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CHROMATOGRAPHIC BEHAVIOUR OF ALIPHATIC AMINES ON PHENOL-IMPREGNATED THIN LAYERS

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SUMMARY

The chromatographic characteristics of 16 aliphatic amines on silica gel plates impregnated with phenol, quinol, pyrogallol, o-cresol, p-chlorophenol and o-chlorophenol were studied and their correlation with the equilibrium constants of the adducts formed by the interaction of amines with o-chlorophenol as impregnant has been attempted. A suitable adsorbent system and a solvent system for the efficient separation of the amines have been developed.

INTRODUCTION

The use of impregnants for improving the thin-layer chromatographic (TLC) separation of phenols[1-3], aromatic amines[4-9] and aliphatic amines[10,11] has been described and seems to offer interesting possibilities for developing new systems for the separation of various classes of compounds. As hydrogen bond formation between the impregnant and aliphatic amines was considered to influence the chromatographic behaviour of the amines on metal salt-impregnated plates[12], it was considered worthwhile to investigate the influence of impregnation with other compounds capable of undergoing hydrogen bond formation with aliphatic amines. This paper describes studies on the chromatographic behaviour of aliphatic amines on silica gel plates impregnated with different phenols, and the determination of equilibrium constants of adducts formed between aliphatic amines and o-chlorophenol and their correlation with hR_F and R_M values.

EXPERIMENTAL

TLC plates (layer thickness 0.5 mm) were prepared by spreading with a Stahl-type applicator a slurry of 50 g of silica gel G (BDH, Poole, Great Britain) and various amounts of impregnants in 100 ml of distilled water, except for o-cresol, for which water–ethanol (9:1) was used. The plates were dried for 24 h at a constant temperature of $60 \pm 1°C$. Different phenols used as impregnants were either recrystallized or redistilled and kept in dark glass containers before use.

TABLE I

SEPARATION OF ALIPHATIC AMINES (hR_F VALUES) ON SILICA GEL G PLATES WITH n-BUTANOL–ACETIC ACID–WATER (35:5:10)

Amine	Non-impregnated silica gel G	Silica gel G impregnated with a 2% (v/v) solution of different phenols					
		Phenol	Quinol	Pyrogallol	o-Cresol	p-Chlorophenol	o-Chlorophenol
Methylamine	28**	29***	20	20	27	23***	26
Dimethylamine	33**	31	21	18	32	25	31
Trimethylamine	35**	35	32	30	37	33	35
Ethylamine	49**	47***	42	40	49	42***	46
Diethylamine	54**	52	40	42	54	46	50
Triethylamine	62**	54	48	44	55	50	53
n-Propylamine	59***	55	50	48	58	55	57
Isopropylamine	66***	61	55	51	61	59	63
Di-n-butylamine	85	82	72	67	82	78	80
Tri-n-butylamine	90	87	79	70	89	81	85
Diethylenetriamine	26*	20***	10	6	20***	15***	17
Ethylenediamine	30*	22***	16	10	22***	21***	22
Cyclohexylamine	82	74	68	64	77	72	76
Allylamine	63***	56	50	45	58	54	60
Diallylamine	70***	63	58	56	63	62	66
Triethanolamine	38***	33	25	25	33	28	38

* Strong tailing.
** Medium tailing.
*** Slight tailing.

Aqueous solutions of amines were applied to the TLC plate by means of a micropipette (Clay Adams, Parsippany, NJ, U.S.A.) and developed with n-butanol–acetic acid–water (35:5:10).

An aqueous solution of cobalt(II) thiocyanate, prepared by dissolving ammonium thiocyanate (3 g) and cobalt(II) chloride (1 g) in 20 ml of distilled water, was used as the spray reagent for detecting all amines on silica gel and phenol-impregnated plates, except for pyrogallol- and quinol-impregnated plates. The amines appeared as blue spots. The colour faded after 2 h, but was restored by spraying with water or keeping the plates in a humid atmosphere. For pyrogallol- and quinol-impreganted plates, a solution of 3 g of ninhydrin in 100 ml of n-butanol + 3 ml of acetic acid was used. After spraying with the ninhydrin solution, the plates were heated at 100°C, when violet-red spots were obtained.

