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EXTENSION TO THE SCHEME OF ROHRSCHNEIDER

I. USE OF ALTERNATIVE BASE STATIONARY PHASES

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SUMMARY

A procedure is presented which extends Rohrschneider's classification scheme and permits the use of any stationary phase as a reference in calculating differences of retention index. By avoiding the use of squalane as reference phase, data obtained at higher temperatures can be analysed. The work shows that Rohrschneider-type schemes are based on the difference in intermolecular interactions between a substance and each of two stationary phases, rather than on polar interactions alone as originally postulated.

INTRODUCTION

Rohrschneider[1] has proposed a scheme in which the retention index of a compound is expressed as the sum of a number of product terms, these terms containing factors characteristic of both the solute and the solvent under consideration. While this scheme and the essentially identical but somewhat more readily applicable scheme of McReynolds[2] have found some acceptance in the classification or comparison of stationary phases, the more important area of retention prediction has been considered by Takacs and his co-workers[3–5] but has otherwise been largely neglected.

In considering intermolecular interaction forces, Rohrschneider assumed dispersion or London forces to be non-polar, and induction, orientation, charge transfer and hydrogen bonding forces to be polar. He then found it possible to eliminate a large portion of the non-polar forces by focussing attention on the difference in retention between a polar and a non-polar (squalane) column:

$$\Delta I^{A} = I_{P}^{A} - I_{Sq}^{A}$$

where

ΔI^{A} = increased retention or index difference due to the polar interacting forces

I_P^A and I_{Sq}^A = retention indices of substance A on a polar and non-polar (squalane) column, respectively.

The index difference ΔI defined in this way was then assumed to be produced additively from portions of the several interactions occurring. Following studies by Pullen and Werner[6,7], it was further assumed that for each type of polar intermolecular attraction, the interaction energy is proportional to a value a characteristic of each solute, and to a value x characteristic of each stationary phase. The index difference ΔI is thus the summation of product terms shown in eqn. 1:

$$\Delta I_P^A = ax + by + cz + du + es \qquad (1)$$

where x, y, z, u, and s are $\Delta I/100$ values for five selected solutes —benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine, respectively— on stationary phase P and a, b, c, d, and e are constants characteristic of substance A.
Thus

$$\Delta I_P^A = I_P^A - I_{Sq}^A = \tfrac{1}{100}[a(I_P^x - I_{Sq}^x) + b(I_P^y - I_{Sq}^y) + c(I_P^z - I_{Sq}^z) + d(I_P^u - I_{Sq}^u) + e(I_P^s - I_{Sq}^s)] \qquad (2)$$

CALCULATIONS BASED ON RETENTION DIFFERENCE OF ANY TWO PHASES

Because of its volatility, squalane sometimes gives rise to experimental difficulties when used as a stationary phase. In any case, squalane is a material of limited general utility. For these reasons it is desirable to avoid the use of squalane in the classification scheme; this has important potential advantages in the further development of Rohrschneider's method since it permits the inclusion of data covering a wide temperature range. We have already reported[8] on the influence of temperature on the polarity of a stationary phase as shown by the variation of the constants x, ..., s on several polysiloxane phases of varying polar character; on the other hand, the temperature dependence of the solute-specific factors a, ..., e does not yet appear to have been studied[4].

Based on eqn. 2, and considering two distinct stationary phases, 1 and 2, it is possible to eliminate squalane entirely as follows:

$$\Delta I_{1,2}^A = I_1^A - I_2^A = \tfrac{1}{100}[a(I_1^x - I_2^x) + b(I_1^y - I_2^y) + c(I_1^z - I_2^z) + d(I_1^u - I_2^u) + e(I_1^s - I_2^s)] \qquad (3)$$

where I_1^A and I_2^A are the retention indices for compound A determined on the two stationary phases 1 and 2, and I_1^x, ..., I_1^s and I_2^x, ..., I_2^s are the retention indices of the five standard substances on columns 1 and 2, respectively.

Eqn. 3 shows that it is possible to determine the substance-specific factors a, ..., e from measurements carried out on any two phases. Alternatively, any other phase can be used as a reference phase instead of squalane. Rohrschneider's original choice of a non-polar solvent for the reference column is seen to have been unnecessarily restrictive.

