

Mathematical Models of Solute Retention in Gas Chromatography as Sources of Thermodynamic Data. Part III. Alkylbenzenes as the Test Analytes

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Abstract

Direct determination of thermodynamic data has always been a complicated and troublesome experimental task. Gas chromatography is among long-established working tools well suited to performing this particular task indirectly. Our own results were first presented in the papers by Ciazynska-Halarewicz and Kowalska (1,2), and this article is Part III in the series. Present experiments are carried out on low- and medium-polarity stationary phases at five different temperatures ranging from 323K to 423K. They enable determination of two thermodynamic properties of the alkylbenzenes, molar enthalpy of vaporization (ΔH_{vap}), and the chemical potential of partitioning of the methylene group between the two phases of the chromatographic system ($\Delta\mu_{p(-CH_2-)}$). These properties are obtained from eight nonempirical models and, as is apparent from their derivation (3–7), the terms of the models have clearly defined physical meaning, which enables calculation of thermodynamic properties.

Introduction

This paper is Part III of a series devoted to an alternative means of acquisition of thermodynamic data by gas chromatography (GC). Part I focused on methyl *n*-alkyl ketones (1), Part II dealt with aldehydes (2), and this paper focuses on simple alkyl aromatic compounds (i.e., alkylbenzenes) as the analytes.

Classical determination of thermodynamic properties entails direct microcalorimetric measurements, which can prove quite complicated because of technical problems. These problems can, however, be overcome with the aid of suitable models (even in the form of simple mathematical equations), combined with appropriate analytical techniques. GC is a practical alternative means for the acquisition of numerical values of some thermodynamic data, specifically the enthalpy of vaporization and enthalpy of solution (1–4,6–16).

If it is agreed that in gas partition chromatography solute retention is achieved as a consequence of a long sequence of thermo-

dynamic equilibria related to the transfer of an analyte from the mobile (gaseous) to the stationary (liquid) phase and vice versa, a similarity between this process and others that depend on vaporization or solution (or both), is immediately apparent. Vaporization and solution are the mutually opposite physical processes and precisely for this reason should be characterized by the same numerical values, although with the opposite signs. This should also be valid for chromatographic processes.

There is another analogy between the transfer of an analyte from a low-polarity stationary phase to the gaseous mobile phase on the one hand and the process of vaporization of the pure liquid on the other. Vaporization of the pure liquid can be approximated by Trouton's rule (for the vast majority of liquids the entropy of vaporization is almost the same and is equal to $85 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1}$). Because of the aforementioned analogy, it seems only justified to accept that Trouton's rule can also be used to describe chromatographic retention.

In GC, thermodynamic data are acquired indirectly (i.e., from source data most often available in the form of retention times), and these measurements are relatively easy and simple. If precise measurements are taken under well-defined and repeatable experimental conditions, the huge amounts of experimental data (points) can be collected in a relatively short period of time. These data, with the analytes' physical characteristics (e.g., boiling points, molar volumes, and volume refractions) are then introduced into specially derived mathematical equations and further processed statistically to obtain the selected thermodynamic magnitudes.

The models of GC retention tested in this paper were devised in the course of the past several years (1–7) (Table I) and are not purely empirical models. Their derivation was based on physicochemical laws (phenomenological thermodynamics included) and chromatographic models. They assume the shape of mathematical equations, with fitting terms that have physical meaning; this makes them attractive candidates for the determination of mathematical magnitudes.

Obviously, these models were founded on certain premises, which have, to some extent, already been introduced, namely: (a) the similarity between the partitioning of an analyte in the chromatographic system and the physical process of vapor-

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ization \leftrightarrow solution, (b) the similarity between the transfer of an analyte in the nonpolar system and vaporization of the pure liquid, (c) the use of Trouton's rule to describe the vaporization of a liquid, and (d) the mutually opposite nature of the processes of vaporization and solution and the resulting equality of the absolute numerical values of some thermodynamic functions (differing only in the sign).

To these assumptions, one more can certainly be added. Because intermolecular interactions can be neglected, the new models should be better suited to systems with low-polarity stationary phases able to participate only in weak nonspecific interactions than to systems with polar stationary phases. Increasing the polarity of the stationary phase makes thermodynamic approximation of the process of retention by the process vaporization \leftrightarrow solution of the liquid analyte virtually impossible because one cannot neglect specific interactions between the analyte and the stationary phase.

