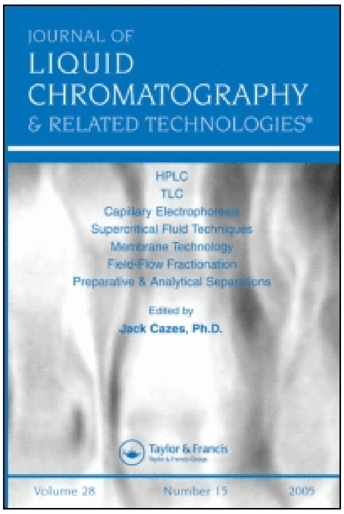

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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S. D. Sharma[a]; Smiti Misra[a]; Reetu Gupta[a]
[a] Analytical Research Laboratory Department of Chemistry, Hindu College, Moradabad, India

To cite this Article Sharma, S. D. , Misra, Smiti and Gupta, Reetu(1993) 'Normal Phase, Reversed Phase and Chelation Thin Layer Chromatographic Studies of Some Toxic Metal Ions in two Component Solvent Systems Containing DMSO: Quantitative Separation of Pb^{2} from $Hg_{2}{}^{2}$, $Hg^{2}{}_{5}$ Tl, Bi^{3}, Sn^{4}, and Sb^{3}', Journal of Liquid Chromatography & Related Technologies, 16: 8, 1833 — 1843

To link to this Article: DOI: 10.1080/10826079308021690

URL: http://dx.doi.org/10.1080/10826079308021690

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(8), 1833-1843 (1993)

NORMAL PHASE, REVERSED PHASE AND CHELATION THIN LAYER CHROMATOGRAPHIC STUDIES OF SOME TOXIC METAL IONS IN TWO COMPONENT SOLVENT SYSTEMS CONTAINING DMSO: QUANTITATIVE SEPARATION OF Pb^{2+} FROM Hg_2^{2+}, Hg^{2+}, Tl^{+}, Bi^{3+}, Sn^{4+}, AND Sb^{3+}

S. D. SHARMA, SMITI MISRA, AND REETU GUPTA
Analytical Research Laboratory
Department of Chemistry, Hindu College
B-3, Jigar Vihar, Moradabad-244 001, India

ABSTRACT

Normal phase, reversed phase and chelation thin layer chromatography of some toxic metal ions was performed in DMSO-HNO_3 and DMSO-HCl systems. The effect of solvent composition on migration of cations has been explained in terms of adsorption, precipitation and specific solvation effect of DMSO. The effect of EDTA and DMSO impregnation on R_F values was studied. TBP and TBA impregnated layers were used for reversed phase thin layer chromatography. The differential migration was utilized to resolve chemically similar elements. Besides it was possible to separate cations of same element having different oxidation states. Quantitative separation of lead from binary mixtures and synthetic alloys, containing Cu^{2+}, Sn^{4+}, Bi^{3+}, Sb^{3+}, Cd^{2+}, Ni^{2+}, Hg_2^{2+} and Hg^{2+} has also been experimentally achieved.

INTRODUCTION

The toxicity of certain metals and metalloids to man and other organisms has long been recognised and has been extensively reviewed.[1-4] The so called heavy metals have been the cause of particular environmental concern. The generally accepted heavy metals are chromium, manganese, iron, cobalt, copper, zinc, molybdenum, silver, mercury, cadmium and nickel. Other metals such as aluminium, beryllium, tin, thallium, lead and bismuth as well as the metalloids arsenic, selenium and antimony and the non-metals boron and tellurium are often included in reviews of metal toxicity. Out of these, thirteen metals were designated as priority pollutants[5] e.g. Pb, Cr, Cu, Cd, Hg, Ni, Ag, Zn, Sb, As, Se, Tl and Be.

