International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 944-948, 2017

Separation of Toxic Metal Cations on Stannous Silicate layers in Micellar TLC

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Abstract : Micellar thin layer chromatographic separation of some toxic metal ions were carried out on a thin layer of stannous silicate using silica gel-G as a binder. Various environmental, industrial and sludge samples were gives good separation in zwitter-ionic surfactant cocamidopropylbetaine (CAPB) containing mobile phase. The nature and the concentration of surfactant also affect the retention factor of toxic metal ions. Effect of some organic additives on separation also studied in current methodology. From several solvent systems acetone in CAPB system was found to be good for separation of metal ions from multicomponent systems. Semi quantitative measurements were also carried out for some metal cation.

Keywords : Zwitter-ionic, Micellar, CAPB, Toxic, Metal.

Introduction

Surfactants modified mobile phases are found to be good solvents for separation of various components from multicomponent systems. The features of micellar and ion-pair versions of thin-layer chromatography and the dynamic and static modifications of stationary phases with surfactants are studied[1]. A micellar high-performance liquid chromatographic method was developed to simultaneously determine ephedrine and pseudoephedrine in human serum[2]. Silica gel in combination with surfactant−mediated eluents has been used for thin−layer chromatography of sixteen metal cations[3]. The main physicochemical methods for identifying and quantifying polyphenol compounds in various plant and food objects (tea, wine) and human biological fluids (urine, plasma, blood serum, saliva) were reviewed, such as chromatography (high-performance liquid chromatography and thin-layer chromatography) and electrophoresis (capillary zone electrophoresis and micellarelectrokinetic chromatography). Different procedures for sample preparation were discussed, including liquid, solid-phase, supercritical fluid extraction, and high-pressure liquid extraction[4].MLC successfully applied for semiquanitative and spectrometry identification of metal ions[5]. Non-ionic surfactant Tween-80 were successfully used as a mobile phase for separation of various metal cations[6]. Thin layer of bismuth silicate were used asadsorbent[7] for separation of toxic metal cations by using aq. surfactants and using other organic solvents.Zwitterionic surfactant cocamidopropylbetaine (CAPB) has been successfully used as mobile phase for separation of various ions. Semi-quantitative determination of UO_2^{2+} also been studied[8].

A current research article explores the utilization of surfactant CAPB for the separation of toxic metal cations on newly developed adsorbent stannous silicate.

Experimental

A Thin Layer Chromatography chamber from Raj Chemicals was used. A labtronics pH Meter was used for determination of pH. CAPB was obtained from Merk. Silica Gel-G, Nitrates and silicates of stannous and sodium were obtained from Loba Chemicals India. All other chemicals were of analytical grade. Salts of various metals were obtained from Loba Chemicals India. Test solutions 1% of these metal ions were prepared in double distilled water. 1% alcoholic dimethylglyoxime, 1% aq. potassium ferrocynide &a freshly prepared dithiozone solution (0.05% in chloroform) was used to detect the metal cations from chromatographic plates. Thin Layer Chromatographic separations for various toxic metal cations were carried on using newly developed stannous silicate thin layer. Plates of stannous silicate were prepared by using method were discussed in[9]. The mobile phase systems were used is listed in Table 1.

Results & Discussion

The results of the study describe herein are summarized in Table 2 and 5 and in Figures 1. The mobility of various toxic metal cations was examined on stannous silicate layer with silica gel-G binder, using aqueous solutions of CAPB in order to optimize the experimental conditions used. The effect of various factors were investigated, including (a) concentration of CAPB in the mobile phase, (b) nature (acidity or basicity) of surfactant containing developer medium, and (c) presence of organic solvents in the mobile phase systems.