Another advantage of the models discussed in this paper is their suitability for the prediction of analyte retention data.

Experimental

Approximately a dozen congeneric alkylbenzenes were investigated on three stationary phases of different polarity, but

with exactly the same liquid stationary phase film thickness (1 μm); all three were capillary columns of identical size (30 m \times 0.32 mm), produced by J&W Scientific (Folsom, CA). The polarities of the stationary phases expressed on the McReynolds scale were 217 for DB-1, 323 for DB-5, and 2188 for DB-Wax. Basic characteristics of these stationary phases are given in Table II.

The experiments were performed under isothermal conditions at five different temperatures from 323K to 423K in 25K intervals by means of a Fisons Instruments (Rodano/Milano, Italy) GC 8000 Series capillary GC equipped with flame ionization detection and cold oncolumn injection. Helium was used as the carrier gas.

All the reagents used (PolyScience, Niles, IL and J.T. Baker, Deventer, the Netherlands) were of standard GC grade.

Results and Discussion

In Table III are collected numerical values of the fitting data (B) and statistical data for the exponential equations (models I, II, VII, and VIII); Table IV contains analogous data for the linear equations (models III–VI). Although the results were evaluated statistically for all five temperatures, we present data only for two out of five measurement temperatures, 323K and 348K.

Table I. Mathematical Models Tested in this Study and Physicochemical Interpretation of the Fitting Terms that Incorporate the Thermodynamic Properties of Interest, ΔH_{vap} and $\Delta\mu_{p(-\text{CH}_2-)}$

Model	Fitting terms, which incorporate thermodynamic properties		Ref.
I $r = A \exp(BT_B) + \text{const.}$	A	$\frac{t_M \beta}{t_{R(\text{st})}} \exp\left(-\frac{\Delta H_{\text{vap}}}{RT_B}\right)$	B $\frac{\Delta H_{\text{vap}}}{RT_B T_C}$ (3)
II $r = A \exp\left(\frac{B}{T_B}\right) + \text{const.}$	A	$\frac{t_M \beta}{t_{R(\text{st})}} \exp\left(\frac{\Delta H_{\text{vap}}}{RT_C}\right)$	B $\frac{\Delta \bar{H}_{\text{vap}}}{R}$ (3)
III $l = A + BT_B$	A	$-\frac{100 \cdot 85 \cdot T_C^*}{\Delta\mu_{p(-\text{CH}_2-)}}$	B $\frac{100 \cdot 85^*}{\Delta\mu_{p(-\text{CH}_2-)}}$ (4,5)
IV $l = A + \frac{B}{T_B}$	A	$\frac{100 \cdot \Delta \bar{H}_{\text{vap}}}{\Delta\mu_{p(-\text{CH}_2-)}}$	B $-\frac{100 \cdot \Delta \bar{H}_{\text{vap}} \cdot T_C}{\Delta\mu_{p(-\text{CH}_2-)}}$ (4,5)
V $\ln k = A + BV_m + C \left(\frac{V_m}{T_B}\right)$	B	$\frac{\Delta H_{\text{vap}}}{RT_C V_m}$	C $-\frac{\Delta H_{\text{vap}}}{RV_m}$ (6)
VI $\ln k = A + BR_m + C \left(\frac{V_m}{T_B}\right)$	B	$\frac{\Delta H_{\text{vap}}}{RT_C V_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	C $-\frac{\Delta H_{\text{vap}}}{RV_m} \cdot \frac{n^2 + 2}{n^2 - 1}$ (6)
VII $r = A \exp\left[BV_m + C \left(\frac{V_m}{T_B}\right)\right] + \text{const.}$	B	$\frac{\Delta H_{\text{vap}}}{RT_C V_m}$	C $-\frac{\Delta H_{\text{vap}}}{RV_m}$ (7)
VIII $r = A \exp\left[BR_m + C \left(\frac{R_m}{T_B}\right)\right] + \text{const.}$	B	$\frac{\Delta H_{\text{vap}}}{RT_C V_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	C $-\frac{\Delta H_{\text{vap}}}{RV_m} \cdot \frac{n^2 + 2}{n^2 - 1}$ (7)

* After the determination of $\Delta\mu_{p(-\text{CH}_2-)}$, the numerical value of the enthalpy of vaporization is obtained from the relationship: $\Delta H_{\text{vap}} = \frac{1}{100} \Delta\mu_{p(-\text{CH}_2-)} + 85T_C$.

