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Comparison of the behaviour of gas–liquid and gas–liquid–solid capillary columns through the determination of thermodynamic characteristics

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Abstract

Interpolation methods, used for the prediction of retention times in programmed temperature capillary gas chromatography, employ equations whose parameters are correlated, through the capacity factor and the phase ratio of the column, with the thermodynamic parameters, that can be calculated by using retention data obtained at various temperatures. Homologous series of organic compounds (linear alkanes and alcohols) were analysed on bonded phase polar, non-polar and carbon layer open tubular columns and the values of some thermodynamic parameters were obtained. Their dependence on the polarity of the liquid phase and of the solutes, film thickness, temperature of the column, was investigated and allowed comparison of the behaviour of the different phases tested.

Keywords: Retention prediction; Thermodynamic potential; Stationary phases, GC

1. Introduction

Some interpolation procedures can predict the retention times in programmed temperature gas chromatography by using retention values measured in isothermal analysis conditions as the input data. Various methods, suggested by several authors [1–9] and by ourselves in papers published previously [10,11] employ numerical terms that properly used yield good results in the prediction of retention times when applied to packed and open tubular columns, bonded-phase gas–liquid columns and carbon or graphite layer capillary columns. The terms and parameters used by the various methods are corre-

lated with the classical thermodynamic function through different relationships, containing constant or column-dependent quantities and cannot therefore be used to compare results obtained by different authors on various types of columns. The possibility of obtaining the values of ΔH and ΔS from the terms of the empirical equations permits the comparison and the classification of columns and stationary phases, independent of the source and previous treatment of the experimental data.

By using retention data measured on bonded phase and carbon layer open tubular columns and simplified equations, the dependence on the thermodynamic functions of the empirical terms of the equations previously used by us was investigated. The values of ΔH and ΔS were calculated, their influence separated by that of other column-depen-

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dent parameters such as phase thickness, diameter and length. As the values of ΔH and ΔS depend on composition and structure of the liquid or solid–liquid layer of the capillary columns and not on geometrical parameters, by using their values instead of composite empirical terms, the behaviour of different columns and the results obtained under different conditions and by various methods can be compared on a common base. Their dependence on temperature and on the analysed compounds can be used for the characterization and classification of the columns, and to show the influence of the porous layer on the solute–solvent interaction in mixed-phase systems.

2. Material and methods

2.1. Instruments and samples

The experiments were performed with fused-silica capillary columns, all of which were 30 m \times 0.32 mm I.D. The liquid–liquid bonded phase columns were non-polar polydimethylsiloxane SPB-1 and polar polyglycol Supelcowax-10 (Supelco, Bellefonte, PA, USA) with nominal film thickness of 0.25 μm . The column Supelcowax-10 is also indicated in the figures and tables as WAX.

The carbon layer capillary columns partially deactivated with polyglycol-terephthalic acid were obtained by courtesy from Supelco (column CL-A) and from the University of Urbino (Italy), Istituto di Scienze Chimiche (column CL-B). The amount of liquid phase on the carbon layer was 16%, both for CL-A and CL-B. The thickness of the stationary film deposited on the inner wall of the capillary was checked with a scanning electron microscope (SEM) by using a Stereoscan Model 440 instrument (Leica, Cambridge, UK). With this method the film thickness (carbon layer plus deactivating liquid phase) of the carbon layer columns was found to be 1.3 μm for CL-A and 0.3 μm for CL-B, while the nominal thickness of 0.25 μm was confirmed for the bonded-phase columns.

The column were installed in a Varian Model 3600 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a capillary split-splitless injector, a constant inlet pressure flow control and a flame

ionization detector. Helium was used as carrier gas. Isothermal conditions were set with an accuracy of $\pm 1^\circ\text{C}$. The analyses were carried out in the range of 60–190 $^\circ\text{C}$, at 10 $^\circ\text{C}$ intervals. Standard solution of *n*-alkanes and *n*-alcohols, at concentrations of 10 mg l $^{-1}$, were injected (amount 10 μl) in the split mode. The retention times were measured with an accuracy of ± 0.005 min by using a Varian DS-650 Data system.

