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APPLICATION OF LINEAR EXTRATHERMODYNAMIC RELATIONSHIPS TO ALCOHOLS, ALDEHYDES, KETONES AND ETHOXY ALCOHOLS

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SUMMARY

The series of five simple and inter-related extrathermodynamic relationships developed by Fellous and co-workers and previously examined with various esters have been further examined by consideration of alcohols, aldehydes, ketones and ethoxy alcohols on stationary phases of varying polar character to determine general application of the relationships.

INTRODUCTION

The five interrelated relationships developed by Fellous and co-workers[1–4] with restricted *n*-alkyl ether data have been summarised in the previous paper[5] where a fairly extensive number of closely related carbonyl compounds, *i.e.* esters, were examined on a variety of stationary phases in an endeavour to determine the value of the relationships on closely related compounds. The present work considers the study of further series of homologous oxygenated compounds including alcohols, aldehydes, ketones and ethoxy alcohols on a similar range of stationary phases to examine any general applicability of the relationships.

EXPERIMENTAL

Gas chromatography used a Hewlett-Packard 5750 research chromatograph interfaced to a 16K P.D.P. 11/40 digital computer. Interfacing was achieved by the use of an LPS 11 Laboratory Peripheral System comprising a 12-bit analog-to-digital converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit digital-to-analog converters. All on-line programming was witten in CAPS II Basic with LPS options. The sampling rate was 0.5 sec. Retention was determined as indices and relative retention, the dead times being determined methamatically.

The data were obtained isothermally at 150° with 12 ft. × 0.25 in. aluminium columns packed with 10% stationary phase on 62–70 mesh acid-washed and silanized Celatom.

TABLE I

RETENTION RELATIVE TO *n*-NONANE AND RETENTION INDICES OF ALCOHOLS, ALDEHYDES KETONES AND ETHOXY ALCOHOLS

	Squalane		*SE-30*		*OV-7*		*OV-17*		*OV-22*		*OV-25*		*QF-1*		*XE-60*	
	t_R/C_9	I_x	t_R/C_9	I	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x
Alcohol																
C_1	0,031	306	0,069	356	0,061	371	0,086	423	0,112	460	0,124	482	0,299	601	0,329	651
C_2	0,045	370	0,098	427	0,10	464	0,136	512	0,161	533	0,203	580	0,348	639	0,426	709
C_3	0,082	473	0,162	530	0,182	578	0,250	630	0,296	655	0,348	688	0,536	746	0,801	850
C_4	0,157	584	0,273	636	0,33	691	0,443	741	0,510	765	0,619	804	0,828	853	1,366	970
