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Thin-layer chromatography of chlorinated anilines on zinc salt-impregnated silica gel thin layers

As reported in previous papers[1,2], isomers of aromatic primary amines showed remarkable separations on silica gel thin layers impregnated with cadmium salts and with acidic mobile phases. In those separations a relationship, which can be expressed by the following equation, was observed between the $\mathrm{p}K_a$ and R_F values of amines:

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

The coefficient of the first-order term, b, was increased on impregnation with the cadmium salt. The coefficient of the second-order term, c, on the other hand, had positive, little changed, and considerably large values. Although there are advantages in handling many aromatic amines with ordinary basicities ($\mathrm{p}K_a$ 2.5–5.0), such tendencies suggested some disadvantages in separating weaker basic amines, such as polyhalogenated anilines.

Little is known on the chromatographic separation of dichloroanilines. A few attempts [3,4] have been reported on the gas chromatography of these compounds, but satisfactory conditions for the separation of the six isomers were not found. Thin-layer chromatography was used by FISHBEIN[5].

Cadmium, in addition, is a toxic element and special caution must be taken when handling thin layers impregnated with cadmium compounds.

This paper reports the results of an attempt to separate halogenated anilines on silica gel thin layers impregnated with zinc salts, which are far less toxic than cadmium compounds. The six isomers of dichloroaniline were separated from each other on thin layers impregnated with zinc chloride or zinc nitrate and with mobile phases containing formic acid. Impregnation with these salts increased b, and decreased a and c in eqn. 1. In particular c was decreased to negative values when the amount of salts on the thin layers was increased.

Experimental

Thin layers of 0.2–0.25 mm thickness were prepared by the method described earlier[1,2]. Activated layers were stored in a constant humidity chamber with saturated sodium dichromate solution. Some layers impregnated with zinc chloride or zinc nitrate were hygroscopic and were therefore stored in a desiccator with activated silica gel.

Thin layers of trimethylsilylated silica gel were prepared by the following procedure. To a suspension containing 50 g of silica gel (E. Merck, less than 0.08 mm for chromatography) in 160 ml of cyclohexane, 34 ml of hexamethyldisilazane were added, and the mixture was refluxed for 1 h. After adding 2 ml of isopropanol, the mixture was refluxed for a further 3 h, and the solid was separated by filtration. The solid was washed with isopropanol, dried at 130° for 3 days, and stored in a desiccator. The silica gel obtained was so hydrophobic that a methanol–water mixture (1:1) was used to prepare thin layers.

4-Methoxyazobenzene, picric acid and 4-(2′-hydroxy-1′-naphthylazo)-2,5-

dimethoxybenzanilide were developed with amines as reference compounds for the correction of R_F values.

The thin layers and solvent mixtures used are listed in Tables I and II, respectively.

The application of *p*-dimethylaminobenzaldehyde solution or exposure to nitrogen oxides followed by spraying with 1-naphthylamine solution was used in order to detect the spots of the amines.

TABLE I

THIN LAYERS USED

No.	*Layer*	*Impregnation*	*Solid: salt ratio (w/w)*
L1	Silica Gel G	None	
L2	Silica Gel G	$ZnCl_2$	2:1
L3	Silica Gel G	$ZnCl_2$	4:1
L4	Silica Gel G	$ZnCl_2$	8:1
L5	Silica Gel G	$ZnCl_2$	16:1
L6	Silica Gel G	$Zn(NO_3)_2 \cdot 6H_2O$	2:1
L7	Silica Gel G	$Zn(CH_3COO)_2 \cdot 2H_2O$	2:1
L8	Silanized silica gel	None	
L9	Silanized silica gel	$Zn(NO_3)_2 \cdot 6H_2O$	2:1

TABLE II

MOBILE PHASES USED

No.	*Proportions of components in solvent mixture*					
	Benzene	*Ethyl acetate*	*Acetic acid*	*Formic acid*	*Methanol*	*Carbon tetrachloride*
S1	39				1	
S2	5	5				
S3	4	1				
S4	6	3	1			
S5	7	2	1			
S6	6	3		1		
S7	7	2		1		
S8		2		1		1

Results

R_F values for the amines are shown in Table III.

