MATHEMATICAL MODELS OF SOLUTE RETENTION IN GAS CHROMATOGRAPHY AS SOURCES OF THERMODYNAMIC DATA.
PART II. ALDEHYDES AS THE TEST ANALYTES

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SUMMARY

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 [1–11]. This paper is the next step in research introduced in other publications [12,13]. Eight different mathematical models (coupling gas chromatographic retention data of analytes with their physicochemical properties) were used to determine the molar heat of vaporization, ΔH_{vap}, and the chemical potential for partitioning of one methylene group between the two phases of the chromatographic system, $\Delta\mu_{p(CH2)}$, for consecutive members of a group of analytes, this time the aldehydes. The experiment was performed on low- and medium-polarity stationary phases in the temperature range 323 to 423 K.

INTRODUCTION

In the determination of certain thermodynamic data for organic compounds gas chromatography can be regarded as a handy alternative to direct, although complicated and troublesome, microcalorimetric methods. Acquisition of thermodynamic data by gas chromatography is achieved indirectly, i.e. from source data most often in the form of the retention times, and these measurements are relatively easy and simple. If precise measurements are made under well-defined and repeatable experimental conditions, huge amounts of the experimental data (points) can be collected in a relatively short time. These data and the analytes' physical characteristics (e.g. boiling points, molar volumes, and volume refraction) are then introduced to the specially derived mathematical equations and further processed statistically to obtain the thermodynamic properties of interest.

The models tested in the work discussed in this paper have been developed during the past several years [12–17] (Table I) and are not the purely empirical models, because their derivation was founded on physicochemical laws, including phenomenological thermodynamics, and on the theories of chromatography. These models are given in form of mathematical equations the terms of which have a physical meaning, which enables derivation of thermodynamic magnitudes from them.

All eight models have been founded on common premises:

(i) the process of retention, which consists in partitioning of the analyte between the stationary and mobile phases can be approximated by the physical process of vaporization and solution;

(ii) transfer of the analyte from the low-polarity liquid stationary phase to the gaseous mobile phase is very similar to (although not identical with) the process of vaporization of the pure liquid;

(iii) vaporization of the liquid is sufficiently well characterized by Trouton's Rule (which says that for most liquids the entropy of vaporization is practically the same – approx. 85 ± 3 J mol^{-1} K^{-1});

(iv) vaporization and solution are the mutually reversible processes; for the sake of simplicity it can be assumed that their characteristic thermodynamic magnitudes are the same in terms of absolute values, but opposite in sign; and

(v) the models discussed do not take into account intermolecular interactions and for this particular reason they are best used to describe chromatographic systems which are characterized by weak non-specific interactions only.

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

EXPERIMENTAL

In previous work [12,13] the performance of Eqs (I)–(VIII) (Table I) was tested for chromatographic results obtained from medium-polarity methyl n-alkyl ketones. In our current study aldehydes (which are slightly less polar than the corresponding ketones) were selected as the test analytes. To measure the retention data needed for further statistical processing and consequently for determination of the thermodynamic properties of interest, the experiment was performed under isothermal conditions, in the range of temperatures from 323 to 423 K (in 25-K intervals). In this experiment three stationary phases of different polarity DB-1, DB-5, and DB-Wax

Table I

Mathematical models tested in this study and physicochemical interpretation of the fitting terms which incorporate the thermodynamic magnitudes of interest, ΔH_{vap} and $\Delta\mu_{p(CH2)}$

Model		Fitting terms, which incorporate thermodynamic properties				Derived in Ref.
I	$r = A\exp(BT_B) + const.$	A	$\dfrac{t_M\beta}{t_{R(st)}}\exp\left(-\dfrac{\Delta H_{vap}}{RT_B}\right)$	B	$\dfrac{\Delta H_{vap}}{RT_B T_c}$	[14]
II	$r = A\exp\left(\dfrac{B}{T_B}\right) + const.$	A	$\dfrac{t_M\beta}{t_{R(st)}}\exp\left(\dfrac{\Delta\overline{H}_{vap}}{RT_c}\right)$	B	$\dfrac{\Delta\overline{H}_{vap}}{R}$	[14]
III	$I = A + BT_B$	A	$-\dfrac{100\cdot 85\cdot T_c}{\Delta\mu_{p(-CH2-)}}$ *	B	$\dfrac{100\cdot 85}{\Delta\mu_{p(-CH2-)}}$ *	[15,16]
IV	$I = A + \dfrac{B}{T_B}$	A	$\dfrac{100\cdot\Delta\overline{H}_{vap}}{\Delta\mu_{p(-CH2-)}}$	B	$-\dfrac{100\cdot\Delta\overline{H}_{vap}\cdot T_c}{\Delta\mu_{p(-CH2-)}}$	[15,16]
V	$\ln k = A + BV_m + C\left(\dfrac{V_m}{T_B}\right)$	B	$\dfrac{\Delta H_{vap}}{RT_c V_m}$	C	$-\dfrac{\Delta H_{vap}}{RV_m}$	[17]
VI	$\ln k = A + BR_m + C\left(\dfrac{R_m}{T_B}\right)$	B	$\dfrac{\Delta H_{vap}}{RT_c V_m}\cdot\dfrac{n^2+2}{n^2-1}$	C	$-\dfrac{\Delta H_{vap}}{RV_m}\cdot\dfrac{n^2+2}{n^2-1}$	[17]
VII	$r = A\exp\left[BV_m + C\left(\dfrac{V_m}{T_B}\right)\right] + const.$	B	$\dfrac{\Delta H_{vap}}{RT_c V_m}$	C	$-\dfrac{\Delta H_{vap}}{RV_m}$	[12]
VIII	$r = A\exp\left[BR_m + C\left(\dfrac{R_m}{T_B}\right)\right] + const.$	B	$\dfrac{\Delta H_{vap}}{RT_c V_m}\cdot\dfrac{n^2+2}{n^2-1}$	C	$-\dfrac{\Delta H_{vap}}{RV_m}\cdot\dfrac{n^2+2}{n^2-1}$	[12]

