



## ENTHALPY-ENTROPY COMPENSATION IN REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY INVESTIGATED FOR THE MOBILE PHASES CONTAINING ALCOHOLS FROM METHANOL TO OCTANOL

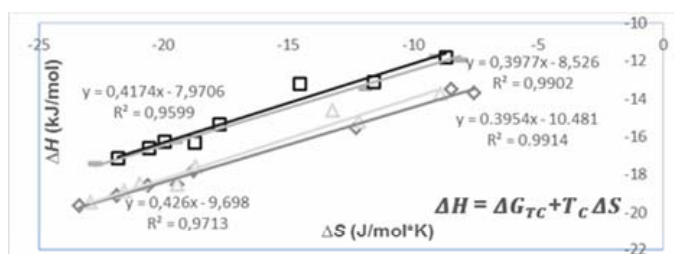
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Retention behaviours of two probe solutes (propylparaben and butylparaben) were studied by reversed-phase liquid chromatography using mobile phases containing methanol with a fixed content of an upper alcohol (from ethanol to octanol) and an aqueous component (with 0.1% phosphoric acid). The van't Hoff analysis of the retention data obtained on the temperature interval 15 - 50°C was used to calculate the standard enthalpy ( $\Delta H^0$ ) and entropy changes ( $\Delta S^0$ ) for the transfer of solutes from mobile to the stationary phase (C18). From the graphical representation of the dependence



between  $\Delta H^0$  and  $\Delta S^0$ , the compensation temperature ( $T_c$ ) was calculated and compared to other data from literature. The values of  $T_c$  varied between 395 K and 426 K (for butylparaben) on a packed HPLC column (Zorbax XDB-C18), while for monolithic column (Chromolith RP-C18) the interval of  $T_c$  variation was very narrow (400 – 402 K) for both studied solutes. This study showed that the compensation effect is observable for the two tested solutes in reversed-phase mechanism by using various mobile phase compositions that differed by the alcohol added to the methanol component in the mobile phase.

### INTRODUCTION

According to the fundamental thermodynamic equation  $\Delta G = \Delta H - T\Delta S$ , the enthalpy change of a system ( $\Delta H$ ), can be written based on entropy change ( $\Delta S$ ) and Gibbs free enthalpy change ( $\Delta G$ ) as follows:

$$\Delta H = \Delta G + T\Delta S \quad (1)$$

For many closely related processes, such as kinetic or partition equilibria, it has been found that the enthalpy and entropy changes are often linearly correlated for a constant temperature  $T$ .<sup>1</sup> This phenomenon, known as enthalpy-entropy compensation (EEC), can be described by the empirical equation between  $\Delta H$  and  $\Delta S$ :

$$\Delta H = a + b\Delta S \quad (2)$$

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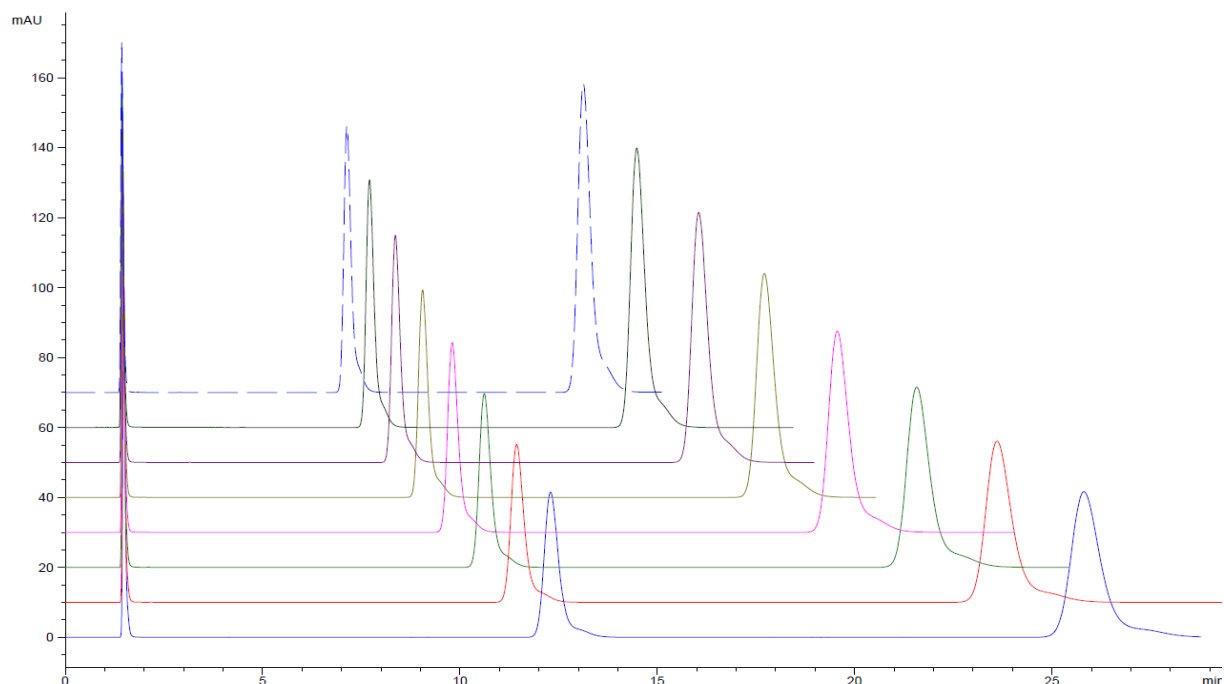


