



ELSEVIER

Journal of Chromatography A, 841 (1999) 263–271

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Retention behaviour of metal ions on tri-*n*-butyl phosphate- and tri-*n*-butyl amine-impregnated silica gel-G layers in oxalic acid–oxalate mobile phases

S.D. Sharma*, S.C. Sharma

Analytical Research Laboratory, Department of Chemistry, Hindu College, B-3, Jigar Colony, Moradabad 244001, India

Received 15 August 1998; received in revised form 16 February 1999; accepted 24 February 1999

Abstract

The chromatographic behaviour of thirty metal ions was studied on tri-*n*-butyl phosphate- (TBP) and Tri-*n*-butyl amine- (TBA) impregnated silica gel-G layers in oxalic acid–oxalate mobile phases. The effects of TBP impregnation, pH of the mobile phase and pK_1 of metal oxalate complexes on R_F values are discussed. For almost all metal ions, there is a sudden change in their chromatographic behaviour at 60% TBP impregnation. The mechanism of migration is explained in terms of adsorption, precipitation and complex formation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Retention behaviour; Metal ions

1. Introduction

In 1958, Winchester [1] used di (2⁻ ethyl hexyl) phosphoric acid loaded on Al₂O₃ to separate a number of rare earths. Since then, reversed-phase thin-layer chromatography (RPTLC) has become very popular and numerous papers have been published. RPTLC of metal ions on silica gel layers during the period up to 1972 has been admirably summarized by Brinkman et al. [2]. Later, the chromatography and physical properties of surface-modified precoated supports for TLC have been reviewed by Fischer et al. [3].

In 1990, the RPTLC of metal ions on silica gel-G layers was studied extensively [4–9]. Similar studies have been performed in our laboratory on some toxic metal ions in two-component systems containing

dimethylsulfoxide (DMSO) [10]. The chromatography of inorganic ions on silica gel layers impregnated with a high-molecular-mass amine using sulphuric acid and sulphuric acid–ammonium sulphate mobile phases has since been carried out and multicomponent ionic mixtures were separated [11–13]. Recently, tri-*n*-butyl phosphate (TBP)-impregnated silica gel-G layers were used for the quantitative separation of some metal ions in an acetone–nitric acid–water system [14].

However, in all such studies, few papers were published using complexing acids as eluants [15,16]. The separation potential of this technique is greatly enhanced if complexation is used. Earlier, we studied the TLC of metal ions using complexing acids and their salts as the mobile phase and established their remarkable utility in the separation of metal ions [17]. As far as we are aware, oxalic acid–oxalate systems have not yet been employed in the RPTLC

*Corresponding author.

of metal ions. The present work is, therefore, undertaken to investigate the RPTLC behaviour of metal ions on silica gel-G layers impregnated with TBP and TBA using these systems as the mobile phase. The results are presented in the following pages.

2. Experimental

2.1. Reagents

Silica gel-G, TBP, TBA, benzene and all other chemicals were of analytical reagent grade from Merck.

The details of the apparatus, test solutions, detectors, preparation of chromatoplates and the chromatographic procedure are the same as reported earlier [10,18].

2.2. Solvent systems

Thirty metal ions were chromatographed in the following seven solvent systems: S_1 , 0.1 M oxalic acid; S_2 , 0.1 M sodium oxalate; S_3 , 0.1 M ammonium oxalate; S_4 , 0.1 M oxalic acid+0.1 M sodium oxalate+0.1 M ammonium oxalate (1:1:1, v/v); S_5 , 0.1 M oxalic acid+0.1 M sodium oxalate (1:1, v/v); S_6 , 0.1 M oxalic acid+0.1 M ammonium oxalate (1:1, v/v); S_7 , 0.1 M sodium oxalate+0.1 M ammonium oxalate (1:1, v/v). The pH values of these systems are 1.50, 7.59, 6.40, 3.55, 2.50, 2.50 and 6.58, respectively. Aqueous nitric acid systems of pH 1.5 (S_8) and pH 2.5 (S_9) were also used.

3. Results and discussion

In the RPTLC of metal ions on TBP- and TBA-impregnated silica gel-G layers, most of the spots are well defined and compact, and tailing is observed only for (a) Fe^{2+} and Fe^{3+} in solvent S_2 , S_3 and S_7 , UO_2^{2+} and Al^{3+} in solvent S_2 on TBP-impregnated layers and (b) Cu^{2+} in solvent S_1 on TBA-impregnated layers. Furthermore, the spots were more compact on TBA-impregnated layers than on TBP-impregnated ones. The R_F values were found to be reproducible and the variation does not exceed 5% of

the average value. The impregnated layers are quite stable and firm, and are capable of withstanding the solvent systems and chemical operations. For metal ion chromatography, 20% TBP-impregnated layers were chosen on the basis of our earlier experience [19].

