MIGRATION OF AMINOALCOHOLS ON PAPER*

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Except for a number of investigations associated with specific biochemical problems[1], there appears to be little information about the paper chromatography of aminoalcohols in general. Thus, although mono-, di- and tri-ethanolamines have been separated on anion-exchange column[2], the most comprehensive reports of this type yet appearing in the literature seem to be those on aminoalcohols derived from amino acids[3], on 2,4-dinitrophenylaminoalcohols derived from amino acids[4,5], and on aminoalcohols related to adrenaline[6]. Confronted with a continuing need for information about the migration properties of a wide variety of aminoalcohols on paper, we have determined R_M values in three different solvent systems for the aminoalcohols given in Table I.

Numerous variations in the migration properties are noted with changes in both solvent system and aminoalcohol structure. For example, solvent B gives extensive tailing of the spots in many cases, sometimes leading to a diffuseness of spot which makes its presence very difficult to detect. On the other hand, solvent A has a tendency to produce lateral diffusion of the spot, with similar though less pronounced effects on sensitivity of detection; this tendency is compensated at least in part by a relatively slow rate of migration and a correspondingly good sensitivity to aminoalcohol structure. Solution C gives very good, coherent spots, but the migration is comparatively rapid, leading to poorer separations than might be desired for certain mixtures.

The extremely rapid migration of N-phenyl-ethanolamine derivatives, (compounds 9, 26 and 38) is especially noticeable in solvents A and C, and a similar behavior is to be seen in the *o*-aminophenols (compounds 67, 68 and 69). A comparison of the R_M values of the N-substituted diethanolamines (compounds 2–9) with those of the N-monosubstituted ethanolamines (compounds 21–26) reveals a practically linear relationship in all three solvent systems. This dependence of the migration rate on the nature of the nitrogen substituent remains the most apparent feature of all the data which have been obtained. It thus appears that the migration rates of aminoalcohols are primarily controlled by the prevailing balance between the basicity of the aminoalcohol and that of the solvent system.

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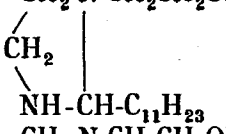
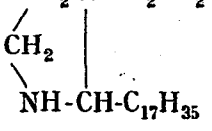
TABLE I

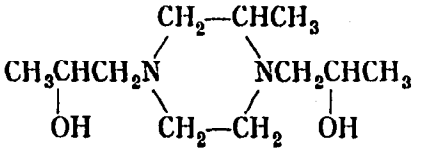
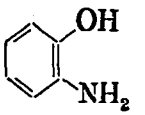
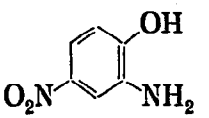
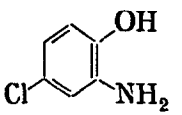
R_F VALUES FOR AMINOALCOHOLS ON WHATMAN NO. 1 PAPER