An approach to the same problem which is similar in some respects to the present work has been investigated by Takacs and his co-workers[4,5]. These authors

consider Rohrschneider's original scheme to have been theoretically faultless but "unsuitable for following some of the more complicated processes because of the possibility of error compensation". They therefore did not base their treatment on Rohrschneider's scheme but chose to use a method which involves the ratios of retention indices, rather than their differences, as shown in eqn. 4 (which applies for constant temperature).

$$\frac{I_P{}^A}{I_{Sq}{}^A} = \sum_{i=1}^{5} f_i \cdot s_i \qquad (4)$$

where f_i is the i-th polarity factor for the stationary phase, given by $f_i = I_P{}^i/I_{Sq}{}^i$, i is the serial number of the standard solute, and s_i is the i-th solute-specific factor characterising the molecular structure of solute A.

Takacs further showed that a similar equation could be derived for any two stationary phases:

$$\frac{I_{P1}{}^A}{I_{P2}{}^A} = \sum_{i=1}^{5} F_i \cdot S_i \qquad (5)$$

where F_i is the i-th polarity factor for any two stationary phases, 1 and 2, *i.e.*, $F_i = I_{P1}{}^i/I_{P2}{}^i$ for a system not based on squalane, and S_i is the i-th solute-specific constant for the same system.

If eqn. 4 is to be compatible with eqn. 2, the solute-specific factors are related by

$$\sum_{i=1}^{5} s_i = 1$$

This relationship appears to hold to within 1 or 2%, indicating that the representation embodied in eqn. 4 is reasonable, although for accurate work a variation of this magnitude could be quite significant. Insufficient information has been published to allow a choice between the two representations. However, it should be noted that the calculation of the retention of isopropanol on PEG-400 (ref. 4) (giving 915.4 index units compared with a measured value of 916.0) is not a reasonable test of the method, since the s-values were obtained from only five stationary phases and least-squares procedures were not used.

It is considered that the approach presented in the present work is to be preferred to that of Takacs at this stage, since it continues to use the well-established concept of retention index differences rather than retention index ratios, and since it incorporates the well-established $x, \ldots, s$ values and leads to $a, \ldots, e$ values similar to those of Rohrschneider, rather than introducing two completely new and different sets of values for what are essentially similar quantities. A decision between the two representations based on their individual accuracies may eventually be possible when further details of Takacs' results are available.

EXPERIMENTAL

The work described here relates specifically to the useful data set provided by Rohrschneider[1]. These data have been re-evaluated using a calculation procedure de-

TABLE I

SUBSTANCE POLARITIES FOR ROHRSCHNEIDER'S DATA BASED ON VARIOUS STATIONARY PHASES

Compound	*Base stationary phase*								
	Squalane	*DC-200*	*Apiezon L*	*DC-710*	*Polyphenyl ether*	*Polypropylene sebacate*	*Carbowax 20M*	*Diethylene glycol succinate*	*TCEP*
	a	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*
2,4-Dimethylpentane	−20.285	−21.034	−21.028	−22.151	−24.772	−20.085	−22.870	−21.537	−21.292
2-Ethyl-1-hexene	20.188	21.891	16.433	21.709	21.414	21.336	20.706	20.945	20.964
Cyclohexane	32.101	32.344	32.161	32.751	38.588	30.314	31.696	33.196	34.698
Toluene	102.870	100.389	101.317	100.579	101.126	101.935	100.378	103.521	101.239
Styrene	120.321	116.592	120.915	116.311	122.757	120.323	117.454	122.735	113.831
Phenylacetylene	116.880	115.120	107.324	114.310	117.229	115.346	115.144	116.823	109.556
Acetone	− 7.138	− 7.668	− 6.233	− 7.458	−12.517	− 9.270	− 8.501	−10.861	− 6.671
Propionaldehyde	10.345	8.190	7.152	10.486	9.211	7.731	8.081	8.538	9.443
Crotonaldehyde	0.370	4.563	7.117	5.081	19.887	5.077	6.293	5.009	2.620
Butyl acetate	− 0.199	4.099	−13.353	4.033	14.263	0.268	2.441	1.954	0.812
Acetonitrile	2.240	1.837	11.526	4.148	6.675	0.681	7.134	2.986	3.439
Nitroethane	− 1.719	0.635	2.329	2.490	4.641	2.452	0.438	2.477	− 2.240
Dioxane	51.191	56.484	45.311	56.750	63.764	54.282	53.241	57.629	55.452
Dibutyl ether	24.821	32.379	17.960	36.194	38.854	29.480	29.585	33.488	29.553
Thiophene	104.392	105.055	102.033	105.425	114.990	105.338	107.304	106.277	105.275
Chloroform	68.964	69.552	66.554	71.854	79.598	72.154	72.581	71.372	68.618
Carbon tetrachloride	70.145	76.084	67.513	75.615	88.019	75.116	77.849	71.744	74.212
Methyl iodide	76.646	79.461	82.469	85.146	95.469	80.698	84.417	83.454	82.493
Ethyl bromide	46.598	46.664	46.441	50.289	50.907	47.790	50.741	45.573	48.161
$C_2F_2Cl_4$	14.176	16.423	1.922	12.427	15.284	13.255	19.789	6.180	11.767
Propanol	− 4.585	0.321	− 4.075	2.301	0.266	0.281	− 1.721	1.050	0.411
Isopropanol	−15.691	−13.090	−17.889	−12.397	22.410	−12.392	−16.895	−16.256	−11.517
Allyl alcohol	22.812	29.389	23.794	29.856	30.152	27.271	27.016	29.045	27.544
tert.-Butanol	−12.677	−13.524	−20.582	−14.480	−30.315	− 8.150	−19.078	−17.163	−11.708
Cyclopentanol	11.563	19.424	14.246	21.526	29.945	20.210	17.619	25.262	16.852

