THE EFFECT OF TEMPERATURE ON THE RETENTION BEHAVIOUR AND POLARITY OF SEVERAL POLYSILOXANE STATIONARY PHASES

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SUMMARY

The effect of temperature on the polarity classification involving five terms as defined by Rohrschneider was examined. It was found that the retention behaviour of the standard substances used to define this polarity classification, as well as the polarity of the several polysiloxane stationary phases used, varied linearly with temperature over a limited temperature range.

INTRODUCTION

For several years, a number of workers have considered the problem of the prediction of retention data under varying conditions. Several approaches have been made to this problem, and most of the more widely accepted methods make use of the Kováts' retention index (I) system[1]. Considerable work has been reported on the variation of this system, as well as with the more basic relative retention (V_R) system, with temperature. Several workers[2–4] have found that a linear relationship exists between relative retention and temperature for the several classes of compounds they examined, while others[5,6] have found that the relative retention is inversely proportional to absolute temperature (T). Chovin and Lebbe[7] derived the following relationship between the relative retentions of two peaks:

$$\log V_R = a + \frac{b}{T}$$

where a and b are constants. This was later expounded by Ettre and Billeb[8], who found that a linear relationship existed between I and T for hydrocarbons on a non-polar phase. Takács *et al.*[9] have shown that the retention index (I) is related to the absolute temperature (T) by the following equation:

$$I^{\text{Stationary phase}}_{\text{Substance}}(T) = A + \frac{B}{T + C}$$

where A, B and C are constants, defined by the substance involved and the properties of the stationary phase. This relationship enables an accurate estimate of I to be made over a large temperature range and has been extensively developed by these workers,

but the constants A, B and C are not easily obtained as they require a knowledge of the molar heats of evaporation of the substances to be characterized as well as fairly extensive experimentation and computation.

Saha and Mitra[4] have made use of temperature *versus* retention index plots in order to predict the retention indices of hydrocarbons on a variety of stationary phases, while Ettre and Billeb[8] have used similar plots with various compounds on squalane and poly(ethylene glycol) 400. The results of these plots are of great use for data prediction and also for selecting conditions for the optimum analysis of multi-component mixtures, as the retention indices may change positively or negatively, depending on the relevant conditions.

The effect of temperature on the polarity of stationary phases has been examined to a lesser extent than its effect on retention indices, but as most modern polarity classification schemes are based on this retention index system, many of the results would appear to be applicable. Of all the polarity schemes, those developed by Rohrschneider[10-12] appear to be the most widely accepted. Lapkin and Makina[13] and Petsev[14] examined the influence of temperature on the polarity of stationary phases based on Rohrschneider's early classification system[10], where a polarity factor (P) was determined as the difference between the logarithm of the ratio of retention of butadiene and n-butane on a polar (P) and non-polar (NP) phase:

$$P = \log \left[\frac{V_P \text{ (butadiene)}}{V_P \text{ (n-butane)}} \right] - \log \left[\frac{V_{NP} \text{ (butadiene)}}{V_{NP} \text{ (n-butane)}} \right]$$

From these results, it was apparent that the polarity varied linearly with temperature, but as expected the rate of change varied with the nature of the stationary phase examined.

In the present work, we studied the influence of temperature on polarity, as defined by Rohrschneider's later classification system[12] for several polysiloxane phases. In this polarity system are included several of the modifications suggested by McReynolds[15], where several higher homologous compounds are used to characterize the stationary liquids, instead of the lower members suggested by Rohrschneider. These changes allow the classification to be more easily and accurately applied.

EXPERIMENTAL

Gas chromatography

The retention data were obtained isothermally between 90° and 150° with 10° increments using 12 ft. $\times$ 1/4 in. O.D. aluminium columns packed with 10% stationary phase on 67–85 mesh acid washed and silanized Celatom support. The equipment consisted of a modified F & M 810/29 research chromatograph with simultaneous flame ionization and thermal conductivity detection and fitted with an improved flow control system. The detector temperature was 220° and the injection temperature was 190°. Helium was used as the carrier gas with an inlet pressure of 45 p.s.i. and a flow-rate of 30 ml/min. With the thermal conductivity detector, the bridge current was 150 mA. The sample size was 1 μl.

