CHROM. 20 951

INFLUENCE OF EXPERIMENTAL CONDITIONS UPON POLARITY PARAMETERS AS MEASURED BY GAS CHROMATOGRAPHY

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(First received May 19th, 1988; revised manuscript received August 15th, 1988)

SUMMARY

The influence of different chromatographic experimental parameters upon empirical, thermodynamic and dispersive force polarity parameters is examined for unusual stationary phases. The parameters considered were found to be sensitive to the column temperature, solute sample size and stationary phase loading.

INTRODUCTION

Polarity parameters have been reported in studies of groups of surfactants, etc., used as the stationary phases in packed chromatographic columns[1–11]. In recent papers the main interest has been in the influence of the structure of these compounds upon their polarities, although some relationships between various polarity parameters were also presented.

The aim of this paper is to explore the influence of different experimental parameters such as the temperature, gas flow-rate, column loading, probe sample size and composition upon some polarity parameters. The results with the present unusual stationary phases should be in conformity with results obtained for more commonly used phases.

EXPERIMENTAL

Experiments were carried out using a Chrom-5 gas chromatograph (Kovo, Czechoslovakia) with flame ionization detection (FID) and an IT2 Integrator (Kovo), or a GCHF 18.3 (Gide, G.D.R.) gas chromatograph with thermal conductivity detection (TCD) or FID. The conditions were: column (1 m × 3 mm I.D.), with stationary phase liquid loadings of 10, 15, 20 or 25% (w/w); support, Porolith (mesh size 0.2–0.5 mm); column temperature, isothermal 50–100°C; carrier gas, helium or nitrogen, 40 ml/min; solute probes, methanol, ethanol, 1-propanol, 1-butanol, 2-butanone, 2-pentanone, benzene, pyridine, 1-nitropropane and C_5–C_{11} n-alkanes; time for column stabilization, overnight; sample sizes both for n-alkanes and polar solutes, 0.1, 0.2 and 0.3 μl. Each measurement was repeated five times and averaged.

The following polarity parameters were considered: retention index, I_R, of

methanol and ethanol; polarity index, PI, of methanol and ethanol, PI $= 100 \log$ $(C - 4.7) + 60$ (ref. 12), where C is the apparent number of carbon atoms in a standard n-alkane having the same retention time as that of the alcohol; coefficient ρ, defined as the ratio of the adjusted retention time of an alcohol to that of n-hexane; partial molal free energies of solution of an hydroxyl, $\varDelta G_s^m(OH)$, or carbonyl group, $\varDelta G_s^m(C=O)$, calculated as described by Risby and co-workers[13–16]; the sum of the differences between the retention indices for the first five McReynolds solutes, $\sum_{i=1}^{5} \varDelta I_i$, on a given stationary phase and on squalane; and Criterion A for n-alkanes calculated according to Ševčik and Löwentap[17]

$$A = \frac{t_{R,n+1} - t_{R,n}}{t_{R,n} - t_{R,n-1}}$$

and the partial molar Gibbs free energy of solution per methylene group, $\varDelta G^E(CH_2)$, as demonstrated by Roth and Novák[19].

Stationary phases
        Surfactant of different structures described in previous papers[1–11] and indicated in Table I were used for temperature studies. The influence of the solute sample size, methods of retention time and of dead time estimation upon the polarity parameters were estimated for the following stationary phases used at 70 and 90°C:
        (1) $C_6H_{13}OCH_2CH(OH)CH_2OCH_2CH_2OC_6H_{13}$;
        (2) $C_4H_9O(CH_2CH_2O)_2CH_2CH(OH)CH_2(OCH_2CH_2)_4C_4H_9$;
        (3) $C_8H_{17}S(CH_2CH_2O)_4H$;
        (4) $C_8H_{17}O(CH_2CH_2O)_2H$;
        (5) $C_8H_{17}OCH_2CH(OH)CH_2OCH_2CH_2OC_8H_{17}$;
        (6) $C_{10}H_{21}NH(CH_2CH_2O)_3H$. These were used in Tables II–IV.