RESULTS AND DISCUSSION

Tertiary amines and aza aromatic compounds act as good electron donors towards phenol in forming strong hydrogen bonds[13,14]. Impregnation of silica gel plates with different phenols was therefore carried out in order to study the chromatographic behaviour of different aliphatic amines on these impregnated plates.

Table I gives the hR_F values of 16 aliphatic amines on silica gel G plates, impregnated with 2% aqueous solution of various phenols, using n-butanol–acetic acid–water (35:5:10) as developing solvent; this system was found to be the most suitable after investigating different proportions of the components. For comparison, aliphatic amines were also chromatographed on non-impregnated silica gel G plates using the same solvent system.

On phenol-impregnated plates, methylamine, ethylamine, ethylenediamine and diethylenetriamine showed slight tailing, and methylamine–dimethylamine–triethanolamine, diethylamine–triethylamine–n-propylamine–allylamine and diethylene-triamine–ethylenediamine were not separated. A difference in hR_F values of ± 3 was taken as a criterion for satisfactory separation. On quinol- and pyrogallol-impregnated plates, tailing of the spots was greatly reduced but the hR_F values of a number of amines were close to each other. Further, on activation the TLC plate turned dark grey with pyrogallol and light brown with quinol as impregnant. With o-cresol as impregnant, the spots of ethylenediamine and diethylenetriamine showed slight tailing, and diethylamine–triethylamine, n-propylamine–allylamine and dimethylamine–triethanolamine were not separated. With p-chlorophenol as impregnant, the spots of methylamine, ethylamine, ethylenediamine and diethylenetriamine showed slight tailing, and methylamine–dimethylamine and triethylamine–n-propylamine–allylamine were not separated. On non-impregnated silica gel G plates the tailing of the spots was much greater than that on impregnated plates. Also, many of the aliphatic amines were not separated.

The best separation of all the aliphatic amines studied was obtained when 2% o-chlorophenol was used as the impregnant. There was no tailing with any of the amines and the hR_F values differed by 3 or more units in each instance. Further, the hR_F values of the amines did not change when a mixture of them was applied and the spots were smallest with o-chlorophenol-impregnated plates.

Influence of o-chlorophenol concentration

Table II gives the hR_F values of amines on thin layers of silica gel containing increasing concentrations of o-chlorophenol. The hR_F values for a particular amine decrease as the concentration of o-chlorophenol increases and becomes almost constant for most of the amines at concentrations higher than 2%. Tailing of spots for some amines was observed when 0.5 or 1% of impregnant was employed. However, no tailing for any of the amines was observed when the concentration of o-chlorophenol was 2%. Hence 2% was the most suitable concentration.

TABLE II

SEPARATION OF ALIPHATIC AMINES (hR_F VALUES) ON SILICA GEL G IMPREGNATED WITH DIFFERENT CONCENTRATIONS OF o-CHLOROPHENOL USING n-BUTANOL–ACETIC ACID–WATER (35:5:10)

Amine	o-Chlorophenol concentration (% v/v)				
	0.5	*1*	*2*	*3*	*5*
Methylamine	28***	28	26	26	26
Dimethylamine	33***	32	31	31	31
Trimethylamine	35***	35	35	35	35
Ethylamine	48***	46	46	46	46
Diethylamine	52***	52	50	50	50
Triethylamine	60***	55	53	53	53
n-Propylamine	59	59	57	57	57
Isopropylamine	66	64	63	63	63
Di-n-butylamine	83	81	80	80	78
Tri-n-butylamine	89	86	85	85	84
Diethylenetriamine	23**	20***	17	17	15
Ethylenediamine	27**	24***	22	22	20
Cyclohexylamine	80	79	76	76	77
Allylamine	63	60	60	60	60
Diallylamine	69	60	66	60	60
Triethanolamine	38	38	38	38	38

** Medium tailing.
*** Slight tailing.

Before discussing the possible role of o-chlorophenol in the silica gel–o-chlorophenol system, it should be noted that the trends of the hR_F values obtained for different amines with non-impregnated silica gel and with silica gel–o-chlorophenol (50:2, w/v)-impregnated layers are similar (Table I). Hence, it is reasonable to assume that the forces responsible for TLC separation in the two instances are similar. It is pertinent to point out that Pires and Roseira[18] accounted for the TLC separation of aromatic amines on silica gel G plates by assuming the presence of a hydrogen bond of the type

Si—OH- - - -N
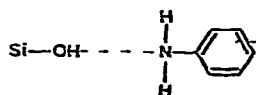
Hence the separation of aliphatic amines on o-chlorophenol-impregnated plates may also be due to hydrogen bond formation between the H atom of the OH group of o-chlorophenol and N atom of the NH₂ group of the amine.

