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Influence of temperature and *n*-alkane pair on the methylene increments to the thermodynamic functions of solution on SE-30 and Carbowax-20M capillary columns

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Abstract

The contributions of the methylene group to the standard free energy, enthalpy and entropy of solution were measured on SE-30 and Carbowax-20M capillary columns. The slight decrease of the absolute value of the free energy increment with the carbon number of the homologues has been confirmed for different temperatures and columns. The absolute values of all increments decrease with temperature, and for Carbowax-20M depend on the film thickness. There is a linear enthalpy–entropy correlation in a series of data measured at different mean temperatures of the range. A short review is included. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The methylene increments of the thermodynamic functions of solution, $\Delta G_{\text{CH}_2}^{\text{S}}$, $\Delta H_{\text{CH}_2}^{\text{S}}$, $\Delta S_{\text{CH}_2}^{\text{S}}$ or the parameters of the linear plot of logarithm of *n*-alkane retention data versus carbon number are important quantities in the practice and theory of gas chromatography (GC). They are the basis of important concepts and methods as: the Kováts retention index system, its connection with other retention and thermodynamic values and molecular structure [1–6], evaluation of the hold-up time and measuring of the retention index with computer systems [1,2,7,8], pre-calculation of temperature-programmed retention data from isothermal ones [9–11] and polarity of the

stationary phase [1,2,4,5,12–15]. Such information for the *n*-alkanes must be associated with the collections of retention indices for complete data exploitation [1,2,9–11]. There are numerous papers on the subject of alkane behavior for dimethylsilicones, Carbowax-20M [1,2,4–6,10–25] and for other typical stationary phases [26–35]. However, the literature data show some scattering in the slope of the *n*-alkane plot or $\Delta G_{\text{CH}_2}^{\text{S}}$ values. They are rather scarce regarding the quantitative slope–temperature relationship, ΔH^{S} , ΔS^{S} or, $\Delta H_{\text{CH}_2}^{\text{S}}$, $\Delta S_{\text{CH}_2}^{\text{S}}$ values [1,2,6,10–12,17–25,30–35]. Moreover, the information concerning the dependence of the latter on the mean temperature within the range and alkane pair is generally insufficient [9–11,22,32–35]. For dimethylsilicones and Carbowax-20M it is practically absent, except for Refs. [10,11,22]. The effect of the

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film thickness or gas–liquid adsorption was studied for *n*-alkanes, as an example, on capillary columns of OV-101 [36] or Carbowax-20M [37,38]. However, the results were not presented in terms of methylene increments of the thermodynamic functions of solution, except in a few cases [14,15]. The effect of gas–liquid adsorption is small for non-polar stationary phases, but it is important for Carbowax-20M and other polar phases, creating column dependence. The present study is based on the retention data for the *n*-alkanes obtained during the measurement of the retention indices of a rather large set of perfumery solutes on SE-30, medium film and thin film Carbowax-20M glass capillary columns [39,40]. It appeared from the need revealed by a trial of generalization of data and development of the theory of the temperature dependence of the retention index [41].

2. Theory and literature information

The linearity of the logarithmic plot of retention values (based on the adjusted retention time, under isothermal conditions) versus carbon number *z* for the members of a homologous series is known from the advent of GC, due to James and Martin [42]. Non-linearity for the inferior homologues is however obvious. For *n*-alkanes, using the retention factor *k* preferred with capillary columns, the relationship is [1–6]:

$$\log k = a' + bz \quad (1)$$

where *a'*, besides the constants included in the intercept of the specific retention volume plot, *a*, also contains the corresponding transformation terms. The parameters *a* and *b* are “phase constants”, roughly depending on stationary phase and temperature. In fact, they also depend on the presence of mixed retention mechanisms, the range of homologues and for the intercept, on the choice of the standard states [4,5,14,15,24,32]. Eq. (1) is based on the additivity of the molar standard free energy of the sorption process, respectively on constancy of the methylene increment, $\Delta G_{\text{CH}_2}^{\text{S}}$ correlated with the slope [1–6]:

$$\Delta G_{\text{CH}_2}^{\text{S}} = -2.303RTb \quad (2)$$

Eq. (2) better corresponds with the alternative definition of the slope based on relative retention of two consecutive homologues with (*z*+1) and *z* carbon atoms, because in this way the explicit part of the methyl group influence is avoided:

$$b = \log r_{z+1, z} = \log t'_{\text{R}, z+1} - \log t'_{\text{R}, z} \quad (3)$$

The numerical value of $\Delta G_{\text{CH}_2}^{\text{S}}$ is the same with different combinations of solute standard states used in gas–liquid partition chromatography, defined with the reference states ideal gas and infinitely diluted solution at the column temperature, but with different concentration units [30,34]. These are usually: (i) unit molar concentrations in gas and solution, or (ii) partial pressure of 1 atm in gas, and unit molar fraction in solution (1 atm = 101 325 Pa). Indeed, the transformation term (independent on solute) between the alternative ΔG^{S} values of the homologues is reduced in the difference involved in the definition of $\Delta G_{\text{CH}_2}^{\text{S}}$.

However, even apparently linear, Eq. (1) is a formal expression of the phenomenon, because in fact there is a non-linearity of the free energy relationship due to the variation of *b* or $\Delta G_{\text{CH}_2}^{\text{S}}$ with the pair of adjacent *n*-alkanes with *z* and (*z*+1) carbon atoms. This can better be seen from the individual *b* or $\Delta G_{\text{CH}_2}^{\text{S}}$ numerical values obtained with Eqs. (2) and (3) [7,26–29], and in other ways [7,26,43]. The general relation for logarithm of retention versus carbon number including the first members of the series is non-linear [1,2,26–29], namely hyperbolic, described with an “universal equation” [27–29]. The absolute value of the negative increment $\Delta G_{\text{CH}_2}^{\text{S}}$ decreases also hyperbolic with the increase of carbon number in the *n*-alkane pair, as shown by Golovnya and Grigoryeva [27–29]. This decrease is marked until octane–nonane, and much slower after. A perfect stabilization is not achieved on different packed and capillary columns, even for the superior *n*-alkanes [7,26–29]. The causes of non-linearity are: (i) intrinsic, connected with the differences among the methyl and methylene groups in the interaction with the stationary phase [2,23,26,29,31,43–46] or with the features described by the statistical models of solution [47] and (ii) artificial, due to the errors in the determination of the hold-up time [7,26]. Rohrschneider [26]

pointed out the same pattern of the variation of the slope b and of the relative vapor pressure for successive n -alkane pairs. The methyl contribution at the thermodynamic functions of solution is greater than of the methylene [23,31]. Golovnya and Grigoryeva [29] observed a high Van der Waals interaction of the solutes with two adjacent methyl groups, diminished by the introduction of methylene groups between them. The marked non-linearity until heptane can be due to the non-equality of the molecular environment in n -alkanes, reflected in the different codification of the bonds in the Takács' retention model [2]. Sugiyama et al. [44] found from a quasi-lattice theory and GC measurements, an about double interaction energy of the contact pair $\text{CH}_3\text{-CH}_3$ compared with the nearly equal $\text{CH}_3\text{-CH}_2$ and $\text{CH}_2\text{-CH}_2$. Korol [45] calculated theoretically a relative value of dispersion interaction energy, finding also a double value for the methyl group and equality between methylene group and oxygen moiety in ethers. The enhanced interaction of the branched alkanes with squalane was explained by a correspondence of the rotation frequencies of the methyl groups in solute and solvent [46]. Gonzales et al. [47] demonstrated the slight non-linearity in the n -alkanes' behavior, using a statistical approach based on the theory of Flory for chain molecules. From another point of view, Vigdergauz and Petrova [43] claim the existence of a fine odd-even alternation effect in b or $\Delta G_{\text{CH}_2}^{\text{S}}$ values obtained with distinct pairs of homologous. This is also due to the difference between the terminal and methylene groups, in some probability of configuration like in *cis/trans* isomers. So, especially in polar series, an increased interaction of the even homologue with the stationary phase can arise.

