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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

PART V. RETENTION OF ALIPHATIC ESTERS ON NON-POLAR, DONOR AND ACCEPTOR STATIONARY PHASES

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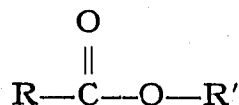
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SUMMARY

The retention behaviour of homologous saturated esters on polysiloxane stationary phases which vary in character from essentially non-polar to those of considerable polar character and exhibiting some donor and acceptor properties is reported. The influence of these factors on the relationship between boiling point and retention as reported on non-polar phases is discussed.

INTRODUCTION

Gas chromatographic retention behaviour of homologous saturated esters on non-polar and several polar stationary phases has previously been reported^{1,2} where the esters were conventionally represented as:



R and R' being the number of carbon atoms of the acid and alcohol chains, respectively. The gas chromatography of aliphatic esters has been extensively documented³ and systematic studies relevant to this work have previously been reviewed¹.

The retention behaviour of homologous saturated esters on the essentially non-polar dimethyl polysiloxane stationary phase was primarily related to the boiling point of the esters as little hydrogen bonding occurred. When this retention data was considered with regard to boiling point, the following features common to retention behaviour were apparent:

(1) The slopes of plots representing esters with the same number of carbon atoms in the acid chain (R) decrease as the value of R increases.

(2) Retention of methyl esters follows boiling points *i.e.* these esters have slightly higher boiling points and retention than expected from the slope of the

corresponding ester plot. The retention behaviour and boiling point of methyl formate shows a linear relationship with the alkyl formates.

(3) The isobutyl and isopentyl esters have boiling points and retention values relatively constantly lower than the corresponding *n*-alkyl esters, while the slopes of the boiling point plot of these series are parallel to those of the *n*-alkyl esters.

(4) The isopropyl esters have boiling points and retention values lower than expected from the appropriate plots of the higher *iso*-esters.

(5) The boiling points of esters where either R or R' or both of them have branched chains similarly tend to follow the retention behaviour.

The retention behaviour of the more polar phenyl substituted polysiloxanes, OV-17 and OV-25, was analogous to that reported on the essentially non-polar phase, however, increased retention was exhibited with the more polar columns. Minor variations were apparent but in most cases these were related to isomerism and a lack of suitable relevant data made a worthwhile conclusion difficult.

With a polar cyanoethyl substituted phase (XE-60) it was apparent that the fit of the points to the various plots was not as satisfactory as with the methyl and methyl phenyl substituted polysiloxanes. This indicated that with this phase there were factors, *i.e.* acceptor character, other than boiling point, affecting the retention behaviour.

Here the retention behaviour of a number of aliphatic esters, essentially similar to those of our previous works^{1,2}, on a variety of silicone stationary phases of varying polar character is reported and the results discussed and compared with earlier observations. The phases were selected as representative of the available types and varied from the essentially non-polar dimethyl polysiloxane to polysiloxanes with *p*-chlorophenyl and phenyl substitutions which exhibit some electron-donating properties and those with trifluoropropyl and cyanoalkyl substitution which exhibit some electron accepting properties.

EXPERIMENTAL

Preparation of esters

The esters where available were of commercial quality and of substantial purity. The remainder of the esters were prepared in the laboratory using conventional esterification or *trans*-esterification procedures and were purified before use.

Stationary phases

The basic structure of the stationary phases used was that of dimethyl polysiloxane. This substance with very low polarity methyl groups was essentially non-polar. However, by varying the degree of substitution of the methyl groups with more polar groups, the polarity of the phases could be varied. In this manner three major classes of stationary phases were obtained: (1) The non-polar; (2) the low to medium polarity electron donating phases; (3) the medium to polar electron accepting phases.

The degree and type of substitution as well as the classification of the polarity in terms of Rohrschneider constants for the polysiloxanes used is shown in Table I.

The Gensil S2116 provided by General Silicones Pty. Ltd., Chatswood, N.S.W.

was a white solid with a relatively sharp melting point *i.e.* 62°, that tended to bleed during use.

The 85% phenyl substituted polysiloxane was an experimental product provided by the Ohio Valley Specialty Chemical Company. The material was a white solid of high molecular weight and with a broad melting point. The majority of the sample melted in the range 135–155° but the sample was not completely molten until 165° and the peaks at 150° were somewhat broader than those obtained with OV-25.

While neither of these materials in their present physical state would be suitable as stationary phases, the retention behaviour due to their substitution is readily evident. The Rohrschneider constants were determined without difficulty and the values obtained were compatible with other polysiloxanes.

TABLE I

COMPOSITION AND ROHRSCHEIDER CONSTANTS OF POLYSILOXANES

Phase	Class	% Methyl replacement	Rohrschneider constants				
			<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i>	<i>s</i>
Gensil S2116 ^a	1	30% stearoyl	0.23	0.50	0.48	0.75	0.56
OV-1 ^b	1	—	0.16	0.20	0.50	0.85	0.48
F-61 ^a	1	11% <i>p</i> -chlorobenzyl	0.31	0.49	0.82	1.08	0.83
OV-17 ^b	2	50% phenyl	1.30	1.66	1.79	2.83	2.47
OV-25 ^b	2	75% phenyl	1.76	2.00	2.15	3.34	2.81
85% Phenyl ^a	2	85% phenyl	1.88	2.33	2.15	5.80	2.95
OV-210 ^b	3	50% trifluoropropyl	1.41	2.13	3.55	4.73	3.04
XE-60 ^b	3	25% cyanoethyl	2.08	3.85	3.62	5.33	3.45
XF-1150 ^a	3	50% cyanoethyl	2.92	4.78	4.54	7.05	4.95

^a Determined in this laboratory.

