Thin Layer Chromatobraphy of Aliphatic Primary Amines

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Introduction

The work described stems from the desire to separate Aliphatic primary amines using T.L.C. technique. There are several reasons why the method of T.L.C. should, where feasible, be considered in preference to paper, column, or gas chromatography when a separation of components in a mixture is attempted. Gasparic (1) determined Rf values of some aliphatic amines. Yasuda (2) using silica gel layer impregnated with cadmium sulphate attempted to find Rf values of some aromatic amines. Bark at. al.[3-5] chromatographed different series of nuclear substituted compounds.

The solvent system were chosen so that the effect of increase in polarity of this particular system could be seen.

Procedure

The chromatoplates were thoroughly washed and dried. Silica gel (30g) was then made into slurry with water (60 ml). This was used to coat five clean plates (20 cm x 20 cm). The layers were than activated in an oven overnight at the temperature of 100°C. These were kept at 104°C - 145°C 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 a double saturation chamber. The elution was carried out in an air oven at a constant temperature of 23°C. The length of run was 14 ± 1 cm from the point of application. The spots were identified. The Rf values were calculated (Table-1).

Discussion

The capacity of the amino group to attract electrons is due to the electronegativity of nitrogen relative to carbon. This unequal sharing of electrons between these two atoms can be transmitted by successive polarization of sigma bonds as in homologous carbon chain[1]

Table 1. Mean Rf values of Alphatic Primary Amines

No. of Compounds		S_1	S_2	S_3	S_4	S_5	S_6
1.	Methylamine	0.03	0.2	0.03	0.04	0.19	0.28
2.	Ethylamine	0.04	0.03	0.05	0.07	0.27	0.36
3.	n-Propylamine	0.06	0.05	0.09	0.08	0.35	0.46
4.	Iso-Propylamine	0.06	0.05	0.08	0.08	0.33	0.43
5.	n-Butylamine	0.09	0.07	0.10	0.10	0.38	0.50
6.	Iso-Butylamine	0.08	0.08	0.40	0.12	0.37	0.48
7.	Pentylamine	0.08	0.06	0.13	0.13	0.45	0.53
8.	Hexylamine	0.08	0.05	0.14	0.13	0.50	0.56
9.	Heptylamine	0.08	0.07	0.15	0.14	0.53	0.58
10.	n-Octylamine	0.09	0.07	0.17	0.15	0.55	0.61
11.	n-Undecylamine	0.09	0.07	0.19	0.06	0.16	0.61
Maxium Variations		±0.01	±0.02	±0.03	±0.01	±0.02	±0.01

S_1 = Chloroform + Methanol (1:1) v/v
S_2 = Chloroform + Methanol (1:3) v/v
S_3 = Chloroform (Sat. with Ammonia) + Methanol (1:1) v/v
S_4 = Chloroform + Methanol, + Acetic Acid (50:50:0) v/v
S_5 = Chloroform + Methanol, + Acetic Acid (50:45:5) v/v
S_6 = Chloroform + Methanol + Acetic Acid (50:40:10) v/v

and the small dipoles produced from such electronic displacement decrease progressively away from the polar group.

The influence of an electronegative group is not limited to transmission along δ bonds of saturated molecule, but it can also be transmitted by a field effect between the amino group and the active centres on the substrate. Considering the chromatographically active functional amino group, hydrogen bonding between the hydrogen atom of the amino group and the oxygen atom of silica could be the cause of amino molecules become attracted and then attached to the substrate layer.

The result of Rf and hence Rm values and subsequently Δ RM (g) values for the methylene group in the homologous series of primary aliphatic amines show that Δ Rm (CH_2) for C_1 - C_4 compound is not constant, altering from 0.16, 0.15, 0.10 and 0.05 units. After C_4 the Δ Rm (CH_2) remains constant as 0.05 units.

This apparent difference to be expected. The electronic effects of the polar amino group will be transmitted across the sigma bonds to the methylene groups, as already indicated the polarization of the bonds becomes progressively weaker as the length of the chain increases. The values suggest that after the C_4 atom, the polarization of the C-C bonds does not occur, thus methylene group added after C_4 all have the same effect.

The solute atoms will be held colse to the surface of the substrate and there may be in some cases some slight penetration of the surface. The interface between the substrate and the mobile phase must therefore be regarded as not a thin line but a region having small but definite thickness.

Above C_4, it is probable that all alkane units are in the mobile phase and this dissolution of the amino, into the mobile phase, will depend upon the number of methylene groups protruding into that phase. If one regards the molecule as being a lever, with a fulcrum at the point of attachment of the amino group to the silica substrate, then one can see that the length of the chain should have a bearing on the distribution.

However the chain is not rigid and it is possible that after a certain length of the chain has been reached further addition of methylene group may result in some spiralling of the chain and not an overall additive increase in the effective length of the chain in the mobile phase. Thus the Δ R_m (CH_2) may decrease again after a certain carbon number. Similarly using an analogous argument, one could not expect the branch chain CH_2 group to have the same effect as a straight chain CH_2 group.

Consideration of the pka values (Table II) shows that there is very little variation in these values for alphatic amines even though the Rf and hence the R_m values vary considerabley. There is no obvious relationship between pka and R_m values. None can be expected, the pka value is a "bulk property", whereas the R_M is a parameter which is essentially only a distribution phenomenon & results from chemical forces exerting an effect over only a few Molecular distances.

Table 2. Aliphatic Primary amines

No. of compounds		Rf	Rm	$\Delta RM_{(g)}$	Pka
1.	Methylamine	0.28	+0.41	–	10.62
2.	Ethylamine	0.36	+0.25	+0.16	10.63
3.	n-Proyplamine	0.44	+0.10	+0.15	10.52
4.	Iso-Propylamine	0.43	+0.12	+0.13	–
5.	n-Butylamine	0.50	+0.00	+0.07	10.60
6.	Iso-Butylamine	0.48	+0.035	+0.03 (5)	–
7.	Pentylamine	0.53	–0.05	–0.05	10.63
8.	Hexylamine	0.56	–0.15	–0.05 (5)	10.64
9.	Hyptylamine	0.58	–0.15	–0.05	10.68
10.	n-Octylamine	0.61	–0.194	–0.05	10.65
11.	n-Undecylamine	0.64	–0.24	–0.05	10.63

References

1. J. Gasparic *Chem. Listy*, 1439 (1961)
2. K. Yasuda, *J. Chromatogr*, 144 (1971)
3. L.S. Bark and R.J.T. Graham, *Talanta*, 839, (1964)
4. L.S. Bark and R.J.T. Garaham, *Talanta*, 1231 (1966)
5. L.S. Bark and R.J.T. Garaham, D. McCormick, *Talanta*, 122 (1965)