To verify this possibility and to establish any correlations between the chromatographic behaviour of aliphatic amines on o-chlorophenol-impregnated plates and the hydrogen bonding therein, equilibrium studies were carried out on hydrogen bond formation between o-chlorophenol and aliphatic amines, using the spectroscopic method of Baba and Suzuki[15].

The increase in absorbance of the shifted band with increase in donor concentration was employed for the calculation of equilibrium constants for hydrogen bond formation. The equilibrium constants were calculated from the following equation given by Baba and Suzuki[15]:

$$\frac{1}{\varepsilon - \varepsilon_f} = \frac{1}{K(\varepsilon_p - \varepsilon_f)} \cdot \frac{1}{C} + \frac{1}{(\varepsilon_p - \varepsilon_f)} \tag{1}$$

where

ε_f = molar extinction coefficient of the non-hydrogen-bonded or free molecole;

ε_p = molar extinction coefficient of the hydrogen-bonded molecule;

ε = molar extinction coefficient as observed in solution in which the concentration of electron donor is ϱ.

By keeping the concentration of the electron acceptor and the cell length constant, throughout a set of spectra, the ε terms in Baba and Suzuki's equation can be replaced with the corresponding absorbances (A) and the equilibrium constant can be evaluated from a plot of $1/(A - A_f)$ versus $1/C$.

All of the studies were confined to the benzenoid absorption region in the range 260–290 nm and at a constant temperature of 30 ± 0.5°C. The solutions of o-chlorophenol and amines were prepared in cyclohexane. A typical spectrum of the system o-chlorophenol–cyclohexylamine is shown in Fig. 1. This shows the presence of isosbestic points which indicate the existence of a 1:1 hydrogen-bonded complex between the OH group of o-chlorophenol and the lone pair of electrons of the N atoms of the amine. Similar behaviour was observed for the other amines.

The values of A and A_f, read at 35,000 cm⁻¹ in each instance, are given in Table III together with the concentration (C) of the amine used in each run.

For calculating the equilibrium constant for hydrogen bond formation in each instance, $1/(A - A_f)$ was plotted against $1/C$ (Figs. 2 and 3). By extrapolation of the line to cut the $1/C$ axis, the value of the equilibrium constant (K) of hydrogen bond formation for each amine was evaluated (Tables III and IV).

For studying the correlation between K and the ΔhR_F values or between log K and ΔR_M, ΔhR_F and ΔR_M were evaluated; the values are given in Table IV and plots of K versus ΔhR_F and log K versus ΔR_M are shown in Fig. 4. It can be seen that the hR_F value for any particular amine is lower on the impregnated than on the non-impregnated silica gel plate, that ΔhR_F increases linearly with K and that ΔR_M is linearly related to log K. These results suggest that amongst the various forces responsible for the TLC separation of amines, hydrogen bond formation plays a prominent role.

TABLE III

CALCULATIONS OF $1/(A - A_f)$ AND $1/C$ FOR ALIPHATIC AMINES WITH o-CHLOROPHENOL

All studies were carried out at 30°C and the absorbance were measured at 35,000 cm⁻¹.