The increment $\Delta G_{\text{CH}_2}^{\text{S}}$ (or the slope b) is one of the measures of the polarity of the stationary phase as pointed out by Kováts and Weiss [12] and other authors [4,5,13–15]. It describes at the same time the dispersion interaction of methylene group with stationary phase and the cavity effect, due to the energy used to break up the cohesion between the solvent molecules. So, $-\Delta G_{\text{CH}_2}^{\text{S}}$ decreases with the increasing of column polarity. Rohrschneider [48] demonstrated the close correlation and interchangeability between the parameters b and a of Eq.

(1) and, respectively, the phase constants l and c in the Abraham polarity model [49].

The dependence of the slope b on the column temperature was reported in [1,2] for several stationary phases including SE-30 ($D=216.65$, $E=-0.302$), OV-1 ($D=215.97$, $E=-0.2898$) and Carbowax-20M ($D=192.70$, $E=-0.287$) as:

$$b = D/T + E \quad (4)$$

Having in view Eqs. (2–4) and general relationship:

$$\Delta G_{\text{CH}_2}^{\text{S}} = \Delta H_{\text{CH}_2}^{\text{S}} - T\Delta S_{\text{CH}_2}^{\text{S}} \quad (5)$$

this corresponds to:

$$D = \Delta H_{\text{CH}_2}^{\text{S}}/2.303R, E = \Delta S_{\text{CH}_2}^{\text{S}}/2.303R \quad (6)$$

A linear relation of b with column temperature t ($^{\circ}\text{C}$) was noted for the two stationary phases of interest here, OV-101 ($b = -0.00126t + 0.4153$) and Superox-20M ($b = -0.0013t + 0.3829$). According to Refs. [27–29], the hyperbolic pattern of the plot $\Delta G_{\text{CH}_2}^{\text{S}}$ versus carbon number of the pair is the same at several temperatures on different stationary phases, and the temperature dependence of $\Delta G_{\text{CH}_2}^{\text{S}}$ is smaller on Carbowax than on non-polar phases.

The generally accepted in practice linear relation of $\log Vg$ on $1/T$, implying the constancy of enthalpy and entropy of solution, is in fact an approximate of the general non-linear case. The coefficients of the non-linear relations include ΔH^{S} , ΔS^{S} but also ΔC_p^{S} , the standard molar heat capacity change at constant pressure during the solution process [34,35]. Défayes et al. [32] used a relation for ΔG^{S} including also ΔC_p^{S} . These expressions are based on the following thermodynamic relations [50], where the asterisk marks a reference temperature:

$$\Delta H_{\text{T}}^{\text{S}} = \Delta H^{\text{S}*} + \Delta C_p^{\text{S}}(T - T^*) \quad (7)$$

$$\Delta S_{\text{T}}^{\text{S}} = \Delta S^{\text{S}*} + \Delta C_p^{\text{S}} \ln(T/T^*) \quad (8)$$

Eq. (7) implies a linear dependence of ΔH^{S} on the mean temperature of the range, with the slope given by ΔC_p^{S} . Vezzani and co-workers [10,11] determined for consecutive small temperature ranges, the functions ΔH^{S} and ΔS^{S} for several solutes including n -alkanes, using the linear dependence of $\log k$

versus $1/T$, on capillary columns of dimethylsilicone and Supelcowax. An almost linear decrease of the absolute values ΔH^S and ΔS^S with the mean temperature of the range was observed. However, it is known that the enthalpy of vaporization of the pure compounds depends non-linearly on temperature, decreasing first slightly, linear on restricted ranges, and then with an accentuate drop until the critical point [33,51]. From the data given by Gallant [51], it results that the vaporization ΔC_p of the pure n -alkanes is higher at a given temperature for the more volatile compounds, because they are closer to the accentuated descending part. As the enthalpy of vaporization with the changed sign is the main part of the enthalpy of solution, the same trends are expected for this quantity. Guermouche and Vergnaud [33] calculated with good results, the activity coefficients and ΔH^S , ΔS^S , ΔG^S values for n -alkanes in squalane, using the enthalpy of vaporization of pure solutes and its non-linear temperature variation (Theisen law). They also found a decrease of the absolute values of ΔH^S and ΔS^S with the mean temperature of the range.

3. Experimental

The same experimental conditions as in the study of the temperature dependence of the retention index of perfumery solutes on SE-30 [39] and Carbowax-20M glass capillary columns [40] were used. Erba Science instruments Fractovap 4160 and Fractovap 2400 equipped with Minigrator or Vidar Autolab integrators were operated with flame ionisation detection with hydrogen as carrier gas, 50 cm/s linear gas velocity, detector and injector temperature 250°C, sampling with split ratio 1:20 of 0.05–0.1% solutions of appropriate mixtures of alkanes in hexane. The SE-30 column prepared by hexamethyl disilazane-(HMDS) silylation and static coating, 40 m×0.35 mm, d_f 0.35 μm , had about 105 000 theoretical plates (TPs). The Carbowax-20M columns prepared by barium carbonate procedure and dynamic coating, had the following characteristics: 51 m×0.43 mm, d_f 0.45 μm , 76 000 TPs and 46 m×0.3 mm, d_f 0.08 μm , 100 000 TPs. Details on preparation and characterization of columns after the Grob procedures, are given in Refs. [39,40]. Some

influence of the BaCO_3 substrate is possible, especially for the thin film column. The hold-up time was determined with methane for the Carbowax columns and from the n -alkane retention times with a program for Hewlett-Packard desk computer [8] for SE-30. The n -alkanes were pure reagents from Fluka (Buchs, Switzerland). The retention factors were determined as a mean of 5–40, mostly 30–40 measurements, with a mean precision of 1–1.5% on SE-30 and Carbowax medium film columns and of 2–2.5% on Carbowax thin film column. The relative retentions of the n -alkane pairs were measured with a precision of about 0.2, 0.5 and 1%, respectively on SE-30, Carbowax d_f 0.45 and 0.08 μm columns.