TABLE I *(continued)*

Compound	*Base stationary phase*								
	Squalane	*DC-200*	*Apiezon L*	*DC-710*	*Polyphenyl ether*	*Polypropylene sebacate*	*Carbowax 20M*	*Diethylene glycol succinate*	*TCEP*
	b	*b*	*b*	*b*	*b*	*b*	*b*	*b*	*b*
2,4-Dimethylpentane	0.389	0.331	0.316	7.099	3.223	3.320	2.459	0.169	0.130
2-Ethyl-1-hexene	− 0.333	2.964	2.032	− 3.570	− 0.439	0.305	0.287	− 0.309	− 0.374
Cyclohexane	−19.938	−18.650	−20.001	−24.227	−25.028	−25.422	−19.534	−19.603	−18.015
Toluene	0.303	− 2.351	− 0.063	2.268	− 0.030	3.247	0.772	0.896	0.351
Styrene	− 2.869	− 9.792	− 4.407	7.983	− 6.698	3.874	− 2.301	− 1.675	− 6.207
Phenylacetylene	1.533	5.624	4.539	0.105	− 1.155	5.198	0.078	2.125	− 2.050
Acetone	− 3.771	− 3.518	− 4.528	− 5.512	− 0.096	− 8.689	− 2.936	− 4.737	− 3.013
Propionaldehyde	− 3.079	− 5.004	− 2.550	−14.826	− 3.730	− 5.964	− 2.665	− 3.249	− 2.604
Crotonaldehyde	−12.111	−17.157	−12.250	− 7.130	−22.531	−13.965	−12.151	−11.860	−13.972
Butyl acetate	−11.080	− 0.973	− 3.577	−24.226	−20.540	−15.927	−11.606	−10.869	−11.641
Acetonitrile	−14.389	−17.981	−18.602	−23.252	−17.427	−20.611	−19.505	−14.230	−13.823
Nitroethane	− 7.583	−11.013	− 7.678	−13.259	− 9.707	− 4.272	− 6.023	− 6.988	− 9.983
Dioxane	− 0.179	7.590	4.742	−11.687	− 6.793	− 1.502	1.975	1.009	0.647
Dibutyl ether	12.672	17.096	19.808	−15.206	7.593	6.853	15.535	13.894	11.873
Thiophene	− 3.458	− 4.174	− 1.845	− 4.576	10.976	− 3.050	− 5.812	− 3.062	− 3.357
Chloroform	29.902	22.264	32.422	26.947	23.680	32.749	28.696	30.163	28.128
Carbon tetrachloride	−14.092	−10.950	− 9.762	−14.383	−23.339	−14.753	−16.356	−14.711	−14.518
Methyl iodide	− 9.756	−18.152	− 9.790	−31.681	−20.186	−11.743	−12.744	− 8.709	− 8.573
Ethyl bromide	− 6.394	−11.340	− 5.624	−21.407	− 8.698	− 6.334	− 9.711	− 6.959	− 6.039
$C_2F_2Cl_4$	−12.958	− 1.246	− 7.294	− 4.904	−14.184	−14.569	−20.033	−15.261	−14.466
Propanol	101.828	103.393	104.268	88.595	102.128	102.988	104.356	102.548	102.567
Isopropanol	92.099	92.591	94.615	87.633	99.519	94.749	96.697	91.378	93.603
Allyl alcohol	113.293	118.449	115.984	104.634	112.393	110.431	115.356	113.976	113.255
tert.-Butanol	72.219	68.941	75.943	82.439	85.808	86.843	79.511	70.843	72.997
Cyclopentanol	79.028	81.110	82.043	64.878	71.302	83.286	81.410	81.543	78.086