2.2. Theory

The equation which describes the dependence of the retention time [$t_R(T)$], on the values of dead time, $t_M(T)$, and capacity factor (k') [4–6,10,12–15] at different temperatures is:

$$t_R(T) = t_M(T) \cdot (1 + k') \quad (1)$$

The k' is correlated to the thermodynamic parameters by the following expression [1–3,8,16–23]:

$$k' = \frac{1}{\beta} \exp\left(\frac{\Delta G}{RT}\right) \quad (2)$$

where ΔG is the free energy of solution or partition of a given compound between the gas and liquid phase, R is the universal gas constant, T the absolute temperature and β is the phase ratio of the column, i.e., the ratio between the volume of the gas phase and that of the liquid phase ($\beta = V_G/V_L$). By taking into account the classical thermodynamic equation:

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

Eq. (2) can be rewritten as:

$$k' = \exp\left(-\ln \beta + \frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) \quad (4)$$

In the methods used to predict the retention times at various temperatures and in different temperature programmed runs [7,10,21–23], this equation is shortened as:

$$k' = \exp\left(\frac{B'}{T} + C'\right) \quad (5)$$

being:

$$B' = \Delta \frac{H}{R}$$

and

$$C' = -\ln \beta - \frac{\Delta S}{R}$$

The empirical values of the composite terms B' and C' can be calculated by using a set of isothermal retention data and can be used successfully for the prediction of the retention times in isothermal or temperature programmed analyses. Whereas the knowledge of B' permits the ΔH value to be easily calculated, R being a known constant,

$$\Delta H + B'R \quad (6)$$

to obtain ΔS from C' values requires the knowledge of the true phase ratio β , that depends on the solid-liquid ratio of the carbon layer columns.

$$\Delta S = (-C' - \ln \beta)R \quad (7)$$

For a given column the term β can be considered as a constant [1,3,7,21–24] while both ΔH and ΔS depend linearly on temperature [10,16,17], according to the following relationships:

$$\Delta H(T) = h_0 + h_1 T \quad (8)$$

$$\Delta S(T) = s_0 + s_1 T \quad (9)$$

It may be impossible to accurately separate ΔH and ΔS notwithstanding the quantity ΔG in Eq. (2) is known. However, for practical purposes it may be sufficient to calculate the values of the thermodynamic constant by using experimental retention values taken at fixed temperature interval, in order to obtain with a step method the trend of ΔH and ΔS versus temperature and compare the characteristics of different stationary phase in the same experimental conditions.

Taking two isothermal runs at temperatures T_1 and T_2 , the following expressions apply:

$$\ln k'(T_1) = -\ln \beta + \frac{\Delta H_1}{RT_1} - \frac{\Delta S_1}{R} \quad (10)$$

$$\ln k'(T_2) = -\ln \beta + \frac{\Delta H_2}{RT_2} - \frac{\Delta S_2}{R} \quad (11)$$

if the ΔT value is small enough to give small changes of k' values, it is reasonable to suppose that the values ϵ_H and ϵ_S :

$$\Delta H_2 - \Delta H_1 = \epsilon_H \quad (12)$$

$$\Delta S_2 - \Delta S_1 = \epsilon_S \quad (13)$$

are negligible with respect of the experimental fluctuations. This allows the system to be simplified and reduced to two equations easily solved:

$$\Delta H = \frac{R(\ln k'_1 - \ln k'_2)T_1 T_2}{T_2 - T_1} \quad (14)$$

$$\Delta S = R \left[\frac{(\ln k'_1 - \ln k'_2)}{T_2 - T_1} T_2 - \ln \beta - \ln k'_1 \right] \quad (15)$$

yielding approximate values of ΔH and ΔS directly calculated by using experimental values of retention measured at small temperature intervals (e.g., 10°C).

The step method suggested here is only valid within the temperature range investigated, but in this range the results are accurate enough being directly connected to experimental measurements of k' values and independent on the fitting of regression analysis.

If the same temperature range is investigated for the different columns tested, the results are comparable and the differences observed between ΔH and ΔS values can be correlated with the interaction mechanism of the stationary phase.

