STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 2, TOM II, 2010

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

THE THERMODYNAMICS AND KINETICS OF SATURATED HYDROCARBON SEPARATION ON A DB-1 COLUMN

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ABSTRACT. Results concerning the thermodynamics and kinetics of separation of some saturated hydrocarbons on a DB-1 non-polar capillary chromatographic column are presented. The effect of temperature on the retention time at constant carrier gas flow was studied in order to determine the adsorption enthalpy and adsorption entropy of the compounds on the poly-dimethyl-siloxane stationary phase. The dependence of the height equivalent to theoretical plate on the carrier gas linear velocities at constant temperature was also determined in order to have access to the optimal linear velocity, the longitudinal diffusion (B) and resistance to mass transfer (C) coefficients. These terms can be determined from the Golay equation. The linearization of the Golay equation is also presented.

Keywords: *gas chromatography, DB-1 capillary column, hydrocarbon isomer separation, adsorption enthalpy, adsorption entropy, Golay equation, longitudinal diffusion coefficient, resistance to mass transfer coefficient.*

INTRODUCTION

The efficiency of the gas chromatographic separation depends on many variables. These variables can be divided in two groups: design- and operational parameters. The design parameters are given by the construction of the chromatographic setup and include the following: the length, the diameter and the polarity of the chromatographic column, the stationary phase film thickness and the carrier gas viscosity. For the separation of a multi-component mixture using a chromatographic system with given design parameters one can vary the operational parameters, i.e the temperature of the column and the carrier gas flow rate. Both can be ramped with a desired rate [1-4].

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The separation of mixtures containing a few components can be made relatively easily by careful and consistent-with-reason variation of the operational parameters. However for the separation of a complex mixture the trial-and-error method might be very time consuming. Numerous examples of difficult-to-separate mixtures can be listed from various fields of chemistry:

- food control and research (separation of carbohydrates, fats, chiral flavor and aroma compounds) [5]
- pharmaceutical and toxicological analysis (screening for drugs and their metabolites in human blood) [6]
- forensic chemistry, analysis of controlled substances (drug profiling, the separation of derivatized amphetamines, opiates from impurities, adulterants and diluents) [7]
- environmental analysis (separation of polychlorinated biphenyls, heterocyclic amines, nitro-polyaromatic hydrocarbon isomers, tetra- and pentachloro-dibenzo-p-dioxin isomers, nitrogen and phosphorous containing pesticides [8], separation of PAHs and PCBs) [9]
- heterogeneous catalysis research (separation of alkane isomers formed in isomerisation/hydroisomerisation and catalytic cracking reactions [10-12], separation of alkane from olefin and water formed in oxidative dehydrogenation and partial oxidation reactions, separation of various partial oxidation products from different substrates) [13].

However a critical reader can identify a few shortcomings in some of the above mentioned literature. In most of the cases the authors report only the retention times, or the chromatogram is shown. The resolution is given very rarely. In several cases it is evident from the chromatograms that the peaks are partly overlapped [9-11]. The use of such a method for quantitative determinations lacks analytical rigor, especially when the authors claim the validation of a new chromatographic method for analytical purposes. It also can be noted that in most of the cases there is no description about the way how the chromatographic method was developed. Seemingly the temperature ramps, holding times and the carrier gas flow rate are set empirically/arbitrarily. In general, the optimization of the chromatographic method with respect to resolution and analysis time is seldom reported. In the following we present through three examples in more detail the above mentioned deficiencies.

Kim and Vane claimed the successful development of a chromatographic method for the simultaneous separation and identification of a mixture containing 40 PAH and PCB compounds [9]. The temperature program and carrier gas flow rate was given. The resolution was given only for the benzo[b]fluoranthene and benzo[k]fluoranthene peak-pair. These were found to be “80% resolved by 2 seconds”. However this is confusing, because the unit of the resolution is not percentage and seconds, but it is a dimensionless number. Some other peaks were characterized only qualitatively by shape and width. No comparison was given between the combined method developed by the authors and the existing method for the individual determination of PAHs and PCBs.