Dead time measurements
        The dead time was calculated from retention times of $C_5–C_9$ n-alkanes by using the Grobler and Balizs[19] method. When TCD was used the air peak time was considered as the dead time. For comparison, the method of Ševčik and Löwentap[20] was considered.

Retention time measurements
        The retention times of solute probes were measured at the peak maxima for symmetrical peaks. When an asymmetric peak was obtained for alcohols or pyridine, three different retention times, corresponding to the peak maximum (max), centre of gravity of the peak (CG) and the median of the peak (MED) were calculated. The elution time of the CG was calculated as

$$t_{R(CG)} = m_1 = \frac{\int_0^\infty t c(t) \, dt}{\int_0^\infty c(t) \, dt} \tag{1}$$

where m_1 denotes the first statistical moment of the peak, t the elution time of each point of the peak and $c(t)$ its concentration[21]. The elution time corresponding to the MED was computed according to the definition of Jönsson[22]. The retention time of the peak maximum was recorded by the integrator.

Statistical calculations

For comparison of polarity parameters calculated from the three retention times estimated by different methods for asymmetrical peaks and for different methods of dead time estimation, a goodness of fit test for the average values was performed according to the F-test and to the Students' t-test.

RESULTS AND DISCUSSION

The results are presented in Tables I–IV and Figs. 1–3. Previous papers[1–11] have shown that, generally, polarity parameters decrease with increasing column temperature. This is supported by the present results for stationary phases comprising some oligooxyethylene derivatives of alcohols, thioalcohols and alkylamines (Table I). In all cases, the retention index, polarity index, coefficient ρ and criterium A decrease with increasing temperature from 50 to 100°C.

Petrowski and Vanatta[23] confirmed the temperature dependence of coefficient ρ and found a linear relationship between ln ρ and the column temperature. The coefficient ρ is, in fact, the retention of the polar solute (alcohol) relative to non-polar n-hexane, and this should change both with the polarity of the stationary phase and with temperature. It is well known that variations in the retention index increase with increasing stationary phase polarity[24].

The influence of carrier gases upon the performance of packed columns was examined by Rohrschneider and Pelster[25]. At temperatures above 70°C they found hydrogen to be the most suitable carrier gas, while below 70°C nitrogen was most suitable. Here, no significant influence of carrier gas upon the polarity parameters considered was observed using helium or nitrogen.

Increase in the column length also did not change the values of any polarity parameters. However, for longer (2 m) columns, longer analysis times, peak broadening and skewing and higher pressure drops increasing the risk of loss of stationary phase were observed. To prevent this one should use, at least for stationary phase–surfactant polarity measurements, relatively short columns, with relatively large support particles, low gas flow-rates and temperatures above the melting point of the stationary phase used, but not so high as to cause bleeding!

The sensitivity of the retention index of two alcohols (methanol and ethanol), the polarity index and the coefficient ρ to the sample size and the stationary phase content is presented in Figs. 1 and 2. These polarity parameters may be sensitive to the sample size of the polar alcohol solute(s), particularly methanol. If they change, their absolute values generally decrease as the sample size of the polar probe increases. The measured I_R of methanol decreases with increasing ratio of the polar probe/standard n-alkanes. The influence of a change in the sample size of n-alkanes is much weaker.

The data presented for dispersive force parameters show that they are sensitive to the sample size of the solute used for their estimation (Table IV). Criterion A increases with increasing sample size of n-alkanes at lower stationary phase loadings.

TABLE I

TEMPERATURE DEPENDENCE OF POLARITY PARAMETERS USING SOME OLIGOOXYETHYLENE DERIVATIVES OF ALCOHOLS, THIO-ALCOHOLS AND ALKYLAMINES AS STATIONARY PHASES

