

## Thin Layer Chromatographic Behaviour of Dithiocarbamates of Arsenic(III), Antimony (III) & Bismuth(III)

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Thin layer chromatographic behaviour of N, N-disubstituted dithiocarbamates of As(III), Sb(III) and Bi(III) on silica gel layers has been studied and the results are discussed on the basis of  $R_m$  versus  $\log X_s$  plots ( $X_s$  = volume fraction of active component in the mobile phase). For a series of particular type of solvents, their molecular areas are found to affect significantly the adsorption and desorption characteristics. The 'thioureide' bond order and the distorted octahedral symmetry of these chelate molecules are found to influence their retention properties.

Separation of neutral chelates by adsorption thin layer chromatography (ATLC) is a recently developed analytical technique<sup>1</sup>. Theoretical basis of this technique was developed by Galik<sup>2</sup> following the 'competition model' of Snyder<sup>3</sup>. According to this model, two similar chelate molecules adsorbing with the same number of bonds can be resolved only when they are solvated to varying degrees by the mobile phase components. We report in this paper the resolution of trisdithiocarbamates of As(III), Sb(III) and Bi(III), having distorted octahedral symmetry<sup>4</sup>, by binary mobile phases of polar solvents diluted with inactive  $\text{CCl}_4$  or cyclohexane. Since the selectivity of ATLC varies exponentially with the molecular area of solute and solvent molecules<sup>5</sup>, Galik's equation has been modified accordingly to explain the differential migration of similar chelate molecules.

### Theoretical Model of ATLC

At constant adsorbent activity ( $\alpha$ ),  $R_m$  is correlated<sup>2</sup> with the formation constants of complexes formed by the adsorption of solute and solvent molecules by Eq. (1),

$$R_m = -m/n \log X_s + C \quad \dots (1)$$

where  $C$  = constant;  $m$  and  $n$  are the number of bonds with which the chelate and solvent molecules get adsorbed; and  $X_s$  is the volume fraction of active component in the mobile phase. The slope of  $R_m$  versus  $\log X_s$  plot, i.e.  $m/n$  is a measure of the degree of adsorption of the chelate molecule. For two similar chelate molecules(1) and (2), adsorbing with the same number of bonds,  $\Delta R_m$  resulting from the change of mobile phase from (A) to (B) is given by Eq. (2),

$$\begin{aligned} \Delta R_m = \text{Constant} &= R_m(1) - R_m(2) \\ &= m/n(\log K_{AZ} - \log K_{BZ}) \quad \dots (2) \end{aligned}$$

where  $K_{AZ}$  and  $K_{BZ}$  are the formation constants of the complexes formed by the adsorption of solvent

molecules (A) and (B) on active sites(Z) of the adsorbent. Soczewinski<sup>6</sup> related  $\Delta R_m$  with the difference in the number of bonds ( $\Delta m$ ) by which the solvent molecules get adsorbed to form complexes

$$\begin{aligned} (R_{m(1)} - R_{m(2)})_A &= (R_{m(1)} - R_{m(2)})_B \\ &+ \log [X_{s(B)}/X_{s(A)}]^{\Delta m} \quad \dots (3) \end{aligned}$$

Snyder<sup>3,7</sup> correlated  $\Delta R_m$  with adsorbent activity ( $\alpha$ ), and molecular area ( $A_e$ ) by Eq. (4)

$$(R_{m(1)} - R_{m(2)})_A = (R_{m(1)} - R_{m(2)})_B + \Delta C \cdot \Delta \epsilon \quad \dots (4)$$

where  $C = \alpha \cdot \Delta A_e$ ;  $\Delta \epsilon = (\epsilon_B - \epsilon_A)$ ;  $A_e = A_{e(B)} - A_{e(A)}$ ; and  $\epsilon$  = solvent strength. At constant  $\alpha$ , Eqs (3) and (4) are equated to get

$$\log [X_{s(A)}/X_{s(B)}]^{\Delta m} = \Delta \mu \cdot \Delta \epsilon \quad \dots (5)$$

where  $\Delta \mu = \Delta C \cdot \Delta m$ . So the change in solvent strength or type results in change in the slope ( $\Delta \mu$ ) rather than  $\Delta m$ . Expressing Eq. (4) in more explicit  $R_f$  values, we get,

$$\left[ \frac{R_{f(2)}(1 - R_{f(1)})}{R_{f(1)}(1 - R_{f(2)})} \right]_A = \left[ \frac{R_{f(2)}(1 - R_{f(1)})}{R_{f(1)}(1 - R_{f(2)})} \right]_B e^{\Delta \mu \cdot \Delta \epsilon} \quad \dots (6)$$