Claude et al. studied the hydro-isomerisation of n-C_{10}–n-C_{24} alkanes [10]. The products were analyzed by on-line gas-chromatography. The temperature program was the following: 10 ºC for 5 minutes than a ramp of 5 ºC/min to 120 ºC followed by the second ramp of 2 ºC/min to 200 ºC and finally the third ramp of 0,1 ºC/min up to 205 ºC. The mono- and multi-branched products eluted in two groups. Although the resolution is not given for the peak-pairs, from the chromatogram one can see that there are partly or totally overlapped peaks. The analysis time was 115-120 minutes, but apparently nothing elutes from the columns before 80 minutes. This means that only about 32% of the chromatogram contains information. The choice of the temperature program is strange because in gas chromatography the use of sub-ambient starting temperature is uncustomary for two reasons. The first reason is that after the completion of a measurement, the GC oven needs to be cooled down from 205 ºC to 10 ºC for the starting another analysis. The cooling is time consuming; therefore the sampling rate is lower than 1 injection/120 minutes. Moreover at that low starting temperature the long chain alkanes are condensing in the column inlet and possibly also in the injector port or valve system and vaporizing when the temperature becomes high enough.

Huybrechts et al. developed a high throughput reactor system for long-chain n-alkane hydroconversion combined with a fast analytical system [11]. They employed a multi-capillary column with poly-dimethylsiloxane stationary phase for the separation of the C_1-C_{10} products. The N_2 carrier gas flow rate was set to 67 ml/min. The temperature was ramped from 40 to 75 ºC by 15 ºC/min. The analysis time was only 3,2 minutes instead of 45 minutes for a conventional 50 m long capillary column. However the authors admitted that there were overlapped peaks, like 2,5-dimethyl-octane and 3,5-dimethyl-octane, 3,4-dimethyl-octane and 3-ethyl-4-methyl-heptane, 4-propyl-heptane and 4,5-dimethyl-octane, 4-ethyl-octane and 2,3-dimethyl-octane, 5-methyl-nonane and 4-methyl-nonane, 3-ethyl-octane and 3-methyl-nonane and 2-methyl-nonane, respectively. Because of the insufficient peak resolution the product selectivities are questionable. Apparently no attempt was undertaken to improve the resolution of peaks. Therefore it can be concluded that the analytical accuracy was sacrificed for fast data acquisition.

Whenever there is a need to separate a complex mixture it is recommended to develop and optimize the chromatographic method based on a rational way. For this purpose the knowledge of the thermodynamic and kinetic parameters of the separation is needed [1-4, 14, 15]. Possibly because of their apparent simplicity, computer programs and expert systems are becoming more and more extensively used for the method development. However these are based on a large number of retention time data determined under various conditions Thus, the method development is possible only for those compounds for which retention data already exists in the databases

and libraries of these programs [4, 16]. Some gas chromatography companies claim that their software enables the user to develop a separation method from a single isothermal run.

The most important thermodynamic quantity of the separation is the adsorption enthalpy (heat of adsorption). This quantity gives information about the interaction between the adsorbent and adsorbate. Based on the strength of interaction the adsorption can be divided into three groups: physical, reversible chemical and irreversible chemical adsorption. The threshold value for the adsorption enthalpy between physical and chemical adsorption is 62,8 kJ/mol (or 15 kcal/mol) [2-4]. The adsorption entropy is connected to the loss of degrees of freedom upon adsorption of the molecules on the surface of the column material. Hence the adsorption entropy has a negative value [4]. From the rate theory one can determine the longitudinal diffusion coefficient and the resistance to mass transfer coefficient.

Besides the fact that all these quantities are indispensable for a rational development of the separation method, they are useful in understanding of the retention mechanism [1-4]. These information could also be explored in the Qualitative Structure Retention Relationship (QSRR) studies, i.e. the knowledge of thermodynamic and kinetic quantities gives a hint of which molecular variable (descriptor) has the greatest effect in the separation. Therefore this approach in QSRR would offer the possibility to reduce the number of variables in a rational way, to those which do have physical meaning in terms of the phenomena implied by the separation. It was already shown that a properly chosen equation involving 2-3 parameters among the physical variables (boiling point, molar refraction, molar volume, van der Waals volume, number of carbon atoms, dipole moment) and topological indices (connectivity index and general index of molecular complexity) gives a good correlation [17].

