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Thin-layer chromatography of aromatic amines on cadmium acetate impregnated silica gel thin layers*

Extending previous work[1], results of investigations regarding the separation of aromatic amine isomers on silica gel layers impregnated with various cadmium salts, *i.e.* sulphate, acetate, phosphate, etc., are now reported. Better mutual separation of some amines, such as anisidines and xylidines, is achieved on cadmium acetate impregnated layers.

The relationship between R'_M value[2] and basicity of the amine was also studied in more detail. A close correlation, which can be expressed by the following equation, was observed from the data obtained on unimpregnated silica gel layers.

$$R'_M = a + b(\mathrm{p}K_a) + c(\mathrm{p}K_a)^2 \qquad (1)$$

Cadmium sulphate impregnation was found to increase b, the coefficient of the first order term of the above equation, and a linear dependence between the difference of the R'_M values and the $\mathrm{p}K_a$ values of the amines, which had been suggested in the previous paper, was also observed in some cases. Cadmium acetate, on the other hand, rather increased the standard deviations between R'_M values and $\mathrm{p}K_a$ values.

Experimental

Thin layers, 0.2–0.25 mm thickness, were prepared according to the method described in the previous paper[1], and the amines were spotted on the layers as 0.5% methanolic solutions.

4-Methoxyazobenzene, picric acid, and 4-(2'-hydroxy-1'-naphthylazo)-2,5-dimethoxy-benzanilide** were developed alongside the amines as reference compounds. The R_F values of the amines were then corrected by means of the correction equation proposed by DHONT *et al.*[3] and the R_F values of the reference compounds.

Results

The corrected R_F values of amines are shown in Table I. A few amines gave spots which tailed; R_F data of such spots are marked st(spot length/spot width being between 2 and 4) or t(ratio more than 4).

Mean R_S values (*ortho* isomer = 1.00) of *meta* and *para* isomers were calculated from the data of toluidines, anisidines, chloroanilines, and bromoanilines and are shown in Table II. Judging from these R_S values, cadmium sulphate impregnation seems to give the best separation of isomers. But experimentally better results were sometimes obtained on cadmium acetate impregnated layers. For example, *ortho* and *meta* isomers of anisidines or six isomers of xylidines were separated from each other only on the latter layers.

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** This compound was obtained by coupling diazotized Naphthol Fast Blue RR and 2-naphthol, and purified by the recrystallization from a benzene–pyridine mixture.

TABLE I

R_F × 100 VALUES AND pK_a VALUES OF AROMATIC AMINES ON UNIMPREGNATED AND IMPREGNATED THIN LAYERS

Ref. 1 = 4-Methoxyazobenzene; ref. 2 = picric acid; ref. 3 = 4-(2′-hydroxy-1′-naphthylazo)-2,5-dimethoxy-benzanilide.
Solvent systems: S_1 = benzene–acetic acid (9:1); S_2 = benzene–acetic acid (8:2); S_3 = benzene–ethyl acetate–acetic acid (10:10:1); S_4 = benzene–ethyl acetate–acetic acid (6:3:1). Layers: L_1 = Unimpregnated layer; L_2 = cadmium sulphate impregnated layer; L_3 = cadmium acetate impregnated layer; L_4 = cadmium phosphate impregnated layer.