3. Results and discussion

Table 1 and Table 2 show the values of B' and C' at various temperatures for compounds of different polarity (*n*-heptanol and *n*-tridecane) analysed on the gas-liquid non-polar (polydimethylsiloxane 0.25 μm), polar (polyethyleneglycol 0.25 μm) and two gas-liquid-solid carbon layer capillary columns (1.3 μm and 0.3 μm respectively for CL-A and CL-B). These two compounds were chosen as probes to show in the figures and tables the behaviour of polar and non-polar solutes because their retention times are similar and therefore allow a easy comparison. Table 3 and Table 4 show ΔH and ΔS values.

The behaviour of these terms as a function of temperature can be summarised as follows. The dependence on temperature of ΔH values (Fig. 1) corresponds to that of B' being the ratio a constant.

For alkanes (*n*-tridecane being taken as an exam-

Table 1
Values of the constant B' for n -tridecane and n -heptanol on the four columns tested

Temperature (K)	$B' \cdot 10^{-3}$ (K)							
	n -Tridecane				n -Heptanol			
	WAX	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
338	5.71				6.42			
343				7.17				6.59
348	5.42			6.95	6.16	4.98	7.00	6.52
358	5.24		7.13		6.04	4.76	6.59	
363				6.36				6.26
368	4.88	6.66	6.85		5.98	4.56	6.25	
378		6.46				4.09		
383	4.17		6.44	5.44	5.35		6.14	5.89
388		6.15				3.93		
398		5.99				3.30		
403	3.80		5.93	4.87	5.11		5.59	5.22
408		5.66				3.43		
418		5.48	5.61	4.19	4.53	2.86	5.43	4.78
423				4.06				4.63
428		5.15	5.26		3.92	2.32	5.21	
438		4.93			3.87	2.30	4.95	
448		4.23			3.26			
458					2.85			

Table 2
Values of the constant C' for n -tridecane and n -heptanol on the four columns tested

Temperature (K)	C'							
	n -Tridecane				n -Heptanol			
	WAX	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
338	-15.32				-16.35			
343				-18.55				-16.40
348	-14.47			-17.90	-15.60	-13.52	-16.60	-16.10
358	-13.96		-17.27		-15.25	-12.91	-15.77	
363				-16.23				-15.45
368	-12.98	-15.92	-16.51		-15.10	-12.35	-14.83	
378		-15.39				-11.09		
383	-11.07		-15.39	-13.76	-13.39		-14.55	-14.46
388		-14.57				-10.68		
398		-14.16				-9.07		
403	-10.13		-14.11	-12.34	-12.80		-13.15	-12.78
408		-13.35				-9.38		
418		-12.92	-13.33	-10.80	-11.38	-8.01	-12.75	-11.70
423				-10.37				-11.34
428		-12.13	-12.51		-9.95	-6.74	-12.24	
438		-11.62			-9.50	-6.60	-11.65	
448		-10.05			-8.47			
458					-7.57			

Table 3
Values of ΔH for *n*-tridecane and *n*-heptanol on the four columns tested

Temperature (K)	$\Delta H \cdot 10^{-3}$ (cal mol ⁻¹)							
	<i>n</i> -Tridecane				<i>n</i> -Heptanol			
	WAX	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
338	11.35				12.75			
343				14.26				13.10
348	10.78			13.71	12.24	9.89	13.91	12.80
358	10.41		14.17		12.00	9.46	13.09	
363				12.63				12.43
368	9.71	13.23	13.62		11.89	9.06	12.41	
378		12.85				8.13		
383	8.29		12.79	10.80	10.62		12.21	11.70
388		12.22				7.82		
398		11.90				6.56		
403	7.56		11.79	9.69	10.16		11.11	10.38
408		11.25				6.81		
418		10.90	11.14	8.66	9.00	5.68	10.78	9.50
423				8.08				9.20
428		10.24	10.45		7.79	4.61	10.35	
438		9.79			7.69	4.57	9.84	
448		8.41			6.48			
458					5.66			

ple) the slope slightly differs between polysiloxane and polyglycol columns; the change of the thickness of the carbon/polyglycol layer shifts the plots towards greater ΔH values. Owing to the predominant effect of hydrogen bonding between the OH groups of the alcohols and the oxygen bridges and end-chain