In this work we proposed to study the separation of some saturated hydrocarbons (n-hexane, 2-methyl-hexane, 3-methyl-hexane, 2,2-dimethyl-butane, 2,2-dimethyl-pentane, methyl-cyclopentane and cyclohexane) on a DB-1 capillary column. In the literature the Kováts retention indices of these compounds are available on DB-1 [18-21] and on various other capillary columns, determined mostly at 60ºC. A very good inter-laboratory reproducibility of the retention index on the same column can be observed. Moreover the intra-laboratory reproducibility of the Kováts retention index on three different columns, DB-1, squalene and SE-30 was also shown [21]. However, up to our best knowledge, the thermodynamic and kinetic parameters of the separation of these compounds on the poly-dimethyl-siloxane stationary phase are still missing. Therefore we aimed to determine these quantities. Since some of these hydrocarbons are the products of n-hexane isomerisation reaction, we also proposed to develop a separation method for a mixture of isomers.

RESULTS AND DISCUSSION

For the determination of the adsorption enthalpy and entropy of the analytes, isothermal chromatographic runs were performed in the temperature interval between 60 and 120ºC, at 2,0 ml/min constant carrier gas flow rate. The plot of retention time of the compounds at different temperatures is shown in Figure 1. The retention times seem to decrease exponentially with the temperature. The curves do not cross each other; therefore the elution order does not change in the studied temperature interval.

At the first glance it can be seen that the peaks are well resolved in the 60-90℃ interval. At higher temperature the dif ference of retention times of the adjacent peaks becomes closer to each other, suggesting the decrease of the resolution.

The elution order is the following: 2,2-dimethyl-butane; 2-methyl-pentane; 3-methyl-pentane; n-hexane; 2,2-dimethyl-pentane; methyl-cyclopentane; cyclohexane. This is in agreement with the literature. The Kováts retention indices corresponding to the compounds listed according to the elution order are the following: 538,0; 569,7; 584,4; 600; 625,7; 630,4; 664,2 [18-21]. The first four members of this elution order show that the retention time decreases with the branching of the carbon chain.

The retention factor (k) for each compound was calculated from the retention time (t_R) and gas holdup time (t_M), respectively, according to the equation (1). The gas holdup time was determined by measuring the retention time of air, which is neither retained nor separated to oxygen and nitrogen by the DB-1 column. The adjusted retention time ($t'_R=t_R-t_M$) is equal with the time the analyte spends on the stationary phase. Therefore the retention factor is the ratio between the times the analyte spends on the stationary phase and in the mobile phase, respectively.

The separation factor (α) has been calculated for the successively eluting peaks, according to the equation 2 and represented in function of temperature. The lower the separation factor, the more difficult to separate the peaks and vice versa. When two peaks are overlapped (partly or totally co-eluting), the separation factor becomes very close to or equal to 1.

$$k = \frac{t_R - t_M}{t_M} = \frac{t'_R}{t_M} \qquad (1)$$

$$\alpha = \frac{k_{i+1}}{k_i} = \frac{t'_{R,i+1}}{t'_{R,i}} \qquad (2)$$

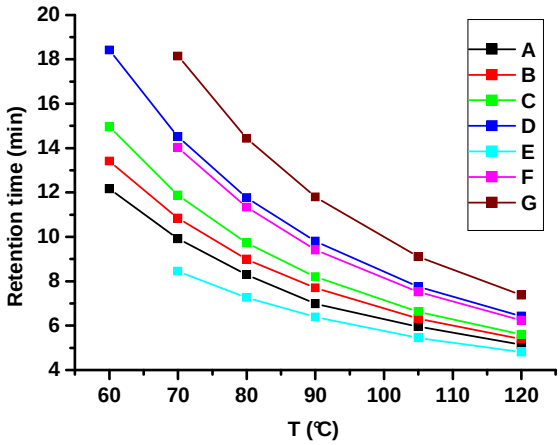

Figure 1. The effect of the temperature on the retention time of the analytes. A: 2-methyl-pentane, B: 3-methyl-pentane, C: n-hexane, D: methyl-cyclopentane, E: 2,2-dimethyl-butane, F: 2,2-dimethyl-pentane, G: cyclohexane.

It can be seen from Figure 2 (a) that the most difficult to separate peak-pair is methyl-cyclopentane and 2,2-dimethyl pentane. Surprisingly, the methyl-cyclopentane and cyclohexane peak-pair is the easiest to separate. The separation of the chain isomers of n-hexane is relatively easy. This separation is the most important from the point of view of n-hexane isomerisation reaction. For kinetic studies the reaction is carried out at low n-hexane conversion. In this case mostly 2-methyl-pentane and 3-methyl-pentane isomers are formed.

