Thin Layer Chromatography of Aromatic Amines.

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The work described here is the result of the attempt to separate aromatic amines using T.L.C. method.

Kosta(1) described R_f values of some aromatic amines using paper chromatography. He also used T.L.C. technique to find R_f values of the same amines. The study of the relationship between the chromatographic behaviour of a series of aromatic amines and their molecular structure necessitate the determination of chromatographic parameters. These parameters could be correlated with the change in the pKa values by the introduction of the same substituent at different positions in the parent compound.

Bark et. al.(2) chromatographed different series of nuclear substituted compounds and from the results of the electronic effects in these nucleus systems, it was not possible to assign group parameters.

The chromatoplates were thoroughly washed and dried. Silica gel (30g) was then made into slurry with water (60ml). This was used to coat five clean plates (20cm x 20cm). The layers were then activated in an oven overnight at the temperature of 100^oC. These were kept at 104^oC-145^oC for about 30 minutes before the cooled plates were used.

The compounds were applied to the layer using the multiple spotting device. The chromatoplates were then eluted in double saturated chamber.(2). The length of run was 14cm from the point of application. The spots were identified. The R_f,R_M and $\Delta RM_{(g)}$ values were calculated (Table-1).

Discussion

The variations in chromatographic behaviour caused by the various substituent groups in the aniline molecule may be correlated with the properties of the molecule which are affected by certain electronic factors. These affect the chromatographically functional group which is the amino group. It must be remembered that in the aromatic molecules the bond system of the molecules readily allows the transfer of electronic effects throughout the aromatic and resonance system.

Halogen Derivatives of Aniline

It has been noticed from the results that the R_M values decrease from ortho to para holagen derivatives. The pKa values for these derivatives are in accordance with their chromatographic behaviour. At the ortho position, halogen atoms withdraw more electron density away from the amino group than do halogens in the other positions. These groups may interfere with the amino group during protonation because of their size and hence oppose the proton acceptance consequently they decrease the electron density on the nitrogen atom of the amino group.

At the meta position there is no effect of the size of the group but a strong inductive effect may be present. At the para position these groups may oppose the participation of the lone-pair of electron of the amino group, in the conjugated system of the nucleus. Moreover, the substituent at para position being further away from the amino group may exercise less effect on the electron density so they increase the electron availability at the nitrogen atom of the amino group. This seems to be the main cause of decrease in the pKa and Δ $Rm_{(g)}$ values in the order ortho, meta and para.

Alkyl Derivatives of Aniline

Methyl and other alkyl groups in amines are not sufficiently electronegative to withdraw electrons from the ring instead the electron withdrawing

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Table 1. No of Solvent Systems

No of Compounds	Name of Compunds	S1			S2			S3			
		R_f	R_m	$\Delta R_{m(g)}$	R_f	R_m	$\Delta R_{m(g)}$	R_f	R_m	$\Delta R_{m(g)}$	PK_a
1.	Aniline	0.58	-0.142		0.78	-0.550	-0.00	0.26	+0.54		4.60
2.	o. Fluoro aniline	0.65	-0.269	-0.127	0.78	-0.550	-0.00	0.34	+0.288	+0.166	3.20
3.	m.Fluoro aniline	0.59	-0.158	-0.016	0.73	-0.432	-0.0118	0.29	+0.389	+0.065	3.50
4.	p. Fluoro aniline	0.47	+0.052	+0.194	0.59	-0.158	-0.392	0.20	+0.502	+0.048	4.60
5.	o. Chloro aniline	0.74	-0.454	-0.312	0.88	-0.865	-0.315	0.41	+0.158	+0.296	2.64
6.	m.Chloro aniline	0.63	-0.231	-0.089	0.81	-0.630	-0.080	0.31	+0.347	+0.107	3.50
7.	p. Chloro aniline	0.56	-0105	-0.037	0.76	-0.501	-0.046	0.26	+0.454	+0.000	3.98
8.	o. Bromo aniline	0.75	-0.477	-0.335	0.90	-0.954	-0.404	0.41	+0.158	+0.096	3.53
9.	M. Bromo aniline	0.63	-0.231	-0.089	0.83	-0.689	-0.139	0.32	+0.327	+0.127	2.54
10.	p. Bromo aniline	0.57	-0.122	-0.02	0.78	-0.550	-0.000	0.28	+0.410	+0.040	3.86
11;	o. Iodo aniline	0.76	-0.501	-0.335	0.93	-0.823	-0.573	0.41	+0.140	+0.314	2.60
12.	m. Iodo aniline	0.66	-0.288	-0.146	0.80	-0.602	-0.052	0.32	+0.327	+0.127	3.61
13.	p Iodo aniline	0.60	-0.176	-0.034	0.75	-0.477	-0.073	0.28	+0.410	+0.010	3.78
14.	o. Nitro aniline	0.67	-0.308	-0.166	0.89	-0.908	-0.908	0.33	+0.308	+0.146	0.26
15.	m. Nitro aniline	0.59	-0.158	-0.016	0.85	-0.753	-0.203	0.25	+0.477	+0.023	2.46
16.	p. Nitro aniline	0.52	-0.035	-0.107	0.84	-0.720	-0.170	0.18	+0.659	+0.305	3.11
17.	o. Methyl aniline	0.52	-0.1.5	-0.037	0.76	-0.5.1	-0.040	0.25	+o.477	+0.023	4.45
18.	m. Methyl aniline	0.55	-0.087	-0.55	0.73	-0.432	-0.118	0.22	+0.550	+0.096	4.72
19.	p. Methyl aniline	0.49	+0.017	-159	0.68	-0.327	-0.233	0.21	+0.602	+0.148	5.10
20.	o. Ethyl aniline	0.60	-0.176	-0.034	0.78	-0.550	-0.000	0.28	+0.410	+0.044	–