^b Determined by SUPINA AND ROSE¹.

It has been found that some minor variations occur with the determination of Rohrschneider constants. The values reported here have been obtained using a column of known characteristics as a control, newly conditioned columns being used in each case.

Gas chromatography

The retention data were obtained on a modified F&M 810/29 Research Chromatograph with simultaneous flame ionisation and thermal conductivity detection and fitted with an improved flow control system. Two 12 ft. × $\frac{1}{4}$ in. O.D. aluminium columns were packed with 10% of the stationary phase on 60–80 mesh acid-washed and silanised Celite 560 and operated isothermally at 150°.

With thermal conductivity detection the following conditions were used: injection temperature, 190°; detector temperature, 220°; bridge current, 150 mA; carrier gas, helium; flow rate, 65 ml/min with an inlet pressure of 40 p.s.i.

The retention data of the esters examined are shown in Table II as net retention (V_g) relative retention (V_R) using nonane as standard, and as retention indices (I_R).

TABLE II

RETENTION DATA FOR ALIPHATIC ESTERS

Compounds	Stationary phases							
	OV-1			F-61			OV-17	
	V_g	V_R	I_R	V_g	V_R	I_R	V_g	V_R
Methyl formate	0.050	0.075	380	0.049	0.070	400	0.037	0.123
Ethyl formate	0.085	0.129	487	0.100	0.143	533	0.066	0.220
Propyl formate	0.145	0.216	592	0.163	0.233	628	0.150	0.380
Butyl formate	0.250	0.375	703	0.270	0.414	733	0.250	0.630
Pentyl formate	0.425	0.645	812	0.482	0.689	831	0.410	1.030
Hexyl formate				0.820	1.172	933	0.710	1.790
Octyl formate				2.281	3.258	1129	1.480	4.930
Isopropyl formate	0.105	0.162	528	0.120	0.172	570	0.375	1.250
2-Methylpropyl formate	0.200	0.301	660	0.248	0.354	707	0.110	0.370
3-Methylbutyl formate	0.350	0.512	774	0.417	0.595	806	0.195	0.650
Methyl acetate	0.093	0.140	506	0.106	0.151	544	0.080	0.260
Ethyl acetate	0.130	0.200	571	0.154	0.220	614	0.100	0.360
Propyl acetate	0.225	0.338	683	0.253	0.362	710	0.180	0.580
Butyl acetate	0.375	0.585	787	0.435	0.621	813	0.300	0.970
Pentyl acetate	0.645	0.980	898	0.729	1.042	910	0.480	1.600
Hexyl acetate				1.216	1.737	1009	0.810	2.700
Octyl acetate				3.309	4.727	1202	2.200	7.960
Isopropyl acetate	0.170	0.259	625	0.181	0.259	647	0.115	0.390
2-Methylpropyl acetate	0.525	0.798	854	0.362	0.517	768	0.240	0.800
3-Methylbutyl acetate				0.623	0.890	882	0.390	1.300
Methyl propionate	0.155	0.235	607	0.167	0.238	629	0.120	0.390
Ethyl propionate	0.220	0.335	679	0.245	0.350	705	0.165	0.550
Propyl propionate	0.375	0.570	787	0.421	0.602	807	0.290	0.950
Butyl propionate	0.630	0.955	891	0.718	1.025	908	0.460	1.530
Pentyl propionate	1.060	1.602	998	1.168	1.668	1003	0.770	2.560
Hexyl propionate				1.973	2.819	1103	1.250	4.160
Octyl propionate				5.271	7.530	1392		
Isopropyl propionate	0.265	0.405	717	0.302	0.433	744	0.210	0.700
2-Methylpropyl propionate	0.520	0.790	853	0.606	0.865	878	0.380	1.260
3-Methylbutyl propionate	0.860	1.304	955	0.992	1.417	971	0.620	2.070
Methyl butyrate	0.260	0.397	714	0.275	0.393	728	0.190	0.630
Ethyl butyrate	0.375	0.565	788	0.410	0.585	800	0.260	0.930
Propyl butyrate	0.605	0.920	884	0.695	0.993	902	0.440	1.570
Butyl butyrate	0.975	1.480	980	1.121	1.602	996	0.690	2.470
Pentyl butyrate	1.550	2.350	1075	1.885	2.693	1094	1.150	4.110
Hexyl butyrate				3.122	4.400	1189	1.070	6.704
Octyl butyrate				8.369	11.955	1380	5.050	18.100
Isopropyl butyrate	0.450	0.680	823	0.504	0.720	840	0.320	1.070
2-Methylpropyl butyrate	0.780	1.180	937	0.916	1.308	955	0.590	1.970
3-Methylbutyl butyrate	1.300	1.970	1039	1.583	2.262	1060	0.995	3.320
Methyl isobutyrate	0.210	0.319	669	0.223	0.318	684		
Ethyl isobutyrate	0.295	0.445	738	0.319	0.456	753	0.213	0.710
Propyl isobutyrate	0.475	0.722	836	0.556	0.794	860	0.340	1.130
Butyl isobutyrate	0.770	1.170	933	0.901	1.287	955	0.550	1.830
Pentyl isobutyrate	1.265	1.870	1032	1.520	2.171	1052	0.930	3.100
Hexyl isobutyrate				2.416	3.452	1143	1.482	4.940
Octyl isobutyrate				6.797	9.710	1340	4.110	13.280
Isopropyl isobutyrate	0.370	0.565	785	0.396	0.566	796	0.240	0.770
2-Methylpropyl isobutyrate	0.660	0.997	900	0.751	1.073	919	0.460	1.490
3-Methylbutyl isobutyrate	1.050	1.590	998	1.266	1.809	1019	0.760	2.460
Methyl pentanoate	0.430	0.650	814	0.484	0.692	832	0.290	1.070
Ethyl pentanoate	0.595	0.900	879	0.705	1.007	903	0.450	1.500