It is interesting to determine the effect of TBP-impregnation on the R_F values of all of the metal ions in 0.1 M oxalic acid and 0.1 M sodium oxalate. For this purpose, plots of R_F versus the percentage TBP-impregnation were drawn for all of the metal ions [Fig. 1]. A cursory inspection of these plots led to the following conclusions.

Pb^{2+} , Cu^{2+} , Hg_2^{2+} , Tl^+ , Cr^{3+} , Ni^{2+} , Co^{2+} , VO^{2+} , Ba^{2+} , Sr^{2+} and Sn^{4+} have almost constant R_F values, irrespective of the percentage TBP impregnation. For Ag^+ and Hg^{2+} , the R_F values remain unchanged until there was 60% TBP impregnation. Beyond this, there is a sudden increase in R_F values, which reached a maximum at 100% TBP impregnation, probably due to less adsorption of these ions on the impregnated layers. For Pd^{2+} , Cd^{2+} , Sb^{3+} , UO_2^{2+} , Fe^{3+} , Ce^{4+} , La^{3+} and Al^{3+} , the R_F values were higher on unimpregnated layers than on impregnated ones. However, the values gradually decreased as we increased the percentage of TBP impregnation. This decrease continued up to 60% impregnation and, beyond this, the R_F remained almost constant, except for Pd^{2+} , which showed an increase in R_F , probably due to less adsorption on TBP-impregnated silica gel-G layers. Thus, maximum adsorption for the majority of the metal ions occurred on 60% TBP-impregnated layers.

The behaviour of Ti^{4+} , Zr^{4+} and Th^{4+} was quite exceptional, as their R_F values did not change appreciably up to the stage of 60% impregnation, but, beyond this level, the values suddenly fell. Furthermore, for Zr^{4+} and Ti^{4+} , the R_F values differed greatly in oxalic acid and sodium oxalate systems and the values were much higher in oxalic acid, probably due to complexation in acidic media. The values have relatively smaller differences for Th^{4+} as it frequently forms oxalate complexes. For Bi^{3+} , the R_F values were generally low, due to hydrolysis, and showed a regular decrease with increasing percentages of TBP impregnation. K^+ , Rb^+ and Cs^+ had almost constant, but high, R_F values, up to the stage of 60% impregnation, due to