† Abbreviations: l = Kováts retention index, k = retention factor, t_M = hold-up time, $t_{R(\text{st})}$ = retention time of the standard solute, β = phase ratio, T_B = boiling point of the analyte, T_C = temperature of the column (of the analysis), R = gas constant, V_m = molar volume, R_m = molar refraction, and n = refractive index.

Table II. Basic Characteristics of the Applied Stationary Phases

Symbol	Composition	Polarity on McReynolds scale
DB-1	100% Polydimethylsiloxane	217
DB-5	95% Polydimethylsiloxane + 5% phenyl	323
DB-Wax	100% Poly(ethylene glycol)	2188

From analysis of the data contained in both tables, it is clearly apparent that all the scrutinized models can be used to predict solute retention under the used conditions. This conclusion is primarily confirmed by the relatively high values of the correlation coefficient (r), the high values of the F -test, the rather insignificant standard errors of estimation, the high values of the explained variance, and the low final losses of the estimated values. The number of cases (n) valid for each system was selected by use of the least-squares of median method.

Table III. Estimates of B for Models I, II, VII, and VIII and Statistical Data from the Estimations for the Analytes Investigated on Three Different Stationary Phases (Examples for Column Temperature $T_c = 323\text{K}$ and 348K)

Model	$T_c = 323\text{K}$					$T_c = 348\text{K}$				
	B	n	Loss	r	r^2 (%)	B	n	Loss	r	r^2 (%)
<i>DB-1</i>										
I	0.0349	18	0.0799	0.9996	99.97	0.0323	21	0.1570	0.9991	99.81
II	-5456.61	18	0.0233	0.9999	99.98	-5530.03	24	0.2893	0.9990	99.79
VII	0.1245	18	0.1312	0.9993	99.86	0.1085	18	0.0749	0.9992	99.84
VIII	0.4336	15	0.0305	0.9998	99.96	0.3920	21	0.1696	0.9990	99.80
<i>DB-5</i>										
I	0.0362	24	1.1745	0.9981	99.62	0.0329	27	0.9423	0.9994	99.88
II	-5733.47	24	2.6624	0.9957	99.13	-6211.90	30	2.1217	0.9989	99.78
VII	0.1346	18	0.2446	0.9994	99.87	0.1030	24	1.3593	0.9990	99.80
VIII	0.4715	18	0.1696	0.9996	99.91	0.3641	24	1.1362	0.9992	99.83
<i>DB-Wax</i>										
I	0.0239	18	0.4843	0.9938	98.76	0.0253	30	4.2084	0.9899	97.99
II	-3866.31	18	0.2179	0.9972	99.40	-4690.63	30	4.9106	0.9882	97.66
VII	0.1354	18	0.0361	0.9993	99.86	0.1076	24	0.1294	0.9995	99.90
VIII	0.5108	18	0.0406	0.9992	99.85	0.3812	27	0.5205	0.9984	99.69

* Abbreviations: n = number of measurements, loss = final loss minimized by means of the least-squares method, r = correlation coefficient, and r^2 = contribution from the explained variance.

Table IV. Fitting Terms B for Models III–VI (Including Their Errors) and Regression Data for the Analytes Investigated on Three Different Stationary Phases (Examples for Column Temperatures $T_c = 323\text{K}$ and 348K)