Stationary phase*	Temp. (°C)	Retention index		Polarity index		Coefficient ρ		Criterion A Alkanes
		Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	
$C_9H_{17}O(EO)_2H$**	50	665	719	88.7	101.0	1.89	2.93	3.580
	60	656	713	86.6	99.0	1.69	2.74	2.475
	70	644	709	83.6	97.6	1.42	2.63	2.310
	80	636	705	82.4	95.1	1.37	2.33	2.680
	90	629	700	79.2	93.2	1.12	2.11	2.220
	100	621	697	73.4	91.2	1.10	1.99	2.143
$C_8H_{17}NH(EO)_2H$	50	764	813	108.2	115.2	4.78	6.33	2.682
	60	756	807	107.7	113.7	4.42	5.97	2.428
	70	753	800	106.3	112.1	4.00	5.63	2.295
	80	744	793	103.2	105.5	3.54	5.07	2.192
	90	742	788	101.1	102.1	3.04	4.80	2.101
	100	738	783	99.5	101.2	2.65	4.73	2.068
$C_8H_{17}S(EO)_3H$	50	703	753	96.2	106.8	2.19	4.12	2.460
	60	694	739	94.7	104.0	2.02	3.87	2.349
	70	689	723	91.3	99.6	1.88	3.55	2.224
	80	655	699	86.8	94.7	1.63	2.49	2.167
	90	648	680	85.6	92.7	1.50	1.93	2.099
	100	635	670	84.0	90.5	1.43	1.66	2.044

* 25% column loading.
** EO = $-CH_2CH_2O-$.

TABLE II

INFLUENCE OF SOLUTE SAMPLE SIZE AND STATIONARY PHASE LOADING ON DISPERSIVE FORCE PARAMETERS AT 90°C

Stationary phase	Loading (%)	Solute sample size (µl)	Criterion A Alkanes	$\Delta G^E(CH_2)$ (J/mol)		
				Alkanes	Alcohols	Ketones
1	10	0.1	2.318	254	103	596
		0.2	2.327	261	102	592
		0.3	2.346	240	99	590
	15	0.1	2.327	265	101	594
		0.2	2.310	233	100	593
		0.3	2.302	218	99	590
	20	0.1	2.328	194	102	592
		0.2	2.329	189	100	590 '
		0.3	2.335	178	99	588
	25	0.1	2.330	172	99	587
		0.2	2.330	173	99	587
		0.3	2.332	172	99	586
2	10	0.1	2.122	273	196	811
		0.2	2.124	271	195	808
		0.3	2.127	268	193	803
	15	0.1	2.127	268	195	808
		0.2	2.129	264	193	806
		0.3	2.131	262	192	803
	20	0.1	2.131	262	193	806
		0.2	2.134	263	192	804
		0.3	2.136	265	191	800
	25	0.1	2.135	267	192	800
		0.2	2.136	266	191	800
		0.3	2.136	267	191	801
4	10	0.1	2.289	199	103	589
		0.2	2.292	192	102	588
		0.3	2.301	187	100	580
	15	0.1	2.293	192	101	582
		0.2	2.298	189	100	580
		0.3	2.297	183	99	577
	20	0.1	2.296	188	102	582
		0.2	2.298	184	101	580
		0.3	2.303	179	99	576
	25	0.1	2.310	174	97	575
		0.2	2.311	175	97	576
		0.3	2.311	174	96	576

The partial molar excess Gibbs free energy of solution per methylene group, $\Delta G^E(CH_2)$, decreases significantly with increasing sample size when n-alkanes are used as the solutes and when estimated at high stationary phase loadings. This parameter generally decreases also when the amount of the stationary phase increases. The

TABLE III

VARIATION OF RETENTION INDEX WITH INCREASING PROBE SAMPLE SIZE FROM 0.1 μl (STEP 0.1 μl) TO $\Delta I_i/0.1$ μl FOR THE FIRST FIVE McREYNOLDS SOLUTES AND THEIR SUM

$\sum\limits_{i=1}^{5} \Delta I_i - \Delta\left(\sum\limits_{i=1}^{5} \Delta I_i\right)$. Sample size of alkanes: 0.1 μl. Temperature: 90°C.

