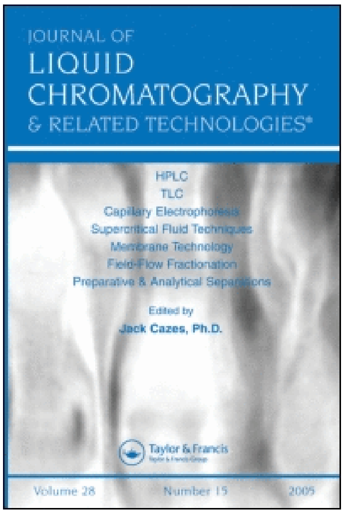

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M. Qureshi[a]; A. Mohammad[a]; N. Fatima[a]
[a] Chemistry Section Z. H. College of Engineering Aligarh Muslim University, Aligarh, India

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REVERSE PHASE THIN-LAYER CHROMATOGRAPHY OF SOME METAL IONS ON BUTYLAMINE IMPREGNATED SILICA GEL G IN FORMIC ACID MEDIUM

M. Qureshi, A. Mohammad, and N. Fatima*
Chemistry Section
Z. H. College of Engineering
Aligarh Muslim University
Aligarh, India

ABSTRACT

Reversed phase thin layer chromatography of metal ions have been performed on s-butylamine and t-butylamine impregnated silica gel thin layers in formic acid and sodium formate systems. Separation potential of impregnated silica gel thin layers was explored. Impregnated silica gel layers were found to be more selective (strongly sorbing) than unimpregnated silica gel chromotoplates. Several important binary and ternary separations were achieved on impregnated thin layers.

INTRODUCTION

Reversed phase chromatography has received considerable attention in analytical chemistry since its introduction in 1958 by Winchester (1) who coupled favourable features of high molecular

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*To whom correspondence should be addressed.

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extractants with chromatographic technique. Reversed phase thin layer chromatography (RPTLC) being relatively a new tool has expanded the scope of separations by normal phase TLC. Now changes in selectivity of a media are possible not only from a varied choice of mobile phases or sorbents but also by modifications of the surface of silica gel G (SG) by reaction with organic silanes of varying chain lengths as well as reacting with various groups including amine, cyano or other ion exchange functions.

A survey of literature revealed that high molecular weight amines and substituted quarternary ammonium salts (2,3), heterocyclic amines (4), tetra substiuted pyrazole (5) and neutral organophosphorous compounds (6) have been extensively used as impregnants of the stationary phase. Solutions of strong monobasic acids such as HCl, HBr, HI, HSCN and $HClO_4$ have been used as eluents. Amongst these acids, Brinkman (3) has nicely established the superiority of HCl over other acids.

Formic acid (FA) is an unusual acid in many ways. It is sufficiently acidic [$Ka(H_2O)$ at 25°C = 1.77×10^{-4}] to prevent hydrolysis of salts, and at the same time it is less acidic than necessary to dissolve the ion exchange materials significantly. Its reducing properties do not permit the oxidation of cations during analysis. It is therefore surprising that very little work appears to have been done on adsorption of cations in FA medium (7-10) and almost no work has been reported on its use as eluent in RPTLC of metal ions.

In this paper, we wish to present the use of FA as eluent for some interesting separations of metal ions on s-butylamine (s-BA) and t-butylamine (t-BA) impregnated SG thin layers.

EXPERIMENTAL

Apparatus

TLC apparatus (Toshniwal, India) was used for the preparation of thin layers on 20x3.5 cm glass plates. The chromatography was performed in 24x6 cm glass jars.

Reagents

SG (E. Merck); s-BA, t-BA and benzene were all of analytical grade from B.D.H. England. Other reagents were of Analar grade.

Test solutions and detectors

Test solutions, 0.1M of chlorides, nitrates or sulphates of cations were prepared in a little of the corresponding acids. Conventional spot test reagents were used for detection purposes (11).

Preparations of thin-layer plates

(a) Preparation of plain or unimpregnated SG thin layer plates

To prepare unimpregnated SG thin layer plates the slurry was first obtained by homogenizing the SG in demineralized water (DMW) in the ratio of 1:3 with constant shaking for 5 min. The resultant slurry was used immediately to coat the clean glass plates with the help of an applicator to give a layer of 250 µm thickness. The plates were air dried in a protected chamber at room temperature (30°C).

