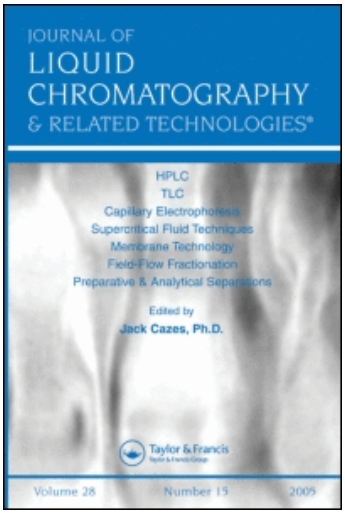

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Correlation Between Chromatographic Behaviour and Stability Constant of Metal Ions on Diethylenetriamine Thin Layer

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CORRELATION BETWEEN CHROMATOGRAPHIC BEHAVIOUR AND STABILITY CONSTANT OF METAL IONS ON DIETHYLENETRIAMINE THIN LAYER.

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ABSTRACT

The stability constants of the complexes formed between diethylenetriamine and the metal ions -V, Th, As, Pb, Zr and Se have been determined by pH metric method and these values, together with the stability constants for the metal ions -Co, Zn, Cd, Hg, Cu, Ni and Ag already reported, have been utilised to show their correlation with chromatographic behaviour of these metal ions on silica gel G plates impregnated with diethylenetriamine.

INTRODUCTION

A reference to the literature(1) showed that TLC separation of different inorganic substances has been attempted by many workers but little attention has been paid to impregnation technique for the TLC separation of metal ions. Lantenschlager and coworkers(2), Baba and coworkers(3) and Qureshi and Akhtar(4) have used aliphatic amines as developing systems. Since aliphatic amines are known to form complexes of varying stability with different metal ions, it was considered worthwhile to try different aliphatic amines to impregnate silica gel for the TLC separation of metal ions, the results of which have already been reported in an earlier communication(5), wherein we have shown that diethylenetriamine is the most satisfactory impregnant for the TLC separation of metal ions under study.

Complex formation between the metal ions and diethylenetriamine may be influencing the chromatographic behaviour on diethylenetriamine-impregnated plate. To confirm this possibility

and to establish the relationship, if any, between the chromatographic behaviour of metal ions on impregnated layer and the stability constants of complexes thus formed, determination of stability constants of these complexes were carried out.

Jonassen et al.(6) reported the stability constants of Ni(II) and Cu(II)-diethylenetriamine complexes while Pruc and Schwarzenbach(7) determined the stability constants for complexes of these ions and with other metal ions also - viz. Co, Zn, Cd, Hg and Ag. Since no study seems to have been made on the complexes formed between metal ions of our study and diethylenetriamine, it was considered necessary to carry out potentiometric studies for the complex formation between diethylenetriamine and rest of the metal ions - V, Th, As, Pb, Zr and Se, the results for which are presented in this paper.

EXPERIMENTAL

The pH values of the solutions were measured on ECIL model No.823 pH-meter, using glass and calomel electrodes. Standard phthalate buffers of pH 4 and 9 were used to calibrate the pH-meter. The titrations were carried out in a thermostated water bath at $30^{\circ} \pm 0.2^{\circ}C$.

The method of Jonassen et al.(6) was used to distil diethylenetriamine. The pH of the solution for different metal ion, in presence of a constant concentration of nitric acid and at constant ionic strength but containing varying concentrations of diethylenetriamine were measured. The results of these studies are depicted in Figure 1.

RESULTS AND DISCUSSION

The stability constants of V, Th, As, Pb, Zr and Se - diethylenetriamine complexes were calculated by using the above data as given in Figure 1 and employing the same method as