Lead is a toxic element which is normally associated with pollution of the atmosphere, as a result of its incorporation into petrol. Because of this perception, it appears that the principal routes via which man is exposed to 'Lead' are considered to be inhalation or ingestion of food contaminated as a result of deposition. Lead in drinking water has not been carefully evaluated, although a trend of ever reducing acceptable concentrations of lead in drinking water is evident. World health organisation set 50 ug/l[6] as the permissible limit for this accumulative poison. DMSO (Dimethyl sulfoxide) offers numerous advantages as a solvent as it has a complex forming tendency with almost all ions, contains no ionisable protons and has a fairly high dielectric constant (ε = 47.5). It has unusual properties as solvent i.e. its ability to solvate metal ions in preference to anions and a specific solvating effect.

The purpose of this study is to investigate the chromatographic behaviour of some toxic metal ions in two component solvent systems containing DMSO. Besides effort has been made to study the chromatographic behaviour of these metal ions on DMSO and EDTA impregnated silica gel-G layers.

For reversed phase thin layer chromatography, TBP and TBA impregnated layers were used. Quantitative separation of lead from a number of other metal ions have also been achieved.

EXPERIMENTAL

Reagents

Silica gel-G (TLC grade) and solvents (analytical grade) from E. Merck were used.

Apparatus

Silica gel-G thin layers on 20x3 cm, glass plates were prepared by thin layer chromatographic applicator (Toshniwal-India). 24x6 cm circular glass jars were used for development. Bausch and Lomb spectronic-20 spectrophotometer was used for quantitative estimations.

Test Solutions

The test solutions were taken as nitrates as far as possible for use with solvent systems containing nitric acid. When HCl containing solvent systems were used most cations were taken as chlorides. Sodium tungstate and sodium molybdate were dissolved in distilled water. Antimony and bismuth were taken as chlorides.

Detectors

Yellow ammonium sulfide, alizarin Red-S, dimethylglyoxime, stannous chloride, potassium ferrocyanide, aluminon, potassium ferricyanide and diphenyl carbazide were used to detect various ions by their usual colour reactions.

Preparation of Chromatoplates

Silica gel-G was slurried with deionised water in the ratio 1:3 with constant stirring for five minutes. The resulting slurry was coated on clean glass plates with the help of an applicator to give a layer of ~0.25 mm thickness. These were first dried in air and then kept at 100°±5°C for 2 hrs in an oven. The plates were cooled to room temperature in a desiccator before use. These activated plates were then impregnated with DMSO or 20% tributyl amine, or 20% tributyl phosphate in benzene. Benzene was evaporated by heating the plates in an electric oven at 100°±5°C for 1 hr. EDTA impregnated plates were also prepared for chromatographic studies.

Solvent Systems

In all, thirteen solvent systems were used. The acid concentration is 1 M in all the cases. The various solvents used are:

Pure DMSO
DMSO + HNO_3 (9:1)
DMSO + HNO_3 (7:3)
DMSO + HNO_3 (5:5)
DMSO + HNO_3 (3:7)
DMSO + HNO_3 (1:9)
DMSO + HCl (9:1)
DMSO + HCl (7:3)
DMSO + HCl (5:5)
DMSO + HCl (3:7)
DMSO + HCl (1:9)
HCl
HNO_3

Procedure

For qualitative studies, cation solutions were spotted on the plates which were developed in the chosen solvent systems by the ascending technique. The ascent of the solvent was fixed at 11 cm in all cases. After development, the plates were dried and the cation spots were detected by using appropriate spraying reagent.

For quantitative work, a stock solution of lead was prepared in demineralized water by dissolving lead nitrate. Known amounts of lead alongwith other metal ions were spotted with the help of a micropipette, and the development was performed in chosen solvent systems. A pilot plate was run simultaneously in order to locate the exact position of the spot on the working plate. The area on the working plate corresponding to the detected spot on the pilot plate was scratched and the mass was eluted with 1:1:3 $H_2SO_4:HNO_3:H_2O$. One ml HCl was added to this solution. The eluent was made oxide free by boiling. After boiling the solution was allowed to cool and lead sulphate was filtered out. The precipitated lead sulphate was treated with ammonium acetate and ammonium hydroxide and lead was determined spectrophotometrically using dithizone in carbon tetrachloride.[7]