(Continued on p. 242)

TABLE I *(continued)*

Compound	*Base stationary phase*								
	Squalane	*DC-200*	*Apiezon L*	*DC-710*	*Polyphenyl ether*	*Polypropylene sebacate*	*Carbowax 20M*	*Diethylene glycol succinate*	*TCEP*
	c	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*
2,4-Dimethylpentane	12.331	12.180	12.163	16.614	12.767	11.779	15.528	11.865	11.865
2-Ethyl-1-hexene	5.482	9.581	7.636	3.513	5.655	5.624	6.530	5.565	5.481
Cyclohexane	−19.407	−17.852	−19.468	−22.229	−20.473	−18.713	−18.776	−18.735	−16.329
Toluene	5.907	2.486	5.322	6.885	5.442	5.066	6.503	7.029	5.842
Styrene	−10.356	−18.985	−11.979	− 3.595	−11.609	−11.769	− 9.621	− 8.057	−15.853
Phenylacetylene	−75.390	−70.735	−73.222	−76.771	−76.506	−76.517	−77.889	−74.347	−81.332
Acetone	94.948	95.189	94.222	93.715	95.599	95.440	96.218	92.966	96.099
Propionaldehyde	72.286	69.766	72.489	64.297	71.793	72.235	72.810	71.875	72.913
Crotonaldehyde	70.044	64.522	70.695	74.180	68.990	71.551	70.393	70.745	67.479
Butyl acetate	59.246	71.708	65.934	50.942	57.693	60.326	58.588	59.754	58.489
Acetonitrile	31.451	27.133	27.923	25.714	30.926	32.371	23.427	31.758	32.408
Nitroethane	46.966	43.153	47.340	43.757	47.193	47.306	49.657	48.267	43.338
Dioxane	43.455	53.253	48.165	36.485	42.823	44.468	47.112	45.950	45.029
Dibutyl ether	33.812	39.899	40.843	16.588	34.110	36.114	38.819	36.488	33.009
Thiophene	−30.027	−30.798	−28.530	−30.628	−31.421	−29.906	−33.662	−29.210	−29.804
Chloroform	−70.344	−79.345	−67.862	−71.903	−71.163	−70.158	−72.080	−69.774	−73.010
Carbon tetrachloride	−49.891	−45.507	−45.443	−49.228	−50.729	−48.564	−53.049	−50.951	−50.194
Methyl iodide	−37.641	−47.292	−36.990	−51.259	−38.829	−36.264	−41.980	−35.389	−35.398
Ethyl bromide	0.323	− 5.532	1.154	− 9.334	0.088	0.591	− 4.799	− 0.754	0.987
$C_2F_2Cl_4$	−32.361	−18.222	−27.591	−27.144	−32.699	−32.247	−43.513	−36.999	−34.804
Propanol	− 0.064	2.334	2.675	− 8.003	0.956	0.877	4.248	1.552	1.424
Isopropanol	14.102	14.980	16.606	11.573	16.146	14.338	21.516	12.777	16.652
Allyl alcohol	−21.719	−14.877	−18.641	−26.521	−20.794	−20.071	−18.065	−20.115	−21.401
tert.-Butanol	30.421	26.439	33.573	37.097	33.202	28.474	41.874	27.718	31.661
Cyclopentanol	−15.778	−12.435	−12.144	−23.869	−15.860	−14.592	−11.462	−10.444	−16.739