| Amine	o-Chlorophenol concentration (M)	No.	A	A_f	$A - A_f$	C	$\dfrac{1}{A - A_f}$	$\dfrac{1}{C}$
Cyclohexylamine	$4.0 \cdot 10^{-4}$	1	0.230	0.18	0.050	$1.9 \cdot 10^{-3}$	20.00	525
		2	0.255	0.18	0.075	$3.0 \cdot 10^{-3}$	13.33	333
		3	0.280	0.18	0.100	$4.2 \cdot 10^{-3}$	10.00	238
		4	0.325	0.18	0.145	$7.0 \cdot 10^{-3}$	6.89	142
		5	0.375	0.18	0.195	$9.8 \cdot 10^{-3}$	5.12	102
Isopropylamine	$5.0 \cdot 10^{-4}$	1	0.250	0.22	0.030	$1.66 \cdot 10^{-3}$	33.33	600
		2	0.270	0.22	0.050	$2.8 \cdot 10^{-3}$	20.00	357
		3	0.350	0.22	0.130	$8.3 \cdot 10^{-3}$	7.10	120
		4	0.380	0.22	0.160	$9.8 \cdot 10^{-3}$	6.30	102
Diallylamine	$4.0 \cdot 10^{-4}$	1	0.195	0.18	0.015	$1.33 \cdot 10^{-3}$	66.60	750
		2	0.210	0.18	0.030	$2.8 \cdot 10^{-3}$	33.33	357
		3	0.225	0.18	0.045	$4.20 \cdot 10^{-3}$	22.22	238
		4	0.250	0.18	0.070	$7.0 \cdot 10^{-3}$	14.30	142
Tri-n-butylamine	$4.0 \cdot 10^{-4}$	1	0.225	0.22	0.005	$1.4 \cdot 10^{-3}$	200.00	714
		2	0.235	0.22	0.015	$2.80 \cdot 10^{-3}$	66.66	357
		3	0.240	0.22	0.020	$4.2 \cdot 10^{-3}$	50.00	238
		4	0.250	0.22	0.030	$7.0 \cdot 10^{-3}$	33.33	142
		5	0.260	0.22	0.040	$9.8 \cdot 10^{-3}$	25.00	102
Diethylenetriamine	$5.0 \cdot 10^{-4}$	1	0.260	0.22	0.040	$0.6 \cdot 10^{-3}$	25.00	1600
		2	0.340	0.22	0.120	$1.8 \cdot 10^{-3}$	8.33	550
		3	0.420	0.22	0.200	$2.8 \cdot 10^{-3}$	5.00	350
		4	0.460	0.22	0.240	$3.5 \cdot 10^{-3}$	4.16	280
		5	0.50	0.22	0.280	$4.5 \cdot 10^{-3}$	3.57	220
Ethylenediamine	$4.8 \cdot 10^{-4}$	1	0.262	0.20	0.062	$1.32 \cdot 10^{-3}$	16.12	757
		2	0.300	0.20	0.100	$2.22 \cdot 10^{-3}$	10.00	450
		3	0.36	0.20	0.160	$4.0 \cdot 10^{-3}$	6.25	250
		4	0.40	0.20	0.200	$5.0 \cdot 10^{-3}$	5.00	200
Triethylamine	$5.2 \cdot 10^{-4}$	1	0.280	0.25	0.030	$1.17 \cdot 10^{-3}$	33.330	854
		2	0.310	0.25	0.060	$2.66 \cdot 10^{-3}$	16.660	375
		3	0.335	0.25	0.085	$4.00 \cdot 10^{-3}$	11.760	250
		4	0.358	0.25	0.108	$5.0 \cdot 10^{-3}$	9.259	200
Di-n-butylamine	$5.1 \cdot 10^{-4}$	1	0.270	0.24	0.030	$1.48 \cdot 10^{-3}$	33.330	675
		2	0.300	0.24	0.060	$3.00 \cdot 10^{-3}$	16.660	333
		3	0.330	0.24	0.090	$5.00 \cdot 10^{-3}$	11.110	200
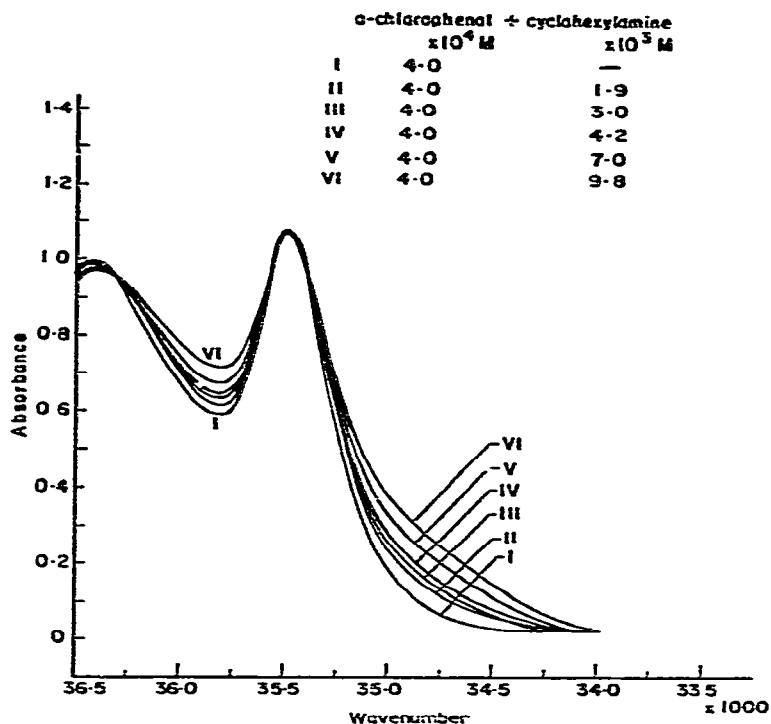
Fig. 1. Absorption spectra of *o*-chlorophenol–cyclohexylamine system in cyclohexane.
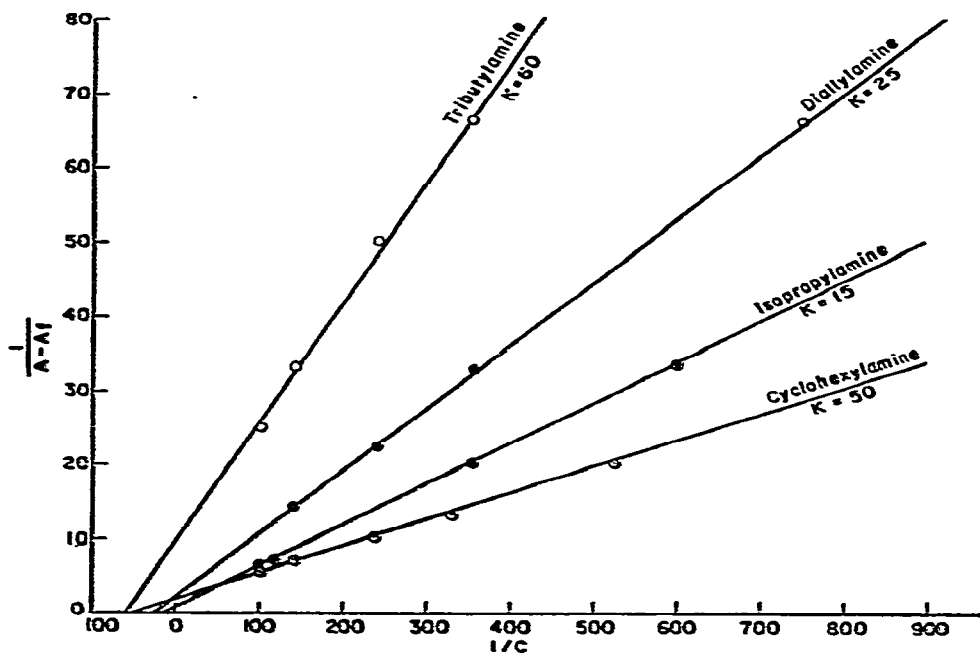