RESULTS AND DISCUSSION

Interesting results were obtained using DMSO-HNO_3 and DMSO-HCl systems. The spots are well-defined and compact. Tailing is observed only for Bi^{3+} and Cd^{2+} in pure DMSO and for Sb^{3+} in HNO_3 and HCl. In order to check the reproducibility of the results, five sets of chromatoplates for each toxicant were developed. It was observed that the variation does not exceed 5% of the average R_F values. The R_F data for various metal ions are given in Table-I. The mechanism of migration can be explained on the basis of adsorption and precipitation in the network of the support. Hydrolysis and solvent-solvent interaction may also play their role in the sorption behaviour of metal ions.

DMSO systems generally take longer time for development than aqueous systems because they are highly viscous liquids (Viscosity of DMSO = 2.473 cP at 20°C) with a low freezing point (18.2°C). In order to correlate the high solvating tendency of DMSO with R_F values of metal ions, plots of R_F versus solvent composition were drawn. (The plots are not given for the sake of brevity). It is evident from the plots that in pure DMSO, the movement for some of the metal ions is either zero (e.g. Mo^{6+}, W^{6+}, Pb^{2+} and Fe^{2+}) or is very low (e.g. Cr^{3+}, As^{3+} and Al^{3+}). With the addition of acid the movement of cations generally increases and is almost constant when the acid concentration is more than 30% with the exception of W^{6+} and Pb^{2+}. Further increase in acid concentration does not affect the R_F values appreciably. This is very much in agreement to the observation made by Janauer[8]

TABLE - I

R_F values of metal ions in DMSO-1M HNO_3 and DMSO-1M HCl Systems of varying compositions

Metal Ions	Pure DMSO	DMSO - HNO_3 9:1	DMSO - HNO_3 7:3	DMSO - HCl 9:1	DMSO - HCl 7:3	1M HCl	1M HNO_3
Be^{2+}	0.40	0.75	0.75	0.55	0.90	0.90	0.98
Al^{3+}	0.10	0.75	0.80	0.55	0.85	0.90	0.95
Cr^{3+}	0.20	0.70	0.70	0.65	0.85	0.90	0.95
Mn^{2+}	0.80	0.85	0.85	0.85	0.85	0.90	1.00
Fe^{2+}	0.00	0.65	0.95	0.55	0.85	0.80	0.95
Fe^{3+}	0.60	0.60	0.70	0.75	0.85	0.80	0.85
Co^{2+}	0.65	0.70	0.80	0.65	0.85	0.90	0.85
Ni^{2+}	0.40	0.75	0.80	0.65	0.90	0.98	1.00
Cu^{2+}	0.60	0.85	0.90	0.75	0.95	0.85	0.85
Zn^{2+}	0.75	0.85	0.85	0.85	0.85	0.90	1.00
As^{3+}	0.10	0.55	0.90	0.55	0.95	0.90	0.85
Se^{4+}	0.60	0.85	0.95	0.85	0.90	0.90	0.90
Mo^{6+}	0.00	0.05	0.75	0.00	0.50	0.90	0.95
Ag^{+}	0.80	0.82	0.95	0.70	0.00	0.00	0.95
Cd^{2+}	T	0.70	0.75	0.75	0.80	0.95	1.00
Sn^{4+}	0.65	0.65	0.95	0.55	0.90	0.90	0.80
Sb^{3+}	0.70	0.70	0.25	0.60	0.20	T	T
Ce^{3+}	0.55	0.60	0.75	0.60	0.85	0.65	0.75
Ce^{4+}	0.55	0.80	0.85	0.80	0.85	0.95	0.90
Hg_2^{2+}	0.35	0.85	0.90	0.65	0.95	0.98	0.98
Hg^{2+}	0.70	0.85	0.95	0.65	0.95	0.98	0.98
Tl^{+}	0.45	0.80	0.85	0.85	0.90	0.85	0.90
Pb^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi^{3+}	T	0.65	0.75	0.60	0.90	0.95	0.75
W^{6+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00

T = Tailing.