S1 = Phenetol + Methanol (90:10) V/V.
S2 = Nitrobenezene + Methanol (90:10) V/V
S3 = Toluene + Methanol (95:5) V/V.

power of the amine is such that the alkyl group loose electrons into the nucleus (they effectively "donate" electrons) This increase of the electron density on the nitrogen atom, tends to increase the pKa value. When the second group is at ortho position, then both of the competing sites are in the plane of the molecules and are equally effected by the mobile phase when the second is at para position, then it is entirely in the hydrocarbon part of the molecule and shows lesser movement by the mobile phase as compared with ortho and meta substituents.

Nitro Derivatives of Aniline.

The $\Delta Rm_{(g)}$ values are found to increase from the ortho, meta to para nitro derivatives of aniline. The nitro groups have great potential of inductive effect and strong opposition of the meso-meric effect of the amino group. Meta nitro aniline is a weaker base than para nitro aniline and ortho nitroaniline is weaker than meta nitro aniline. The order of $\Delta Rm_{(g)}$ values is ortho meta and para.

Table II

$\Delta Rm_{(g)}$ values in S_2 solvent.

$\Delta Rm_{(g)}$	Groups							
	NH2	OCH3	CH3	F	Cl	Br	I	NO_2
ortho	+0.659	+0.121	+0.023	+0.166	+0.296	+0.296	+0.314	+0.146
meta	+0.926	+0.266	+0.096	+0.065	+0.107	+0.127	+0.127	+0.023
para	+0.056	+0.659	+0.148	+0.048	+0.000	+0.040	+0.010	+0.205