Phase	Loading (%)	Probe					$\sum\limits_{i=1}^{5} \Delta I_i$
		X' Benzene	Y' 1-Butanol	Z' 2-Pentanone	U' 1-Nitropropane	S' Pyridine	
2	10	+0.5	−0.5	+1.0	+1.2	−12.5	−10.3
	15	0.0	+0.6	+1.0	+1.3	−11.6	− 8.7
	20	+2.3	−0.7	−1.0	+2.0	− 8.6	− 1.0
	25	+0.2	−0.1	+1.0	+0.7	− 2.5	− 0.7
3	10	+1.3	+0.3	0.0	+0.6	− 5.8	− 3.6
	15	0.0	0.0	0.0	0.0	− 3.0	− 3.0
	20	−0.3	−0.6	+0.3	+0.6	− 3.0	− 3.0
	25	0.0	0.0	0.0	0.0	− 0.3	− 0.3
4	10	0.0	+1.0	0.0	+0.3	−21.0	−19.7
	15	+1.0	−1.0	−0.3	+0.3	− 7.7	− 7.7
	20	−0.6	0.0	0.0	0.0	− 2.7	− 3.3
	25	+0.2	0.0	0.0	+0.3	− 0.8	− 0.3

sample size dependence is much weaker when alcohols and ketones are used as the probe solutes and is insignificant for higher liquid loadings of stationary phase.

The sensitivity of the retention index to variations in column liquid loading, support activity and sample size has been examined by several workers[24,26–31]. Vernon and Suratman[24] have pointed out that the sample size and sample composition influence the retention index. These effects were much stronger on a polar than on a non-polar phase. The present work suggests they are stronger with non-polar solute probes.

Jönsson and Mathiasson[29] have concluded that in the presence of surface adsorption, both on the surface of the support and on the surface of the liquid phase, the retention volume usually varies with sample size. Accurate measurements of retention data thus require the retention volume to be corrected for adsorption[27–30]. It was found[30] that the contribution from adsorption varies strongly with sample size. Adsorption effects, of course, decrease significantly with increasing stationary phase loadings as possibly shown in Table III. Both column loadings and sample size ought to be high in order to keep the variation in retention index as small as possible[31]. The effect of the sample size of polar probes depends significantly upon the column loading (Figs. 1–3). Increasing the amount of the stationary phase decreases the influence of the sample size, and usually 25% loadings gave the most consistent results for each polarity parameter.

Observed variations may be attributed both to the adsorption effects of polar probes (see Mathiasson et al.[31]) and of n-alkane reference compounds. These results
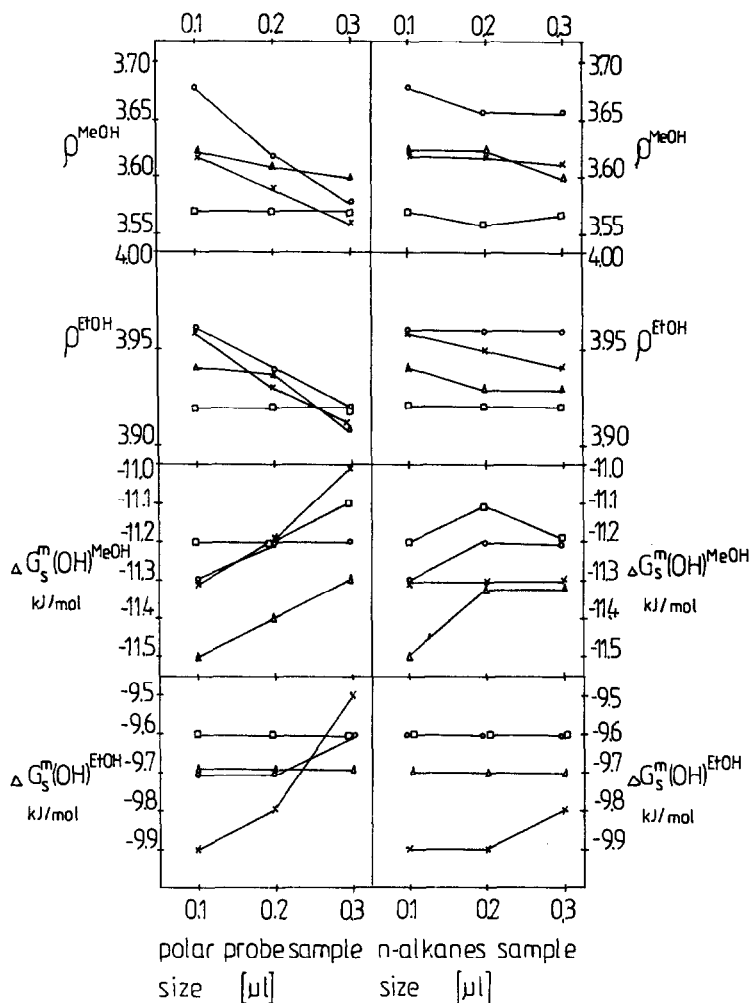
Fig. 1. The influence of the sample size of the solute probe on the polarity parameters considered. Stationary phase: $C_8H_{17}O(CH_2CH_2O)_2H$. Liquid phase loading (%): $\times$, 10; $\bigcirc$, 15; $\triangle$, 20; $\square$, 25. Sample sizes of reference n-alkanes and polar probes were 0.1 μl for both halves of the figure.