Stationary phases

Four of the phases used consisted of polysiloxanes. The simplest was OV-1

(methylpolysiloxane), but the other three phases, OV-17, OV-210 and XF-1150, each had 50% of the methyl groups replaced with phenyl, trifluoropropyl and cyanoethyl groups, respectively. The fifth phase was squalane, a C-30 branched-chain hydrocarbon. The retention data obtained are shown in Table I.

TABLE I

VARIATION OF RELATIVE RETENTION VOLUMES AND RETENTION INDICES WITH TEMPERATURE

Stationary phase	Column temp. (°C)	Benzene		Butanol		2-Pentanone		Nitropropane		Pyridine	
		V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Squalane	90	0.128	648	0.089	603	0.113	634	0.144	663	0.195	699
	100	0.142	648	0.096	595	0.123	632	0.161	663	0.210	699
	110	0.157	649	0.103	594	0.136	631	0.172	662	0.230	701
	120	0.170	651	0.113	594	0.147	630	0.185	663	0.244	702
	130	0.185	650	0.123	590	0.161	628	0.201	662	0.264	703
	140	0.201	650	0.133	587	0.169	623	0.217	660	0.283	703
	150	0.213	652	0.139	582	0.180	624	0.225	660	0.296	703
OV-1	90	0.180	657	0.177	654	0.200	671	0.284	721	0.318	736
	100	0.197	658	0.192	654	0.213	669	0.304	722	0.345	741
	110	0.211	658	0.200	650	0.229	668	0.316	719	0.362	741
	120	0.228	659	0.213	646	0.243	668	0.334	719	0.383	742
	130	0.248	659	0.224	643	0.263	670	0.355	721	0.410	743
	140	0.264	659	0.243	642	0.276	672	0.371	720	0.425	742
	150	0.281	660	0.255	641	0.293	672	0.384	722	0.444	746
OV-17	90	0.369	762	0.372	766	0.473	798	1.009	901	1.009	901
	100	0.389	762	0.383	760	0.483	795	0.999	900	1.020	903
	110	0.415	767	0.396	761	0.494	794	0.997	899	1.026	904
	120	0.428	765	0.403	756	0.504	791	1.004	901	1.049	907
	130	0.451	770	0.417	754	0.515	790	0.998	900	1.065	911
	140	0.483	773	0.424	752	0.531	789	0.986	897	1.077	912
	150	0.500	777	0.434	750	0.536	786	0.976	896	1.102	917
OV-210	90	0.497	777	0.664	826	1.540	972	3.267	1099	1.675	985
	100	0.508	779	0.664	825	1.536	974	3.200	1105	1.700	992
	110	0.522	781	0.655	824	1.505	976	3.102	1110	1.688	994
	120	0.553	784	0.670	822	1.500	981	3.011	1112	1.689	1003
	130	0.573	785	0.705	825	1.496	984	2.870	1119	1.645]	1003
	140	0.605	789	0.713	826	1.463	984	2.761	1123	1.611	1010
	150	0.628	794	0.744	831	1.463	987	2.707	1132	1.634	1014
XF-1150	90	1.158	926	3.192	1100	2.634	1068	8.827	1274	5.248	1186
	100	1.196	930	3.032	1101	2.620	1075	8.496	1291	5.153	1200
	110	1.213	936	2.852	1102	2.562	1082	8.160	1307	5.018	1213
	120	1.238	941	2.787	1105	2.559	1088	7.969	1317	4.977	1222
	130	1.215	945	2.580	1107	2.421	1094	7.329	1338	4.627	1237
	140	1.255	952	2.507	1107	2.400	1100	7.200	1351	4.571	1245
	150	1.269	958	2.388	1109	2.374	1107	6.974	1365	4.465	1259

