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Thin-Layer Chromatographic Behavior and Separation of Thallium Valancies I and III as Their Neutral *N,N*-Disubstituted Dithiocarbamates

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Thin-Layer Chromatographic Behavior and Separation of Thallium Valancies I and III as Their Neutral *N,N*-Disubstituted Dithiocarbamates

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Abstract

Thallium(I) and (III) species have been separated quantitatively as their neutral *N,N*-disubstituted dithiocarbamates on silica gel layers. The effects of solvent strength, chelate type, and adsorbent deactivation on their resolutions are discussed. The effect of charge density perturbations at the N atom of the "thioureide" bond on adsorption characteristics are discussed with infrared absorption frequencies. Slopes of R_m vs $\log X_s$ plots (X_s = fraction of more polar component in the mobile phase) showed strong adsorption of monomeric Tl(III) dithiocarbamates through three adsorption sites. However, they are found to migrate ahead of polymeric Tl(I) dithiocarbamates with mobile phases of solvent strength greater than 0.15 ε° or of solubility parameters (δ_T) greater than 8.8.

INTRODUCTION

Since thallium(I) species are highly poisonous (*1*), their determination and differentiation from thallium(III) species is essential in checking the toxicity of this heavy metal. Though separations of these species have been reported earlier by different chromatographic techniques (*2, 3*), their separation as neutral chelates has not been studied in spite of the advantages of chromatographic separation after chelation (*2*). *S,S*-donor *N,N*-disubstituted dithiocarbamate ion (dtc) complexes of these heavy metal ions give neutral chelates with significant differences in such physical properties as solubility, stability, and color (*4, 5*). This work reports the quantitative separation of

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Tl(I) and Tl(III) dithiocarbamates derived from different amines on silica gel layers and discusses their migratory behavior with the slopes of R_m vs $\log X_s$ plots for binary mobile phases.

EXPERIMENTAL

The sodium salts of dithiocarbamic acids were prepared from dimethylamine, diethylamine, di-*n*-propylamine, di-*n*-butyl amine, *N*-methylaniline, dibenzylamine, piperidine, and morpholine following a standard procedure (*6*). At 0 to 5°C, amine, carbon disulfide (both in dioxane), and sodium hydroxide in a minimum quantity of water were mixed in equimolar proportions with constant stirring. The sodium salts, formed as white solids, were separated by filtration and recrystallized from isopropanol.

Thallium(I) dithiocarbamates were prepared by treating Tl(I) ions (from Tl_2SO_4) with the sodium salt of the ligand in 1:1 molar proportions in aqueous solutions. The white chelates formed were washed repeatedly with water, dried, and recrystallized from chloroform. The results of their elemental analyses (C, H, N, and S) confirmed their monochelate composition (thallium and ligand in the ratio 1:1). Molecular weight determination (cryoscopic) in benzene corresponded to dimeric compositions, indicating their polymeric nature even in solution, as reported earlier (*7*).

Thallium(III) dithiocarbamates were prepared by treating the Tl(III) ions (prepared from Tl(I) by oxidation with H_2O_2) (*8*) and the sodium salt of the ligand in 1:3 molar proportions. The yellowish orange solids precipitated were repeatedly washed with water, dried, and recrystallized from chloroform. The results of their elemental analyses confirmed their trischelate composition (thallium and ligand in the ratio 1:3). Molecular weight measurements confirmed the monomeric nature for all types of Tl(III) dithiocarbamates, supporting the earlier observation for tris(diethyldithiocarbamate) thallium(III) (*9*).

