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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

PART IV. INFLUENCE OF STATIONARY PHASE POLARITY
ON RETENTION OF UNSATURATED ESTERS

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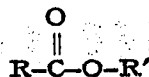
SUMMARY

The retention behaviour of a number of homologous series of unsaturated esters on polysiloxane stationary phases of increasing polar character is reported.

INTRODUCTION

An earlier report¹ has described the gas chromatography of several series of homologous unsaturated esters on the essentially non-polar Methyl Polysiloxane Stationary Phase SE-30.

Esters may be conveniently represented as



where the carbon numbers of the acid and alcohol chains are R and R' respectively. Studies of alkanes² and of fatty esters³⁻⁵ show that the introduction of a double bond in the acid chain produces a reduction in retention on a non-polar stationary phase. With simple esters where R = 2, *i.e.* acrylates and propionates, this effect has been observed; similarly where R = 1, 2 or 3 and R' = 2, *i.e.* vinyl and ethyl esters, decreased retention is also experienced¹.

When the hydrogen of the α -carbon atom of the acrylate ester (R) was replaced by a methyl group (the methacrylate esters) increased retention was observed when compared to the appropriate saturated ester. A greater increase in retention was observed with substitution of the β -carbon atom (R) (the crotonate esters) when compared with the butyrate esters. The replacement of a hydrogen atom in vinyl acetate with a methyl group (isopropenyl acetate) also produced increased retention compared with the saturated ester.

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TABLE I
RETENTION DATA FOR UNSATURATED ESTERS

Ester	Stationary phase											
	SE-30			OV-17			OV-25			XE-60		
	V_R^a	V_R^b	I_R	V_R^a	V_R^b	I_R	V_R^a	V_R^b	I_R	V_R^a	V_R^b	I_R
Methyl acrylate	0.128	0.194	569	0.140	0.450	743	0.110	0.512	766	0.120	0.78	844
Ethyl acrylate	0.205	0.310	664	0.165	0.550	784	0.155	0.720	831	0.160	1.03	911
Propyl acrylate	—	—	—	0.280	0.930	887	0.260	1.21	939	0.232	1.55	1006
Butyl acrylate	0.595	0.903	878	0.470	1.57	987	0.445	2.02	1040	0.380	2.45	1111
Pentyl acrylate	0.960	1.455	978	0.870	2.80	1108	0.715	3.28	1142	0.580	3.75	1210
Hexyl acrylate	1.595	2.42	1068	1.415	4.55	1200	1.155	5.30	1240	0.895	5.78	1312
Isopropyl acrylate	—	—	—	0.195	0.65	816	0.180	0.835	865	0.165	1.06	914
2-Methylpropyl acrylate	—	—	—	0.410	1.32	953	0.330	1.51	986	0.300	1.94	1055
Methyl methacrylate	0.217	0.329	677	0.210	0.680	829	0.175	0.830	865	0.160	1.02	909
Ethyl methacrylate	0.320	0.482	756	0.249	0.830	863	0.245	1.12	920	0.210	1.40	980
Propyl methacrylate	0.528	0.798	856	0.402	1.34	957	0.375	1.79	1016	0.315	2.10	1085
Butyl methacrylate	0.884	1.34	962	0.690	2.30	1068	0.640	2.94	1118	0.485	3.24	1179
Pentyl methacrylate	1.46	2.212	1064	1.23	3.97	1176	1.035	4.75	1214	0.760	4.90	1272
Hexyl methacrylate	2.40	3.64	1165	2.07	6.68	1281	1.630	7.60	1312	1.115	7.43	1369
Octyl methacrylate	—	—	—	5.10	17.00	1463	3.905	18.45	1489	—	—	—
2-Methylpropyl methacrylate	0.750	1.135	928	0.620	1.94	1032	0.475	2.21	1060	0.410	2.64	1128
3-Methylbutyl methacrylate	—	—	—	4.05	13.51	1416	3.025	14.42	1439	—	—	—
Ethyl crotonate	0.441	0.667	820	0.430	1.39	965	0.395	1.80	1016	0.340	2.12	1086
Propyl crotonate	0.710	1.075	917	0.670	2.23	1065	0.625	2.87	1112	0.535	3.35	1188
Butyl crotonate	1.190	1.804	1021	1.10	3.67	1157	1.005	4.74	1210	0.760	4.90	1272
Pentyl crotonate	1.905	2.89	1119	1.84	6.13	1265	1.515	7.22	1307	1.170	7.55	1372

