



Solvation molar enthalpies and heat capacities of *n*-alkanes and *n*-alkylbenzenes on stationary phases of wide-ranging polarity

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ARTICLE INFO

Article history:

Received 6 July 2010

Received in revised form 1 October 2010

Accepted 5 October 2010

Available online 30 October 2010

Keywords:

Gas chromatography

Retention factor

Molar enthalpy of solvation

Molar heat capacity of solvation

Hydrocarbon

Stationary phase

ABSTRACT

A comparison of the most usual gas chromatographic methods for the calculation of partial molar enthalpies of solvation ($\Delta_{\text{sol}}H^{\circ}$) has been carried out. Those methods based on the fitting of $\ln V_{\text{g}}$ or $\ln(k/T)$ vs. $1/T$ and $\ln(k/T)$ vs. $(1/T + T_{\text{a}})$ and the temperature arrangement, T_{a} are the most adequate ones for obtaining $\Delta_{\text{sol}}H^{\circ}$ values. However, the latter is the only reliable option for $\Delta_{\text{sol}}H^{\circ}$ estimation when commercial WCOT capillary columns are used, since in this case the estimation of some variables involved in the V_{g} determination is less accurate or even impossible. Consequently, in this paper, $\Delta_{\text{sol}}H^{\circ}$ obtained from $\ln(k/T)$ vs. $(1/T + T_{\text{a}})$ fitting at 373.15 and 298.15 K for *n*-alkanes and *n*-alkylbenzenes on 12 commercial capillary columns coated with stationary phases covering the 203–3608 McReynolds polarity range are reported. Moreover, molar heat capacities of solvation at constant pressure ($\Delta_{\text{sol}}C_{\text{p}}^{\circ}$) have also been calculated using this method. A clear influence on $\Delta_{\text{sol}}H^{\circ}$ of the type and content of the substitution group in the stationary phase was observed. In addition, a linear relationship of $\Delta_{\text{sol}}C_{\text{p}}^{\circ}$ with the van der Waals volume of the *n*-alkanes and the temperature gradient of density of the stationary phase was found. The effect of the size of the hydrocarbon on both thermodynamic variables was also investigated.

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1. Introduction

Gas chromatography (GC) is, besides a powerful tool for the analysis of complex mixtures, an alternative to the calorimetric and static methods for measuring physicochemical parameters of solutes [1]. The earliest physical measurements by GC date from 1955, when methods for obtaining boiling points, distribution constants, and enthalpies and entropies of solvation for a volatile solute dissolved in a non-volatile solvent were described [2]. While calorimetric [3,4] and static methods [5] are still employed, GC has become an easy way to study the thermodynamics of the interaction of a volatile solute with a non-volatile solvent. First, it is cheaper and easier to apply. No especial experimental skills are necessary either, small amount of material are required, and impure solute samples and mixtures can be handled. Second, it is very precise, so much so as retention magnitudes (retention time, t_{R} ; retention factor, k ; specific retention volume, V_{g} ; etc.). This implies careful pressure/flow regulation of the carrier gas and oven temperature control, conditions easily achieved nowadays. Third, it is possible to obtain values in a wide range of temperatures, since the chromatographic column is inside an oven. Finally, GC exper-

iments are rather quick, and much infinite-dilution information is obtained in one run.

The measurement of thermodynamic parameters by GC is possible because the gas chromatographic process is similar to a solvation process. Basically, it consists in a distribution of the analyte between the two phases, the mobile phase or carrier gas and the immobile or stationary phase (SP). This process can be approached in thermodynamic terms, for instance, $\Delta_{\text{sol}}G^{\circ}$, $\Delta_{\text{sol}}H^{\circ}$, $\Delta_{\text{sol}}S^{\circ}$, etc. where these symbols stand for partial molar solvation Gibbs energy, enthalpy and entropy increments when a mole of solute is transferred from the mobile to the stationary phase. The increment of the infinite dilution partial molar Gibbs solvation energy for the transference of a solute from the carrier gas to the stationary phase ($\Delta_{\text{sol}}G^{\circ}$) is given as:

$$\Delta_{\text{sol}}G^{\circ} = -RT \ln K \quad (1)$$

where R is the gas constant, T , the temperature of the chromatographic column, and K , the distribution constant of the solute between the mobile and the stationary phase.

It is known that the Gibbs–Helmholtz's equation relates partial molar Gibbs energies of solvation with partial molar enthalpies ($\Delta_{\text{sol}}H^{\circ}$) and entropies ($\Delta_{\text{sol}}S^{\circ}$) of solvation, according to Eq. (2). On the other hand, the solvation process involves the condensation and mixing of the pure solute with the solvent (stationary phase), so $\Delta_{\text{sol}}H^{\circ}$ can be divided into two parts (Eq. (3)), the enthalpy of

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vaporization ($\Delta_{\text{vap}}H^{\circ}$) and the excess enthalpy of mixing (H^{E}), i.e. the energy consumed or released when one mole of pure solute dissolves in an infinite quantity of stationary phase.

$$\Delta_{\text{sol}}G^{\circ} = \Delta_{\text{sol}}H^{\circ} - T\Delta_{\text{sol}}S^{\circ} \quad (2)$$

$$\Delta_{\text{sol}}H^{\circ} = -\Delta_{\text{vap}}H^{\circ} + H^{\text{E}} \quad (3)$$

This excess magnitude is a measure of the relative freedom or randomness of the solute molecule in the two phases [6], while the solvation enthalpy is a measure of the relative magnitudes of the molecular forces between solute and stationary phase. The excess enthalpy can be calculated calorimetrically or by GC measurements, in the last case, from experimental $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{vap}}H^{\circ}$ values or from the activity coefficient at infinite dilution (γ_1^{∞}) [2]. H^{E} values for a great variety of compounds, mainly *n*-alkanes, have been determined in polysiloxanes [7–9], poly(ethylene glycol) [7], ionic liquids [10–16], and other non-volatile substances [17–22].

In order to obtain experimentally all these thermodynamic quantities it is necessary to relate them to some absolute chromatographic magnitude, as V_{g} . Rearranging Eqs. (1) and (2) (Eq. (4)), and keeping in mind the relationship between V_{g} and K (Eq. (5)), the expression that allows to calculate $\Delta_{\text{sol}}H^{\circ}$ from the slope of the $\ln V_{\text{g}}$ vs. $1/T$ plot (Eq. (6)) is obtained:

$$\ln K = -\frac{\Delta_{\text{sol}}H^{\circ}}{RT} + \frac{\Delta_{\text{sol}}S^{\circ}}{R} \quad (4)$$

$$V_{\text{g}} = \frac{273.15RK}{M} \quad (5)$$

$$\ln V_{\text{g}} = -\frac{\Delta_{\text{sol}}H^{\circ}}{RT} + \frac{\Delta_{\text{sol}}S^{\circ}}{R} + C \quad (6)$$

where M is the molar mass of the stationary phase and C is a temperature-independent constant. This method has allowed to calculate $\Delta_{\text{sol}}H^{\circ}$ values of different families of solutes in polysiloxanes [7–9,23–25], poly(ethylene glycols) [7,23–25], squalane [26], other polymers [18,19,21,22] and non-volatile substances [17,27] in a limited range of temperatures, in which $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}S^{\circ}$ are considered to be independent from the temperature. Although WCOT capillary columns are very popular nowadays, most of these $\Delta_{\text{sol}}H^{\circ}$ values have been obtained using packed columns. The reason lies in the variables that must be measured to obtain V_{g} values (Eq. (7)), namely, the volumetric flow-rate of the dry carrier gas at the column outlet, at the column temperature and ambient pressure (F_{c}); the mass of stationary phase in the column (W_{S}); the James and Martin's correction factor (j); the experimental retention time of the solute (t_{R}); and the retention time of an unretained substance in the chromatographic system (t_{M} , hold-up time).

$$V_{\text{g}} = \frac{F_{\text{c}}}{W_{\text{S}}} j (t_{\text{R}} - t_{\text{M}}) \frac{273.15}{T} \quad (7)$$

The low F_{c} and W_{S} values on capillary columns introduce additional sources of error [28], which produce inaccurate results. In order to overcome this problem, and bearing in mind the relationship between K and k (Eq. (8)), some chromatographers have used the $\ln k$ vs. $1/T$ plot [29,30] or even the $\ln(1/t'_{\text{R}})$ vs. $1/T$ plot [31] to calculate $\Delta_{\text{sol}}H^{\circ}$:

$$K = \beta k = \beta \frac{t'_{\text{R}}}{t_{\text{M}}} = \beta \frac{t_{\text{R}} - t_{\text{M}}}{t_{\text{M}}} \quad (8)$$

where β is the phase ratio and t'_{R} is the adjusted retention time of the solute.

