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Note

Thin-layer chromatography of aromatic amines on silica gel thin layers impregnated with manganese salts*

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As was stated in previous papers,[1-3] the use of acidic mobile phases on silica gel thin layers, impregnated with cadmium or zinc salts, sometimes achieved remarkable mutual separations of the isomers of aromatic primary amines. R_F values of aromatic amines on silica gel thin layers with acidic solvents have a relationship with the dissociation constants of the compounds, as is expressed in the following equation.

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

where $R'_M = \log(1/R'_F - 1)$, $\mathrm{p}K_a$ = the dissociation constant and a, b and c are constants.

Such impregnations cause considerable changes in value of the coefficients of the equation, *i.e.*, generally increasing a and decreasing b. The donation of the unshared electrons of the amino group in the sample molecule to the metal or silica gel surface may give a good explanation of this behaviour. Observed values are, however, sometimes so varied that other factors might play a part.

This paper reports the results of an attempt at the chromatographic separation of aromatic amines on silica gel thin layers impregnated with manganese salts. Since these salts are expected to form less stable complexes with amines than other salts, the effects of factors other than charge transfer may appear more clearly on these layers.

EXPERIMENTAL

Thin layers of 0.2–0.25 mm thickness were prepared in the manner described earlier, and stored in a constant humidity chamber with saturated sodium dichromate solution.

Samples were spotted on the layers as 0.5% methanolic solutions and detected by spraying 4-dimethylaminobenzaldehyde solution or by exposure to nitrogen oxides.

4-Methoxyazobenzene, picric acid, and 4-(2′-hydroxy-1′-naphthylazo-)-2,5-dimethoxybenzanilide were developed together with amines as reference compounds for the correction of R_F values.

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RESULTS AND DISCUSSION

Corrected R_F values of the amines are shown in Table I.

Some monosubstituted amines, such as toluidines, naphthylamines and monohalogenated anilines, showed improved mutual separations on manganese salt im-

TABLE I

R_F VALUES AND pK_a VALUES OF AROMATIC AMINES

L1 = Silica gel without impregnation; L2 = silica gel–$Mn(CHO_2)_2 \cdot 2H_2O$ (6:1); L3 = silica gel–$Mn \cdot Na_2EDTA \cdot 2H_2O$ (2:1); L4 = silica gel–$Mn(C_2H_3O_2)_2 \cdot 4H_2O$, (4:1). S1 = benzene–acetic acid (9:1); S2 = benzene–ethyl acetate–acetic acid (6:3:1); S3 = benzene–ethyl acetate–acetic acid (7:2:1); S4 = benzene–ethyl acetate–formic acid (6:3:1); S5 = benzene–ethyl acetate–formic acid (7:2:1).