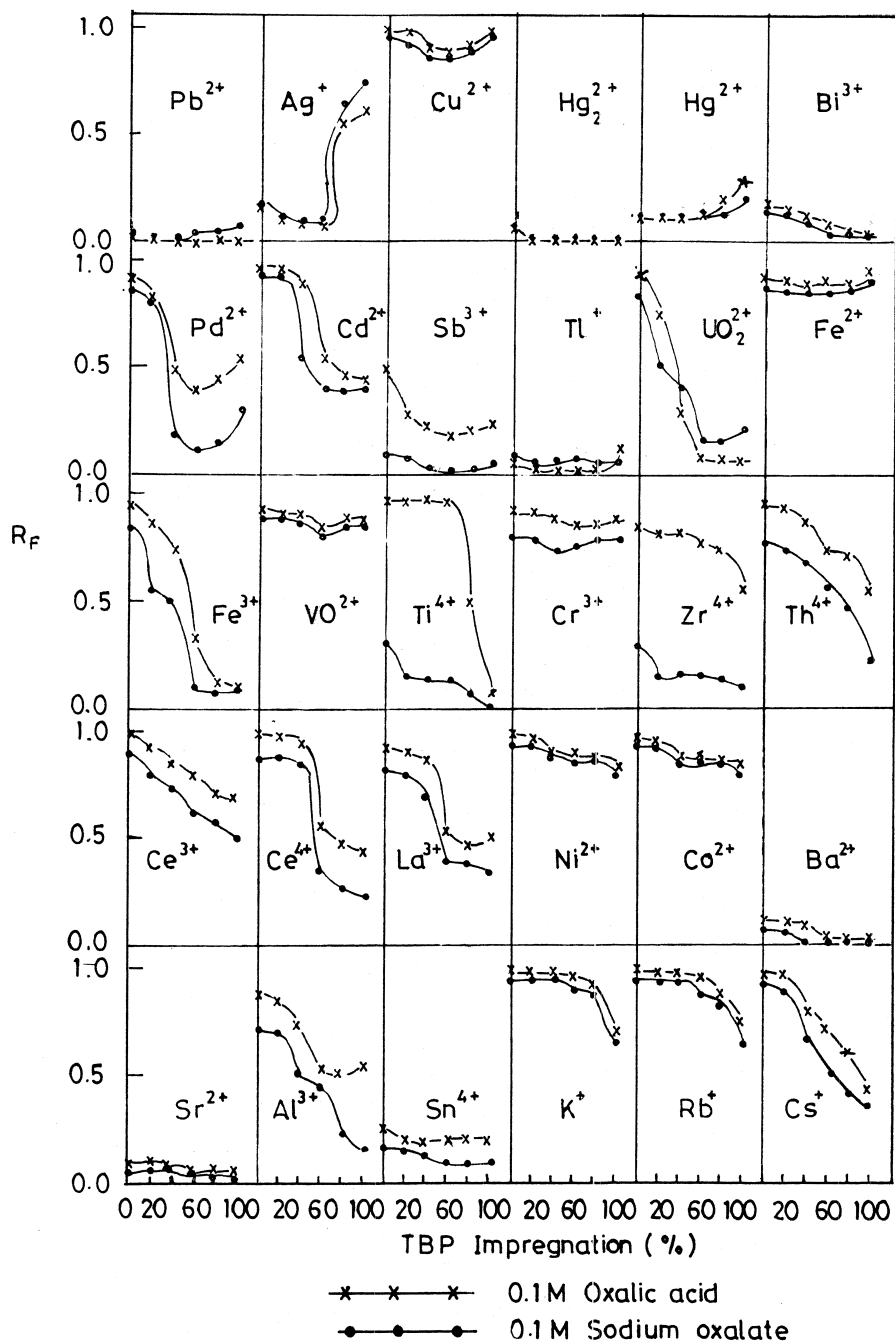


Fig. 1. Plots of R_F vs. TBP impregnation.

the fact that they do not normally form complexes. A further increase in the percentage of TBP impregnation caused a gradual decrease in their R_F values,

probably due to higher adsorption as a result of the increasingly non-polar nature of the layer. It was very much in evidence that there was a change in the

chromatographic behaviour of almost all of the metal ions at the stage of 60% TBP impregnation.

To study the effect of pH on the movement of metal ions, values of R_F versus pH on 20% TBP- and TBA-impregnated layers were plotted (Fig. 2a and b). Metal ions are grouped on the basis of the similarity in their chromatographic behaviour on both of the impregnated layers. The salient features are:

3.1. On TBP and TBA impregnated layers

Pb^{2+} , Hg_2^{2+} , Ag^+ , Bi^{3+} , Ba^{2+} and Sr^{2+} had zero or low R_F values at all pH values studied, due to their precipitation (Table 1). Sn^{4+} gave low R_F values, probably due to the formation of $[\text{Sn}(\text{C}_2\text{O}_4)]^{4-}$ [20], which is strongly adsorbed on these layers. In contrast, Cd^{2+} , Th^{4+} , Ce^{3+} , Ni^{2+} and Co^{2+} give high R_F values (≥ 0.70) over the whole pH range, which may be due to the formation of soluble oxalate complexes. The R_F values of metal ions such as UO_2^{2+} , Fe^{3+} , Ti^{4+} , Sb^{3+} and Zr^{4+} suddenly decrease with increasing pH in the lower pH range. However, the values become constant in neutral or alkaline media. For Ti^{4+} , Sb^{3+} and Zr^{4+} , this may be due to hydrolysis in these media. The decrease in R_F with increasing pH for UO_2^{2+} and Fe^{3+} in the lower pH range is more pronounced on TBA-impregnated layers than on TBP-impregnated ones, due to slight polarity of TBP in comparison to non-polar TBA. TBP is very slightly soluble in H_2O (0.04 per 100 parts at 20°C) whereas TBA is insoluble.

3.2. On TBP impregnated layers

Hg^{2+} and Tl^+ gave low R_F values at all pH values studied, probably due to the higher dissociation constants of their oxalate complexes. However, Cu^{2+} , Pd^{2+} , VO^{2+} , Cr^{3+} , Ce^{4+} , Fe^{2+} and Al^{3+} gave high R_F values at all pH values studied. Formation of their soluble complexes with oxalate ion may be the reason for it.

3.3. On TBA impregnated layers

The R_F values of metal ions such as Cu^{2+} , Cr^{3+} ,

Tl^+ , Fe^{2+} and Pd^{2+} gradually decrease with an increase in pH and, in the higher pH range, the R_F value becomes almost constant with increasing pH. The R_F values for Hg^{2+} and Ce^{4+} decrease sharply and become minimal at pH 3.5. With further increases in the pH, the R_F values remain unchanged. In case of Hg^{2+} , this may be due to a precipitation mechanism, whereas, for Ce^{4+} , which exists in the form of hydrated ion, $[\text{Ce}(\text{H}_2\text{O})]^{4+}$, hydrolysis occurs except at low pH [20], thereby giving rise to low R_F values. The R_F values for VO^{2+} and Al^{3+} decrease continuously with increasing pH and reach almost 0.10 for VO^{2+} at pH 7.6.

