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Note

Kováts' retention indices of pyridine bases on stationary phases of medium polarity

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Kováts' retention indices[1] are used extensively in gas chromatographic (GC) identification, and the experience gained from its usage has shown that it is a most convenient means of expressing chromatographic retention data. They can be applied to the characterization of both the solute and the stationary phase.

Gas chromatographic data for the alkylpyridine bases are scarce, and have been obtained by use of glycerine, Apiezon[2,3], Amin 220, Triton X-305 and Carbowax-1000[3] phases. In this work, Kováts' retention indices have been determined for alkylpyridines on phases of medium polarity which are more widely used in chromatography.

EXPERIMENTAL

The analysis was performed on a gas chromatograph equipped with a katharometer and by use of steel columns (1.0 m × 0.30 mm). The carrier gas (helium) flow-rate was 33 ml/min and the column temperatures were 90, 100, 110 and 120°. The stationary phases used were dinonyl sebacate (DNS), dioctyl sebacate (DOS), diheptyl sebacate (DHS), diheptyl phthalate (DHP), dibenzyl phthalate (DBP), dibenzyl sebacate (DBS) and dibenzyl succinate (DBSU). Chromaton N AW HMDS (0.43–0.60 mm) was used as the solid support. The amount of liquid phase was 30%.

RESULTS AND DISCUSSION

The specific retention volumes of pyridine and 12 derivatives were determined. The retention indices were calculated from the retention volumes[4]. The results are given in Table I. The data show that the retention indices of homologous alkylpyridines increase by about 100 units with increasing molecular weight. 2-Methylpyridine and 2,4,6-trimethylpyridine are exceptions. We suggest that the methyl group in the 2-position screens the pyridine nitrogen atom and reduces the interaction of the sorbate with the liquid phases.

The retention indices of the pyridine bases exhibit approximately linear dependences on the boiling point (Fig. 1) and the polarity* of the stationary phases (Fig. 2).

* Relative polarity of stationary phases as defined by Rohrschneider.

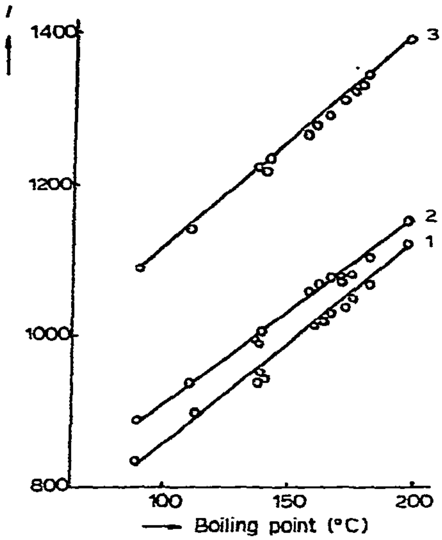

Fig. 1. Dependence of the retention indices on the boiling points of the pyridine bases. 1 = Dioctyl sebacate, 2 = diheptyl phthalate, 3 = dibenzyl succinate.

Increasing the length of the ester function of the stationary phase results in a reduction of the retention index, and the graphic dependence was rectilinear (Fig. 3).

Values of the temperature coefficient $\Delta I/\Delta T$ are presented in Table II. The table shows that the values depend not only on the number of substituents in the alkylpyridines, but also on their position with respect to the nitrogen atom. The lowest

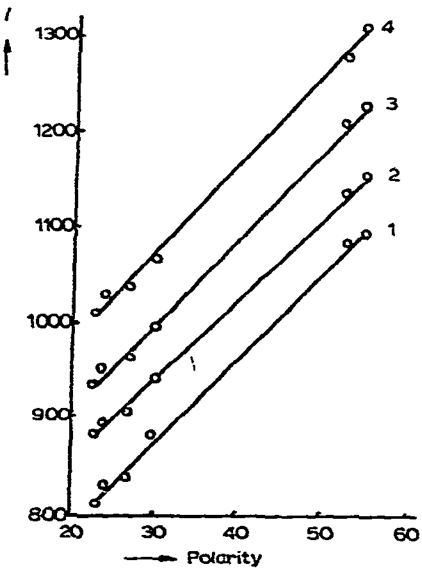

Fig. 2. Dependence of the retention indices on the relative polarities of the stationary phases as defined by Rohrschneider. 1 = Pyridine, 2 = 2-methylpyridine, 3 = 4-methylpyridine, 4 = 2,3 dimethylpyridine.