However, in these plots the dependence of β on temperature is not considered, introducing a bias in the results. Therefore, other authors [32,33] have used $\ln(k/T)$ instead of $\ln k$, by means of the following two equations:

$$\ln \left(\frac{k}{T} \right) = -\frac{\Delta_{\text{sol}}H^{\circ}}{RT} + \frac{\Delta_{\text{sol}}S^{\circ}}{R} + C' \quad (9)$$

$$\begin{aligned} \ln \left(\frac{k}{T} \right) &= -\frac{\Delta_{\text{sol}}H^{\circ}_{T_0}}{RT} + \frac{\Delta_{\text{sol}}C_{\text{p}}^{\circ}}{R} T_{\text{a}} + C'' \\ &= -\frac{\Delta_{\text{sol}}H^{\circ}_{T_0}}{RT} + \frac{\Delta_{\text{sol}}C_{\text{p}}^{\circ}}{R} \left(\frac{T_0}{T} + \ln T \right) + C'' \end{aligned} \quad (10)$$

where C' and C'' are constants, T_{a} is the temperature arrangement and T_0 is a single reference temperature.

Eq. (10) bears in mind the enthalpy and entropy dependence on temperature by introducing the change in molar heat capacity of a solute at a constant pressure ($\Delta_{\text{sol}}C_{\text{p}}^{\circ}$), and allows to estimate the solvation enthalpy outside the range of temperatures studied [31].

Taking into account the possibilities that GC offers to obtain enthalpies of solvation, and the discrepancies in their calculation methods, infinite dilution partial molar solvation enthalpies ($\Delta_{\text{sol}}H^{\circ}$) of some *n*-alkanes and *n*-alkylbenzenes on 12 polymers determined between 323.15 and 423.15 K are presented in this work. A comparison of the different expressions used to estimate $\Delta_{\text{sol}}H^{\circ}$ by GC was carried out. Its dependence on polarity and composition of the stationary phase, as well on the size of the hydrocarbon was studied. Other magnitude, the change in molar heat capacity of a solute at a constant pressure ($\Delta_{\text{sol}}C_{\text{p}}^{\circ}$), was also calculated.

2. Experimental

2.1. Apparatus

Gas chromatographs HP-5890A and HP-5890 Series II (Agilent, Palo Alto, CA, USA) with split/splitless injection systems, flame ionization detectors (FID), back-pressure regulators and WIKA Tronic 891.13.500 pressure transducers (Alexander Wiegand, Klingenberg, Germany) with numeric monitors PM-2900 (Félix Mateo, Barcelona, Spain) were used. Electronic integrators Spectra Physics SP4270 (Newport Corp., CA, USA) and the Clarity Lite chromatographic software for data acquisition and data processing for Windows 98 (Data Apex Ltd., Prague, Czech Republic) were used.

2.2. Chromatographic columns

Most of experiments were carried out on the commercial chromatographic columns shown in Table 1, ordered by increasing polarity. All columns are fused-silica WCOT type, with stationary phases (SP) that span practically all the polarity range of preferred stationary phases [34]. But for the ZB-WAX column, that have poly(ethylene glycol) as SP, the rest of columns belong to the poly(dimethyl siloxane) type with different functional groups. So, five of them are poly(phenylmethyl siloxanes) with 0–50% of phenyl group (TRB-1, TRB-5A, TRB-20, TRB-35 and TRB-50), covering the low to medium polarity zone. Other five columns have only 3-cyanopropyl groups at several substitution percentages (BPX70 and TR-CN100) or mixed with phenyl groups (TRB-1301, BP10 and TRB-225), that confer them medium to high polarity. Finally, the VB-210 column is a poly(3,3,3-trifluoropropylmethyl siloxane) of medium polarity. BP columns were from SGE (International Pty. Ltd., Victoria, Australia); VB-210, from ValcoBond Capillary Columns (VICI Gig Harbor, WA, USA); ZB-Wax, from Zebron GC columns (Phenomenex, CA, USA); and TRB and TR-CN columns were from Teknokroma (San Cugat del Vallés, Barcelona, Spain).

Experiments for the comparison of enthalpy estimation methods were carried out on two glass WCOT columns prepared in our laboratories from borosilicate glass tube by the static method [35,36]. The column TFPS00 was $30.1 \text{ m} \times 0.225 \text{ mm} \times 0.300 \text{ }\mu\text{m}$, and prepared with a solution of 5.20 mg cm^{-3} of poly(dimethyl siloxane). The other glass WCOT column (TFPS50), was $25.7 \text{ m} \times 0.216 \text{ mm} \times 0.300 \text{ }\mu\text{m}$, and prepared with a solution

Table 1
Characteristics of the 12 commercial chromatographic columns studied.

Column name	Stationary phase chemical composition	Supplier ^a	Dimensions ^b	Polarity	Methyl group (%) ^c
TRB-1	Poly(dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	203	100
TRB-5A	Poly(5% diphenyl 95% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.50 μm	324	95
TRB-20	Poly(20% diphenyl 80% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	571	80
TRB-1301	Poly(6% 3-cyanopropylphenyl 94% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	596	94
BP10	Poly(14% 3-cyanopropylphenyl 86% dimethyl siloxane)	SGE	60 m × 0.25 mm × 0.25 μm	772	86
TRB-35	Poly(35% diphenyl 65% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	875	65
TRB-50	Poly(50% diphenyl 50% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	1007	50
VB-210	Poly(3,3,3-trifluoropropylmethyl siloxane)	VICI Gig Harbor	60 m × 0.25 mm × 0.20 μm	1574	50
TRB-225	Poly(50% 3-cyanopropylphenyl 50% dimethyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.25 μm	1843	50
ZB-WAX	Poly(ethylene glycol)	Phenomenex	30 m × 0.25 mm × 0.50 μm	2403	0
BPX70	Poly(70% biscyanopropyl 30% dimethyl silphenylene-siloxane)	SGE	60 m × 0.25 mm × 0.25 μm	3037	30
TR-CN100	Poly(biscyanopropyl siloxane)	Teknokroma	30 m × 0.25 mm × 0.20 μm	3608	0

^a See Section 2.2 for more details.

^b Column length × internal diameter × film thickness.

^c Percentage of methyl groups in the siloxane chain. ZB-WAX was considered to have a 0% methyl content.

of 7.32 mg cm⁻³ of poly(3,3,3-trifluoropropylmethyl siloxane). Both polymers were previously synthesised in our laboratories [35].