The resolution of the adjacent peaks has been calculated (equation 3). A resolution larger than 1,5 means baseline resolution of the adjacent peaks. The shapes of the resolution versus temperature curves are very similar to the retention factor versus temperature curves. Based on these figures it can be seen that an isothermal chromatographic method operating in the temperature interval between 80-105ºC is good with respect to the resolution of the peaks and the analysis time. The analysis time in case of an isothermal method at 80ºC would be roughly of 15 minutes. However the optimal method among the studied ones is the isothermal run at 105ºC. In this case the analysis time is reduced to about 10 minutes. The analysis time might be reduced further by developing a temperature programmed chromatographic method.

$$R_s = \frac{2 \cdot (t_{R,i+1} - t_{R,i})}{w_{i+1} + w_i} = \frac{2 \cdot (t'_{R,i+1} - t'_{R,i})}{w_{i+1} + w_i} \qquad (3)$$

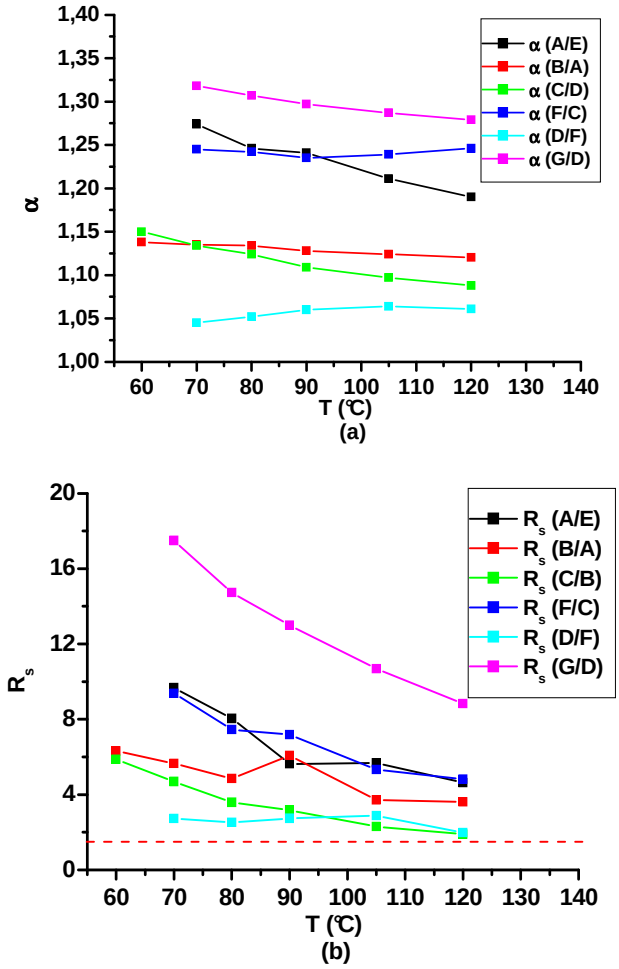

Figure 2. (a) The effect of the temperature on separation factor (α) of the successively eluting analytes. (b) The effect of the temperature on retention factor (R_s) of the successively eluting analytes. The dotted horizontal line at R_s=1,5 stands for the limit of baseline separation. The componds in both figures are: A: 2-methyl-pentane, B: 3-methyl-pentane, C: n-hexane, D: methyl-cyclopentane, E: 2,2-dimethyl-butane, F: 2,2-dimethyl-pentane, G: cyclohexane

The temperature programmed method can be developed experimentally, by trying different heating rates, starting- and end temperatures. The hold times at starting and end temperature can also be varied, but then the parameter space will be very large. Therefore a large number of experiments need to be done.

The other approach in method development is the modeling of the retention times under temperature programmed conditions. This is possible once the adsorption enthalpy and entropy is extracted from the isothermal runs [1-4, 14, 15].

For the determination of the thermodynamic quantities, the specific retention volume (V_g) was calculated (equation 4) at different column temperatures (T).

$$V_g = \frac{F_c \cdot j \cdot (t_R - t_M) \cdot 273}{m_{sp} \cdot T} \quad (4)$$

For the calculation of V_g, the adjusted retention time was determined and normalized with the mass of the stationary phase (m_{sp}). The flow rate of the carrier gas (F_c) should be constant for the measurements at different temperatures (i.e. the GC was operated in constant flow mode). Because the inlet and outlet pressure (p_i and p_o, respectively) is different at different column temperatures, the pressure drop along the column also changes significantly with the variation of the temperature. Therefore the requirement for isothermal and isobaric operation mode is apparently infringed. To overcome this, the retention volume data should be corrected with the James-Martin correction factor (equation 5) [1-4].

