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Miceller Thin Layer Chromatography of Various Heavy Metal Cations Using Non Ionic Surfactant

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Abstract: Various metal cations were separated by using miceller thin layer chromatography. Non ionic surfactant Tween-80 were used as a mobile phase whereas silica gel- G used as stationary phase. Effect of (a) concentration of Tween-80 in the mobile phase, (b)acidity or basicity of surfactant containing developer medium, (c) presence of alcohols in the mobile phase systems, and (d)the presence of strong and weak electrolytes in the mobile phase systems. Semiquantitative determination of Ni^{2+} by spot area measurement was attempted.

Keywords: Metal, miceller, chromatography, Tween-80, surfactant, electrolyte.

1. Introduction

TLC has been successfully utilized for various purposes, such as the separation of metal ions from a water sample [1], the characterization of the mobility of metal [2], and the estimation of concentration of toxic metal in industrial waste [3].The use of aqueous surfactant solution as a mobile phase in TLC was pioneered by Armstrong and Terrill [4]. Using a surfactant as the mobile phase gained popularity and became more widely applied due to its operational simplicity, cost effectiveness, relative non-toxicity and enhanced separation efficiency [5-8]. The use of silica gel and an alumina layer with surfactant – mediated mobile phase systems [9-14] has been used to separate various inorganic species.

In the present study a new mobile phase solvent system was developed, implanting a non ionic surfactants Tween-80, when employed as a mobile phase, Tween-80 may be used to separate various metal ions under a range of different conditions.

We herein describe the continuation of our earlier work on TLC [15-19], and discuss our systematic study of the separation and selectivity of mobile phases for different metal ions using TLC with silica gel 'G' in thin layers.

2. Material and Methods

2.1 Chemicals and Reagents: Silica gel 'G' and Tween-80 were obtained from Merk, Dimethylglyoxime, dithizone, potassium ferrocyanide, carbon tetrachloride, methanol, ethanol, propanol, butanol, glacial acetic acid, and HCl were obtained from SD Fine India. All other chemicals were of analytical reagent grade.

2.2 Metal ion Studied: Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Bi^{3+}, U^{6+}, V^{5+},Zr^{4+}, Sb^{3+}, Pb^{2+}, Ag^{+}, Th^{4+}, Mo^{6+}, As^{3+},and W^{6+}.

2.3 Test Solution: TLC was performed using a standard aqueous solution (1%) of the chloride, nitrate or sulphate salts of the metal ions listed.

2.4 Detection: Fe^{3+}, Cu^{2+},U^{6+}, V^{5+}, Zr^{4+},and Th^{4+} were detected using 1% aqueous potassium ferrocyanide; Zn^{2+}, Cd^{2+}, Hg^{2+}, Bi^{3+}, Sb^{3+}, Pb^{2+}, Ag^{+}, Mo^{6+}, As^{3+}, and W^{6+} using 0.5% dithizone in carbon tetrachloride; and Ni^{2+}, and Co^{2+} using a 1% solution of alcoholic dimethylglyoxime.

2.5 Stationary Phase: Silica gel 'G' was used as the stationary phase.

2.6 Mobile Phase: The following solvent systems were used as mobile phases: (i) pure water mobile system, (ii) aqueous systems with surfactant : Tween-80 (1%, 3%, 5% and 7%), (iii) aqueous surfactant systems with developer media: 7% aqueous Tween-80 in buffer solution of pH(2.3 ,4.5, 6.7, 8.3 & 11.9), (iv)alcohol systems with added surfactant: solvent systems consisting of aqueous solution 7% Tween-80 with methanol, ethanol, propanaol and butanol at different volume ratio (10%, 20% and 30%), and (v) strong and weak electrolyte systems with added surfactant: solvent systems consisting of aqueous solution 7% Tween-80 with strong electrolyte NaCl and weak electrolyte acetic acid at different volume ratio (10%,and 20%).