TABLE -II

Precipitation of the cations in the solvents used (acid concentration is 1M in all cases)

	Cations + Solvent		
Solvent Systems	Cations which precipitate	Cations which do not precipitate	Adsorbent
DMSO		Fe^{2+}, Mo^{6+}, Pb^{2+}, W^{6+}	Silica gel-G
HNO_3	W^{6+}		" "
HCl		W^{6+}	" "
DMSO:HNO_3 (9:1)		Mo^{6+}, Pb^{2+}, W^{6+}	" "
DMSO:HNO_3 (7:3 and 5:5)		Pb^{2+}, W^{6+}	" "
DMSO:HNO_3 (3:7) and (1:9)	Sb^{3+}, W^{6+}	Pb^{2+}	" "
DMSO:HCl (9:1)		Mo^{6+}, Pb^{2+}, W^{6+}	" "
DMSO:HCl (7:3), (5:5) (3:7) and (1:9)	Ag^+, Pb^{2+}		" "
DMSO:HNO_3 (1:1)	Sb^{3+}, W^{6+}	Pb^{2+}	DMSO impregnated Silica gel-G
DMSO:HCl (1:1)	Sb^{3+}, W^{6+}, Tl^+, Ag^+	Pb^{2+}	" "
DMSO:HCl (1:1)	Ag^+, W^{6+}	Pb^{2+}	EDTA Impregnated Silica gel-G
DMSO:HNO_3 (1:1)	W^{6+}	Ag^+, Pb^{2+}	TBP Impregnated Silica gel-G
DMSO:HCl (1:1)	Ag^+, Tl^+, W^{6+}	Pb^{2+}	" "
DMSO:HNO_3 (1:1)	Ag^+, W^{6+}	Pb^{2+}	TBA Impregnated Silica gel-G
DMSO:HCl (1:1)	Ag^+, W^{6+}	Pb^{2+}	" "

that in DMSO-HNO_3 systems, the DMSO is most effective when acid concentration is 0.10-0.60M.

The novel feature of this study is a significant difference in R_F values of chemically similar elements leading to fantastic separation possibilities (Table-I) which were realised in practice. Thus in DMSO-HNO_3 and DMSO-HCl systems, Ag^+ was separated from Pb^{2+}, Hg_2^{2+}, Hg^{2+} and Cu^{2+}; Cr^{3+} from Mo^{6+}, Mn^{2+} and Se^{4+}; Fe^{2+} from Fe^{3+}, Mn^{2+} and Co^{2+}; Hg^{2+} from Hg_2^{2+} and Cd^{2+}; Bi^{3+} from Sb^{3+} and Pb^{2+}; Ce^{3+} from Ce^{4+} and Fe^{3+} from Co^{2+} and Mn^{2+}. Other binary and ternary separations actually achieved on these layers are: Ni^{2+} from Co^{2+} and Cu^{2+}; Zn^{2+} from Be^{2+} and Cu^{2+}; As^{3+} from Sb^{3+} and Se^{4+}; Sn^{4+} from Bi^{3+}, Pb^{2+} and Sb^{3+}; Pb^{2+} from Tl^+. In pure DMSO, ternary separations e.g. Fe^{2+}-Ni^{2+}-Co^{2+} and W^{6+}-Mo^{6+}-Cr^{3+} are also achieved.

The above separation possibilities arise from two effects:

(i) DMSO being an aprotic dipolar solvent with 'hard' oxygen and 'soft' sulphur, is a strong solvating agent for cations. It also decreases the dielectric constant leading to the formation of non-dissociated complexes.

(ii) The presence of HCl is responsible for the formation of chloro complexes.