The metal ions that have R_F values of zero or that are less than 0.10 do so owing to: (a) precipitation; (b) strong adsorption due to high charge and (c) complex formation

On mixing a solution of a metal ion with TBP followed by the addition of different solvents, it was found that, for Pb^{2+} , Hg^{2+} , Hg_2^{2+} , Ag^+ , Bi^{3+} , Ba^{2+} and Sr^{2+} , a precipitate was obtained. In such cases, the zero or very low R_F values on TBP-impregnated layers are, therefore, due to a precipitation mechanism. For TBA-impregnated layers, a similar experiment was carried out and various metal ions were precipitated (Table 1). In this case also, zero or very low R_F values were due to precipitation. However, the low R_F values for Tl^+ and Hg^{2+} on TBP-impregnated layers are probably due to the higher values of the dissociation constants of their oxalate complexes ($\text{p}K_1$ for Tl^+ is 2.03) and the low R_F value for Sb^{3+} is due to hydrolysis. On TBA-impregnated layers, the low R_F value for UO_2^{2+} is probably due to the formation of anionic complexes [21] such as $[\text{UO}_2(\text{C}_2\text{O}_4)_2]^{2-}$ or $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$ and for Ti^{4+} in the higher pH range (i.e. beyond 6), is due to its hydrolysis in alkaline media.

To study the effects of complexation, R_F values for all of the metal ions were determined in nitric acid (pH values of 1.5 and 2.5) in order to compare them with the R_F data obtained in oxalic acid–oxalate systems having the same pH on TBP- and TBA-impregnated silica gel-G layers. The R_F data for those metal ions that showed considerable variations are given in Table 2. In the case of 20% TBP-impregnated layers, a plot of R_F versus metal ions for oxalic acid and nitric acid indicates that most of the metal ions have higher R_F values in

