

Mathematical Models of Solute Retention in Gas Chromatography as Sources of Thermodynamic Data. Part IV. Aliphatic Alcohols as the Test Analytes

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Abstract

This study is the fourth consecutive part belonging to the cycle devoted to an alternative approach to deriving certain thermodynamic magnitudes. The previous three papers were dedicated, respectively, to ketones, aldehydes, and alkylbenzenes. In our present study (similar to the previous ones) the following working procedure is adopted. With the aid of capillary gas chromatography, the retention times are obtained for a wide variety of the aliphatic alcohols. The analyses are carried out isothermally on stationary phases of different polarity and at five different measuring temperatures. These data constitute an experimental basis for further processing with the aid of the specially devised mathematical equations. The fitting parameters of these equations, due to their physicochemical meaning, enable determination of certain thermodynamic data. Nine equations used in this study are the relationships coupling the selected retention data [relative retention (r), non-reduced relative retention (r_G), the retention factor (k), or the Kováts retention index (I)] and a variety of the physical magnitudes [the boiling point of the analyte (T_b), its molar volume (V_m), or its molar refraction (R_m)]. These relationships are tested with respect to their performance to predict the molar enthalpy of vaporization (ΔH_{vap}) of the analytes of interest (i.e., of aliphatic alcohols). Evaluation of the equations' performance is carried out through a comparison of the numerical values generated from this approach with those originating from the other methods, and a very good agreement was found between these two series of the data. The best molar enthalpy vaporization values (ΔH_{vap}) are obtained from the retention data originating from the most polar of the three investigated stationary phases (i.e., DB-Wax). Models V and VIII proved the best performing ones among the nine models tested in this study.

Introduction

In our earlier papers (1–3), the idea of applying the capillary gas chromatography (GC) and the specially devised mathematical equations (based on the theory of physical chemistry and the theory of chromatography) was successfully employed for the

determination of the thermodynamic data [i.e., the molar enthalpies of vaporization (ΔH_{vap})] for the selected ketones, aldehydes, and alkylbenzenes. These relationships are the one- or two-parameter linear or exponential equations, and their fitting parameters have a clearly defined physicochemical meaning. From the numerical values of these parameters (obtained when applying the relevant statistical procedures), the thermodynamic data of interest can finally be estimated.

The idea of deriving the thermodynamic data from the GC results is not new, and it was extensively discussed in the literature (4–13) as a novel area of application of this particular separation technique to the physicochemical studies. Investigations directly preceding this cycle of papers were presented in publications (14–19) as an attractive alternative for microcalorimetric measurements.

It is the aim of this paper to estimate the molar enthalpies of vaporization (ΔH_{vap}) for a wide selection of aliphatic alcohols in the way analogous to that presented in the literature (1–3) and to compare the obtained data with those already existing in literature.

Theory

Our procedure of deriving the numerical data of the molar enthalpy of vaporization (ΔH_{vap}) from the GC results is stepwise, with individual steps fully analogous to those extensively described in the preceding papers from this series (1–3). They comprise acquisition of the respective retention time values for the test analytes in a data base form, data processing, statistical evaluation of the computational results and drawing of the relevant conclusions.

In our study, nine different mathematical relationships, which are given in Table I, are employed. For the sake of brevity, their derivation is not introduced; however, in the last column of Table I, the references are given to these papers, which provide detailed derivations (as the discussed relationships are not purely empirical, but the semi-empirical models). In Table II, the physicochemical and chromatographic relationships utilized for the

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purpose of derivation are summarized.

The relationships summarized in Table II are very simple; therefore, it can rightfully be concluded that the mathematical models derived from these presumptions contain numerous simplifying assumptions. These assumptions were extensively discussed in the literature (1–3), so an interested reader is referred to those earlier papers.

It seems that the analytes discussed in this study (aliphatic alcohols), due to their considerable polarity, are going to provide a very demanding test of an overall correctness for models I–IX [as compared with the less polar alkylbenzenes, aldehydes, and ketones, previously employed as the test analytes (1–3)]. This happens so because the original assumptions upon which models I–IX were built focus on such analyte–stationary phase systems, in which the predominant role is played by the dispersive intermolecular interactions and not by those involving the localized hydrogen bonds. However, in the case of the aliphatic alcohol–DB–Wax stationary phase system, the localized inter-

molecular interactions will certainly play a significant enough (or even predominant) role. If models I–IX perform well, even in the case of alcohols, then they can rightfully be considered as “universal” and not only “local” (i.e., applicable to a limited group of the low polar analytes only), and, once again, GC will be confirmed as a precise tool, well suited for the derivation of thermodynamic data.