OH groups of the polyglycol with respect of gas–solid interactions, the values of all for Supelcowax and for the two carbon layer columns differ only slightly for *n*-heptanol, showing a small divergence with increasing temperature. A decreasing slope with increasing the thickness of the carbon layer is also observed. Lower ΔH values are found on polysiloxane. This agrees with the values of the difference in apparent carbon number of linear alkanes and alcohols, ΔC [26,27], equal to 2.75 for SPB-1, 7.5 for Supelcowax and ranging from 6.0 to 6.4 for CL-A and from 6.5 to 7.2 for CL-B. The change of polarity with temperature [25] of carbon layer columns CL-B is greater (about 10% in the range 60–180°C with respect of 6% for CL-A) as shown by the greater slope.

Fig. 1 also shows the inversion of the ΔH values for tridecane and heptanol on the polar and non-polar gas–liquid columns, according to the well known greater affinity of the solutes with the liquid phases having a similar polarity. When the analysed compound has a polarity similar to the modifying liquid added to the carbon layer (*n*-heptanol vs. polyglycol) the gas–liquid interaction may be predominant. A small difference of ΔH is therefore observed be-

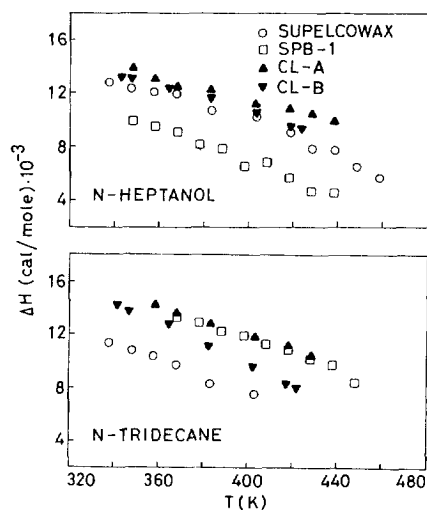


Fig. 1. Temperature dependence of the ΔH values for *n*-heptanol and *n*-tridecane on the four columns tested.

tween Supelcowax, CL-A and CL-B, and the slightly greater values for carbon layer columns may be ascribed to residual gas–solid mechanism. When the polarity of the probe (*n*-tridecane) is quite different from that of the modifying liquid, the interaction of the carbon layer becomes predominant and the column behaves with a polarity similar to that of the probe. In fact, the lower part of Fig. 1 shows that the ΔH values of tridecane measured on SPB-1 and on CL-A are nearly coincident, while those measured on Supelcowax are much smaller. The lower values and the different slope of the CL-B column with respect to CL-A for both polar and non-polar compounds can be ascribed to the smaller thickness of the carbon layer ($0.3 \mu\text{m}$ instead of $1.3 \mu\text{m}$) of this column and to different origin and treatment of the graphitized carbon. The different slope also agrees with the change of polarity of the CL-A and CL-B columns with temperature, observed previously [25].

Fig. 2 and Fig. 3 show the values of C' and those of ΔS calculated by using Eq. (7). The C' values for alkanes differ between gas–liquid polysiloxane and polyglycol columns, but are similar, except for the greater slope of CL-B, on non-polar gas–liquid SPB-1 and gas–liquid–solid columns with a reduced

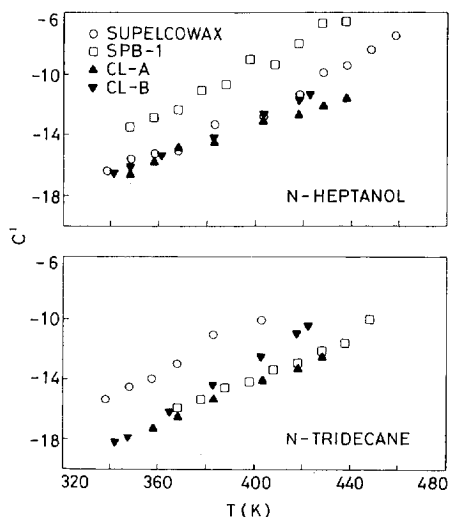


Fig. 2. Temperature dependence of the constant C' for *n*-heptanol and *n*-tridecane on the four columns tested.

