

Thin Layer Chromatographic Behaviour of Dithiocarbamates of Zinc(II), Cadmium(II) & Mercury(II)

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Thin layer chromatographic behaviour of dithiocarbamates of zinc(II), cadmium(II) and mercury(II) derived from different types of amines has been studied. The effect of highly polar amines in the mobile phase on the migratory behaviour of these chelates has been discussed based on the slope values derived from R_m versus $\log X_s$ plots (X_s = fraction of more polar component i.e. amine in the eluent).

The separation of neutral dithiocarbamates of Zn(II), Cd(II) and Hg(II) derived from diethylamine using different chromatographic techniques has been reported in literature¹⁻⁴. Except for our recent work on the TLC behaviour of dithiocarbamates⁵ and carbodithioates⁶ derived from heterocyclic amines and acyclic amines, not much work is reported in literature⁷. We have presently reported the migratory behaviour of dithiocarbamates of Zn(II), Cd(II) and Hg(II), derived from different amines using a variety of mobile phases. The influence of different amines in the mobile phase on the migratory characteristics of these chelates is also discussed.

Materials and Methods

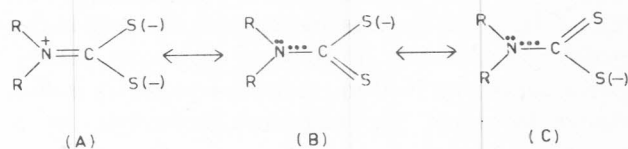
Sodium dithiocarbamates were prepared from diethylamine, dimethylamine, di-*n*-propylamine, di-*n*-butylamine, N-methylaniline, dibenzylamine, piperidine and morpholine following the procedure reported earlier⁸. Dithiocarbamates of Zn(II), Cd(II) and Hg(II) were prepared by metathetical reactions of their respective metal chlorides at pH 7 with aqueous solution of (10%, w/v) sodium salts of the ligands⁹. The precipitated chelates were repeatedly crystallised from chloroform. Thin layers of silica gel G (BDH) of thickness 0.25 ± 0.02 mm on clean glass plates were kept at 125° for 30 min and then equilibrated under laboratory humidity for 12 hr in order to obtain reproducible R_f measurements.

For binary mobile phases, benzene or chloroform was mixed with non-polar cyclohexane in various proportions. For ternary mobile phases, 2 to 15% of an amine was added to a diluent (mixture of benzene-cyclohexane). Solvent mixtures were prepared just before use. Aliphatic amines like methyl, ethyl, isopropyl, *n*-butyl, *n*-propyl, dimethyl, diethyl and heterocyclic amines like pyrrolidine, piperidine, morpholine and pyridine were employed in ternary mobile phases. All reagents and solvents employed were of analytical grade.

Fresh chloroform solutions of 30 to 50 μ g of chelates were spotted 1.5 cm from the lower end of the chromatostrips. The solvent front was allowed to move up by 10 cm from the spotted region in closed chambers pre-equilibrated with solvent vapours.

Results and Discussion

Simple solvents as mobile phases—The hR_f values listed in Table I indicate the possibility of separation of binary mixtures of Zn and Cd as their dithiocarbamates of all types and ternary mixtures of Zn, Cd and Hg dithiocarbamates derived from heterocyclic amines only. The migratory order of dithiocarbamates is $Zn \geq Hg > Cd$. With respect to different N-alkyl substituents, the migratory order is: Morp.dtc < Dime.dtc < Me.ph.dtc < Pip.dtc < Die.dtc < Dipr.dtc < Dibut.dtc < Dibenz.dtc. Mobilities increase with increase in basic strength (pK_a) of the amine from which the chelates are derived (Fig. 1). Among S, S donor bidentate ligands, the polar resonance form (A) is the characteristic of dithiocarbamates¹⁰.



The contribution of form (A) increases with increase in electron releasing capability of the amine¹¹. Though piperidine is more basic ($pK_a = 11.2$) than diethylamine ($pK_a = 10.9$), pip.dtc chelates are uniformly slow moving than the Die.dtc chelates. The rigid heterocyclic piperidine ring resists the electron flow from N to C atom and decreases the contribution of (A)¹² by accumulating more electron density on N-atom, thereby making the chelate molecule to adsorb strongly on silica gel surface.