C_5	0,298	694	0,499	742	0,59	802	0,758	896	0,859	870	1,036	907	1,21	947	2,189	1076
C_6	0,546	797	0,789	852	1,054	910	1,298	951	1,472	978	1,771	1015	1,86	1053	3,516	1182
C_7	0,997	899	1,288	953	1,757	1010	2,211	1055	2,5	1084	2,953	1117	2,79	1154	5,591	1286
C_8	1,807	1001	2,169	1058	3,046	1115	3,766	1158	4,178	1188	4,971	1221	4,215	1256	8,867	1390
C_9	3,164	1097	3,61	1162	5,177	1217	6,307	1259	7,02	1292	8,307	1324	6,363	1351	14,099	1494
iso-C_3			0,101	447	0,133	598	0,171	556	0,198	574	0,229	604	0,402	675	0,513	750
iso-C_4			0,212	595	0,281	653	0,353	697	0,4	716	0,481	753	0 681	805	1 036	908
sec.-C_4	0,116	533	0,187	570	0,246	627	0,336	674	0,351	689	0,414	723	0,629	785	0,826	857
tert.-C_4	0,076	460	0,126	491	0,156	539	0,214	589	0,21	586	0,243	616	0,465	711	0,484	737
2-me-C_5	0,454	767	0,675	820	0,868	873	1,126	912	1,196	936	1,387	962	1,606	1017	2,843	1135
Aldehyde																
C_1	0,015	187	0,037	229	0,023	180	0,082	401	0,089	414	0,059	333	0,079	291	0,284	607
C_2	0,034	323	0,073	367	0,081	423	0,145	512	0,125	482	0,111	460	0,34	638	0,293	626
C_3	0,064	430	0,126	479	0,135	537	0,235	606	0,228	603	0,23	604	0,515	756	0,553	762
C_4	0,120	537	0,201	574	0,26	646	0,368	693	0,391	711	0,44	735	0,852	869	0,873	862
C_5	0,221	642	0,352	688	0,466	757	0,653	806	0,695	827	0,766	846	1,399	987	1,469	987
C_6	0,406	746	0,573	788	0,785	857	1,089	505	1,138	926	1,265	947	2,166	1098	2,357	1092
C_7	0,737	848	0,042	889	1,321	957	1,508	1004	1,871	1026	2,076	1047	3,283	1197	3,708	1195
Ketone																
C_1C_1	0,057	412	0,16	465	0,152	534	0 208	592	0 229	603	0,268	637	0,677	808	0,6	736
C_1C_2	0,113	528	0,198	574	0,265	641	0,354	696	1,383	707	0,47	749	0,989	903	0,931	884
C_1C_3	0,197	623	0,313	666	0,424	733	0,551	783	0,621	804	0,736	839	1,446	995	1,445	983
C_1C_4	0,368	730	0,531	773	0,736	839	0,939	888	1,05	910	1,206	937	2,27	1106	2,363	1093
C_1C_5	0,661	829	0,87	873	1,23	939	1,563	986	1,729	1011	2,014	1040	3,43	1208	3,704	1193
C_1C_6	1,188	929	1,457	978	2,093	1042	2,622	1089	2,841	1111	3,318	1140	5,264	1314	5,888	1297
C_1-iso-C_4	0,278	582	0,424	727	0,557	785	0,702	830	0,763	845	0,897	878	1,807	1051	1,765	1028
Ethoxy alcohol																
C_1	0,127	548	0,226	608	0,331	685	0,443	741	0,552	780	0,703	828	0,833	864	1,621	1003
C_2	0,208	632	0,348	694	0,498	764	0,647	815	0,775	849	1,022	904	1,10	932	2,052	1057
C_4	0,692	837	0,966	898	1,393	963	1,790	1014	2,026	1042	2,592	1095	2,479	1129	4,773	1249
C_6	2,192	1033	2,871	1099	3,952	1165	5,087	1218	5,512	1244	7,031	1298	5,748	1334	11,521	1450