4. Results and discussion

The $\Delta G_{\text{CH}_2}^S$ increments were determined for each column, temperature and pair of homologues having $z+1$ and z carbon atoms, using Eqs. (2) and (3). If one of the homologues was not available, the pair $z+2$, z was considered, obtaining the $2b$ value. The standard deviation (J mol^{-1}) was for SE-30 between 0 and 50 (mean 12), for Carbowax $d_f=0.45$ μm , between 4 and 100 (mean 31), and for Carbowax $d_f=0.08$ μm , between 6 and 150 (mean 28). Generally, higher errors were for the extremes of the investigated temperature ranges. The results are summarized in Tables 1 and 2. The mean values and the corresponding standard deviations of $\Delta G_{\text{CH}_2}^S$ for all the investigated pairs at each temperature are given at the bottom of the columns in Tables 1 and 2. The $\Delta G_{\text{CH}_2}^S$ values obtained from the slope of the linear regression of $\log k$ versus the carbon number in the homologous series are also included. The corresponding $\log k-z$ equations are reported in Tables 3 and 4, respectively for SE-30 and Carbowax-20M columns. In Fig. 1, $-\Delta G_{\text{CH}_2}^S$ is represented function of column temperature for different alkane pairs, on the SE-30 and Carbowax $d_f=0.45$ μm columns. In Fig. 2, the same data are shown as graphics of $-\Delta G_{\text{CH}_2}^S$ versus the current number of the alkane pair at different temperatures, for a better visualization of the decrease from a pair to another and a possible observation of the odd/even alternation effect [43].

Table 1

The increments $-\Delta G_{\text{CH}_2}^{\text{S}}$ as a function of the temperature and pair of n -alkanes with z and $z+1$ carbon atoms, for the SE-30 column

$z+1, z$	$-\Delta G_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹)														
	80°C	90°C	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C	180°C	190°C	200°C	210°C	220°C
8, 7	2114		1964												
9, 8	2092	2029	1960	1914	1850	1810	1756	1710							
10, 9	2092	2029	1967	1905	1850	1791	1737	1691							
11, 10	2094	2017	1944	1874	1830	1769	1735	1700	1639						
12, 11	2085	2015	1946	1877	1835	1781	1737	1687	1625	1596	1553				
13, 12		2009	1954	1880	1837	1783	1737	1693	1641	1601	1555				
14, 13				1878	1826	1783	1731	1678	1634	1600	1543	1513			
15, 14					1841	1777	1731	1676	1625	1584	1528	1486	1452	1400	
16, 15						1754	1710	1654	1615	1574	1536	1487	1451	1405	
18, 16/2								1650	1604	1563	1519	1474	1428	1381	
19, 18								1647	1604	1548	1505	1458	1415	1369	1340
21, 19/2													1407	1364	1335
22, 21													1388	1355	1324
23, 22														1344	1306
24, 23														1341	1306
Mean	2095	2018	1956	1888	1837	1781	1734	1679	1623	1581	1534	1484	1424	1374	1322
s	11	9	9	17	10	16	13	22	15	20	18	20	25	23	18
From Eq. (1)		2018	1985	1884	1840	1776	1729	1669	1621	1585	1532	1484	1422	1375	1325
D.r. ^a	5.6	5.4	3.3	7.2	2.4	5.0	4.3	6.5	4.9	7.7	6.9	9.3	8.9	6.9	7.7

^a Decrease rate of $-\Delta G_{\text{CH}_2}^{\text{S}}$ with the current number of the pair obtained by linear regression, including the missing pairs.

The $-\Delta G_{\text{CH}_2}^{\text{S}}$ values are lower on Carbowax-20M because of the higher polarity of the stationary phase [12–15], as may be seen in Fig. 1 and Tables 1 and 2. The thin film Carbowax column has apparently a less polar character than the medium film column, that is a little higher absolute values of $\Delta G_{\text{CH}_2}^{\text{S}}$. This corresponds with the observations made by Poole et al. [14,15] for the pure gas–liquid partition value of $\Delta G_{\text{CH}_2}^{\text{S}}$ in Carbowax-20M comparatively with that affected by interfacial phenomena. The bunch of lines for the 0.08 μm film column in a representation as in Fig. 1 is closer to that of SE-30 compared with the 0.45 μm film column.

The $-\Delta G_{\text{CH}_2}^{\text{S}}$ increments on a given column decrease as expected [27–29] with the increase of pair carbon numbers, as shown in Figs. 1 and 2. This effect is more evident on Carbowax, as it is well illustrated in Fig. 1 and in the decrease rates at each temperature mentioned in the last rows of the Tables 1 and 2 for the corresponding capillary columns. The decrease rate, very small taking into consideration the level of experimental errors, but generally obvious, was evaluated from the linear regression of $-\Delta G_{\text{CH}_2}^{\text{S}}$ in function of the current number of pairs.

The correlation was fair for SE-30 (r^2 between 0.4 and 0.9) and better for Carbowax (r^2 among 0.7 and 0.99). The decreasing rate is about the same at different temperatures and ranges of investigated pairs. The general means (J mol⁻¹ per pair) for SE-30, Carbowax medium- and thin-film columns are respectively, 6.1 ± 2.0 , 9.0 ± 1.6 and 10.0 ± 2.0 . Besides the general molecular reasons of this behavior as discussed above, the gas–liquid adsorption of the n -alkanes on Carbowax-20M also plays a part. This effect increases for the thinner films and for higher homologues [37,38]. The groups available for the interaction with alkanes are practically for SE-30 only methyl, and for Carbowax-20M only methylene and etheric oxygen. From the point of view of the literature information on the dispersion energy it is to be expected that the effect of n -alkane pair should be greater for SE-30 than for Carbowax-20M. The larger cavity effect during the solution process and the gas–liquid adsorption on Carbowax, compensates and modifies this situation. Regarding the fine even/odd alternation effect, if it exists, it is obscured by the propagation of the errors made in the consecutive ratios $r_{z+1, z}$, and practically is not revealed by Fig.

Table 2

The increments $-\Delta G_{\text{CH}_2}^{\text{S}}$ as a function of the temperature and pair of n -alkanes with z and $z+1$ carbon atoms, for the Carbowax-20M columns with film thicknesses of 0.45 and 0.08 μm