Model	$T_c = 323\text{K}$					$T_c = 348\text{K}$				
	$B \pm s_B$	n	r	F	s	$B \pm s_B$	n	r	F	s
<i>DB-1</i>										
III	3.47 ± 0.02	18	0.9998	49512.4	1.5044	3.56 ± 0.03	24	0.9993	16233.4	3.2737
IV	-568745 ± 2958	15	0.9998	36964.8	0.8544	-610593 ± 11015	21	0.9969	3072.8	4.3692
V	0.11 ± 0.00	18	0.9995	8191.7	0.0234	0.11 ± 0.00	24	0.9983	3092.7	0.0411
VI	0.37 ± 0.01	18	0.9996	10136.9	0.0211	0.35 ± 0.01	21	0.9994	7033.6	0.0156
<i>DB-5</i>										
III	3.56 ± 0.03	24	0.9993	16442.2	3.2539	3.74 ± 0.04	30	0.9986	10412.0	5.7469
IV	-610435 ± 11134	21	0.9968	3005.8	4.4165	-574367 ± 13779	27	0.9929	1737.7	12.0428
V	0.13 ± 0.00	24	0.9983	3101.6	0.0477	0.10 ± 0.01	30	0.9967	2042.0	0.0708
VI	0.46 ± 0.02	24	0.9986	3792.6	0.0432	0.35 ± 0.02	30	0.9972	2382.8	0.0656
<i>DB-Wax</i>										
III	2.78 ± 0.04	18	0.9982	4565.8	4.2111	2.88 ± 0.06	30	0.9940	2296.9	9.4229
IV	-415363 ± 5616	18	0.9985	5469.7	3.8486	-463948 ± 13203	30	0.9888	1234.8	12.7853
V	0.14 ± 0.00	21	0.9982	2466.2	0.0378	0.10 ± 0.00	27	0.9984	3697.4	0.0285
VI	0.50 ± 0.00	21	0.9987	3415.0	0.0322	0.37 ± 0.01	27	0.9979	2863.2	0.0324

* Abbreviations: n = number of measurements, r = correlation coefficient, F = the Fischer–Snedecor test value with the confidence level $p < 0.0000$ for each individual case, and s = the standard estimation error.

Table V. Numerical Values of ΔH_{vap} Calculated from the *B* Terms of Models I and IV–VIII for the Investigated Analytes and Data Taken from the Literature*

Analyte	ΔH_{vap} (kJ/mol)								
	Data calculated from the model						Data taken from the literature		
	I	IV	V	VI	VII	VIII	(a) [†]	(b)	(c)
Benzene	33.11		26.85	25.98	29.71	30.48	27.1	28.30	30.03
	32.91		28.23	26.81	27.89	29.69			
Toluene	35.97		32.11	30.86	35.53	36.21	31.1	32.31	32.62
	35.75		33.76	31.84	33.36	35.27			
<i>o</i> -Xylene	39.13		36.49	35.56	40.38	41.71			35.49
	38.90		38.37	36.68	37.92	40.63			
<i>m</i> -Xylene	38.63		37.12	35.69	41.08	41.87			35.03
	38.40	43.14 [‡]	39.04	36.82	38.57	40.78			
<i>p</i> -Xylene	38.57	41.93 [‡]	37.25	35.69	41.23	41.87	35.6		34.98
	38.34		39.17	36.82	38.71	40.78			
Ethylbenzene	38.35		37.00	35.45	40.94	41.58	34.7		34.78
	38.12		38.90	36.57	38.44	40.50			
Cumene	39.94		42.03	39.99	46.51	46.92			36.22
	39.70		44.20	41.26	43.67	45.70			
<i>n</i> -Propylbenzene	40.50		42.13	40.15	46.62	47.10	38.5		36.73
	40.26		44.30	41.42	43.77	45.88			

* The stationary phase was DB-1. Examples are given for two working temperatures, $T_c = 323\text{K}$ (upper values) and 348K (lower indented values).

[†] (a) ΔH_{vap} , DB-1, $T = 318\text{--}388\text{K}$ (10); (b) $-\Delta H_{sol}$, SE-30, $T = 333\text{--}373\text{K}$ (8); and (c) approximate values (independent of the stationary phase), calculated from Trouton's rule.

[‡] Mean values of the analyte studies.

Table VI. Numerical Values of ΔH_{vap} Calculated from the *B* Terms of Models I and IV–VIII for the Investigated Analytes and Data Taken from the Literature*

Analyte	ΔH_{vap} (kJ/mol)									
	Data calculated from the model						Data taken from the literature			
	I	IV	V	VI	VII	VIII	(a) [†]	(b)	(c)	(d)
Benzene	34.34		31.36	32.23	32.12	33.15	25.4			30.03
	33.63		26.35	26.48	27.58	26.72				
Toluene	37.31		37.50	38.28	38.41	39.37	29.3			32.62
	36.53		31.52	31.74	31.67	32.76				
<i>o</i> -Xylene	40.59		42.62	44.10	43.66	45.36		43.43	43.22	35.49
	39.75		35.82	36.57	35.99	37.74				
<i>m</i> -Xylene	40.07		43.36	44.26	44.42	45.53				35.03
	39.23	45.17 [‡]	36.44	36.70	36.62	37.88				
<i>p</i> -Xylene	40.01	37.47 [‡]	43.51	44.27	44.57	45.53	33.3	42.38	42.59	34.98
	36.57		36.71	39.17	36.75	37.88				
Ethylbenzene	39.77		43.21	43.96	44.26	45.22	32.8			34.78
	38.95		36.32	36.45	36.49	37.62				
Cumene	41.43		49.09	49.60	50.29	51.02				36.22
	40.56		41.26	41.13	41.46	42.44				
<i>n</i> -Propylbenzene	42.01		49.20	49.80	50.40	51.22	36.1			36.73
	41.29		41.35	41.14	41.55	42.62				