ary phases

25	85% Phenyl					OV-210			XE-60		
	V_R	I_R	V_R	V_R	I_R	V_R	V_R	I_R	V_R	V_R	I_R
16	0.170	542	0.320	0.105	489	0.110	0.365	704	0.057	0.350	653
15	0.260	631	0.072	0.241	634	0.159	0.531	776	0.090	0.560	766
10	0.450	740	0.126	0.420	740	0.251	0.837	865	0.130	0.810	851
10	0.774	840	0.229	0.763	852	0.396	1.319	964	0.210	1.310	966
15	1.280	949	0.393	1.309	960	0.606	2.020	1068	0.330	2.060	1070
10	2.040	1042	0.663	2.210	1058	0.933	3.110	1172	0.490	3.060	1164
10	5.500	1244	1.880	6.265	1257	2.108	7.025	1367	1.170	7.310	1365
14	0.250	624	0.074	0.245	637	0.201	0.671	823	0.090	0.560	766
10	0.566	788	0.158	0.526	786	0.339	1.129	930	0.168	1.040	912
15	1.000	894	0.324	1.079	920	0.497	1.655	1019	0.265	1.660	1026
71	0.330	678	0.087	0.289	699	0.161	0.535	778	0.080	0.500	741
30	0.440	731	0.126	0.421	741	0.224	0.748	835	0.110	0.690	816
36	0.780	849	0.213	0.711	840	0.336	1.121	929	0.170	1.070	918
50	0.210	938	0.371	1.236	947	0.518	1.725	1030	0.260	1.630	1024
35	2.000	1040	0.623	2.078	1045	0.794	2.645	1134	0.400	2.500	1118
75	3.600	1158	0.971	3.238	1131	1.162	3.872	1222	0.620	3.880	1219
25	0.490	745	2.978	9.925	1345	2.643	8.810	1421	1.490	9.310	1438
25	0.910	884	0.142	0.474	741	0.266	0.887	877	0.125	0.780	844
35	1.560	990	0.276	0.921	890	0.469	1.563	1006	0.213	1.320	966
35	1.560	990	0.513	1.710	1011	0.692	2.305	1100	0.335	2.100	1085
05	0.512	764	0.146	0.486	768	0.214	0.712	835	0.114	0.760	836
40	0.700	829	0.211	0.703	840	0.305	1.018	905	0.150	1.000	900
55	1.180	933	0.357	1.189	940	0.473	1.575	1007	0.230	1.555	1006
10	1.955	1035	0.592	1.972	1034	0.717	2.390	1108	0.390	2.440	1110
85	3.140	1132	1.040	3.485	1142	1.088	3.625	1209	0.600	3.750	1210
85	5.050	1228	1.656	5.520	1234	1.602	5.341	1297	0.930	5.820	1314
85	12.950	1420	4.386	14.620	1422	3.561	11.870	1491	2.320	14.500	1524
65	0.770	847	0.243	0.810	865	0.353	1.178	926	0.190	1.190	941
10	1.500	983	0.454	1.513	986	0.669	2.231	1092	0.305	2.000	1060
50	2.500	1086	0.827	2.755	1100	0.986	3.286	1187	0.472	3.150	1170
70	0.780	850	0.219	0.730	845	0.326	1.086	902	0.170	1.130	930
25	1.070	914	0.333	1.109	926	0.445	1.482	992	0.230	1.440	988
95	1.800	1018	0.543	1.811	1020	0.677	2.258	1096	0.360	2.250	1090
45	2.930	1117	0.930	3.100	1122	1.019	3.395	1193	0.535	3.350	1188
30	4.780	1215	1.463	4.875	1205	1.520	5.065	1290	0.820	5.120	1283
30	7.580	1311	2.280	7.600	1297	2.310	7.700	1388	1.255	7.800	1381
35	19.200	1494	6.303	21.010	1492	4.995	16.650	1576	2.940	18.370	1576
55	1.190	933	0.375	1.250	953	0.527	1.757	1036	0.250	1.660	1026
70	2.350	1073	0.660	2.200	1257	0.910	3.034	1168	0.435	2.720	1131
35	3.800	1171	1.221	4.070	1172	1.367	4.555	1261	0.685	4.280	1236
75	0.830	865	0.168	0.561	796	0.276	0.919	882	0.160	1.190	941
80	1.400	970	0.256	0.853	878	0.373	1.244	951	0.270	1.690	1028
75	2.210	1060	0.388	1.292	959	0.584	1.947	1060	0.615	2.800	1141
80	3.540	1152	0.651	2.170	1058	0.856	2.854	1152	0.660	4.100	1244
25	5.700	1250	1.042	3.472	1147	1.298	4.327	1248	1.050	6.570	1341
25	14.550	1443	1.751	5.835	1246	1.380	6.460	1345	2.325	15.500	1541
85	0.860	868	4.536	15.120	1430	4.374	14.580	1543	0.185	1.230	952
80	1.730	1010	0.256	0.853	878	0.409	1.363	973	0.360	2.250	1090
15	2.860	1108	0.483	1.609	1000	0.702	2.339	1104	0.550	3.440	1192
100	1.400	970	0.813	2.709	1100	1.151	3.838	1221	0.300	2.000	1060
10	1.900	1029	0.423	1.410	971	0.508	1.693	1022	0.370	2.310	1100
10	1.900	1029	0.569	1.896	1029	0.650	2.168	1086			