d_f (μm)	$z+1, z$	$-\Delta G_{\text{CH}_2}^{\text{S}}$ (J mol^{-1})										
		120°C	130°C	140°C	150°C	160°C	170°C	180°C	190°C	200°C	220°C	
0.45	12, 11	1725	1679	1636	1600							
	13, 12	1713	1664	1615	1585	1539						
	14, 13	1706	1650	1615	1567	1540						
	15, 14	1696	1654	1606	1563	1520	1482	1440				
	16, 15	1677	1638	1585	1555	1508	1472	1433				
	18, 16/2		1613	1574	1530	1480	1451	1405	1366	1337		
	19, 18		1610	1570	1522	1485	1448	1411	1375	1338		
	21, 19/2			1553	1514	1472	1432	1400	1361	1319		
	22, 21				1497	1461	1422	1377	1351	1305		
	23, 22				1489	1442	1412	1374	1337	1301		
	24, 23					1439	1400	1359	1328	1282		
	Mean		1703	1644	1594	1542	1489	1440	1400	1353	1314	
	s		18	26	28	37	37	29	29	18	22	
From Eq. (n)		1694	1661	1589	1550	1486	1441	1401	1368	1321		
D.r. ^a		11.3	10.3	9.2	9.7	9.1	8.3	7.9	5.8	9.6		
0.08	13, 12	1760	1710	1645								
	14, 13	1748	1680	1641	1607							
	15, 14	1725	1667	1634	1600	1571						
	16, 15	1725	1673	1630	1587	1558	1514	1482				
	18, 16/2	1709	1651	1614	1562	1523	1495	1461				
	19, 18	1715	1661	1600	1547	1508	1462	1418			1338	
	21, 19/2				1543	1516	1472	1428			1349	1278
	22, 21				1503	1451	1420	1390			1315	1240
	23, 22				1492	1454	1422	1385			1315	1245
	24, 23					1526	1485	1442	1395		1296	1228
	Mean		1730	1674	1627	1552	1508	1461	1423		1323	1248
	s		20	20	17	41	44	36	37		21	21
	From Eq. (n)		1722	1666	1619	1552	1522	1477	1420		1303	1248
D.r. ^a		8.2	7.1	7.5	10.4	11.4	10.8	11.8		9.9	13.3	

^a As in Table 1.

Table 3

The equations $\log k$ versus carbon number z , for the n -alkanes at different temperatures, on the SE-30 column

T (°C)	z Range	n	a	b	r^2	T (°C)	z Range	n	a	b	r^2
90	7–12	6	-2.5101	0.2902	1.0000	160	10–19	9	-2.4808	0.1954	1.0000
100	7–13	7	-2.5502	0.2778	0.9999	170	11–19	8	-2.5132	0.1868	0.9999
110	8–14	7	-2.4695	0.2445	1.0000	180	11–19	8	-2.4953	0.1766	0.9999
120	7–15	9	-2.5017	0.2443	1.0000	190	13–19	6	-2.4832	0.1673	1.0000
130	8–16	9	-2.4777	0.2300	1.0000	200	14–22	7	-2.4461	0.1570	1.0000
140	8–16	9	-2.4979	0.2185	1.0000	210	14–24	9	-2.4331	0.1486	1.0000
150	8–19	11	-2.4799	0.2059	0.9999	220	18–24	6	-2.4153	0.1403	0.9999

Table 4

The equations $\log k$ versus carbon number z , for the n -alkanes at different temperatures, on Carbowax-20M columns with film thicknesses of 0.45 and 0.08 μm

T ($^{\circ}\text{C}$)	$d_f=0.45 \mu\text{m}$					$d_f=0.08 \mu\text{m}$				
	z Range	n	a	b	r^2	z Range	n	a	b	r^2
120	11–16	6	-3.0477	0.2250	1.0000	11–19	8	-3.5702	0.2287	1.0000
130	11–19	8	-3.0434	0.2151	0.9998	12–19	7	-3.5556	0.2158	1.0000
140	11–21	9	-2.9543	0.2009	0.9999	12–19	7	-3.5107	0.2046	1.0000
150	11–23	11	-2.9565	0.1913	0.9999	11–23	12	-3.4380	0.1914	1.0000
160	12–24	11	-2.8964	0.1792	0.9999	14–24	9	-3.4726	0.1835	0.9997
170	14–24	9	-2.8735	0.1698	0.9999	15–24	8	-3.4703	0.1741	0.9998
180	14–24	9	-2.8719	0.1615	0.9999	15–24	8	-3.4361	0.1636	0.9998
190	16–24	7	-2.8757	0.1542	1.0000	18–24	6	-3.3658	0.1470	1.0000
200	16–24	7	-2.8214	0.1458	0.9999	19–24	5	-3.3821	0.1346	0.9999
220										

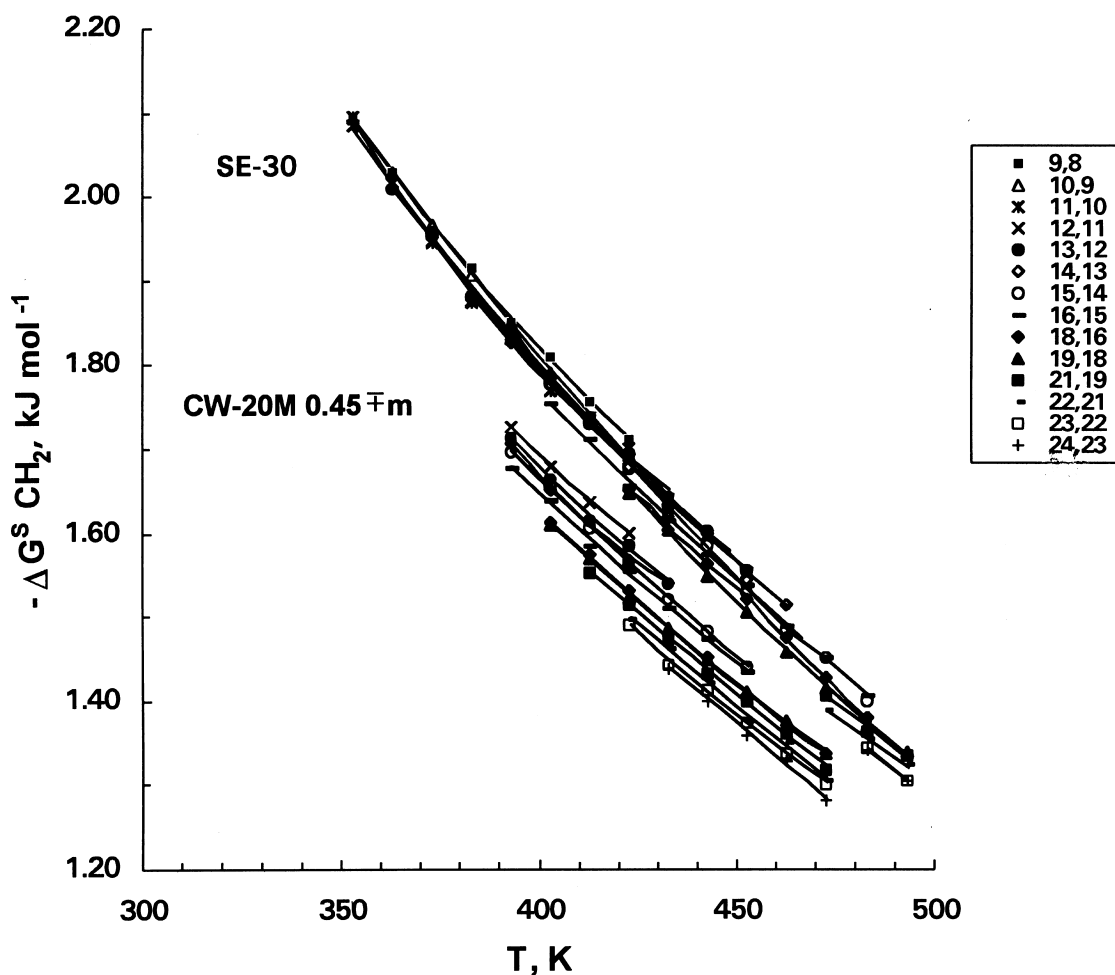


Fig. 1. The increment $\Delta G_{\text{CH}_2}^{\text{S}}$ on the SE-30 and the medium film Carbowax (CW)-20M glass capillary columns as a function of temperature for different n -alkane pairs.