Fig. 1 – Eight overlaid chromatograms recorded for standard solutions of uracil, propylparaben and butylparaben (elution order) separated on Zorbax XDB-C18 column at 8 different temperatures (15 - 50°C), for a mobile phase containing 50% methanol (with 1% hexanol as hydrophobic additive) and 50% aqueous component (0.1% H<sub>3</sub>PO<sub>4</sub>), v/v.

The EEC correlation plot between  $\Delta H$  and  $\Delta S$  is characterized by the slope  $b$  identified as the compensation temperature ( $T_C$ ), and the intercept  $\Delta G = \text{constant} = a$ . In practice, this dependence can be polynomial, when the concept of EEC is no longer valid.<sup>2,3</sup>

For the compensation temperature, the enthalpy change from eq. 1 becomes:

$$\Delta H = \Delta G_{T_C} + T_C \Delta S \quad (3)$$

In principle, the value of the slope should be close to the value of temperature  $T$  used for correlation. In practice, due to the experimental errors, the magnitudes of the intercept and slope calculated from EEC plot are uncertain.<sup>4,5</sup> It is considered from statistical point of view that EEC is real when  $T_C > T$  for  $T$  used for the correlations, but in the case  $T_C < T$  the correlation is affected by large errors and the correlation is no longer valid.<sup>3</sup>

For HPLC processes, EEC can be studied using  $\Delta H$  and  $\Delta S$  calculated from van't Hoff plots, for homologous series of  $n$  compounds (e.g. alkylbenzenes, or alkylphenols). When EEC takes place,  $\Delta H$  versus  $\Delta S$  plot should be linear with slope equally to  $T_C$ , and the intercept gives the value of Gibbs free enthalpy change  $\Delta G_{T_C}$ . Thus, it has been found that EEC takes place for some classes of studied compounds, but with different

compensation temperature for different separation mechanisms. Thus, in normal phase mechanism (NP-HPLC) the compensation process takes place around 150 K, while in reversed-phase mechanism (RP-HPLC) the compensation takes place at higher temperatures, being situated within the range 500 and 1,000 K.<sup>6</sup> For example, according to an extensive study, the value of  $T_C$  for a group of five halogenated benzylamines was calculated to 560 K.<sup>7</sup> Linear dependences between  $\Delta H$  and  $\Delta S$  have been observed also in gas chromatography and used to explain the retention mechanism of various target compounds.<sup>8,9</sup>

This study takes into consideration a new experimental design in order to investigate EEC in RP-HPLC, but this time various mobile phases having in their composition a series of different hydrophobic additives at the same concentration level are used. These additives are the series from ethanol to octanol, added to the organic component (methanol) of the mobile phase in a fixed concentration. The possibility of employing these alcohols in the composition of mobile phase has been already used in explaining the retention mechanism in RP-HPLC,<sup>10</sup> with useful utilizations in current applications.<sup>11-15</sup> In the present work the thermodynamics based on van't Hoff approach is studied for the retention of two hydrophobic probe solutes using this series of alcohols as additives in

the mobile phase in order to evaluate EEC in RP-HPLC, and to compare the outcome with data reported by the literature.<sup>6,7</sup>

## EXPERIMENTAL

The HPLC experiments were performed with a Agilent LC system, model 1100, having the following components: degasser, binary pump, autosampler, column thermostatted compartment and variable wavelength UV detector. Data acquisitions were achieved with the aid of Agilent Chemstation. Two HPLC columns were used in this study: Zorbax XDB-C18 (150 mm length, 4.6 mm i.d. and 5  $\mu$ m particle diameter) and Chromolith RP-C18 (100 mm length, 4.6 mm. i.d.). UV detection was made at 254 nm.