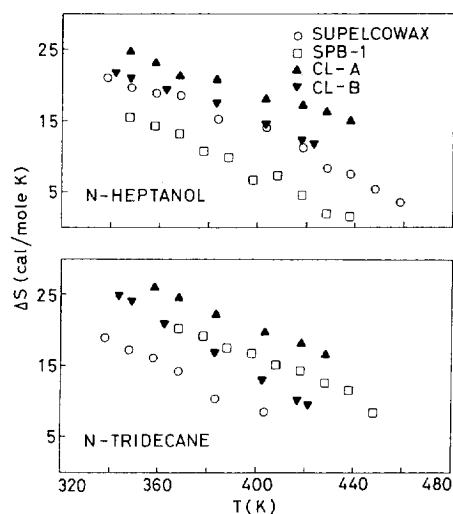


Fig. 3. Temperature dependence of the ΔS values for *n*-heptanol and *n*-tridecane on the four columns tested.

amount of polar liquid phase. An opposite behaviour is shown by *n*-heptanol, the C' values for the Supelcowax and the carbon layer columns being similar in this instance and the values are higher, though near parallel, for SPB-1. The comparison of Fig. 2 and Fig. 3 shows the advantage of using ΔS values for the characterization of stationary phases instead of the composite term C' . In fact, whereas the values of C' for the two carbon-layer columns are very similar (differing slightly in the slope as a function of temperature) and also are close to the values for alcohols on the polar column and for alkanes on the non-polar one, the different behaviour of columns with different thickness of the carbon layer is also observed when the values of ΔS are shown (Fig. 3). The distance between the lines for CL-A and CL-B columns is greater, owing to the influence of the term β (see Eq. 7) directly depending on the phase thickness and the correlation between C' and ΔS is not so simple as that between B' and ΔH . If β is taken as a constant independent on temperature being negligible the difference of thermal expansion of the column and of the phase layer, its value can be calculated merely by using the geometrical parameters of the capillary column, i.e., the internal radius, r , and the liquid phase film

thickness, d [28], respectively proportional to the void volume of the column i.e., to the volume of the gas phase V_G and of the liquid phase V_L :

$$\beta = \frac{V_G}{V_L} = \frac{r^2 L}{(r+d)^2 L - r^2 L} = \frac{r^2}{2rd} = \frac{r}{2d} \quad (16)$$

The ΔS values obtained by using Eq. (7), depend therefore on the exact knowledge of the film thickness. By using the value of 0.25 μm for Supelcowax and SPB-1, 1.3 and 0.3 μm for CL-A and CL-B respectively, the ΔS values shown in Table 4 and Fig. 3 were calculated and found to behave linearly as a function of temperature; the same inversion between the plots of tridecane and heptanol found for ΔH is also observed by changing from polar to non-polar column.

By using a polydimethylsiloxane column with a nominal film thickness of 3 μm (DB-1, 30 m \times 0.32 mm I.D.; J & W Scientific, Folsom, CA, USA) the validity of the β value calculated with Eq. (16) was checked. As an example, the ΔS at 90°C for n -tridecane is 20.14 $\text{cal mol}^{-1} \text{K}^{-1}$ for 0.25 μm and

19.75 $\text{cal mol}^{-1} \text{K}^{-1}$ for 3 μm column; the two values correspond well enough. However, SEM examination of the two columns showed that the true average thickness of the phase in the column with nominal film 3 μm thick was equal to 3.5 μm . By using this value, a ΔS of 20.07 $\text{cal mol}^{-1} \text{K}^{-1}$ was found for tridecane, better approaching the value measured on the 0.25 μm column. This confirms that, whereas C' depends on the geometrical parameters of the column and on the film thickness, the ΔS value only depends for classical gas-liquid chromatography on the type of liquid phase and, if measured for columns of known geometrical parameters, may be used to calculate the unknown film thickness of other columns. For carbon layer columns or other capillary types having inert material bonded to the inner surface and supporting the liquid phase (PLOT=porous layer open tubular) the β value cannot be simply obtained by measuring the geometrical thickness of the composite layer (phase plus supporting medium) and an effective β value should be determined by taking into account the amount of modifying liquid phase, the increased