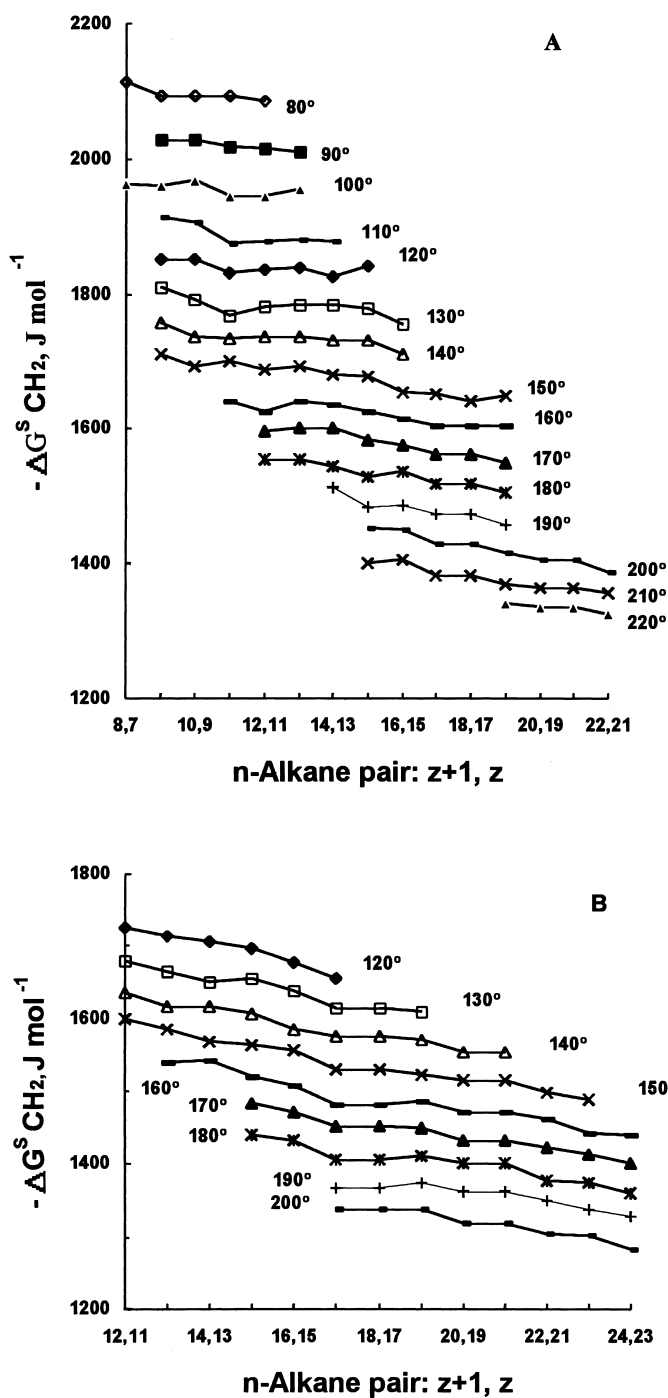


Fig. 2. The increment $\Delta G^S_{CH_2}$ for different column temperatures as a function of the *n*-alkane pair on the columns: (A) SE-30 and (B) Carbowax-20M, d_f 0.45 μm .

2. The monotone decrease of the absolute value $\Delta G_{\text{CH}_2}^{\text{S}}$ of with successive pairs, which produces a continuous slight diminution of the slope b , results in an apparent good linearity of the $\log k$ versus carbon number plot (Tables 3 and 4). In most cases, the $\Delta G_{\text{CH}_2}^{\text{S}}$ obtained from the slope of the line is satisfactory in practice. However, for the calculation of the thermodynamic functions based on the retention index, especially connected with the pre-calculation of temperature-programmed data [9–11,22] it is better to consider n -alkane pair effect. In our study on the temperature dependence of the retention index [41], the differences in thermodynamic functions between investigated solutes and the reference alkanes were calculated using the $\Delta G_{\text{CH}_2}^{\text{S}}$ values for each temperature and the specific alkane pair from Tables 1 and 2.

The numerical values for b or $-\Delta G_{\text{CH}_2}^{\text{S}}$ from literature for dimethylsilicones and Carbowax-20M columns are compared rather well with our data. For dimethylsilicones, the $\Delta G_{\text{CH}_2}^{\text{S}}$ values obtained with Eq. (4) for SE-30 [1], but not with that for OV-1 [2],

correspond to our data, in the limits of ± 0.3 –2%. The values for OV-101 according to the b versus t ($^{\circ}\text{C}$) equation given in [19] are reasonably compared with ours only until 120°C . The data from [4–6,13–18,21,25] are also compatible, especially [16,18] where capillary columns were used. As expected, in the case of Carbowax-20M, the differences are higher, until 500 J mol^{-1} . The concordance of our data on the medium film column with those from [16,19] is in the limits of 0.4–2% in the 120 – 160°C range and 3–15% in the 160 – 200°C range. The deviations are much higher for the data obtained with packed columns [1,21].

The enthalpy and entropy increments $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ at different temperatures were calculated as the intercept and slope of the linear regression according to Eq. (5), of $\Delta G_{\text{CH}_2}^{\text{S}}$ against T , on 20- and 30°C -wide ranges. The data from Tables 1 and 2 were used for each alkane pair. Indeed, the differences between the pairs of homologues at each temperature are about of the same order of magnitude with the general level of the experimental

Table 5

The average values for the studied n -alkane pairs^a of increments $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ on the SE-30 glass capillary column at different temperatures^b, and the standard deviations^c

T ($^{\circ}\text{C}$)	z Range	n	$-\Delta H_{\text{CH}_2}^{\text{S}}$ (kJ mol^{-1})	s (kJ mol^{-1})	$-\Delta S_{\text{CH}_2}^{\text{S}}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	s ($\text{J mol}^{-1} \text{K}^{-1}$)	T ($^{\circ}\text{C}$)	z Range	n	$-\Delta H_{\text{CH}_2}^{\text{S}}$ (kJ mol^{-1})	s (kJ mol^{-1})	$-\Delta S_{\text{CH}_2}^{\text{S}}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	s ($\text{J mol}^{-1} \text{K}^{-1}$)
90	7–12	5	4.51	0.16	6.84	0.46	155	11–16	5	3.64	0.11	4.64	0.24
95	8–12	4	4.43	0.21	6.63	0.60	160	11–19	8	3.54	0.16	4.42	0.37
100	7–13	6	4.39	0.18	6.51	0.50	165	11–19	8	3.56	0.13	4.46	0.30
105	8–13	5	4.21	0.06	6.03	0.19	170	11–19	8	3.53 ^c	0.16	4.41 ^c	0.38
110	8–13	5	4.07	0.07	5.69	0.17	175	12–19	7	3.56	0.11	4.48	0.27
115	8–13	5	4.01	0.10	5.51	0.27	180	13–19	5	3.58	0.12	4.54	0.27
120	8–14	6	3.84	0.15	5.09	0.37	185	14–19	4	3.51	0.05	4.38	0.13
125	8–14	6	3.80	0.15	4.99	0.35	190	14–19	4	3.45	0.15	4.26	0.34
130	8–15	7	3.82	0.16	5.04	0.39	195	14–19	4	3.51	0.08	4.39	0.20
135	8–15	7	3.77	0.16	4.91	0.39	200	14–19	4	3.49	0.11	4.36	0.26
140	8–16	8	3.75	0.11	4.88 ^c	0.25	205	18–19	1	3.31	–	4.00	–
145	10–16	6	3.72	0.15	4.82	0.35	210	18–19	1	3.19	–	3.75	–
150	11–16	5	3.75	0.10	4.90 ^c	0.24	215	22–24	2	3.10	0.11	3.64	0.23
s_{mean}	($N=24$)										0.13		0.31
σ	($N=128$)										0.11		0.26