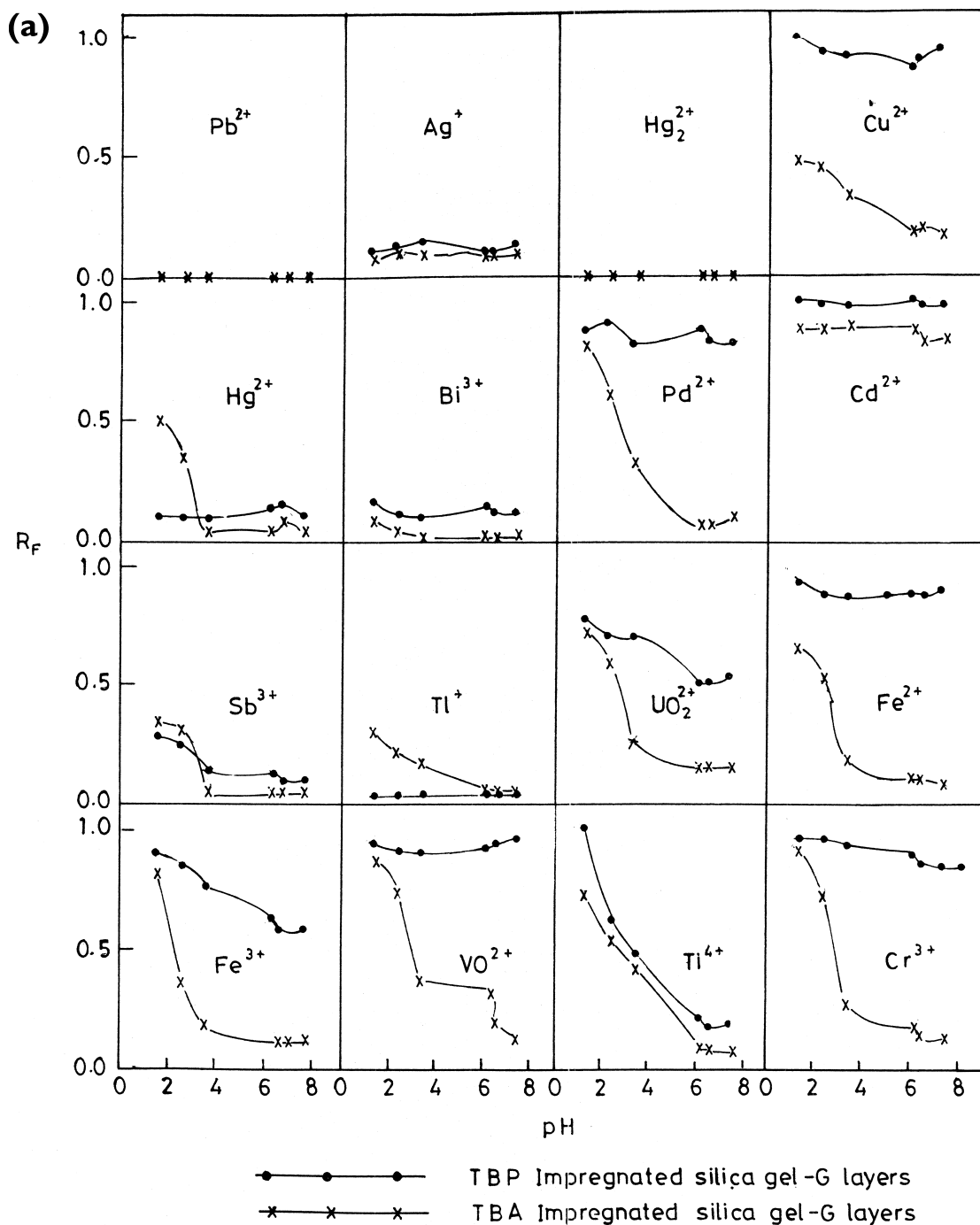


Fig. 2. Plots of R_F vs. pH.

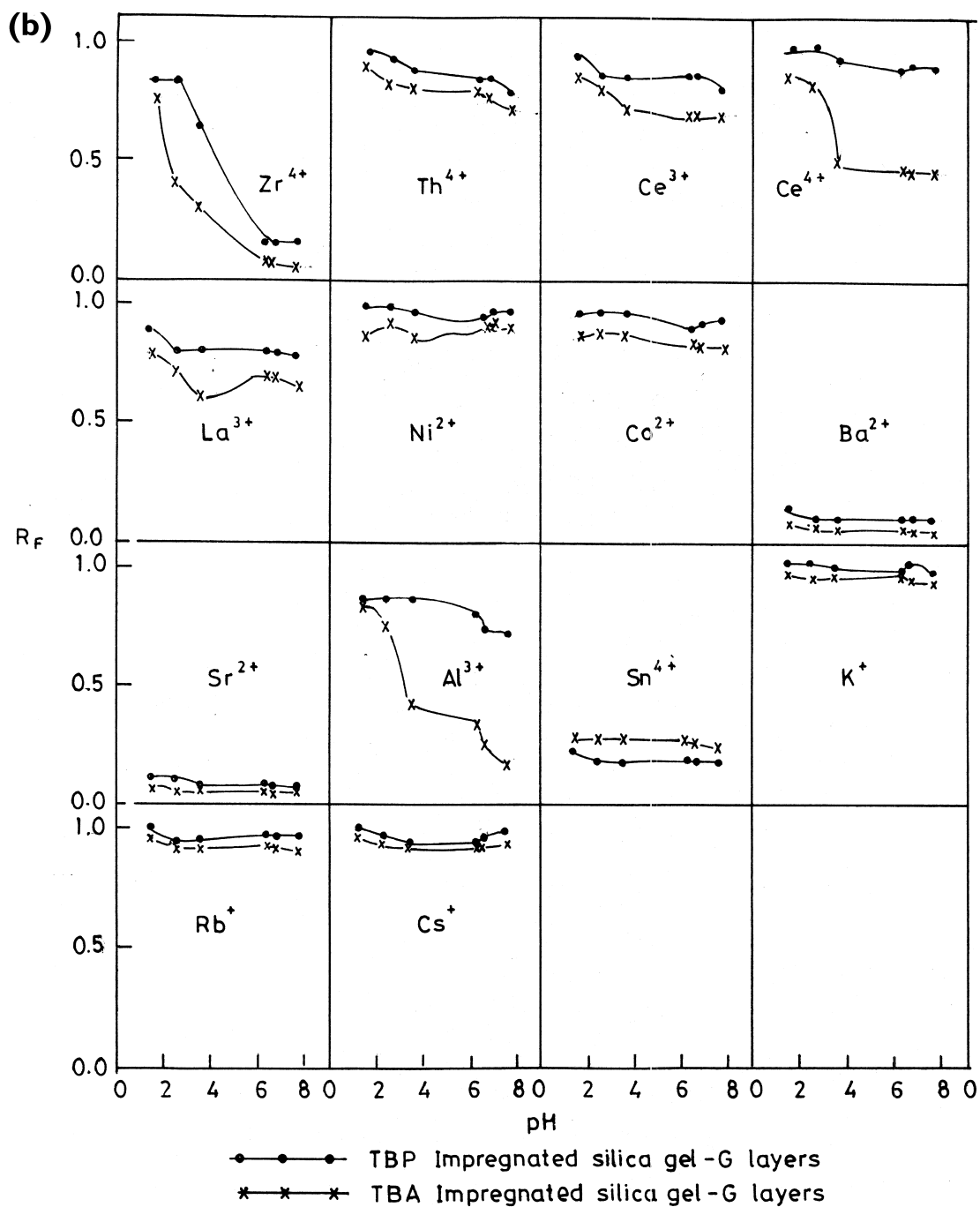


Fig. 2. (continued)

