.84), Fe^{3+} (0.02) from Co^{2+} (0.52) and Cr^{6+} (0.82).

Because inorganic ions (e.g. Fe^{3+} , Cu^{2+} or Ni^{2+} etc.) are used as catalysts in a variety of chemical reactions, they might be present as impurities in organic compounds. Similarly, organometallic compounds can contain trace amounts of organic impurities. It is evident from Tables VI and VII that mixtures of metal ions could be separated in the presence of organic (amines or phenolic) impurities; likewise, amines or phenols could be separated in the presence of inorganic impurities.

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Table VII

Separation of amines and phenols in the presence of inorganic impurities on TBP (0.001 M)-impregnated silica layers developed with mobile phases M₆ or M₁₇

Impurities	Separation (<i>R_F</i>)
Fe ³⁺	p-DAB (0.45) from ID (0.70), p-DAB (0.44) from L-TRYP (0.76), o-Crol (0.74) from m-Crol (0.00), o-Crol (0.74) from p-Crol (0.00), m-APh (0.70)/p-APh (0.83) from o-APh (0.00)
Cu ²⁺	p-DAB (0.46) from ID (0.71), p-DAB (0.45) from L-TRYP (0.75), o-Crol (0.73) from m-Crol (0.00), o-Crol (0.75) from p-Crol (0.00), m-APh (0.73)/p-APh (0.84) from o-APh (0.02)
Ni ²⁺	p-DAB (0.47) from ID (0.72), p-DAB (0.45) from L-TRYP (0.74), o-Crol (0.72) from m-Crol (0.00), o-Crol (0.76) from p-Crol (0.02), m-APh (0.72)/p-APh (0.82) from o-APh (0.00)
Co ²⁺	p-DAB (0.46) from ID (0.71), p-DAB (0.45) from L-TRYP (0.74), o-Crol (0.73) from m-Crol (0.00), o-Crol (0.76) from p-Crol (0.00), m-APh (0.73)/p-APh (0.83) from o-APh (0.00)
UO ₂ ²⁺	p-DAB (0.48) from ID (0.70), p-DAB (0.46) from L-TRYP (0.75), o-Crol (0.73) from m-Crol (0.00), o-Crol (0.75) from p-Crol (0.00), m-APh (0.72)/p-APh (0.82) from o-APh (0.00)

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