Thin-Layer Chromatographic Study

Thin layers (thickness 0.25 ± 0.02 mm) were made from silica gel supplied by B.D.H. on clean glass plates (15 × 8 cm) with aqueous slurries. The air-dried plates were activated at 110°C for an hour. Fifty to 60 μg of chelates in 10 to 20 μL of chloroform solutions were spotted 1.5 cm from the lower end of the chromatostrips with microsyringes. The plates were developed by ascending techniques at 29°C in closed glass chambers preequilibrated with eluent vapors (for 1 hr). The solvent front was allowed to move up 13 cm from the spotted regions. The colorless zones of Tl(I) chelates were visualized by spraying the plates with 5% copper sulfate solution (in ethanol:water 1:1). Binary mobile phases were made just before use. All solvents and reagents employed were of analytical grade. IR spectra were taken in Nujol mulls with a Perkin-Elmer 199 spectrometer. Elemental analyses (C and H) were made with a Perkin-Elmer 140-B Elemental Analyzer. Nitrogen was estimated by the micro-Kjeldahl method and sulfur by gravimetry as $BaSO_4$. Beckmann Model 25 UV Visible Spectrophotometer was employed for spectrophotometric estimations of chelates after separation and elution.

RESULTS AND DISCUSSION

Simple nonpolar organic solvents, as mobile phases, resolved the dithiocarbamates of Tl(I) and Tl(III), and the resolution was found to increase with an increase in solvent strength ε°, i.e., in the order, xylene < toluene < benzene < chloroform < ethylene chloride < dichloromethane.

Trischelates of Tl(III) are faster moving than monochelates of Tl(I) (Table 1). The greater mobility of Tl(III) chelates corresponds with their greater extraction constants (*10, 11*). The polymeric nature of Tl(I) dithiocarbamates even in solution causes these chelates to be retained strongly on an adsorbent surface. In addition, the influence of the "lone pair" effect accumulates more electron density on the N atom, the adsorbing site, as evidenced from IR ν (C$\overset{...}{-}$N) absorption frequencies (Table 1). With respect to N-alkyl substituents, the mobilities of these chelates are in the order Morph.dtc < Dime.dtc < Pip.dtc < Me.ph.dtc < Die.dtc < Dipr.dtc < Dibenz.dtc < Dibut.dtc. The presence of an aromatic ring in the N-atom substituent and the increase in hydrophobic N-alkyl chain length decreases their resolution with an increase in solvent strength (Table 1).

Since the "dtc" moiety adsorbs on —OH groups of the silica gel surface via H-bond formation through the N atom of the "thioureide" bond, the increased electron density on the N atom will favor its adsorption. With an increase in the basic strength (pK_a) of the amine, the electron flow from the N to the C atom of the thioureide bond increases with a corresponding decrease in adsorption of the chelate molecule (Table 1). However, the chelate derived from heterocyclic piperidine shows restricted migration though it is more basic than acyclic diethyl amine. The rigid heterocyclic ring controlling the electron flow from N to C in the chelate molecule accumulates a greater charge density on the N atom (*12*) and favors its strong adsorption.

For dithiocarbamates, C$\overset{...}{-}$N bond order is an indirect measure of the electron density on the N atom (*4*). Greater IR ν(C$\overset{...}{-}$N) frequencies will

TABLE 1

hR_f Values[a] of Some *N,N*-Disubstituted Dithiocarbamates of Tl(I) and Tl(III) with Simple Mobile Phases