2.3. Chromatograms

Methane (from natural gas), *n*-alkanes (from *n*-pentane to *n*-pentadecane) and *n*-alkylbenzenes (benzene, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene) were chromatographed isothermally from 323.15 to 423.15 K in increments of 10 K (±0.1 K) using nitrogen as carrier gas. In order to simplify the notation throughout the manuscript, temperatures are given hereafter without the decimal places. Moreover *n*-butanol, 2-pentanone, 1-nitropropane and pyridine were also injected at 393 K for calculating stationary phase polarity. Chromatograms were recorded with retention times expressed in hundredths of a minute.

On the other hand, to obtain thermodynamic magnitudes at infinite dilution, independence of the solute retention times on the amount injected are necessary. Therefore, mixtures of *n*-alkanes and *n*-alkylbenzenes containing amounts of these compounds that decreased as the hydrocarbon chain increased were prepared. 0.05–0.1 μL of these mixtures was completed up to 1 μL with methane and injected in a split ratio of 100:1 at least three times. Under such conditions, symmetric peaks were obtained for all the compounds on all the stationary phases and temperatures, with relative standard deviation for retention times lower than 0.34% except for the TR-CN100 column (<0.84%). Solutes were purchased from Merck (Darmstadt, Germany), Carlo Erba Reagenti (Rodano, Milano, Italy) and Sigma-Aldrich Co. (St. Louis, MO, USA) with a purity of 98–99.5%, sufficed for gas chromatographic use.

2.4. Mathematical treatment

Stationary phase polarity was calculated as the sum of the first five McReynolds' constants (ΔI_i) at 393 K [37]. Specific retention volumes were determined by Eq. (11), that allows reliable values of V_g in capillary columns since magnitudes difficult to measure, such as column head and outlet pressures, column length, internal diameter, mass and film thickness of the stationary phase, and flow rate of the carrier gas at column temperature outlet, are not involved [28,38]:

$$V_g = \frac{k}{c_s} \left(1 - \frac{c_s}{2\rho_s} \right)^2 \frac{273.15}{T} \quad (11)$$

where c_s is the concentration of the SP solution used to prepare the capillary column and ρ_s is the SP density.

Hold-up times (t_M) were calculated by the LQG method [39]. Thus, retention times of a mixture of several *n*-alkanes including methane were used to obtain the values of the four parameters, *A*, *B*, *C* and *D*, of Eq. (12), that were used to calculate the respective hold-up time through Eq. (13) at each chromatographic condition.

$$t_R = A + \exp(B + Cz^D) \quad (12)$$

$$t_M = A + \exp B \quad (13)$$

As mentioned in Section 1, different methods for obtaining partial molar enthalpies of solvation at infinite dilution by GC are described in the bibliography. According to theory (Eq. (6)), $\Delta_{sol}H^0$ is obtained from the slope of the $\ln V_g$ vs. $1/T$ plot (Method A, reference method). Other possibilities employed in the literature are $\ln k$ vs. $1/T$ (Method B) and $\ln(1/t'_R)$ vs. $1/T$ (Method C) plots, and recently the $\ln(k/T)$ vs. $1/T$ plot by Eq. (9) (Method D) or the $\ln(k/T)$ vs. $(1/T + T_a)$ plot by Eq. (10) (method E). For the sake of clarity, all of them are gathered in Table 2 including the physicochemical meaning of their fitting parameters.

Microsoft Office Excel 2007 (Microsoft Corp., Redmond, WA, USA) was used for data handling and basic calculations, and the Statgraphics Centurion XV program (StatPoint Technologies, Warrenton, VA, USA) for univariate and multivariate linear regressions. Non-linear regressions necessary for t_M estimation were carried out using Microcal Origin 6.0 (OriginLab Corp., Northampton, MA, USA).

3. Results and discussion

3.1. Comparison of the different methods for $\Delta_{sol}H^0$ calculation

In order to compare and check the different methods for obtaining $\Delta_{sol}H^0$ values by GC, some *n*-alkanes and *n*-alkylbenzenes were injected at 353, 373, 393 and 413 K in two capillary columns, TFPS00 and TFPS50 (see Section 2.2 for details). Both columns were prepared in our laboratories, since it is necessary to know the amount of stationary phase in the column to calculate V_g values. Using the experimental retention times of *n*-alkanes and *n*-alkylbenzenes, their t'_R , k and V_g values were calculated (see Table S1 in Supplementary Data section). All of them were fitted to the different models studied and gathered in Table 2. The $1/T$ coefficient (a parameter) was multiplied by the gas constant (R) to obtain the $\Delta_{sol}H^0$ for all the compounds in the middle of the temperature interval (383 K). Table 3 shows the values obtained by each method. As can be seen, methods D and E give the same results as method A (reference method), whereas the enthalpy values for methods B and C are 7–14% lower than the others. Differences stem from considering β constant with temperature in methods B and C. According to these

Table 2
Mathematical models tested in this study and physicochemical interpretation of the fitting terms a , b and c .

Method	Equation	Parameter		
		a	b	c
A	$\ln V_g = a \frac{1}{T} + b$	$-\frac{\Delta_{\text{sol}}H^{\circ}}{R}$	$\frac{\Delta_{\text{sol}}S^{\circ}}{R} - \ln \frac{M}{273.15R}$	
B	$\ln k = a \frac{1}{T} + b$	$-\frac{\Delta_{\text{sol}}H^{\circ}}{R}$	$\frac{\Delta_{\text{sol}}S^{\circ}}{R} - \ln \beta$	
C	$\ln \left(\frac{1}{t_r} \right) = a \frac{1}{T} + b$	$\frac{\Delta_{\text{sol}}H^{\circ}}{R}$	$-\frac{\Delta_{\text{sol}}S^{\circ}}{R} - \ln \frac{\beta}{t_M}$	
D	$\ln \left(\frac{k}{T} \right) = a \frac{1}{T} + b$	$-\frac{\Delta_{\text{sol}}H^{\circ}}{R}$	$\frac{\Delta_{\text{sol}}S^{\circ}}{R} + \ln \frac{W_S R}{M V_M^{\circ}}$	
E	$\ln \left(\frac{k}{T} \right) = a \frac{1}{T} + b T_a + c^a$	$-\frac{\Delta_{\text{sol}}H_{T_0}^{\circ}}{R}$	$\frac{\Delta_{\text{sol}}C_p^{\circ}}{R}$	$\frac{\Delta_{\text{sol}}S_{T_0}^{\circ}}{R} + \ln \frac{W_S R}{M V_M^{\circ}} - \frac{\Delta_{\text{sol}}C_p^{\circ}}{R} \left(1 + \frac{\ln T_0}{R} \right)$

^a $T_a = ((T_0/T) + \ln T)$, T_a being the temperature arrangement [33], T the temperature of the experiment (column temperature) and T_0 a single reference temperature.

Table 3
Partial molar enthalpies of solvation at 383 K on TFPS00 and TFPS50 columns.