TABLE I *(continued)*

Compound	*Base stationary phase*								
	Squalane	*DC-200*	*Apiezon L*	*DC-710*	*Polyphenyl ether*	*Polypropylene sebacate*	*Carbowax 20M*	*Diethylene glycol succinate*	*TCEP*
	d	*d*	*d*	*d*	*d*	*d*	*d*	*d*	*d*
2,4-Dimethylpentane	− 1.151	− 0.714	− 0.700	− 4.792	− 0.100	− 2.318	− 3.897	− 0.934	− 0.450
2-Ethyl-1-hexene	− 2.220	− 7.562	− 1.741	− 0.798	− 2.847	− 3.103	− 3.601	− 2.909	− 2.634
Cyclohexane	2.395	0.510	2.404	5.016	1.384	5.389	1.818	2.975	− 0.107
Toluene	− 4.416	0.390	− 3.361	− 4.571	− 3.296	− 4.958	− 4.249	− 2.054	− 3.573
Styrene	12.726	24.023	13.429	7.394	13.338	10.322	12.900	16.229	18.175
Phenylacetylene	58.812	54.038	62.026	61.196	59.989	58.374	62.279	61.724	64.858
Acetone	7.211	7.111	7.210	8.578	8.320	10.191	6.231	6.058	6.505
Propionaldehyde	6.967	10.629	8.343	15.016	7.928	9.493	7.150	7.982	7.186
Crotonaldehyde	30.662	35.595	27.100	24.663	25.105	28.639	28.179	26.980	30.467
Butyl acetate	11.303	− 4.633	13.497	18.125	8.088	12.794	11.123	10.128	11.053
Acetonitrile	82.068	87.201	79.808	87.164	81.137	85.169	89.520	81.915	81.099
Nitroethane	71.078	74.667	68.941	72.734	68.603	67.494	67.245	69.586	72.688
Dioxane	−11.510	−24.711	−11.574	− 6.549	−15.143	−12.801	−16.417	−12.374	−14.339
Dibutyl ether	−18.283	−27.965	−19.262	− 5.113	−23.459	−18.844	−25.682	−21.389	−20.455
Thiophene	18.270	18.930	18.483	18.487	16.206	17.592	21.394	18.241	17.729
Chloroform	49.951	60.181	49.602	50.442	47.207	47.107	50.672	48.517	51.143
Carbon tetrachloride	20.296	13.150	18.862	17.550	15.067	17.700	21.202	15.295	18.290
Methyl iodide	25.045	35.245	21.909	35.647	19.893	23.451	27.276	23.060	21.168
Ethyl bromide	16.311	23.067	15.889	24.711	15.085	15.608	20.705	14.530	15.257
$C_2F_2Cl_4$	27.107	9.942	30.019	22.478	27.119	28.213	23.888	23.772	29.297
Propanol	4.814	0.329	2.910	10.255	1.943	1.605	− 1.125	2.491	1.612
Isopropanol	− 6.404	− 8.330	− 6.886	− 5.095	− 6.453	− 9.235	−14.458	− 9.373	− 9.589
Allyl alcohol	19.834	9.609	17.522	22.034	16.203	18.315	14.171	16.859	17.220
tert.-Butanol	−10.352	− 5.445	− 8.510	−16.447	− 7.464	−18.171	−21.206	−12.299	−11.321
Cyclopentanol	14.943	8.339	11.508	19.380	8.663	8.484	7.874	13.353	12.553

(Continued on p. 244)