Table 4
Values of ΔS for n -tridecane and n -heptanol on the four columns tested

Temperature (K)	ΔS (cal mol ⁻¹ K ⁻¹)							
	n -Tridecane				n -Heptanol			
	Wax	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
338	18.98				21.02			
343				25.75				21.49
348	17.30			24.35	19.54	15.39	24.80	20.43
358	16.27		26.13		18.85	14.18	23.15	
363				21.16				19.60
368	14.33	20.16	24.62		18.54	13.08	21.29	
378		19.12				10.57		
383	10.53		22.40	16.25	15.15		20.74	17.63
388		17.49				9.76		
398		16.67				6.56		
403	8.68		19.86	13.41	13.98		17.94	14.29
408		15.06				7.18		
418		14.21	18.30	10.50	11.16	4.45	17.15	12.15
423				9.51				11.43
428		12.65	16.67		8.30	1.93	16.14	
438		11.62			7.42	1.65	14.96	
448		8.50			5.38			
458					3.57			

Table 5
 ΔH and ΔS values for *n*-alkanes at two temperatures (348K and 418K) on the four columns tested

Column Temperature (K)	$\Delta H \cdot 10^{-3}$ (cal mol ⁻¹)				ΔS (cal mol ⁻¹ K ⁻¹)			
	WAX	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
z ^a	348	418	348	418	348	418	348	418
7		5.89				7.18		
8		7.58				10.82		
9		9.11	4.93			13.89	3.00	
10		10.48	6.83	8.03	9.47	16.45	6.88	13.72
11		11.70	8.11	12.39	10.95	18.55	9.40	15.69
12	9.55	12.84	9.69	13.50	10.15	20.39	12.19	16.90
13	10.77		10.90	11.14	13.71		14.21	18.30
14	11.89	7.87	12.01	12.18	14.74	8.76	16.10	19.82
15	12.95	9.14		15.58	11.75	10.99		15.35
16	14.00	10.24		13.05	13.02			17.52
18	15.80	12.42		15.16	16.36			21.18
20	14.25			16.95				24.55
22	15.99				21.97			

^a Number of C atoms.

Table 6
 ΔH and ΔS values for *n*-alcohols at two temperatures (348K and 418K) on the four columns tested

Column Temperature (K)	$\Delta H \cdot 10^{-3}$ (cal mol ⁻¹)				ΔS (cal mol ⁻¹ K ⁻¹)			
	WAX	SPB-1	CL-A	CL-B	WAX	SPB-1	CL-A	CL-B
z ^a	348	418	348	418	348	418	348	418
4				8.90				13.60
5	10.13	6.74	8.88	10.26	16.00	9.01	21.90	14.49
6	11.24	7.90	11.53	11.61	17.92	12.53	23.41	15.90
7	12.24	9.00	12.72	12.80	19.54	15.39	24.80	17.15
8	13.22	10.28	13.90	13.78	21.07	17.85	25.70	18.36
9	14.10	11.43	14.80	15.80	22.50	19.85	26.70	19.68
10	12.41	13.58	15.80	12.64	12.07	21.71	20.70	12.38
12	14.23		13.46	15.30	16.95		23.23	16.55
13	15.04	13.55	16.17	16.66	20.75	18.21	24.38	22.58

^a Number of C atoms.

surface exposed to the interaction with the solute molecules due to the porosity of the layer and to the additive effect of a support not completely inert.

The regular behaviour of the plots of ΔH and ΔS as a function of temperature confirms that the hypothesis of the linear dependence is a suitable approximation and therefore that the thermodynamic functions may be calculated, by using isothermal data, with the methods previously tested for the prediction of retention times [10,11] and correlated with the polarity and interaction mechanism of the column. However, the experimental fluctuations observed ($\pm 4\%$ for B' and ΔH and $\pm 6\%$ for ΔS values) explains why equations using values of t_R measured at only three temperatures [5,6] yield less accurate values of the thermodynamic functions. While calculation methods increase their confidence as the number of available starting data increases, whereas methods using three isothermal data only accurately predict retention times in programmed temperature runs, they are less convenient for the determination of ΔH and ΔS values that should be calculated by using retention data obtained in several isothermal runs at small temperature intervals. When the interval between isothermal runs, i.e., the difference between the k' values of Eq. (10) and Eq. (11), is small, the values of ΔH and ΔS obtained with the simplified equation of the step method suggested better approximate those that could be obtained with more complex methods. The ΔT interval used in this research (10°C) yields values precise enough to compare the behaviour of the various columns tested.