Solute	$-\Delta_{\text{sol}}H_{373}^{\circ}$ (kJ mol ⁻¹)									
	TFPS00 ^a					TFPS50 ^a				
	Method A ^b	Method B	Method C	Method D	Method E	Method A ^b	Method B	Method C	Method D	Method E
<i>n</i> -Pentane	23.77	20.60	20.48	23.77	23.71					
<i>n</i> -Hexane	27.78	24.60	24.48	27.77	27.70					
<i>n</i> -Heptane	31.79	28.61	28.49	31.78	31.69	27.27	24.09	23.92	27.26	27.19
<i>n</i> -Octane	35.80	32.63	32.50	35.80	35.70	30.75	27.58	27.40	30.75	30.66
<i>n</i> -Nonane	39.82	36.65	36.52	39.82	39.70	34.22	31.05	30.87	34.21	34.11
<i>n</i> -Decane	43.84	40.66	40.54	43.83	43.70	37.68	34.51	34.33	37.67	37.56
<i>n</i> -Undecane	47.85	44.67	44.55	47.84	47.70	41.15	37.98	37.80	41.15	41.02
<i>n</i> -Dodecane						44.62	41.45	41.27	44.61	44.47
<i>n</i> -Tridecane						48.09	44.91	44.73	48.08	47.93
Benzene	29.09	25.92	25.79	29.08	29.03	29.29	26.11	25.93	29.28	29.20
Toluene	32.63	29.46	29.33	32.63	32.56	32.40	29.22	29.05	32.39	32.30
Ethylbenzene	36.18	33.01	32.88	36.18	36.09	35.51	32.33	32.16	35.50	35.40
<i>n</i> -Propylbenzene	39.72	36.55	36.42	39.71	39.62	38.62	35.44	35.27	38.61	38.50
<i>n</i> -Butylbenzene	43.61	40.43	40.31	43.60	43.49	41.74	38.56	38.38	41.73	41.60

^a For characteristics of these WCOT columns see Section 2.2.

^b See Section 2.4 and Table 2 for method identification.

results, $\ln V_g$ or $\ln(k/T)$ are the adequate magnitudes to fit against $1/T$ or $(1/T + T_a)$ when $\Delta_{\text{sol}}H^{\circ}$ values are estimated. This fact is very important when commercial capillary columns are used, since the knowledge of the amount of stationary phase or the β is rarely available.

Bearing in mind that the main aim of this work is to calculate $\Delta_{\text{sol}}H^{\circ}$ on commercial WCOT columns, methods D and E seem to be the best choice. Their authors indicate that they are equivalent [33], although method E offers the possibility of estimating $\Delta_{\text{sol}}C_p^{\circ}$ values and allows to determine $\Delta_{\text{sol}}H^{\circ}$ values outside the temperature range studied, for example at 298 K, that is a standard reference temperature for thermodynamic magnitudes. Therefore, in the following, we have adopted the method E (based on Eq. (10)) to calculate $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}C_p^{\circ}$ values.

3.2. Determination of $\Delta_{\text{sol}}H^{\circ}$ on different commercial stationary phases

Retention factors of *n*-alkanes and *n*-alkylbenzenes on 12 different polymeric stationary phases have been obtained in the 323–423 K temperature range. Mean values are summarized in Table S2 in Supplementary Data section. These k values were fitted to the Eq. (10) by multiple linear regression at $T_0 = 373$ K (middle point of the temperature interval studied), but also at $T_0 = 298$ K. Excellent regression models with adjusted correlation coefficients higher than 0.999992, Fisher's factors between 3.0×10^5 and 1.6×10^9 , and standard errors between 0.003 and 0.00009, were obtained. The residual plots do not show any significant trend.

It is important to note that pure thermodynamic quantities of solvation only can be obtained when the mechanism of retention is exclusively the gas–liquid partitioning. Although in our case symmetric peaks were obtained, this fact does not preclude the presence of adsorption effects [1]. Interfacial adsorption at the liquid interface has been observed for solutes with limited solubility in the bulk liquid SP, particularly non-polar solutes on polar SPs as poly(ethylene glycols) (as the ZB-WAX column) [40–42] or poly(biscyanoalkyl siloxanes) (as the BPX70 and TR-CN100 columns) [40,43–45]. Therefore, in these cases the thermodynamic magnitudes come from the combination of adsorption and solvation processes. González et al. [42] quantified the average contribution of interfacial adsorption for *n*-alkanes in capillary columns coated with poly(ethylene glycols) as a function of temperature and film thickness. Bearing in mind their conclusions, only k values above 373 K for the ZB-WAX column were considered to obtain its $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}C_p^{\circ}$ values, because for a capillary column with 0.5 μm of film thickness the interfacial adsorption contribution to the retention process is expected to be below 2%, good enough to obtain reliable thermodynamic quantities of solvation in this SP. On the other hand, it was not possible to quantify the contribution of interfacial adsorption to the retention process for the columns with SPs of high content of biscyanopropyl group (BPX70 and TR-CN100 columns), because there are not commercially available columns with higher film thicknesses. However, taking into account the limited data published about these SPs, it was considered worthwhile to keep in the paper the enthalpies and heat capacities calculated in both columns, although in principle they must be

Table 4
Partial molar enthalpies of solvation at 373 K on the commercial columns studied.

Solute	$-\Delta_{\text{sol}}H_{373}^{\circ}$ (kJ mol ⁻¹) ^a											
	TRB-1	TRB-5A	TRB-20	TRB-1301	BP10	TRB-35	TRB-50	VB-210	TRB-225	ZB-WAX ^b	BPX70 ^c	TR-CN100 ^c
<i>n</i> -Pentane	24.27	24.15	23.77		23.49							
<i>n</i> -Hexane	28.36	28.26	27.85	27.80	27.52	26.45	26.01		25.17			
<i>n</i> -Heptane	32.43	32.37	31.93	31.84	31.57	30.41	29.86		28.89	24.17		
<i>n</i> -Octane	36.50	36.47	35.98	35.89	35.61	34.32	33.72	31.42	32.66	27.68	31.08	
<i>n</i> -Nonane	40.57	40.58	40.04	39.94	39.66	38.28	37.56	34.91	36.40	31.28	34.90	
<i>n</i> -Decane	44.63	44.69	44.11	43.99	43.71	42.22	41.41	38.42	40.16	34.82	38.74	38.53
<i>n</i> -Undecane	48.70	48.79	48.17	48.04	47.75	46.16	45.25	41.93	43.91	38.39	42.58	42.62
<i>n</i> -Dodecane	52.77	52.90	52.22	52.09	51.80	50.10	49.09	45.44	47.66	41.94	46.40	46.70
<i>n</i> -Tridecane			56.28	56.14		54.04	52.94	48.94	51.41	45.49	50.25	50.81
<i>n</i> -Tetradecane						57.99		52.45	55.16	49.05	54.08	54.91
<i>n</i> -Pentadecane								55.96			57.92	59.00
Benzene	29.26	29.66	30.51	30.31	30.52	30.76	31.02	29.52	31.61	31.60	31.98	32.76
Toluene	33.04	33.48	34.26	34.06	34.27	34.42	34.60	32.78	35.06	34.33	35.23	35.97
Ethylbenzene	36.82	37.31	38.04	37.80	38.01	38.09	38.16	36.03	38.50	37.06	38.49	39.18
<i>n</i> -Propylbenzene	40.60	41.13	41.79	41.54	41.76	41.75	41.72	39.28	41.95	39.78	41.75	42.42
<i>n</i> -Butylbenzene	44.37	44.96	45.55	45.29	45.51	45.41	45.28	42.53	45.39	42.51	45.00	45.63

^a Calculated by method E (Eq. (10)) at $T_0 = 373$ K.^b The temperature range considered was 373–423 K, instead of the 323–423 K range taken for the rest of the columns.^c Partial molar enthalpy of sorption (solvation + adsorption).

considered as thermodynamic sorption quantities ($\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}C_p^{\circ}$).