The effect of Cl^- ion concentration on the R_F values of metal ions can be explained. In general, in DMSO-HCl systems, as the chloride ion concentration increases, the R_F value of the ion also increases. This may be due to increase in the solubility of the metal chloride in DMSO. It appears that DMSO promotes the formation of non-dissociated chloro compounds and DMSO compounds by mass action and a decrease in the dielectric constant. This explanation was given by Birze[9] and Fritz[10] for the increase in R_F values of Bi^{3+} with increase in chloride ion concentration in the DMSO-

HCl media. The same explanation may hold good for other cations as well.

The behaviour of Ag^+, Sb^{3+} and Pb^{2+} is some what exceptional. Ag^+ and Sb^{3+} show high R_F values *in* pure DMSO. Ag+ is highly polarisable and hence interacts strongly with DMSO. When HCl is added both H^+ and Ag^+ ions compete for DMSO and since DMSO interacts more strongly with H^+ ions, the R_F falls suddenly. Birze found that the solubility of AgCl in DMSO-HCl mixture is very tricky[9]. Unless a set order of addition of reagents i.e. DMSO, $AgClO_4$, H_2O and HCl, is used, AgCl does not dissolve. In our case the order of the addition of reagents is different than the one suggested by Birze and hence AgCl should not dissolve significantly causing almost zero R_F in increasing HCl concentration. Sb^{3+} and Pb^{2+} exhibit lower R_F values with increasing HCl concentrations due to the precipitation of their respective chlorides. Other ions which have zero R_F may do so owning to precipitation. In order to simulate conditions on thin layers, appropriate solvent was added to the cationic solutions. Few cations precipitated under these conditions (Table-II). In these cases precipitation mechanism holds good.

Observations were made to study the effect of ligands (DMSO or EDTA) on retention factor of metal ions. Except Pb^{2+} and W^{6+} other toxic metal ions give high R_F in DMSO:HCl or DMSO:HNO_3 *systems on unmodified silica gel-G or* DMSO or EDTA modified layers. Retention factor for Pb^{2+} and W^6+ is zero in DMSO:HCl or DMSO:HNO_3 systems on unmodified silica gel layers or on DMSO or TBP or TBA modified silica gel-G layers. But W^{6+} has a zero R_F on EDTA modified layers in DMSO-HCl media due to precipitation (Table-II). On EDTA modified layers the R_F *is as high as* 0.95 *and* 0.70 for Pb^{2+} and W^{6+} in DMSO-HNO_3 systems respectively. Brintzinger[11] and his coworkers regarded the complex Pb[Pb(EDTA)]H_2O as a salt, since it gave the usual qualitative tests for Pb^{2+}. Obviously, these tests were afforded by the uncomplexed lead ion.

Phase reversal also affect retention factor of few metal ion. R_F values are generally low on TBA modified layers. Ag^+ shows zero R_F on TBP or TBA modified layers. This is probably due to its interaction with the adsorbent. It has been shown by Murray et.al[12] that cations are preferably exchanged when the gel has a negative surface charge, but that Ag^+ is considerably exchanged even when the gel has a positive charge. They have explained this by the assumption that the adsorption of Ag^+ is due to Ag^+-matrix interaction.

The most important advantage of this work lies in the fact that we have been able to quantitatively separate Pb^{2+} (10 µg) from mixtures containing larger amounts of other metals such as Be^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+},Fe^{2+},Fe^{3+},Co^{2+},Ni^{2+},Cu^{2+}, Zn^{2+}, As^{3+}, Se^{4+}, Mo^{6+}, Ag^+, Cd^{2+}, Sn^{4+}, Sb^{3+}, Ce^{3+}, Ce^{4+}, Hg_2^{2+}, Hg^{2+}, Tl^+ and Bi^{3+}. It has been observed that the method works well within an error range of 5%. Thus the technique presents a solution to the problem of separating Pb^{2}+ from other toxic metals. The method works satisfactorily even when we wish to separate Pb^{2+} from alloys e.g. leaded bronze, Darcet, Solder, Frary metals, Type metal alloy, Wood and Antimony bronze. Some determinations to this effect have actually been performed by preparing synthetic mixtures of metals with Pb^{2+} and separating lead in such mixtures on these layers.

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