Experimental

The GC measuring conditions

The chromatographic analyses were carried out for 27 different aliphatic alcohols, among them, the homologous series with several or about a dozen representatives (see Table III). Moreover, *n*-alkanes were also chromatographed as the reference compounds used for determination of the Kováts retention indices with alcohols. All these compounds were of the GC standard purity grade (PolyScience Corporation, Niles, IL and J.T. Baker, Deventer, The Netherlands).

The chromatographic conditions were exactly the same ones, as in the case of the earlier employed test analytes and are described in the following sections.

Stationary phases

The stationary phases were: DB-1 (100% polydimethylsiloxane), polarity on the McReynolds scale 217 (low polar); DB-5 (95% polydimethylsiloxane + 5% phenyl), polarity 323 (low polar); and DB-Wax (100% polyethylene glycol), polarity 2188 (medium polar).

Apparatus and measuring conditions

Experiments were performed with a Fisons Instruments (Rodano/Milan, Italy) GC 8000 series capillary GC with on column injection (the sample aliquot 0.1 µL) and flame ionization detection (493 K). Helium was employed as carrier gas (purity 6.0; $F_c = 1.35 \text{ cm}^3 \text{ min}^{-1} = \text{const.}$) Isothermal chromatography was performed in the temperature range of 323 to 423 K at 25 K intervals.

Analysis was performed on three different capillary columns (Agilent Technologies, Palo Alto, CA/formerly J&W Scientific, Folsom, CA), each with a length of 30 m, an internal diameter of 0.32 mm, and stationary phase film thickness of $d_f = 1 \text{ µm}$.

Computer programs

Acquisition and immediate processing of the chromatographic data were performed by means of the computer program Chromax (Artur Dzieniszewski, Pol-Lab, Warsaw, Poland). The programs Statistica 5.1. PL (StatSoft, Tulsa, OK) and Matlab 6.5.0 (The MathWorks, Natick, MA)

Table I. Mathematical Models Tested in this Study and Physico-Chemical Interpretation of the Fitting Parameters, which Incorporate the Thermodynamic Properties of Interest (All Symbols Are Explained in the Glossary)

Model	Fitting Parameter		Derivation
	B	C	
I $r = A \exp \left[BV_m + C \left(\frac{V_m}{T_B} \right) \right]$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m}$	$-\frac{\Delta H_{\text{vap}}}{RV_m}$	(20)
II $r = A \exp \left[BR_m + C \left(\frac{R_m}{T_B} \right) \right]$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	$-\frac{\Delta H_{\text{vap}}}{RV_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	(20)
III $r_G = A \exp \left[BV_m + C \left(\frac{V_m}{T_B} \right) \right] + \text{const.}$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m}$	$-\frac{\Delta H_{\text{vap}}}{RV_m}$	(21)
IV $r_G = A \exp \left[BR_m + C \left(\frac{R_m}{T_B} \right) \right] + \text{const.}$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m} \cdot \frac{n^2 + 2}{n^2 - 2}$	$-\frac{\Delta H_{\text{vap}}}{RV_m} \cdot \frac{n^2 + 2}{n^2 - 2}$	(1,21)
V $r_G = A \exp(BT_B) + \text{const.}$	$\frac{\Delta H_{\text{vap}}}{RT_B T_c}$		(14)
VI $1nk = A + BV_m + C \left(\frac{V_m}{T_B} \right)$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m}$	$-\frac{\Delta H_{\text{vap}}}{RV_m}$	(17)
VII $1nk = A + BR_m + C \left(\frac{R_m}{T_B} \right)$	$\frac{\Delta H_{\text{vap}}}{RT_c V_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	$-\frac{\Delta H_{\text{vap}}}{RV_m} \cdot \frac{n^2 + 2}{n^2 - 1}$	(17)
	A	B	
VIII $l = A + BT_B$	$-\frac{100 \cdot \Delta H_{\text{vap}} \cdot T_c}{T_B \cdot \Delta \mu_{p(-CH_2-)}}$	$\frac{100 \cdot \Delta H_{\text{vap}}}{T_B \cdot \Delta \mu_{p(-CH_2-)}}$	(15,16)
IX $l = A + \frac{B}{T_B}$	$\frac{100 \cdot \Delta \bar{H}_{\text{vap}}}{\Delta \mu_{p(-CH_2-)}}$	$-\frac{100 \cdot \Delta \bar{H}_{\text{vap}} \cdot T_c}{\Delta \mu_{p(-CH_2-)}}$	(15,16)

were used for statistical analysis of the data. Excel (Microsoft Corporation, Redmond, WA) was used for other computations.