TABLE I *(continued)*

Compound	*Base stationary phase*								
	Squalane	*DC-200*	*Apiezon L*	*DC-710*	*Polyphenyl ether*	*Polypropylene sebacate*	*Carbowax 20M*	*Diethylene glycol succinate*	*TCEP*
	e	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*
2,4-Dimethylpentane	0.753	0.938	0.945	− 3.059	− 0.490	− 0.292	1.210	1.979	1.195
2-Ethyl-1-hexene	0.006	− 1.627	− 1.813	1.724	− 0.144	− 0.466	− 0.173	0.209	− 0.051
Cyclohexane	27.533	26.985	27.586	30.073	30.054	29.798	27.595	25.173	24.953
Toluene	− 2.111	− 0.562	− 1.493	− 2.884	− 1.551	− 2.912	− 1.540	− 6.965	− 1.924
Styrene	− 3.118	0.342	− 1.651	− 9.104	− 0.775	− 5.419	− 2.467	−12.121	1.637
Phenyl acetylene	5.896	4.705	4.332	7.281	7.799	4.986	6.444	0.985	11.059
Acetone	6.612	6.638	7.254	7.767	4.926	8.771	6.885	13.228	5.711
Propionaldehyde	4.079	5.294	4.053	11.376	4.770	5.657	4.616	4.642	3.688
Crotonaldehyde	12.216	13.239	11.276	8.203	16.236	11.810	10.771	12.546	13.988
Butyl acetate	17.694	12.889	12.115	25.053	21.934	19.247	17.102	16.958	18.193
Acetonitrile	− 0.016	1.457	2.810	5.137	1.395	2.466	− 0.786	− 0.768	− 0.853
Nitroethane	− 3.189	− 2.380	− 3.729	− 0.475	− 2.801	− 5.242	− 3.855	− 6.022	− 0.356
Dioxane	36.914	32.794	32.836	43.000	39.432	36.683	36.233	30.171	35.363
Dibutyl ether	− 6.014	− 9.355	−12.217	9.118	− 4.900	− 5.061	− 7.424	−11.816	− 5.795
Thiophene	12.706	12.840	11.435	13.200	16.247	12.364	12.203	10.343	12.458
Chloroform	− 4.673	− 1.885	− 6.867	− 3.405	− 2.088	− 6.355	− 5.475	− 5.374	− 2.611
Carbon tetrachloride	27.077	24.580	23.080	26.183	30.531	26.197	25.376	33.461	26.962
Methyl iodide	17.823	20.425	16.934	29.807	21.967	17.600	16.168	12.510	15.603
Ethyl bromide	9.034	10.921	8.271	17.664	9.926	8.756	8.308	13.352	8.390
$C_2F_2Cl_4$	30.964	25.990	27.128	26.285	31.652	31.712	30.185	46.741	33.019
Propanol	− 4.484	− 6.153	− 7.033	2.414	− 5.593	− 5.950	− 5.404	− 7.717	− 6.022
Isopropanol	5.464	4.710	3.261	7.608	1.281	3.833	5.366	11.245	3.190
Allyl alcohol	−19.687	−23.085	−22.587	−15.673	−20.382	−19.688	−20.887	−22.511	−20.311
tert.-Butanol	4.822	6.260	2.266	− 1.192	− 1.858	− 1.168	5.781	13.926	3.792
Cyclopentanol	15.750	13.232	12.234	22.604	17.990	12.384	14.072	1.088	16.037

scribed elsewhere[9,10]. Briefly, the program used permits the choice of any stationary phase as the base phase (equivalent to squalane in the Rohrschneider and McReynolds classification systems). Using the chosen base phase, retention index differences are calculated for all the observations. Column polarity factors $x, \ldots, s$ are then assigned in terms of the column behaviour for benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine, the same five standard substances used by Rohrschneider.

The substance-specific factors, $a, \ldots, e$, are calculated using a standard least-squares criterion which minimises the sum of the squared errors, applied to all stationary solvent phases for each substance separately. The values of $a, \ldots, e$ obtained in this way, using squalane as the base column, differ slightly from those obtained by Rohrschneider, whose method of calculation used a different criterion. The relative merits of these two approaches are discussed elsewhere[10].

To permit a comparison of results using different stationary phases, the differences between the calculated and observed values were used to calculate both the root mean square error and the average absolute error for each substance, for each column, and for the complete data set.

RESULTS AND DISCUSSION

Substance-specific factors $a, \ldots, e$ have been calculated for the 30 substance 23 column data set of Rohrschneider, using each of the 23 columns as the base stationary phase. Table I lists a representative sample of the results obtained; it includes values for three non-polar phases (squalane, DC-200, and Apiezon L), three medium polarity phases (DC-710, polyphenyl ether and polypropylene sebacate) and three highly polar phases (Carbowax 20M, diethylene glycol succinate and 1,2,3-tris-(cyanoethoxy)propane (TCEP)).