	XF-1150		OV-105		OV-225		SILAR 5CP		SILAR 7CP		SILAR 9CP		SILAR 10C		OV-275	
	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x	t_R/C_9	I_x
Alcohol																
C_1	2.172	1102	2.619	1157	0.382	692	0.560	765	1.352	978	1.591	1027	1.97	1094	1.945	1083
C_2	2.427	1130	2.729	1168	0.506	753	0.754	834	1.915	989	1.772	1056	2.136	1117	2.162	1112
C_3	3.092	1193	3.308	1220	0.816	856	1.237	949	2.213	1104	2.757	1177	3.216	1234	3.161	1217
C_4	4.443	1288	4.63	1309	1.386	971	2.098	1072	3.482	1221	4.248	1295	4.873	1353	4.852	1335
C_5	6.32	1379	6.406	1396	2.242	1075	3.413	1185	5.356	1332	6.448	1409	7.21	1465	7.154	1441
C_6	9.034	1472	9.067	1489	3.676	1181	4.493	1289	8.086	1438	9.497	1514	10.42	1570	10.303	1592
C_7	13.221	1571	12.946	1584	5.905	1284	5.954	1294	12.946	1541	14.009	1621	14.874	1672	14.789	1641
C_8	19.236	1668	18.601	1681	9.399	1384	8.568	1399	17.919	1643	20.32	1723	21.454	1777	21.234	1741
C_9	28.585	1771	27.474	1785	15.072	1487	13.457	1504	26.520	1744	31.50	1825	30.789	1880	30.554	1841
iso-C_3	2.407	1128	2.623	1158	0.417	757	0.778	841	1.391	985	1.724	1049	2.003	1098	1.945	1083
iso-C_4	3.742	1243	3.919	1265	1.077	916	1.603	1010	2.702	1156	3.323	1238	3.802	1282	3.753	1264
sec.-C_4	3.148	1198	3.351	1223	0.866	869	1.294	960	2.150	1097	2.628	1164	3.007	1215	2.911	1194
tert.-C_4	2.332	1120	2.535	1148	0.523	750	0.726	826	1.272	962	1.522	1015	1.749	1060	1.757	1055
2-me-C_5	7.462	1422	7.469	1437	2.882	1129	4.247	1236	6.414	1379	7.575	1453	8.349	1507	8.338	1483
Aldehyde																
C_1	0.963	825	1.235	898	0.321	655	0.444	697	0.938	882	1.355	983	1.657	1041	1.585	1027
C_2	0.944	820	0.939	820	0.278	624	0.596	775	0.897	871	1.049	913	1.203	951	1.368	989
C_3	1.388	921	1.406	933	0.535	761	0.929	878	1.334	975	1.675	1040	1.931	1084	1.887	1075
C_4	2.105	1030	2.106	1040	0.866	869	1.455	966	1.957	1076	2.413	1140	2.719	1179	2.698	1175
C_5	3.332	1150	3.241	1155	1.390	978	2.974	1075	3.019	1189	3.62	1255	3.993	1290	4.210	1292
C_6	4.968	1255	4.831	1261	2.319	1086	3.219	1182	4.544	1297	5.53	1365	6.094	1405	5.903	1388
C_7	7.361	1357	7.141	1364	3.677	1188	4.964	1289	6.743	1401	7.991	1466	8.682	1504	8.313	1483
Ketone																
C_1C_1	1.606	966	1.636	977	0.509	786	4.816	854	1.429	995	1.985	1090	2.295	1137	2.193	1116
C_1C_2	2.328	1062	2.351	1072	0.954	890	1.481	995	2.278	1115	2.830	1188	3.202	1233	3.099	1217
C_1C_3	3.252	1149	3.234	1156	1.436	978	2.085	1077	3.141	1198	4.02	1212	4.251	1330	4.19	1300
C_1C_4	5.115	1266	4.776	1269	2.308	1080	3.297	1186	4.78	1306	5.751	1372	6.274	1425	6.145	1395
C_1C_5	7.536	1366	7.306	1370	3.717	1183	5.063	1288	9.086	1408	8.111	1479	8.746	1520	8.574	1490
C_1C_6	11.307	1472	10.951	1476	5.912	1283	7.827	1391	10.476	1508	11.69	1580	12.387	1619	12.24	1536
C_1-iso-C_4	3.664	1179	3.60	1184	1.707	1014	2.382	1108	3.439	1221	4.108	1291	4.523	1331	4.502	1314
Ethoxy alcohol																
C_1	4.56	1233	4.554	1245	1.645	1008	2.725	1140	5.108	1323	6.762	1420	6.626	1430	5.852	1375
C_2	5.29	1271	5.222	1281	2.109	1052	3.44	1193	5.848	1358	7.444	1447	8.711	1508	8.313	1484
C_4	11.055	1465	10.674	1471	4.982	1249	7.815	1384	11.931	1542	14.319	1624	16.194	1682	15.616	1658
C_6	24.532	1673	23.265	1078	12.588	1460	18.868	1590	24.67	1741	29.523	1821	32.314	1876	30.953	1846