The mobile phase had the composition (v/v): 50% organic component and 50% aqueous component (with 0.1% H<sub>3</sub>PO<sub>4</sub>). The organic component was methanol that contained only one additive (from ethanol to octanol) in volumetric concentration of 1% additive, or 1.5%. The flow rate was set up to 1 mL/min, and the retention time for studied solutes was measured for column temperature fixed at 15; 20; 25; 30; 35; 40; 45 and 50°C. The two studied solutes (propylparaben and butylparaben) were injected as standard solutions with concentration of 200  $\mu$ g/mL in methanol, with the injection volume of 1  $\mu$ L.

Column dead-time ( $t_0$ ) was determined from the retention time of uracil, injected into the column simultaneously with studied solutes for different mobile phase compositions and temperatures. An example of separations for the three compounds used for this study at the temperature values indicated above is given in Fig. 1.

## RESULTS AND DISCUSSION

The thermodynamic model for the partition process<sup>16,17</sup> of an eluted solute gives the dependence of the natural logarithm (ln) of retention factor  $k$  of a solute on the standard enthalpy ( $\Delta H^0$ ) and entropy changes ( $\Delta S^0$ ) for its transfer from mobile to the stationary phase by the well-known van't Hoff equation, written in the form:

$$\ln k = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} + \ln \Psi \quad (4)$$

where,  $\Psi$  is the phase ratio, namely the ratio between the volume of stationary phase to the volume of mobile phase from the chromatographic column,<sup>18-22</sup>  $T$  is the column temperature, and  $R$  is the universal gas constant (8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>). The van't Hoff plot, representing the dependence between the experimental values of  $\ln k$  and  $1/T$ , are used for estimating  $\Delta H^0$ . The value of  $\Delta S^0$  can

be calculated considering that  $\Psi$  is temperature invariant.<sup>23</sup> However, recent studies have shown that  $\Psi$  can vary with temperature, depending on the organic modifier used for the mobile phase composition.<sup>24,25</sup> A more complicated situation is encountered when the dependence of  $\ln k$  on  $1/T$  is nonlinear,<sup>26</sup> a behavior that is attributed to the multiple interactions or the existence of multiple molecular forms of the solute in mobile phase whose interactions with the stationary phase are characterized by different free enthalpies of interaction.<sup>27,28</sup> However, for the present evaluated system the van't Hoff dependencies were found to be linear.

The values of regression parameters  $a$  (intercept) and  $b$  (slope) from van't Hoff plots ( $\ln k = a + \frac{b}{T}$ ) for the two solutes were used to calculate the values of the standard enthalpy ( $\Delta H^0$ ) and entropy changes ( $\Delta S^0$ ) as follows:

$$\Delta H^0 = -b \times R \quad (5)$$

$$\Delta S^0 = R (a - \ln \Psi) \quad (6)$$

The regression parameters were calculated from van't Hoff plots for the two columns, and different additives in the mobile phase composition: methanol (abbreviated by MeOH), ethanol (EtOH), propanol (PrOH), butanol (BuOH), pentanol (PnOH), hexanol (HxOH), heptanol (HpOH) and octanol (OcOH). The values of  $\Delta S^0$  were calculated with the eq. 6, using a value for  $\Psi$  equal to 0.1135 for the Zorbax column and 0.1121 for the Chromolith column, which were determined from previous retention experiments on these columns.<sup>29</sup> The values of  $\Delta H^0$  and  $\Delta S^0$  calculated from the HPLC separations carried out on the two mentioned columns, at different temperatures and mobile phase compositions are listed in Tables 1 – 4. These tables show that, excepting a few particular situations due to the possible experimental errors, the absolute values of  $\Delta H^0$  and  $\Delta S^0$  assigned to the transfer of the solute from the mobile to the stationary phase decrease with the increase of the hydrophobic character of the additive added in mobile phase (upper alcohols), explained by the competition adsorption between the additive and solute molecules for the C18 sites from the stationary phase surface.<sup>10</sup>