Raw data processing

Building of the experimental data base for further mathematical and statistical processing

Retention times were measured for 27 aliphatic alcohols with the straight and branched carbon chains at five different measuring temperatures (323, 348, 373, 398, and 423 K) and using three stationary phases of different polarity. However, the geometrical parameters of the employed columns (i.e. their length, inner diameter, and the film thickness) were identical in order to facilitate direct comparisons among the obtained numerical data. The analyses were run with a constant carrier gas flow rate, and they lasted no longer than 100 min (as a sound compromise between the maximum number of the separated compounds and still reliable values of the retention time). In order to multiply the measured data, each analyte was chromatographed three times in the given working conditions.

Retention times of *n*-alkanes (indispensable for calculation of the Kováts retention indices; see models VIII and IX) were measured in an analogous way.

Through transformation of the measured retention times, the experimental data base was built containing such retention parameters, as relative retention (*r*), non-reduced relative retention (*r_c*), logarithm of the retention factor ($\ln k$), and the Kováts retention index (*I*).

Selection of the relevant data (building of the computational data base)

Then the computational database was derived from the experimental one, preliminarily using the statistical least median of squares (LMS) procedure. With the aid of this procedure for each of the nine models and for each kind of the applied chromatographic conditions, an individual set of valid data was selected, with the outlier points eliminated. These purified data sets were then statistically processed.

As the LMS procedure applies to the linear equations only, the exponential equations had to be linearized first.

Derivation of statistical parameters (enabling assessment of the predictive power with respect to retention) and of the fitting parameters for models I-IX

The double goal of this step was attained with aid of a single statistical procedure, adequate to a given type of the model considered. With the

Table II. Thermodynamic and Chromatographic Relationships, Employed for Derivation of Models I-IX from Table I; by 'x' Applicability of a Given Relationship to Derivation of a Given Model Was Indicated (All Symbols Are Explained in the Glossary)

Equation	Model				
	I, II	III, IV	V	VI, VII	VIII, IX
$1/n K_p = \frac{\Delta\mu_p}{RT_c}$	x	x	x		x
$\Delta\mu_p = \Delta H_{vap} - T_c \Delta S_{vap}$	x	x	x	x	x
$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_B} = const. = 85$ (the Trouton's Rule)	x	x	x	x	x
$k = K_p \beta$	x	x	x		x
$\frac{l}{100} = \frac{\Delta\mu_p}{\Delta\mu_{p(-CH_2-)}} \cong z$					x
$\Delta H_{vap} \sim V_m$	x	x		x	

Table III. Physicochemical Properties of Aliphatic Alcohols Used in the Gas Chromatographic Investigations (All Symbols are Explained in the Glossary)