Eluent	Chelate	Dime.[b]	Die.	Dipr.	Dibut.	Me.ph.	Dibenz.	Pip.	Morph.
Benzene	Tl(I)	33.8	58.7	83.6	92.7	39.3	88.8	47.2	5.5
	Tl(III)	46.2	68.3	89.0	97.4	66.5	97.0	66.7	9.0
Toluene	Tl(I)	21.5	44.8	68.6	90.2	30.3	75.7	40.9	0
	Tl(III)	29.6	53.2	73.5	98.1	45.5	92.2	51.6	5.0
Xylene	Tl(I)	12.9	24.7	62.5	88.3	23.5	70.5	19.9	0
	Tl(III)	21.8	32.5	67.6	91.9	34.4	88.5	28.0	0
Chloroform	Tl(I)	52.3	74.6	92.6	96.9	68.4	93.6	69.3	0
	Tl(III)	64.8	83.3	97.8	98.9	91.4	97.8	81.4	26.3
Dichloromethane	Tl(I)	60.9	81.8	100	100	73.4	100	72.2	0
	Tl(III)	83.8	91.0	100	100	93.7	100	88.9	29.8
Ethylene dichloride	Tl(I)	51.3	80.4	100	100	56.4	100	64.4	0
	Tl(III)	73.3	86.7	100	100	85.8	100	79.2	34.5
IR ν(C=N)	Tl(I)	1490	1475	1460	1470	1450	1450	1470	1450
	Tl(III)	1498	1488	1480	1475	1465	1470	1480	1468
pK_a of the amine (from which the ligand is derived)		10.76	10.92	11.18	11.28	4.85	—	11.22	8.33

[a] Layers of silica gel with about 2% H_2O.

[b] Dime = dimethyl dithiocarbamate; Die = diethyl dithiocarbamate; Dipr. = di-*n*-propyl dithiocarbamate; Dibut. = di-*n*-butyl dithiocarbamate; Me.ph. = *N*-methyl,*N*-phenyl dithiocarbamate; Dibenz. = dibenzyl dithiocarbamate; Pip. = 1-piperidine carbodithioate; Morph. = morpholine-4-carbodithioate.

TABLE 2

Effect of Thin Layer Deactivation by H_2O on the Resolution of Some Dithiocarbamates of Tl(I) and Tl(III)

Chelate[a] (metal ion)	% H_2O (on layers)	hR_f values of eluents[b]					
		1	2	3	4	5	6
Die. (Tl(I))	2	33.2	22.2	8.2	54.8	69.7	59.1
(Tl(III))	2	46.9	35.7	19.9	70.7	82.7	79.3
Pip. (Tl(I))	2	22.8	21.9	10.6	48.3	62.5	53.1
(Tl(III))	2	43.2	36.8	18.5	69.5	80.0	75.5
Die. (Tl(I))	3	58.8	44.8	24.5	74.6	81.8	80.4
(Tl(III))	3	68.3	51.6	32.0	83.3	88.9	86.7
Pip. (Tl(I))	3	47.2	40.4	19.9	68.3	72.2	64.0
(Tl(III))	3	66.7	53.2	28.0	81.4	90.9	79.2
Die. (Tl(I))	4	73.2	61.6	56.7	78.9	90.9	83.1
(Tl(III))	4	78.6	63.7	62.4	84.8	98.2	86.8
Pip. (Tl(I))	4	56.7	48.8	36.3	73.2	78.7	71.7
(Tl(III))	4	75.0	55.3	41.1	83.8	90.8	87.3

[a] Die. = diethyl dithiocarbamate; Pip. = 1-piperidine carbodithioate.

[b] 1 = benzene; 2 = toluene; 3 = xylene; 4 = chloroform; 5 = dichloromethane; 6 = ethylene chloride.

indicate a low electron density on N and weak adsorption of the chelate molecules. In contrast to this expectation, the mobilities are found to increase with a decrease in IR $\nu(C\overset{\cdots}{-}N)$ frequencies (Table 1). Though inductive effects should increase with an increase in N-alkyl chain length, the growing mass of the N-alkyl chain kinematically retards the electron flow to the N atom via hyperconjugation of α-CH_2 groups (*13*). This, along with the electron flow to donor sites in conjugation with the—C(S)S group, decreases the $C\overset{\cdots}{-}N$ bond order. The −I effect of phenyl groups in Me.ph.dtc and Dibenz.dtc and the electron-withdrawing heterocyclic ring O atom in Morph.dtc chelates restrict the electron flow from N to C, resulting in a decreased $C\overset{\cdots}{-}N$ bond order and $\nu(C\overset{\cdots}{-}N)$ IR absorption frequencies as well as the pK_a values of the respective amines. The ring O atom of Morph.dtc, acting as an additional adsorbing site, makes the chelate molecule adsorb strongly in spite of a low charge density on the N atom.