(b) Preparation of amine impregnated SG thin layers

Impregnated SG thin layers were obtained by impregnating the support either directly or indirectly.

i) Direct impregnating method: 20 gm of SG was well shaken in a mortar with 60 ml of 30% (V/V) amine (s- or t-BA) solution in benzene for at least 4 min. The resultant slurry was spread over glass plates with the help of an applicator to obtain a layer of

250 µm thickness. Benzene was allowed to evaporate at room rempera- ture.

ii) Indirect impregnating method: Glass plates were covered with a 250 µm layer of an aqueous slurry of SG. After drying at 100 ± 5°C for 2h, the chromatoplates were impregnated by placing them in chromatographic chambers and developing with a solution of 30% (V/V) s-or t-BA solution in benzene. Benzene was allowed to evaporate at room temperature.

Indirect impregnating method was found unsuitable for chromatographic studies because it suffered two main drawbacks:

I. Solution required few hours (≈5h) to reach the top of the plate.

II. Two solvent fronts were appeared on the impregnated chromatoplates. It seems that both the components of the solvent mixture ascend with different rate on SG coated plate.

Therefore, the chromatoplates obtained by direct impregnating method were selected for detailed studies.

Solvent systems

The following solvent systems were used as mobile phase:

S_1	1.0M HCOOH
S_2	1.0M HCOONa
S_3	1.0M HCOOH + 1.0M HCOONa (1:1)
S_4	1.0M HCOOH + 1.0M HCOONa (2:8)
S_5	1.0M HCOOH + 1.0M HCOONa (4:6)
S_6	1.0M HCOOH + 1.0M HCOONa (6:4)
S_7	1.0M HCOOH + 1.0M HCOONa (8:2).

Procedure

The sample solution was loaded (1 or 2 drops) on unimpreg- nated or butylamine impregnated SG chromatogplates with the help of glass capillaries and the spots were allowed to dry at room temperature. The solvent ascent was always 10 cm. The R_L and R_T were measured after detection and R_f values were evaluated.

RESULTS AND DISCUSSION

Reversed phase chromatography on SG impregnated with the s- or t-BA gave excellent results. Few aspects of this study are worthy to note:

1. Thin layers prepared by direct impregnating method were of good quality and they yielded always reproducible results. These results are in consonance with the recent findings of Hulshoff and Perrin (12) for non-aqueous stationary phase.
2. The time of run with all solvent systems was only 15-20 min. The addition of 3% NaCl, NaBr, NH_4Br, LiCl or $CaCl_2$ in the mobile phase did not increase the migration rate of mobile phase.
3. Thin layer plates impregnated with 30% amine solution were found to be most appropriate and convenient to handle for chromatography of metal ions. At lower degree of impregnation, results were not good while at higher impregnation tailing started and a longer time required for developing the chromatoplates. Over 50% impregnation the disagreeable smell of amines made it impossible to prepare the chromatoplates.
4. Impregnated SG thin layers were more selective (strongly sorbing) for metal ions than unimpregnated SG thin layers in all solvent systems.
5. s-BA impregnated SG thin layers showed stronger sorbing strength (higher selectivity) for metal ions than t-BA impregnated SG plates in 1.0M HCOOH (pH = 13) while reverse is true in 1.0M COONa(pH=6.2).

Results obtained have been summarized in figures 1-3 and tables 1-2. The R_f values for only those cations which gave compact spots were taken for plotting the figures. The results of these studies revealed that impregnated SG thin layers offered

TABLE 1

Binary and Ternary Separations Achieved Experimentally on 30% s-BA Impregnated SG Thin Layers (Development Time=20 min.)