Isopropyl crotonate	0.540	0.818	863	0.435	1.50	978	0.385	1.77	1015	0.337	2.24	1090
2-Methylpropyl crotonate	0.978	1.481	983	0.900	2.80	1094	0.780	3.58	1156	0.630	4.06	1232
3-Methylbutyl crotonate	1.61	2.44	1082	1.413	4.71	1208	1.255	5.92	1257	0.980	6.32	1332
Vinyl acetate	0.115	0.173	548	0.096	0.320	679	0.070	0.341	688	0.086	0.571	770
Vinyl propionate	0.190	0.286	648	0.150	0.490	763	0.125	0.580	790	0.135	0.870	861
Vinyl butyrate	0.310	0.466	750	0.260	0.810	859	0.200	0.950	892	0.200	1.29	963
Vinyl pentanoate	—	—	—	0.380	1.29	950	0.340	1.56	990	0.280	2.00	1060
Vinyl hexanoate	—	—	—	0.635	2.08	1037	0.565	2.59	1095	0.430	3.07	1162
Vinyl isobutyrate	—	—	—	0.150	0.518	773	0.175	0.815	857	0.145	1.04	912
Vinyl 3-methylbutyrate	—	—	—	0.285	0.950	889	0.250	1.15	928	0.210	1.50	996
Vinyl 4-methylpentanoate	—	—	—	0.500	1.64	998	0.450	2.09	1050	0.350	2.50	1118
Allyl formate	0.130	0.200	571	0.120	0.380	714	0.100	0.455	743	0.120	0.780	844
Allyl acetate	0.210	0.310	670	0.190	0.600	801	0.155	0.720	831	0.144	0.960	892
Allyl propionate	0.340	0.521	770	0.310	0.970	895	0.260	1.18	933	0.230	1.48	995
Allyl butyrate	0.520	0.790	853	0.500	1.60	990	0.400	1.84	1020	0.355	2.29	1096
Allyl pentanoate	0.880	1.33	960	0.830	2.60	1090	0.660	3.07	1123	0.535	3.45	1192
Allyl hexanoate	1.430	2.16	1056	1.375	4.30	1192	1.075	4.89	1219	0.830	5.35	1294
Allyl octanoate	—	—	—	—	—	—	—	—	—	1.960	12.66	1490
Allyl isobutyrate	0.430	0.649	815	0.324	1.08	916	0.295	1.37	961	0.280	1.81	1041
Allyl 3-methylbutyrate	0.710	1.082	915	0.620	1.94	1032	0.500	2.29	1065	0.410	2.64	1130
Allyl 4-methylpentanoate	—	—	—	—	—	—	0.885	4.02	1181	0.640	4.27	1240
Isopropenyl acetate	0.185	0.274	644	0.140	0.460	744	0.130	0.605	782	0.095	0.680	815
Isopropenyl propionate	—	—	—	0.220	0.749	846	0.210	0.970	894	0.165	1.10	921
Isopropenyl butyrate	—	—	—	0.385	1.263	944	0.340	1.58	988	0.225	1.60	1012
Isopropenyl pentanoate	—	—	—	0.600	1.97	1036	0.570	2.60	1095	0.365	2.60	1022
Isopropenyl hexanoate	—	—	—	1.005	3.30	1138	0.895	4.16	1189	—	—	—
Isopropenyl isobutyrate	—	—	—	0.265	0.870	875	0.250	1.17	928	0.200	1.43	988
Isopropenyl 3-methylbutyrate	—	—	—	—	—	—	0.410	1.91	1029	0.330	2.20	1084
Isopropenyl 4-methylpentanoate	—	—	—	0.795	2.61	1092	0.715	3.33	1144	0.510	3.40	1184

^a Corrected for dead volume.

^b Relative to nonane.

The present work reports the retention behaviour of unsaturated esters of the types described previously, together with those where $R' = 3$ and has both a straight chain (the allyl esters) and also a branched chain (isopropenyl esters). The esters were examined on several stationary phases of increasing polar character. The results are compared with those of fatty esters where decreased and increased retention is observed with the introduction of unsaturation on substantially non-polar and polar stationary phases, respectively.