Alcohol	Summaric equation	n	d ²⁰	M	V _m	R _m	T _B
Methanol	CH ₃ OH	1.325	0.790	32.04	40.56	8.16	337.65
Ethanol	C ₂ H ₅ OH	1.362	0.790	46.07	58.32	12.93	351.45
1-Propanol	C ₃ H ₇ OH	1.384	0.800	60.10	75.12	17.56	370.40
1-Butanol	C ₄ H ₉ OH	1.399	0.810	74.12	91.51	22.15	391.15
1-Pentanol	C ₅ H ₁₁ OH	1.410	0.810	88.15	108.83	26.96	411.15
1-Hexanol	C ₆ H ₁₃ OH	1.418	0.820	102.18	124.61	31.40	430.15
1-Heptanol	C ₇ H ₁₅ OH	1.424	0.820	116.20	141.71	36.18	449.15
1-Octanol	C ₈ H ₁₇ OH	1.429	0.830	130.23	156.90	40.46	466.15
1-Nonanol	C ₉ H ₁₉ OH	1.433	0.830	144.26	173.81	45.21	488.15
1-Decanol	C ₁₀ H ₂₁ OH	1.437	0.830	158.29	190.71	49.98	504.65
1-Undecanol	C ₁₁ H ₂₃ OH	1.440	0.830	172.31	207.60	54.71	521.50
1-Dodecanol	C ₁₂ H ₂₅ OH	1.440	0.830	186.34	224.51	59.17	534.65
2-Propanol	C ₃ H ₇ OH	1.377	0.786	60.10	76.46	17.59	355.55
2-Butanol	C ₄ H ₉ OH	1.397	0.810	74.12	91.51	22.04	372.65
2-Hexanol	C ₆ H ₁₃ OH	1.414	0.810	102.18	126.15	31.49	410.15
2-Heptanol	C ₇ H ₁₅ OH	1.421	0.820	116.20	141.71	35.94	433.15
2-Octanol	C ₈ H ₁₇ OH	1.423	0.820	130.23	158.82	40.48	452.15
3-Hexanol	C ₆ H ₁₃ OH	1.415	0.819	102.18	124.76	31.24	408.15
2-Methyl-1-propanol	C ₄ H ₉ OH	1.396	0.802	74.12	92.42	22.18	381.15
2-Methyl-1-butanol	C ₅ H ₁₁ OH	1.411	0.820	88.15	107.50	26.67	401.15
3-Methyl-1-butanol	C ₅ H ₁₁ OH	1.405	0.810	88.15	108.83	26.69	404.65
2-Methyl-2-butanol	C ₅ H ₁₁ OH	1.405	0.818	88.15	107.76	26.41	384.65
2-Methyl-1-pentanol	C ₆ H ₁₃ OH	1.418	0.824	102.18	124.00	31.25	421.15
4-Methyl-2-pentanol	C ₆ H ₁₃ OH	1.411	0.802	102.18	127.41	31.64	405.15
2-Methyl-3-pentanol	C ₆ H ₁₃ OH	1.417	0.819	102.18	124.76	31.37	401.15
3-Methyl-3-pentanol	C ₆ H ₁₃ OH	1.418	0.824	102.18	124.00	31.25	396.00
2,4-Dimethyl-3-pentanol	C ₇ H ₁₅ OH	1.425	0.829	116.20	140.17	35.84	412.65

exponential equations (Models I–V), the non-linear estimation by means of the quasi-Newton method was applied and with the linear equations (Models VI–IX), the one- or two-parameter linear regression was used. Consequently, several statistical parameters were calculated, enabling evaluation of a given data set. The parameters were: the correlation coefficient (R), the error of the fit of a given model to the data used for its construction [the root mean square error (RMS)], and the error of the predictive performance of the model [(the root mean square error of cross-validation (RMSCV)]. In this work, the leave-one-out approach was used to determine the RMSCV values. Besides, these two types of the error were also given in the standardized form (as %RMS and %RMSCV), to enable direct comparisons among the results originating from the different working conditions. For the standardization purpose, the respective error value was divided by the mean value of the dependent variable and multiplied by the factor of 100.

The numerical values of RMS and RMSCV (and also those of their standardized analogues) ought to be as low as possible because only then is evidence available of good fitting (RMS) and

of good predictive power (RMSCV) of the model. The respective numerical data were obtained for each model considered and for all the applied analytical conditions. The obtained values of RMS and RMSCV fall within the range from 0.1 to several units and their percentage analogues in the most cases do not exceed the level of several percent. The correlation coefficient values (R) in the most cases exceed the 0.98–0.99 level.

From this analysis it comes out that statistical parameters referring to each and every stationary phase are very good. In that way, the indispensable condition with respect to all the assessed models is fulfilled, namely their outstanding ability to predict the analytes retention is confirmed. It can also rightfully be claimed that the statistically best results were obtained for the most polar of the three stationary phases (i.e., for DB-Wax). No evident impact has been revealed of the working temperature on statistical parameters of interest.

Examples of the statistical results are shown in Table IV, and they refer exclusively to the best performing stationary phase (i.e., to DB-Wax). As mentioned in the preceding part of this study, the statistical processing of the database resulted in derivation of the fitting parameters A, B, and C for each individual model also. Numerical values of the fitting parameters that are valid for our further computations are also given in Table IV.

Results and Discussion

The last step was a comparison of the molar enthalpy of vaporization values (ΔH_{vap}) (calculated upon our experimental data from the fitting parameters of Models I–IX) with the analogous enthalpy values found in the literature and in certain cases calculated from the approximative Trouton's Rule also (see Table V). The data taken from the literature originate from the different (and not always chromatographic) experimental and computational approaches and, of course, from the different working conditions. In this study, it was assumed that the numerical values of thermodynamic magnitudes are approximately constant within a considered range of temperatures (100K), thus allowing for a direct comparison of the data originating from the different working temperatures (even if this assumption is somewhat rough).