Binary mobile phases—At constant temperature and humidity, the mobility of a chelate molecule (Z) with a

binary mobile phase containing a polar solvent (S) as the active component, is given by Eq. (1)

$$R_m = \text{Constant} - \log K_{ZS_x} - (m/n + x) \log X_s \quad \dots (1)$$

where K_{ZS_x} is the solvation or adduct formation constant of the chelate molecule (Z) with x molecules of

Table 1— hR_f Values of Dithiocarbamates of Zn(II), Cd(II) and Hg(II) using Simple Mobile Phases

Metal	hR_f values for dithiocarbamate used*							
	1	2	3	4	5	6	7	8
	Eluent:benzene							
Zn	62	80	94	97	66	97	81	8
Cd	0	49	73	94	33	89	39	0
Hg	55	73	87	93	77	96	62	15
	Toluene							
Zn	53	76	79	98	54	95	69	4
Cd	0	41	55	91	21	84	27	0
Hg	38	68	87	99	65	93	51	6
	Xylene							
Zn	36	63	81	92	40	87	56	0
Cd	0	28	39	70	20	62	21	0
Hg	30	48	73	88	45	86	38	0
	Carbon tetrachloride							
Zn	7	20	36	51	6	36	12	0
Cd	0	6	8	15	8	15	0	0
Hg	4	10	33	44	30	39	9	0
	Chloroform							
Zn	67	85	88	94	76	90	77	16
Cd	0	70	78	92	65	84	60	0
Hg	65	89	97	95	75	91	88	53

* hR_f values are the averages of minimum five experiments.

- (1) Dimethyl dithiocarbamate; (2) diethyl dithiocarbamate; (3) di-*n*-propyl dithiocarbamate; (4) di-*n*-butyl dithiocarbamate; (5) N-methyl, N-phenyl dithiocarbamate; (6) dibenzyl dithiocarbamate; (7) 1-piperidine carbodithioate; and (8) morpholine-4-carbodithioate.

Table 2—Slopes of R_m versus $\log X_s$ Linear Plots for Zn(II), Cd(II) and Hg(II) Dithiocarbamates using Binary Mobile Phases

Chelate	I			II		
	Zn(II)	Cd(II)	Hg(II)	Zn(II)	Cd(II)	Hg(II)
Dime.dtc	1.43	—	—	1.82	—	—
Die.dtc	1.43	2.50	2.22	2.35	2.67	2.00
Dipr.dtc	1.37	2.50	2.22	2.50	2.99	2.35
Dibu.dtc	1.33	3.08	2.35	2.86	3.08	2.33
Me.ph.dtc	1.43	2.67	2.43	2.50	2.97	2.00
Dibenz.dtc	1.82	3.33	2.35	3.00	3.08	2.41
Pip.dtc	1.44	2.67	2.38	2.67	2.86	2.66
Morph.dtc	1.25	—	—	2.31	—	—

The slopes given are the average of minimum six batches of chromatograms. All are negative values, but expressed as positive values by convention.

(I)= Active component is benzene; and (II) chloroform with cyclohexane as the diluent.

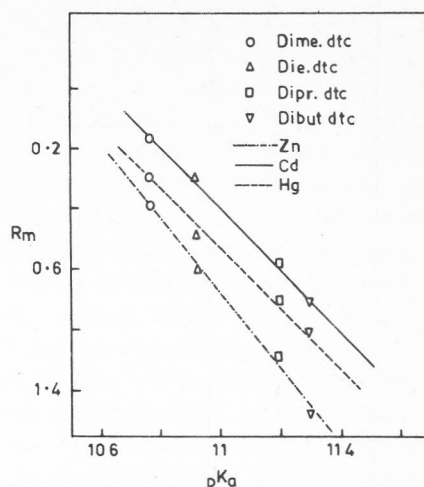


Fig. 1—Dependence of R_m values on pK_a values of the amines from which the dithiocarbamates are derived

active solvent (S) and X_s is the volume fraction of the active component in the mobile phase. Under chromatographic conditions (K_{ZS_x} becomes constant) Eq. (1) assumes the form

$$R_m = \text{Constant} - (m/n + x) \log X_s \quad \dots (2)$$

Thus the plots of R_m versus $\log X_s$ should be linear with slope values dependent on degree of solvation or adduct formation and are proportional to $m/n + x$. The slopes presented in Table 2 for different types of dithiocarbamates are in the order: Cd > Hg > Zn for benzene-cyclohexane system and Cd > Zn > Hg for chloroform-cyclohexane system. The slow migration of Cd and Hg chelates despite their favourable extraction constants^{13,14} is due to the presence of stable dimeric species^{8,15} in solution. The greater mobility of Zn chelates is due to the disintegration of dimeric species into monomeric species in solution by solvation with even less polar solvents like benzene, chloroform etc. With relatively more polar chloroform containing mobile phases, these chelates show almost

equal mobility and similar R_m versus $\log X_s$ slopes. Though the slope has to decrease with increase in solvent strength¹⁶, relatively weak benzene (planar, molecules with greater molecular area)¹⁷ containing mobile phases show lower slope values than strong chloroform (non-planar) containing mobile phases. This shows predominance of secondary solvent effects like molecular area influencing the mobility of these neutral chelates in non-polar mobile phases. Highly stable mercury chelates with greater extraction constants do not show significant changes in slopes with small polarity changes of the mobile phases.