Table 1. List of Mobile Phase

Symbol	Composition
A1	1% aqueous CAPB
A2	3% aqueous CAPB
A3	5% aqueous CAPB
A4	7% aqueous CAPB
A5	5% aqueous CAPB at pH 2.3
A6	5% aqueous CAPB at pH 4.6
A7	5% aqueous CAPB at pH 6.7 (Actual pH of CAPB Solution)
A8	5% aqueous CAPB at pH 8.3
A9	5% aqueous CAPB at pH 9.15
S1	5% aqueous CAPB: ethanol (9:1) (V/V)
S2	5% aqueous CAPB: ethanol (8:2) (V/V)
S3	5% aqueous CAPB: ethanol (7:3) (V/V)
S4	5% aqueous CAPB: methanol (9:1) (V/V)
S5	5% aqueous CAPB: methanol (8:2) (V/V)
S6	5% aqueous CAPB: methanol (7:3) (V/V)
S7	5% aqueous CAPB: propanol (9:1) (V/V)
S8	5% aqueous CAPB: propanol l (8:2) (V/V)
S9	5% aqueous CAPB: butanol (9:1) (V/V)
S10	5% aqueous CAPB: butanol (8:2) (V/V)
S11	5% aqueous CAPB: Acetone (9:1) (V/V)
S12	5% aqueous CAPB: Acetone (8:2) (V/V)
S13	5% aqueous CAPB: Acetone (7:3) (V/V)

a) Variation of Concentration of CAPB :

In order to study the effect of the concentration of zwitterionic CAPB surfactants on the mobility of the metal cations, TLC experiments were performed on stannous silicate with varying concentrations of CAPB, using surfactants - mediated mobile phase systems. The R_F values of the metal cations obtained in pure water (zero surfactant concentration) and in an aqueous solution of CAPB at different concentration (1%, 3%, 5% and 7%), are listed in Table 2.

Table 2R_F value of the metal cations obtained on stannous silicate layers developed with aqueous and solution of CAPB as different concentration level.

R_F value							R_F value					
Metal Ions		**CAPB**					**Metal Ions**		**CAPB**			
	Pure water	**1%**	**3%**	**5%**	**7%**			**Pure water**	**1%**	**3%**	**5%**	**7%**
Cu^{2+}	0.15T	0.17	0.20	0.30	0.31		**Co^{2+}**	0.29T	0.32T	0.45	0.60	0.60sp
Zn^{2+}	0.12T	0.14	0.21	0.32	0.31		**Hg^{2+}**	0.37T	0.43T	0.55	0.87	0.89sp
Pb^{2+}	0	0	0	0	0		**Ag^{+}**	0	0	0	0	0
Fe^{3+}	0.07	0.10	0.14	0.21	0.20		**Zr^{4+}**	0.25T	0.30	0.37	0.40	0.44
Ni^{2+}	0.31T	0.35T	0.40	0.55	0.60sp		**VO^{2+}**	0.23T	0.24	0.30	0.37	0.32
Sb^{3+}	0.19T	0.20	0.24	0.35	0.39sp		**Cd^{2+}**	0.21T	0.24	0.35	0.41	0.46
As^{3+}	0.11	0.11T	0.15	0.30	0.29		**Bi^{3+}**	0.21	0.23T	0.33	0.45sp	0.51sp
UO_2^{2+}	0.09	0.09	0.14	0.25	0.28sp		**W^{6+}**	0	0	0	0	0
Th^{4+}	0	0	0	0	0		**Mo^{6+}**	0	0	0	0	0

T- Tailed Spot, SP- Spread Spot

From the data shown in Table 1 the following conclusions may be drawn:

1. In water mobile phase system maximum metalions produced tailing. Among all these metal ions, higher mobility shown by Hg^{2+}.
2. At all concentration range, metal ions such as Pb^{2+}, Ag^{+} Th^{4+}, W^{6+} and Mo^{6+} remain at the point of application that is they are strongly retained on the stannous silicate layer. When concentration of CAPB increased gradually from 1% - 7% changes in mobilities were observed. Results were obtained in case of 1% were similar with water mobile phase system. At 7% concentration of CAPB, most of the metal ions produced tailed spot.
3. Highly compact spot, fast separation and good results were obtained in case of 5% CAPB. Maximum metal ions wereget separated with high difference in there R_F values with other metal ions, which opens opportunities for its selective separation from multicomponent mixture of metal cations. Hence 5% CAPB mobile phase system is considered for further studies.

b) Effect of Nature of Medium:

Effect of acidic and basic pH on migration of heavy metal ions on stannous silicate layer was examined. For that various solvent systems at various pH were utilized for this study. Results are shown in Table 3.