Hence, it is virtually impossible to judge which of these data are more reliable than the other; thus, the comparison is not easy. In order to solve this problem, the following procedure was adopted. For each reference data set, possibly closest to our experimental conditions, first the minimum and the maximum value was chosen, and then, this range was expanded from both sides by the margin of 10%, in order to accommodate the anticipated experimental and/or computational errors contained within the data taken from the literature.

Table IV. Statistical Evaluation of Models I–IX and of the Values of the Fitting Parameters A, B, and C, Together with the Respective Errors (for Each Model the Values of these Parameters Only Are Given, Which Are Used for Calculation of the Molar Enthalpies of Vaporization) (N—the Number of Valid Cases) –Column: DB-Wax, Selected Examples

Eq.	Tc [K]	Fitting parameter		N	RMS	%		R	
		B ± s _B	C ± s _C			RMS	RMSCV		
I	323	0.156 ± 0.001	-60.752 ± 0.612	27	0.46	7.6	0.44	7.4	0.9923
	373	0.120 ± 0.000	-57.252 ± 0.236	42	0.76	5.0	0.82	5.4	0.9987
	423	0.108 ± 0.000	-52.059 ± 0.273	60	0.79	14.1	0.83	14.8	0.9876
II	323	0.706 ± 0.005	-274.388 ± 2.411	27	0.90	7.8	0.83	7.2	0.9941
	373	0.473 ± 0.001	-224.044 ± 0.963	42	0.88	5.8	0.95	6.2	0.9982
	423	0.457 ± 0.002	-210.091 ± 1.265	54	0.67	15.2	0.71	16.2	0.9777
III	323	0.173 ± 0.001	-67.022 ± 0.531	27	0.36	6.0	0.40	6.7	0.9952
	373	0.117 ± 0.000	-54.950 ± 0.258	39	0.23	5.4	0.25	5.9	0.9978
	423	0.099 ± 0.000	-45.554 ± 0.220	48	0.08	5.0	0.08	5.3	0.9919
IV	323	0.707 ± 0.004	-274.635 ± 1.819	27	0.39	6.5	0.39	6.6	0.9940
	373	0.472 ± 0.001	-223.853 ± 0.945	51	0.21	4.8	0.23	5.2	0.9982
	423	0.399 ± 0.002	-181.794 ± 1.098	66	0.12	7.8	0.12	8.2	0.9791
V	323	0.048 ± 0.001		30	0.57	10.3	0.64	11.7	0.9896
	373	0.029 ± 0.000		48	0.31	6.0	0.34	6.6	0.9990
	423	0.026 ± 0.000		63	0.20	6.6	0.22	7.4	0.9984
VI	323	0.159 ± 0.002	-59.970 ± 0.859	27	0.09	4.5	0.10	5.1	0.9937
	373	0.116 ± 0.000	-54.468 ± 0.095	42	0.05	4.2	0.06	4.4	0.9969
	423	0.110 ± 0.001	-50.541 ± 0.251	51	0.13	-26.9	0.14	-28.5	0.9829
VII	323	0.643 ± 0.009	-241.077 ± 4.074	27	0.11	5.2	0.12	5.8	0.9919
	373	0.462 ± 0.001	-213.497 ± 0.448	42	0.06	4.7	0.06	5.0	0.9962
	423	0.392 ± 0.003	-166.774 ± 1.616	57	0.18	-33.1	0.20	-35.4	0.9676
		A ± s _A	B ± s _B						
VIII	323	-629.0 ± 7.3	4.5 ± 0.0	33	11.30	1.1	12.21	1.2	0.9946
	373	-992.7 ± 4.2	5.5 ± 0.0	48	13.59	1.1	14.19	1.1	0.9982
	423	-1270.7 ± 4.1	6.1 ± 0.0	60	28.78	2.1	29.65	2.2	0.9954
IX	323	2580 ± 10	-589410 ± 3668	30	16.86	1.6	18.21	1.8	0.9885
	373	3600 ± 9	-951980 ± 3565	60	31.40	2.4	32.73	2.6	0.9848
	423	4200 ± 7	-119940 ± 2814	51	28.43	2.1	29.92	2.2	0.9959

For the eight out of the nine models (Models I–IV and VI–IX), the enthalpy of vaporization can be calculated from the two fitting parameters (B and C or A and B) and in the case of Model V from one fitting parameter (B) only. It is evident that a vast number of the enthalpy of vaporization values were calculated, and the totality of them are presented in the literature (27). Although each model performs very well in the case of each stationary phase considered, for the sake of this study, the best performing ones were selected, and these are given in Table VI (these data correspond with the fitting parameters contained in Table IV).