TABLE II

SLOPE (*a*) AND INTERCEPT (*b*) VALUES OF ALDEHYDES KETONES AND ETHOXY ALCOHOLS, WITH *n*-ALCOHOLS AS REFERENCE SERIES CALCULATED FROM EQN. 1

Homolog	*Squalane*	*SE-30*	*OV-7*	*QF-1*	*XE-60*	*OV-225*	*SILAR 5CP*	*XF-1150*
Slope a (ref. homolog:ethanol)								
Aldehydes	1.07466	1.03186	1.0873	1.29538	0.950055	0.963575	1.08473	1.1393
Ketones	1.01429	0.996488	0.996488	0.902676	1.07378	1.02056	0.987228	1.30231
Ethoxy alcohols	0.979258	1.03232	0.870849	1.02583	0.812005	0.894985	0.914125	1.17909
Intercept b								
Aldehydes	−0.116	−0.138	−0.128	−0.049	−0.150	−0.184	−0.135	−0.416
Ketones	0.363	0.27	0.292	0.442	0.255	0.212	0.212	0.167
Ethoxy alcohols	0.611	0.567	0.571	0.483	0.600	0.586	0.648	0.268

RESULTS AND DISCUSSION

Relative retention and index values of the compounds examined are shown in Table I. The values calculated from eqn. 1 (ref. 5)

$$\log t'_{R(\mathrm{ROEt})} = a \log t'_{R(\mathrm{ROMe})} + b \qquad (1)$$

for a correlation relating two series of homologs on a common stationary phase are shown in Table II, the correlation coefficients being 0.99 in each case. Figs. 1a and 1b show plots of slope and intercept against stationary phase polarity and consider alcohols as reference homologs to establish the relationship with aldehydes, ketones

TABLE III

REGRESSION COEFFICIENTS (*a* AND *b*) FOR ALCOHOLS, ALDEHYDES, KETONES AND ETHOXY ALCOHOLS FROM EQN. 2 AND ETHOXY ALCOHOLS CONSIDERING BEHAVIOUR ON TWO STATIONARY PHASES

Stationary phase	*a*	*b*	*r*	*a*	*b*
SE-30	1	0	1	1	0
Squalane	1.16078	−0.141057	0.998806	1.19792	−0.105789
OV-7	1.07535	0.126447	0.997469	1.16581	0.161945
OV-11	1.07588	0.176085	0.998319	1.32597	0.226067
OV-17	1.04361	0.227621	0.997881	0.979623	0.275766
OV-22	1.02982	0.273565	0.99909	0.988379	0.286161
OV-25	1.03415	0.348724	0.998834	1.09057	0.34355
QF-1	0.776077	0.354404	0.999038	1.00771	0.556862
XE-60	0.960641	0.631364	0.997947	0.873797	0.571791
OV-225	0.949079	0.650517	0.998427	0.862646	0.563535
OV-105	0.628954	1.03287	0.990001	0.672671	0.848606
XF-1150	0.676535	1.03549	0.9941	0.721491	0.8691
SILAR 5CP	0.897395	0.795905	0.99231	0.837839	0.752183
SILAR 7CP	0.817583	0.972064	0.993224	0.640518	0.77274
SILAR 9CP	0.801887	1.04461	0.993139	0.664143	0.894475
SILAR 10CP	0.75582	1.07458	0.990883	0.633315	0.927781
OV-275	0.756951	1.07083	0.991004	0.614353	0.915722

OV-25	*OV-17*	*OV-11*	*SILAR 7CP*	*SILAR 9CP*	*SILAR 10CP*	*OV-275*	*OV-22*	*OV-105*
1.0762	0.943252	1.2447	0.855817	0.907415	0.934581	0.903524	0.981965	1.1639
0.928398	0.912685	0.890437	0.999812	0.921482	0.939857	0.977036	0.952829	1.40458
0.866043	0.897262	0.86772	0.853689	0.815341	0.893362	0.931931	0.885286	1.28953
−0.184	−0.065	−0.181	−0.154	−0.152	−0.169	−0.143	−0.117	−0.452
0.283	0.299	0.283	0.123	0.168	0.138	0.112	0.294	0.277
0.617	0.591	0.578	0.617	0.663	0.600	0.552	0.583	0.149

and ethoxy alcohols. With non-polar to medium polarity phases the slopes decrease from aldehydes to ketones to ethoxy alcohols, but on highly polar phases ketones exhibit the greatest slope. Fig. 1b shows that the intercepts are the greatest occur for the ethoxyalcohols and are reduced with ketones and lowest with aldehydes, which is basically the opposite of the results shown in Fig. 1a. The value of the intercept indicates the retention increment between series on a phase. The possibility of separation can be estimated from the intercept values.