Fig. 2. Plot of $1/(A - A_f)$ versus $1/C$.

TABLE IV

pK_a VALUES, EQUILIBRIUM CONSTANTS, ΔhR_F VALUES AND ΔR_M VALUES

| Amine	pK_a	Equilibrium constant of adducts		Adsorbent				Difference between hR_F and R_M	
				Non-impregnated silica gel		Silica gel + 2% o-chlorophenol (50:2, w/v)			
		K	$Log\ K$	hR_F	R_M	hR_F	R_M	ΔhR_F	ΔR_M
Triethylamine	11.010	70	1.840	62**	−0.213	53	−0.052	9	−0.161
Isopropylamine	10.720	15	1.170	66***	−0.288	63	−0.231	3	−0.057
Di-n-butylamine	10.560	45	1.650	85	−0.753	80	−0.602	5	−0.151
Tri-n-butylamine	10.830	60	1.778	90	−0.954	85	−0.753	5	−0.201
Diethylenetriamine		95	1.977	26*	0.454	17	0.689	9	−0.235
Ethylenediamine	10.712	80	1.900	30*	0.368	22	0.550	8	−0.192
Cyclohexylamine	10.660	50	1.698	82	−0.659	76	−0.551	6	−0.158
Diallylamine		25	1.397	70***	−0.368	66	−0.288	4	−0.080