Hence the mobility or selectivity is an exponential function of solvent strength and its molecular area. So two similarly adsorbing chelate molecules without truly equal molecular areas ( $A_s$ ) can be resolved by judicious choice of solvent strength or type. Accordingly Eq. (1) due to Galik can be modified as

$$R_m = -\mu/N \log X_s + C \quad \dots (7)$$

where  $\mu = m \cdot \alpha \cdot A_s$  and  $N = n \cdot \alpha \cdot A_e$

### Materials and Methods

Sodium salts of the dithiocarbamic acids were prepared from dimethylamine, diethylamine, di-*n*-propylamine, di-*n*-butylamine, N-methylaniline, dibenzylamine, piperidine and morpholine following

the standard procedures<sup>8</sup>. Neutral dithiocarbamates of As(III), Sb(III) and Bi(III) were prepared by metathetical reactions between the aqueous solutions of metal ions and ligand in 1:3 molar proportions<sup>4</sup> below pH 7. These were recrystallised from chloroform.

TLC studies were made by allowing the mobile phase to move up by 10 cm from spotted region in closed chambers preequilibrated with eluent vapours at 29°C. Layers (thickness  $0.25 \pm 0.02$  mm) were activated at 125°C for 1 hr and kept for 24 hr in the open so that the thin layers acquire the relative humidity prevailing in the laboratory. Fresh chelate solutions in benzene were spotted 1.5 cm from the lower end of the chromatostrips with microsyringes. Binary mobile phases were prepared just before use. Colourless zones of As and Sb chelates were visualised by spraying with 5% CuSO<sub>4</sub> solution. Pilot chromatograms were run to facilitate their quantitative elution and determination.

### Results and Discussion

*Simple mobile phases*—These trischelates have highly distorted octahedral symmetry due to lone pair of electrons on the central metalloid atom<sup>4</sup>. The bulky organic ligands make these chelates to adsorb by the same number of bonds via lone pair of electrons on N-atom of ligand moiety. However, the data in Table 1 show parallel movement of As and Sb chelated while the movement of Bi chelates is slow. The greater degree

of  $\pi$ -back donation (Bi  $\rightarrow$  S; IR  $\nu_{N=C}$  around  $1475\text{ cm}^{-1}$ )<sup>9,10</sup> and the less electronegative character of Bi(III) facilitates greater availability of lone pair of electrons on N-atom for adsorption. Though the equally moving As and Sb chelates have insignificant  $\pi$ -back donation<sup>4,10</sup> (IR  $\nu_{N=C}$  around  $1485\text{ cm}^{-1}$ ) small differences manifested in their molecular area by electronegativity and ionic radii variations<sup>11</sup> aid their resolution (of some chelate types) by higher hydrocarbons. This shows the effect of molecular area of the solvents, as well as solutes in achieving the required selectivity. Mobilities of different types of chelates are in the order: Morph. dte  $\ll$  Dime. dte < Pip. dte < Die. dte < Me.ph.dte < Dipr. dte < Dibut. dte < Dibenz. dte. The mobility increases with increase in N-alkyl chain length of the ligand (Fig. 1) and with the basicity of the amines from which they are derived, with the exception of Me.ph.dte and Dibenz.dte. Though piperidine is more basic than diethylamine, Pip.dte is found to be slow moving than Die.dte (Table 2). The controlled electron flow from N to C atom in the rigid heterocyclic ring<sup>10</sup> decreases the 'thioureide' bond order and makes the chelate to adsorb strongly. Morph.dte chelates with strongly adsorbing ring O-atom show negligible migration.