Table 3- Effect of Nature of CAPB on Mobilities.

R_F value							R_F value					
Metal Ions		**CAPB**					**Metal Ions**		**CAPB**			
	pH 2.3	**pH 4.6**	**pH 6.7**	**pH 8.3**	**pH 11.9**			**pH 2.3**	**pH 4.6**	**pH 6.7**	**pH 8.3**	**pH 11.9**
Cu^{2+}	0.10	0.25T	**0.44**	0.27T	0.15sp.		**Co^{2+}**	0.20sp	0.20T	**0.66**	0.26T	0.17sp
Zn^{2+}	0.14	0.27T	**0.4**	0.20T	0.17sp.		**Hg^{2+}**	0.11	0.22T	**0.89**	0.26T	0.17sp
Pb^{2+}	0.00	0	**0**	0	0		**Ag^{+}**	0.00	0	**0**	0	0
Fe^{3+}	0.18	0.33T	**0.39**	0.32T	0.15sp		**Zr^{4+}**	0.12sp	0.23T	**0.62**	0.25T	0.15sp
Ni^{2+}	0.23	0.27T	**0.65**	0.25T	0.14sp		**VO^{2+}**	0.13sp	0.26T	**0.63**	0.23T	0.12sp
Sb^{3+}	0.11	0.19T	**0.27**	0.16T	0.15sp		**Cd^{2+}**	0.14	0.25	**0.6**	0.18T	0.11sp
As^{3+}	0.18	0.11T	**0.25**	0.15T	0.11sp		**Bi^{3+}**	0.16sp	0.23T	**0.6**	0.13T	0.06sp
UO_2^{2+}	0.11	0.12T	**0.44**	0.30T	0.11sp		**W^{6+}**	0.00	0	**0**	0	0
Th^{4+}	0.00	0	**0**	0	0		**Mo^{6+}**	0.00	0	**0**	0	0

T- Tailed spot, sp- Spread Spot (Actual pH of CAPB nearly 6.7)

From Table 3 it was concluded that, change in pH of mobile phase gave maximum changes in migration factor with respect to pH of solution. Spreading and tailing were observed at highly acidic and basic pH, and hence no further studies were carried out for this section.

c) Effect of Addition of Organic Solvents in Mobile phase :

To study the retention behaviour of metal ions on stannous silicate layer, hybrid- mobile phase systems comprising of micelle 5% CAPB– water- organic solvent (acetone, methanol, ethanol, propanaol and butanol) were also used and better chromatographic separation in terms of increase in migration of metal ions by these mobile phases over aqueous micellar mobile phase systems was observed. From this section following trends were observed,

1. As compared to aqueous surfactant mobile phase system, there were improvement in migration of metal ions expect Pb^{2+}, Th^{4+}, Ag^{+}, W^{6+} and Mo^{6+}. Improvement of migration was examined from compactness and less time for separation point of view. Among all organic mobile phase good separation was observed in case of acetone added mobile phase systems. And so, 5% aq. CAPB with acetone (9:1, V/V) are carried out for various separations like binary, quaternary, from sludge and various environmental samples.

Applications-

1. After preparation of plates separation and quantitative estimation of various metal cations were carried by using spot area measurement method as described in[9]. 5% CAPB+ acetone (9:1 v/v) solvent was found to be good for quantitative estimation of Cu^{2+}, Ni^{2+} and Cd^{2+}. The recovery of Cu^{2+}, Ni^{2+} and $Cd^{2+}$was 85 ± 12 %. Results are shown in Figure 1.