RESULTS AND DISCUSSION

Rohrschneider's polarity classification is based on the difference in behaviour of the retention indices of five standard substances on a non-polar squalane phase

and the phase to be characterized. Rohrschneider chose the retention behaviour of benzene, ethanol, 2-butanone, nitromethane and pyridine as being representative of induction, orientation, charge transfer and hydrogen bonding forces, with the assumption that they would characterize polar intermolecular interactions. Several of these substances were unsatisfactory as standards as they had small retention volumes, which tended to make their determination difficult and unreliable. McReynolds[15] suggested that higher homologues would be better substituted, *i.e.*, butanol for ethanol
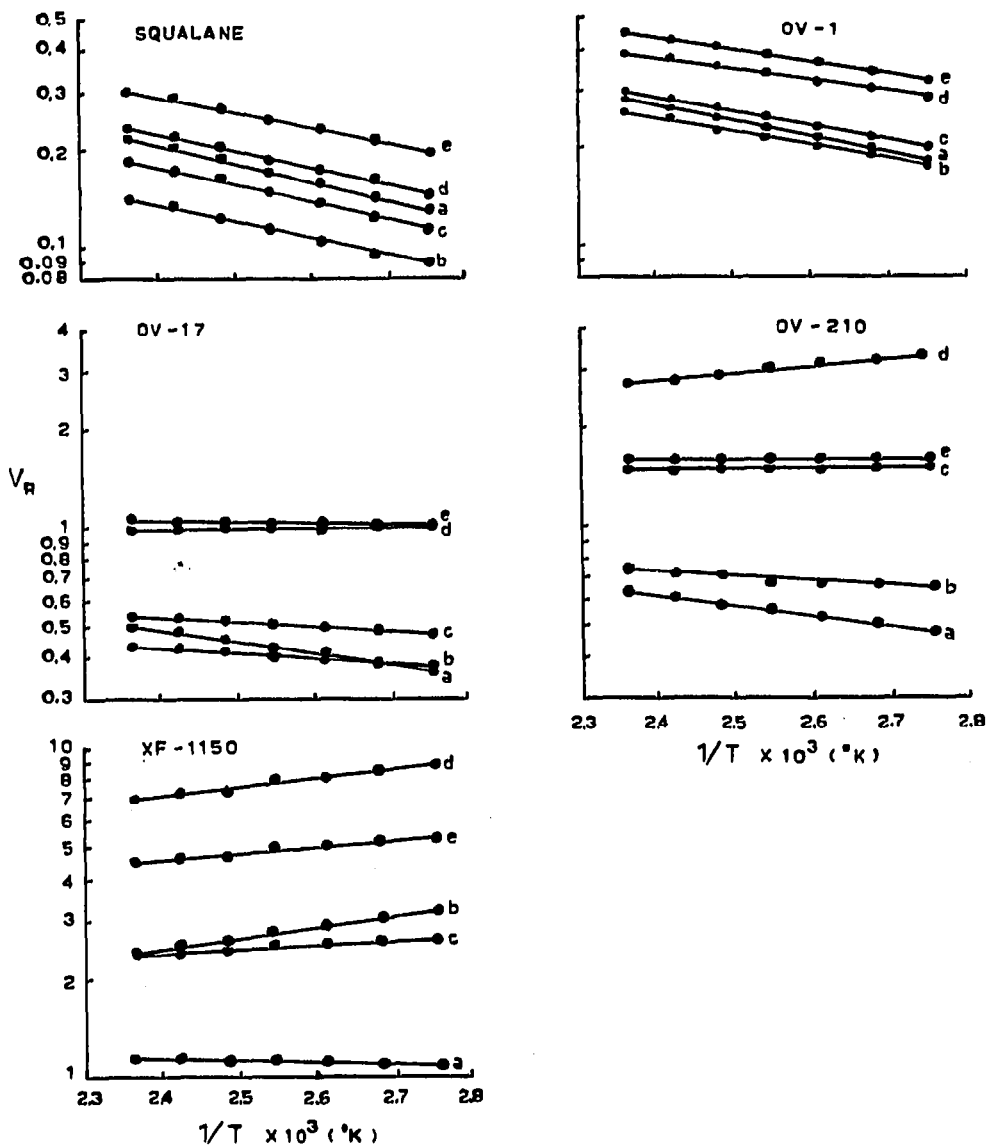