*Binary mobile phases: (A) With benzene/halogenated hydrocarbons as the active component*—When the simple solvents listed in Table 1 are diluted with inactive cyclohexane (or CCl<sub>4</sub>) better resolutions are achieved (Table 2), proving the increase in selectivity

Table 1— $hR_f$  Values with Simple Solvents as Mobile Phases

Eluent	$hR_f$ of metal chelates of								
	Metal	Dime.	Die.	Dipr.	Dibut.	Me.ph.	Dibenz.	Pip.	Morph.
Benzene	As	33.0	54.7	79.3	90.6	71.7	96.3	50.0	7.0
	Sb	37.6	61.8	85.4	93.3	66.3	90.2	58.4	4.9
	Bi	22.8	42.1	68.6	86.3	51.9	88.2	38.0	0
Toluene	As	18.4	38.5	64.1	85.3	57.4	82.7	28.3	3.0
	Sb	19.2	39.1	73.4	89.6	42.1	81.3	26.2	0
	Bi	6.5	21.3	59.0	85.2	38.8	83.5	24.8	0
Xylene	As	7.3	16.4	38.2	67.3	39.1	65.5	11.6	0
	Sb	6.3	18.0	50.0	61.9	26.4	76.2	15.7	0
	Bi	0	9.3	32.5	69.1	14.2	63.2	5.4	0
Chloroform	As	35.5	59.3	77.0	86.3	57.3	88.1	55.3	8.9
	Sb	40.9	68.2	81.0	88.1	69.1	97.1	60.1	7.3
	Bi	31.9	53.3	67.0	79.3	63.3	92.6	58.6	4.3
Dichloromethane	As	65.1	82.9	88.3	98.0	88.1	100.0	80.8	14.4
	Sb	71.6	91.9	100.0	100.0	95.6	100.0	82.7	12.7
	Bi	67.9	88.8	100.0	100.0	99.2	100.0	80.3	9.3

Humidity = 80 to 82%

Dime = Dimethyl dithiocarbamate; Die = Diethyl dithiocarbamate;

Dipr = Di-*n*-propyl dithiocarbamate; Dibut = Di-*n*-butyl dithiocarbamate;

Ne. ph. = N-methyl, N-phenyl dithiocarbamate; Dibenz = Dibenzyl dithiocarbamate;

Pip. = 1-Piperidine carbodithioate; Morph = Morpholine-4-carbodithioate.

with decrease in solvent strength<sup>5</sup>. Though the slopes of  $R_m$  versus  $\log X_s$  plots should decrease with solvent strength<sup>2</sup>, weaker benzene (planar, with larger molecular area)<sup>3</sup> containing mobile phases show lower slopes than stronger  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  (non-planar, with low molecular area) containing mobile phases (Table 3). Thus molecular area can be used to determine the solute adsorption in addition to solvent strength, solute type and other secondary solvent effects like aromatic localisation, etc. The slopes are in the order: Pip.dtc > Dime.dtc. > Me.ph.dtc >

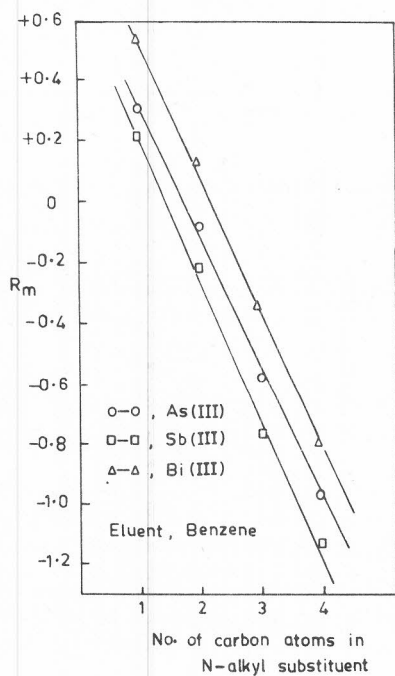


Fig. 1—Dependence of  $R_m$  values on the number of carbon atoms in N-alkyl substituents

Dibenz.dtc > Die.dtc > Dipr.dtc > Dibut.dtc. Though the slopes with these trischelates are greater than those with bischelates of the bivalent elements (Table 3), their correlation with chelate stoichiometry as done earlier<sup>2</sup> is less pertinent because the adsorption of these chelates is influenced not only by the N-alkyl substituents but also by their molecular symmetry and electronegativity of the central ions.