2.7 Thin - layer chromatography

A. Preparation of Plates: The TLC plates were prepared by mixing silica gel with demineralised water in ratios of 1:2 by weight with constant shaking to obtain homogeneous slurry. The slurry was then immediately applied to the glass plates using the dipping method. The plates were allowed to dry overnight at room temperature and were used following day in TLC.

B. Procedure: Test solutions were spotted onto thin- layer plates with the help of micropipette positioned about 1.0 cm above the lower edge of the TLC plates. The spots were air dried and the plates were then developed with the given mobile phase using by the one dimensional ascending technique in glass jars. The development distance

C. Separation: For the separation, the metal ions to be separated were mixed in equal amounts. A test solution of the resultant mixture was spotted onto the activated TLC plate, and was then air dried. The plates were developed to a distance of 10 cm. The spots were detected and the separated metal cations were identified by their R_F values

D. Limits of Detection: The limits of detection of the metal cations were determined by spotting different amounts of metal ion onto the TLC plates, developing the plates using the method describe above, and then detecting the spots. This method was repeated with a successive decrease in the amount of metal ion used until spots were not detected. The minimum detectable amount on the TLC plates was taken as the limit of detection.

E. Semi- quantitative determination by spot- area measurement- For semi quantitative determination by spot- area measurement method, 0.01ml volume from a series of standard solution (0.5-2%) of Ni^{2+} were spotted on thin layer plates. The plates were developed with (7% aqueous Tween-80 + 10% Methanol). After detection the spots were copied onto tracing paper from the chromatoplates and then the area of each spot was calculated.

3. Results and Discussion

The results of the study describe herein are summarized in Table1and 2 and in Figures 1 to 3. The mobility of 18 metal cations was examined on silica gel layers, using aqueous solutions of Tween-80 in order to optimize the experimental conditions used. The effect of various factors was investigated, including (a) concentration of Tween-80 in the mobile phase, (b) acidity or basicity of surfactant containing developer medium, (c) presence of alcohols in the mobile phase systems, and (d) the presence of strong and weak electrolytes in the mobile phase systems.

a) **Variation of Concentration of Tween-80 :** In order to study the effect of the concentration of non ionic Tween-80 surfactants on the mobility of the metal cations, TLC experiments were performed on silica layers with varying concentrations of non ionic Tween-80, 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 Tween-80 at different concentration (1%, 3%, 5% and 7%), are listed in Table 1.

Table 1. R_F value of the metal cations obtained on silica gel layers developed with pure water and aqueous solution of Tween-80 as different concentration level.

METAL	$R_F$value				
		Tween-80			
	Pure water	1%	3%	5%	7%
Cu^{2+}	0.15T	0.20T	0.26	0.30	0.35
Zn^{2+}	0.12T	0.19T	0.23	0.28	0.32
Pb^{2+}	0	0	0	0	0.09
Fe^{3+}	0.07	0.17T	0.22	0.28	0.33
Ni^{2+}	0.31T	0.37T	0.41	0.46	0.52
Sb^{3+}	0.19T	0.18T	0.20T	0.19	0.19
As^{3+}	0.11	0.15	0.17	0.18	0.19
UO_2^{2+}	0.09	0.12T	0.17	0.22	0.27
Th^{4+}	0	0	0	0	0
Co^{2+}	0.29T	0.33T	0.37	0.41	0.53
Hg^{2+}	0.37T	0.40T	0.57	0.61	0.73
Ag^{+}	0	0	0	0	0
Zr^{4+}	0.25T	0.28T	0.32	0.37	0.40
VO^{2+}	0.23T	0.28	0.32	0.37	0.40
Cd^{2+}	0.21T	0.27T	0.33	0.40	0.48
Bi^{3+}	0.21	0.23T	0.28	0.33	0.36
W^{6+}	0	0	0	0	0
Mo^{6+}	0	0	0	0	0

T- Tailed Spot

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

1. In pure water, all metal ions except Pb^{2+}, Ag^{+} Th^{4+}, W^{6+} and Mo^{6+} show little mobility. Maximum metal ions found to produce tailed spot. Among all these metal ions, Hg^{2+} ($R_F \approx 0.37$) show higher mobility as compared to other metal ions facilitates their separation from all other metal ions studied.