Amine	pK_a	R_F												
		L1				*L2*					*L3*		*L4*	
		S1	*S2*	*S4*	*S5*	*S1*	*S2*	*S3*	*S4*	*S5*	*S1*	*S3*	*S1*	*S3*
Aniline	4.6					6	23	23	4	2	19	40	15	30
o-Toluidine	4.4	26	46			17	35	38	5	4	29	54	28	45
m-Toluidine	4.7	17	37			10	25	28	3	3	19	44	18	30
p-Toluidine	5.1	12	25			6	15	18	3	2	12	31	10	19
o-Anisidine	4.5	19	49		8	12	32	32	3	3	26	47	27	42
m-Anisidine	4.2	18	46			9	27	27	4	3	21	36	18	31
p-Anisidine	5.3	5	13			3	5	6	4	2	7	10	5	7
o-Chloroaniline	2.6	62	70		44	57	66	64	51	50	61	70	61	66
m-Chloroaniline	3.3	44	61		18	36	55	53	17	17	46	60	45	55
p-Chloroaniline	3.8	32	53		9	23	44	41	7	9	35	50	31	46
o-Bromoaniline	2.6	64	74		48	60	68	67	55	58	63	71	67	69
m-Bromoaniline	3.5	45	65		20	42	56	57	19	25	44	61	51	61
p-Bromoaniline	3.9	35	58		11	29	45	41	11	12	37	52	39	54
o-Iodoaniline		55	63	51	44	57	66	68	55	43	63	72		
m-Iodoaniline		31	57	17	13	29	54	54	19	9	43	59		
p-Iodoaniline		22	49	11	8	22	46	45	12	4	25	51		
1-Naphthylamine	4.0	33	64			22	50	46	8	7	36	57	30	57
2-Naphthylamine	4.1	24	55			13	39	36	5	4	27	48	20	43
2,3-Xylidine	4.7	15	37			9	22	20	3	3	21	43	18	34
2,4-Xylidine	4.9	13	33			7	18	17	4	3	19	37	15	27
2,5-Xylidine	4.5	20	47			12	20	29	4	4	27	49	22	41
2,6-Xylidine	4.0	35	61			27	51	46	8	10	43	62	45	58
3,4-Xylidine	5.2	9	23			6	11	10	4	3	10	23	10	18
3,5-Xylidine		15	36			8	19	17	4	3	16	37	10	28
2,3-Dichloroaniline	1.8			63	66	55	64	68	66	65	61	68	58	65
2,4-Dichloroaniline	2.0			62	63	54	64	61	65	63	60	68	56	66
2,5-Dichloroaniline	1.5	71	87	67	69	65	71	68	71	70	65	73	58	70
2,6-Dichloroaniline	0.4			70	73	72	72	67	74	74	71	77	63	70
3,4-Dichloroaniline	3.0			38	27	43	53	55	37	35	46	58	42	54
3,5-Dichloroaniline	2.4			59	52	56	62	62	62	59	54	65	50	61
o-Aminodiphenyl	3.8	59					67		22					
p-Aminodiphenyl	4.2	27					38		8					
o-Phenetidine	4.5	26					38		6					
p-Phenetidine	5.3	9					7		4					
N-Methylaniline	4.8					10	35	32	4	4	27	53		
N,N-Dimethylaniline	5.1					9	26	29	2	2	31	55		
N-Methyl-*m*-toluidine	4.9					8	25	26	3	3	24	47		
N,N-Dimethyl-*m*-toluidine	4.7						21	24	2	3	25	48		

pregnated layers. In particular, complete separation, which has never been achieved on ordinary layers, was obtained for the *o*- and *m*-anisidines on L3 and L4. However, an improved but still incomplete separation of six isomers of xylidine and inferior results for dichloroanilines were also obtained. Attempts to employ the layers impregnated with manganese sulphate or chloride resulted in failure, because the layers swelled up and broke down in the developing chambers. Manganese nitrate was also found impracticable, as the layers turned black when they were heated for activation. A strange phenomenon was observed on the layers impregnated with an increased amount of manganese acetate: the solvent fronts always stopped midway through developing, within a few centimeters from the start points, and soon started to recede.

Though considerable reduction of R_F values was sometimes observed on manganese salt impregnated layers, especially on L2, Table II shows that changes in value of the coefficients of the equation on these layers are generally smaller than, or opposite to those obtained on other layers impregnated with cadmium or zinc salts. This suggests that the ease of complex formation of manganese salts with amines is, as expected, less than those of cadmium and zinc.

TABLE II

COEFFICIENTS OF EQUATION 1

L5: silica gel-$3CdSO_4 \cdot 8H_2O$ (2:1); L6: silica gel-$Cd(C_2H_3O_2)_2 \cdot 2H_2O$ (2:1). L7: silica gel-$ZnCl_2$ (2:1). For solvent systems and other layers see Table I.