$$j = \frac{3}{2} \cdot \frac{\left[\left(\frac{p_i}{p_o}\right)^2 - 1\right]}{\left[\left(\frac{p_i}{p_o}\right)^3 - 1\right]} \quad (5)$$

We show here the simplification of the above equation for calculation of the James-Martin correction factor for large difference between the inlet and outlet pressure. When the relative pressure is higher than 6, the 2nd and 3rd power of the relative pressure is so high that the −1 term may be omitted from both the numerator and denominator of the above formula. Then it may be simplified further by canceling the power and the equation 6 will be equivalent with equation 5. The equivalence of these equations with the condition of p_r>6 is demonstrated by the Figure 3.

$$j = \frac{3}{2} \cdot \left(\frac{p_i}{p_o}\right)^{-1} \quad (6)$$

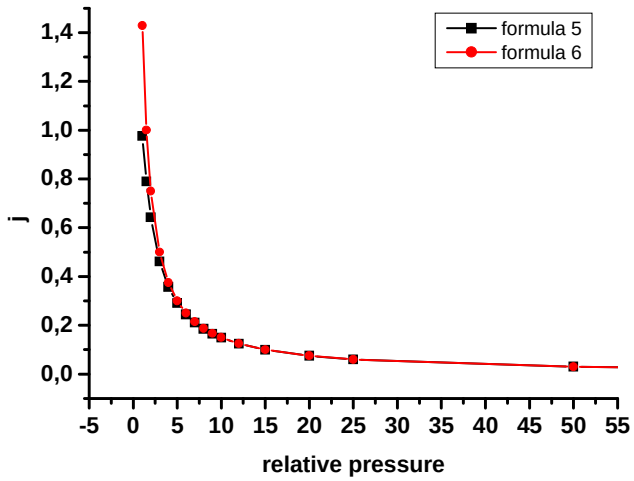

Figure 3. The James-Martin factor at different relative pressures.

Since the chromatographic experiments were done in a GC-MS setup, the end of the column is placed in the chamber of the mass spectrometer, where the pressure (p_o) is in the order of 10^{-8} bar. The inlet pressure (p_i) is slightly higher than the atmospheric pressure. Therefore the relative pressure (p_i/p_o) is in the order of 10^8. Because the above mentioned condition concerning the relative pressure is fulfilled, we used the simple equation (6) to calculate the James-Martin correction factor.

The logarithm of the specific retention volume was represented in function of the reciprocal temperature (Figure 4). The adsorption enthalpy was calculated from the slope of the straight line; while the adsorption entropy was calculated from the intercept, based on the equation (7) [1-4, 14]. The older literature [1] might be misleading with respect of the adsorption enthalpy. There the adsorption enthalpy is considered to be identical with the evaporation heat of the solute from a solution. However from the energetic point of view the adsorption-desorption equilibrium is not identical with the condensation-evaporation equilibrium.

The adsorption-desorption equilibrium involved by gas chromatography implies only adsorbate-adsorbent interactions at low adsorbate concentration (infinite dilution). In this case it is possible to determine the adsorption enthalpy of the adsorbate (analyte) on the adsorbent (stationary phase).

At higher adsorbate concentration the adsorbate-adsorbate interactions will have a contribution besides the adsorbate-adsorbent interaction. Therefore the apparent enthalpy will be a combination of the adsorption and condensation enthalpy.

$$\ln(V_g) = -\frac{\Delta H_{ads}}{R \cdot T} + \frac{\Delta S_{ads}}{R} \qquad (7)$$