Table 1

The values of the regression parameters and thermodynamic parameters calculated from van't Hoff plots, for the column Zorbax XDB-C18 and and 1 mL/min mobile phase containing 50% methanol (with 1% hydrophobic additive) and 50% aqueous component (with 0.1% H<sub>3</sub>PO<sub>4</sub>)

Additive	Propylparaben		Butylparaben		Propylparaben		Butylparaben	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
MeOH	-4.43	1961.5	-4.52	2228.5	-16.31	-18.78	-18.53	-19.47
EtOH	-4.91	2096.3	-4.99	2360.5	-17.43	-22.75	-19.63	-23.38
PrOH	-4.66	2011.5	-4.81	2296.1	-16.72	-20.66	-19.09	-21.88
BuOH	-4.53	1954.9	-4.66	2234.1	-16.25	-19.53	-18.57	-20.64
PnOH	-4.33	1870.0	-4.44	2139.6	-15.55	-17.89	-17.79	-18.80
HxOH	-3.61	1617.6	-3.65	1864.9	-13.45	-11.91	-15.51	-12.28
HpOH	-3.15	1434.3	-3.09	1645.2	-11.92	-8.11	-13.68	-7.57
OcOH	-3.27	1415.0	-3.20	1619.3	-11.76	-9.10	-13.46	-8.49

\* Note: MeOH indicated methanol with no added C2-C8 alcohol

Table 2

The values of the regression parameters and thermodynamic parameters calculated from van't Hoff plots, for the column Zorbax XDB-C18 and and 1 mL/min mobile phase containing 50% methanol (with 1.5% hydrophobic additive) and 50% aqueous component (with 0.1% H<sub>3</sub>PO<sub>4</sub>)

Additive	Propylparaben		Butylparaben		Propylparaben		Butylparaben	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
MeOH	-4.43	1961.5	-4.52	2228.5	-16.31	-18.78	-18.53	-19.47
EtOH	-4.80	2056.8	-4.93	2337.0	-17.10	-21.82	-19.43	-22.93
PrOH	-4.65	1996.4	-4.77	2270.5	-16.60	-20.58	-18.88	-21.56
BuOH	-4.58	1951.4	-4.70	2223.6	-16.22	-19.95	-18.49	-20.94
PnOH	-4.31	1841.7	-4.43	2111.2	-15.31	-17.76	-17.55	-18.74
HxOH	-3.57	1572.9	-3.64	1823.7	-13.08	-11.61	-15.16	-12.16
HpOH	-3.22	1417.1	-3.25	1648.4	-11.78	-8.69	-13.70	-8.90
OcOH	-3.93	1586.2	-3.77	1756.6	-13.19	-14.56	-14.60	-13.24

Table 3

The values of the regression parameters and thermodynamic parameters calculated from van't Hoff plots, for the column Chromolith RP-C18 and 1 mL/min mobile phase containing 50% methanol (with 1% hydrophobic additive) and 50% aqueous component (with 0.1% H<sub>3</sub>PO<sub>4</sub>)

Additive	Propylparaben		Butylparaben		Propylparaben		Butylparaben	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
MeOH	-5.82	2104.5	-5.94	2376.4	-17.50	-30.19	-19.76	-31.16
EtOH	-5.73	2075.7	-5.84	2345.1	-17.26	-29.48	-19.50	-30.38
PrOH	-5.69	2052.0	-5.80	2321.6	-17.06	-29.10	-19.30	-30.03
BuOH	-5.75	2055.0	-5.89	2331.0	-17.09	-29.61	-19.38	-30.75
PnOH	-5.14	1849.3	-5.23	2108.6	-15.38	-24.57	-17.53	-25.29
HxOH	-4.72	1684.7	-4.80	1940.5	-14.01	-21.07	-16.13	-21.75
HpOH	-4.48	1565.6	-4.37	1760.9	-13.02	-19.03	-14.64	-18.18
OcOH	-3.99	1354.7	-4.01	1585.3	-11.26	-15.01	-13.18	-15.18

Linear dependences between  $\Delta H^0$  and  $\Delta S^0$  calculated from van't Hoff plots were obtained for the two tested solutes and for the eight compositions of mobile phase, which differ by the nature of the alcohol added to the methanol component in mobile phase. These representations for both used HPLC columns are shown in Fig. 2 and 3. They show a high correlation between the two thermodynamic parameters ( $R^2 > 0.9000$ ),

indicating that EEC effect is real and the HPLC process can be characterized by a compensation temperature ( $T_C$ ). Thus, these representations were used to obtain the regression parameters for the linear dependence fitted by eq. 2, with slope multiplied by  $10^3$  (to bring  $\Delta H^0$  and  $\Delta S^0$  at the same kJ units), indicating the compensation temperature ( $T_C$ ). The values of  $T_C$  are given in Table 5.