* The stationary phase was DB-5. Examples are given for two working temperatures, $T_c = 323\text{K}$ (upper values) and 348K (lower indented values).

[†] (a) ΔH_{vap} , DB-5, $T = 318\text{--}388\text{K}$ (3,10); (b) ΔH_{vap} , $T = 298\text{K}$ (11); (c) ΔH_{vap} , DB-5MS, $T = 313\text{--}351\text{K}$ (11); and (d) approximate values (independent of the stationary phase) calculated from Trouton's rule.

[‡] Mean values of the analyte studies.

One must also emphasize that at the other three temperatures, the statistical data again confirm the possibility of using the models for prediction of the analyte retention.

The high statistical validity makes it possible to use the models for acquisition of thermodynamic data, the main purpose of these approaches. The equations presented enable calculation of numerical values of the molar enthalpy of vaporization (ΔH_{vap}) and the chemical potential of partitioning of one methylene group between the phases of the chromatographic system ($\Delta\mu_{\text{p}(-\text{CH}_2-)}$).

Tables V–VII show numerical values of ΔH_{vap} for the analytes studied, determined by the use of the relationships verified in this paper and taken from literature.

Even preliminary comparison clearly reveals good correlation between the calculated data and those taken from the other sources. Data taken from the literature are, in a sense, scattered (most obviously for different stationary phases) because they originate from different references, were derived with the aid of various different methods, and use stationary phases similar to those used in our experiment, although not identical. Similarly, the working temperatures cited in the literature are not the same as those employed in our experiment. Owing to the widely accepted assumption that thermodynamic magnitudes are stable over a relatively wide range of temperatures, however, we can compare data taken from the other sources with our own. This comparison very much favors the results derived with the aid of the models investigated in this paper. The last columns in Tables V–VII

contain identical values of ΔH_{vap} , calculated by the use of the universal Trouton's rule, which couples the magnitude of ΔH_{vap} with the boiling point of a given substance T_{B} ($85 = \Delta H_{\text{vap}}/T_{\text{B}}$). Because of the approximate nature of Trouton's rule, the results obtained should also be regarded as approximate only, because they are independent of the chemical nature and polarity of the stationary phase and of the temperature of gas chromatographic analysis.

The quality of agreement of the thermodynamic data given in literature with those calculated using relationships I–VIII is certainly affected by, for example, the discrepancy between the temperatures at which chromatography was carried out and the temperature at which the physicochemical data used in our models (refraction index, density, molar volume, and molar refraction) were measured (usually 20°C, or 293K). The lowest measurement temperatures in our GC experiments were 323K and 348K (50 and 75°C), and with increasing measurement temperatures, the computational discrepancies also increase because the nonchromatographic magnitudes occurring in the equations largely depend on the aforementioned physicochemical values. Thus, it seems that our choice of these two temperatures, at which considerable numbers of errors are minimized, is well founded.

With all eight equations, the numerical values of ΔH_{vap} can be derived from the two fitting terms shown in Table I. Usually, however, one of the terms provides results that are clearly superior. Usually, the greater is the number of the individual physical magnitudes involved in a given fitting term, the better

Table VII. Numerical Values of ΔH_{vap} Calculated from the *B* Terms of Models I and IV–VIII for the Investigated Analytes and Data Taken from the Literature*