justify the standard liquid loading of 25% used in previous works[1-11] where the sample size varied between 0.2 and 0.3 μl.

A significant variation consequent upon the sample size of polar probes is observed (for lower liquid loadings) for the sums of the first five McReynolds probes, $\sum_{i=1}^{5} \Delta I_i$ (Fig. 3), particularly due to the retention index of pyridine (Table III). Vernon and Rayakorn[26] have found pyridine and butanol to show exceptionally high solute–support interactions but this was not found here for butanol.

In several cases, chromatographic peaks were broadened and skewed, especially those of pyridine and to a minor degree methanol and ethanol. What is the proper

TABLE IV

POLARITY PARAMETERS CALCULATED FROM RETENTION TIMES OF POLAR SOLUTES ESTIMATED BY DIFFERENT METHODS*

MeOH = methanol; EtOH = ethanol; BuOH = butanol; Py = pyridine.

Phase	PI^{MeOH} calc. from**			ρ^{EtOH} calc. from			I_R^{BuOH} calc. from			I_R^{Py} calc. from		
	$t'_{R,max}$	$t'_{R,MED}$	$t'_{R,CG}$	$t'_{R,max}$	$t'_{R,MED}$	$t'_{R,CG}$	$t'_{R,max}$	$t'_{R,MED}$	$t'_{R,CG}$	$t'_{R,max}$	$t'_{R,MED}$	$t'_{R,CG}$
1	89.4	89.2	89.1	1.77	1.76	1.76	855	853	852	929	911	903
2	107.2	107.0	106.8	3.96	3.94	3.90	1008	1003	1000	1100	1084	1072
3	97.2	97.1	96.9	4.10	4.10	4.09	839	837	836	960	955	948
4	83.6	83.5	83.5	2.63	2.60	2.57	918	917	916	1035	1030	1026
5	72.5	72.4	72.3	1.34	1.33	1.30	836	834	833	892	890	887
6	103.6	103.6	103.5	5.06	5.05	5.03	935	934	932	909	902	898

* Stationary phase loading 25%; probe sample size 0.1 μl; temperature 70°C for PI and ρ, and 90°C for I_R.