(continued on p. 38)

TABLE II (continued)

Compounds	Stationary phases							
	OV-1			F-61			OV-17	
	V_G	V_R	I_R	V_G	V_R	I_R	V_G	V_R
Propyl pentanoate	0.975	1.480	980	1.154	1.648	1000	0.760	2.460
Butyl pentanoate	1.545	2.340	1074	1.899	2.794	1098	1.240	4.010
Pentyl pentanoate	2.455	3.720	1170	3.010	4.300	1184	1.850	6.400
Hexyl pentanoate				4.879	6.970	1292	3.000	10.200
Octyl pentanoate				12.887	18.410	1463		
Isopropyl pentanoate	0.725	1.110	921	0.844	1.206	940	0.505	1.680
2-Methylpropyl pentanoate	1.300	1.970	1027	1.554	2.220	1058	0.990	3.330
3-Methylbutyl pentanoate	2.060	3.120	1134	2.632	3.760	1158	1.585	5.280
Methyl 3-methylbutyrate	0.335	0.508	764	0.365	0.521	780	0.270	0.900
Ethyl 3-methylbutyrate	0.490	0.740	840	0.504	0.782	858	0.339	1.130
Propyl 3-methylbutyrate	0.785	1.190	937	0.923	1.319	959	0.570	1.900
Butyl 3-methylbutyrate	1.250	1.890	1030	1.483	2.118	1048	0.920	3.060
Pentyl 3-methylbutyrate	1.975	2.990	1125	2.377	3.395	1139	1.650	5.300
Hexyl 3-methylbutyrate				4.053	5.790	1240	2.590	8.350
Octyl 3-methylbutyrate				10.493	14.990	1421		
Isopropyl 3-methylbutyrate	0.605	0.920	883	0.677	0.967	899	0.370	1.230
2-Methylpropyl 3-methylbutyrate	1.040	1.580	994	1.212	1.731	1009	0.730	2.430
3-Methylbutyl 3-methylbutyrate	1.665	2.520	1088	1.992	2.845	1107		3.950
Methyl hexanoate	0.700	1.060	913	0.800	1.143	930	0.550	1.830
Ethyl hexanoate	0.970	1.470	980	1.139	1.628	998	0.750	2.680
Propyl hexanoate	1.560	2.360	1077	1.840	2.629	1088	1.390	4.350
Butyl hexanoate	2.475	3.750	1170	3.063	4.375	1185	2.340	7.300
Pentyl hexanoate	3.940	5.960	1268	4.928	7.040	1278	3.630	11.720
Hexyl hexanoate				8.022	11.460	1369	5.310	17.700
Octyl hexanoate				12.113	31.590	1564		
Isopropyl hexanoate	1.175	1.780	1018	1.385	1.978	1000	0.920	3.070
2-Methylpropyl hexanoate	2.035	3.080	1131	2.491	3.558	1147	1.695	5.650
3-Methylbutyl hexanoate	3.250	4.930	1227	4.081	5.830	1242	2.755	9.180
Methyl 4-methylpentanoate	0.580	0.880	876	0.666	0.952	893	0.500	1.650
Ethyl 4-methylpentanoate	0.825	1.250	947	0.970	1.386	965	0.648	2.160
Propyl 4-methylpentanoate	1.295	1.960	1038	1.595	2.278	1061	1.050	3.500
Butyl 4-methylpentanoate	2.105	3.200	1138	2.576	3.680	1152	1.655	5.520
Pentyl 4-methylpentanoate	3.315	5.020	1232	4.110	5.871	1243	3.080	9.450
Hexyl 4-methylpentanoate				6.741	9.630	1338	3.975	13.250
Octyl 4-methylpentanoate				17.591	25.130	1523		
Isopropyl 4-methylpentanoate	0.995	1.510	985	1.176	1.680	1003	0.770	2.490
2-Methylpropyl 4-methylpentanoate	1.750	2.650	1100	2.129	3.042	1117	1.500	4.700
3-Methylbutyl 4-methylpentanoate	2.805	4.250	1198	3.511	5.015	1213	2.470	7.700

DISCUSSION OF RESULTS

The plots of the logarithm of relative retention *versus* number of carbon atoms in the alcohol chain (R') for *n*- and *iso*-esters produced a series of linear relationships. The plots of these esters is shown in Fig. 1 where an example is taken from each class of phase examined. The 85% phenyl phase and OV-210 being representative of the electron donor and electron acceptor phases, respectively. The behaviour exhibited by the non-polar phases was similar to that of the donor phases.