With retention relative to nonane, an intercept of at least 0.4 would achieve a good separation. The relationship between ethoxy alcohols and alcohos gives an intercept of 0.57 on OV-7, which indicates that homologs of the two series are well separated on the phase. For best separation the value of *a* must also be considered

r	*a*	*b*	*r*	*a*	*b*	*r*
1	1	0	1	1	0	1
0.999914	1.19764	−0.110447	0.999817	1.12496	−0.163312	0.999683
0.995411	1.03627	0.148677	0.999818	0.979598	0.151409	0.999935
0.979823	0.998872	0.19448	0.999464	0.955001	0.217892	0.99988
0.999235	1.00154	0.247334	0.999422	0.966646	0.263967	0.999885
0.997562	1.00003	0.28837	0.999171	0.912962	0.320733	0.99976
0.998166	0.988981	0.354853	0.999083	0.997871	0.429359	0.999969
0.984565	0.81873	0.5794	0.999291	0.76745	0.405837	0.99968
0.991602	0.910171	0.615972	0.999074	0.784875	0.69532	0.998809
0.98513	0.953791	0.620575	0.998139	0.813065	0.718564	0.998758
0.969829	0.753606	0.894073	0.995096	0.658929	1.05175	0.996211
0.986091	0.779554	0.912118	0.995697	0.679153	1.06621	0.996618
0.992856	0.876282	0.749905	0.996811	0.773279	0.912988	0.998736
0.983269	0.781412	0.885153	0.995999	0.638009	1.09151	0.996718
0.973743	0.701341	0.941259	0.993729	0.598539	1.18094	0.994358
0.968162	0.670462	0.969177	0.993379	0.621506	1.22277	0.999955
0.976517	0.693226	0.971104	0.994535	0.646033	1.19964	0.99913

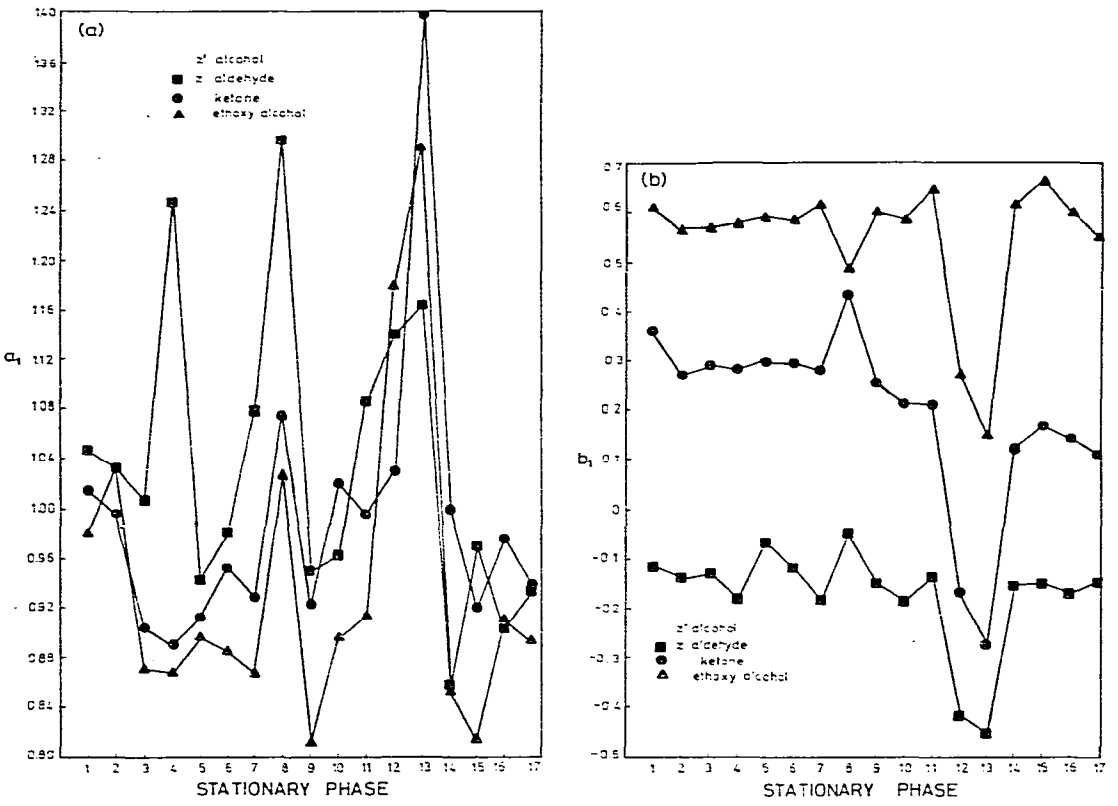

Fig. 1. Plots showing slopes (a) and intercepts (b) of relationship concerning behaviour of homologous compounds and homologous alcohols on a single stationary phase (eqn. 1). The stationary phases used are (1) squalane; (2) SE-30; (3) OV-7; (4) OV-11; (5) OV-17; (6) OV-22; (7) OV-25; (8) QF-1; (9) XE-60; (10) OV-225; (11) SILAR 5CP; (12) XF-1150; (13) OV-105; (14) SILAR 7CP; (15) SILAR 9CP; (16) SILAR 10CP; (17) OV-275.

such that $a > 1$ and $b > 0.4$. With two homologs related to a reference homolog then separation of the two could occur when $a_1 - a_2 > 0$ and $b_1 - b_2 > 0.4$.