The six isomers of dichloroaniline were separated from each other on L2, L3 and L6 thin layers and with S7 or S8 as the mobile phase with a run of 15 cm. Monohalogenated anilines or more basic amines, on the other hand, gave tailing spots with low R_F values, and were therefore incompletely separated.

Solvents containing acetic acid were found to be inferior to those containing formic acid in the separation of 2,3-, 2,4- and 3,5-dichloroanilines.

TABLE III

R_F VALUES OF AROMATIC AMINES ON ZINC SALT-IMPREGNATED THIN LAYERS

Amine	pK_a	*L1*								*L2*			*L3*		*L4*				*L5*		*L6*		*L7*	*L8*	*L9*
		S1	*S2*	*S3*	*S4*	*S5*	*S6*	*S7*	*S8*	*S4*	*S6*	*S7*	*S6*	*S7*	*S4*	*S5*	*S6*	*S7*	*S6*	*S7*	*S6*	*S7*	*S4*	*S7*	*S7*
2,3-Dichloroaniline	1.8	57	78	71	70	63	63	66	56	37	43	28	37	34	69	69	39	36	47	40	46	45	66	74	28
2,4-Dichloroaniline	2.0	56	77	71	68	61	62	63	53	33	37	23	31	26	65	67	34	30	42	33	39	36	65	74	23
2,5-Dichloroaniline	1.5	64	81	76	73	67	67	69	64	55	57	45	51	49	74	73	53	53	62	53	62	60	71	74	44
2,6-Dichloroaniline	0.4	69	83	80	77	73	70	73	73	89	79	80	77	76	79	77	71	73	73	71	79	77	74	76	72
3,4-Dichloroaniline	3.0	46	72	67	61	49	38	27	17	26	27	14	21	10	33	35	20	15	23	13	15	13	44	68	16
3,5-Dichloroaniline	2.4	53	79	72	68	62	59	52	41	37	35	20	28	20	58	60	29	26	37	24	26	24	59	74	18
2,4,5-Trichloroaniline		61			71	69	69		65	78	76	68	68	64	76	72	67	63	69	63	72	69	70		
2,4,6-Trichloroaniline		70			77		73		72	88	81	88	82	81	81	79	79	76	79	73	81	79	75		
2-Chloroaniline	2.6		79	75	70	62		44							54	60		11		22	19	18	60	67	10
3-Chloroaniline	3.3		74	68	59	42		18							23	27		7		8	12	10	36	61	9
4-Chloroaniline	3.8		70	63	49	27		9							18	14		5		8	10	8	20	60	9
2-Bromoaniline	2.6	57			71	65		49	42			8			59	65		13		23	24	21	61		
3-Bromoaniline	3.5	46			61	44		20	11			7			29	29		7		11	15	11	37		
4-Bromoaniline	3.9				54	29		11							22	18		7		10	13	9	20		
2-Anisidine	4.5	24			43	18		8	1			2			11	8		2		4			20		
4-Aminophenol	5.5	4			4				0			0			0	2		0		0			2		
Ref. 1		71	86	81	75	73	72	75	72	92	87	58	79	80	79	78	74	75		73	80	79	73		
Ref. 2		0	7	2	20	28	54	55	34			4									67	65	11		
Ref. 3		51	81	76	68	60	63	64	54	87	54	11†	60†	57†	55	52	58	57		51	72	68	67		

Thin layers impregnated with zinc chloride or nitrate adsorbed atmospheric moisture when left in the ambient atmosphere, and amines migrated too near the solvent front on such layers. The storage of these thin layers in a desiccator therefore seemed essential for satisfactory separations.

Impregnations with zinc phosphate, silicate and formate were also attempted. Probably owing to the poor solubilities of these salts in water, however, little improvement in the separation was effected on these layers. Impregnation with zinc sulphate was also impracticable, as the layers swelled up and broke down in the development chamber with acidic solvents.