	Aminoalcohol	Formula	A		B		C	
			R_F	R_x*	R_F	R_x*	R_F	R_x*
1	Triethanolamine	$N(CH_2CH_2OH)_3$	0.22	1.16	0.45	1.41	0.62	1.15
2	Diethanolamine	$HN(CH_2CH_2OH)_2$	0.21	1.11	0.47	1.47	0.62	1.15
3	N-Methyl-diethanolamine	$CH_3N(CH_2CH_2OH)_2$	0.25	1.32	0.66	2.06	0.62	1.15
4	N-Ethyl-diethanolamine	$C_2H_5N(CH_2CH_2OH)_2$	0.33	1.74	0.76	2.38	0.66	1.22
5	N-*n*-Butyl-diethanolamine	n-$C_4H_9N(CH_2CH_2OH)_2$	0.52	2.74	0.88	2.75	0.77	1.43
6	N-Isopropyl-diethanolamine	i-$C_3H_7N(CH_2CH_2OH)_2$	0.39	2.05	0.83	2.60	0.65	1.20
7	N-*tert.*-Butyl-diethanolamine	*tert.*-$C_4H_9N(CH_2CH_2OH)_2$	0.46	2.16	0.87	2.72	0.73	1.35
8	N-Benzyl-diethanolamine	$C_6H_5CH_2N(CH_2CH_2OH)_2$	0.50	2.63	0.89	2.78	0.81	1.50
9	N-Phenyl-diethanolamine	$C_6H_5N(CH_2CH_2OH)_2$	0.89	4.68	0.83	2.60	1.00	—
10	N,N,N′,N′-Tetrakis-(hydroxyethyl)-ethylenediamine	$[CH_2N(CH_2CH_2OH)_2]_2$	0.29	1.53	0.48	1.50	0.66	1.22
11	N,N,N′-Tris-(2-hydroxypropyl)-N′-(2-hydroxyethyl)-ethylenediamine	$CH_3CH(OH)CH_2$ $\vert$ N-$CH_2CH_2N[CH_2CH(OH)CH_3]_2$ $\vert$ $HOCH_2CH_2$	0.54	2.84	0.80	2.50	0.79	1.46
12	N,N,N′,N′-Tetrakis-(2-hydroxypropyl)-ethylenediamine	$[CH_2N(CH_2CH(OH)CH_3)_2]_2$	0.59	3.10	0.78	2.44	0.82	1.51
13	N,N,N′,N′-Tetrakis-(2-hydroxybutyl)-ethylenediamine	$[CH_2N(CH_2CH(OH)CH_2CH_3)_2]_2$	0.76	4.00	0.84	2.62	0.90	1.67
14	Diethyleneglycolamine		0.23	1.21	0.39	1.22	0.62	1.15
15	2-Amino-2-hydroxymethyl-1,3-propanediol	$H_2NC(CH_2OH)_3$	0.18	0.95	0.52	1.63	0.74	1.37
16	2-Amino-1,3-propanediol	$H_2NCH(CH_2OH)_2$	0.17	0.90	0.33	1.03	0.57	1.06
17	2-Amino-2-methyl-1,3-propanediol	$H_2NC(CH_3)(CH_2OH)_2$	0.23	1.21	0.49	1.53	0.68	1.26
18	2-Amino-2-ethyl-1,3-propanediol	$H_2NC(C_2H_5)(CH_2OH)_2$	0.37	1.95	0.58	1.81	0.68	1.26
19	2-Ethylamino-2-methyl-1,3-propanediol	$C_2H_5NHC(CH_3)(CH_2OH)_2$	0.34	1.79	0.70	2.18	0.76	1.41
20	2-Dimethylamino-2-methyl-1,3-propanediol	$(CH_3)_2NC(CH_3)(CH_2OH)_2$	0.28	1.47	0.69	2.16	0.68	1.26
21	Ethanolamine	$H_2NCH_2CH_2OH$	0.19	1.00	0.32	1.00	0.54	1.00
22	N-Methyl-ethanolamine	$CH_3NHCH_2CH_2OH$	0.25	1.32	0.54	1.69	0.60	1.11
23	N-Ethyl-ethanolamine	$C_2H_5NHCH_2CH_2OH$	0.32	1.68	0.70	2.18	0.67	1.24
24	N-*tert.*-Butyl-ethanolamine	*tert.*-$C_4H_9NHCH_2CH_2OH$	0.50	2.63	0.80	2.50	0.76	1.41
25	N-Benzyl-ethanolamine	$C_6H_5CH_2NHCH_2CH_2OH$	0.55	2.90	0.88	2.75	0.82	1.52
26	N-Phenyl-ethanolamine	$C_6H_5NHCH_2CH_2OH$	0.88	4.63	0.87	2.72	1.00	—