From Fig. 1 it is evident that both positive and negative deviations occur for

primary phases

5			85% Phenyl			OV-210			XE-60		
	V_R	I_R	V_0	V_R	I_R	V_0	V_R	I_R	V_0	V_R	I_R
5	3.000	1126	0.900	3.000	1117	0.976	3.253	1184	0.580	3.630	1205
0	4.860	1218	1.415	4.715	1203	1.464	4.880	1279	0.850	5.670	1304
5	7.500	1312	2.334	7.780	1300	2.183	7.277	1375	1.260	8.400	1395
5	12.060	1404	3.657	12.190	1384	3.183	10.610	1468	1.870	12.460	1491
5	29.800	1589	9.270	30.900	1565	6.825	22.750	1650	4.230	28.150	1679
0	2.000	1040	0.607	2.023	1040	0.751	2.504	1120	0.400	2.500	1118
5	3.740	1166	1.081	3.633	1149	1.293	4.310	1246	0.710	4.440	1251
5	6.210	1268	1.844	6.145	1251	1.898	6.325	1341	1.000	6.650	1344
5	1.100	915	0.284	0.945	892	0.441	1.470	991	0.215	1.410	982
5	1.440	972	0.425	1.416	972	0.594	1.980	1065	0.775	1.720	1029
0	2.250	1063	0.700	2.332	1069	0.882	2.940	1158	0.420	2.620	1126
0	3.580	1156	1.118	3.725	1159	1.298	4.325	1249	0.630	4.050	1225
5	5.450	1243	1.859	6.195	1256	1.914	6.380	1341	0.980	6.120	1320
0	9.140	1345	3.033	10.110	1365	2.844	9.480	1438	1.465	9.160	1418
			7.950	26.500	1539	6.189	20.630	1628	3.425	21.420	1616
0	1.490	976	0.483	1.611	999	0.795	2.759	1134	0.305	1.910	1053
5	2.860	1108	0.858	2.861	1105	1.128	3.759	1217	0.520	3.250	1179
0	4.700	1200	1.508	5.025	1213	1.770	5.900	1324	0.795	4.960	1276
0	2.250	1063	0.671	2.238	1060	0.735	2.451	1115	0.434	2.700	1130
5	3.000	1128	0.915	3.050	1120	0.990	3.299	1186	0.520	3.260	1171
5	4.900	1219	1.150	5.000	1213	1.484	4.945	1284	0.830	5.190	1286
5	7.640	1310	2.240	8.000	1308	2.244	7.420	1380	1.260	7.880	1382
5	12.120	1406	3.915	13.050	1401	3.336	11.120	1478	1.960	12.200	1482
5	19.680	1508	6.435	21.450	1496	4.836	16.120	1569	2.720	18.090	1577
			16.035	53.450	1673	10.530	35.100	1757	6.220	41.400	1766
5	3.300	1143	1.017	3.391	1140	1.149	3.830	1224	0.580	3.630	1205
5	6.020	1258	1.887	6.290	1260	1.985	6.615	1352	1.040	6.510	1339
20	9.520	1357	3.182	10.605	1359	2.883	9.610	1445	1.565	9.790	1433
5	1.840	1020	0.540	1.800	1019	0.710	2.367	1105	0.355	2.250	1090
50	2.560	1090	0.735	2.450	1075	0.949	3.162	1176	0.455	2.840	1142
50	3.960	1180	1.215	4.050	1170	1.430	4.765	1275	0.700	4.380	1244
50	6.370	1270	1.950	6.500	1265	2.112	7.040	1369	1.060	6.630	1344
35	10.000	1360	3.129	10.430	1358	3.012	10.400	1464	1.615	10.100	1441
35	15.800	1466	5.046	16.820	1450	4.710	15.700	1560	2.450	15.300	1540
35	40.600	1650	13.023	43.410	1632	10.365	34.550	1753	5.625	35.200	1734
35	2.660	1095	0.818	2.725	1198	1.113	3.710	1214	0.517	3.200	1173
55	4.800	1220	1.508	5.025	1216	1.830	6.100	1334	0.855	5.350	1294
35	7.790	1316	2.555	8.515	1312	2.778	9.260	1435	1.380	8.030	1391

methyl and isopropyl esters, respectively, however an examination of the deviations from linearity with respect to the changing effects of column polarity and increasing homologous series produced no definite trend and their behaviour was attributed to the effects of boiling point. The increase of the methyl esters being due to the slightly polar methyl group being adjacent to the polar ester group allowing the transmission of the effect of the dipole through a greater length in the molecule, which increases the cohesive forces and thus the boiling point. The decrease in boiling points for the isopropyl esters can be attributed to molecular shapes⁶. When branching occurs the shape of the molecule approaches a sphere and hence the intermolecular forces are