* Strong tailing.
** Medium tailing.
*** Slight tailing.
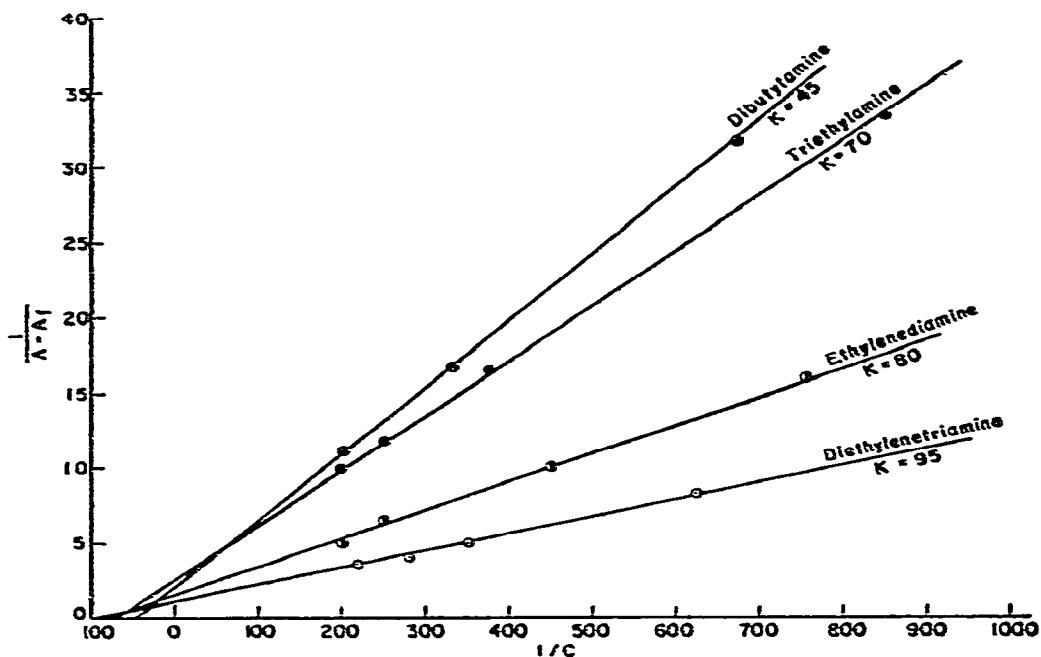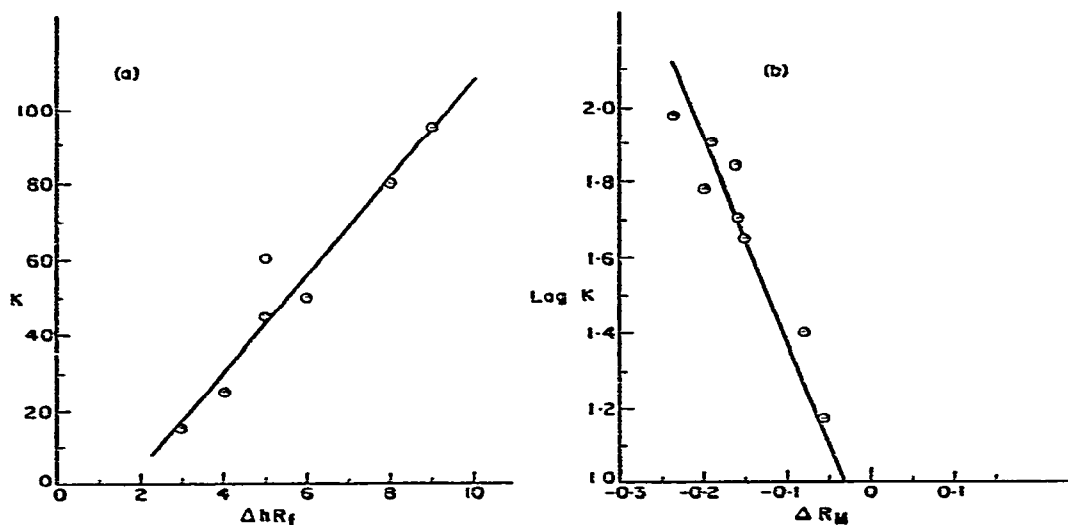
Fig. 3. Plot of $1/(A - A_f)$ versus $1/C$.