With an increase in adsorbent deactivation by water molecules, the mobilities increased as expected in addition to the decrease in resolution between Tl(I) and Tl(III) chelate molecules. This decrease is more prominent with less strong mobile phases (Table 2).

TABLE 3

Slopes of R_m vs log X_s Plots for Some Dithiocarbamates of Thallium(I) and Thallium(III)

Binary mobile phase	Dime.		Die.		Pip.	
Active component: diluent	Tl(I)	Tl(III)	Tl(I)	Tl(III)	Tl(I)	Tl(III)
(20 to 80)						
C_6H_6:CCl_4	1.55	2.09	1.51	1.85	1.21	2.35
$CHCl_3$:CCl_4	1.92	2.35	1.98	2.16	1.67	2.51
C_6H_6:Cy.H.[a]	2.21	2.81	2.11	2.91	2.57	3.23
$CHCl_3$:Cy.H.	2.35	3.08	2.22	3.13	2.66	3.33
(80 to 100)						
CH_2Cl_2:C_6H_6	2.22	3.19	1.68	2.35	2.05	2.50
CH_2Cl_2:$CH_3C_6H_5$	2.05	2.67	1.51	2.60	1.25	1.43
CH_2Cl_2:$(CH_3)_2C_6H_4$	1.38	1.82	1.25	1.43	1.54	1.67

[a] Cy.H. = cyclohexane.

Binary Mobile Phases

Binary mobile phases containing benzene, chloroform, dichloromethane, etc. as active components with cyclohexane or carbon tetrachloride as the inactive diluent also resolved these chelates. At constant temperature and humidity, the mobility (R_m) of a neutral chelate molecule is proportional to the fraction of active component (X_s) in the mobile phase (*14*), i.e., $R_m = \log X_s(-m/n) + C$, where C is a constant and m and n are the number of bonds with which the chelate and active solvent molecules, respectively, are adsorbed. So the slope (m/n) of the straight line plot of R_m vs log X_s is a measure of the degree of adsorption of chelate molecules. The uniformly greater slopes shown by Tl(III) chelates (Tables 3 and 4) with all types of mobile phases indicate their strong adsorption through N atoms of three "dtc" moieties. The greater slopes observed for Tl(I) chelates with single adsorption site per molecule than expected is due to their polymeric nature and the lone pair effect. It is also found that Tl(III) chelates, usually faster moving than Tl(I) chelates with simple nonpolar mobile phases (Table 1), are found to be slower moving for binary mobile phases with solvent strengths below 0.11 ε° for N-alkyl derivatives and 0.15 ε° for heterocyclic derivatives (Figs. 1a, 1b, 2a, and 2b). This variation in mobility with solvent strength shows the predominance of solubilizing property over the adsorption characteristics of the chelate molecules. Binary mobile phases of chloroform with benzene, with a solvent strength around 0.25 ε° (*15*) and a solubility

TABLE 4[a]

Slopes of R_m vs log X_s Plots of Binary Mobile Phases Containing 2 to 15% of a Ketone/Ester/Alcohol as the Active Component with Carbon Tetrachloride as the Diluent