(ii) *With ketones/dioxan/tetrahydrofuran in carbon tetrachloride as active components*—Binary mobile phases containing 4 to 15% (v/v) of a ketone in  $\text{CCl}_4$  resolve these chelates on thin layers. Greater than 4% concentration of acetone, dioxan, etc. and 8% concentration of methyl ethyl ketone, tetrahydrofuran, etc. offer good resolutions (Fig. 2). Chelates derived from dialkyl amines and cyclic amines are well resolved by mobile phases containing acyclic and cyclic ketones respectively (Fig. 3). Slopes of  $R_m$  versus  $\log X_s$  plots for some chelates presented in Table 4 show the mobilities in the order As > Sb > Bi. The slopes are found to

Table 2— $hR_f$  Data of Some Binary Mobile Phases with Benzene/Halogenated Hydrocarbons as Active Components

Chelate	Eluent	$hR_f$ values		
		As	Sb	Bi
Dime.	$\text{CHCl}_3$ -Cy.H(1:1)	13.4	30.0	0
Die.	$\text{C}_6\text{H}_6$ - $\text{CCl}_4$ (8:2)	44.1	60.4	31.3
	$\text{NO}_2\text{C}_6\text{H}_5$ - $\text{CCl}_4$ (12:88)	43.7	79.9	59.8
	$\text{C}_6\text{H}_6$ -Cy.H(7:3)	59.9	73.1	44.9
Dipr.	$\text{C}_6\text{H}_6$ - $\text{CCl}_4$ (1:1)	32.6	58.2	44.2
	$\text{CHCl}_3$ - $\text{CCl}_4$ (6:4)	53.1	78.8	68.3
	$\text{ClC}_6\text{H}_5$ - $\text{CCl}_4$ (7:3)	58.1	72.8	31.5
	Dibut.	$\text{CHCl}_3$ -Cy.H(1:1)	50.5	79.2
Pip.	$\text{CHCl}_3$ - $\text{CCl}_4$ (1:1)	17.9	30.4	5.3

CyH = Cyclohexanone

Table 3—Slopes of  $R_m$  versus  $\log X_s$  Plots for Binary Mobile Phases Containing Benzene/Halogenated Aliphatic Hydrocarbons as Active Components with Cyclohexane as Diluent

Active component (20 to 80 % v/v)	Metal	Slopes of metal chelates of						
		Dime.	Die.	Dipr.	Dibut.	Me.ph.	Dibenz.	Pip.
Benzene	As	2.38	1.85	1.48	1.40	2.25	1.67	3.50
	Sb	1.91	1.64	1.38	1.21	2.35	1.86	2.53
	Bi	2.64	2.01	1.43	1.67	2.63	2.08	3.22
	(Zn)	(1.43)	(1.43)	(1.37)	(1.33)	(1.48)	(1.62)	(1.42)
$\text{CHCl}_3$	As	2.86	2.61	2.61	2.61	2.86	3.08	3.33
	Sb	2.79	2.78	2.27	2.17	3.64	2.61	3.67
	Bi	4.00	3.68	2.61	2.52	3.33	3.86	4.0
	(Zn)	(1.82)	(2.35)	(2.50)	(2.86)	(2.50)	(3.00)	(2.76)
$\text{CH}_2\text{Cl}_2$	As	2.67	2.48	2.51	2.02	1.74	2.53	3.08
	Sb	2.48	2.52	2.11	2.09	2.61	2.35	3.33
	Bi	3.73	3.38	2.55	2.27	3.14	2.78	3.45
$\text{ClCH}_2\text{CH}_2\text{Cl}$	As	2.33	2.17	2.14	1.77	1.32	2.23	2.69
	Sb	2.17	2.21	1.85	1.83	2.28	2.06	2.91
	Bi	3.26	2.86	2.23	1.99	2.75	2.43	3.02