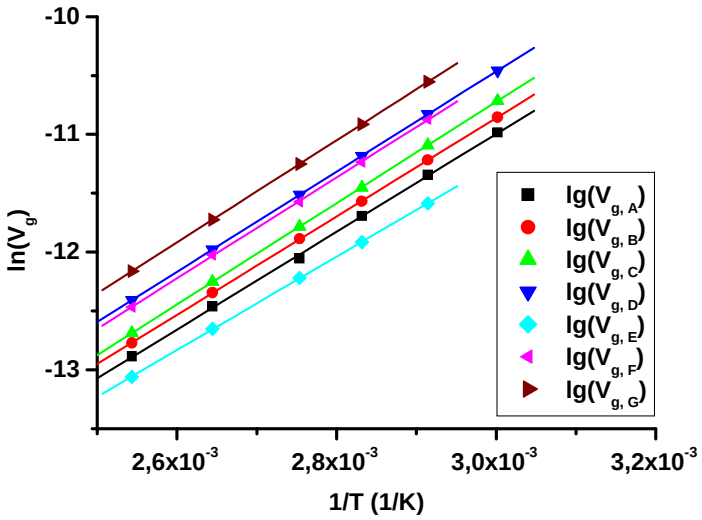

Figure 4. Plot of the logarithm of the specific retention volume (V_g) in function of the reciprocal temperature. A: 2-methyl-pentane, B: 3-methyl-pentane, C: n-hexane, D: methyl-cyclopentane, E: 2,2-dimethyl-butane, F: 2,2-dimethyl-pentane, G: cyclohexane.

In order to show that the thermodynamics of the adsorption and condensation is different, in the Table 1 we compiled the phase change thermodynamic quantities amongst the determined adsorption enthalpy and entropy. For comparison, we also determined the adsorption thermodynamic quantities for polar compounds like water, methanol and acetonitrile.

The magnitude of the adsorption enthalpy indicates physical adsorption of all the studied compounds on the stationary phase. The numerical values of adsorption enthalpy are close to each other regardless of the polarity of the analyte. This is not unexpected since the stationary phase is not polar. It can also be seen that the adsorption enthalpy of all the hydrocarbons are is 3 up to 4,5 kJ/mol more negative than the enthalpy of condensation. In case of the water and methanol the case was observed, however for the acetonitrile the adsorption enthalpy and condensation enthalpy are found to be equal within experimental errors.

The adsorption entropy determined from the Figure 3 has a significant negative value. This means that upon adsorption the degrees of freedom of the molecules are significantly reduced. The adsorption entropy of the hydrocarbons is almost the same. Compared to them the adsorption entropy of water, methanol and acetonitrile is more negative.

The condensation entropy is not readily available. However the vaporization entropy can be calculated based on the equation 8 [22]. The data needed for the calculation of the vaporization entropy are available. The enthalpy of vaporization is numerically equal to the absolute value of the condensation enthalpy (equation 9). Therefore the absolute value of the condensation entropy is equal with the vaporization entropy (equation 10). The values are close to 87-89 J/mol·K predicted by the Trouton's rule. However the water and methanol is a well known exception from the Trouton's rule due to hydrogen bonding.

It can be noted that the adsorption entropy is roughly 2,3 times more negative than the condensation entropy of the compounds. This also indicates that the thermodynamic parameters of adsorption and condensation are very different.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{boil}} \qquad (8)$$

$$\Delta H_{vap} = -\Delta H_{con} \qquad (9)$$

$$\Delta S_{vap} = -\Delta S_{con} \qquad (10)$$

When the average linear velocity of the carrier gas is increased the retention times and peak widths are decreasing and vice versa. For the optimization of the average linear velocity (u), and the determination of the kinetic parameters the Golay equation was used [1-4]. The Golay equation is similar to the van Deemter equation which is applicable in case of the packed columns. However in the capillary columns there is no eddy diffusion, therefore the Golay equation does not contain the first term of the van Deemter equation.

The height equivalent of the plate theory (H) was determined at different carrier gas flow rates. On plot (5) one can see that the minimum of the curves correspond roughly to the optimal average linear velocity of 23 cm/s (or 0,8 ml/min carrier gas flow rate). However, if the resolution at higher carrier gas flow rate is satisfactory as it was shown above, one may apply higher flow rate to shorten the analysis time [3].

Table 1. The thermodynamic parameters of the adsorption of the componds on poly-dimethyl-siloxane stationary phase. ΔH_{ads} – adsorption enthalpy, ΔS_{ads} – adsorption entropy, ΔH_{con} – enthalpy of condensation [22, 23], T_{boil} – boiling point at atmospheric pressure [23], ΔS_{con}– the condensation entropy, ΔH_{con}-ΔH_{ads} – the absolute difference between the enthalpy of condensation and the adsorption enthalpy. A: 2-methyl-pentane, B: 3-methyl-pentane, C: n-hexane, D: methyl-cyclopentane, E: 2,2-dimethyl-butane, F: 2,2-dimethyl-pentane, G: cyclohexane, H: water, I: methanol, J: acetonitrile.