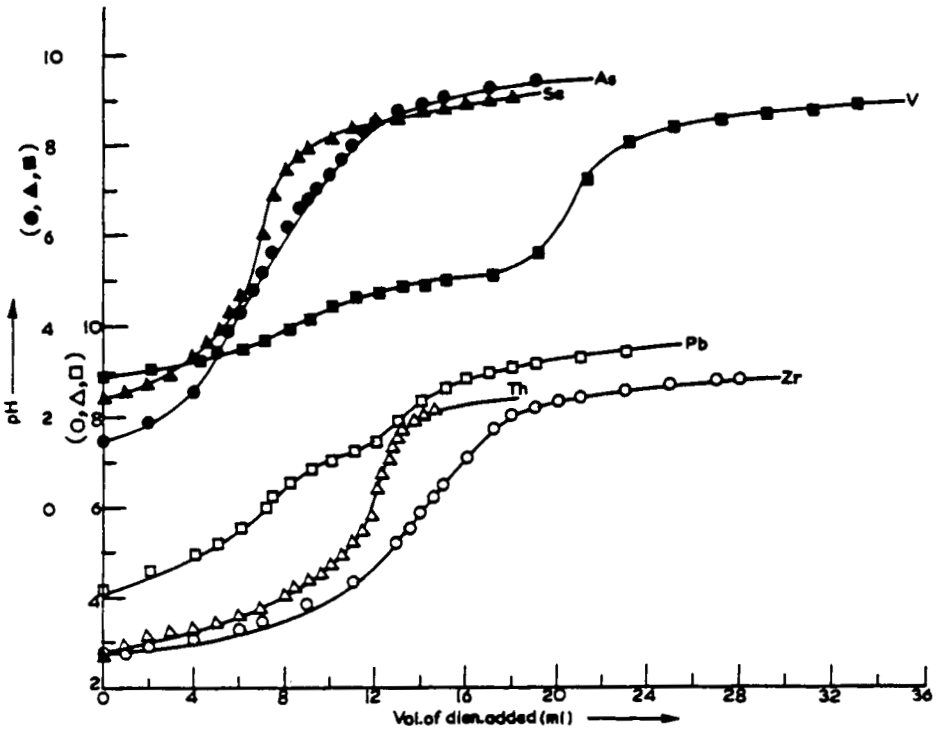

Fig.1_ Plots of pH vs. volume of dien. added.

used by Jonassen et al.(6). The plots of $\bar{n}$ Vs. p[dien] for the evaluation of stability constants are given in Figure 2. The values of the stability constants obtained from the formation curves along with the values reported by Prue and Schwarzenbach(7) for the complexes formed, with other metal ions, are tabulated under Table-1.

To find out the relationship between the migration behaviour of metal ions on diethylenetriamine impregnated plate and the stability constants of their complexes, the value of ΔhRf (difference in the hRf value on plain silica gel and on impregnated plate)(5) for different metal ions and also the value of ΔR_M

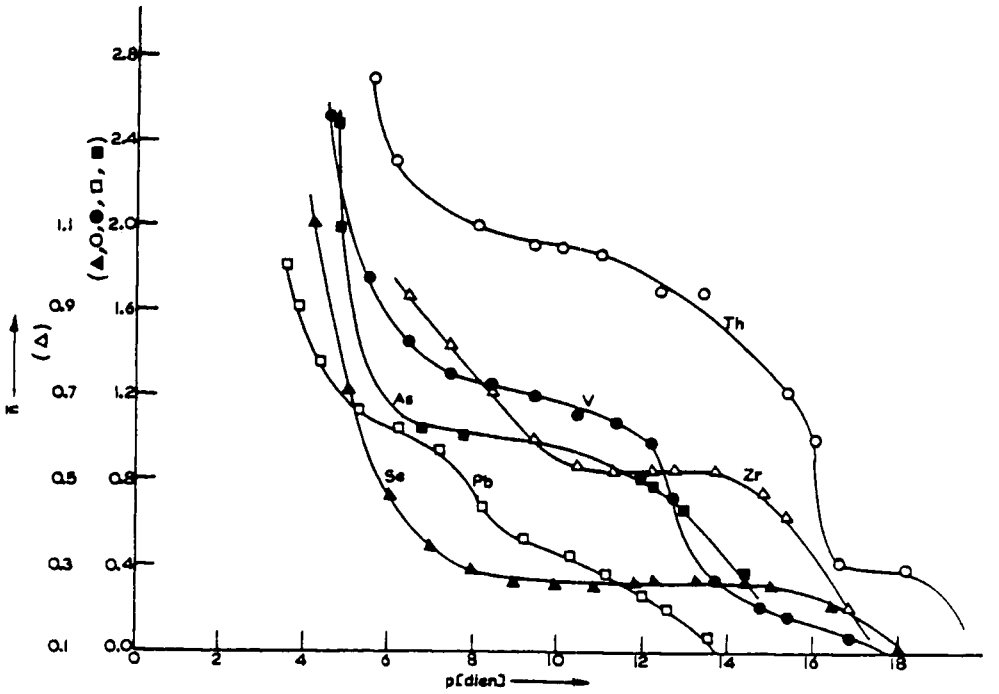

Fig.2 - Formation curves of the metal-dien complexes.

and from the R_M values of metal ions on unimpregnated and impregnated plates were calculated. These values of ΔhRf, R_M and ΔR_M are also tabulated in Table-1, along with the stability constants of the complexes. The plots of log K and ΔR_M (Figure 3) and log K and ΔhRf (Figure 4) were drawn. The linear plot obtained in both the cases showed that the movement of metal ions on impregnated plate depends upon the stability constant of the complex formed between the metal ion and the impregnant.