It will be seen that the values based on squalane vary slightly from the values originally calculated by Rohrschneider[1]. They agree with the values calculated by Leary *et al.*[9] using a standard least-squares criterion.

The substance-specific factors calculated in this way agree with each other surprisingly well. No particular trends were observed for any of the base stationary phases. It is apparent that it is possible to develop a Rohrschneider-type characterisation scheme by considering the difference in intermolecular interactions between any two phases, as has been implied by Takacs and his co-workers[4].

Table II shows the prediction capabilities of the method when the base or comparative stationary phase is varied. Total differences between the observed and calculated results for the complete data set are presented as the average absolute error, and the root mean square error. Again, no systematic trends were evident with any particular type of stationary phase. The values of error with squalane (the conventionally used material) as base, while low, were slightly higher than those with TCEP, the most polar phase included in the study. This indicates that the predictive behaviour of the method is not affected by changing the base column.

While in this work we have used the available data of Rohrschneider to facilitate our comparisons, it is evident that many of the phases he employed were commercial materials of unspecified composition which have not found subsequent acceptance and for some of which the stability is unknown. From work in this laboratory it has been noted that the Rohrschneider constants for XF-1150 vary

TABLE II

ERRORS IN THE CHANGE OF BASE CALCULATIONS

Stationary phase	*Error (calculated—observed)*	
	Average absolute	*RMS*
Squalane	3.25	4.97
DC-200	3.73	5.72
Apiezon L	3.39	5.33
Diethyl hexyl sebacate	3.52	5.60
Celanese ester No. 9	3.77	5.95
Diisodecyl phthalate	3.75	5.66
DC-710	3.55	5.32
QF-1	3.22	4.97
Ucon LB-550X	3.35	5.12
Acetyl tributyl citrate	3.94	6.21
Tricresyl phosphate	4.09	6.11
Polyphenyl ether	3.67	5.56
Marlophen 87	3.47	5.46
Polypropylene sebacate	3.88	5.96
Marlophen 814	3.40	5.10
Neopentyl glycol succinate	3.27	5.08
XF-1150	3.77	6.17
Carbowax 20M	3.26	4.96
Carbowax 4000	3.23	4.90
Reoplex 400	3.42	5.17
Diethylene glycol sebacate	3.28	5.08
Ethylene glycol bis(cyanoethyl) ether	3.35	5.16
Tris(cyanoethoxy)propane	3.20	4.90
Average	3.51	5.37

continuously with use; with this phase higher errors were obtained in the present calculations. With the other commercial ester materials it is similarly suggested that the high errors might be attributed to variation in composition with use as has been reported with various polyesters[11].

The work reported here suggests that Rohrschneider's scheme can be readily extended to include a wider temperature range. Because of the volatility of squalane, operating temperature has been restricted to a maximum of between 100 and 120°. A higher operating temperature is possible if a suitable base stationary phase is chosen; this needs not necessarily be non-polar in character, but should be non-volatile, stable in composition and capable of giving accurate and reproducible results. This will allow the accepted classification schemes of Rohrschneider and later of McReynolds to be retained with minimum alteration.

Table III lists the stationary phase polarity constants based on the most polar phase, TCEP, which is also the phase giving the most accurate prediction of retention indices. This table shows that while the individual column polarities appear to be considerably different to those based on squalane, this difference is more apparent than real since each $x, \ldots, s$ value for a particular column is equal to its value based

TABLE III

STATIONARY PHASE POLARITY CONSTANTS BASED ON TRIS(CYANOETHOXY)PROPANE

Values in parentheses are based on squalane.