Retention data of unsaturated esters has been tabulated by SCHUPP AND LEWIS⁶. Allyl esters (C_8-C_{18}) have been examined previously on an Apiezon M column⁷ while systematic studies relevant to this work have been previously reviewed¹.

EXPERIMENTAL

Preparation of esters

The esters where available were of commercial quality and of substantial purity. The remainder of the esters were prepared using esterification or transesterification procedures with an acidic ion-exchange resin as catalyst.

Chromatography

The retention data were obtained isothermally at 150° using 12 ft. \times $1/4$ in. O.D. aluminium columns packed with 10% stationary phase (Methyl Silicone Polymer SE-30, Methyl Phenyl Silicone Polymers OV-17 and OV-25 and Methyl Cyanoethyl Silicone Polymer XE-60) each on 60-80 mesh acid washed and silanised Celite 560. The equipment, conditions and calibration procedures were as previously reported¹.

The retention data of the esters examined are shown in Table I as net retention (V_0), relative retention (V_R) using nonane as standard, and as retention indices (I_R).

DISCUSSION OF RESULTS

The influence of a double bond in the acid chain (R) is observed by comparison of the homologous acrylate, methacrylate and crotonate esters with the propionate, isobutyrate and butyrate esters as shown in Fig. 1. Figs. 1a and b show plots of relative retention *versus* the number of carbon atoms in the alcohol chain (R') on SE-30 and XE-60 stationary phases. The slopes of all of the esters on SE-30 were essentially parallel, the minor variations apparent having been previously described¹. With the XE-60 phase plots representing the acrylate and butyrate esters intercepted (*i.e.* decreased retention due to the double bond being more apparent with the higher alkyl esters) while the plot representing the crotonate esters showed a considerably greater increase in retention on the more polar phase.

London forces, due to the interaction of two rapidly changing instantaneous dipoles, exist to varying degrees between all molecules. With non-polar molecules these are the sole attractive forces. The London forces do not exhibit any special selectivity and the retention behaviour in non-polar systems is determined by the boiling point of the compounds. This effect is observed with simple saturated normal and isoalkyl esters on SE-30 (ref. 8) as is the reduction of retention due to branching as described by JAMES AND MARTIN⁸.

The behaviour of fatty esters on non-polar stationary phases was suggested by

JAMES^{4,5} to follow that of hydrocarbons. The attractive forces are influenced by the chain length, branching, unsaturation, location of double bond and the presence of conjugation.

Linear relationships between chain length and retention of homologous compounds are usually obtained and greater methylene separation factors are observed

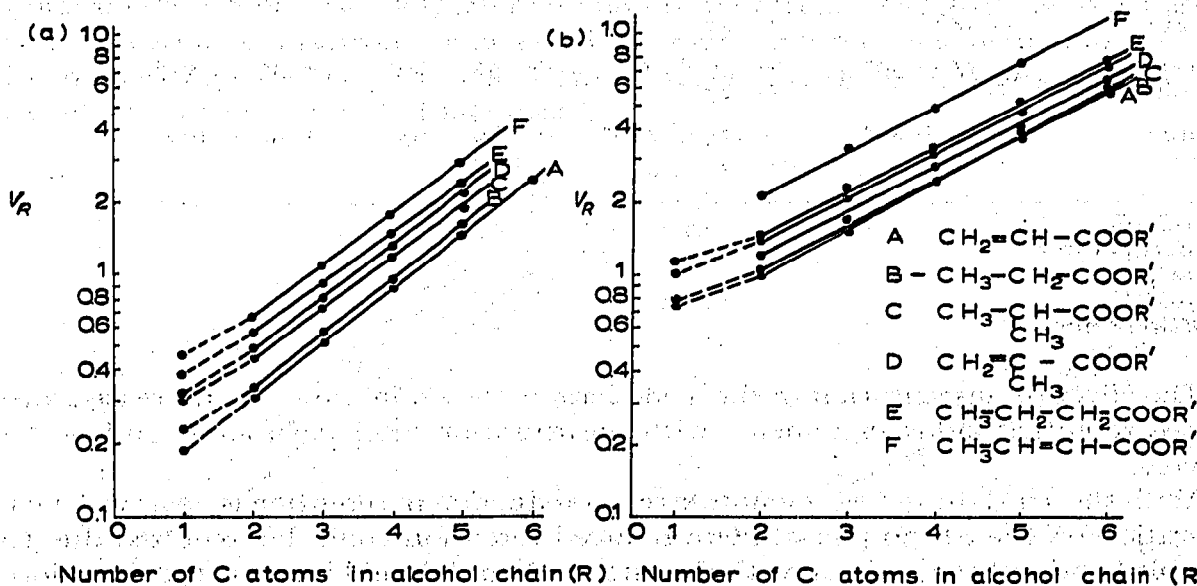


Fig. 1. Plot of logarithm of relative retention *versus* number of carbon atoms in the alcohol chain of unsaturated esters on (a) SE-30 and (b) XE-60 stationary phases.