^a Averages of the values for the number n of homologues pairs, in the indicated range of the carbon number, z ; temperatures are the means of the 20 or 30°C -wide ranges.

^b The individual values for each pair were calculated by linear regression with Eq. (5) at the mean temperature of the range of 90, 100, ... 210°C from three points $\Delta G_{\text{CH}_2}^{\text{S}}$ versus T for 20°C -wide temperature ranges, and at 95, 105, ... 215°C with four points, for 30°C -wide temperature ranges.

^c s = The standard deviations associated with the reported increments, s_{mean} = their mean for all the N temperatures; σ = the mean of the standard deviations of the regression parameters for all the N temperatures and alkane pairs.

Table 6

The average values of increments $-\Delta H_{\text{CH}_2}^{\text{S}}$ and $-\Delta S_{\text{CH}_2}^{\text{S}}$ on the Carbowax-20M glass capillary columns $d_f=0.45$ and $0.08 \mu\text{m}$, at different temperatures, for the studied n -alkane pairs^a

T (°C)	$d_f=0.45 \mu\text{m}$					$d_f=0.08 \mu\text{m}$						
	z Range	n	$-\Delta H_{\text{CH}_2}^{\text{S}}$ (kJ mol ⁻¹)	s (kJ mol ⁻¹)	$-\Delta S_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹ K ⁻¹)	s (J mol ⁻¹ K ⁻¹)	z Range	n	$-\Delta H_{\text{CH}_2}^{\text{S}}$ (kJ mol ⁻¹)	s (kJ mol ⁻¹)	$-\Delta S_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹ K ⁻¹)	s (J mol ⁻¹ K ⁻¹)
130	11–16	5	3.51	0.07	4.60	0.18	12–19	6	3.75	0.22	5.09	0.50
135	11–16	5	3.41	0.06	4.34	0.16	13–19	5	3.58	0.22	4.74	0.57
140	11–19	7	3.33	0.08	4.19	0.22	13–19	5	3.40	0.36	4.29	0.91
145	12–19	6	3.33	0.10	4.19	0.25	14–19	4	3.33	0.32	4.15	0.80
150	12–21	7	3.28	0.13	4.10	0.34	15–19	3	3.37	0.22	4.25	0.56
155	14–21	5	3.25	0.06	4.06	0.13	15–19	3	3.30	0.15	4.09	0.40
160	14–23	7	3.19	0.09	3.94	0.17	15–24	7	3.15	0.16	3.81	0.38
165	14–23	7	3.18	0.09	3.91	0.15	15–24	7	3.15	0.17	3.81	0.41
170	14–24	8	3.12	0.12	3.80	0.26	15–24	7	3.16	0.29	3.86	0.65
175	16–24	6	3.06	0.06	3.69	0.12	18–24	5	3.21	0.21	3.99	0.44
180	16–24	6	3.08	0.13	3.72	0.27	18–24	5	3.22	0.26	4.01	0.56
185	16–24	6	3.08	0.05	3.72	0.11	18–24	5	3.23	0.25	4.03	0.55
190	16–24	6	3.06	0.10	3.70	0.22	18–24	5	3.23	0.25	4.03	0.55
195							19–24	4	3.14	0.17	3.84	0.35
200							19–24	4	3.12	0.13	3.87	0.30
210							19–24	4	3.00	0.08	3.55	0.15
s_{mean}	($N=13$)			0.09		0.20		($N=16$)	0.22			0.51
σ	($N=81$)			0.09		0.22		($N=70$)	0.12			0.26

^a Explanations as in Table 5.

errors (as results from s , s_{mean} and σ , defined as follows). Consequently, the average values of $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ for the several indicated pairs are reported together with the corresponding standard deviations s , as may be seen in Table 5 for SE-30 and Table 6 for the two Carbowax columns. The mean of the s values for all temperatures, s_{mean} , and the average of the standard deviations associated with the regression parameters for all the individual regressions, σ , are reported also in the last rows of

Tables 5 and 6. The only case with a significant difference between pairs seems to be the Carbowax-20M $d_f=0.08 \mu\text{m}$ column, where the s or s_{mean} values are about double when compared with σ .

Table 7 summarizes the information regarding the global concept based on the Eqs. (1), (4) and (6), obtained with the slope values from the Tables 3 and 4. The general means of the $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ values at different temperatures from Tables 5 and 6 were included for comparison. Higher apparent

Table 7

The parameters of the equation $b=(D/T)+E$, obtained with data from Tables 3 and 4, and the corresponding $-\Delta H_{\text{CH}_2}^{\text{S}}$ and $-\Delta S_{\text{CH}_2}^{\text{S}}$ values, comparatively with the general means of the values reported in Tables 5 and 6^a

Column	Range (°C)	Eq. (4)				$-\Delta H_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹)		$-\Delta S_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹ K ⁻¹)	
		D	E	n	r	Eq. (6)	Mean ^a	Eq. (6)	Mean ^a
SE-30	90–220	201.248	-0.2685	14	0.9961	3.85	3.73	5.14	4.91
Carbowax-20M d_f 0.45 μm	120–200	186.554	-0.2499	9	0.9989	3.57	3.22	4.78	4.00
Carbowax-20M d_f 0.08 μm	120–220	183.795	-0.2407	9	0.9988	3.52	3.27	4.61	4.09

^a Means of the 24, 13 and 16 values for different temperatures, respectively for SE-30 and the two columns of Carbowax.

values of $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ are obtained with the global concept. These are of the same order of magnitude and sign with the global and rather spread out values reported in literature for dimethylsilicones [1,2,17–25], namely $-\Delta H_{\text{CH}_2}^{\text{S}}$ between 4.5 and 3.4 kJ mol^{-1} and $-\Delta S_{\text{CH}_2}^{\text{S}}$ between 5.8 and 4.1 $\text{J mol}^{-1} \text{K}^{-1}$. For Carbowax-20M the literature data [1,2,21,23,24] indicate $-\Delta H_{\text{CH}_2}^{\text{S}}$ between 3.7 and 3.0 kJ mol^{-1} and $-\Delta S_{\text{CH}_2}^{\text{S}}$ between 5.5 and 3.3 $\text{J mol}^{-1} \text{K}^{-1}$.