Indisputably, Models V and VIII proved the best and provided excellent numerical values of the molar enthalpy of vaporization of aliphatic alcohols, independent of the assumed measuring conditions. The only exception were the last two analytes, 3-methyl-3-pentanol and 2,4-dimethyl-3-pentanol. For these two compounds no measured vaporization enthalpies were available in the literature; so the only reference was the values computed from the Trouton's Rule, and, for this reason, the data from our

experiment falls beyond the scope of the satisfactory results. Thus, Models V and VIII can be considered as relatively insensitive to the working temperature and to the polarity of the applied stationary phase, although the fitting parameter B (which incorporated the working temperature of the column and, in that way, better characterized the measuring conditions than parameter C) provided the better values of the enthalpy of vaporization.

When it comes to discussing the polarity of the stationary phases, the results originating from the most polar DB-Wax are considerably better than those measured with use of the less polar DB-1 and DB-5. In chemical terms, DB-Wax is 100% polyethylene glycol, having in its structure the same hydroxyl functionality as aliphatic alcohols. Thus, it can be deduced that the particularly good quality of the results obtained with use of DB-Wax is influenced by structural similarity between the analytes and the stationary phase. Besides in the case of DB-Wax, the highest numerical values of the molar enthalpy of vaporization were obtained. This result clearly demonstrates an increased energetical input needed for disruption of intermolecular inter-

Table V. The Enthalpy of Vaporization Values (ΔH_{vap}) of the Investigated Analytes Taken from Literature or Calculated from the Trouton's Rule (the Numerical Values Are Ascribed to the Respective Chromatographic Columns); in Certain Cases the Vaporization Enthalpies Missing in the Literature Were Extrapolated from the Relationship: Enthalpy of Vaporization = f (Number of Carbon Atoms in a Molecule of the Given Homologue)

Numerical values of ΔH_{vap} taken from literature [kJ mol ⁻¹]										
Experimental column	All columns*					DB-WAX*		DB-1*	DB-5*	
	a	b	c	d	e	f	g	h	i	j
Alcohol										
Methanol	35.21	37.43	37.60	13.53	28.70	33.89	31.00	16.50	19.90	37.32
Ethanol	38.56	42.32	42.30	17.77	29.87	37.94	33.50		23.80	42.24
1-Propanol	41.44	47.45	47.50	22.02	31.48	42.15	37.20	24.00	27.50	47.49
1-Butanol	43.29	52.35	52.30	26.19	33.25	46.00				52.43
1-Pentanol	44.36	57.02	57.00	30.62	34.95	49.90				56.90
1-Hexanol	44.50	61.61	61.10	34.72	36.56	53.58				61.59
1-Heptanol	50.70	66.81	66.80	38.97	38.18	58.14				66.82
1-Octanol	53.10	70.98	70.10	43.24	39.62	62.37				70.96
1-Nonanol	55.72	76.86	76.90	47.48	41.49	66.29				76.86
1-Decanol	58.23	91.96	80.90	51.72	42.90	70.34				81.50
1-Undecanol	60.75	86.47	84.70	55.97	44.33	74.39				86.52
1-Dodecanol	63.26	91.37	90.00	60.21	45.45	78.44				91.96
2-Propanol	39.85	45.39	45.30	20.32	30.22		33.60	23.20	22.10	
2-Butanol	40.75	49.72	49.70	24.47	31.68					
2-Hexanol	41.01	58.46	58.30	32.81	34.86					
2-Heptanol	43.49	62.81	62.64	36.94	36.82					
2-Octanol	44.40	67.17	66.97	41.11	38.43					
3-Hexanol			58.60		34.69					
2-Methyl-1-propanol	41.82	50.82	50.80		32.40					
2-Methyl-1-butanol		55.16	54.10		34.10					
3-Methyl-1-butanol	44.07	55.61	54.30		34.40					55.65
2-Methyl-2-butanol	39.04	50.10		26.05	32.70					50.17
2-Methyl-1-pentanol	50.20		59.40		35.80					
4-Methyl-1-pentanol	44.46	60.47	60.50		34.44					
2-Methyl-3-pentanol			56.00		34.10					
3-Methyl-3-pentanol					33.66					
2,4-Dimethyl-3-pentanol					35.08					

* a = measurement at the boiling point, p = 1atm (22); b = 298K (22); c = 298.15K, GC: HP-5 (23); d = GC: C78, 358-418K (24); GC: C78, 363-483K [25]; e = the Trouton's Rule; f = GC: Carbowax 1540, 343-363K (26); g, h, i = (4); j = 298K (10).

actions of the analyte–stationary phase type, pronounced the most in the case of this most polar stationary phase.