Fig. 4. (a), Relationship between K and ΔhR_F; (b), relationship between log K and ΔR_M.

In order to establish whether there was any correlation between the $\Delta R'_M$ values and the basicities of the amines, $\Delta R'_M$ values were calculated with the help of conversion factors given by Snyder[16], by taking ε as 1.1 and tabulated pK_a values[17]. The values are given in Table V and the plot of pK_a versus $\Delta R'_M$ is shown in Fig. 5. It

TABLE V

pK_a AND $\Delta R'_M$ VALUES

Amine	pK_a	A*		B**		Difference
		hR_F	R'_M	hR_F	R'_M	($\Delta R'_M$)
Methylamine	10.657	28	0.35	26	0.40	−0.05
Dimethylamine	10.732	33	0.24	31	0.29	−0.05
Trimethylamine	9.810	35	0.20	35	0.20	0.00
Ethylamine	10.807	49	−0.07	46	−0.01	−0.06
Diethylamine	10.489	54	−0.17	50	−0.09	−0.08
Triethylamine	11.010	62	−0.33	53	−0.15	−0.18
n-Propylamine	10.704	59	−0.27	57	−0.23	−0.04
Isopropylamine	10.720	66	−0.42	63	−0.35	−0.07
n-Butylamine	10.560	85	−1.16	80	−0.87	−0.29
Tri-n-butylamine	10.830	90	−2.00	85	−1.16	−0.84
Diethylenetriamine	—	26	0.40	17	0.64	−0.24
Ethylenediamine	10.712	30	0.31	22	0.50	−0.19
Cyclohexylamine	10.660	82	−0.97	76	−0.71	−0.26
Allylamine		63	−0.35	60	−0.29	−0.06
Diallylamine		70	−0.53	66	−0.15	−0.38
Triethanolamine		38	0.14	38	0.14	0.00

* A = Non-impregnated silica gel.
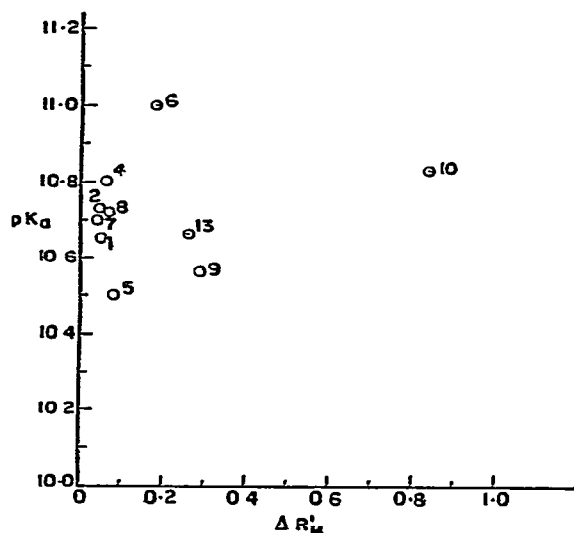** B = silica gel G + 2% o-chlorophenol (50:2, w/v).

Fig. 5. Relationship between pK_a and $\Delta R'_M$. 1 = Methylamine; 2 = dimethylamine; 4 = ethylamine; 5 = diethylamine; 6 = triethylamine; 7 = n-propylamine; 8 = isopropylamine; 9 = n-butylamine; 10 = tri-n-butylamine; 13 = cyclohexylamine.

can be seen that no correlation exists between the pK_a value of an amine and the $\Delta R'_M$ value, unlike the behaviour observed by Yasuda[4] in the TLC separation of aromatic amines on silica gel layers impregnated with cadmium sulphate.

It therefore seems that the TLC behaviour of aliphatic amines on silica gel G thin layers and o-chlorophenol-impregnated layers is due to hydrogen bond formation between the amine and silica gel in the former instance and between the amine and silica gel as well as o-chlorophenol in the latter.

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