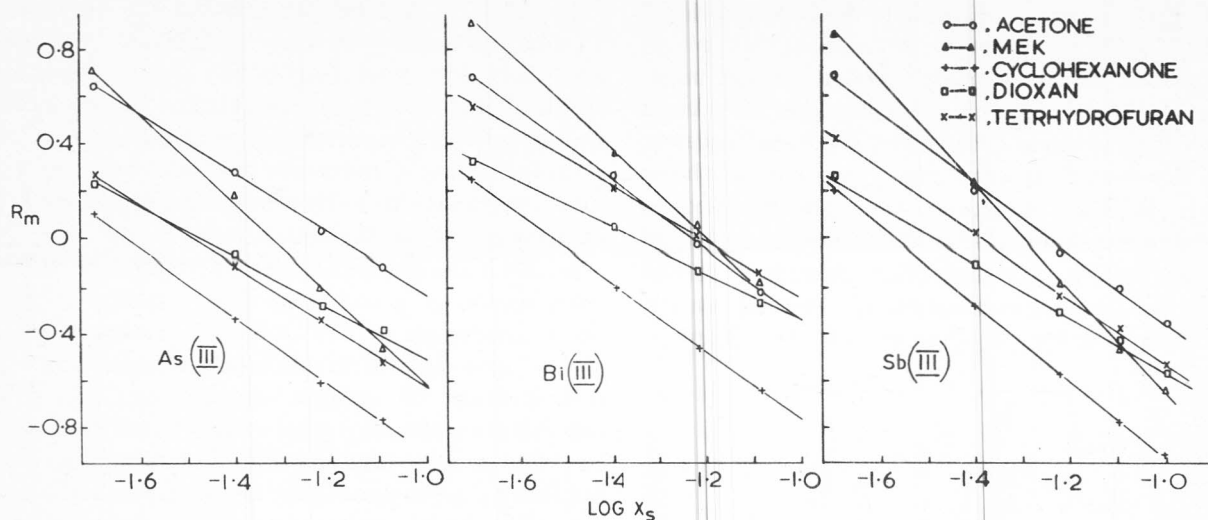


Fig. 2— $R_m$  versus  $\log X_s$  plots for 1-piperidine carbodithioates of As(III), Sb(III) and Bi(III). [Mobile phases: ketones as the active components (2 to 15% v/v) with  $CCl_4$  as the diluent

decrease, in general, with increase in molecular area and  $pK_a$  of the ketones, dioxan and THF as shown below with tris(diethyldithiocarbamato)antimony(III);

	Acetone	MEK	Cyclo-hexanone	Dioxan	THF
$pK_a$	-7.2	-7.2	-6.8	-3.2	-2.0
Slope	1.38	1.29	1.25	1.18	1.11

Larger slopes observed with acetophenone (Table 4) show its weak adsorption due to  $-I$  effect of the phenyl group adjacent to the adsorbing site. Lengthy N-alkyl chain and N-phenyl group give lower slopes due to their fast migration because of weak adsorption and greater lipophilicity. Like ketones, esters also resolve these chelates but with more compact spots facilitating their quantitative elution and determination.

(III) *With alcohols as active components*—Slopes of  $R_m$  versus  $\log X_s$  plots presented in Table 4 show the migratory behaviour of these chelates in the order: As < Sb > Bi. Since sorption mechanism is accepted for highly polar alkanols<sup>7</sup> as mobile phases, the comparatively more polar chelate molecules may be presumed to be sorbed strongly on the primarily adsorbed layer of polar alkanol molecules resulting in their restricted migration. The slopes are found to decrease with molecular area of the alkanols. Isoalcohols show greater slopes than *n*-alcohols. The anomalous behaviour of methanol (lower slopes) can be explained by its free and strong adsorption at any position on adsorbent surface. The slopes are in the order: Morph.dtc > Pip.dtc > Dime.dtc > Die.dtc > Dipr.dtc > Dibut.dtc > Dibenz.dtc > Me.ph.dtc. The intersecting  $R_m$  versus  $\log X_s$  linear plots of As and Sb chelates (Fig. 4) around 5% (v/v) of alkanol (in  $CCl_4$ )

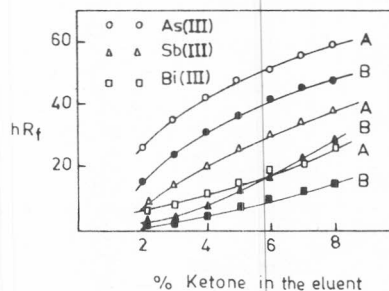


Fig. 3—Plots of  $hR_f$  versus per cent of active component (ketones) in the binary mobile phase with carbon tetrachloride as the diluent for morpholine-4-carbodithioates. [A = dioxan; B = tetrahydrofuran.]