Analyte	ΔH_{vap} (kJ/mol)									
	Data calculated from the model						Data taken from the literature			
	I	IV	V	VI	VII	VIII	(a) [†]	(b)	(c)	(d)
Benzene	22.67		32.31	35.14	32.31	35.91	40.79	29.2	32.23	30.03
	25.86		26.66	28.32	27.66	28.87				
Toluene	24.63		38.64	41.74	38.64	42.66	42.71	32.5	35.24	32.62
	28.09		31.88	33.64	33.03	34.30				
<i>o</i> -Xylene	26.80		43.92	48.08	43.92	49.14	45.82			35.49
	30.56		36.24	38.75	37.60	39.51				
<i>m</i> -Xylene	26.45		44.68	48.26	44.68	49.32	44.88			35.03
	30.17	39.35 [‡]	36.87	38.90	38.26	39.66				
<i>p</i> -Xylene	26.41	39.33 [‡]	44.84	48.26	44.84	49.33	44.78	35.7		34.98
	30.13		37.00	38.90	38.39	39.66				
Ethylbenzene	26.26		44.53	47.93	44.53	48.99	44.58	35.4		34.78
	29.95		36.74	38.63	38.12	39.39				
Cumene	27.35		50.59	54.08	50.59	55.27	45.58			36.22
	31.19		41.74	43.59	43.31	44.44				
<i>n</i> -Propylbenzene	27.74		50.70	54.30	50.70	55.49	46.36	38.2		36.73
	31.63		41.84	43.76	43.41	44.62				

* The stationary phase was DB-Wax. Examples are given for two working temperatures, $T_c = 323\text{K}$ (upper values) and 348K (lower indented values).

[†] (a) ΔH_{vap} , PEG 4000, $T = 373\text{K}$ (4); (b) ΔH_{vap} , DB-Wax, $T = 318\text{--}388\text{K}$ (10); (c) $-\Delta H_{\text{sol}}$, PEG 20000, $T = 333\text{--}373\text{K}$ (8); and (d) approximate values (independent of the stationary phase) calculated from Trouton's rule.

[‡] Mean values of the analyte studies.

the agreement observed between the numerical value of ΔH_{vap} derived experimentally and the data taken from literature. Models I and II are an exception to this rule. For these the excessive complexity of the A term makes its usage for our purpose almost impossible. The only difference between the physical description of the pairs of suitable terms from the remaining models is the measurement temperature (T_c), which seems a decisive factor (except for model III) enhancing agreement between the computed data and those taken from literature.

Incidentally, with each of the eight models, better results were always obtained when using the B term. For this reason, numerical values of only B are given in Tables III and IV; these are used further for the calculation of the numerical values of ΔH_{vap} given in Tables V–VII.

Careful study of the numerical values of ΔH_{vap} revealed that more satisfactory results were obtained from the use of the low-polarity stationary phases (i.e., DB-1 and DB-5) than from the medium-polarity phase DB-Wax.

Particularly good results were obtained by the use of models I and V–VIII. The relatively large number of physicochemical properties combined in the B terms of all these models enables more precise description of the considered chromatographic system and, hence, ensures greater accuracy of the obtained results.

Model III furnished results that were too high. This might be because of the relatively higher error of this approach—computation of ΔH_{vap} from another thermodynamic property ($\Delta\mu_{\text{p}(-\text{CH}_2-)}$), which will be discussed later. Thus, we simply excluded computational results derived from model III.

Results derived from model II are not included in Tables V–VII. From this model we can obtain mean values of the enthalpy of vaporization only, one and the same for an entire population of the analytes. For the three stationary phases considered, these were exclusively negative numerical values because they were derived from B , which was also negative. The negative values of B derived from model II were in such striking contrast with analogous results from all the other models that they were disregarded without further discussion. It is also possible to obtain mean ΔH_{vap} values from model IV. In this instance, the values were positive as expected and of the correct order of magnitude, but again they were identical for all the analytes considered and, consequently, could be regarded only as rough approximations.

For the medium-polarity stationary phase (DB-Wax), the generally somewhat different performance of the individual models was repeated, but with simultaneous worsening of the ΔH_{vap} values derived. In summary, comparison of the thermodynamic values obtained resulted in differentiation of the stationary phases in terms of their polarity; significantly better agreement between the thermodynamic data derived from our models and those originating from literature was achieved for the less polar stationary phases. This is understandable because unwanted intermolecular interactions not mirrored by the models do not occur on the low polarity stationary phases. With increasing stationary phase polarity, specific interactions become more probable, leading to an evident worsening of the results.