Compound	**$-\tilde{\Delta}H_{ads}$ (kJ/mol)**	**$-\tilde{\Delta}S_{ads}$ (J/molK)**	**$-\tilde{\Delta}H_{con}$ (kJ/mol)**	**T_{boil} (K)**	**$-\tilde{\Delta}S_{con}$ (J/molK)**	ΔH_{con}-ΔH_{ads} **(kJ/mol)**
A	34,5±0,4	214,1±2,7	30,0±0,1	334,0±0,1	89,9±0,3	4,5±0,4
B	34,8±0,1	213,7±0,5	30,3±0,1	336,4±0,4	90,1±2,7	4,5±0,9
C	35,8±0,1	215,6±0,3	31,1±0,9	341,9±0,3	91,0±0,3	4,7±0,1
D	36,6±0,8	212,3±0,2	31,7±0,1	345,0±0,2	91,9±0,3	3,7±0,1
E	33,0±0,1	211,6±0,6	27,8±0,1	322,9±0,1	86,1±0,3	5,2±0,1
F	35,6±0,2	213,3±1,3	32,5±0,1	352,3±0,3	92,3±0,3	3,1±0,2
G	36,0±0,1	211,9±0,4	33,0±2,0	353,9±0,2	93,2±5,7	3,0±2,0
H	34,7±0,8	237,2±4,9	40,7	373,2±0,4	109,1	-6,0
I	31,2±1,0	223,9±3,4	37,0±2,0	337,8±0,3	109,5±5,9	-5,8±2,2
J	33,6±0,2	219,2±1,4	33,3±0,3	354,8±0,4	93,9±0,9	0,2±0,4

For the determination of the longitudinal diffusion term (B) and resistance to mass transport term, one can perform a nonlinear fitting procedure according to the Golay equation 11.

$$H = \frac{B}{u} + C \cdot u \qquad (11)$$

Here we present the linearization of the Golay-equation. Both sides of the equation 11 were multiplied by the average linear velocity of the carrier gas (u). The resulted equation 12 is still nonlinear, but after performing $H \cdot u = Y$ and $u^2 = X$ variable changes, it can be transformed into the linear equation 13. Then the B and C parameters can be determined according to the conventional linear fitting procedure (Figure 6).

$$H \cdot u = B + C \cdot u^2 \qquad (12)$$

$$Y = B + C \cdot X \qquad (13)$$

The value of the longitudinal diffusion coefficient (B) is high and the resistance to mass transfer (A) is small. This is a known feature for a GC-MS system, because there is a very large pressure drop along the column [3,4]. The variation of B and C values with the structure of the compounds is difficult to interpret. However the numerical values of the longitudinal diffusion coefficient are statistically close to each other.

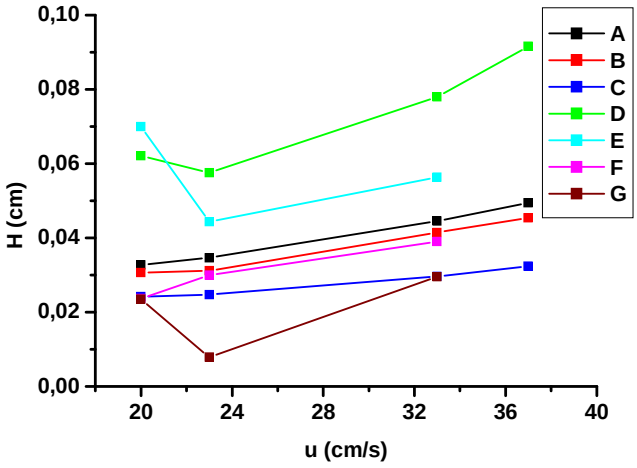

Figure 5. The effect of the carrier gas linear velocity on the height equivalent of the plate theory. A: 2-methyl-pentane, B: 3-methyl-pentane, C: n-hexane, D: methyl-cyclopentane, E: 2,2-dimethyl-butane, F: 2,2-dimethyl-pentane, G: cyclohexane.