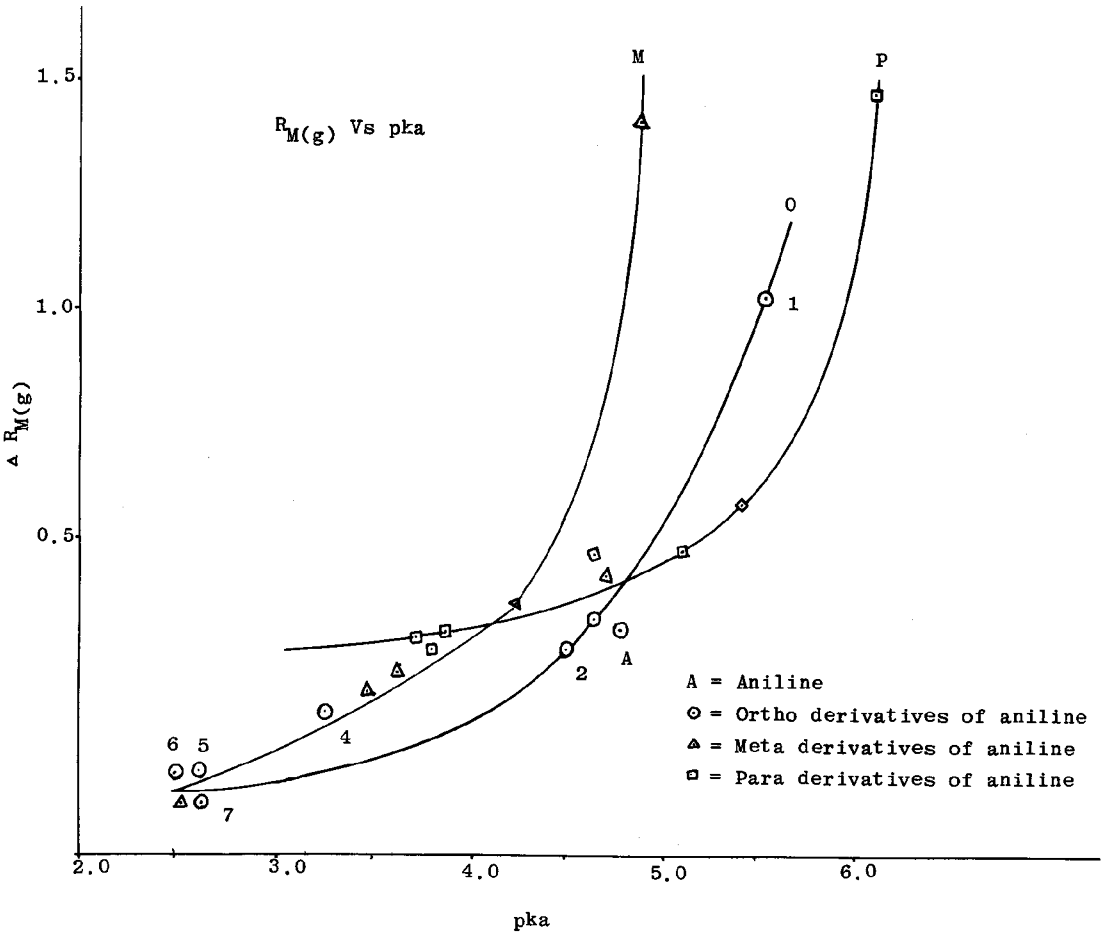

Fig. 1

Correlation of the chromatographic behaviour and the molecular structure of the aniline derivatives

An examination of the Table (1) shows that in every case studied the ortho isomer moves faster i.e. is less strongly adsorbed than the meta and para isomers. This would be expected if it were assumed that in the ortho isomer, amino hydrogens were less effective in hydrogen bonding formation on the substrate silica gel as compared with meta and para isomers.

Further examination of Table (1) shows that the considerable differences which exist between the $\Delta Rm_{(g)}$ values of the ortho and para isomers of aniline derivatives, indicate that factors in addition to hydrogen bonding play important role in the adsorption of the nuclear substituted anilines. As mentioned earlier, these factors are steric hindrance. Inductive effects and geometrical arrangment of the substituent about the benzene ring. The degree of steric hindrance depends on the position and the size of the substituent group; the magnitude of the inductive effect depends upon the electronic charge of the solvents used. Kirkpatrick and Arenbergs$^{(3)}$ determined and arranged the pKa values of the aniline derivatives.

If these pKa values are compared with the corresponding $\Delta Rm_{(g)}$ values determined then the $\Delta Rm_{(g)}$ values are not in the same increasing order as these pKa values. In the values of the ortho, meta and para derivatives. there in no linear relationship between these parameters Fig(I).

Since the order of the pKa values is to some extent a measure of the ionisation of the -NH bond caused by H bonding between the H atom and the HOH molecule, one could expect that the H bonding between the H atom and the H-O-Si-entity of the substrate, would be directing the order of the adsorption in to that similar to the order of pKa values.

Since the above table (ii) and fig (i) indicate no linear relationship but do indicate an overall tendency for the $\Delta Rm_{(g)}$ value to increase as the pKa value increases, we must consider other effects as playing significant roles in determining the chromatographic distribution. These factors may include the effect of the solvent and both the solute and the substrate, the effective dipole mements of solute which may be related to the manner in which solute molecules present themselves to the active sites on the substrate.

References

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