At the other temperatures, the general scheme of the observed regularities is the same as at the lowest temperatures (i.e., results are better for the low-polarity stationary phases than for the medium-polarity phase). Elevation of the temperature of the experiment slightly increases the differences between the numerical values of ΔH_{vap} calculated by the use of the models tested and those taken from the literature. Although we lack comparative (i.e., reference) data valid for higher temperatures, we still noticed an interesting division of the investigated retention models into two groups. For models V–VIII, ΔH_{vap} values calculated at 20°C from the formulas containing large numbers of physicochemical properties were substantially larger than those calculated at higher temperatures. In contrast, for models with physicochemical rather simple fitting terms, similar breakdown is not evident. Once again this observation confirms the correctness of our choice of the temperatures of 323K and 348K as the most representative for the entire investigation.

As already mentioned, in model III (and also in model IV) we must first calculate the magnitude $\Delta\mu_{\text{p}(-\text{CH}_2-)}$, known as the chemical potential of partitioning of one methylene group H ($>\text{CH}_2$) in order to be able to calculate ΔH_{vap} . The most convenient way of determining the numerical value of $\Delta\mu_{\text{p}(-\text{CH}_2-)}$ is to use the B term from model III. The results, with the respective statistical information, are given in Table VIII.

High correlation coefficients (r) (certainly better on the low-polarity phases than on the medium-polarity phase), high numerical values of the F -test, and the relatively low standard errors (s , s refers to the retention index, the order of its numerical value is in the range of 10^2 – 10^3) give evidence of the high

Table VIII. Fitting B Terms for Model III (Including Their Errors) and the Regression Data for the Analytes Investigated on Three Different Stationary Phases at Five Different Measurement Temperatures

T_c (K)	$B \pm s_B$	n	r	F	s
DB-1					
323	3.47 ± 0.02	18	0.9998	49512.4	1.5044
348	3.56 ± 0.03	24	0.9993	16232.4	3.2737
373	3.69 ± 0.03	30	0.9990	13768.9	4.9326
398	3.83 ± 0.04	33	0.9987	11715.9	7.4037
423	3.79 ± 0.05	30	0.9978	6344.5	7.4615
DB-5					
323	3.56 ± 0.03	24	0.9993	16442.2	3.2539
348	3.74 ± 0.04	30	0.9986	10412.0	5.7469
373	4.01 ± 0.06	33	0.9970	5182.7	11.6492
398	4.10 ± 0.07	33	0.9960	3841.2	13.8514
423	4.16 ± 0.08	33	0.9945	2804.5	16.4243
DB-Wax					
323	2.78 ± 0.04	18	0.9982	4565.8	4.2111
348	2.88 ± 0.06	30	0.9940	2296.9	9.4229
373	3.08 ± 0.07	33	0.9930	2199.8	13.7654
398	3.31 ± 0.06	36	0.9941	2875.8	17.5722
423	3.40 ± 0.06	36	0.9852	3508.2	16.3613

* Abbreviations: n = number of measurements, r = correlation coefficient, F = the Fischer-Snedecor test value with the confidence level $p < 0.0000$ in each individual case, and s = the standard estimation error.

statistical validity of the model equations; this makes them suitable for the determination of $\Delta\mu_{p(-CH_2-)}$.

Selected $\Delta\mu_{p(-CH_2-)}$ data calculated from Model III and data taken from the literature are listed in Table IV, this time for all five working temperatures employed in the experiment.

As for ΔH_{vap} , the reference values of $\Delta\mu_{p(-CH_2-)}$ again originate from a variety of different sources, and refer to similar, but not identical, stationary phases and temperatures derived for different methyl group-containing compounds. Some numerical values taken from the literature are positive, whereas others are negative, which emphasizes a lack of consistency among the authors in achieving thermodynamic equilibrium in the vaporization \leftrightarrow solution process.

Numerical values of $\Delta\mu_{p(-CH_2-)}$ calculated from the data from our experiment are all positive, which corresponds well with the positive ΔH_{vap} values and most probably confirms a shift in the thermodynamic equilibrium of the analyte partitioning between the two phases towards vaporization.

For each individual temperature only one value of $\Delta\mu_{p(-CH_2-)}$ is provided, obviously a mean value, calculated for one $-CH_2-$ group. It must be stressed that the numerical value of $\Delta\mu_{p(-CH_2-)}$ refers to the methylene group of *n*-alkanes and is almost independent of the nature of the analyte. As a consequence, $\Delta\mu_{p(-CH_2-)}$ can be determined even from results focused on the determination of Kováts retention indices for analytes lacking methylene groups in their structure.