Table 4 lists the $\Delta_{\text{sol}}H^{\circ}$ values at 373 K for the *n*-alkanes and *n*-alkylbenzenes in the studied WCOT columns ordered by the polarity of the SP. All values are negative, indicating an exothermic process, so the solvation process is favoured by the enthalpic component. As a general rule, the $\Delta_{\text{sol}}H_{373}^{\circ}$ values of the *n*-alkanes become less negative when the SP polarity increases, since dispersion forces decrease accordingly. However, a closer look at the values showed a dependence on substitution percentage and type of functional group in the SP. Thus, Fig. 1 shows the plot of $\Delta_{\text{sol}}H_{373}^{\circ}$ values for *n*-undecane vs. the percentage of methyl groups in the SP for all the polymers studied. The substitution of methyl by phenyl groups into the siloxane chains increases the enthalpy of the solvation process (less negative $\Delta_{\text{sol}}H_{373}^{\circ}$), because the contribution of dispersion interactions decreases [46]. For a given content, e.g. at 50% of methyl groups, $\Delta_{\text{sol}}H_{373}^{\circ}$ for *n*-alkanes also increases by the introduction of 3-cyanopropyl groups and even more if the groups are 3,3,3-trifluoropropyl, as SPs with these groups are more cohesive [46–48] and therefore, the solvation of the *n*-alkanes on them is more difficult. So, the solubility of *n*-

alkanes on these stationary phases decreases as compared with the poly(dimethyl siloxane). The lowest solubility for these compounds (highest $\Delta_{\text{sol}}H_{373}^{\circ}$) seems to correspond to the ZB-WAX (a non polysiloxane-type polymer). At this stage it is important to highlight the behaviour of the TR-CN100 column. Although it has 0% of methyl groups, as the ZB-WAX, it shows the same $\Delta_{\text{sol}}H_{373}^{\circ}$ value as BPX70 (30% of methyl group content). Bearing in mind that it is a highly cohesive and polar SP [49], the cavity formation necessary for the subsequent *n*-alkane insertion and activation of the solute-stationary phase interactions is hindered. Therefore, the *n*-alkane molecules remain adsorbed on the surface of the SP, since the opposing forces of cavity formation (requires energy) and dispersion interactions (provide energy) favours the embedding of the *n*-alkane in the interface as compared to its solvation in the SP. The solvation properties of this interfacial region resemble those of the bulk solvent, with the exception that the interfacial region is less cohesive [50]. Hence, some dispersion interactions can be established, giving a value of enthalpy lower than that of the ZB-WAX column and of the same order as in the BPX70 column.

The opposite trend was found for *n*-alkylbenzenes. In general, $\Delta_{\text{sol}}H_{373}^{\circ}$ decreases (more negative values) as the SP polarity increases, since the dipolar interactions with the stationary phase favour the solvation process. Again, a dependence of the enthalpy on the type and content of substitution group was found. Fig. 2 shows the plot of the $\Delta_{\text{sol}}H_{373}^{\circ}$ values for benzene in all the chromatographic columns according to the percentage of methyl group in the polymer. The presence of phenyl and 3-cyanopropyl groups favours the solvation of the *n*-alkylbenzenes in proportion to the amount of those groups in the SP. This effect is more important in phenylcyanopropyl, methylcyanopropyl and biscyanopropyl siloxanes due to the higher dipole moment and stronger electronic affinity of the cyanopropyl group as compared with the phenyl group. This increase of the interactions with the π electrons of the aromatic compounds results in a more favourable solvation process [46,48]. As seen with *n*-alkanes, once more the VB-210 column shows a high enthalpy value, due to the absence of electron lone pair interactions in the SP, neither as donor nor as acceptor. The strong electronegativity of fluorine atoms makes the fluoroalkanes little prone to give unshared electron pairs to molecules with stable empty molecular orbitals. Furthermore, fluorine cannot act as electron acceptor either, since the trifluoropropyl group does not have stable empty molecular orbitals. On the other hand, the stationary phases without methyl groups (ZB-WAX and TR-CN100) show close enthalpy values, although higher (less negative) in the ZB-WAX,

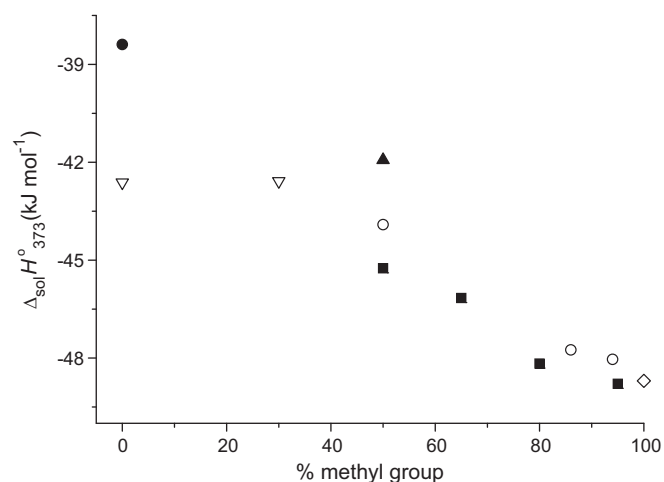


Fig. 1. Variation of the molar solvation enthalpy of *n*-undecane at 373 K with the methyl content of the polymer: (●) poly(ethylene glycol), (◇) poly(100% dimethylsiloxane) and poly(dimethylsiloxanes) with (■) diphenyl, (○) phenylcyanopropyl, (▲) trifluoropropylmethyl or (▽) biscyanopropyl groups.

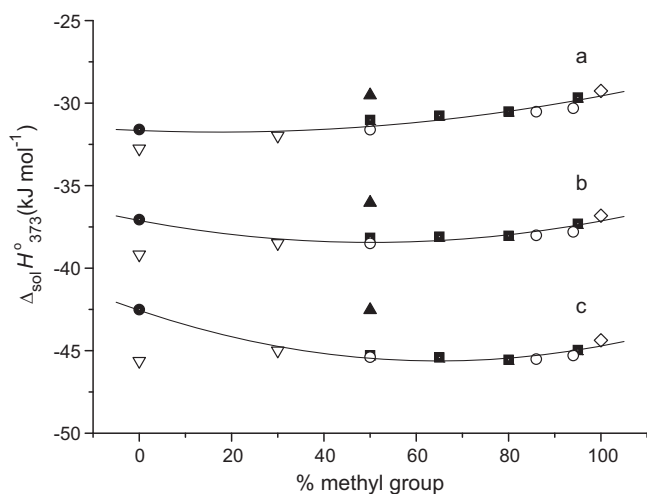


Fig. 2. Variation of the molar solvation enthalpy of (a) benzene, (b) *n*-ethylbenzene and (c) *n*-butylbenzene at 373 K with the methyl content of the polymer (symbols as in Fig. 1).

as poly(ethylene glycols) are slightly less dipolar/polarizable than poly(biscyanopropyl siloxanes) [46]. In fact, the TR-CN100 column shows the lowest (more negative) values for benzene in all the SPs studied, indicating that, in contrast to the *n*-alkanes, the additional polar solute-SP interactions of benzene with the 3-cyanopropyl groups result in a preference for absorption over adsorption. When the alkyl chain length of the aromatic ring increases, $\Delta_{\text{sol}}H_{373}^{\circ}$ decreases (more negative) in all columns, but at different rates, according to the magnitude of the dipolar/polarizable and electron lone pair interactions as compared with dispersion interactions. For *n*-alkylbenzenes, a balanced combination of these polar and non-polar forces results in a curved variation of $\Delta_{\text{sol}}H_{373}^{\circ}$ with the percentage of methyl groups in the SP, being more evident from benzene to *n*-butylbenzene (Fig. 2). However, VB-210 and TR-CN100 columns do not follow this behaviour. The former because cannot give polar interactions with the aromatic moiety, and the latter because the *n*-alkylbenzenes are partially adsorbed on the surface of the SP, as seems to indicate the low values of enthalpy (even lower than that of BPX70 column). Moreover, the contribution of interfacial adsorption to the retention process increases with the length of the alkyl chain, as can be seen in Fig. 2.