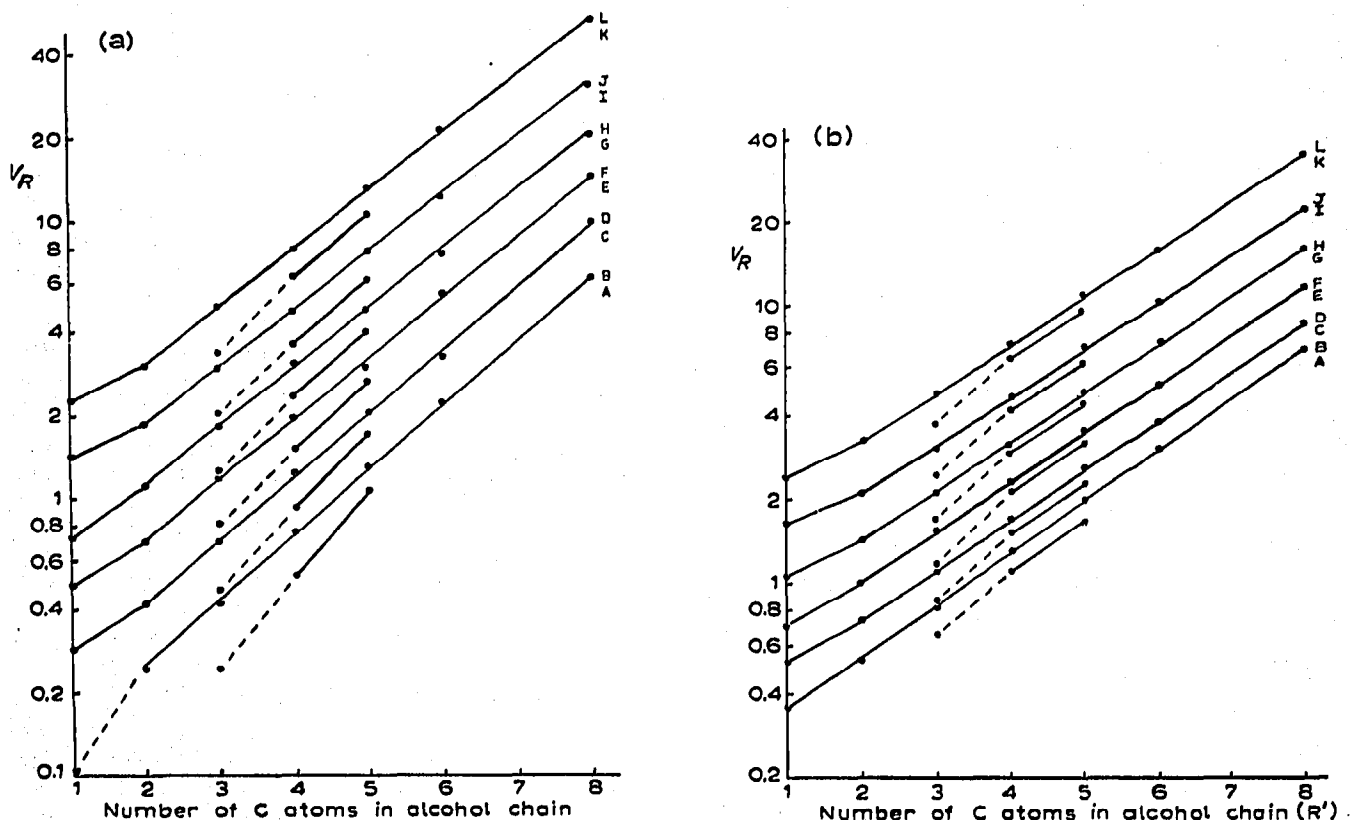


Fig. 1. Plots of the logarithm of the relative retention volume *vs.* the number of carbon atoms in the alcohol chain of saturated esters on (a) 85% Phenyl and (b) OV-210 stationary phases with the alcohol chain (R') forming both *n*- and *iso*-esters while the acid chain (R) is linear. A = HCOO-*iso*-R'; B = HCOOR'; C = CH₃COO-*iso*-R'; D = CH₃COOR'; E = C₂H₅COO-*iso*-R'; F = C₂H₅COOR'; G = C₃H₇COO-*iso*-R'; H = C₃H₇COOR'; I = C₄H₉COO-*iso*-R'; J = C₄H₉COOR'; K = C₅H₁₁COO-*iso*-R'; L = C₅H₁₁COOR'.

overcome at a lower temperature. With isopropyl esters this effect will be maximised.

With all plots it appeared that the lower homologs had maximum slopes that decreased as R increased. This trend is better observed from Table III, where the methylene increments for the alcohol chain are tabulated. It is apparent that the increments decrease as R increases. The effect of column polarity is not so great, although it appears that for the lower homologs, *i.e.* where R equals 0 to 2, that the increments decrease as column polarity increases or more noticeably that the range

TABLE III

METHYLENE INCREMENTS FOR ALCOHOL CHAIN OF *n*-ALKYL ESTERS

	OV-1	F-61	OV-17	OV-25	85% Phenyl	OV-210	XE-60
Formate	108	99	102	102	104	99	100
Acetate	109	98	102	106	101	98	103
Propionate	106	98	100	99	97	98	104
Butyrate	96	97	98	97	94	97	98
Pentanoate	97	93	96	93	89	94	97
Hexanoate	96	94	97	96	92	95	98

of the increments is reduced, especially on the accepting columns. Both effects probably result from "general" polarity. The former being a dilution effect, *i.e.* a methylene group has less effect on larger molecules, while the latter is due to the fact that the non-polar methylene group will have more influence on non-polar columns where boiling points influence separation.

An obvious feature of Fig. 1 is that for the OV-210 column it appears that the separation of the lower homologs is reduced. With the formate and acetate esters the donor hydrogen and methyl groups will be adjacent to the acceptor carboxyl and the acceptor properties of the compounds will be at a minimum due to the transmission of the dipole induced in the chain. Thus the retention of these compounds will be increased on an acceptor column as the acceptor properties of the substances should be minimised. This in turn will reduce the acceptor/acceptor repulsion in the column and increase the relative retention of these lower members with respect to the higher members. When methylene groups are introduced into the acid chain the transmission of the induced dipole in the chain will diminish in a geometrical progression⁶ as the valency linkage increases. Hence due to the weak donating effect of the methyl group, the acceptor properties of the ester will be dependent upon the decreasing interaction between the carbonyl group and the methyl group. As the methyl group moves further away from the carbonyl group this increased retention is not observed to the same extent, *i.e.* as R becomes greater than 3.