	Dime.		Die.		Dipr.		Me.ph.		Dibenz.		Pip.	
Active component	A	B	A	B	A	B	A	B	A	B	A	B
Ketones												
Acetone	1.08	1.33	1.54	1.67	1.38	1.67	1.33	1.67	1.48	1.54	1.14	1.33
MEK	1.25	1.33	1.15	1.29	1.54	1.60	1.03	1.21	1.33	1.54	1.14	1.33
MIBK	1.14	1.25	1.11	1.48	1.11	1.43	1.11	1.21	1.00	1.25	1.14	1.21
Cyclohexanone	1.11	1.40	0.98	1.23	1.00	1.25	1.21	1.38	1.05	1.21	1.03	1.43
Dioxan	1.21	1.38	1.25	1.60	1.21	1.54	1.33	1.43	1.25	1.82	1.18	1.58
Acetophenone	0.80	1.48	0.80	1.25	0.98	1.04	—	1.11	0.98	1.14	0.83	1.14
Esters												
Methyl acetate	1.01	1.11	1.14	1.21	1.00	1.21	1.01	1.11	1.08	1.67	0.85	1.33
Ethyl acetate	1.05	1.21	1.21	1.33	1.29	1.43	1.54	1.74	1.18	1.76	1.38	1.54
Butyl acetate	1.08	1.43	1.60	1.29	1.39	0.98	1.25	1.25	1.08	1.25	1.11	1.38
Alcohols												
Methanol	1.74	2.45	1.67	2.42	2.48	3.08	1.66	2.76	1.54	1.82	2.22	2.67
Ethanol	1.38	2.32	1.27	1.27	2.11	2.67	1.22	2.66	1.12	1.67	1.95	2.35
Propanol	0.95	1.29	0.95	0.95	0.95	2.01	1.14	1.91	0.88	1.35	1.74	1.21
Isopropanol	1.61	2.0	1.29	1.91	1.11	2.85	1.60	1.91	0.87	2.11	1.61	—
Isobutanol	0.91	1.33	0.87	1.48	0.88	1.82	1.25	2.16	1.38	1.67	1.33	—
Isoamyl alcohol	1.14	1.48	1.11	1.21	1.25	1.38	1.21	1.54	1.25	1.29	0.88	1.25

[a] MEK = methyl ethyl ketone; MIBK = methyl isobutyl ketone; A = Tl(I) dithiocarbamates; B = Tl(III) dithiocarbamates.

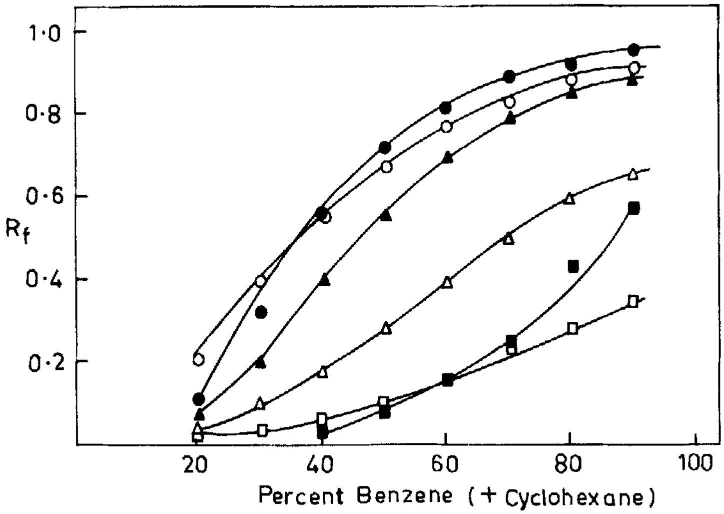

FIG. 1a. Plots of R_f vs percentage of benzene in the binary mobile phase with cyclohexane as the diluent. Dibutyl dithiocarbamate of Tl(I) (○) and Tl(III) (●). Dibenzyl dithiocarbamate of Tl(I) (△) and Tl(III) (▲). 1-Piperidine carbodithioate of Tl(I) (□) and Tl(III) (■).