Solvents	Separations achieved
S_1 V	VO^{2+}(0.2) - Fe^{3+}(0.9) - Al^{3+}(0.62)
	VO^{2+}(0.2) - Fe^{3+}(0.9) - Fe^{2+}(0.45)
	VO^{2+}(0.2) - Fe^{3+}(0.9) - Th^{4+}(0.62)
	VO^{2+}(0.2) - Fe^{3+}(0.9) - Uo_2^{2+}(0.62)
	VO^{2+}(0.2) - Fe^{3+}(0.9) - Cr^{3+}(0.62)
	Bi^{3+}(0.15) - Fe^{3+}(0.9) - Al^{3+}(0.62)
	Bi^{3+}(0.15) - Mo^{6+}(0.9) - Al^{3+}(0.62)
	Bi^{3+}(0.15) - Cd^{2+}(0.92) - Al^{3+}(0.62)
	Bi^{3+}(0.15) - Tl^{+}(0.87) - Fe^{2+}(0.45)
S_2	Cr^{3+}(0.25) - Cu^{2+}(0.82), Cr^{3+}(0.25) - Co^{2+}(1.0)
	Bi^{3+}(0.0) - Cu^{2+}(0.82), Bi^{3+}(0.0) - Tl^{+}(0.94)
	Pb^{2+}(0.0) - Cd^{2+}(1.0), Pb^{2+}(0.0) - Cu^{2+}(1.82)
S_3	Fe^{2+}(0.1) - Al^{3+}(0.52) - Co^{2+}(1.00)
	Fe^{2+}(0.1) - Cu^{2+}(0.5) - Co^{2+}(1.0)
	Fe^{2+}(0.1) - Zn^{2+}(0.62) - Co^{2+}(1.0)
	Fe^{2+}(0.1) - Th^{4+}(0.57) - Co^{2+}(1.0)
	Fe^{2+}(0.1) - Uo_2^{2+}(0.55) - Co^{2+}(1.0)
	Fe^{2+}(0.1) - Bi^{3+}(0.4) - Ni^{2+}(1.0)
	Fe^{2+}(0.1) - Cu^{2+}(0.52) - Ni^{2+}(1.0)
S_4	Fe^{3+}(0.3) - Co^{2+}(1.0), Tl^{+}(0.61) - Se^{4+}(0.9)
S_5	Ag^{+}(0.1) - Tl^{+} (0.72), Ag^{+}(0.1) - Cd^{2+}(0.45)
S_6	Cu^{2+}(0.25) - Ni^{2+}(1.0), Bi^{3+}(0.05) - Tl^{+}(0.5)
S_7	W^{6+}(0.0) - Th^{4+}(0.7), Mo^{4+}(0.0) - Th^{4+}(0.7)
	Zr^{4+}(0.0) - Uo_2^{2+}(0.47)
	Zr^{4+}(0.0) - Th^{4+}(0.7), MO^{4+}(0.0) - Cr^{3+}(0.53)

TABLE 2

Binary and Ternary Separations Achieved Experimentally on 30% t-BA Impregnated SG thin Layers (Development time = 20 min)

Solvents	Separations achieved
S_1	Pb^{2+}(0.0) - Zn^{2+}(0.58) - Cr^{3+}(0.92)
	Pb^{2+}(0.0) - Fe^{2+}(0.54) - Cr^{3+}(0.92)
	Pb^{2+}(0.0) - UO_2^{2+}(0.81) - Fe^{2+}(0.54)
	Pb^{2+}(0.0) - Cu^{2+}(0.95) - Fe^{2+}(0.54)
	Pb^{2+}(0.0) - Fe^{3+}(1.0)) - Fe^{2+}(0.54)
	Pb^{2+}(0.0) - Bi^{3+}(0.65) - Cd^{2+}(1.0)
	Zr^{4+}(0.0) - Th^{4+}(0.85) - Fe^{2+}(0.54)
	Zr^{4+}(0.0) - Ni^{2+}(1.0) - Fe^{2+} (0.54)
	Zr^{4+}(0.0) - Al^{3+}(0.85) - Fe^{2+}(0.54)
	Zn^{2+}(0.58) - Cd^{2+}(1.0), Zn^{2+}(0.58) - Cu^{2+}(0.95)
S_2	Cu^{2+}(0.0) - Ni^{2+}(1.0) - Tl^{+}(0.67)
	Cu^{2+}(0.0) - Co^{2+}(1.0), Cu^{2+}(0.0) - Fe^{2+}(0.35)
S_3	Vo^{2+}(0.2) - Uo_2^{2+}(0.55), Cu^{2+}(0.42) - Ni^{2+}(1.0)
	Th^{4+}(0.62) - Zr^{4+}(0.0), Fe^{3+}(0.10) - Cr^{3+}(0.52)
S_4	Zr^{4+}(0.0) - Uo_2^{2+}(0.43), - Zr^{4+}(0.0) - Th^{4+}(0.47)
	Cu^{2+}(0.58) - Ag^{+}(0.12), - Cu^{2+}(0.58) - Cr^{3+}(0.21)
S_5	Cd^{2+}(0.45) from a mixture of Al^{3+}, Vo^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Zr^{4+}, and Ag^{+}.
	Tl^{+}(0.77) from a mixture of Zr^{4+}, Cu^{2+}, Zn^{2+} and Uo_2^{2+}.
	Th^{4+}(0.60) from a mixture of Zn^{2+}, Bi^{3+}, Al^{3+} and Zr^{4+}.