** t'_{max}, t'_{MED}, t'_{CG} = retention times for the maximum, median or centre of the peak, respectively.
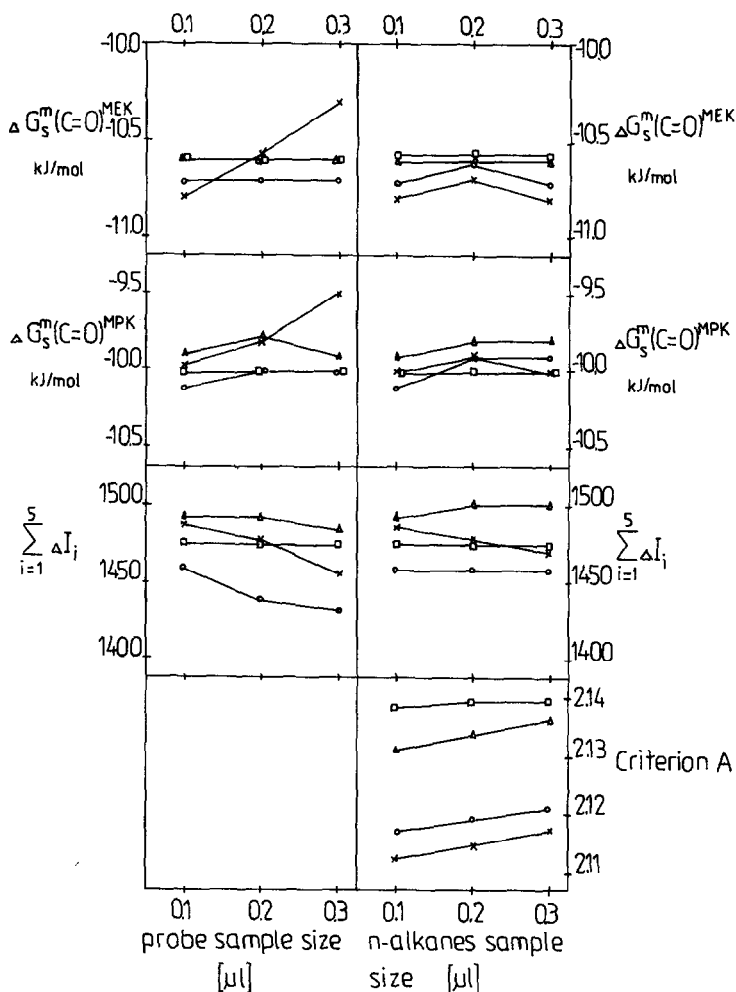
Fig. 2. The influence of the sample size of the solute probe on the polarity parameters. Stationary phase: $C_4H_9O(CH_2CH_2O)_2CH_2CH(OH)CH_2(OCH_2CH_2)_4OC_4H_9$. Other details as in Fig. 1.

measure of the retention time of non-symmetrical chromatographic peaks? The characterization of the elution profiles was extensively examined[32–37], Jönsson in a series of papers[22,38–40] studied the problem of the correct measure of retention time in linear, non-ideal elution chromatography. He examined relationships between three different retention measures (the maximum of the peak, the median and the centre of gravity) and the skew and the width of the elution peak observed. For symmetric peaks these three measures of retention time (or retention volume) would be identical, but the elution peak is generally skewed and the degree of skewness depends on the nature of the peak broadening mechanisms[22,39]. Generally, the correct measure of the retention time is the median, while the maximum and the centre of gravity are different from the true retention time.
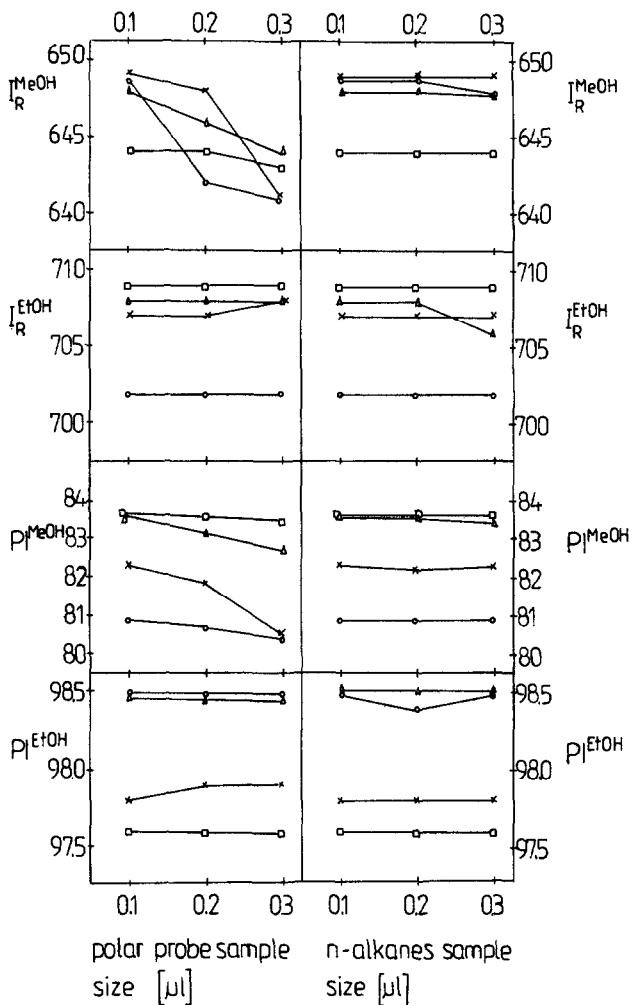
Fig. 3. The influence of the solute sample size on the polarity parameters. Stationary phase: $C_4H_9O(CH_2CH_2O)_2CH_2CH(OH)CH_2(OCH_2CH_2)_4OC_4H_9$. $\Delta G_s^m(C=O)^{MEK}$ and $\Delta G_s^m(C=O)^{MPK}$ = partial molal Gibbs free energies of solution of the carbonyl group for 2-butanone and 2-pentanone, respectively. Other details as in Fig. 1.