TABLE I

KOVÁTS' RETENTION INDICES OF PYRIDINE AND SOME ALKYLPYRIDINES

Stationary phase	Temperature (°C)	Pyridine	2-Methyl pyridine	3-Methyl pyridine	4-Methyl pyridine	2,6-Dimethyl pyridine	2,5-Dimethyl pyridine	2,4-Dimethyl pyridine	2,3-Dimethyl pyridine	3,5-Dimethyl pyridine	3,4-Dimethyl pyridine	3-Ethyl pyridine	4-Ethyl pyridine	2,4,6-Trimethyl pyridine
DNS	90	813	881	930	932	942	996	999	1013	1050	1075	1023	1028	944
	100	815	883	933	934	944	998	1002	1016	1054	1079	1026	1031	945
	110	817	885	936	937	945	1000	1004	1020	1059	1085	1030	1035	947
	120	819	887	938	940	946	1003	1007	1023	1063	1089	1033	1039	948
DOS	90	826	894	945	948	951	1010	1014	1026	1064	1091	1036	1041	953
	100	828	895	947	950	953	1012	1016	1029	1067	1094	1039	1044	954
	110	830	897	949	953	954	1014	1019	1032	1070	1098	1042	1047	956
	120	831	899	951	956	955	1016	1021	1034	1073	1102	1044	1050	957
DHS	90	837	906	958	962	963	1023	1025	1040	1077	1107	1050	1053	962
	100	838	907	959	964	964	1025	1027	1042	1079	1110	1051	1055	963
	110	840	909	961	966	965	1026	1029	1044	1082	1113	1055	1057	964
	120	841	910	962	967	967	1028	1030	1046	1084	1116	1056	1061	965
DHP	90	880	939	998	1004	994	1057	1060	1070	1116	1149	1088	1095	993
	100	881	940	999	1005	995	1058	1061	1071	1117	1150	1089	1097	994
	110	882	941	1000	1007	996	1059	1063	1073	1119	1152	1091	1098	995
	120	884	943	1002	1008	997	1061	1064	1074	1121	1154	1092	1100	996
DBP	90	1082	1134	1210	1220	1180	1261	1269	1288	1341	1391	1305	1320	1181
	100	1084	1136	1213	1223	1182	1263	1272	1291	1344	1394	1307	1323	1183
	110	1087	1138	1215	1226	1184	1265	1274	1294	1348	1398	1310	1326	1185
	120	1090	1141	1217	1229	1186	1268	1277	1297	1351	1402	1314	1330	1186
DBS	90	869	927	993	997	979	1048	1056	1071	1118	1154	1084	1089	979
	100	872	929	995	1000	981	1050	1058	1074	1121	1157	1086	1092	981
	110	974	931	998	1002	983	1052	1061	1077	1124	1161	1089	1095	982
	120	876	933	1000	1005	985	1055	1063	1079	1127	1164	1092	1098	984
DBSU	90	1095	1146	1228	1233	1185	1270	1288	1297	1359	1399	1321	1335	1185
	100	1097	1147	1230	1235	1186	1272	1290	1299	1362	1402	1323	1338	1186
	110	1098	1149	1231	1237	1187	1273	1292	1301	1365	1405	1325	1341	1187
	120	1099	1150	1233	1238	1189	1275	1294	1304	1367	1408	1328	1343	1189

TABLE II

VARIATION OF RETENTION INDICES WITH TEMPERATURE, $\Delta I/\Delta T$

Stationary phase	*Pyridine*	2-*Methyl pyridine*	3-*Methyl pyridine*	4-*Methyl pyridine*	2,6-*Dimethyl pyridine*	2,5-*Dimethyl pyridine*	2,4-*Dimethyl pyridine*	2,3-*Dimethyl pyridine*	3,5-*Dimethyl pyridine*	3,4-*Dimethyl pyridine*	3-*Ethyl pyridine*	4-*Ethyl pyridine*	2,4,6-*Trimethyl pyridine*
DNS	0.20	0.20	0.26	0.26	0.13	0.23	0.27	0.33	0.43	0.46	0.33	0.37	0.13
DOS	0.17	0.17	0.20	0.26	0.13	0.20	0.23	0.26	0.30	0.37	0.26	0.30	0.13
DHS	0.13	0.13	0.13	0.17	0.13	0.16	0.17	0.20	0.23	0.30	0.23	0.27	0.10
DHP	0.13	0.13	0.13	0.16	0.10	0.13	0.13	0.13	0.16	0.17	0.13	0.17	0.10
DBP	0.27	0.23	0.27	0.30	0.20	0.23	0.26	0.30	0.33	0.36	0.30	0.33	0.17
DBS	0.23	0.20	0.23	0.26	0.20	0.23	0.23	0.26	0.30	0.33	0.27	0.30	0.16
DBSU	0.13	0.13	0.16	0.17	0.13	0.17	0.20	0.23	0.26	0.30	0.23	0.26	0.13

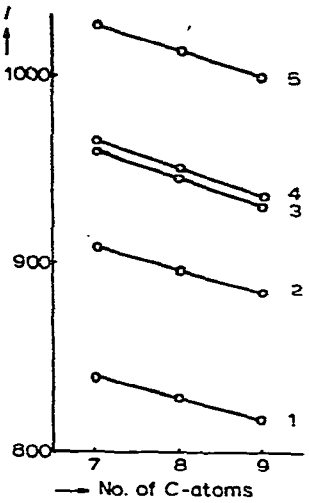

Fig. 3. Dependence of the retention indices on the lengths (number of carbon atoms) of the ester function of the stationary phase. 1 = Pyridine, 2 = 2-methylpyridine, 3 = 3-methylpyridine, 4 = 4-methylpyridine, 5 = 2,5-dimethylpyridine.

values of $\Delta I/\Delta T$ were obtained for bases having substituents close to the nitrogen atom; the largest values were obtained for 3,5- and 3,4-dimethylpyridine. These values of $\Delta I/\Delta T$ can be used for the group identification of pyridine bases in analysed mixtures[5].

The observed dependence of the retention index on the physicochemical properties of the bases and stationary phases can be used to study the intermolecular solute–solvent interaction.

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