The great deviation of Se from the linear curve may be due to the uncertainity in the computation of ΔhRf or ΔR_M because of great tailing. On the other hand, the great departure of As from the linear curve may be due to the fact that the hRf

TABLE-1

Metal ion	Stability constant log K	On plain silica gel		Silica gel G impregnated with 0.5% diethylenetriamine in 100 ml water		Difference	
		hRf	R_M	hRf	R_M	ΔhRf	ΔR_M
Co	8.1 ±	78	-0.550	54	-0.070	24	-0.480
Zn	8.9 ±	82	-0.659	38	+0.213	44	-0.872
Ni	10.7 ±	74	-0.454	42	+0.140	32	-0.594
Fe	6.2	79	-0.575	71	-0.389	08	-0.186
Cu	16.0 ±	84	-0.072	22	+0.550	62	-1.270
V	13.5	76	-0.61	26	+0.454	50	-0.555
Th	16.4	80	-0.602	13	+0.826	67	-1.428
As	13.7	37	+0.231	28	+0.410	09	-0.179
Pb	4.05	63	-0.231	61	-0.194	02	-0.037
Cd	8.45 ±	75	-0.477	56	-0.105	19	-0.372
Hg	7.00 ±	96	-1.380	81	-0.630	15	-0.750
Ag	6.10 ±	53	-0.052	40	+0.176	13	-0.228
Zr	15.8	0	0	0	0	0	∞
Se	5.75	67	-0.308	21	+0.575	46	-0.803

± The values taken from the work of Frue and Schwarzenbach(7).

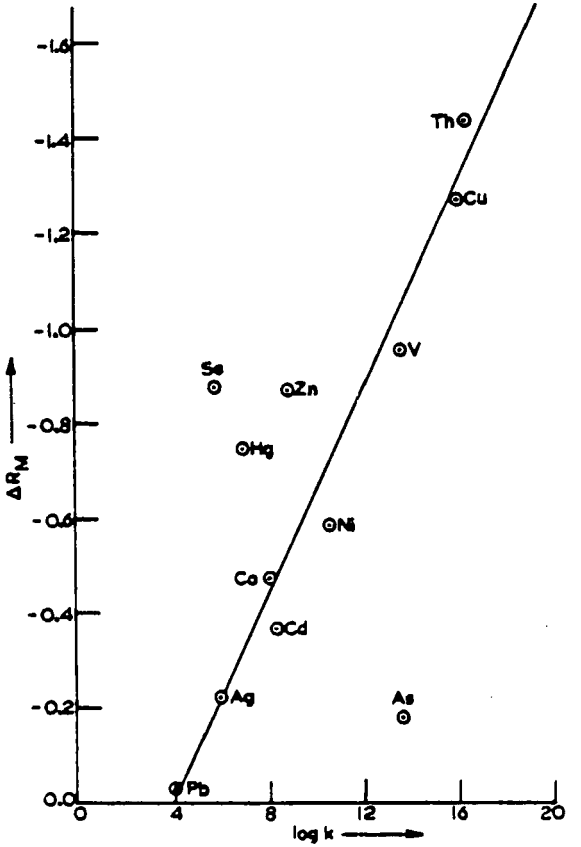

Fig.3 - Relationship between log k and ΔR_M.

value of As on un-impregnated plate was the lowest amongst the ions tried (except for Zr) indicating the existence of strong interaction between silica gel and As and, therefore, the addition of the impregnant will naturally not influence the chromatographic behaviour appreciably as a result of complex formation. Zr showed an anomalous behaviour obviously because of its lack of movement, both on un-impregnated and impregnated plates.

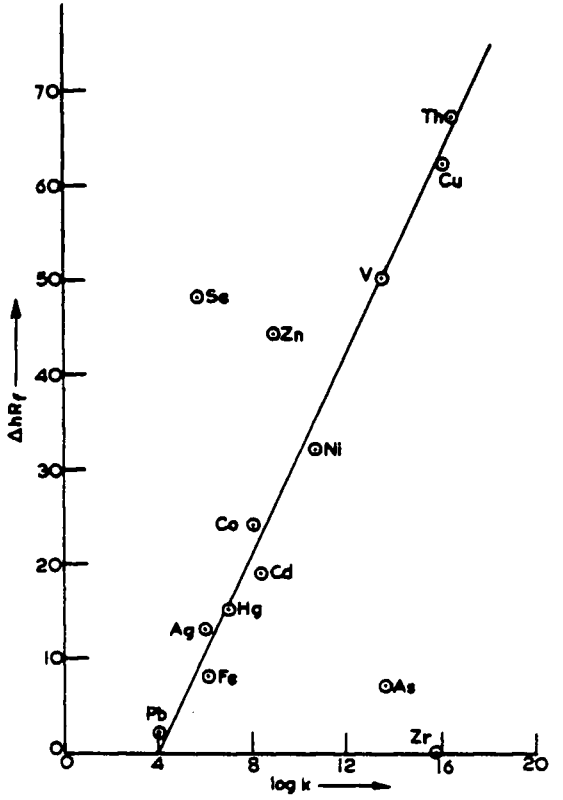

Fig.4_Relationship between logk and ΔhRf.

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