Amines	R_F × 100 value														pK_a value
	S_1				S_2				S_3			S_4			
	L_1	L_2	L_3	L_4	L_1	L_2	L_3	L_4	L_1	L_2	L_3	L_1	L_2	L_3	
o-Toluidine	26	13	22	24	28	18t	34st[a]	20	47	41	52	46	22st	41	4.4
m-Toluidine	17	8	12	15	12	11t	26t[a]	12	34	30t	33	37	14st	26	4.7
p-Toluidine	12	4	8	9	17	9t	20t	9	24	17st	23	35st	6st	18st	5.1
o-Anisidine	19	11st	18	20st	28	11t	29t	16st	47	36t	44st	49	22st	31	4.5
m-Anisidine	18	8st	13	16st	26	11t	27t	16st	34	35t	35st	46	20st	26	4.2
p-Anisidine	5	1	6	5	12	4t	19t	3	13	14t	11	13	3	5	5.3
2,3-Xylidine	15	6	26t	18	20	18st	32st	16	36	41st	52	37st	16st	27	4.7
2,4-Xylidine	13	5	23t	15	18	17st	31st	14	33	36st	46	33	13st	23	4.9
2,5-Xylidine	20	10	31t	23	26	22st	38st	19	45	48t	56	47	22	34	4.5
2,6-Xylidine	35	27	49	41	45	41	57	37	62	70	76	61	46	59	4.0
3,4-Xylidine	9	4	12	13	13	12st	22st	9	22	21t	23st	23	6	12	5.2
3,5-Xylidine	15	6	18t	18	17	14st	29st	14	32	36t	34st	36	14st	22	
o-Chloroaniline	62	64	70	60	65	71	70	62	80	87	84	70	72	75	2.6
m-Chloroaniline	44	33	34	44	49	44	44st	44	71	70	63	61	57	50	3.3
p-Chloroaniline	32	15	25	30	37	26st	35st	30	60	45st	48	53	36	39st	3.8
o-Bromoaniline	64	64	73	62	66	73	74	66	81	85	85	74	73	77	2.6
m-Bromoaniline	45	36	36	45	51	49	44st	47	71	71	64	65	60	53	3.5
p-Bromoaniline	34	18	26	34	40	32	35st	30	62	54	51	58	43	41	3.9
1-Naphthylamine	33	27st	35st	37	40	35st	47	49	67	64	67	64st	47st	51	4.0
2-Naphthylamine	24	18	23	27	37	20t	34st	37t	56	28t	52t	55t	24t	36t	4.1
o-Aminobenzoic acid	44	43st	13	41	58	52		55	66		13st				2.1
m-Aminobenzoic acid	14	10	3	14	25	11		24	47		4				3.1
p-Aminobenzoic acid	33	31	12	33	47	42		44	54		17st				2.4
o-Aminobiphenyl	59	51	65	60	61		76		82		86				3.8
p-Aminobiphenyl	27	10t	21	26	33		39		69		50				4.3
o-Phenethidine	26	14t	29	24	30		41		69		61				4.5
p-Phenethidine	9	4	6	12	13		19		21		16				5.3
2,5-Dichloroaniline	71	70	73	65	74	80	75	69	77	78	80	87			1.5
Ref. 1	15	47	4	19	24	65	11	31	23	60	8t	12	54	7	
Ref. 2	74	74	85	72	79	88	91	77	79	80	86	88	90	94	
Ref. 3	45	62	74		60	74	86	63	75	85	90	72	75	83	

[a] For explanation of st and t, see text.

TABLE II

MEAN R_S VALUES OF ISOMERS (R_F VALUE OF *ortho*-ISOMER = 1.00)
For solvent systems and thin layers, see Table I.

	S_1				S_2			
	L_1	L_2	L_3	L_4	L_1	L_2	L_3	L_4
meta isomer	0.75	0.61	0.56	0.72	0.80	0.73	0.73	0.76
para isomer	0.44	0.23	0.35	0.42	0.56	0.44	0.56	0.40

	S_3			S_4		
	L_1	L_2	L_3	L_1	L_2	L_3
meta isomer	0.80	0.84	0.73	0.87	0.79	0.71
para isomer	0.58	0.49	0.47	0.58	0.28	0.42

Discussion

The relationship between the R'_M and pK_a values of amines is clearly shown in Figs. 1–6, in which the R'_M values of amines on various layers are plotted against the pK_a values of amines. This shows that the amino group in the amines takes the leading role in the adsorption to the surface of silica gel, and the contribution of the other groups towards the adsorption may be much smaller than that of the amino group, since the adsorption energy[4] of the amino group to the silica gel is much larger than that of the other groups. As is shown in Figs. 1–3, the R'_M values of the amino-