2. When aqueous surfactant Tween-80 solutions at different concentration level (1%, 3% 5% and 7%) were used as mobile phase, metal ions such as Ag^+ Th^{4+}, W^{6+} and Mo^{6+} did not show any mobility in all concentration of Tween-80. Pb^{2+} shows little mobility ($R_F \approx 0.09$) at 7% Tween-80.
3. All metal ions except Pb^{2+}, Sb^{3+}, Th^{4+}, Ag^+, W^{6+} and Mo^{6+} show increasing mobility were observed as soon as there were increasing concentration of Tween -80 from 1% to 7%.
4. In all concentrations range of Tween-80, Sb^{3+} shows nearly same mobility in range of ($R_F \approx$ 0.18-0.20).
5. In 1% Tween-80 mobile phase, maximum metal ions show tailed spot. Spot compactness increases as soon as concentration of Tween-80 increases.
6. In 7% Tween-80 mobile phase, Hg^{2+} shows higher mobility ($R_F \approx 0.73$) facilitates their separation from all other metal ions studied, whereas as the mid R_F of Ni^{2+}, Co^{2+}, Zr^{4+} and VO^{2+} opens opportunities for its selective separation from multicomponent mixture of metal cations.
7. 7% aqueous Tween-80 mobile phase was judged to be favorable for further studies as more compact spot for cations were realized with this mobile phase system.

b) **Effect of Acidity and Basicity of Medium:** Thin layer chromatography of metal ions was performed using aqueous 7% Tween-80 solution prepared in borate phosphate buffer of different pH values (pH-2.3, 4.6, 6.7, 8.3 and 11.9). The results obtained with the buffered surfactant solutions have been summarized in Table 2. The following conclusions may be drawn from these results:

Table 2. Mobility of metal cation developed with buffered surfactant solution of different pH.

Metal	R_F value				
	pH 2.3	pH 4.6	pH 6.7	pH 8.3	pH 11.9
Cu^{2+}	0.14sp.	0.23T	0.40	0.21T	0.11sp.
Zn^{2+}	0.11sp.	0.24T	0.41	0.19T	0.12sp.
Pb^{2+}	0	0	0	0	0
Fe^{3+}	0.13sp	0.27T	0.35	0.30T	0.14sp
Ni^{2+}	0.17sp	0.21T	0.60	0.21T	0.12sp
Sb^{3+}	0.13sp	0.11T	0.25	0.15T	0.15sp
As^{3+}	0.14sp	0.14T	0.25	0.14T	0.11sp
UO_2^{2+}	0.11sp	0.13T	0.41	0.27T	0.11sp
Th^{4+}	0	0	0	0	0
Co^{2+}	0.15sp	0.23T	0.62	0.27T	0.17sp
Hg^{2+}	0.11	0.24T	0.87	0.27T	0.17sp
Ag^+	0	0	0	0	0
Zr^{4+}	0.13sp	0.26T	0.61	0.24T	0.15sp
VO^{2+}	0.12sp	0.28T	0.63	0.23T	0.13sp
Cd^{2+}	0.11sp	0.27T	0.59	0.18T	0.11sp
Bi^{3+}	0.14sp	0.23T	0.57	0.11T	0.12sp
W^{6+}	0	0	0	0	0
Mo^{6+}	0	0	0	0	0

T- Tailed spot *sp- Spread Spot*

1. Change in pH of mobile phase systems had high effect on the mobilities of all metal cations except Pb^{2+}, Th^{4+}, Ag^+, W^{6+} and Mo^{6+}.
2. With strongly acidic (pH = 2.3) and strongly basic (pH = 11.9) mobile phase systems all metal ions showed little mobility with spread spots. Whereas at slightly acidic (pH= 4.6) and slightly basic (pH =