The variation of $-\Delta H_{\text{CH}_2}^{\text{S}}$ values from Tables 5 and 6 with column temperature is represented comparatively for the three columns in Fig. 3. The $-\Delta S_{\text{CH}_2}^{\text{S}}$ versus T plot is practically of the same pattern, in spite of the basic difference described by

Eqs. (7) and (8). A decrease of the absolute values of $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ increments with column temperature, and a non-linearity of the dependencies are observed, for the both quantities. The experimental points were fitted with fourth-order polynomial equations for the SE-30 and the Carbowax thin film columns where a larger temperature interval was used, and with second-order polynomial equations for the Carbowax medium film column.

An ΔH – ΔS compensation effect, partially combined with the propagation of the errors between the slope and intercept of Eq. (5) is observed. The equations relating the two series of data for different mean temperatures are the following. For the SE-30 column and temperatures 90–215°C:

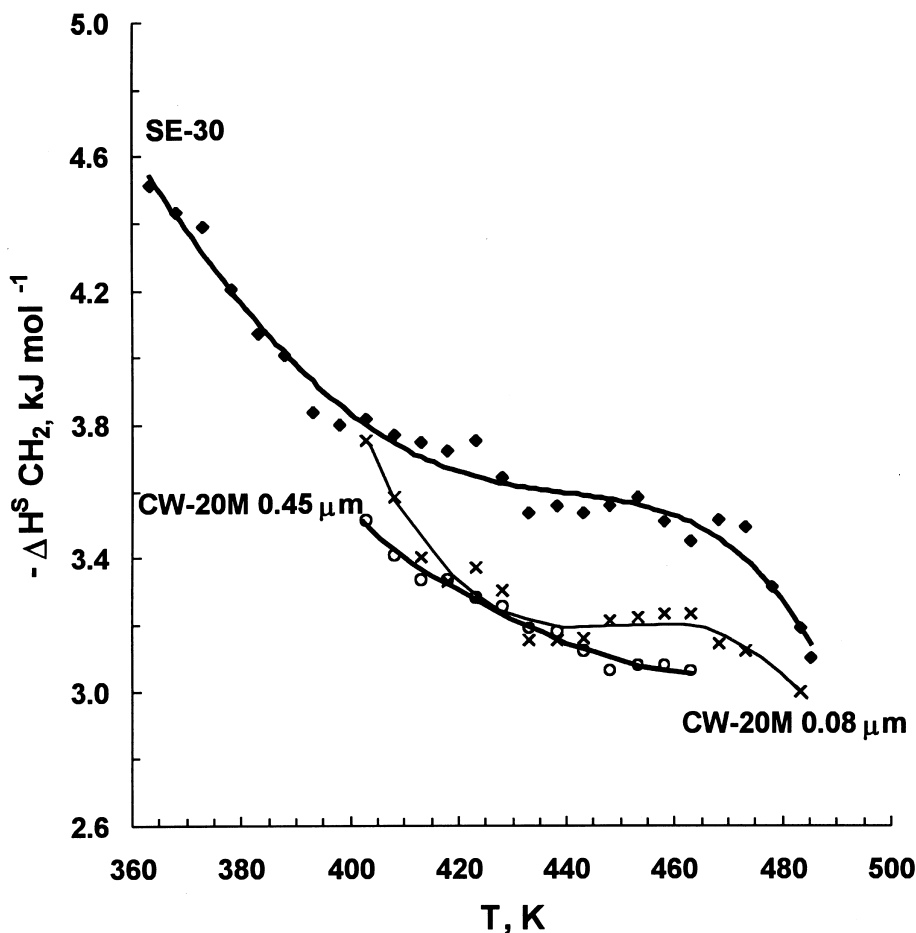


Fig. 3. The average increment $\Delta H_{\text{CH}_2}^{\text{S}}$ for several n -alkane pairs as a function of the mean temperature of the range, for the glass capillary columns of SE-30 and of Carbowax-20M having the film thicknesses 0.45 and 0.08 μm .

$$\Delta H_{\text{CH}_2}^{\text{S}} = 0.4304\Delta S_{\text{CH}_2}^{\text{S}} - 1.6196, r^2 = 0.9923;$$

$$n = 26$$

For Carbowax-20M d_f 0.45 μm column, 130–190°C:

$$\Delta H_{\text{CH}_2}^{\text{S}} = 0.5123\Delta S_{\text{CH}_2}^{\text{S}} - 1.1741, r^2 = 0.9982;$$

$$n = 13$$

and for Carbowax-20M d_f 0.08 μm column, 130–210°C:

$$\Delta H_{\text{CH}_2}^{\text{S}} = 0.4916\Delta S_{\text{CH}_2}^{\text{S}} - 1.2618, r^2 = 0.9939;$$

$$n = 16$$

The slope of the curve $\Delta H_{\text{CH}_2}^{\text{S}}$ against T must be ΔC_p^{S} in accordance with Eq. (7). A dependence of ΔC_p^{S} on the mean temperature of the range and implicitly on the n -alkane pairs used for obtaining the experimental points is observed. The greater slope in Fig. 3 for the range 90–130°C in the case of SE-30, and in some measure in the range 130–140°C for the two Carbowax-20M columns, is probably connected with the higher volatility of the n -alkane pairs involved in the means (see Tables 5 and 6). Indeed, the pairs with the carbon numbers 9, 8; 11, 10; 12, 11; 13, 12 on SE-30 had individual curves $-\Delta H_{\text{CH}_2}^{\text{S}}$ versus T , with a higher slope comparative-

ly with the other superior homologues. Their weight in the mean values on indicated temperature range is very high. The same is valid for the pairs 13, 12 and 14, 13 for Carbowax. In the ranges 130–200°C on SE-30, 140–190°C on Carbowax-20M 0.45 μm and 135–200°C on Carbowax-20M 0.08 μm , the pattern is linear and the decrease rate is lower. The inferior pairs named above have reduced weights in the means. The properties of other involved pairs is expected to be closer to each other with the increasing carbon number [51]. The final larger decrease at higher temperatures observed in the curves from Fig. 3 is possible to be produced by the non-linear behavior of the molar heat capacity change with temperature, but also by the higher experimental errors. In the case of the thin film Carbowax column, the high contribution of the gas–liquid adsorption superposed with other effects, explains probably the plateau in the range 160–190°C. The increased order in the condensed phase and the corresponding compensation effect produce from the same reason, more negative values for the both increments comparatively with the medium film column. The above aspects regarding the variation of $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ with the mean temperature of the range are the expected trends [10,11,33–35,51] as discussed in Section 2.