Eqn. 2 presents the reverse situation to eqn. 1 such that the behaviour of one homologous series is considered on two stationary phases.

$$\log t'_{R(\varphi_1)} = a_2 \log t'_{R(\varphi_2)} + b_2 \tag{2}$$

where φ_1 and φ_2 are stationary phases and a_2 and b_2 are regression coefficients.

Table III shows the coefficients a_2, and b_2 and the correlation coefficients for alcohols, ketones, aldehydes and ethoxyalcohols with SE-30 as the reference stationary phase. Acceptable correlation coefficients are shown for all series except the aldehydes where the values are poor and further deteriorate as the phase polarity is increased, *i.e.* the difference in the phases is increased. The slope a_2 expresses the relative polarity of the phase φ_1 to phase φ_2, the value a_2 being inversely proportional to the polarity. The relative polarities of the phases examined are shown in Table IV, and considerable variations in the sequences are shown by comparison with the general polarities expressed in terms of McReynolds data (Fig. 2).

TABLE IV

TABULATION OF STATIONARY PHASE POLARITY WITH REFERENCE TO FUNCTIONAL CLASSES SHOWN AND COMPARED TO McREYNOLDS CLASSIFICATION

Stationary phase	*Alcohol*	*Aldehyde*	*Ketone*	*Ethoxy alcohols*	*McReynolds*
Squalane	1	2	1	1	1
OV-11	2	1*	6	5	4
OV-7	3	3	2	3	3
OV-17	4	8	3	4	5
OV-25	5	4	7	7	7
OV-22	6	7	4	6	6
SE-30	7	6	5	2	2
XE-60	8	9	9	9	9
OV-225	9	10*	8	8	10
SILAR 7CP	10	15*	12	15	14
SILAR 5CP	11	11	10	10	11
SILAR 9CP	12	14*	15	17	15
QF-1	13	5*	11	11	8
OV-275	14	17*	16	14	17
SILAR 10CP	15	16*	17	16	16
XF-1150	16	12*	13	12	12
OV-105	17	13*	14	13	13

* Correlation was poor.

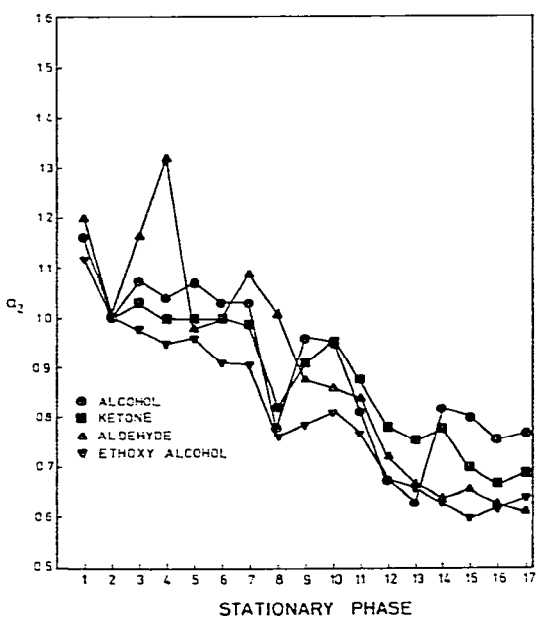

Fig. 2. Plots showing slopes and general polarity of alcohols, aldehydes, ketones and ethoxy alcohols on a stationary phase relative to SE-30 considering eqn. 2. The stationary phases used are shown in Fig. 1.