promising potentialities for the rapid separations of metal ions in FA medium. Interestingly, all separations were achieved on 30% (s-BA or t-BA) impregnated SG layers. Thus a large number of important binary and ternary separations of metal ions were actually achieved on impregnated SG thin layers in different solvent systems. These separations have been summarized in tables 1-2. The separations such as: VO^{2+} - Fe^{3+} - Fe^{2+}, Zn^{2+} - Fe^{2+} - Ni^{2+}, Th^{4+} - Fe^{2+} - Zr^{4+}, VO^{2+} - Fe^{3+} - UO_2^{2+}, Zn^{2+} - Cu^{2+}, Zn^{2+} - Cd^{2+}, Cu^{2+} - Ni^{2+}, W^{6+} - Th^{4+}, Th^{4+} - Zr^{4+}, Pb^{2+} - Bi^{3+}, Cr^{3+} - Fe^{3+}, Mo^{6+} - Th^{4+} and Tl^{+} - Se^{4+} are interesting and show the advantage of reversed phase chromatography in FA medium.

Figure 1 summarizes the effect of degree of impregnation of s- and t-BA on the R_f values of metal ions in 1.0M HCOOH. It is evident from Fig.1 that both impregnants showed remarkable difference in sorbing strength (selectivity) towards most of the metal ions only at 30% impregnation. VO^{2+}, Fe^{2+}, Cu^{2+}, Th^{4+}, Cr^{3+}, Al^{3+} gave minimum R_f values (strongly sorbing) on 30% s-BA impregnated SG thin layers. Fe^{3+} showed maximum R_f value on this support. On SG impregnated with 30% t-BA only four metal ions such as VO^{2+}, Fe^{2+}, Zn^{2+} and Mo^{6+} showed minimum R_f values while Fe^{3+}, Cu^{2+}, UO_2^{2+}, Th^{4+}, Cd^{2+} and Cr^{3+} gave maximum R_f values. At lower degree of impregnation (10-20%) all the metal ions showed similar trend of R_f values on both the impregnated supports. Th^{4+} and Mo^{6+} are only the exceptions. Similarly at higher degree of impregnation (40-50%) all the metal ions leaving Cr^{3+} showed similar trend of R_f values on these supports. Therefore, 30% impregnated SG thin layers were chosen for detailed study and interestingly many important separations were achieved on these chromotoplates with quite ease and rapidity.

Figure 2 revealed how the selectivity of plain SG thin layers increases on impregnation with s-BA or t-BA. To compare the