When the relative retention was plotted against the number of carbon atoms in the acid chain (R) in Fig. 2 linear relationships were obtained on the non-polar

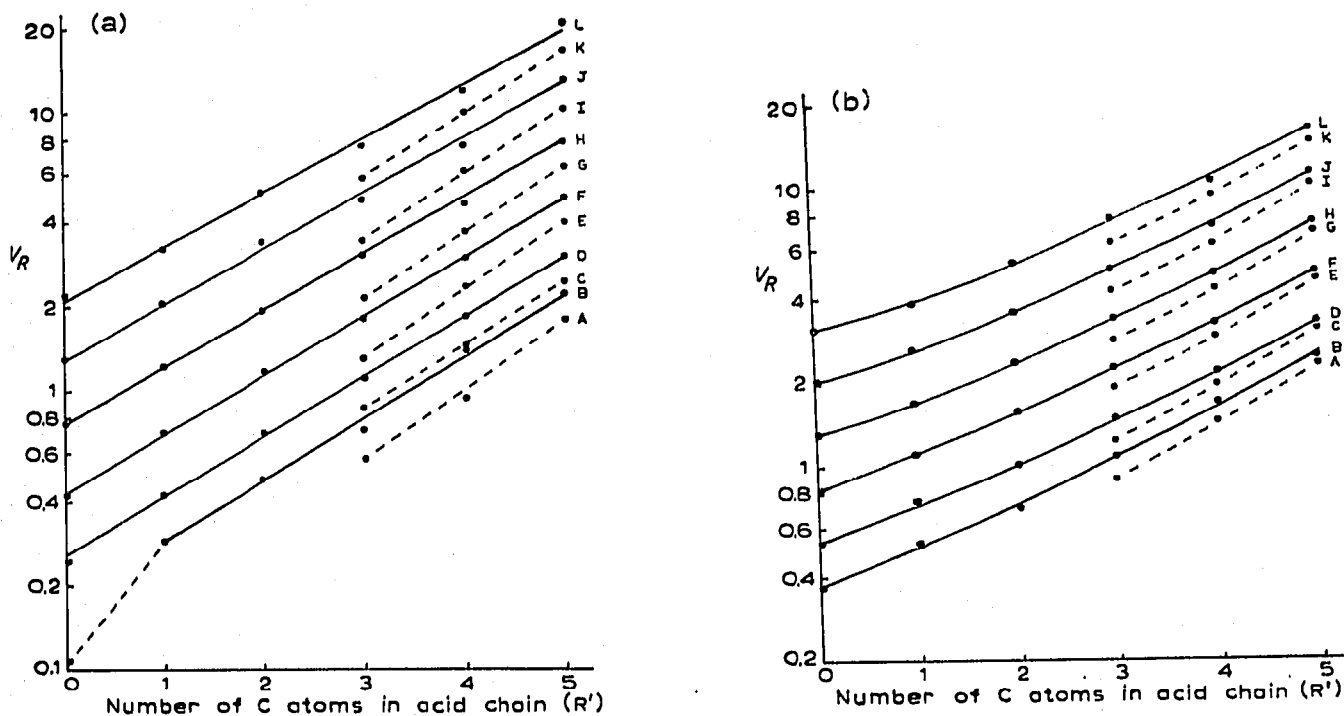


Fig. 2. Plots of the logarithm of the relative retention volume *vs.* the number of carbon atoms in the acid chain for saturated esters on (a) 85% Phenyl and (b) OV-210 stationary phases with R of both *normal*- and *iso*-structure while the alcohol chain is linear. A = *iso*-RCOOCH₃; B = RCOOCH₃; C = *iso*-RCOOC₂H₅; D = RCOOC₂H₅; E = *iso*-RCOOC₃H₇; F = RCOOC₃H₇; G = *iso*-RCOOC₄H₉; H = RCOOC₄H₉; I = *iso*-RCOOC₅H₁₁; J = RCOOC₅H₁₁; K = *iso*-RCOOC₆H₁₃; L = RCOOC₆H₁₃.

TABLE IV

METHYLENE INCREMENTS FOR THE ACID CHAIN OF *n*-ALKYL ESTERS

	SE-30	F-61	OV-17	OV-25	85% Phenyl	OV-210	XE-60
Methyl	102	97	98	96	98	84	97
Ethyl	99	93	99	99	97	82	91
Propyl	97	92	97	96	94	84	87
Butyl	93	90	97	94	91	83	83
Pentyl	91	89	97	92	88	82	78
Hexyl	—	87	—	93	88	79	83
Octyl	—	87	—	—	83	78	81

and donor phases where the 85% phenyl phase is representative of the type of behaviour observed. The acceptor phases no longer produced linear relationships. This would be expected from a study of the alcohol plot Fig. 1 where the separation between the homologs increased with R, *i.e.* the lower formate, acetate and propionate series showed a considerable interaction and increased retention with the acceptor phases. From Table IV the methylene increments can be seen for the acid chain (R). It should be noted that the values for the polar XE-60 and OV-210 acceptor columns are averages of a non-linear slope, and therefore possibly misleading. However, they do show similar trends to Table III. It is interesting to compare the values from the two tables where it is noted that the values in Table IV are generally lower than the corresponding ones in Table III which indicates that a methylene group has more effect in the alcohol chain (R') than in the acid chain (R). This explains why the