Fig. 1. Plots of the logarithm of the relative retention volume (V_R) *versus* the reciprocal of the absolute temperature (T) on the five stationary phases for the standard substances. a, Benzene; b, butanol; c, 2-pentanone; d, nitropropane; e, pyridine.

2-pentanone for 2-butanone and nitropropane for nitromethane, as the polar properties of each class of compound would not be radically affected. It was considered that benzene and pyridine had sufficiently large retention volumes and remained as standards. The additional substances suggested by McReynolds were not included[16].

A further problem associated with Rohrschneider's system is the relatively low upper temperature limit of the standard non-polar phase (squalane) of 100° (ref. 17), which restricts the retention index prediction properties of the system, although McReynolds[15] has reported data at 120°. In this work, the column temperature was varied from 90° to 150° in 10° increments (Table I) in order to obtain McReynolds' constants. At 150°, the column life of squalane was short owing to high column bleed, but the experimental time at these higher temperatures was short and with frequent calibration the results were extremely reproducible, $viz.$, $\pm$ 1 unit, which enabled usable trends to be obtained.

The effect of temperature on relative retention can be seen in Fig. 1, where a linear relationship for all standard compounds on phases of varying polarity existed when log V_R was plotted against $1/T$. However, it should be noted that excellent correlations also existed when V_R was plotted against T, these being slightly lower than those obtained for the plots in Fig. 1. This is apparent from Table II, where the correlation coefficients of the V_R $versus$ T and log V_R $versus$ $1/T$ plots are compared for benzene.

TABLE II

CORRELATION COEFFICIENTS FOR BENZENE PLOTS

Stationary phase	V_R versus T	Log V_R versus $1/T$
Squalane	0.997	0.999
OV-1	1.000	1.000
OV-17	0.997	0.997
OV-210	0.998	0.997
XF-1150	0.932	0.935