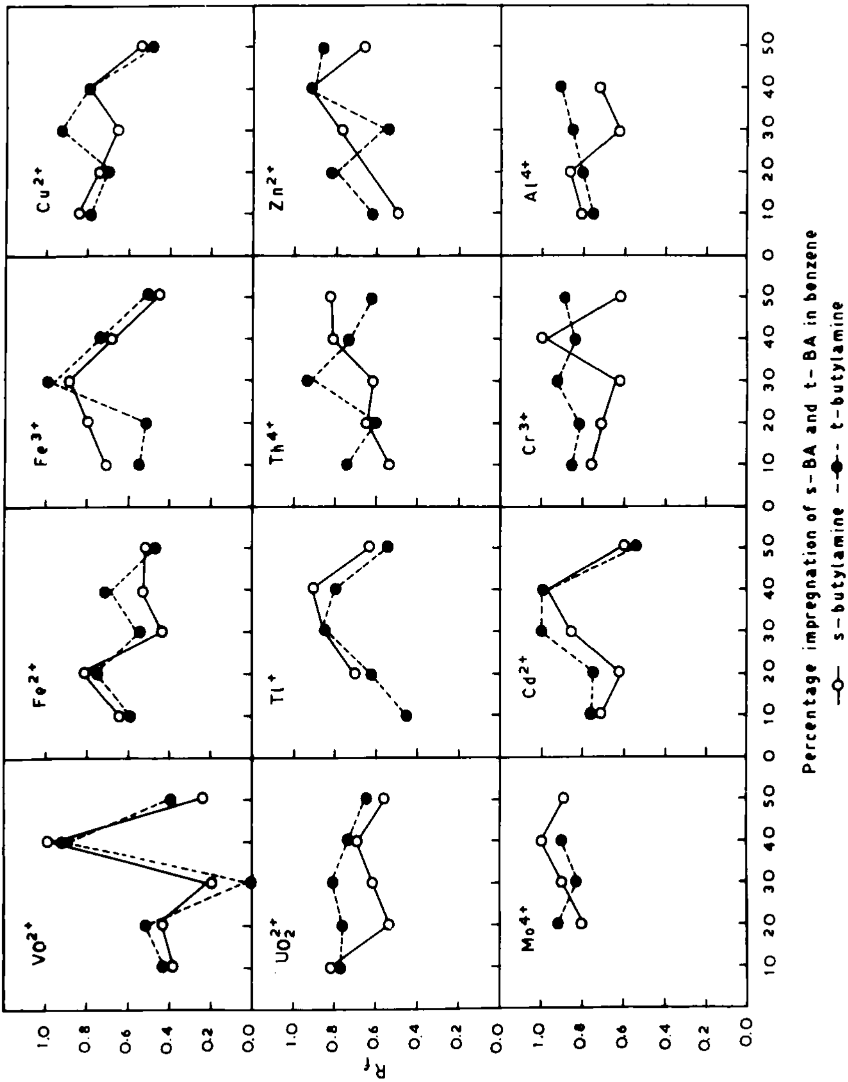

FIGURE 1 Plot of R_f vs. percentage impregnation of s-butylamine or t-butylamine.

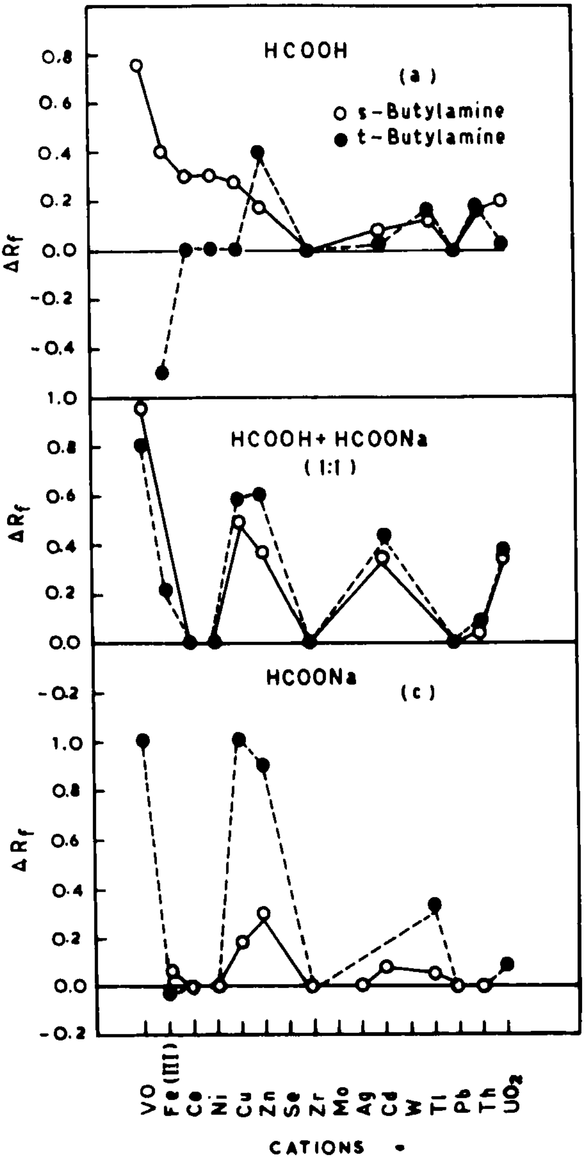

FIGURE 2 Comparison between selectivities of butylamines impregnated and unimpregnated silica gel thin layers in 1.0M HCOOH, 1.0M HCOONa and 1.0M HCOOH + 1.0M HCOONa(1:1) solvent systems.

selectivity of impregnated and unimpregnated SG thin layers the difference in R_f values i.e. ΔR_f (R_f on plain or unimpregnated SG - R_f on impregnated SG) have been plotted in Fig. 2. It is clear from Fig. 2 that the selectivity (sorbing strength) of plain SG is drastically enhanced on impregnation with 30% s-BA or t-BA in all three chosen solvent systems (1.0M HCOOH, 1.0M HCOONa, and 1.0M HCOOH + 1.0M HCOONa)as indicated by positive ΔR_f values for most of the metal ions. In HCOOH, SG impregnated with s-BA was more selective than plain SG for most of metal ions (Fig. 2a). In comparison to unimpregnated SG thin layer s-BA impregnated chromatoplates showed highest selectivity for VO^{2+} (more positive value of ΔR_f) and minimum for Cr^{4+} and Pb^{2+}($\Delta R_f = 0$) while t-BA impregnated layers showed highest selectivity for Zn^{2+} and least selectivity for Fe^{3+} (negative ΔR_f value).