Ternary mobile phases—Chemical interaction of Zn and Cd diethyl dithiocarbamates with cyclic and acyclic amines resulting in the formation of adducts has been reported earlier¹⁸⁻²¹. Ternary mobile phases containing 2 to 15% of an amine in benzene + cyclohexane (the proportion of benzene is kept constant at 60%) as diluent significantly alter the adsorption and desorption characteristics of Zn and Cd chelates. The adsorption and desorption characteristics of highly stable dimeric Hg(II) chelates remain unaffected in these ternary mobile phases, except for the enhanced migration corresponding to the preferential adsorption of polar amines. The mobilities of Zn chelates are less than those of Cd chelates (Figs 2 and 3). The slow migration of Zn chelates is due to the stronger adsorption of adducts formed with the amines in the eluent. The slopes of R_m versus $\log X_s$ plots for different amines and dithiocarbamates provide following useful observations.

(i) **Slopes versus pK_a of amines in the mobile phase**—Though the slopes of R_m versus $\log X_s$ plots should decrease with increase in polarity of amine (pK_a) in the mobile phase, Zn chelates show greater slopes indicating their strong adsorption in the presence of more basic amines (Table 3). Figure 4 shows the linear variation of slopes with pK_a of the amine in the mobile phase for bis(diethyl dithiocarbamato)zinc(II). When the adduct forming amine approaches the vacant coordination site of Zn, the electron density distribution changes as in Scheme 1.

The resultant decrease in thioureide (N-C) bond order and the increased electron density on N-atom make the chelate to adsorb strongly via H-bond formation with -OH groups on adsorbent surface. Slopes are also found to increase with pK_a values of the

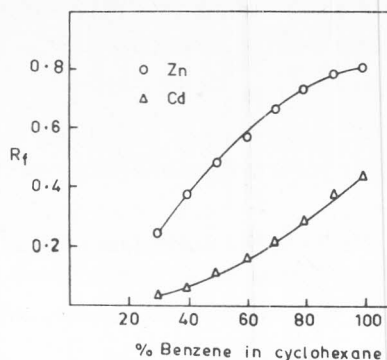


Fig. 2— R_f versus % benzene in the binary mobile phase with cyclohexane as the diluent for diethyl dithiocarbamates of Zn and Cd

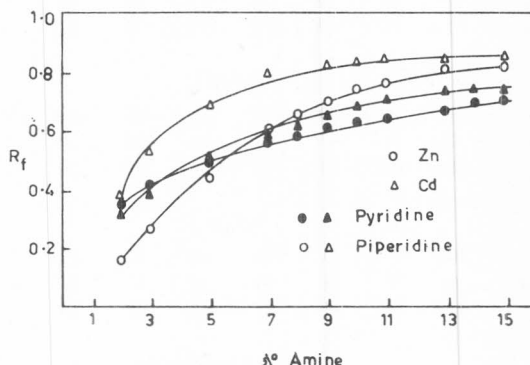


Fig. 3— R_f versus % amine in the ternary mobile phase with benzene (60%) + cyclohexane as the diluent for diethyl dithiocarbamates of Zn and Cd

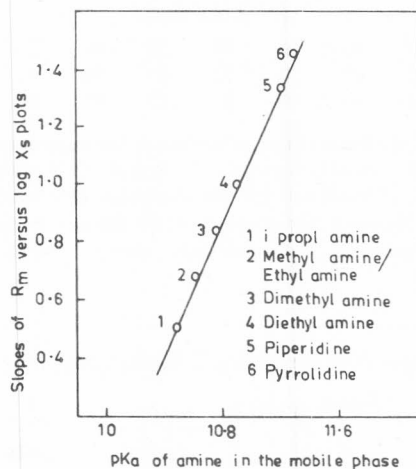
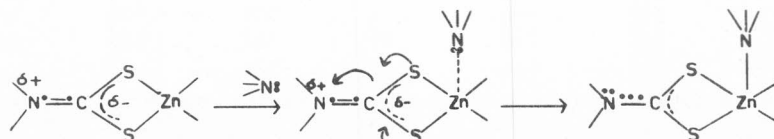


Fig. 4—Dependence of slopes of R_m versus $\log X_s$ plots on pK_a of amines in the ternary mobile phase for diethyl dithiocarbamate of Zn(II)