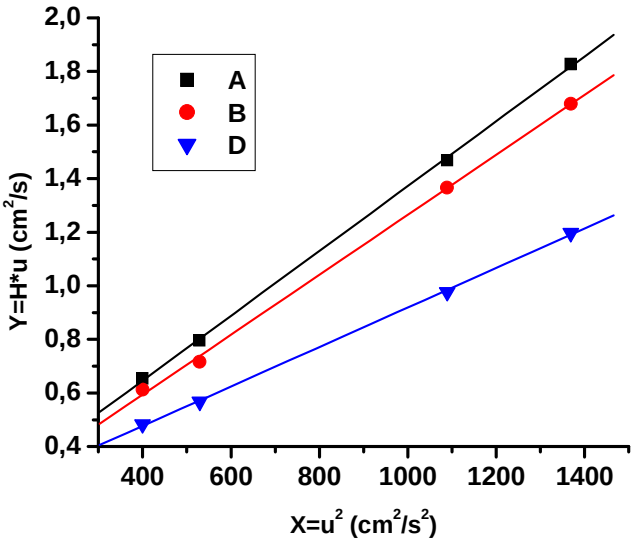

Figure 6. Fitting the linearized Golay equation. 2-methyl-pentane, B: 3-methyl-pentane, D: methyl-cyclopentane, the other compounds were omitted for clarity reasons.

Table 2. The longitudinal diffusion coefficient and resistance to mass transport of the compounds. (a) - because hexane was the solvent, and its peak was not symmetric (tailing) and much broader and compared to the other peaks, the data were omitted from this table.

Compound name	B (cm^2/s)	C (s)
2-methyl-pentane	1,62 ± 0,15	1,21 ± 0,02
3- methyl-pentane	1,46 ± 0,24	1,12 ± 0,03
n-hexane	(a)	(a)
methyl-ciklopentane	1,82 ± 0,11	0,74 ± 0,01
2,2-dimethyl-butane	1,41 ± 0,27	1,15 ± 0,06
2,2-dimethyl-pentane	1,73 ± 0,30	1,02 ± 0,04
ciklohexane	2,26 ± 0,35	0,99 ± 0,06

CONCLUSIONS

Jennings et al. pointed out in the preface of their textbook [3] that although chromatography is a very powerful analytical technique, many researchers are using it only as a means to an end and sometimes the better understanding of the chromatographic principles is lacking. However, due to the fact that it is such a powerful technique, even with little knowledge it is still possible to generate useful data. For the improvement of the data quality and quantity, the scientists who employ chromatography are encouraged for a more comprehensive understanding of their specific separation problem.

In this paper we proposed to follow these recommendations for the rational development of the separation method for some saturated hydrocarbons. In the first approach isothermal chromatographic runs were performed. An optimal chromatographic method was chosen with respect of resolution and analysis time. We also reported the thermodynamic and kinetic parameters of the separation process. These data will be used for the estimation of the retention times under temperature programmed conditions.

EXPERIMENTAL SECTION

The chromatographic measurements were performed on a GC-MS (Agilent 6890 GC coupled with Agilent 5975B MSD) setup. Two solutions have been prepared:

(a) 2-methyl-pentane and 3-methyl-pentane in n-hexane, and

(b) 2,2-dimethyl-butane, 2,2-dimethyl-pentane and cyclohexane in n-hexane as solvent. The concentration of all the compounds was approximately 1,0 vol%.

The sampling was performed via an automatic liquid sampler equipped with a 10 μl syringe. A volume of 1,0 μl solution has been injected in the liner heated up to 150℃. The split ratio was set to 1:15 for all the measurements. Helium was used for the split-flow.

DB-1 type non-polar column chromatographic column was used, which is suitable for general separation purposes. The length of the column was 60 m, the diameter was 320 μm, the thickness of the stationary phase was 5,0 μm. The stationary phase consists of 100% poly-dimethyl-siloxane. The characteristics of this stationary phase are the following: dispersion index=9, dipole index=0, acid-base index=0 [3]. Helium was used as carrier gas.

The first series of measurements consisted of isothermal runs at 60, 70, 80, 90, 105 and 120℃, and at constant carrier gas flow rate of 2,0 ml/min, respectively. In the second experiment series the carrier gas flow rate was set to 2,0; 1,6; 0,8 and 0,6 ml/min, respectively, while the column temperature was kept constant at 60℃. The average linear velocity of the carrier gas corresponding to the above flow rates were 37, 33, 23 and 20 cm/s, respectively. The variation of average linear velocities in a wider interval was not possible because of technical reasons. Flow rates lower than 0,6 ml/min could not be achieved because the pressure at the inlet of the column would be below the threshold level of 0,1 bar. However the upper limit of carrier gas flow rate of 2,0 ml/min was determined by the pumping capacity of the turbo-molecular pump of the MS detector.

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