The weakest basic amines, *i.e.*, 2,6-dichloroaniline and 2,4,6-trichloroaniline, gave only faint and transient colour spots with *p*-dimethylaminobenzaldehyde, but were detected clearly by exposure to nitrogen oxides followed by spraying with 1-naphthylamine solution.

Disscussion

The coefficients of eqn. 1 for some combinations of thin layers and solvents are given in Table IV, in which an increase in *b*, and a decrease in *a* and *c* by the impregnation with zinc salts can be seen clearly. As shown in Fig. 1, each coefficient also seems to bear some relationships to the amount of zinc chloride on the layers. These phenom-

TABLE IV

COEFFICIENTS IN EQUATION 1

Thin layer	*Mobile phase*	*a*	*b*	*c*
L1	S1	−0.37	−0.11	0.07
	S2	−1.07	0.12	0.01
	S3	−0.91	0.16	−0.01
	S4	−0.48	−0.28	0.10
	S5	−0.55	−0.08	0.08
	S6	−0.42	−0.25	0.14
	S7	−0.79	0.13	0.07
	S8	−0.62	−0.04	0.07
L2	S4	−2.43	2.08	−0.39
	S6	−1.15	0.84	−0.11
	S7	−1.19	0.93	−0.07
L3	S6	−1.09	0.88	−0.11
	S7	−1.11	0.78	−0.02
L4	S4	−0.98	0.19	0.05
	S5	−0.78	−0.04	0.10
	S6	−0.76	0.50	−0.02
	S7	−0.99	0.76	−0.05
L5	S6	−0.75	0.30	0.04
	S7	−0.83	0.57	−0.02
L6	S6	−1.23	0.85	−0.08
	S7	−1.13	0.76	−0.05
L7	S4	−0.67	0.00	0.07
L8	S7	−0.70	−0.03	0.04
L9	S7	−0.67	0.92	−0.11

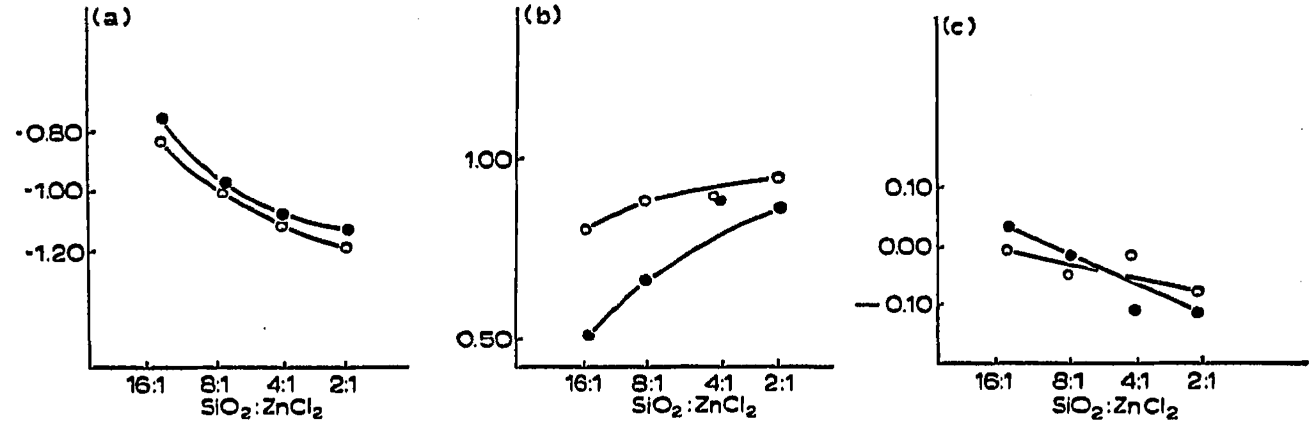
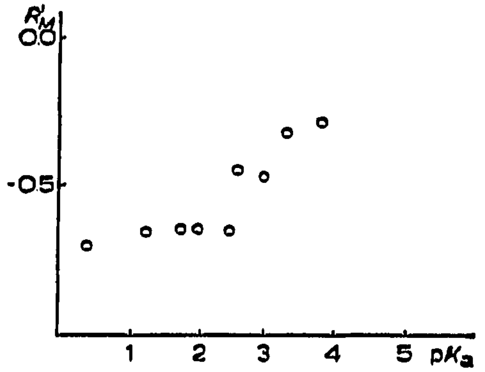