Scheme 1

Table 3—Slopes of R_m versus $\log X_s$ Plots for Zn(II) and Cd(II) Dithiocarbamates using Ternary Mobile Phases Containing Benzene (60%) and Cyclohexane as Diluents and an Amine as the Active Component

Amine in the mobile phase	Metal	Slopes* of plots for dithiocarbamates					
		1	2	3	4	5	6
Piperidine	Zn	1.33	0.86	0.74	1.11	0.56	1.25
	Cd	1.67	1.18	1.11	1.69	1.00	1.49
Morpholine	Zn	0.44	0.48	0.53	—	0.11	0
	Cd	0.83	0.59	0.50	0.63	0.42	0.91
Diethylamine	Zn	1.00	0.83	0.67	0.77	0.42	0.87
	Cd	1.78	1.43	1.43	1.00	0.83	1.39
<i>n</i> -Butylamine	Zn	0.09	+0.28	+0.28	+0.67	0.33	0.67
	Cd	1.43	1.43	0.44	1.03	0.63	1.47
Isopropylamine	Zn	0.50	0.54	0.41	0.56	0.67	0.67
	Cd	1.05	1.54	1.71	1.43	1.18	1.67
Benzylamine	Zn	+0.21	+0.22	+0.28	0.63	+0.22	0.63
	Cd	1.00	0.50	0.50	0.63	0.33	0.63
Pyridine	Zn	0.71	0.67	0.11	0.77	0.29	0.67
	Cd	0.91	1.11	0.33	1.00	0.35	0.92
Methylaniline	Zn	0.46	0.24	+0.40	0.56	+0.37	0.40
	Cd	1.43	1.11	0.83	1.11	1.25	1.22

*All slopes are negative except those indicated and are average of minimum six batches of chromatograms.

(1) Die.dtc; (2) Dipr.dtc; (3) Dibut.dtc; (4) Me.ph.dtc; (5) Dibenz.dtc; and (6) Pip.dtc.

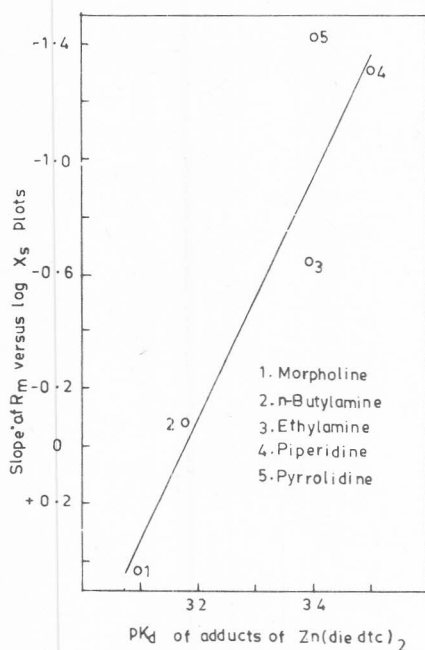


Fig. 5—Slopes (of R_m versus $\log X_s$ plots) versus pK_a of adducts of diethyl dithiocarbamate of Zn(II) with various amines

adducts (Fig. 5) proving the increased adsorption with increased adduct stability.

(ii) *Slopes versus pK_a of amines from which the chelates are derived*—With a particular amine in the mobile phase, the slope values are found to decrease with increase in pK_a of the amine from which the chelate is derived (Fig. 6). The electron flow from N to donor sites opposes the adduct forming tendency and hence adsorption.

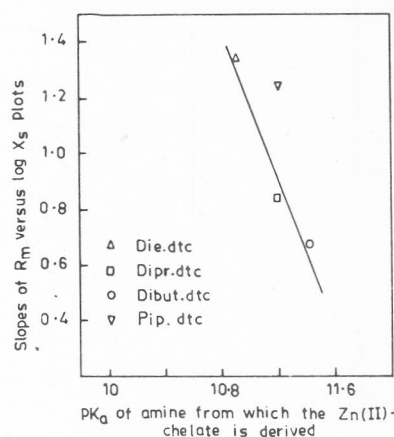


Fig. 6—Dependence of slopes (of R_m versus $\log X_s$ plots) (with benzene + cyclohexane as the diluent) on pK_a of amines from which the dithiocarbamates are derived

Dependence of slopes on steric factors—Less negative slopes in the case of Zn chelates in the presence of diethylamine and with other bulky amines like benzylamine, *n*-butylamine etc., indicate the influence of steric factors in adduct formation and hence on adsorption.

The abnormal behaviour of Zn dithiocarbamates, observed earlier¹⁶ while correlating the extraction constants with R_m values is now explained by solvation or adduct formation of chelate molecules with active and polar components of the mobile phases.

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