Table 1
Precipitation of metal ions in the mixture of impregnating material and solvent

Solvent system	Metal ion +TBP+solvent		Metal ion+TBA+solvent	
	P	NP	P	NP
S ₁	Pb ²⁺ , Hg ₂ ²⁺ , Ag ⁺ , Bi ³⁺	Tl ⁺ , Ba ²⁺ , Sr ²⁺ , Hg ₂ ²⁺	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺	Ba ²⁺ , Sr ²⁺
S ₂	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Sb ³⁺ , Tl ⁺	Pb ²⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Pd ²⁺ , Sb ³⁺ , Tl ⁺ , Fe ²⁺ , Fe ³⁺ , Cu ²⁺ , Cr ³⁺ , Zr ⁴⁺ , Ba ²⁺ , Sr ²⁺ , Hg ₂ ²⁺ , Ag ⁺ , Hg ₂ ²⁺	Ti ⁴⁺ , UO ₂ ²⁺
S ₃	Pb ²⁺ , Hg ₂ ²⁺ , Ag ⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Sb ³⁺ , Tl ⁺	Pb ²⁺ , Cu ²⁺ , Hg ₂ ²⁺ , Hg ₂ ²⁺ , Pd ²⁺ , Sb ³⁺ , Tl ⁺ , Fe ²⁺ , Fe ³⁺ , Cr ³⁺ , Zr ⁴⁺ , Ba ²⁺ , Sr ²⁺ , Bi ³⁺	Ti ⁴⁺ , UO ₂ ²⁺
S ₄	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Sb ³⁺ , Tl ⁺	Pb ²⁺ , Hg ₂ ²⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Sb ³⁺ , Tl ⁺ , Fe ²⁺ , Fe ³⁺ , Ba ²⁺ , Sr ²⁺	NIL
S ₅	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Tl ⁺	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Tl ⁺ , Ba ²⁺ , Sr ²⁺	NIL
S ₆	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Tl ⁺	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Ba ²⁺ , Sr ²⁺	NIL
S ₇	Pb ²⁺ , Ag ⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Ba ²⁺ , Sr ²⁺	Hg ₂ ²⁺ , Sb ³⁺ , Tl ⁺	Pb ²⁺ , Hg ₂ ²⁺ , Hg ₂ ²⁺ , Bi ³⁺ , Pd ²⁺ , Sb ³⁺ , Tl ⁺ , Fe ²⁺ , Fe ³⁺ , Cr ³⁺ , Zr ⁴⁺ , Ba ²⁺ , Sr ²⁺ , VO ²⁺	UO ₂ ²⁺ , Ti ⁴⁺

P, metal ions that precipitate.

NP, metal ions that do not precipitate.

oxalic acid media, probably because of the formation of anionic metal oxalate complexes, except for Ag²⁺, Hg₂²⁺, Ba²⁺ and Sr²⁺. The lower R_F values for Ag⁺ and Hg₂²⁺ ions are due to precipitation, whereas the higher dissociation constants of the oxalate complexes of Ba²⁺ and Sr²⁺ may be the reason for their lower R_F values (pK_1 for Ba²⁺ is 2.3 and for Sr²⁺ is 2.54). A similar explanation may also be given for the higher R_F values for most of the metal ions in oxalic acid–sodium oxalate media. The same trend was also observed on 60% TBP-impregnated layers. However, for most of the metal ions, the difference in R_F values in nitric acid and oxalic acid media on 60% TBP-impregnated layers is much higher in comparison to that observed on 20% TBP-impregnated ones due to the lesser adsorption of the oxalate complexes on these layers. TBA-impregnated layers also showed the same trend. The plots are not given for the sake of brevity.

The plots of R_F versus pK_1 of metal oxalates [22] are interesting (Fig. 3). At $pK_1 > 2.60$, the R_F suddenly increases considerably, due to very low

dissociation. Furthermore, the R_F values for most of the metal ions are higher on TBP-impregnated layers than on TBA-impregnated ones as TBP is slightly polar in contrast to TBA, which is non-polar. However, the difference in R_F is more pronounced in the case of Cu²⁺, Fe³⁺ and Zr⁴⁺. The oxalates of zirconium are regarded essentially as covalent molecules or as complexes [20], showing lesser migration on TBA-impregnated layers in oxalic acid–oxalate media. Fe³⁺ forms a tris-oxalato complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and Cu²⁺ forms $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ [20], having higher R_F values on TBP-impregnated layers.