Table 5
Slopes of the plots (*m*) at two temperatures of partial molar enthalpies of solvation vs. the number of carbon atoms (*z*) of the alkyl side chain and difference from the slope of the plot corresponding to *n*-alkanes (Δm).

Column	$\Delta_{\text{sol}}H_{373}^{\circ}$			$\Delta_{\text{sol}}H_{298}^{\circ}$		
	<i>m</i>		Δm^a	<i>m</i>		Δm^a
	<i>n</i> -Alkanes	<i>n</i> -Alkylbenzenes		<i>n</i> -Alkanes	<i>n</i> -Alkylbenzenes	
TRB-1	-4.07	-3.78	0.29	-4.65	-4.34	0.31
TRB-5A	-4.11	-3.83	0.28	-4.61	-4.27	0.34
TRB-20	-4.06	-3.76	0.30	-4.57	-4.25	0.32
TRB-1301	-4.05	-3.74	0.31	-4.59	-4.28	0.31
BP10	-4.04	-3.75	0.29	-4.53	-4.18	0.35
TRB-35	-3.94	-3.66	0.28	-4.36	-4.07	0.29
TRB-50	-3.85	-3.56	0.28	-4.32	-3.92	0.40
VB-210	-3.51	-3.25	0.26	-4.01	-3.76	0.25
TRB-225	-3.75	-3.44	0.31	-4.25	-3.85	0.40
ZB-WAX ^b	-3.56	-2.73	0.83	-4.10	-3.01	1.09
BPX70 ^c	-3.84	-3.26	0.58	-4.43	-3.70	0.73
TR-CN100 ^c	-4.09	-3.22	0.87	-4.99	-3.95	1.04

All values in kJ mol^{-1} .

^a $\Delta m = m(\textit{n}\text{-alkylbenzenes}) - m(\textit{n}\text{-alkanes})$.

^{b,c} As in Table 4.

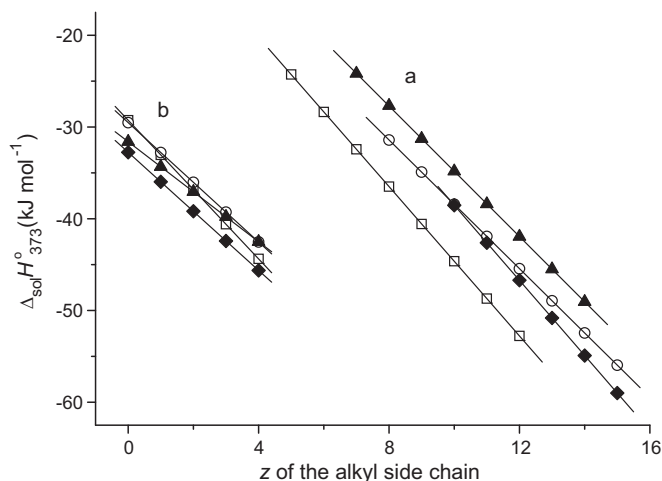


Fig. 3. Dependence of infinite dilution partial molar enthalpy of solvation on the length of the chain attached to a methyl (a) or phenyl (b) group at 373 K on several stationary phases: (□), TRB-1; (○), VB-210; (▲), ZB-WAX; (◆), TR-CN100.

The decrease of $\Delta_{\text{sol}}H_{373}^{\circ}$ with the hydrocarbon chain length could be quantified as the slope of the plot of $\Delta_{\text{sol}}H_{373}^{\circ}$ vs. the number of carbon atoms (*z*) of the molecule for a given homologous series. In all cases, linear relationships with adjusted correlation coefficients higher than 0.9999990, Fisher's factors between 1.6×10^6 and 4.6×10^8 , and standard errors between 0.01 and 0.0006 were obtained. The values of the slopes are presented in Table 5, and Fig. 3 shows the dependence of $\Delta_{\text{sol}}H^{\circ}$ on *z* for *n*-alkanes and *n*-alkylbenzenes at 373 K in some of the chromatographic columns studied. The slopes represent, in each case, the contribution to the solvation enthalpy per methylene group of that homologous series. Accepting the additivity principle, the slope of the lines will represent the contribution of the methylene group to the corresponding thermodynamic parameter in the series. The slope value deduced from the plots of the *n*-alkanes is considered as the real contribution of the methylene group [51]. In all other instances, the "polar" group at the end of the hydrocarbon chain (phenyl in our case) has an effect on the nearby methylene groups, modifying their contribution to the thermodynamic parameters. The net effect for a specific "polar" group may be deduced from the differences in the slopes (Δm). Thus, the phenyl group produces a decrease in the slope, so each new methylene group in the *n*-alkylbenzenes contributes less than in the *n*-alkanes to their

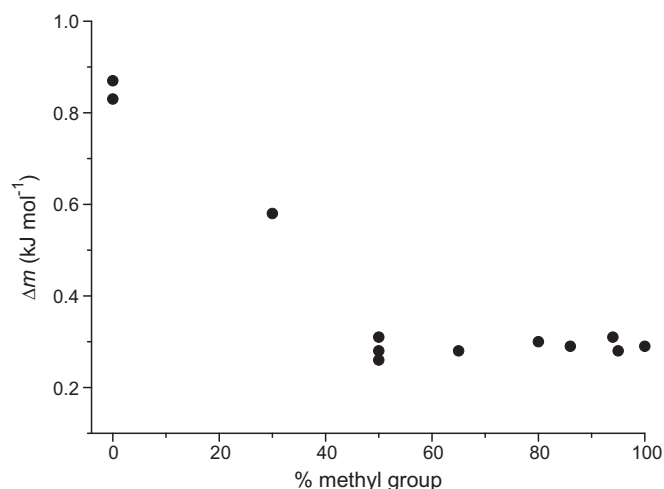


Fig. 4. Effect of phenyl moiety on the contribution of the methylene group of a homologous series to the partial molar enthalpy of solvation.

$\Delta_{\text{sol}}H_{373}^{\circ}$, and consequently, to their solubility in the SP. This effect is similar for all the SPs with methyl contents between 50 and 100%, but it has a higher magnitude (the process is less exothermic) for the other three columns studied, that is, the more polar ones (Fig. 4).

Values of $\Delta_{\text{sol}}H^{\circ}$ at 298 K for the *n*-alkanes and *n*-alkylbenzenes in the studied WCOT columns were also calculated. They are listed in Table 6, ordered by the polarity of the stationary phases. Like the values at 373 K, all of them are negative but with higher absolute values, since dispersion forces may not have a temperature term, but they are strongly distance-dependent. For that reason, the strengthening of solvent–solvent interactions that makes cavity formation more difficult at lower temperatures also increases the dispersion interactions by diminishing the average distance between solute and solvent molecules. The dependence of $\Delta_{\text{sol}}H_{298}^{\circ}$ on type and content of functional group in the SP is also present, and similar conclusions can be drawn.

The plots of $\Delta_{\text{sol}}H_{298}^{\circ}$ vs. *z* for *n*-alkanes and *n*-alkylbenzenes were in all cases linear, with adjusted correlation coefficients higher than 0.999990, Fisher's factors between 2.1×10^5 and 6.3×10^6 , and standard errors between 0.05 and 0.007. The slope values of the lines (Table 5), are more negative than those at 373 K, but show a similar trend of Δm values with the percentage of

methyl groups in the SP (see last column in Table 5). The effect of the phenyl group of the alkylbenzenes on the value of $\Delta_{\text{sol}}H_{298}^{\circ}$ is higher than at 373 K, especially on the SP with low methyl content.