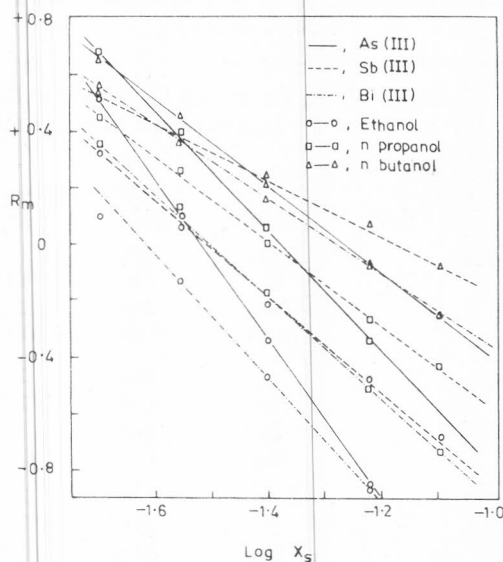


Fig. 4—Plots of  $R_m$  versus  $\log X_s$  plots for 1-piperidine carbodithioates of As(III), Sb(III) and Bi(III). [Mobile phase: alcohols as the active component with  $CCl_4$  as the diluent]

Table 4—Slopes of  $R_m$  versus  $\log X_s$  Plots of Some N, N-Disubstituted Dithiocarbamates of As(III), Sb(III) and Bi(III)

Eluent* (Active component 2 to 15% v/v)	Die.			Dipr.			Dibut.			Me.ph.			
	As	Sb	Bi	As	Sb	Bi	As	Sb	Bi	As	Sb	Bi	
Acetone	1.18	1.38	1.87	0.95	1.27	1.54	0.91	1.09	1.18	1.00	1.11	1.33	
MEK	1.25	1.29	1.65	1.13	1.16	1.00	1.10	1.03	1.10	0.92	1.05	1.02	
THF	0.91	1.11	1.10	1.18	1.60	2.00	1.54	2.11	2.05	1.08	1.67	1.11	
Cyclohexanone	1.27	1.25	1.45	1.00	1.18	1.48	0.83	1.13	1.25	0.87	1.11	1.43	
Dioxan	0.91	1.18	1.05	1.00	0.83	0.93	0.83	0.83	0.83	0.81	1.08	0.96	
Acetophenone	2.27	2.86	2.83	2.50	2.86	2.42	1.68	1.98	2.22	1.35	2.22	2.22	
		Dime.			Die.			Dibenz			Morph.		
Methanol	1.98	1.18	2.67	2.00	1.48	1.96	1.38	1.29	1.67	2.78	2.67	2.85	
Ethanol	1.82	1.38	2.88	2.22	1.60	2.28	1.48	1.48	1.80	2.80	2.25	2.48	
n-Propanol	1.48	1.00	1.95	1.91	1.43	1.78	1.33	1.11	0.95	2.18	2.11	2.28	
n-Butanol	0.95	0.87	0.91	1.11	1.01	1.00	1.01	0.71	0.95	1.95	2.00	2.11	
Isopropanol	2.00	1.67	2.50	1.74	1.43	2.50	1.43	1.33	1.54	2.72	2.54	—	
Isobutanol	1.60	1.11	2.11	1.43	1.29	1.81	1.33	1.14	1.04	2.67	1.80	1.93	
Isoamyl alc.	0.91	0.87	0.83	1.33	1.11	1.67	1.18	0.88	0.91	1.81	1.48	1.56	
Diacetone alc.	0.77	0.71	0.80	1.29	0.83	1.38	1.13	1.11	0.91	1.60	1.45	1.55	

Humidity = 76%; MEK = methyl ethyl ketone; THF = Tetrahydrofuran.

\* Carbon tetrachloride as diluent.

show their better resolutions with mobile phases containing more than 8% (v/v) of alkanol.

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