Stationary phase	*x*		*y*		*z*		*u*		*s*	
Squalane	−6.00	(0.0)	−8.71	(0.0)	−7.94	(0.0)	−11.53	(0.0)	−9.40	(0.0)
DC-200	−5.85	(0.15)	−8.15	(0.56)	−7.47	(0.47)	−10.75	(0.78)	−8.96	(0.44)
Apiezon L	−5.68	(0.32)	−8.32	(0.39)	−7.69	(0.25)	−11.05	(0.48)	−8.85	(0.55)
Diethyl hexyl sebacate	−5.27	(0.73)	−7.06	(1.65)	−6.79	(1.15)	− 9.33	(2.20)	−8.16	(1.24)
Celanese ester No. 9	−5.17	(0.83)	−6.95	(1.76)	−6.66	(1.28)	− 9.17	(2.36)	−7.94	(1.46)
Diisodecyl sebacate	−5.17	(0.83)	−7.06	(1.65)	−6.51	(1.43)	− 9.00	(2.53)	−7.86	(1.54)
DC-710	−4.95	(1.05)	−7.21	(1.50)	−6.33	(1.61)	− 9.02	(2.51)	−7.50	(1.90)
QF-1	−4.91	(1.09)	−6.85	(1.86)	−4.94	(3.00)	− 7.59	(3.94)	−6.99	(2.41)
Ucon LB-550X	−4.86	(1.14)	−5.95	(2.76)	−6.26	(1.68)	− 8.41	(3.12)	−7.32	(2.08)
Acetyl tributyl citrate	−4.64	(1.36)	−6.05	(2.66)	−5.83	(2.11)	− 7.83	(3.70)	−7.07	(2.33)
Tricresyl phosphate	−4.26	(1.74)	−5.49	(3.22)	−5.36	(2.58)	− 7.39	(4.14)	−6.45	(2.95)
Polyphenyl ether	−4.25	(1.75)	−6.440	(2.27)	−5.60	(2.34)	− 8.27	(3.26)	−6.56	(2.84)
Marlophen 87	−4.22	(1.78)	−4.99	(3.72)	−5.41	(2.53)	− 7.04	(4.49)	−6.06	(3.34)
Polypropylene sebacate	−4.07	(1.93)	−5.33	(3.38)	−5.36	(2.58)	− 7.17	(4.36)	−6.13	(3.27)
Marlophen 814	−3.78	(2.22)	−4.480	(4.23)	−5.020	(2.92)	− 6.18	(5.35)	−5.62	(3.78)
Neopentyl glycol succinate	−3.32	(2.68)	−3.83	(4.88)	−4.07	(3.87)	− 5.40	(6.13)	−4.19	(5.21)
XF-1150	−3.14	(2.86)	−3.91	(4.80)	−3.45	(4.49)	− 4.71	(6.82)	−4.51	(4.89)
Carbowax 20M	−2.82	(3.18)	−3.38	(5.33)	−4.13	(3.81)	− 4.51	(7.02)	−4.36	(5.04)
Carbowax 4000	−2.78	(3.22)	−3.25	(5.46)	−4.08	(3.86)	− 4.38	(7.15)	−4.23	(5.17)
Reoplex 400	−2.44	(3.56)	−2.96	(5.75)	−3.50	(4.44)	− 4.10	(7.43)	−3.45	(5.95)
Diethylene glycol succinate	−1.07	(4.93)	−1.13	(7.58)	−1.80	(6.14)	− 2.03	(9.50)	−1.03	(8.37)
Ethylene glycol bis(cyanoethyl) ether	−0.81	(5.19)	−1.11	(7.60)	−0.94	(7.00)	− 1.12	(10.41)	−1.28	(8.12)
Tris(cyanoethoxy)propane	0.0	(6.00)	0.0	(8.71)	0.0	(7.94)	0.0	(11.53)	0.0	(9.40)

on squalane, minus a constant. The same numerical differences still exist between polar and non-polar phases, thus allowing easy column selection —an important feature of Rohrschneider's original scheme.

REFERENCES

1 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
2 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
3 L. Káplár, C. Szita and J. Takács, *J. Chromatogr.*, 65 (1972) 115.
4 J. Takács, Zs. Szentirmay, E. B. Molnár and D. Králik, *J. Chromatogr.*, 65 (1972) 121.
5 Zs. Szentirmay, G. Tarján and J. Takács, *J. Chromatogr.*, 73 (1972) 11.
6 I. A. Pullen and R. L. Werner, *Nature (London)*, 206 (1965) 393.
7 I. A. Pullen and R. L. Werner, *Spectrochim. Acta*, 21 (1965) 1257.
8 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 84 (1973) 231.
9 J. J. Leary, S. Tsuge and T. L. Isenhour, *J. Chromatogr.*, 82 (1973) 366.
10 P. Souter, *J. Chromatogr.*, 92 (1974) 231.
11 P. Magidman, S. F. Herb, R. A. Barford and R. W. Riemenschneider, *J. Amer. Oil Chem. Soc.*, 39 (1962) 137.