3.3. Determination of $\Delta_{\text{sol}}C_p^{\circ}$ on different commercial stationary phases

In addition to its usefulness for obtaining solvation enthalpies, Eq. (10) can also be used to evaluate molar heat capacities of solvation at a constant pressure. However, it is important to point out that the estimation of $\Delta_{\text{sol}}C_p^{\circ}$ values (Table 7) with Eq. (10) has a higher error than that of $\Delta_{\text{sol}}H^{\circ}$. Thus, the average error in $\Delta_{\text{sol}}H^{\circ}$ was ± 0.006 (0.02%) and ± 0.03 (0.08%) kJ mol^{-1} at 373 and 298 K, respectively, but ± 0.4 $\text{J mol}^{-1} \text{K}^{-1}$ (0.8%) in $\Delta_{\text{sol}}C_p^{\circ}$. All values in Table 7 are positive, as expected, since $\Delta_{\text{sol}}C_p^{\circ}$ is a measure of the temperature dependence of $\Delta_{\text{sol}}H^{\circ}$, indicating that the absolute value of $\Delta_{\text{sol}}H^{\circ}$ increases with temperature. The dependence on polarity or type-content of substituent group in the stationary phase is not as evident as that for $\Delta_{\text{sol}}H^{\circ}$.

Good straight lines were obtained for the $\Delta_{\text{sol}}C_p^{\circ}$ vs. *z* graphs for all compounds. No deviation from this linear relationship was observed in any case, even for higher *n*-alkanes on polar stationary phases (Fig. 5), on the contrary to those obtained by Görgenyi et al. [23]. However, it is important to point out the high values of $\Delta_{\text{sol}}C_p^{\circ}$ for *n*-alkanes in the TR-CN100. As Görgenyi et al. [23] indicated, this may be connected with the formation of a structure in the SP, like the adsorption of these compounds on its surface. Then all *n*-alkanes studied should be adsorbed on the surface of the TR-CN100 stationary phase, in agreement with the low values of $\Delta_{\text{sol}}H^{\circ}$ found for this SP and the data from literature [40,43].

The linear dependence of $\Delta_{\text{sol}}C_p^{\circ}$ on *z* or other molecular size magnitudes (molar volume, van der Waals volume, McGowan volume, etc.) is shown in Fig. 5, as all these magnitudes are linearly related for *n*-alkanes. However, Görgenyi et al. [23] found that $\Delta_{\text{sol}}C_p^{\circ}$ also fluctuates with the temperature gradient of the density of the SP (ρ'). In order to check this for the 12 SPs studied, a multiple linear regression for the *n*-alkanes was carried out. The van der Waals volumes (V_x) [52] and ρ' values were used as independent variables. The ρ' values for all the SPs were obtained from Ref. [53], but for TRB-1 and VB-210 [34], and BPX70 and TR-CN100 [54]. In all cases, for polymers with the same percentage of substituent groups the same density was taken, except for TRB-1301 and BP10 columns, for which it was assumed that the density was that for the OV-105 stationary phase. Fig. 6 shows the results,

Table 6
Partial molar enthalpies of solvation at 298 K on the commercial columns studied.

Solute	$-\Delta_{\text{sol}}H_{298}^{\circ}$ (kJ mol^{-1}) ^a											
	TRB-1	TRB-5A	TRB-20	TRB-1301	BP10	TRB-35	TRB-50	VB-210	TRB-225	ZB-WAX ^b	BPX70 ^c	TR-CN100 ^c
<i>n</i> -Pentane	26.69	26.89	25.73		26.24							
<i>n</i> -Hexane	31.26	31.61	30.34	30.47	30.69	29.43	28.23		28.20			
<i>n</i> -Heptane	35.93	36.15	34.98	35.03	35.26	33.76	32.66		32.30	27.13		
<i>n</i> -Octane	40.62	40.78	39.52	39.68	39.79	38.16	36.92	35.54	36.70	31.05	35.70	
<i>n</i> -Nonane	45.23	45.39	44.07	44.26	44.33	42.54	41.27	39.57	40.94	35.29	40.16	
<i>n</i> -Decane	49.90	50.01	48.63	48.85	48.86	46.85	45.56	43.58	45.14	39.35	44.70	45.95
<i>n</i> -Undecane	54.56	54.61	53.21	53.42	53.39	51.24	49.87	47.58	49.43	43.48	49.06	50.84
<i>n</i> -Dodecane	59.20	59.23	57.78	58.01	57.93	55.59	54.18	51.58	53.64	47.55	53.49	55.85
<i>n</i> -Tridecane			62.34	62.59		59.95	58.51	55.61	57.89	51.64	57.90	60.84
<i>n</i> -Tetradecane						64.33		59.64	62.12	55.75	62.32	65.86
<i>n</i> -Pentadecane								63.65			66.74	70.90
Benzene	32.05	32.90	33.03	32.95	33.74	33.94	34.10	32.79	35.07	35.12	35.51	35.71
Toluene	36.42	37.17	37.30	37.24	37.93	38.05	38.00	36.58	38.90	38.16	39.18	39.68
Ethylbenzene	40.78	41.42	41.53	41.54	42.13	42.10	41.94	40.32	42.74	41.15	42.87	43.67
<i>n</i> -Propylbenzene	45.08	45.70	45.77	45.81	46.30	46.17	45.84	44.09	46.62	44.14	46.58	47.57
<i>n</i> -Butylbenzene	49.40	49.98	50.05	50.07	50.47	50.25	49.77	47.83	50.44	47.18	50.28	51.53

^a Calculated by method E (Eq. (10)) at $T_0 = 298$ K.

^{b,c} As in Table 4.

Table 7
Molar heat capacities of solvation on the commercial columns studied.

Solute	$\Delta_{\text{sol}}C_p^{\circ}$ (J mol ⁻¹ K ⁻¹) ^a											
	TRB-1	TRB-5A	TRB-20	TRB-1301	BP10	TRB-35	TRB-50	VB-210	TRB-225	ZB-WAX ^b	BPX70 ^c	TR-CN100 ^c
<i>n</i> -Pentane	32.3	36.6	26.2		36.7							
<i>n</i> -Hexane	38.6	44.6	33.4	35.6	42.2	39.7	29.6		40.3			
<i>n</i> -Heptane	46.7	50.4	40.7	42.6	49.2	44.7	37.3		45.4	39.5		
<i>n</i> -Octane	54.9	57.5	47.1	50.4	55.6	51.2	42.7	55.0	53.8	44.9	61.6	
<i>n</i> -Nonane	62.2	64.2	53.7	57.6	62.3	56.8	49.4	62.1	60.4	53.5	70.1	
<i>n</i> -Decane	70.2	71.0	60.3	64.8	68.7	61.8	55.3	68.8	66.4	60.4	79.4	98.8
<i>n</i> -Undecane	78.1	77.6	67.2	71.8	75.2	67.7	61.5	75.4	73.6	67.8	86.4	109.6
<i>n</i> -Dodecane	85.8	84.4	74.1	79.0	81.8	73.2	67.8	81.9	79.8	74.9	94.4	122.1
<i>n</i> -Tridecane			80.8	86.1		78.7	74.3	88.9	86.4	82.0	102.0	133.7
<i>n</i> -Tetradecane						84.6		95.8	92.8	89.3	109.9	146.0
<i>n</i> -Pentadecane								102.5			117.6	158.6
Benzene	37.1	43.3	33.6	35.1	42.9	42.4	41.0	43.5	46.1	46.9	47.1	39.4
Toluene	45.1	49.2	40.5	42.4	48.8	48.3	45.4	50.6	51.2	51.0	52.8	49.4
Ethylbenzene	52.8	54.9	46.6	49.8	54.8	53.4	50.4	57.2	56.5	54.6	58.3	59.8
<i>n</i> -Propylbenzene	59.8	60.9	53.1	56.8	60.5	58.9	55.0	64.2	62.3	58.1	64.5	68.7
<i>n</i> -Butylbenzene	67.0	66.9	60.1	63.8	66.2	64.6	59.9	70.7	67.3	62.3	70.5	78.7

^a Calculated by method E (Eq. (10)).