27	N,N-Dimethyl-ethanolamine	$(CH_3)_2NCH_2CH_2OH$	0.27	1.42	0.13	0.41	0.61	1.13
28	N-Methyl-N-ethyl-ethanolamine	$C_2H_5N(CH_3)CH_2CH_2OH$	0.31	1.63	**	—	0.67	1.24
29	N,N-Diethyl-ethanolamine	$(C_2H_5)_2NCH_2CH_2OH$	0.34	1.79	0.79	2.47	0.72	1.33
30	N,N-Diallyl-ethanolamine	$(CH_2=CHCH_2)_2NCH_2CH_2OH$	0.59	3.10	**	—	0.82	1.52
31	β-(N-Pyrrolidino)-ethanol	$(CH_2)_4NCH_2CH_2OH$	0.31	1.63	0.78	2.44	0.68	1.26
32	β-(N-Piperidino)-ethanol	$(CH_2)_5NCH_2CH_2OH$	0.40	2.10	0.84	2.62	0.72	1.33
33	β-(4-Methylhexamethylenimino)-ethanol	$CH_3CH(CH_2)_4NCH_2CH_2OH$	0.54	2.84	0.90	2.82	0.81	1.50
34	β-(2-Undecyl-1-imidazolino)-ethanol		0.75	3.95	0.92	2.88	0.89	1.65
35	β-(2-Heptadecenyl-1-imidazolino)-ethanol		0.77	4.05	0.93	2.90	0.95	1.76
36	β-(4-Methyl-1-piperazino)-ethanol	$CH_3N(CH_2)_4NCH_2CH_2OH$	0.23	1.21	0.70	2.18	0.62	1.15
37	β-(N-Morpholino)-ethanol	$O(CH_2)_4NCH_2CH_2OH$	0.31	1.63	0.67	2.10	0.67	1.24
38	N-Ethyl-N-phenyl-ethanolamine	$C_6H_5N(C_2H_5)CH_2CH_2OH$	0.91	4.79	0.92	2.88	1.00	—
39	N-(2-Aminoethyl)-ethanolamine	$H_2N(CH_2)_2NHCH_2CH_2OH$	0.13	0.68	0.40	1.25	0.47	0.87
40	1,4-Bis-(2-hydroxyethyl)-piperazine	$[(CH_2)_2NCH_2CH_2OH]_2$	0.13	0.68	0.43	1.34	0.55	1.02
41	1-Phenyl-2-methyl-ethanolamine	$H_2NCH(CH_3)CH(C_6H_5)OH$	0.53	2.79	0.88	2.75	0.87	1.61
42	1-Phenyl-2,2-dimethyl-ethanolamine	$H_2NC(CH_3)_2CH(C_6H_5)OH$	0.59	3.10	0.86	2.68	0.90	1.67
43	1-Phenyl-2-methyl-N-methyl-ethanolamine	$CH_3NHCH(CH_3)CH(C_6H_5)OH$	0.57	3.00	0.89	2.78	0.89	1.65
44	1-Phenyl-2-methyl-N,N-dimethyl-ethanolamine	$(CH_3)_2NCH(CH_3)CH(C_6H_5)OH$	0.55	2.90	0.86	2.68	0.88	1.63
45	2-Ethyl-ethanolamine	$H_2NCH(C_2H_5)CH_2OH$	0.35	1.89	0.76	2.38	0.71	1.32
46	2,2-Dimethyl-ethanolamine	$H_2NC(CH_3)_2CH_2OH$	0.40	2.10	0.70	2.18	0.70	1.30
47	2-Pyridyl-methyl-phenyl-carbinol	$(C_5H_4N)C(CH_3)(C_6H_5)OH$	0.62	3.26	0.90	2.82	0.87	1.61
48	2-Pyridyl-diphenyl-carbinol	$(C_5H_4N)C(C_6H_5)_2OH$	0.94	4.95	1.00	—	0.76	1.41
49	β-(2-Pyridyl)-ethanol	$(C_5H_4N)CH_2CH_2OH$	0.72	3.79	**	—	**	—
50	3-Amino-1-propanol	$H_2N(CH_2)_3OH$	0.24	1.26	0.43	1.34	0.55	1.02
51	3-Diethylamino-1-propanol	$(C_2H_5)_2N(CH_2)_3OH$	0.44	2.32	0.83	2.60	0.69	1.28
52	4-Amino-1-butanol	$H_2N(CH_2)_4OH$	0.24	1.26	0.46	1.44	0.61	1.13
53	1-Methyl-4-diethylamino-1-butanol	$(C_2H_5)_2N(CH_2)_3CH(CH_3)OH$	0.57	3.00	0.88	2.75	0.79	1.46
54	5-Amino-1-pentanol	$H_2N(CH_2)_5OH$	0.32	1.68	0.58	1.81	0.66	1.22
55	6-Amino-1-hexanol	$H_2N(CH_2)_6OH$	0.38	2.00	0.71	2.22	0.72	1.33