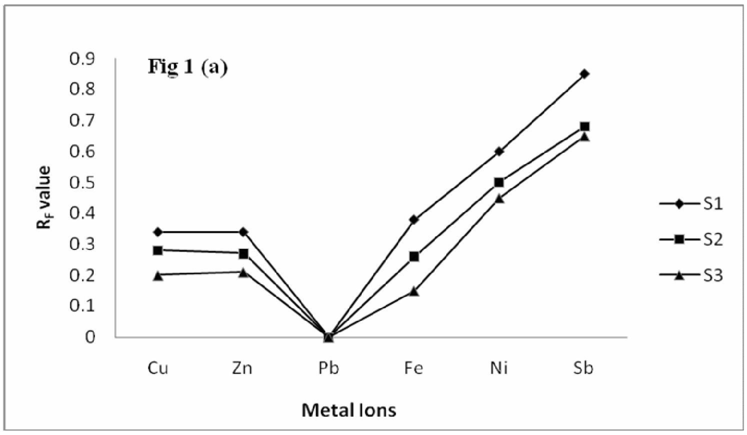
8.3) all metal ions showed increased mobility as compare to strongly acidic and basic pH respectively. At this pH range all metal gave tailed spots.

3. Compact spot of all metal ions except Pb^{2+}, Th^{4+}, Ag^{+}, W^{6+} and Mo^{6+} were visualized in neutral range of pH (pH= 6.7).
4. Pb^{2+}, Th^{4+}, Ag^{+}, W^{6+} and Mo^{6+}, did not show any mobility irrespective of the fact whether mobile phase medium used was acidic or basic or neutral in nature.

c) **Effect of Addition of Alcohols:** to investigate the retention of metal cations on silica layer, hybrid-mobile phase systems comprising of micelle 7% Tween-80 – water- alcohol (methanol, ethanol, propanaol and butanol) were also used and better chromatographic separation in terms of promotion of differential migration of metal ions by these mobile phases over aqueous miceller mobile phase systems was observed. The R_F values of metal cations were determined with surfactant – water – alcohol mobile phases consisting of methanol (10%, 20% and 30%), ethanol (10%, 20% and 30%), propanol (10%, 20% and 30%) and butanol (10%, 20% and 30%) and 7% aqueous Tween-80. In all cases, a general trend of decreasing R_F value with the increasing in molecular weight alcohol. Higher mobility was observed in methanol containing mobile phase system and compact spot obtained in these systems within a short space of time. However, in different concentration range of methanol mobility were decreases with increasing concentration of methanol. The representative plots are given in Figure 1(a), (b) and (c).

The retention mechanism is connected with the adsorption of surfactnt on the surface of the stationary phase. As long as the surface of the silica gel layer is saturated by the adsorbed surfactant that is there are no more free silanol groups on the layer for the interaction, metal ions move faster showing higher R_F value.

The addition of alcohol to the mobile phase leads to the reduction in the adsorbed amount of surafctant on the stationary phase, which causes an incraese in retention of solutes and a change in selectivity. Thus, in the presence of alcohol the silica layers are not completely saturated by adsorbed surfactant and there are still free silanol groups, the interaction between them and the metal cations affects the retention pattern. In general, the better separation possibilities were realized with mobile phase containing 10% methanol. In this case also metal ions such as Pb^{2+}, Th^{4+}, Ag^{+}, W^{6+} and Mo^{6+} did not show any mobility at all alcohol added mobile phase systems. Thus, low molecular weight alcohol (methanol) provides superior separation of metal cations compared to high molecular weight alcohol (butanol).