Table 4

The values of the regression parameters and thermodynamic parameters calculated from van't Hoff plots, for the column Chromolith RP-C18 and 1.5 mL/min mobile phase containing 50% methanol (with 1% hydrophobic additive) and 50% aqueous component (with 0.1% H<sub>3</sub>PO<sub>4</sub>)

Additive	Propylparaben		Butylparaben		Propylparaben		Butylparaben	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
MeOH	-5.98	2155.0	-6.13	2437.0	-17.92	-31.54	-20.26	-32.78
EtOH	-6.01	2158.9	-6.17	2443.3	-17.95	-31.81	-20.31	-33.14
PrOH	-5.99	2142.9	-6.15	2425.4	-17.82	-31.64	-20.16	-32.94
BuOH	-5.83	2080.0	-5.99	2361.6	-17.29	-30.30	-19.63	-31.59
PnOH	-5.46	1944.5	-5.61	2221.3	-16.17	-27.22	-18.47	-28.42
HxOH	-4.75	1688.1	-4.92	1972.0	-14.03	-21.27	-16.40	-22.73
HpOH	-4.76	1649.1	-4.69	1856.2	-13.71	-21.36	-15.43	-20.84
OcOH	-4.20	1416.8	-4.25	1656.2	-11.78	-16.75	-13.77	-17.16

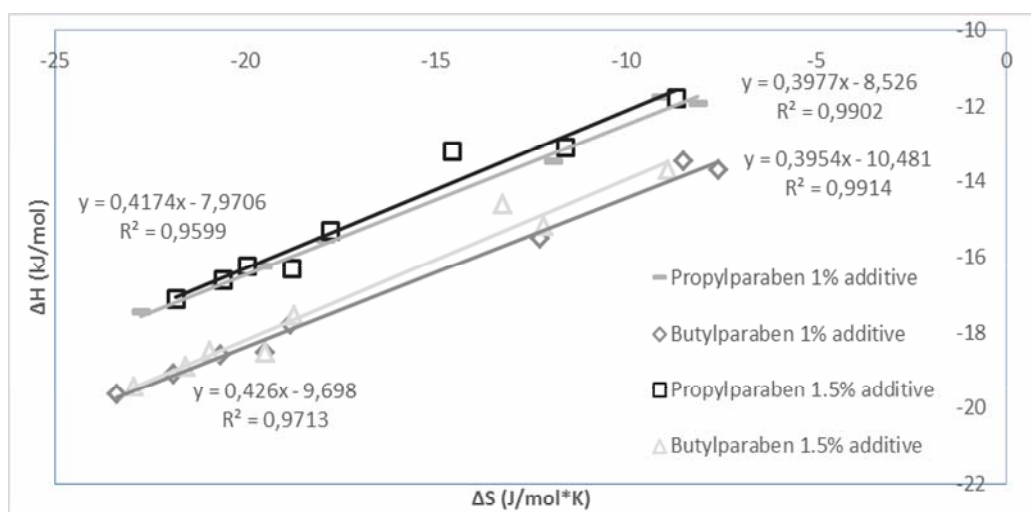


Fig. 2 – Representation between  $\Delta H^0$  and  $\Delta S^0$  obtained for the two studied solutes on Zorbax XDB-C18 column, for 1% and 1.5% upper alcohol added to methanol component in mobile phase.