Fig. 1. Relationships between the coefficients in eqn. 1 and the SiO_2: $ZnCl_2$ ratio: (a) *a*; (b) *b*; (c) *c*. Mobile phase: ●, S6; ○, S7.



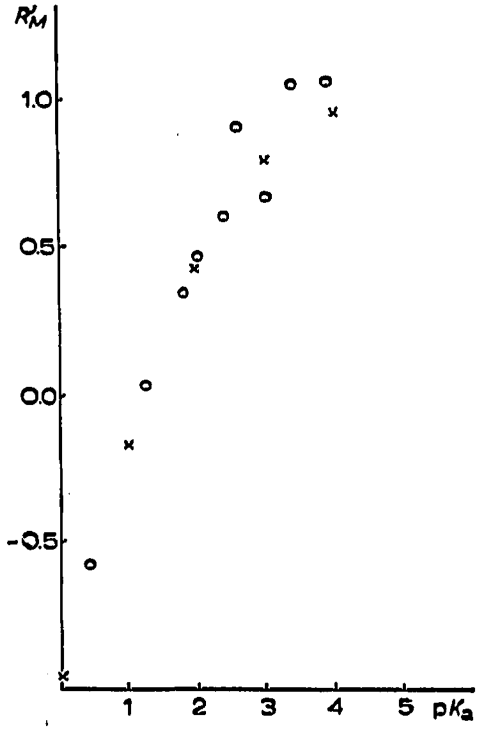


Fig. 2. Relationship between R'_M and pK_a valves of amines on layer L8 with S7 as the mobile phase.

Fig. 3. Relationship between R'_M and pK_a values of amines on layer L9 with S7 as the mobile phase. ○, Experimental values; ×, calculated values.

ena suggest that the basicities of amines are primarily responsible for the improved separation, and the mechanism of this separation has some similarities with ligand-exchange chromatography[6] in which the electron donation from amines to metal atoms plays a major role. The results for the development of silanized layers, shown in Figs. 2 and 3, also suggest that the ordinary adsorption mechanism with silica gel plays only a minor role in separations on such thin layers.

There is a possibility of controlling the coefficients of eqn. 1, and as shown in Figs. 4–6, good consistency between the values obtained and those in eqn. 1 may also