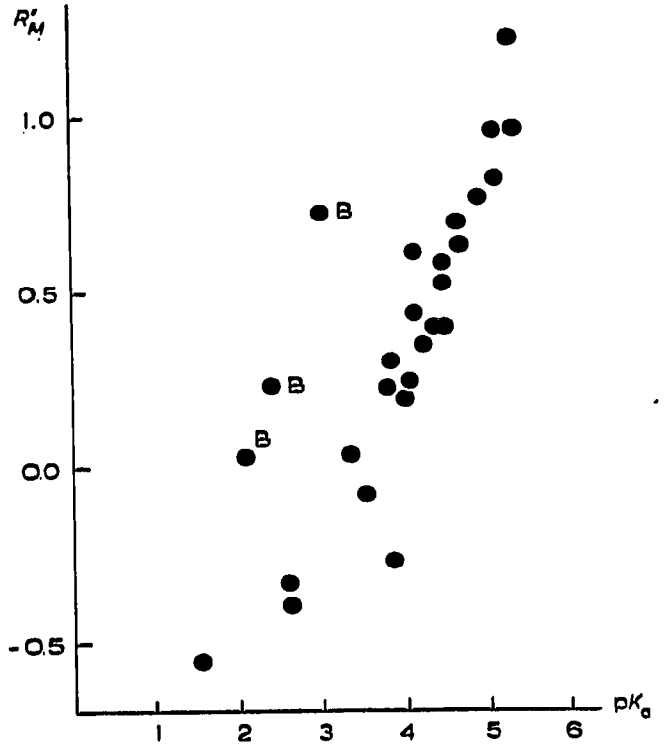

Fig. 1. Relationships between the R'_M and pK_a values of amines on unimpregnated silica gel thin layers. Solvent system: benzene–acetic acid (9:1). B = Aminobenzoic acid.