From Fig. 1, it is apparent that as the temperature increased for non-polar phases, $i.e.$, squalane and OV-1, the relative retention for the five standard substances increased. As the polarity of the phases increased, the behaviour of these substances apparently changed. On OV-17, the relative retention of nitropropane decreased slightly, while with OV-210, the relative retentions of nitropropane, pyridine and 2-pentanone also decreased with increase in temperature. Finally, with XF-1150, the trends observed on the non-polar phases were almost reversed, benzene being the only substance to show an increase in relative retention with temperature. From these plots in Fig. 1, the effect of varying the polarity of the stationary phase can be seen on the relative retention volumes and the elution order of the five standard substances. As expected, the relative retention volumes increased considerably with polarity. It is apparent that nitropropane is fairly susceptible to a change in polarity, as its relative retention increased dramatically on the more polar phases, but the other standard substances that also have acceptor groups present tended to show an increase in their relative retentions with respect to benzene. This effect was most evident with the two stationary phases that also have pendant acceptor groups present, $i.e.$, OV-210 and XF-1150, which contain 50% of trifluoropropyl and cyanoethyl groups, respectively, hence explaining the predominance of this interaction with these phases.
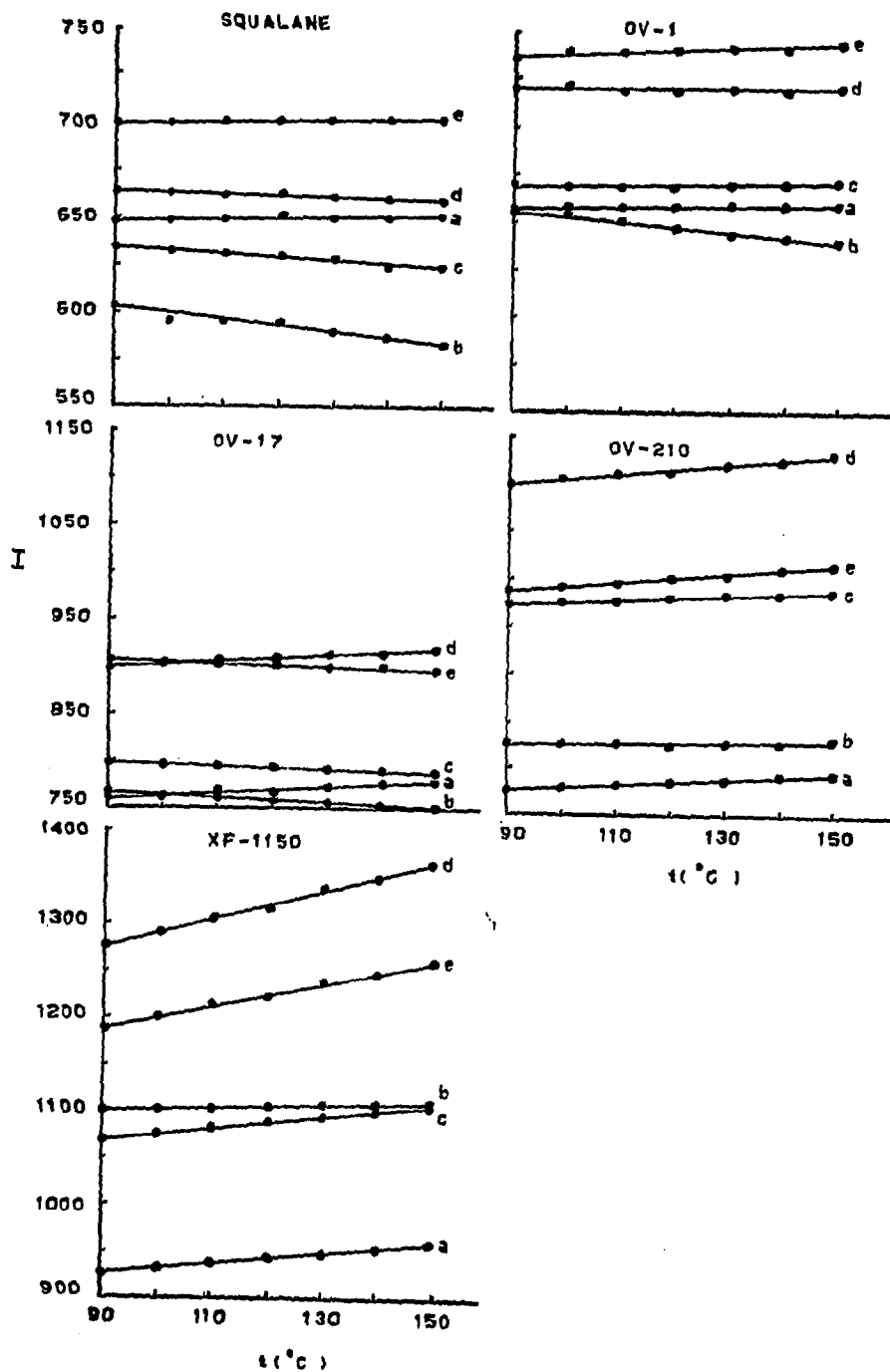
Fig. 2. Plots of Kováts indices (*I*) versus temperature (°C) on five stationary phases for the standard substances. a, Benzene; b, butanol; c, 2-pentanone; d, nitropropane; e, pyridine.

In Fig. 2, plots of Kováts indices *versus* temperature are shown for the five phases. It is apparent that a linear relationship exists between I and T similar to that found by Ettre and Billeb[8] for various hydrocarbons on non-polar phases. As they suggested, this I *versus* T relationship appears to be valid for other classes of compounds on polar phases, although we have evaluated this behaviour only on polysiloxanes. They also found large deviations from a straight line for benzene on squalane, but this effect was not evident in this work, as the aromatic substances evaluated (benzene and pyridine) behaved linearly with only small random deviations.