^{b,c} As in Table 4.

the values for the TR-CN100 and BPX70 columns deviating from the model. But for these values, the equation of the final model with all terms statistically significant at the 95.0% confidence level was:

$$\Delta_{\text{sol}}C_p^{\circ} = (-13.89 \pm 3.77) + (0.645 \pm 0.020)V_x - (0.737 \pm 0.280)\rho' \times 10^4 \quad (14)$$

with an adjusted correlation coefficient of 0.964, a Fisher's factor of 540 and a standard error of 4.69 for the 83 experimental values of $\Delta_{\text{sol}}C_p^{\circ}$. The deviation of the values for TR-CN100 was in accordance with the results obtained so far, indicating the interfacial adsorption of *n*-alkanes. However, this is not the case for the BPX70 column, because the $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}C_p^{\circ}$ values do not show any hint of adsorption on the surface of the SP, although it would be expected for such a high content of cyano groups in the SP. The reason of this anomalous behaviour could be found in the presence of silphenylene groups in the backbone, that makes the SP less cohesive and therefore, promoting the solvation process [55]. Consequently, and according to Eq. (4), the use of ρ' of a polysiloxane instead of the more rigid poly(silphenylene-siloxane) could explain the deviation of BPX70 values in Fig. 6. However, for the

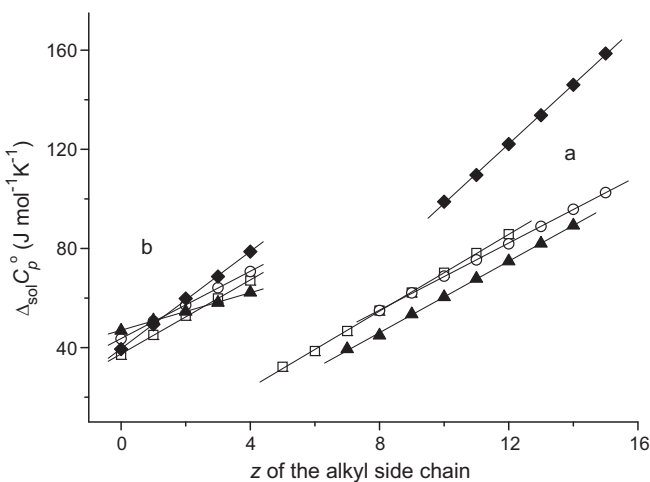


Fig. 5. Dependence of molar heat capacities of solvation on the length of the chain attached to a methyl (a) or phenyl (b) group on several stationary phases (symbols as in Fig. 3).

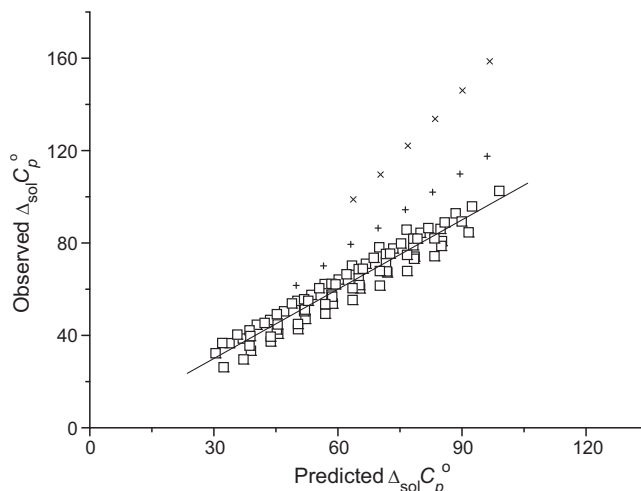


Fig. 6. Plot of the observed vs. predicted values of the molar heat capacity of solvation obtained by Eq. (14). Data from BPX70 (+) and TR-CN100 (x) columns were not considered in the fitting.

moment we do not have enough experimental evidence to support this.

4. Conclusions

The results obtained confirm that gas chromatography allows to calculate reliable $\Delta_{\text{sol}}H^{\circ}$ values by relating $\ln V_g$ or $\ln(k/T)$ to $1/T$ and $\ln(k/T)$ to $(1/T + T_a)$, provided that retention times are due only to the gas–liquid partitioning mechanism. Other methods that related $\ln k$ or $\ln(1/t'_R)$ to $1/T$ give $\Delta_{\text{sol}}H^{\circ}$ values 7–14% lower, because the phase ratio dependence on temperature is not considered. Therefore, when commercial capillary columns are used, Eq. (10) is recommended for $\Delta_{\text{sol}}H^{\circ}$ calculations. Bearing in mind these facts, retention factors of *n*-alkanes and *n*-alkylbenzenes on 12 commercial capillary columns covering a broad stationary phase polarity spectrum were estimated for the 323–423 K temperature range. All these values were fitted to Eq. (10), obtaining $\Delta_{\text{sol}}H^{\circ}$ values at 373 K (middle point of the temperature interval studied) and 298 K, with an average error lower than 0.08%. $\Delta_{\text{sol}}C_p^{\circ}$ values were also obtained, with an average error lower than 0.8%.

The $\Delta_{\text{sol}}H^{\circ}$ values for the *n*-alkanes become less negative when the content of methyl groups in the stationary phase decreases.

The introduction of phenyl, 3-cyanopropyl or 3,3,3-trifluoropropyl groups into the siloxane chains produces an increase of their $\Delta_{\text{sol}}H^{\circ}$ values, the latter being more important for the same percentage. The opposite situation was found for benzene and other light *n*-alkylbenzenes, except for the VB-210 column, where an increase of $\Delta_{\text{sol}}H^{\circ}$ was noticed. For the higher *n*-alkylbenzenes on the more polar stationary phases a balance of dispersion and polar interaction forces is observed.

The effect of the phenyl moiety on the contribution of the methylene group to the $\Delta_{\text{sol}}H^{\circ}$ of *n*-alkylbenzenes was found to be similar for the SP with methyl contents between 50 and 100%, but of higher magnitude for the rest of the columns studied (the more polar ones). Both $\Delta_{\text{sol}}H^{\circ}$ and $\Delta_{\text{sol}}C_{\text{p}}^{\circ}$ were perfectly correlated to *z* for all the compounds studied. Moreover, for $\Delta_{\text{sol}}C_{\text{p}}^{\circ}$ a linear relationship with the van der Waals volume of the *n*-alkanes and the temperature gradient of density of the stationary phase was found. The high values of $\Delta_{\text{sol}}C_{\text{p}}^{\circ}$ for *n*-alkanes in the TR-CN100 column, along with their low values of enthalpy, corroborate that all *n*-alkanes studied are adsorbed on the surface of this stationary phase. Finally, the BPX70 column did not show the interfacial adsorption expected for the *n*-alkanes, probably due to the presence of silphenylene groups into the backbone.

Acknowledgements

This work was carried out under Projects CTQ2006-10512/BQU of Ministerio de Ciencia e Innovación (Spain) and ANALISYC II (S2009/AGR-1464) of the Comunidad de Madrid (Spain). Thanks are given to Dr. J.M. Takács for valuable comments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.10.019.

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