In HCOOH + HCOONa (1:1) and HCOONa solvent systems, both the impregnated supports were more selective than plain SG support for all metal ions (Fig. 2b-c). Ni^{2+}, Co^{2+}, Zr^{4+} and Pb^{2+} are only exceptions which showed the same selectivity towards impregnated and unimpregnated supports. It is also interesting to note from the comparison of Figs. 2a,b & c that when plain SG thin layers were taken as standard than the s-BA impregnated chromatoplates showed stronger sorbing strength (more selectivity) in HCOOH and weaker sorbing strength (lower selectivity) in HCOONa than t-BA impregnated thin layers for most of metal ions. In mixed solvent system (HCOOH + HCOONa, 1:1) both the impregnated supports showed comparable sorbing strength.

It is worthwhile at this juncture to make a comparison between the selectivities of s-BA impregnated SG and t-BA impregnated SG thin layers in different solvent systems. For this purpose the ΔR_f values (R_f on SG impregnated with t-BA - R_f on SG impregnated with s-BA) have been plotted in Fig.3. In 1.0M HCOOH

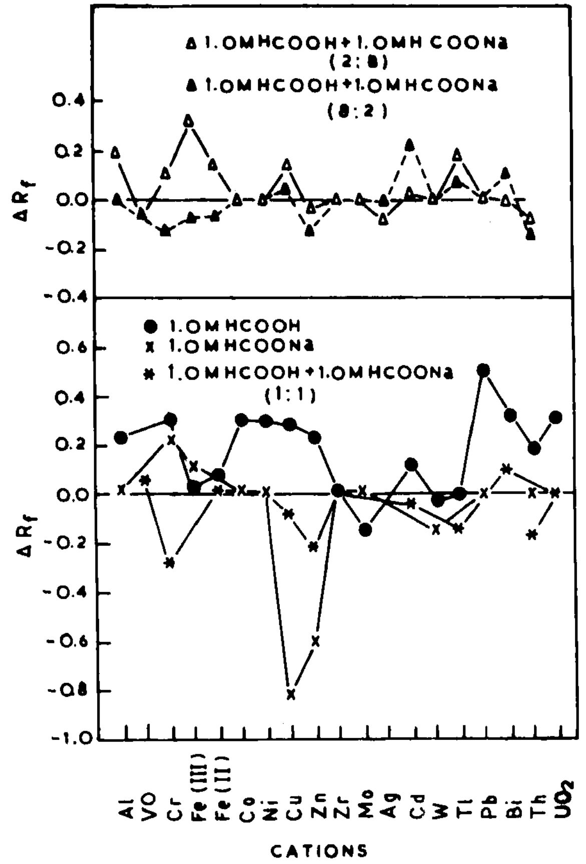

FIGURE 3 Comparison between selectivities of s-butylamine and t-butylamine impregnated silica gel thin layers in different solvent systems.

(pH = 1.3), s-BA impregnated SG plates showed stronger sorbing strength towards most of metal ions compared to t-BA impregnated plates as indicated by positive ΔR_f values. But a reversal trend was observed in 1.0M HCOONa (pH = 6.2) where t-BA showed more sorbing strength than the s-BA impregnant. In this solvent system a strong sorption of Cu^{2+} on t-BA impregnated SG thin layers is an unique feature which leads to the selective separation of Cu^{2+}. In equimolar mixture of HCOOH and HCOONa (pH = 3.2) t-BA showed stronger sorbing tendency towards many metal ions in comparison to s-BA. However, when 1.0 HCOOH + 1.0M HCOONa(2:8, pH = 2.3) was used as mobile phase, many metal ions showed almost similar chromatographic behaviour (ΔR_f = zero). Al^{3+}, Fe^{3+}, Fe^{2+}, Cu^{2+} and Tl^{+} were strongly sorbed on s-BA impregnated SG chromatoplates. In 1.0M HCOOH + 1.0M HCOONa (8:2, pH = 4.6) again t-BA impregnated plates showed strong sorption towards most of the metal ions but Cd^{2+}, Tl^{+} and Bi^{3+} were strongly sorbed on s-BA impregnated SG thin layers.

In general, s-BA impregnated SG layers were more selective (stronger sorbing) for metal ions at lower pH value of the mobile phase (pH = 1-2.5) than t-BA impregnated SG layers while at higher pH value of mobile phase (pH = 3-6.2) reverse is true.

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