The effect of temperature on these retention indices was different to that on relative retentions, and in many instances the behaviour was the opposite. With XF-1150 and OV-210, the retention indices of the standard substances increased with temperature while the relative retentions decreased or remained fairly constant. On the less polar OV-17, OV-1 and squalane phases, the trends for pyridine and benzene were similar, *i.e.*, I and V_R increased with temperature, except for pyridine, where both parameters decreased. However, for butanol the trends in I and V_R were opposites, *i.e.*, V_R increased and I decreased. The behaviour of nitropropane and 2-penta-

TABLE III

VARIATION OF McREYNOLDS' CONSTANTS WITH TEMPERATURE

Stationary phase	Column temp. (°C)	McReynolds' constants				
		X'	Y'	Z'	U'	S'
OV-1	90	0.09	0.54	0.34	0.57	0.39
	100	0.09	0.54	0.37	0.58	0.39
	110	0.09	0.55	0.39	0.58	0.40
	120	0.09	0.55	0.41	0.59	0.40
	130	0.09	0.55	0.43	0.59	0.41
	140	0.09	0.56	0.45	0.60	0.41
	150	0.08	0.56	0.47	0.61	0.42
OV-17	90	1.17	1.64	1.63	2.38	2.01
	100	1.19	1.64	1.63	2.38	2.03
	110	1.20	1.64	1.63	2.37	2.05
	120	1.22	1.65	1.63	2.37	2.06
	130	1.24	1.65	1.63	2.37	2.08
	140	1.26	1.66	1.63	2.37	2.10
	150	1.28	1.66	1.63	2.37	2.12
OV-210	90	1.28	2.24	3.38	4.35	2.87
	100	1.30	2.27	3.42	4.41	2.91
	110	1.32	2.30	3.46	4.47	2.95
	120	1.34	2.33	3.51	4.52	2.99
	130	1.36	2.35	3.55	4.58	3.03
	140	1.39	2.38	3.60	4.64	3.07
	150	1.41	2.41	3.64	4.70	3.11
XF-1150	90	2.77	4.99	4.34	6.12	4.88
	100	2.82	5.03	4.42	6.27	5.00
	110	2.88	5.08	4.51	6.43	5.11
	120	2.91	5.12	4.59	6.59	5.22
	130	2.96	5.17	4.67	6.74	5.33
	140	3.01	5.21	4.75	6.90	5.44
	150	3.06	5.26	4.84	7.06	5.55

none was variable. Opposite behaviour occurred for 2-pentanone on OV-17 and squa-
lane while similar behaviour was observed on OV-1. For nitropropane, the opposite
behaviour was apparent on squalane and OV-17 while similar trends were present in
I and V_R on OV-1.

The effect of column polarity on the retention indices and elution order was
essentially similar to that observed when the effect of polarity on the relative retention
volumes was considered, as this retention index system is an empirical method of
representing relative retention volumes in terms of normal paraffins and while the
slopes of the corresponding V_R and I versus temperature plots will change, owing to
a difference in temperature coefficients between the hydrocarbons and standard sub-
stances on phases of varying polarity, the magnitude of the retention indices and the
elution order will be very similar to those observed with the V_R plots.