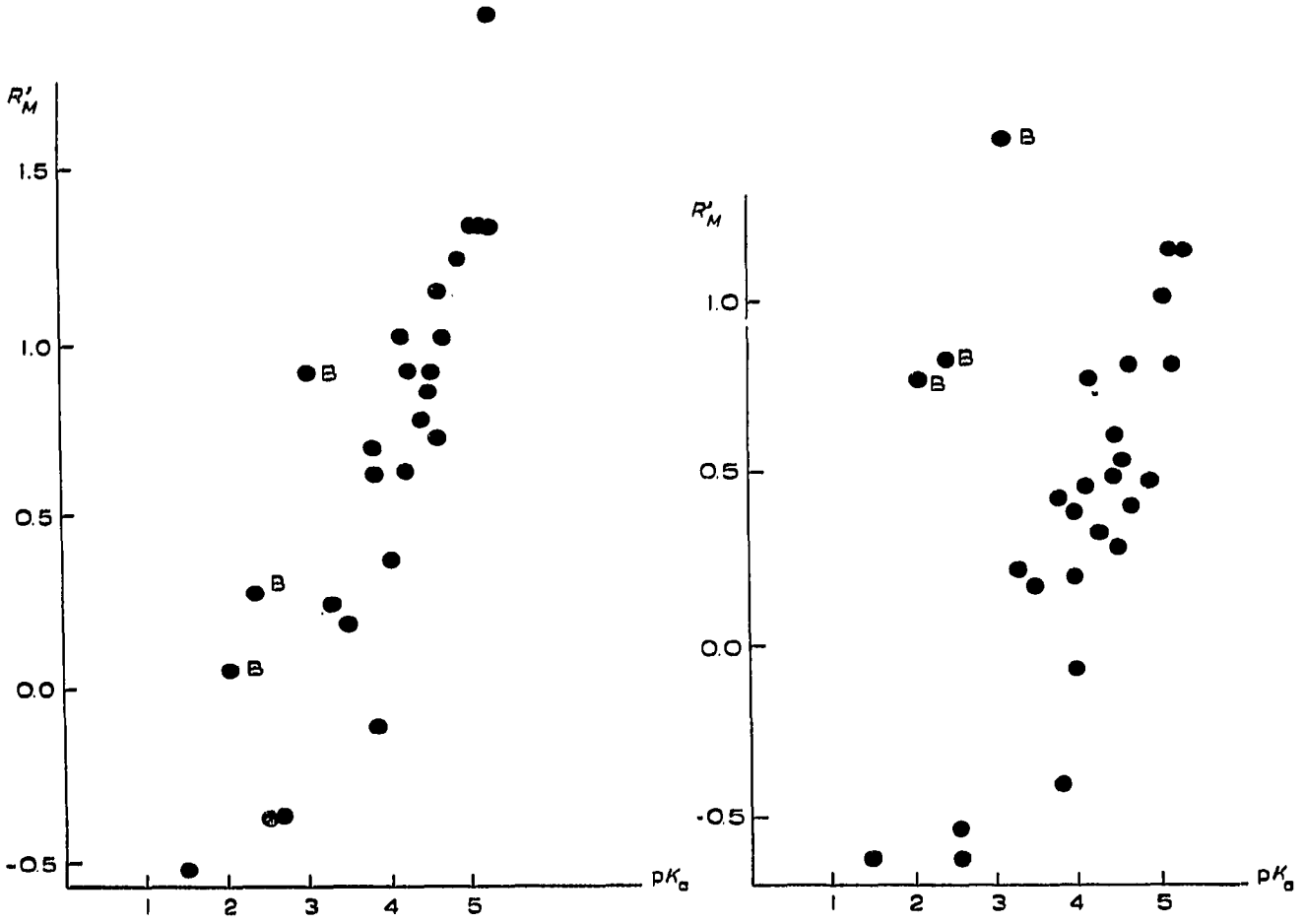

Fig. 2. Relationships between the R'_M and pK_a values of amines on cadmium sulphate impregnated silica gel thin layers. Solvent system: benzene–acetic acid (9:1). B = Aminobenzoic acid.

Fig. 3. Relationships between the R'_M and pK_a values of amines on cadmium acetate impregnated silica gel thin layers. Solvent system: benzene–acetic acid (9:1). B = Aminobenzoic acid.

benzoic acids have properties which differ from those of the other amines. This may be due to the larger adsorption energy of the carboxyl group as opposed to that of the amino group.

The relationship between the R'_M and pK_a values of the amines can be expressed as the general equation (1). The coefficients of each of the terms were calculated and are shown in Table III. The R'_M values of the aminobenzoic acids were, however, omitted from the calculation, since the values were far from normal.

Impregnation with cadmium sulphate increased b, the coefficient of the first order term, and, as is shown in Figs. 7 and 8, the $\Delta R'_M$ values, *i.e.*, the differences between the R'_M values on layers impregnated with salt and on unimpregnated layers, were found to have a clear relationship with the pK_a values of the amines. This may suggest that the amino group of the amines, or more correctly, an unshared electron pair in the amino group, also plays a part in the adsorption of the amino groups on cadmium sulphate. As the pK_a values of aromatic amines generally increase in the order of the *ortho*, *meta* and *para* isomers, good separation can be expected on