The working temperature of the column seems the most efficient tool in controlling intermolecular interactions of the analyte–stationary phase type. And indeed, on the most polar stationary phase (DB-Wax), the best results were obtained at the highest working temperatures. With the low polar stationary phases, intermolecular interactions between the analytes and the stationary phase are apparently weaker and the considerably better enthalpies of vaporization were, in this case, obtained at the lower temperatures. It seems that with the low polar stationary phases, the decisive role is played by the lowest possible difference between the working temperature of the column and (in the most cases ambient) temperature of determination of certain tabulated physicochemical magnitudes, employed in Models I–IX (like, e.g., the density, molar volume, or molar refraction of the test analytes).

With one and the same stationary phase, an impact of the measuring temperature on the numerical values of the enthalpy of

vaporization is also observable. The higher the measuring temperature, the lower the enthalpy of vaporization of any given analyte becomes, as the energy input necessary to transfer its molecules from the liquid to the gaseous phase becomes lower.

The above comments are of the general nature only and of course, certain deviations from the observed regularities can happen, which, however, do not disqualify the models and the assumed approach. Summing up, an excellent agreement between the molar enthalpies of vaporization, ΔH_{vap} , obtained from this experiment for aliphatic alcohols and those taken from the literature gives evidence of the fact that this approach can be viewed as universal and applicable to a wide spectrum of the organic compounds and compound classes.

Conclusions

The mathematical models tested in this study perform well statistically and allow a reliable prediction of the retention and

Table VI. The Enthalpy of Vaporization Values (ΔH_{vap}), Calculated Upon the Experimental Gas Chromatographic Data from the Fitting Parameters (B or C) for the Two Best Performing Models (eqs V and VIII) Out of the Nine Tested Ones (DB-Wax, Examples Valid for the Three Working Temperatures: the Lowest, the Medium, and the Highest—Corresponding with Table IV).

The ΔH_{vap} values [kJ mol ⁻¹] calculated with use of the fitting parameters of eq.									
Alcohol	V			VIII					
	323	373	423	323		373		423	
T _c [K]									
parameter	B	B	B	B	C	B	C	B	C
Methanol	43.50	30.35	30.86	14.08	16.35	11.69	14.48	11.24	11.31
Ethanol	45.28	31.59	32.12	22.32	25.91	18.52	22.95	17.82	17.93
1-Propanol	47.72	33.29	33.85	30.31	35.19	25.15	31.16	24.20	24.34
1-Butanol	50.40	35.16	35.75	38.23	44.37	31.72	39.30	30.52	30.70
1-Pentanol	52.97	36.96	37.58	46.54	54.02	38.61	47.84	37.15	37.37
1-Hexanol	55.42	38.67	39.31	54.19	62.90	44.96	55.70	43.26	43.51
1-Heptanol	57.87	40.37	41.05	62.43	72.47	51.80	64.18	49.85	50.14
1-Octanol	60.06	41.90	42.60	69.82	81.05	57.94	71.78	55.75	56.07
1-Nonanol	62.89	43.88	44.61	78.03	90.57	64.74	80.21	62.29	62.65
1-Decanol	65.02	45.36	46.12	86.27	100.13	71.58	88.68	68.87	69.27
1-Undecanol	67.19	46.88	47.66	94.43	109.61	78.35	97.07	75.39	75.83
1-Dodecanol	68.88	48.06	48.86	102.12	118.54	84.73	104.98	81.53	82.00
2-Propanol	45.81	31.96	32.49	30.35	35.23	25.18	31.20	24.23	24.37
2-Butanol	48.01	33.50	34.06	38.03	44.15	31.56	39.10	30.37	30.54
2-Hexanol	52.84	36.87	37.48	54.35	63.08	45.09	55.87	43.39	43.64
2-Heptanol	55.81	38.94	39.59	62.02	71.99	51.46	63.76	49.52	49.80
2-Octanol	58.25	40.64	41.32	69.86	81.09	57.96	71.81	55.77	56.10
3-Hexanol	52.59	36.69	37.30	53.92	62.59	44.74	55.43	43.05	43.30
2-Methyl-1-propanol	49.11	34.26	34.83	38.28	44.44	31.76	39.35	30.56	30.74
2-Methyl-1-butanol	51.68	36.06	36.66	46.04	53.44	38.20	47.32	36.76	36.97
3-Methyl-1-butanol	52.13	36.37	36.98	46.07	53.47	38.22	47.35	36.78	36.99
2-Methyl-2-butanol	49.56	34.58	35.15	45.58	52.91	37.82	46.86	36.39	36.60
2-Methyl-1-pentanol	54.26	37.86	38.49	53.93	62.60	44.75	55.44	43.06	43.31
4-Methyl-1-pentanol	52.20	36.42	37.03	54.60	63.38	45.30	56.13	43.59	43.84
2-Methyl-3-pentanol	51.68	36.06	36.66	54.15	62.85	44.93	55.66	43.23	43.48
3-Methyl-3-pentanol	51.02	35.60	36.19	53.93	62.60	44.75	55.44	43.06	43.31
2,4-Dimethyl-3-pentanol	53.17	37.09	37.71	61.86	71.80	51.33	63.59	49.39	49.67