The data from Tables 5 and 6 were used for the calculation of the “phase constants” entering in the theoretical expressions for the relation between

Table 8

The approximate molar standard heat capacity changes during the solution process for the SE-30 and Carbowax-20M columns on the indicated temperature ranges, calculated as the slope of $\Delta H_{\text{CH}_2}^{\text{S}}$ versus T curves^a

Range (°C)	Implied alkanes	ΔC_p^{S} (J mol ⁻¹ K ⁻¹)		
		SE-30	Carbowax ($d_f=0.45 \mu\text{m}$)	Carbowax ($d_f=0.08 \mu\text{m}$)
90–125	7–12 to 8–14	21.9 ^b		
120–200	8–14 to 14–19	4.9 ^c		
130–140	12–19 to 13–19			35.0 ^d
140–210	13–19 to 19–24			4.1 ^e
130–190	11–16 to 16–24		7.2 ^f	
190–215	14–19 to 22–24	17.6 ^g		

^a r = Correlation coefficient, n = number of points.

^b r = 0.9907, n = 8.

^c r = 0.9449, n = 17.

^d r = 0.9999, n = 3.

^e r = 0.8134, n = 14.

^f r = 0.9676, n = 13.

^g r = 0.8890, n = 6.

different equations of the temperature dependence of the retention index and thermodynamic significance of their parameters [41].

The approximate (global for several pairs) molar heat capacity changes obtained as the slopes of the different linear sections of the dependence $\Delta H_{\text{CH}_2}^{\text{S}}$

against T for the three columns are summarized in Table 8. The data are of the same order of magnitude with the values calculated from the published information. Except for [32], the $\Delta C_{\text{p}}^{\text{S}}$ values were reported for a single n -alkane, for example octane [34], hexane [35], dodecane [10], but the methylene

Table 9
Example of $\Delta H_{\text{CH}_2}^{\text{S}}$ and $\Delta S_{\text{CH}_2}^{\text{S}}$ values, calculated on different temperature ranges, centered on the same mean temperature^a

Column	Pair	T (°C)	Range (°C)	ΔT	N	$-\Delta H_{\text{CH}_2}^{\text{S}}$ (kJ mol ⁻¹)	$\Delta S_{\text{CH}_2}^{\text{S}}$ (J mol ⁻¹ K ⁻¹)	r^2
SE-30	13, 12	130	120–140	20	3	3.80±0.59	5.00±1.48	0.998
			110–150	40	5	3.70±0.09	4.74±0.22	0.999
			100–160	60	7	3.82±0.13	5.05±0.32	0.995
			90–170	80	9	3.84±0.10	5.08±0.25	0.995
			Mean			3.79±0.10	4.97±0.25	
	135	135	120–150	30	4	3.71±0.20	4.78±0.48	0.998
			110–160	50	6	3.71±0.06	4.78±0.15	0.999
			100–170	70	8	3.78±0.11	4.93±0.27	0.995
			90–180	90	10	3.81±0.09	4.99±0.22	0.996
			Mean			3.75±0.08	4.87±0.18	
	140	140	130–150	20	3	3.60±0.15	4.50±0.37	1.000
			120–160	40	5	3.73±0.09	4.82±0.22	0.999
			110–170	60	7	3.69±0.05	4.71±0.06	0.999
			100–180	80	9	3.75±0.09	4.86±0.11	0.996
			Mean			3.69±0.11	4.72±0.16	
	145	145	130–160	30	4	3.68±0.14	4.70±0.35	0.999
			120–170	50	6	3.69±0.08	4.71±0.17	0.999
			110–180	70	8	3.67±0.04	4.67±0.10	0.999
			Mean			3.68±0.02	4.69±0.05	
			Carbowax-20M $d_f=0.45 \mu\text{m}$	19, 18	150	140–160	20	3
130–170	40	5				3.26±0.11	4.09±0.27	0.998
Mean						3.29±0.36	4.17±0.11	
155	155	140–170		30	4	3.23±0.24	4.03±0.19	0.996
		130–180		50	6	3.22±0.09	3.99±0.20	0.998
		Mean				3.23±0.09	4.01±0.27	
160	160	150–170		20	3	3.09±0.00	3.70±0.00	1.000
		140–180		40	5	3.19±0.13	3.92±0.08	0.975
		130–190		60	7	3.19±0.07	3.92±0.16	0.998
		Mean				3.16±0.12	3.85±0.32	
165	165	150–180		30	4	3.09±0.00	3.69±0.00	1.000
		140–190		50	6	3.15±0.04	3.84±0.09	0.998
		130–200		70	8	3.16±0.06	3.87±0.13	0.998
		Mean				3.13±0.10	3.80±0.25	

^a The data from Tables 1 and 2 were used; N =number of temperature points; r =correlation coefficient of the regression line Eq. (5); ΔT =the extension of the temperature range; the confidence limits of the regression coefficients were calculated from the corresponding standard deviations and the Student factors, $t(N-2, 95\%)$; the confidence limits of the mean were calculated as the products of the standard deviation with $t(N, 95\%)/N^{1/2}$.

contribution could be approximately evaluated dividing with the carbon number. So, the ΔC_p^S values for the methylene unit in $\text{J mol}^{-1} \text{K}^{-1}$ were of 7.3 in a branched paraffinic stationary phase of infinite molecular mass around 130°C [32], 6 in the $n\text{-C}_{36}$ alkane as stationary phase around 100°C [34], 7 in Squalane and triethylene glycol around 50°C [35], 16.7 on a SPB-1 capillary column of dimethylsilicone type and 14.4 on a Supelcowax capillary column around $120\text{--}130^\circ\text{C}$ [11].

Finally, a practical aspect must be considered, connected with the importance of the mean temperature of the range rather than the range itself, when the thermodynamic functions are compared. Table 9 gives examples of $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ values on SE-30 and Carbowax columns, calculated on progressively wider temperature ranges centered on the same mean temperature, using respectively a greater number of $\Delta G_{\text{CH}_2}^S - T$ points. The values are rather constant in the limits of experimental errors. The mean temperature of the range brings statistically perceptible modification of $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ values generally only when is shifted with over 20°C increments. However, the systematic trends shown in Figs. 2 and 3 are obvious.

5. Conclusions

The methylene increments of the free energy, enthalpy and entropy of solution were measured and compared on the same SE-30 and Carbowax-20M glass capillary columns used in the evaluation of temperature dependence of the retention index for comprehensive groups of perfumery solutes [39,40]. All are negative contributions and their absolute values decrease with the column temperature. The order of magnitude of ΔC_p^S was evaluated. The n -alkane pair effect was significant only in the case of $\Delta G_{\text{CH}_2}^S$, because for $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ it was generally covered by the experimental errors. With an almost constant cavity effect for each column, the general decreasing of $-\Delta G_{\text{CH}_2}^S$ with the carbon number of the homologue pair, means a decrease of the dispersion interaction methylene group-stationary phase. The effect of the interfacial phenomena for the thin film ($0.08 \mu\text{m}$) Carbowax-20M column is

obvious. An apparently less polar character, a higher entropy change and a modification of the pattern of the $\Delta H_{\text{CH}_2}^S$ and $\Delta S_{\text{CH}_2}^S$ versus T plots were observed, comparatively with the $0.45 \mu\text{m}$ column. An enthalpy-entropy compensation effect acts when temperature changes.

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