Thin-layer	*Solvent*	*Coefficient*		
		a	*b*	*c*
L1	S1	−0.58	−0.10	0.08
	S2	−0.48	−0.28	0.10
	S3	−0.55	−0.08	0.08
	S5	−0.79	−0.13	0.07
L2	S1	−0.55	−0.04	0.08
	S2	−0.46	−0.22	0.09
	S5	−1.04	0.30	0.05
L3	S1	−0.03	−0.29	0.09
	S3	−0.28	−0.29	0.09
L4	S1	−0.44	−0.09	0.07
	S3	−0.55	−0.14	0.06
L5	S1	−0.69	−0.10	0.10
L6	S1	−0.96	0.09	0.05
L7	S5	−1.19	0.93	−0.07

Fig. 1 not only confirms the existence of the relationship between R'_M values and pK_a values of amines which had previously been reported on the other layers but also reveals the existence of considerable deviations between obtained values and values calculated from the equation. The detailed examination of such deviations revealed that *ortho* isomers, with few exceptions, tend to have lower R'_M values than those calculated. No clear relationship was observed between adsorption energies of substituted groups and these deviations, but as shown in Table III, the size of group seems to have some influences on them. N-Substituted amines, in addition, have similar tendencies to those of *ortho* isomers, since the steric effect of *ortho*-substituted

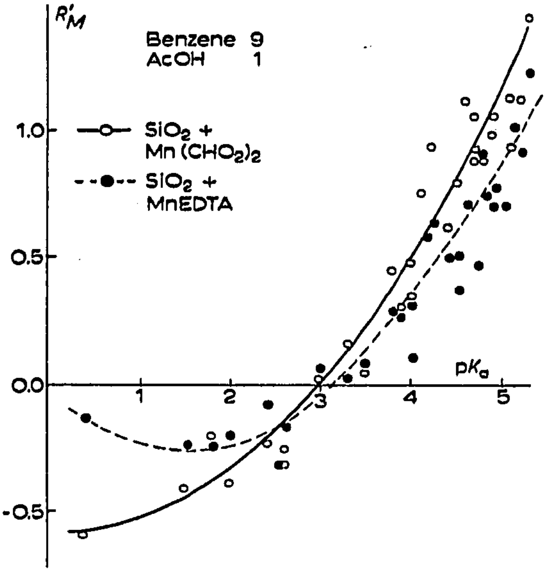

Fig. 1. Relationships between the R'_M values and pK_a values of aromatic amines on manganese salt impregnated thin layers.

TABLE III

RELATIONSHIPS BETWEEN DEVIATIONS IN R'_M VALUE AND SUBSTITUTED GROUPS

Substituted group	*[R'_M (calculated) − R'_M (obtained)] × 100*									
	L1			*L2*					*L3*	
	S1	*S2*	*S5*	*S1*	*S2*	*S3*	*S4*	*S5*	*S1*	*S3*
Methyl	−7	−4		−13	−12	−18			−13	−17
Methoxy	−5	−16		3	−11	−12			−17	−17
Chloro	1	25	0	−8	2	0	−5	−9	−10	3
Bromo	−4	−14	−10	−6	−3	−7	−13	−25	−24	−5
Phenyl	−41				−43		−25			
Ethoxy	−13				−23					

groups on amino groups may be considered to be one of the factors which control R_F values.

As pK_a values of anisidines increase in the order of *m*- > *o*- > *p*-, the steric effect of an *ortho*-substituted methoxy group acts against the main factor in separation, *i.e.* charge transfer, and therefore yields a poor separtion of *o*- and *m*-isomers on either unimpregnated or cadmium (excepting cadmium acetate) or zinc salt impregnated layers. But manganese salt impregnated layers, in which the charge transfer mechanism does not apply, can yield a unique separation of such isomers, based on a different mechanism: steric effect.

The role of the anions of the salts and the influence of crystal structures on the controlling of R_F values were beyond the consideration of this work. The comparison of data obtained on L2, L3, and L4, will also be of importance and is expected to be studied in further investigations.

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