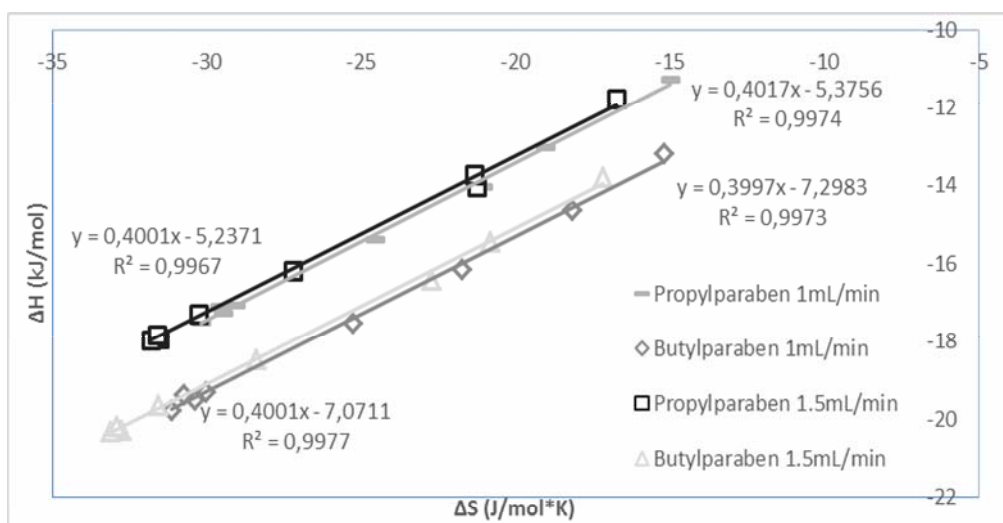


Fig. 3 – Representation between  $\Delta H^0$  and  $\Delta S^0$  obtained for the two studied solutes on Chromolith RP-C18 column, 1 and 1.5 mL/min flow rate for the mobile phase containing 1% upper alcohol added to methanol component.

Table 5

The values of compensation temperature  $T_C$  calculated from the slope of  $\Delta H = f(\Delta S)$  plots, for various chromatographic conditions

Zorbax XDB-C18	Propylparaben (1 % additive)	Butylparaben (1 % additive)	Propylparaben (1.5 % additive)	Butylparaben (1.5 % additive)
	397.69 ± 30.06 K	395.41 ± 27.89 K	417.39 ± 64.78 K	425.96 ± 55.54 K
Chromolith RP-C18	Propylparaben (1 mL/min)	Butylparaben (1 mL/min)	Propylparaben (1.5 mL/min)	Butylparaben (1.5 mL/min)
	401.69 ± 15.70 K	399.75 ± 15.93 K	400.06 ± 17.46 K	400.12 ± 14.51 K

As shown in Table 5, the values of  $T_C$  for the two chromatographic columns are not very different. Thus, the values of  $T_C$  varied between 395 K and 426 K (for butylparaben) on packed HPLC column (Zorbax XDB-C18), while for the monolithic column (Chromolith RP-C18) the interval of  $T_C$  variation was very narrow (400 – 402 K) for the both studied solutes. These values are however lower than the interval of variation of  $T_C$  reported by the literature for the reversed-phase mechanism in case of series of homologous series of solutes.

Due to the errors affecting the measurement process, the values of  $T_C$  represent only an estimate, characterized by the average and the confidence interval where this parameter is situated.<sup>4,30,31</sup> This confidence interval can be written as follows:<sup>6,7</sup>

$$T_C \pm t(n-2, 1-\alpha) \times V(T_C) \quad (7)$$

In expression (7) the statistical parameter  $V(T_C)$  can be calculated with the formula:

$$V(T_C) = \frac{\sum_{i=1}^n (\Delta H_i - \Delta G_{T_C} - T_C \Delta S_i)^2}{(n-2) \sum_{i=1}^n (\Delta S_i - \langle \Delta S \rangle)^2} \quad (8)$$

where  $\langle H \rangle$  and  $\langle S \rangle$  represent the average values of these thermodynamic parameters, and  $\langle G_{T_C} \rangle$  is Gibbs free enthalpy change at temperature  $T_C$ . The value of the Student's  $t$  corresponds to  $(n-2)$  degrees of freedom and a confidence level  $(1-\alpha)$ . ANOVA approach was applied to this case ( $n=8$ ;  $\alpha=0.95$ ), which finally gave the confidence intervals for the computed  $T_C$  indicated also in Table 5.

## CONCLUSIONS

This study showed that the compensation effect is observable for the two tested solutes (propyl and

butylparaben) in reversed-phase mechanism by using eight mobile phase compositions that differed by the C2-C8 alcohol added to the methanol component in mobile phase. The interval of variation for compensation temperature was estimated approximately to 395 – 425 K, slightly below the typical range reported in the literature (500 – 1000 K), but this effect is caused by the addition of hydrophobic additives in the mobile phase composition. This study also showed that, excepting for some specific situations, the absolute values of  $\Delta H^0$  and  $\Delta S^0$  assigned to the transfer of the solute from the mobile to the stationary phase decrease with the increase of the hydrophobic character of the alcohol added in mobile phase, which may be explained by the competition adsorption between the additive and solute molecules for the C18 sites from the stationary phase surface.

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