with non-polar stationary phases where London forces are at their maximum. With polar phases the methylene separation factors are lowered as the London forces are reduced.

The introduction of a double bond into a saturated fatty ester was shown by JAMES AND MARTIN⁹ to reduce retention on a non-polar phase, a conclusion now widely apparent. Maximum interaction occurs with methylene groups and this is reduced with the ethylenic group.

With polar stationary phases specific interactions occur between polarisable double bonds and the ester groups in addition to the London interactions which operate in the opposite direction. For each non-interacting double bond an approximately equivalent retention increase is observed on a polar phase conversely on a non-polar phase decreased retention occurs. While conjugated fatty esters have not been extensively studied the limited data available show increased retention occurring on both polar and non-polar phases; conjugation with the ester carbonyl is similarly anomalous^{9,10}.

Some polar character is exhibited by saturated esters due to the carbonyl structure. Although the dipole moment is not great the degree of polarisability is higher. The dipole moment of esters is little influenced by unsaturation although the polarisability is increased. Increased retention on a polar phase would be expected with an unsaturated ester of similar boiling point to a saturated ester. The reverse effect would be expected on a non-polar stationary phase.

TABLE II
EFFECT OF THE PRESENCE OF UNSATURATION IN THE ACID CHAIN

Esters	Stationary phase			
	SE-30	OV-17	OV-25	XE-60
Acrylate	- 15 - 20 ^a	o + 15 ^a		o + 20 ^d
Propionate	- 38 ^b	+ 27		
Methacrylate	+ 15 + 30 ^a	+ 90 + 95 ^a	+ 55 + 60 ^a	+ 30 + 60 ^a
Isobutyrate	+ 8 ^b	+ 27 ^c		
Crotonate	+ 30 + 40 ^c	+ 125 + 130 ^c	+ 80 + 95 ^a	+ 90 + 100 ^a
Butyrate	+ 68 ^b	+ 98 ^b	+ 102 ^b	

- ^a n -C₃-C₆
^b Methyl ester.
^c n -C₂-C₄.
^d n -C₁-C₆.
^e Ethyl ester.

The effect of unsaturation in the acid chain is shown in Table II. Increased and decreased retention index increments with unsaturation are shown as + and - respectively.

With the acrylate and propionate esters a reduction in retention is observed with unsaturation on the SE-30 phase. Here reduced retention could be expected due to the double bond but conjugation with the ester carbonyl should increase the retention. This system with the stationary phases of increasing polarity shows the anticipated increase in retention. The methacrylate and crotonate esters on the phases show greater retention than the corresponding saturated esters. The methacrylates due to their branched chain have lower retention than the crotonates on each phase.

With fatty esters the introduction of unsaturation produces little relative effect on boiling point but with simple esters variations in boiling point are more apparent especially with the low polarity phase.

With the same total chain length acrylates and propionates have virtually identical boiling points and the boiling points are not of consequence. Methacrylates have slightly higher boiling points than butyrates and some increase in retention could be expected. Crotonates have substantially higher boiling points than butyrates and a greater increase in the retention could be expected. It thus seems that the boiling

TABLE III
EFFECT OF THE PRESENCE OF UNSATURATION IN ALCOHOL CHAIN

Esters	Stationary phase			
	SE-30	OV-17	OV-25	XE-60
Vinyl	- 20 - 40	- 18 - 30	- 20 - 40	- 20 - 40
Ethyl				
Alkyl	- 30 - 30	+ 3 + 10	+ 3 + 5	- 9 + 25
Propyl				
Isopropenyl	+ 19 ^a	+ 15 + 35	+ 45 + 60	- 15 - 20

^a Isopropenyl acetate.

point of simple unsaturated esters on a non-polar phase plays a very significant role in determining the retention.