(continued on p. 80)

TABLE 1 (*continued*)

	Aminoalcohol	*Formula*	*A*		*B*		*C*	
			R_F	R_x*	R_F	R_x*	R_F	R_x*
56	Dihydroxymethyl-ethylenediamine		0.17	0.90	0.36	1.12	0.58	1.07
57	Tri-isopropanolamine	$N(CH_2CHOHCH_3)_3$	0.45	2.36	**	—	0.81	1.50
58	Di-isopropanolamine	$HN(CH_2CHOHCH_3)_2$	0.37	1.95	0.72	2.25	0.75	1.39
59	Isopropanolamine	$H_2NCH_2CHOHCH_3$	0.26	1.37	0.52	1.63	0.60	1.11
60	N-Cyclohexyl-isopropanolamine	$C_6H_{11}NHCH_2CHOHCH_3$	0.66	3.47	0.89	2.78	0.87	1.61
61	N,N-Dimethyl-isopropanolamine	$(CH_3)_2NCH_2CHOHCH_3$	0.32	1.68	**	—	0.65	1.20
62	1,4-Bis-(2-hydroxypropyl)-2-methyl-piperazine		0.46	2.42	0.85	2.66	0.78	1.44
63	1-Diethylamino-3-amino-2-propanol	$(C_2H_5)_2NCH_2CH(OH)CH_2NH_2$	0.21	1.11	0.77	2.40	0.50	0.93
64	N-(2-Aminoethyl)-isopropanolamine	$H_2N(CH_2)_2NHCH_2CHOHCH_3$	0.21	1.11	0.57	1.78	0.52	0.96
65	1,3-Diamino-2-propanol	$(H_2NCH_2)_2CHOH$	0.07	0.37	0.40	1.25	0.39	0.72
66	1,4-Bis-(dimethylamino)-2,3-diphenyl-2,3-butanediol	$[(CH_3)_2NCH_2C(C_6H_5)OH]_2$	0.43	2.26	0.87	2.70	0.85	1.58
67	*o*-Aminophenol		0.65	3.42	0.80	2.50	1.00	—
68	4-Nitro-2-aminophenol		0.87	4.58	0.58	1.81	1.00	—
69	4-Chloro-2-aminophenol		0.86	4.52	0.87	2.72	1.00	—

* R_x refers to ethanolamine.
** No spot could be detected.

EXPERIMENTAL

The solvent systems employed are well known ones which have been used before:

Solvent A: *n*-Butanol, 77%: acetic acid, 6%: water, 17% (ref. [3]).

Solvent B: *n*-Butanol saturated with 0.1% aqueous NH_3 (ref. [3]).

Solvent C: Pyridine, 42%: ethyl acetate 25%: water, 25%: acetic acid, 8% (ref. [7]).

Whatman No. 1 paper was spotted with methanolic solutions of the several aminoalcohols 1 in. from the bottom of a sheet 9.25 in. wide by 8 in. high. When the spots were dry, the sheet was stapled into a cylinder, and set into a dish resting on a glass plate and containing the solvent. The whole assembly was covered by a bell-jar and sealed at the base with clay. With solutions A and B, the migration was allowed to proceed 4 h. With solution C, which moved more rapidly, migration was stopped after 3 h. Upon removal of the paper cylinder, the solvent front was marked while still wet. After air-drying, the sheet was sprayed with 0.25% ninhydrin in 1:1 pyridine–ethanol and heated 5 min at 105° to bring out the color of the spots.

SUMMARY

The migration of 69 aminoalcohols on Whatman No. 1 paper has been determined in three different developing solvents. The general behavior of the migrating spots in the three solvents is indicated. Variations in migration rates with structural characteristics of the aminoalcohols are briefly discussed.

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