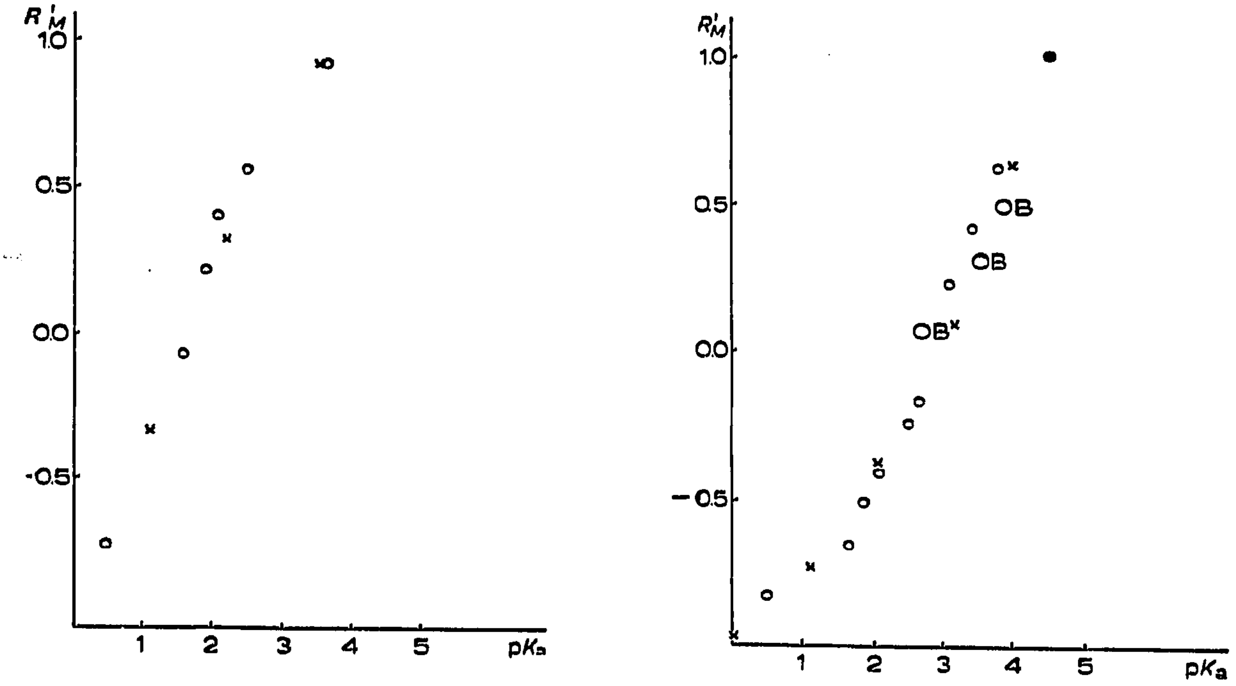


Fig. 4. Relationship between R'_M and pK_a values of amines on layer L3 with S7 as the mobile phase. ○, Experimental values; ×, calculated values.

Fig. 5. Relationship between R'_M and pK_a values of amines on layer L4 with S4 as the mobile phase. ○, Experimental values; OB, bromoanilines; ●, *p*-anisidine; ×, calculated values.

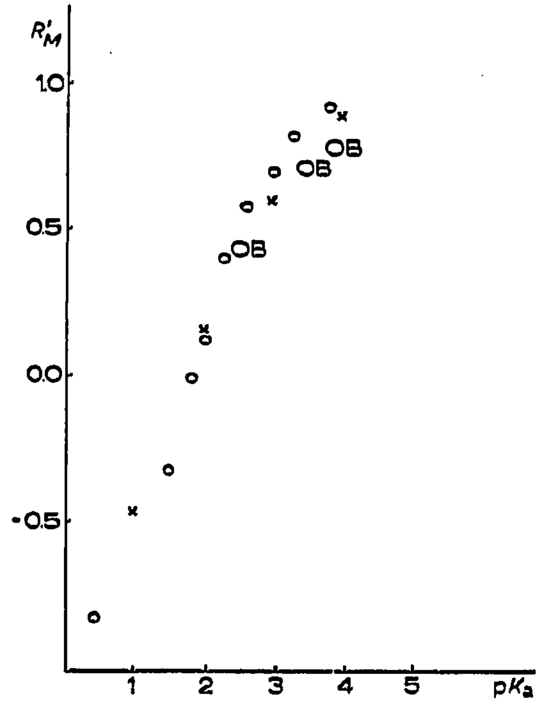


Fig. 6. Relationship between R'_M and pK_a values of amines on layer L6 with S6 as the mobile phase. ○, Experimental values; OB, bromoanilines; ×, calculated values.

suggest the possibility of obtaining adequate R_F values of amines if their pK_a values are known or of estimating approximate pK_a values of amines from their R_F values.

As shown in Figs. 5 and 6, bromoanilines showed similar tendencies to the chlorinated homologues, but always showed slightly lower R'_M values than those expected from eqn. 1. Such deviations may be due to differences in the energies of adsorption[7] of chlorine and bromine atoms to silica gel and the area of the gel occupied by those atoms[7]. The addition of a term to the equation to take account of the effects of other substituted groups may sometimes be advantageous so as to make the agreement of the equation with the experimental results more satisfactory. This correction term will be studied in detail in future investigations.

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