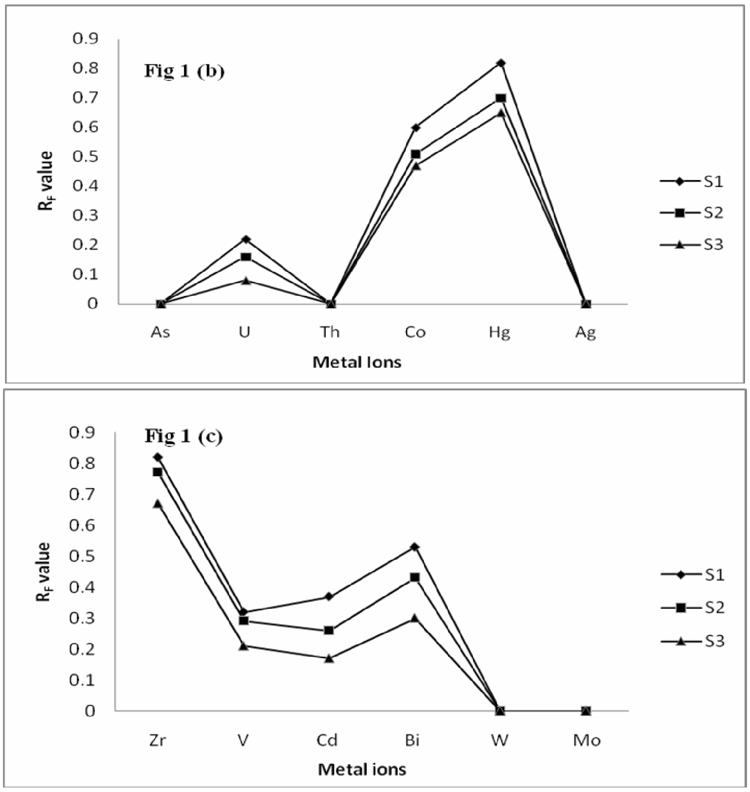


Fig 1 (a,b and c): Mobility of metal cations on silica gel layers developed with 7% aqueous Tween-80 containing different amounts of alcohols.
Mobile systems: S1- 7%Tween-80 + 10% methanol **,S2**- 7%Tween-80 + 20% methanol**,**
S3- 7%Tween-80 + 30% methanol

d). Effect of Addition of Strong and Weak Electrolyte: The effect of addition of weak electrolyte (CH_3COOH) and strong electrolyte (NaCl) at different concentration levels in the eluent 7% aqueous Tween-80 on the mobility of metal cations was examined. The RF value of metal cations were determined with surfactant – water – electrolyte mobile phase consisting of NaCl (10% and 20%) and CH_3COOH (10% and 20%) and 7% Tween-80. From the available data in Fig.2 (a, b and c), following trends are noticeable:

1. Higher mobility and compact spots were obtained in mobile phase containing weak elctrolytes CH_3COOH as comapred to mobile phase containing strong electrolye NaCl.
2. In acetic acid added mobile phase system, mobility were found to decreases as sson as concentartion of acetis caid increases from 10% to 20%.
3. Pb^{2+}, Th^{4+}, Ag^{+}, W^{6+} and Mo^{6+} did not show any mobility in all cases of mobile phase containing both of electrolytes.