4. Conclusion

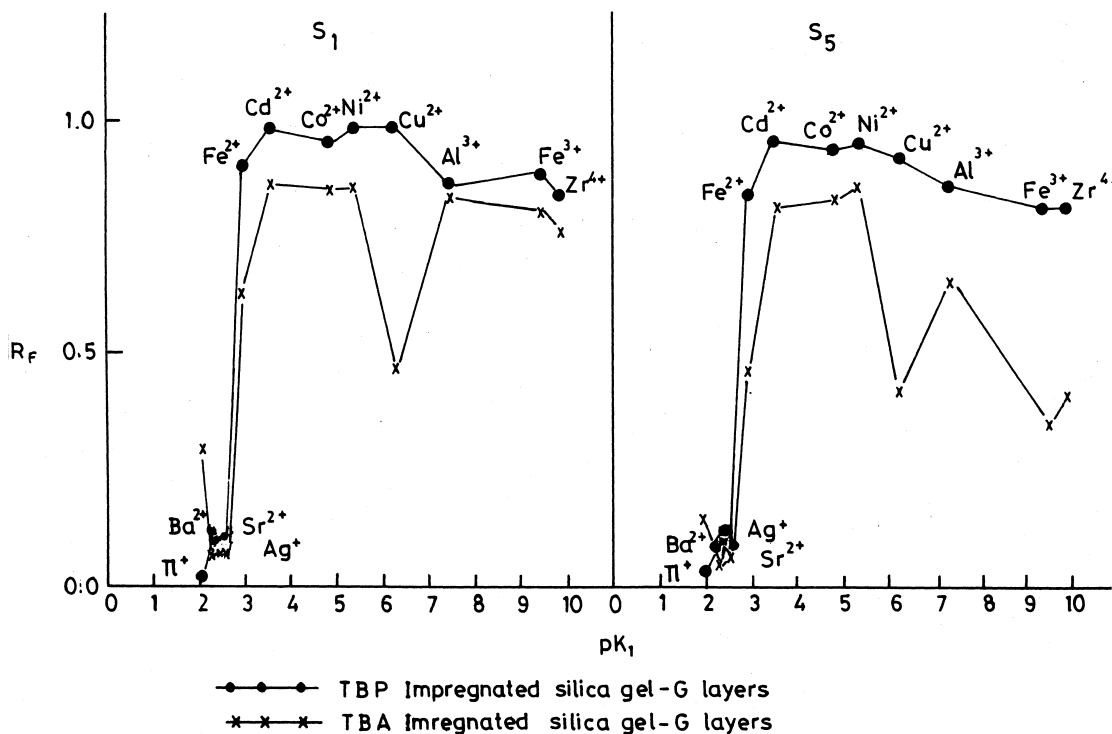
The effect of TBP impregnation on R_F values is quite interesting and metal ions exhibit a sudden change in chromatographic behaviour at 60% TBP-impregnation on silica gel-G layers. The pH effect on the movement of most of the metal ions is significant only in the low pH range, i.e., 1.50 to

Table 2

 R_F values of some metal ions on impregnated silica gel-G layers in aqueous nitric acid and oxalic acid–oxalate media