The similar behaviour of the ΔH plots for purely gas-liquid bonded phase and gas-liquid-solid carbon layer columns with the same polar liquid (polyglycol) shows that the approach used for the calculation is valid for both types and that with increasing temperature no abrupt change of the mechanism takes place. The effect of the carbon layer shifts the ΔH plots towards higher values. This effect seems to be correlated with the thickness of the layer and with the amount of liquid phase added to the graphitized carbon.

The values of the thermodynamic functions ΔH and ΔS obtained with the described method fairly agree with the available literature data on both packed and capillary columns [2,19,23]. Their dependence on the type and molecular mass of the

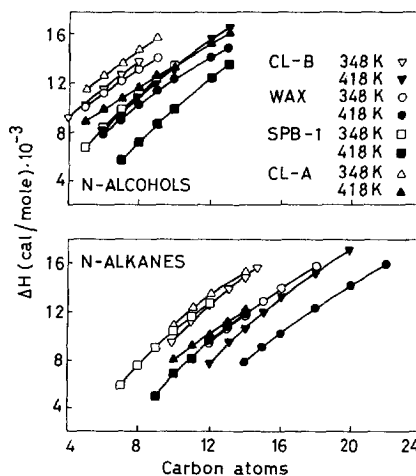


Fig. 4. Dependence of ΔH values on the number of carbon atoms. The values at two temperatures (348 K and 418 K) are shown.

analyte is shown in Table 5 and Table 6 where their values are reported at two temperatures as a function of the number of carbon atoms of the solute. The increasing temperature shifts the plots corresponding to the various columns towards decreasing values of ΔH and ΔS with a slope which differs between gas-liquid and gas-liquid-solid columns, as shown in Fig. 4 and Fig. 5.

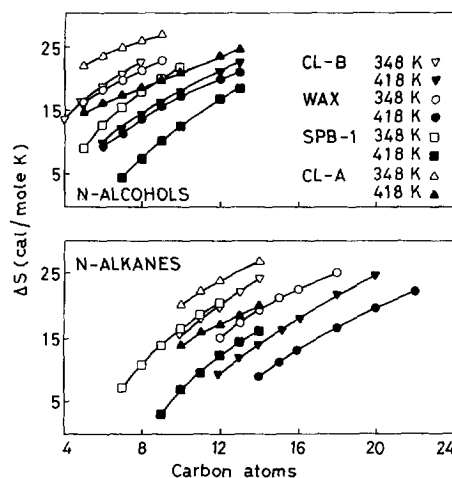


Fig. 5. Dependence of ΔS values on the number of carbon atoms. The values at two temperatures (348 K and 418 K) are shown.

4. Conclusions

The determination of thermodynamic values with the equations and methods previously used for the prediction of retention times in programmed temperature gas chromatography gives accurate results if several isothermal analyses are used as the source of data.

The method allows the ΔH and ΔS values to be calculated when simplified equations are applied to retention data obtained in isothermal runs, and their accuracy increases with increasing numbers of temperature tested. A ΔT interval of 10–15°C was found suitable to show the different behaviour of various types of capillary columns. The change in the intercept and in the slope of the ΔH and ΔS plots as a function of temperature is correlated with the concentration of liquid phase in the porous layer and with its absolute amount (i.e., with the thickness of the layer). These effects seem to act synergistically and have different importance depending on the polarity of the compound analysed and of the liquid phase. Further experiments with different liquid/solid ratios and various layer thicknesses would clarify this phenomenon and permit explanation of the general behaviour of mixed-mechanism columns and confirmation of the usefulness of thermodynamic characteristics in order to predict the behaviour of both gas–liquid and gas–liquid–solid columns.

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