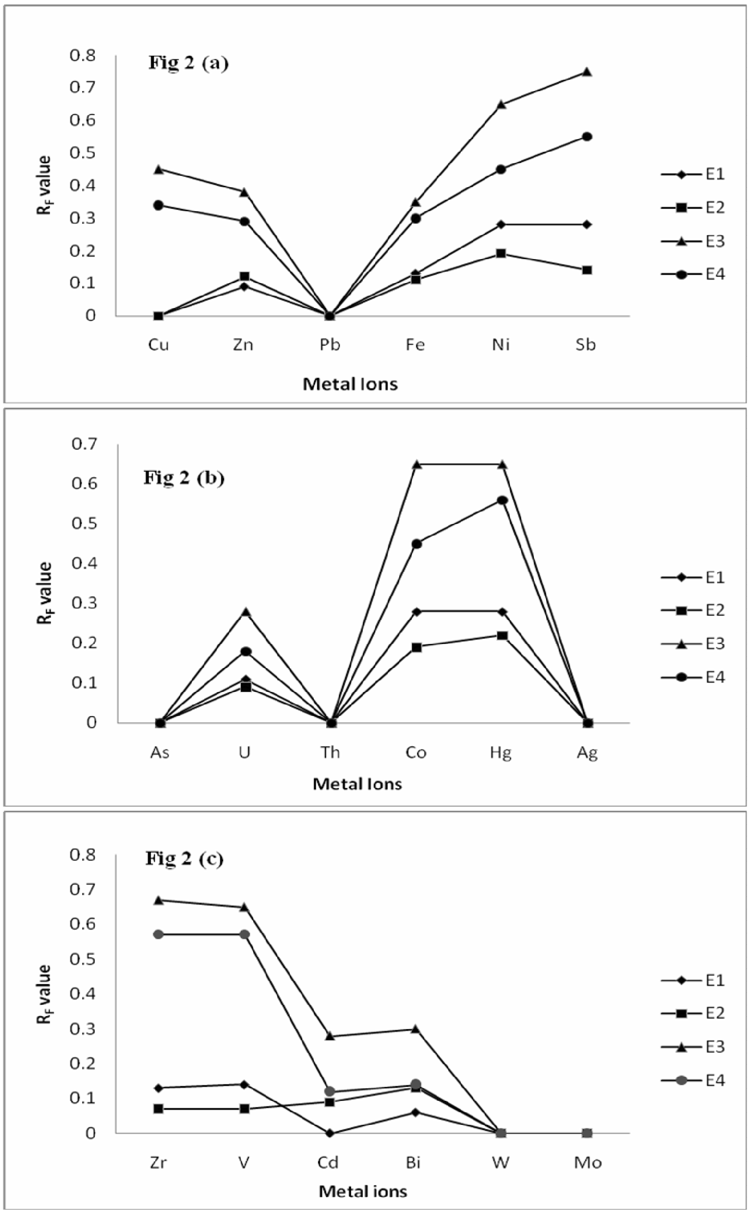


Fig 2 (a,b and c): Mobility of metal cations on silica gel layers developed with 7% aqueous Tween-80 containing different amounts of electrolytes.

Mobile systems: E1- 7%Tween-80 + 10% NaCl,**E2-** 7%Tween-80 + 20% NaCl, **E3**- 7%Tween-80 + 10% CH_3COOH, **E4** - 7%Tween-80 + 10% CH_3COOH.

Semi-quantitative Estimation of Ni^{2+}

An attempt has been made to determine the recovery of Ni^{2+} spiked into water using spot area measurement method by using 7% aqueous Tween-80 + 10% methanol mobile phase system. A linear relationship obtained when the amount of sample spotted was plotted against area of the spot follows the empirical equation ζ=km, where ζ is the area of the spot, m is the amount of solute and k is a constant. Representative plot for Ni^{2+} has been shown in Figure 3 respectively. The linearity is maintained upto 300 µg/spot. At higher concentration a positive deviation from linear law was observed. The accuracy and precision was around $Ni^{2+} =$ ±35 %.

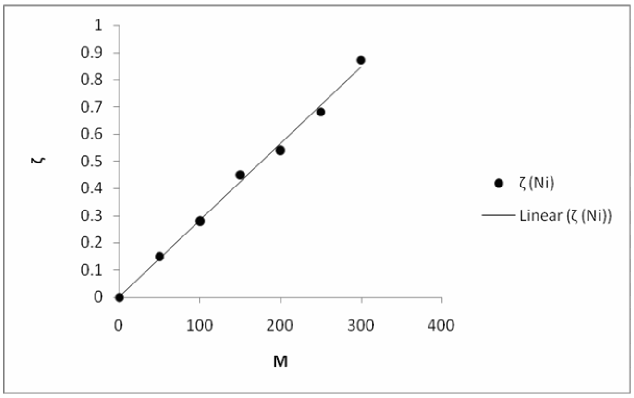


Fig 3. : Calibration curve for semiquantitative determination of Ni^{2+}.
Stationary Phase:-Silica Gel 'G', Mobile phase: 7% aqueous Tween-80 + 10% methanol

Application:

The proposed method was applied for identification of various toxic metal ions in spiked industrial waste water, river and power plant ash after separation on silica gel layer. The result listed in Table 1 and 2 and Fig 1-3 clearly demonstrated that this method is very useful for separation and identifaication of metal cations from environmental sample as well as from their multicomponent mixtures using Tween -80 with or without organic additives on silica gel layers.

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