thermodynamic parameters of the investigated analytes. Hence it can be deduced that they are physicochemically sound.

All the investigated models allow very good (i.e., well coinciding with the data taken from literature) numerical values of the molar enthalpy of vaporization (ΔH_{vap}) to be obtained for the investigated aliphatic alcohols. Models V and VIII proved the two best performing ones. The fitting parameter B provides better results than the other fitting parameters.

With an increase of the stationary phases' polarity, correlation between the thermodynamic data originating from our experiment and those taken from literature is improving. The best numerical data of the molar enthalpy of vaporization (ΔH_{vap}) were obtained with use of the most polar stationary phase (DB-Wax). This finding evidently means that the non-negligible intermolecular interactions between the polar stationary phase and the polar analytes did not invalidate the application of our approach.

With an increase of the stationary phases' polarity, the numerical values of the molar enthalpy of vaporization (ΔH_{vap}) also increase. In the other words, the more pronounced the intermolecular interactions, the more difficult (and the more energy-consuming) the vaporization of the respective analytes becomes.

With an increase of the column temperature, the quality of the results obtained from the medium polar stationary phase improves and that from the low polar stationary phases deteriorates.

In the past, the approach of an alternative derivation of the thermodynamic data (assumed in this study) has performed well with the three analyte groups (i.e., alkylbenzenes, aldehydes, and ketones). Presently, an analogous outcome with the considerably

more polar class of compounds (aliphatic alcohols) was obtained, and, hence, this approach can rightfully be considered as universal. Thus the technique of capillary GC seems a practical and handy alternative for microcalorimetry and allows a reliable derivation of certain thermodynamic data.

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Glossary of Terms

Symbol	Explanation
r_G	Non-reduced relative retention (unitless)
r	Relative retention (unitless)
k	Retention factor (unitless)
I	Kováts retention index (unitless)
β	Phase ratio (unitless)
T_c	Measurement temperature (column temperature) [K]
T_B	Boiling point of the analyte [K]
V_m	Molar volume of the analyte [cm ³ mol ⁻¹]
R_m	Molar refraction of the analyte [cm ³ mol ⁻¹]
n	Refractive index of the analyte (unitless) (20°C, $\lambda = 589\text{nm}$)
z	Number of carbon atoms C in a molecule of the <i>n</i> -alkane
d^{20}	Density at 20°C [g cm ⁻³]
M	Molar weight [g mol ⁻¹]
R	Universal gas constant (8.314 J mol ⁻¹ K ⁻¹)
ΔH_{vap}	Enthalpy of vaporization of the analyte [J cm ⁻³]
$\overline{\Delta H_{vap}}$	Mean molar vaporization enthalpy of the analyte [J mol ⁻¹]
$\Delta\mu_{p(-CH_2-)}$	Chemical potential of partitioning of one methylene group between two phases of chromatographic system [J mol ⁻¹]
$\Delta\mu_p$	Chemical potential of partitioning of the analyte between two phases of chromatographic system [J mol ⁻¹]
K_p	Equilibrium constant for partitioning of the analyte between the stationary and mobile phases (unitless)
ΔS_{vap}	Entropy of vaporization of the analyte [J mol ⁻¹ K ⁻¹]

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