The effect of unsaturation in the alcohol chain is shown in Table III, while Figs. 2a-b show plots of the esters obtained using SE-30 and XE-60 stationary phases respectively. With vinyl and ethyl esters reduced retention is experienced with the unsaturated esters on all four stationary phases. Increased retention on the more polar phases is not observed, the reduction being little affected by the four stationary phases. Terminal unsaturation in a chain is responsible for some reduction in retention in comparison to other positions of unsaturation but the results observed would not be expected from studies of fatty esters.

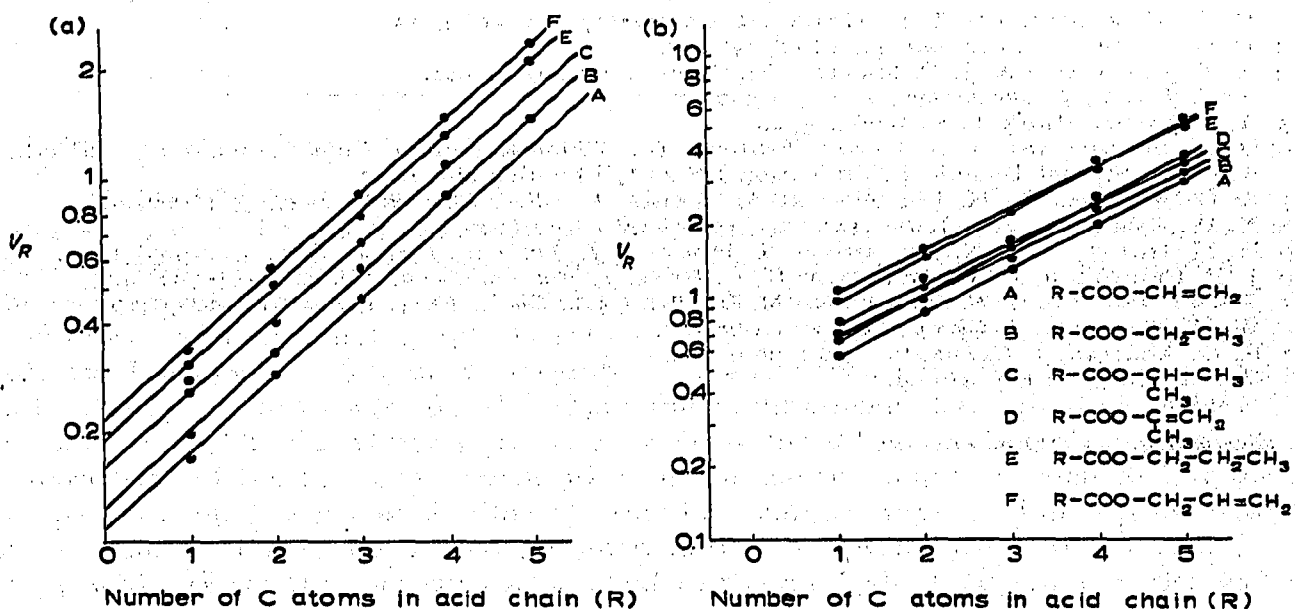


Fig. 2. Plot of logarithm of relative retention *versus* number of carbon atoms in the acid chain of unsaturated esters on (a) SE-30 and (b) XE-60 stationary phases.

Allyl esters exhibited reduced retention on the SE-30 stationary phase and increased retention on the more polar phases. While these results may be as anticipated, terminal unsaturation present as with the vinyl esters and the added methylene group in a non-conjugated environment would not be expected to be significant.

Isopropenyl acetate showed an increase in retention on the non-polar phase similar to that shown by the methacrylate esters.

The majority of the structural arrangements including unsaturation, location of the double bond, *i.e.* terminal or conjugated unsaturation and the presence of branching existing in the simple esters examined have been studied in detail with fatty esters. It is well known that the particular location of a double bond^{11,12} or methyl group¹³ along a chain will influence retention due to interactions that occur. It is apparent from this work that studies of fatty esters provide little information relevant to the simpler compounds due to the significant effect of interactions that are present.

The $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}$ structure of the methacrylate and isoprenyl esters is not widely experienced in fatty esters and its behaviour is not apparent from a consideration of

fatty ester studies of the individual effects of branching and the position of unsaturation.

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