TABLE V

TABULATION OF INTERCEPTS OF RELATIONSHIP CONSIDERING BEHAVIOUR OF A HOMOLOGOUS SERIES ON TWO STATIONARY PHASES (EQN. 2)

Stationary phase	*Alcohol*	*Aldehyde*	*Ketone*	*Ethoxy alcohols*
Squalane	−0.141	−0.106	−0.110	−0.163
SE-30	0.0	0.000	0.000	0.000
OV-7	0.126	0.162	0.149	0.151
OV-11	0.176	0.226	0.194	0.218
OV-17	0.228	0.276	0.247	0.269
OV-22	0.274	0.286	0.288	0.321
OV-25	0.349	0.343	0.355	0.429
QF-1	0.354	0.557	0.579	0.406
XE-60	0.631	0.571	0.616	0.695
OV-225	0.650	0.563	0.621	0.719
SILAR 5CP	0.706	0.752	0.750	0.913
SILAR 7CP	0.972	0.772	0.885	1.091
OV-105	1.033	0.849	0.894	1.052
XF-1150	1.035	0.869	1.066	1.066
SILAR 9CP	1.045	0.894	0.941	1.181
OV-275	1.070	0.916	0.971	1.200
SILAR 10CP	1.075	0.927	0.969	1.223

The intercepts (b_2) are shown in Table V where, as might be expected, the values are generally increased with increasing phase polarity.

The relationship between structural parameters and retention data is shown in eqn. 3:

$$\log t'_R = \varrho^*\sigma^* + h(n - 3) \tag{3}$$

where σ^* = polar constant of substituent as determined by Taft[6]. n = number of hydrogen atoms bonded to the α-carbon atom; ϱ^* and h = regression coefficients.

If $n = 3$ (CH_3 is substituent), $\sigma^*_{CH_3} = 0$ (by definition of Taft) and $\log t'_{CH_3} = 0$ or $t'_{CH_3} = 1$, which shows that the relative retention of all compounds should be calculated relative to that of a compound where CH_3 is a substituent to satisfy the relationship. With relative retentions calculated relative to nonane a corrective term is included such that eqn. 3 becomes:

$$\log t'_{R(\text{rel. to any compound})} = \varrho^*\sigma^* + h(n - 3) + \log t'_{R(\text{rel. to } CH_3Z)} \tag{3a}$$

The equation is now of the form $y = a_1 \times a_1 + a_2 \times a_2 + b$, where a general multiple linear regression analysis is used. In the alcohol series, there are 11 compounds available for examination, with isopropyl and *tert.*-butyl alcohols being of the type $n + 1$.

With esters[5], ketones and the aldehyde series, only compounds where $n = 2$ are available and for these compounds the relationship

$$\log t'_R = \varrho^*\sigma^* + h(n - 3) + b \tag{3b}$$

is reduced to

$$\log t'_R = \varrho^*\sigma^* - h + b \tag{3c}$$

and subsequently

$$\log t'_R = \varrho^*\sigma^* - h' \tag{3d}$$

where $h' = (h + b)$ and ϱ^* and h' can be calculated from the line of best fit determined by linear regression as shown in Table VI. Verification of eqn. 3 is shown in Fig. 3, where relative retention times of a homologous series of alcohols on OV-11 are plotted against the polar constant σ^* for eleven compounds with $n = 1$ and 2.