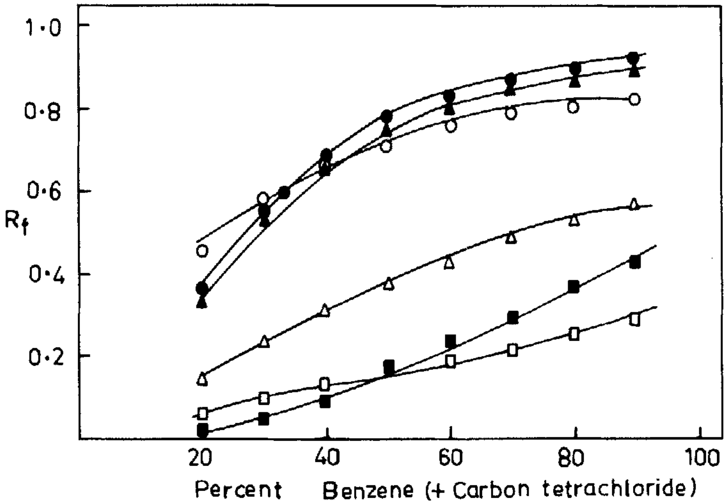

FIG. 1b. Plots of R_f vs percentage of benzene in the binary mobile phase with carbon tetrachloride as the diluent. Dibutyl dithiocarbamate of Tl(I) (○) and Tl(III) (●). Dibenzyl dithiocarbamate of Tl(I) (△) and Tl(III) (▲). 1-Piperidine carbodithioate of Tl(I) (□) and Tl(III) (■).

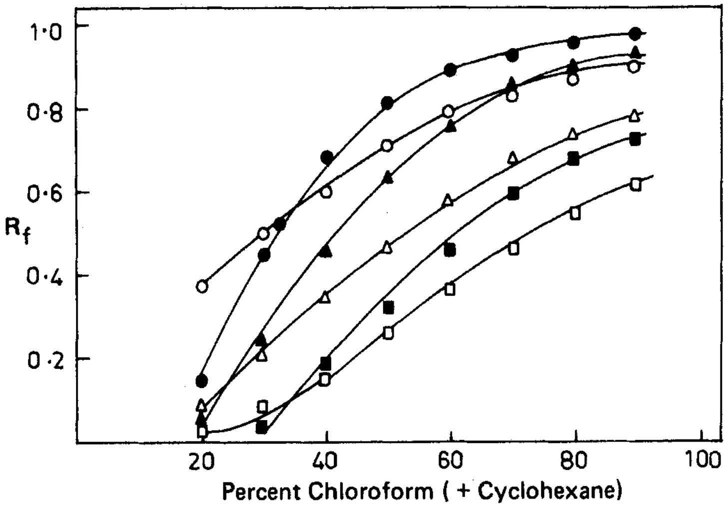

FIG. 2a. Plots of R_f vs percentage of chloroform in the binary mobile phase with cyclohexane as the diluent. Dibutyl dithiocarbamate of Tl(I) (○) and Tl(III) (●). Dibenzyl dithiocarbamate of Tl(I) (△) and Tl(III) (▲). 1-Piperidine carbodithioate of Tl(I) (□) and Tl(III) (■).

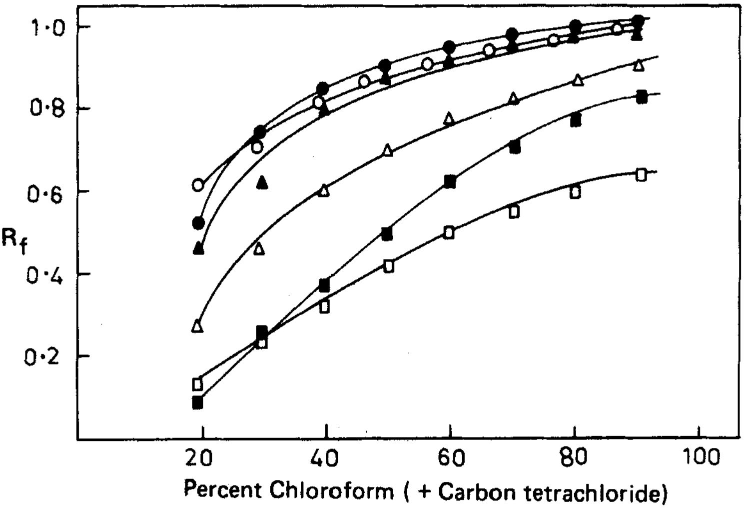

FIG. 2b. Plots of R_f vs percentage of chloroform in the binary mobile phase with carbon tetrachloride as the diluent. Dibutyl dithiocarbamate of Tl(I) (○) and Tl(III) (●). Dibenzyl dithiocarbamate of Tl(I) (△) and Tl(III) (▲). 1-Piperidine carbodithioate of Tl(I) (□) and Tl(III) (■).