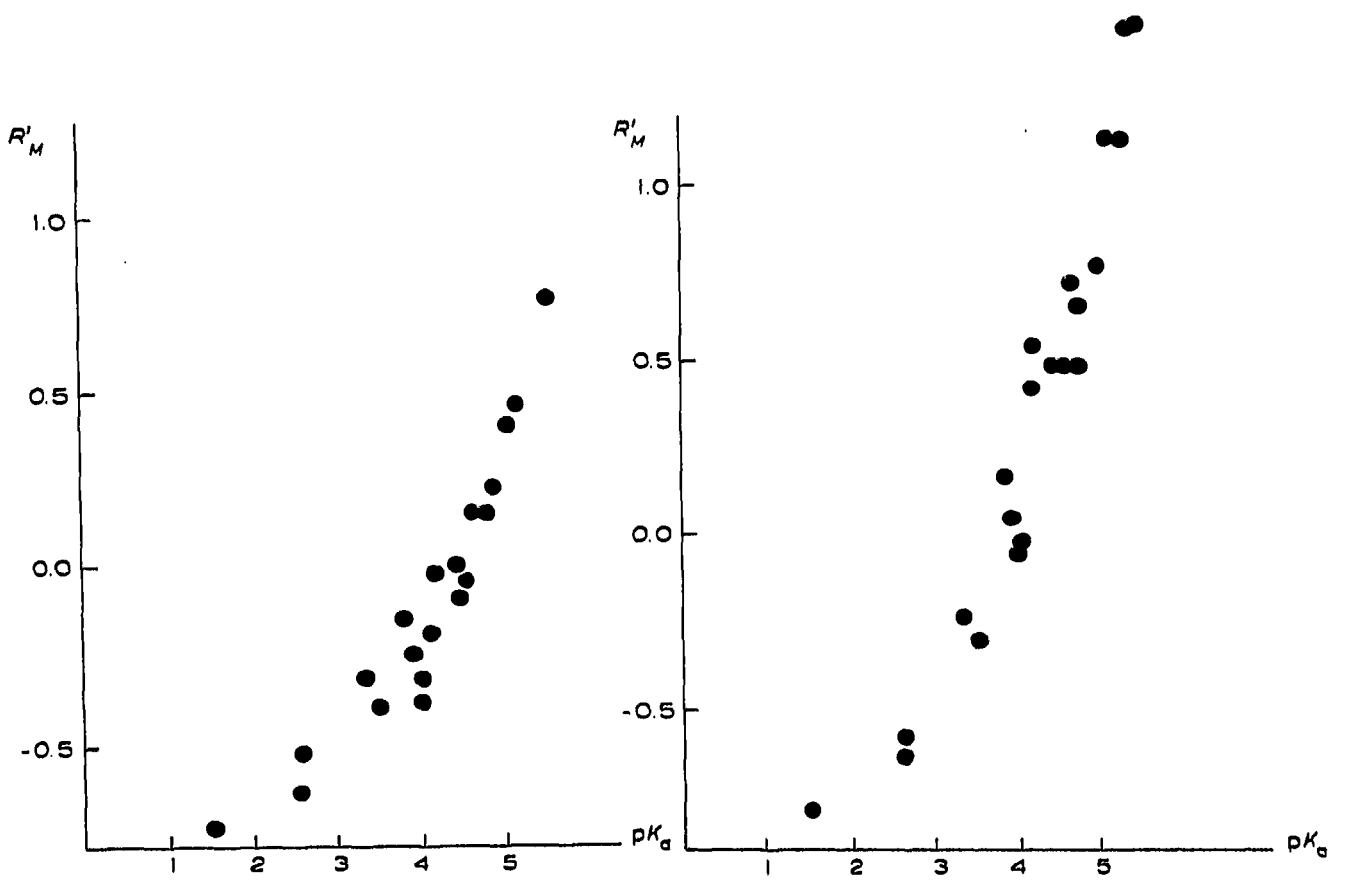

Fig. 4. Relationships between the R'_M and pK_a values of amines on unimpregnated silica gel thin layers. Solvent system: benzene–ethyl acetate–acetic acid (6:3:1).

Fig. 5. Relationships between the R'_M and pK_a values of amines on cadmium sulphate impregnated silica gel thin layers. Solvent system: benzene–ethyl acetate–acetic acid (6:3:1).

TABLE III

COEFFICIENTS OF EQUATION (1) FOR THE FOLLOWING RELATIONSHIP BETWEEN R'_M AND pK_a: $(X = pK_a; y = R'_M)$ $y = a + b(X - \bar{X}) + c(X - \bar{X})^2$

For solvent systems and their layers, see Table I.

Solvent system	*Thin layer*	$\bar{X}$	*a*	*b*	*c*	*Standard deviation*	*Fo 1st order*[a]	*Fo 2nd order*[a]
S_1	L_1	4.11	0.37	0.47	0.05	0.13	241	12
	L_2	4.11	0.68	0.62	0.06	0.21	181	7.1
	L_3	4.11	0.36	0.48	0.05	0.25	73	1.7
S_3	L_1	4.23	−0.15	0.57	0.14	0.26	87	5.4
	L_2	4.17	−0.08	0.68	0.07	0.26	106	1.0
	L_3	4.23	−0.09	0.36	0.07	0.30	49	0.5
S_4	L_1	4.04	−0.09	0.36	0.06	0.10	217	28
	L_2	4.04	0.31	0.60	0.08	0.13	368	27
	L_3	4.04	0.21	0.49	0.05	0.18	139	5.4

[a] *Fo* means that the F-test was made from observed values.

cadmium sulphate impregnated layers. Unsatisfactory results were, however, sometimes obtained on this layer, especially for the separation of amines with similar pK_a values.