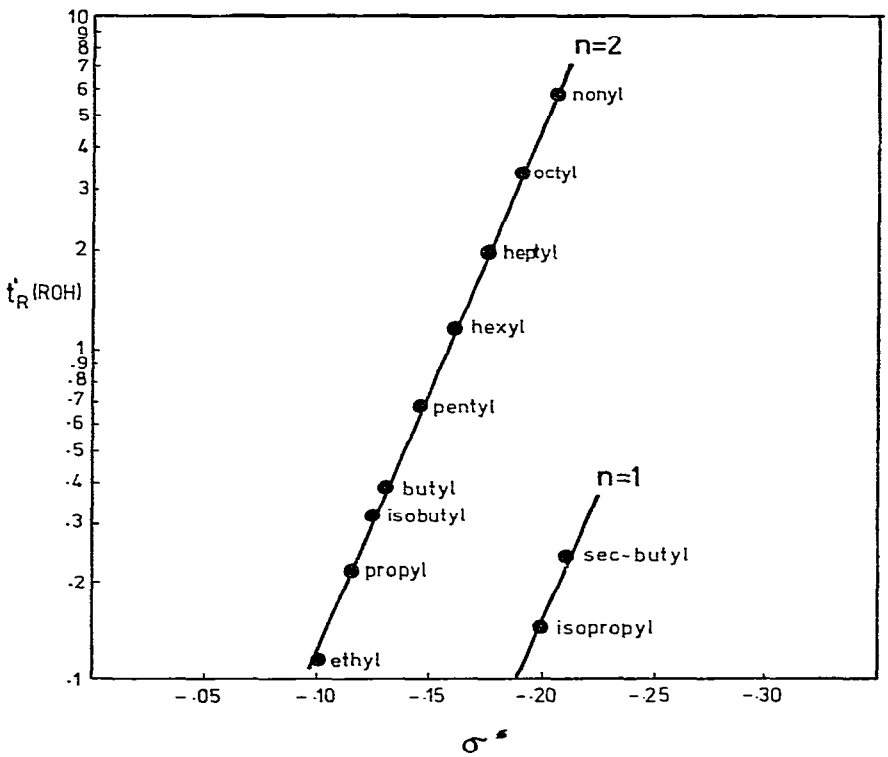

Fig. 3. Plots of log relative retention and polar constants (σ^*) in terms of eqn. 4.

The polar factor ϱ^* is indicative of the stationary phase to polar effects. The data are shown in Fig. 4 where QF-1 as expected shows elevated value swith all the carbonyl compound while both the acceptor and donor phases show little evidence of any systematic behaviour related to the known structures of the phases. Similarly the hyperconjugation factors h do not indicate any systematic behaviour.

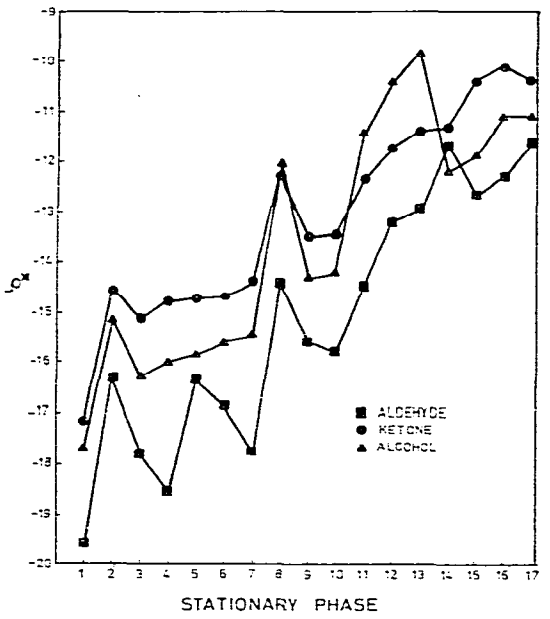

Fig. 4. Plot showing polar factor (ϱ^*) and stationary phase polarity in terms of eqn. 4. The stationary phases used are shown in Fig. 1.

Eqn. 4 introduces a steric factor E_s and thus eqn. 4 is eqn. 3 + E_s and on examination of the experimental data modification as with eqn. 3 to consider data of the type $t'_{R\cdot CH_3Z}$. is necessary.

$$\log t'_R = \sigma^*\varrho^* + \sigma E_s + h(n - 3) \tag{4}$$

where E_s is the Taft steric parameter and σ is a constant adjusted to give the best fit of the data and simuitaneously determined with p* and h.

The values calculated (Table VII) do not follow any obvious pattern with either stationary phase polarity or type of compounds.

The relationship shown in eqn. 5 indicates a scale of polarity with ϱ^* and a_2 from eqn. 1

$$\varrho^*_{(\varphi)} = \lambda a_2 + \beta \tag{5}$$

where λ and β are regression coefficients.

Correlation coefficients of $\gamma = 0.993$, 0.994 and 0.949 were obtained for eqn. 5 when applied to alcohols, ketones and aldehydes, respectively. These values compare favourably with the corresponding tabulated values of $\gamma = 0.780$, 0.974 and 0.951 at the 0.001 probability level and the appropriate degrees of freedom. While these values together with those for homologous esters indicate some utility of the relationships as a means of stationary phase classification, general application is unlikely owing to the limited availability of basic data necessary for use in the application of the relationship.

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