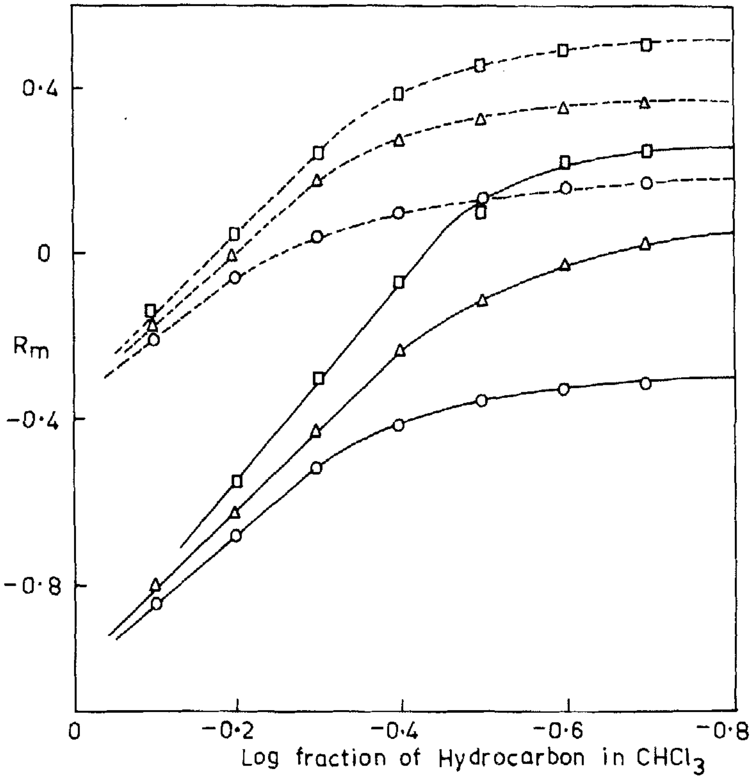

FIG. 3. Plots of R_m vs log X_s for *N*-methyl,*N*-phenyl dithiocarbamates of Tl(I) (- -) and Tl(III) (——). X_s = Fraction of hydrocarbon in chloroform; benzene (○), toluene (△), and xylene (□).

parameter around 9.2 δ_T (*15, 16*), showed better resolutions for these valencies with most of the chelate types (Fig. 3).

Binary mobile phases containing moderately polar ketones or esters as the active component also resolved these chelates with the same migratory behavior as with nonpolar mobile phases (Table 4). However, the low solubility parameters of these mobile phases containing 2 to 20% active component are not strong enough to desorb Tl(III) chelate molecules. However, with highly polar alcohol molecules as the active component, Tl(III) chelates migrated fast. Comparatively weak "sorption" of Tl(III) chelates on the primarily absorbed layers of polar alcohol molecules (*17*) may account for their fast migration in addition to their greater solvent strength and solubility parameters. R_m vs log X_s slopes were also found to decrease with an increase in the molecular area of the active component (Table 4). Iso alcohols with branched chain structure showed greater slopes than straight-chain *n*-alcohols. Spectrophotometric estimation of Tl(I) chelates, after separation and elution with nonpolar solvents, showed their chromatographic stability and quantitative separation. Tl(I) chelates were converted into Cu(II) chelates by metal-exchange reaction and allowed their spectrophotometric estimation at 436 nm (*5*).

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