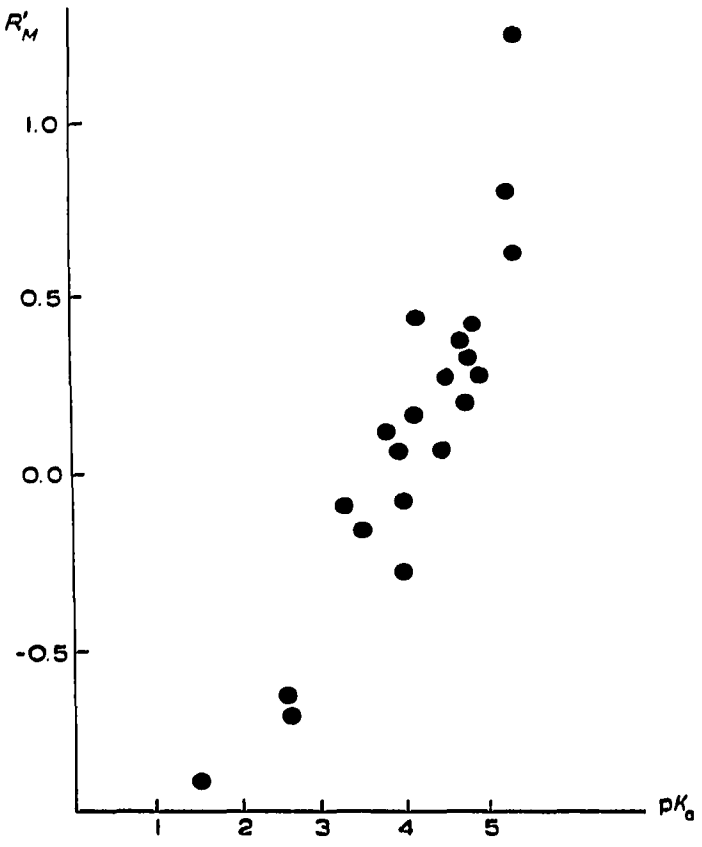

Fig. 6. Relationships between the R'_M and pK_a values of amines on cadmium acetate impregnated silica gel thin layers. Solvent system: benzene–ethyl acetate–acetic acid (6:3:1).

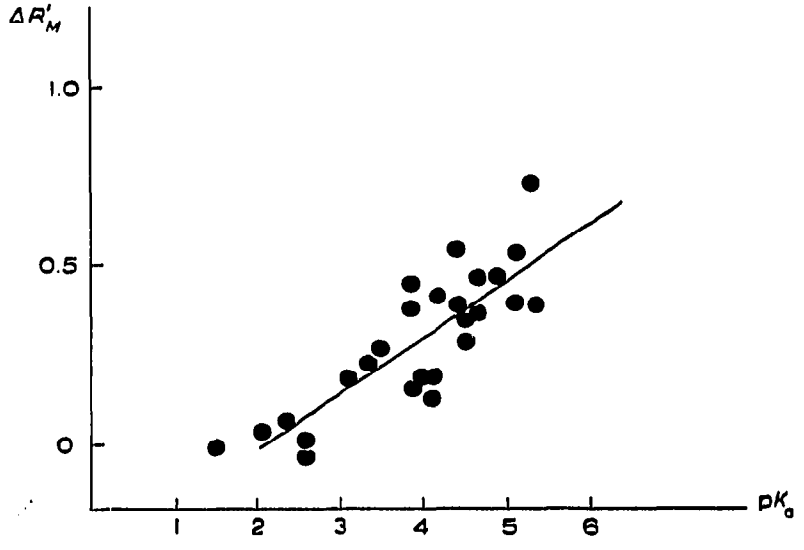

Fig. 7. Relationships between the $\Delta R'_M$ and pK_a values of amines on cadmium sulphate impregnated silica gel thin layers. Solvent system: benzene–acetic acid (9:1). $\Delta R'_M = 0.16\,[pK_a] - 0.34$; $r = 0.84$.