The change in stationary phase polarity with temperature can be found from
the differences, divided by 100, between the values for the standard substances on
squalane and the stationary phase to be characterized. These results are apparent in
Table III and Fig. 3, where the results are tabulated and plotted according to the re-
gression lines in order to minimize the random errors obtained when determining the
retention volumes and indices, as the differences are often small and can be accen-
tuated, especially on the non-polar OV-1 phase. These regression coefficients can be
found in Table IV. The effect of temperature on column polarity is variable, OV-1
and OV-17 showing the least variation of the four phases evaluated. As expected, the
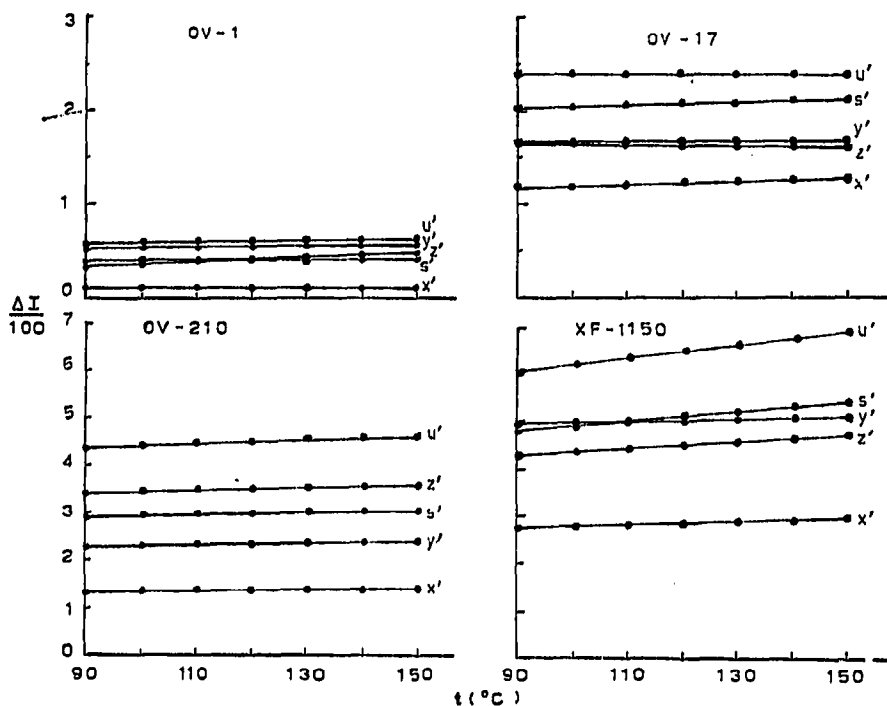greatest variation was obtained on the more polar phase, XF-1150, where the U,

Fig. 3. Plots of McReynolds' constants *versus* temperature (°C) for the phases characterized.

TABLE IV

REGRESSION COEFFICIENTS OF McREYNOLDS' CONSTANTS OF THE FORM $\frac{\Delta I}{100} = mT + b$

Stationary phase	X'		Y'		Z'		U'		S'	
	m	b	m	b	m	b	m	b	m	b
OV-1	−0.00018	0.110	0.00046	0.494	0.00215	0.150	0.00057	0.519	0.00043	0.350
OV-17	0.00189	0.996	0.00043	1.597	−0.00004	1.634	−0.00018	2.394	0.00182	1.846
OV-210	0.00207	1.096	0.00286	1.983	0.00443	2.977	0.00568	3.843	0.00393	2.516
XF-1150	0.00471	2.349	0.00454	4.579	0.00821	3.603	0.01568	4.704	0.01111	3.884

factor showed a positive rate of change of +0.157 units per 10°. In comparison, the smallest rate of change was found with Z' on OV-17, where a negative change of 0.0004 units per 10° was obtained. With almost all phases the polarity increased with temperature, except for several cases with OV-1 and OV-17 phases, where the negative change was small enough to be considered to be constant over the temperature range considered.

It is apparent that if the polarity of phases is to be considered at higher (or lower) temperatures than that of published data, especially for polar phases or non-polar phases that differ markedly in structure to squalane, consideration should be given to temperature effects when standard substances are used, as here, to characterize the stationary phase to be examined. While these simple linear relationships applied in this work probably do not give the most accurate estimate of polarity and retention behaviour for substances at different temperatures, over a small temperature range, as considered here, they proved to be fairly accurate and within normal experimental errors and they provide a useful estimate of these important characteristics.

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