For these values, excellent correlation was also observed between the computed and reference $\Delta\mu_{p(-CH_2-)}$ values obtained on the low-polarity stationary phases, whereas for the medium-polarity phase the correlation was worse (the respective numerical values were slightly too high). This is obviously because of intermolecular interactions between the stationary phase and the analytes. If one stationary phase is focused on, a general trend of decreasing $\Delta\mu_{p(-CH_2-)}$ values with increasing working temperature is noticed, thus implying easier (i.e., less energetic) transfer of the methylene group from one phase to another. The numerical values of $\Delta\mu_{p(-CH_2-)}$, calculated by the use of the *A* term of model III, are all too high.

Conclusion

All the models tested in this study are characterized by very high statistical performance and can, therefore, be used to predict the retention of the investigated analytes in capillary GC and to derive the two thermodynamic properties, molar enthalpy of vaporization (ΔH_{vap}), and chemical potential of the partitioning of one methylene group ($\Delta\mu_{p(-CH_2-)}$).

The computed numerical values of the thermodynamic properties were very similar to data taken from the literature. It became clear that these models provided better thermo-

Table IX. Numerical Values of $\Delta\mu_{p(-CH_2-)}$, the Chemical Potential of the Partitioning of One Methylene Group between the Stationary and Mobile Phases Calculated from Model III and Taken from the Literature

		$\Delta\mu_{p(-CH_2-)} \text{ (J/mol)}$									
		$T_c = 323K$		$T_c = 348K$		$T_c = 373K$		$T_c = 398K$		$T_c = 423K$	
Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
DB-1											
2447	2282 (a)*	2388	2112 (a)	2303	1964 (a)	2220	1722 (a)	2243	1555 (a)		
	-2363 (b)		-2221 (b)		-2079 (b)		-1937 (b)		-1795 (b)		
	-2594 (c)		-2388 (c)		-2182 (c)		-1976 (c)		-1771 (c)		
	2591 (d)		2385 (d)		2178 (d)		1972 (d)		1765 (d)		
					1987 (e)		-1937 (h)				
					2009 (f)		-1860 (i)				
					1859 (g)		-1952 (j)				
DB-5											
2388	2399 (k)	2273	2152 (k)	2121	1978 (k)	2072	1821 (k)	2046	1636 (k)		
	1913 (l)		1839 (l)		1765 (l)		1691 (l)		1661 (l)		
					1935 (m)		-1916 (o)				
					2032 (n)						
DB-Wax											
3059	1897 (p)	2952	1725 (p)	2756	1607 (p)	2568	1448 (p)	2497	1263 (p)		
	-2035 (q)		-1919 (q)		-1793 (q)		-1672 (q)		-1550 (q)		
					1639 (r)		1674 (s)		1364 (r)		
							-1674 (t)				
							-1816 (u)				

* (a) OV-101 (17); (b) OV-101, based on reference (18); (c) PDMS, based on reference (18); (d) PDMS, based on reference (4); (e) SE-30, $T = 383.15K$ (5); (f) OV-1, $T = 383.15K$ (5); (g) OV-101, $T = 383.15K$ (5); (h) SE-30, $T = 394.6K$ (19); (i) OV-101, $T = 393.2K$ (20); (j) PDMS, $T = 393.2K$ (20); (k) OV-3 (17); (l) SE-54 (17); (m) SE-52, $T = 383.15K$ (5); (n) OV-3, $T = 383.15K$ (5); (o) OV-3, $T = 394.6K$ (19); (p) Carbowax 20M (17); (q) Superox 20M, based on reference (18); (r) PEG-20M (5); (s) PEG-20M, $T = 394.6K$ (5); (t) CW 20M, $T = 394.6K$ (19); and (u) CW 20M, $T = 393.2K$ (20).

dynamic results if the fitting terms involved physicochemical properties characteristic of the considered analytes.

Each model produced more accurate thermodynamic data if low-polarity stationary phases (and lower measurement temperatures) were used because these conditions lead to less pronounced intermolecular interactions not taken into account in the model assumptions. Thus, it can be concluded that the retention models studied differentiate among stationary phases with regard to their polarity.

GC can easily be used as a convenient means of acquiring thermodynamic data.

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