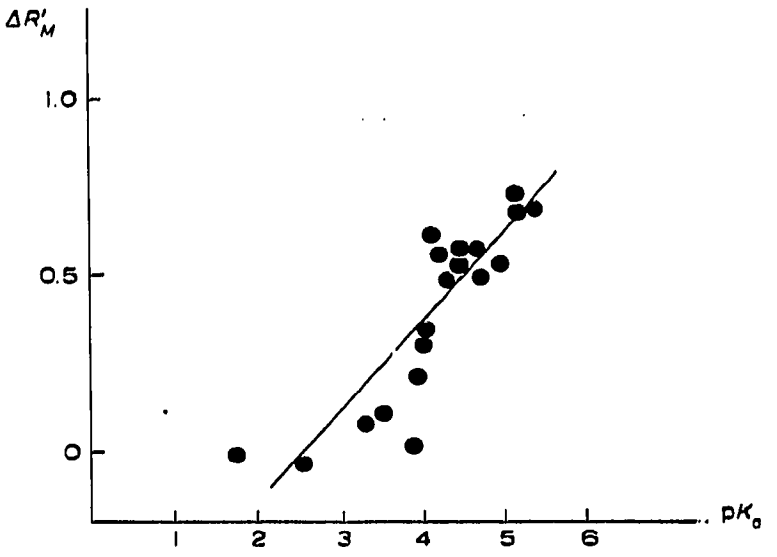

Fig. 8. Relationships between the $\Delta R'_M$ and pK_a values of amines on cadmium sulphate impregnated silica gel thin layers. Solvent system: benzene–ethyl acetate–acetic acid (6:3:1). $\Delta R'_M = 0.25\,[pK_a] - 0.63$; $r = 0.89$.

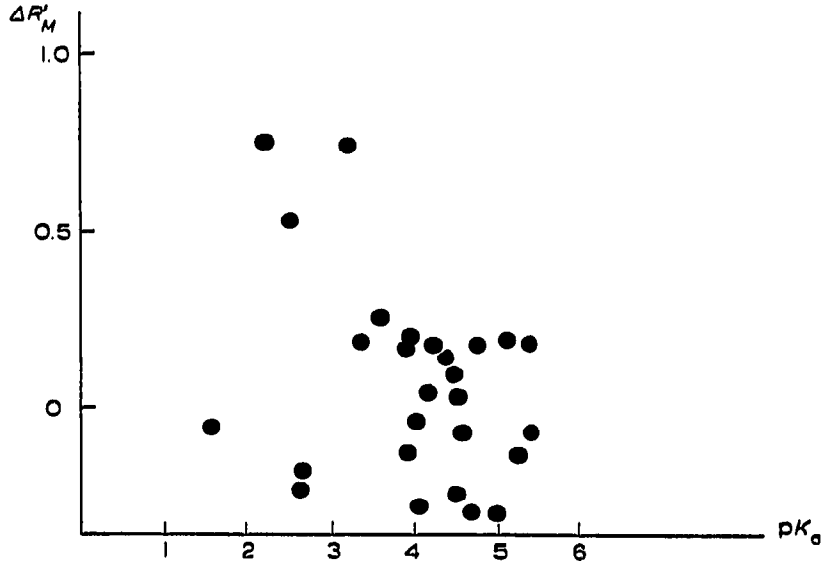

Fig. 9. Relationships between the $\Delta R'_M$ and pK_a values of amines on cadmium acetate impregnated silica gel thin layers. Solvent system: benzene–ethyl acetate–acetic acid (6:3:1).

Cadmium acetate, on the other hand, had the effect of increasing the standard deviations in the equation. As is shown in Fig. 9, the $\Delta R'_M$ values have little correlation with the pK_a values on cadmium acetate impregnated layers. Supposedly, impregnation with the latter salt introduces some new factors which affect the separation mechanism on the layers. A characteristic of the separation of amines on cadmium acetate impregnated layers was the partial reduction of the tailing of spots, but these unknown factors may be considered to be primarily responsible for it.

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Industrial Research Institute, Osaka Pref.,
Osaka (Japan)

KENJI YASUDA

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