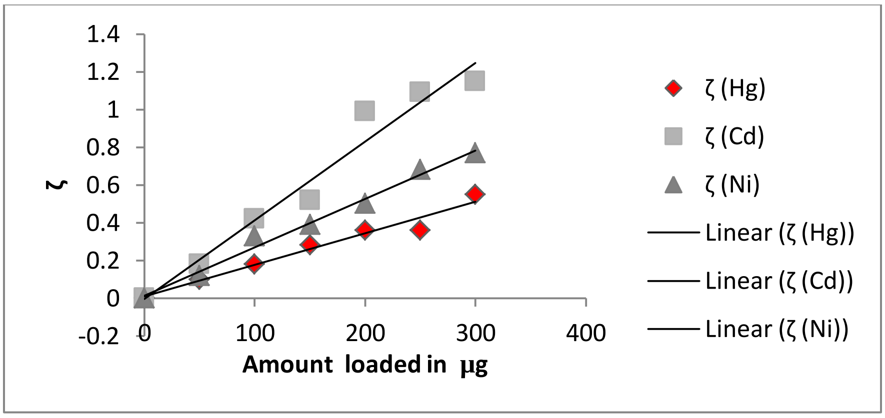

Figure 1.Semi-quantitative Estimation

2. Various metal ions were separated from binary, ternary and quaternary separation in influence of other metal ions. Results were shown in Table 4,

Table 4 – Binary, Ternary & Quaternary Separations.

S. No.	Components	S 11	S. No.	Components	S 11
		(R_f values of metal ions)			(R_f values of metal ions)
A	Cd^{2+}& Zn^{2+}	Zn^{2+} – 0.19 & Cd^{2+}– 0.67	H	UO_2^{2+} , Ni^{2+} & Hg^{2+}	UO_2^{2+}– 0.24, Ni^{2+}– 0.67 & Hg^{2+} – 0.89
B	Co^{2+}& Cu^{2+}	Cu^{2+}– 0.16 & Co^{2+}– 0.52	I	Pb^{2+}, Fe^{3+}& Hg^{2+}	Pb^{2+}– 0.00, Fe^{3+}– 0.09 & Hg^{2+}– 0.90
C	Ni^{2+}& Hg^{2+}	Ni^{2+}– 0.50 & Hg^{2+}– 0.89	J	Hg^{2+} , Ni^{2+}, UO_2^{2+}& Pb^{2+}	UO_2^{2+} –0.19 , Pb^{2+}– 0.00 Hg^{2+}– 0.80 & Ni^{2+}– 0.60
D	Zn^{2+}& Ni^{2+}	Zn^{2+}– 0.17 & Ni^{2+}– 0.51			
E	Cu^{2+}& Hg^{2+}	Cu^{2+}– 0.15 & Hg^{2+}– 0.90			

F	Pd^{2+}& UO_2^{2+}	Pd^{2+}– 0.00 & UO_2^{2+}– 0.23			
G	UO_2^{2+}& Hg^{2+}	UO_2^{2+} – 0.19 & Hg^{2+}– 0.84			

3. Separation of various metal ions from spiked, sludge and various environmental sample, results are shown in Table 5,

Table 5- Separation of various metal ions from spiked, sludge and various environmental sample

Spiked Samples		**R_f values of metal ions**		
A	Sludge Sample	Cu^{2+} – 0.22	Cd^{2+}– 0.67	Hg^{2+}– 0.86
B	Industrial waste water	Zn^{2+}– 0.20	Cd^{2+}– 0.70	Hg^{2+-}– 0.89
C	River Water	Zn^{2+}– 0.19	Cd^{2+}– 0.69	Hg^{2+}– 0.89
Environmental Samples				
A	Industrial waste water	Fe^{3+} –0.09	Cu^{2+}– 0.23	Hg^{2+}– 0.84
B	Ground water	Fe^{3+}–0.11	Cu^{2+}–0.24	Cd^{2+}– 0.69
C	Mineral samples	Fe^{3+}–0.09	Cd^{2+}–0.69	Hg^{2+}– 0.85
D	Effluent treated sludge sample	Fe^{3+}–0.10	Cu^{2+}–0.28	Hg^{2+}– 0.86

Acknowledgement-

The authors would like to thank the principal of Bhiwapur Mahavidyalaya, the principal and head of the Department of Chemistry, and Director of Dr. Ira Nimdeokar P. G. & Research Centre for Chemistry Hislop College Nagpur, and M.S. India for the provision of the research facilities used in our study.

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