Metal ions	20% TBP impregnation				60% TBP		20% TBA impregnation			
	S_8	S_1	S_9	S_6	S_8	S_1	S_8	S_1	S_9	S_6
Ag ⁺	0.80	0.10	0.70	0.12	0.33	0.05	0.15	0.06	0.15	0.10
Cu ²⁺	0.93	0.98	0.85	0.92	0.50	0.88	0.60	0.45T	0.73	0.42
Hg ₂ ²⁺	0.42	0.00	0.33	0.00	0.26	0.00	0.30	0.00	0.13	0.00
Hg ²⁺	0.22	0.10	0.20	0.10	0.25	0.10	0.30	0.50	0.10	0.34
Pd ²⁺	0.18	0.85	0.15	0.88	0.30	0.40	0.15	0.80	0.08	0.60
Sb ³⁺	0.03	0.28	0.03	0.25	0.08	0.18	0.03	0.33	0.03	0.28
Tl ⁺	0.06	0.02	0.08	0.02	0.10	0.02	0.08	0.30	0.09	0.20
UO ₂ ²⁺	0.23	0.76	0.26	0.68	0.30	0.07	0.35	0.70	0.28	0.56
Fe ²⁺	0.50	0.90	0.05	0.84	0.20	0.90	0.35	0.63	0.03	0.50
Fe ³⁺	0.50	0.88	0.04	0.83	0.19	0.33	0.35	0.80	0.03	0.33
VO ₂ ⁺	0.93	0.92	0.88	0.88	0.35	0.85	0.35	0.85	0.36	0.70
Ti ⁴⁺	0.25	0.98	0.15	0.60	0.03	0.98	0.18	0.70	0.15	0.50
Cr ³⁺	0.55	0.92	0.70	0.92	0.45	0.86	0.30	0.88	0.29	0.69
Zr ⁴⁺	0.10	0.83	0.05	0.80	0.13	0.78	0.13	0.75	0.13	0.40
Th ⁴⁺	0.75	0.95	0.85	0.93	0.35	0.75	0.44	0.90	0.13	0.82
Ce ³⁺	0.50	0.93	0.18	0.85	0.30	0.88	0.15,	0.85	0.15	0.80
La ³⁺	0.58	0.89	0.06	0.80	0.22	0.53	0.10	0.78	0.09	0.72
Ba ²⁺	0.93	0.12	0.85	0.07	0.98	0.04	0.95	0.06	0.95	0.03
Sr ²⁺	0.88	0.10	0.81	0.10	0.95	0.06	0.98	0.06	0.93	0.05
Al ³⁺	0.51	0.85	0.72	0.85	0.30	0.53	0.30	0.84	0.16	0.73

T, tailing.

Fig. 3. Plots of R_F vs pK_1 in solvents S_1 and S_5 .

3.55, whereas in the higher pH range, i.e., 6.40 to 7.59, R_F values change slightly or remain almost constant. Furthermore, the R_F values for metal ions increase suddenly when the pK_1 of their metal oxalates exceeds 2.60.

References

- [1] J.W. Winchester, Rep. U.S. At. Energy Comm., CF-58-12-43 (1958).
- [2] U.A.Th. Brinkman, G. De Vries, R. Kuroda, J. Chromatogr. 85 (1973) 187.
- [3] W. Fischer, H.E. Hauck, W. Jost, Proc. Chromatogr. Soc. Int. Symp (1988) 139.
- [4] M. Ajmal, A. Mohammad, N. Fatima, J. Ahmad, J. Planar Chromatogr. 3 (1990) 181.
- [5] I. Skvore, N. Zambeli, S. Iskria, O. Hadzija, J. Chromatogr. 498 (2) (1990) 428.
- [6] Li. Huanran, Rong Qing Xin, Li. Lunxing, Fenxi Huaxue 18 (1) (1990) 53.
- [7] H. Yiyuvin, S.M. Khopkar, Anal. Lett. 23 (4) (1990) 635.
- [8] K.S. Panesar, O.V. Singh, S.N. Tandon, Anal. Lett. 23 (1990) 125.
- [9] A. Jain, O.V. Singh, S.N. Tandon, J. Planar Chromatogr.-Mod TLC 3 (1990) 79.
- [10] S.D. Sharma, S. Misra, R. Gupta, J. Liq. Chromatogr. 16 (1993) 1833.
- [11] S. Tsuneo, J. Satoshi, I. Noriko, T. Yohko, J. Planar Chromatogr.-Mod TLC 7 (2) (1994) 98.
- [12] S. Tsuneo, K. Mayumi, T. Yoshimi, J. Planar Chromatogr.-Mod TLC 8 (2) (1995) 152.
- [13] S. Tsuneo, T. Yoshimi, K. Michiko, J. Planar Chromatogr.-Mod TLC 8 (6) (1995) 469.
- [14] S.D. Sharma, S. Misra, S.C. Sharma, J. Ind. Chem. Soc. 75 (1998) 81.
- [15] K.S. Panesar, O.V. Singh, S. N Tandon, J. Planar Chromatogr.-Mod TLC 5 (1992) 289.
- [16] M. Qureshi, A. Mohammad, N. Fatima, J. Liq. Chromatogr. 8 (1985) 1279.
- [17] M. Qureshi, B.M. Sethi, S. D Sharma, J. Liq. Chromatogr. 7 (7) (1984) 1345.
- [18] M. Qureshi, S.D. Sharma, Anal. Chem. 45 (1973) 1283.
- [19] M. Qureshi, B.M. Sethi, S.D. Sharma, J. Liq. Chromatogr. 6 (1983) 165.
- [20] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 2nd edition, Willey Eastern Ltd. (1966) 461, 1068, 917, 860 and 906.
- [21] A.A. Grinberg, in: An Introduction to the Chemistry of Complex Compounds, Addison Wesley, Reading, 1962, p. 338.
- [22] J. Lurie, in: Handbook of Analytical Chemistry, Mir Publishers, Moscow, 1975, p. 294.