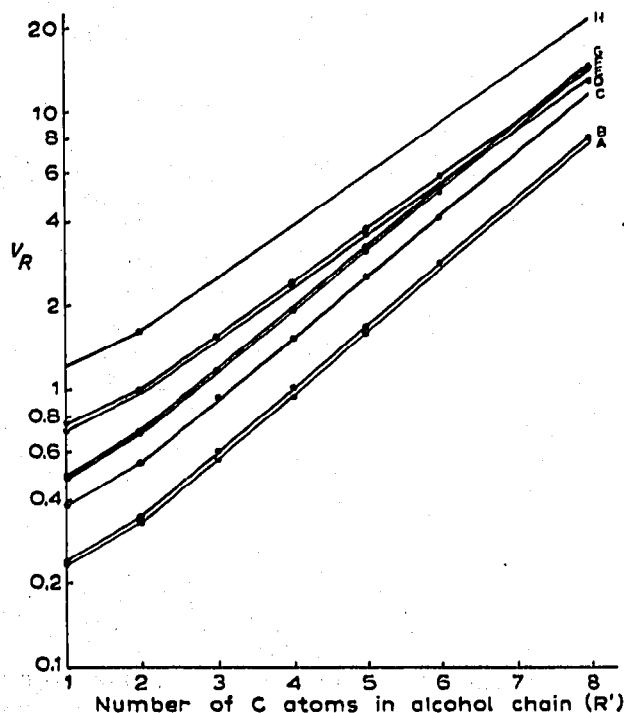


Fig. 3. A plot of the logarithm of the relative retention volume *vs.* number of carbon atoms in the alcohol chain for *n*-alkyl propionate esters on stationary phases of varying polarity. A = OV-1; B = F-61; C = OV-17; D = OV-210; E = XE-60; F = OV-25; G = 85% Phenyl; H = XF-1150.

relative retention of the lower alcohol homolog was not increased with respect to the higher alcohol homolog as experienced with the acid homologs in Fig. 2 on acceptor columns. It is probable that the presence of the ether linkage allows a better transmission of the dipole between the low polarity methyl group and the polar carbonyl group of the ester in the alcohol chain due to polarisation of the adjacent methylene groups, resulting in a similar increase in relative retention for the lower and higher alcohol homologs.

The effect of isomerism in the acid chain did not appear to be affected significantly by column polarity and as previously discussed, followed the corresponding boiling point trends which were most probably due to surface areas.

The effect of column polarity on the saturated esters is shown in Fig. 3 with a plot of log retention *versus* number of carbon atoms in the alcohol chain for the propionate esters. From this figure it is apparent that there are two sets of parallel plots, the first having the steeper slope consisting of the electron donor and non-polar stationary phases. The second set with lower slope consists of the electron acceptor columns. This change in slope can again be explained in terms of polar interactions. As the number of carbon atoms in the alcohol chain increases, the overall acceptor properties will similarly increase as previously explained. Consequently on an acceptor column because of like/like repulsions the slope will be lower than on a donor column.

It was not surprising that the donor and non-polar phases had similar slopes

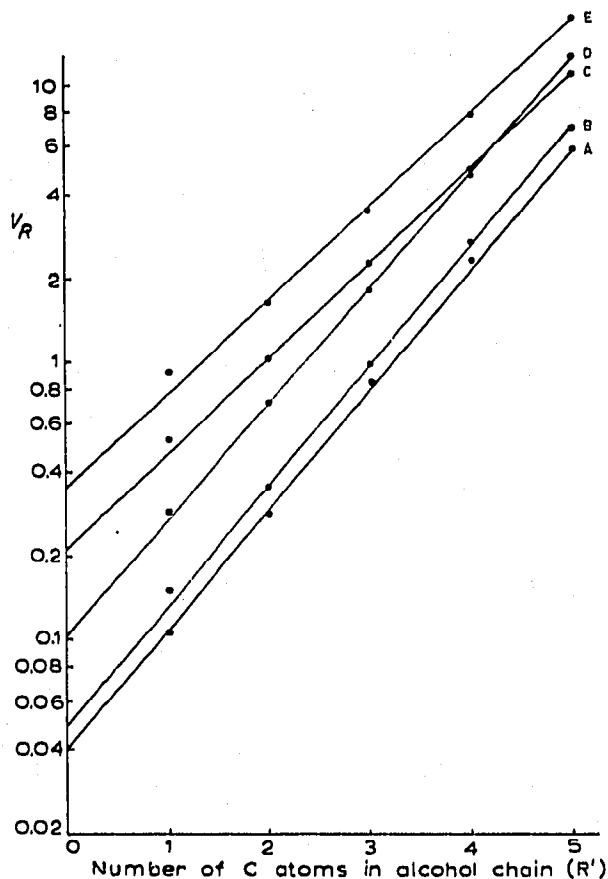


Fig. 4. Plots of the logarithm of relative retention volume *vs.* the number of carbon atoms in the alcohol chain of normal saturated esters where $R = R'$ on: A = Gensil S2116; B = F-61 C = OV-210; D = 85% phenyl; E = XF-1150.

TABLE V

THE EFFECT OF THE CARBOXYL GROUP ON RETENTION

<i>Columns</i>	<i>Retention</i>
Gensil S2116	275
OV-1	304
F-61	353
OV-17	410
OV-25	550
85% Phenyl	495
XE-60	520
OV-210	541
XF-1150	641

as the two classes of phases have exhibited very similar retention behaviour throughout this study. From a consideration of Rohrschneider constants it would be expected for donor columns that dominant donor factors x and y would be present, even allowing for the fact that the constants have very little physical meaning. This, however, does not happen and it appears that the effect of introducing phenyl groups into the dimethyl siloxane polymer is to increase the "general polarity" of the column. The acceptor phases do have some dominant acceptor factors u and s confirming the presence of their acceptor behaviour, however, there still appears to be present a large "general polarity" as exhibited by the magnitude of the remaining factors.

The effect of the carboxyl group on the retention of the n -alkyl esters was found from Fig. 4 where esters with the same number of carbon atoms in the acid and alcohol chains, *i.e.* when $R = R'$, were plotted against log relative retention. This relationship was linear and by extrapolating the plot to zero, *i.e.* $R = R' = 0$, the relative contribution of carboxyl group was obtained. The retention of the carboxyl group for the columns used is shown in Table V. As expected the net retention of the group increased with increasing polar character of the column.

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