Using three different measures for retention time for some solute probes, three sets of polarity parameters were determined (Table IV). Different retention times were obtained by measuring to the median (MED), centre of gravity (CG) or maximum of the peak. The polarity parameters calculated from three sets of retention times are generally close to each other for alcohols as the observed differences are random and statistically insignificant. However, differences in the retention time and retention index of pyridine are high, systematic and significant on all six stationary phases examined.

Another factor which might influence the polarity parameters is the method of

the dead time estimation. Many workers have extensively examined the problem of dead time estimation[41–52]. Wainwright and Haken[52] reviewed the methods of presentation of retention data, measurement and calculation of column dead time, and presented procedures for its calculation. They pointed out that the dead time can be determined most accurately by using at least four n-alkanes and the calculation method of Grobler and Balizs[19]. The methods using three consecutive n-alkanes and the direct calculation methods of Peterson and Hirsch[53], Sevčik[45] or Sevčik and Löwentap[20] were also recommended[51]. Whilst different values of the dead time were obtained here, the values of the polarity parameters were not influenced by the method of dead time estimation as the observed differences are random and statistically insignificant.

In the case of stationary phases with significantly low molecular masses, one should take into account possible bleeding. The differences in the amounts of liquid phase, weighed before and after the experiment (after extraction from the support), confirmed that no significant loss of the liquid phase took place during the polarity measurements at the standard temperature.

CONCLUSIONS

The column temperature significantly influences all the polarity parameters considered. They decrease with increasing temperature (Table I), although not always due to a decrease in the stationary phase polarity.

An increase in the amount of liquid stationary phase decreases the sensitivity of the polarity parameters to changes in the sample size, both of the polar probes and the reference n-alkanes (Figs. 1 and 2). An increase in the sample size of the polar probe decreases (for liquid loadings below 20%) the values of the retention index, polarity index and coefficient ρ, while the partial molal free energies of solution of hydroxyl, $\Delta G_s^m(OH)$, and carbonyl, $\Delta G_s^m(C=O)$, groups were sometimes increased. Dispersive force parameters, such as criterion A, slightly increase with increasing sample size of the n-alkanes. The partial molar excess Gibbs free energy of solution per methylene group, $\Delta G^E(CH_2)$, slightly decreases with increasing solute sample size if the stationary phase loading is less than 25%. This may be attributed to support activity and could be reduced by blocking the active sites on the support surface by using a silanized support.

The influence of the carrier gas, the column length and the method of dead time estimation upon the polarity parameters is statistically insignificant.

It was found that the skewness of alcohols' peaks is small and differences between the polarity parameters calculated from different retention times are random and insignificant. The peaks for pyridine are highly skewed and the retention indices calculated from different retention times are quite different. They may be arranged in the following order: $I_{R,max} > I_{R,MED} > I_{R,CG}$.

No significant loss of the stationary phase during polarity measurement has been observed. Differences between the amount of the liquid phase before and after chromatographic measurements were generally below 0.2%.

ACKNOWLEDGEMENT

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