*After determination of $\Delta\mu_{p(CH2)}$ the numerical value of the enthalpy of vaporization is obtained from the relationship: $\Delta H_{vap} = \dfrac{I}{100}\Delta\mu_{p(-CH2-)} + 85T_c$

Explanation of symbols:

Chromatographic properties: r – relative retention; I – Kováts retention index, k – retention factor, t_M – hold-up time, $t_{R(st)}$ – retention time of standard solute, β – phase ratio

Physicochemical properties: T_B – boiling point of analyte, T_c – temperature of column (of analysis), R – gas constant, V_m – molar volume, R_m – molar refraction, n – refractive index

Thermodynamic properties: ΔH_{vap} – molar vaporization enthalpy of the analyte, $\Delta\overline{H}_{vap}$ – mean molar vaporization enthalpy of the analyte, $\Delta\mu_{p(CH2)}$ – chemical potential of partitioning of one methylene group between two phases of chromatographic system

(J&W Scientific, Folsom, CA, USA) yet with identical dimensions (30 m × 0.32 mm i.d.) and film thickness (1 μm) were used; 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.

The reagents used in our experiment (manufactured by PolyScience Corporation, Niles, IL, USA and J.T. Baker, Deventer, The Netherlands) were of GC standard grade and were analyzed by use of a Fisons Instruments (Rodano/Milano, Italy) GC 8000 Series capillary gas chromatograph equipped with flame ionization detection (FID) and cold on-column injection. Helium was used as carrier gas.

RESULTS AND DISCUSSION

Numerical values obtained for the B terms of the exponential equations (models I, II, VII, and VIII) and data from statistical analysis are listed in Table II; analogous data for the linear equations (Models III–VI) are given in Table III. Statistical evaluation was performed for results from

Table II

Estimates of B for Models I, II, VII and VIII and statistical data from the estimation (n – number of measurements, loss – final loss, minimized by means of the least squares method, r – correlation coefficient, r^2 –contribution from the explained variance) for the analytes investigated on three different stationary phases (an example for column temperature $T_c = 323$ K)

Model	B	n	Loss	r	r^2 (%)
DB-1					
I	0.0389	18	3.8273	0.9995	99.91
II	−6318.40	18	13.8678	0.9983	99.66
VII	0.1167	18	3.2407	0.9996	99.92
VIII	0.4606	18	5.4488	0.9993	99.87
DB-5					
I	0.0397	21	0.8289	0.9998	99.97
II	−6483.31	21	4.2283	0.9991	99.82
VII	0.1285	15	0.6658	0.9998	99.97
VIII	0.5269	15	1.6435	0.9996	99.92
DB-Wax					
I	0.0386	18	1.2719	0.9997	99.94
II	−6285.37	18	3.5972	0.9991	99.83
VII	0.1302	15	0.6925	0.9998	99.96
VIII	0.6099	15	0.2639	0.9999	99.98

Table III

Fitting terms B for Models III–VI (including their errors) and the regression data (n – number of measurements, r – correlation coefficient, F – the Fischer–Snedecor test value with the confidence level $p < 0.0000$ for each individual case, s – the standard estimation error) for the analytes investigated on three different stationary phases (an example for column temperature $T_c = 323$ K)

Model	$B \pm s_B$	n	r	F	s
DB-1					
III	3.77 ± 0.06	21	0.9977	4056.6	9.3589
IV	-576565 ± 14025	15	0.9962	1690.1	10.0141
V	0.09 ± 0.00	21	0.9973	1686.4	0.0949
VI	0.31 ± 0.02	21	0.9971	1525.3	0.0997
DB-5					
III	3.68 ± 0.07	21	0.9966	2794.1	11.0147
IV	-447849 ± 14751	18	0.9914	921.8	13.0004
V	0.12 ± 0.00	18	0.9992	4722.0	0.0464
VI	0.43 ± 0.02	21	0.9964	1249.5	0.1052
DB-Wax					
III	4.13 ± 0.05	15	0.9991	7583.9	5.0579
IV	-615935 ± 11789	15	0.9976	2729.8	8.4176
V	0.11 ± 0.01	18	0.9982	2048.2	0.0759
VI	0.39 ± 0.03	18	0.9974	1462.1	0.0898

all three stationary phases, although as an example we present data for one of the five measurement temperatures only – 323 K. 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 these measurement conditions. Such a conclusion is first of all apparent from the relatively high values of the correlation coefficient, r, from the high values from the F-test, and from the rather insignificant standard errors of estimation, the high values of the explained variance, and by the low final losses of the estimated values. The number of cases (n) valid for each system was selected by use of the LMS (least squares of median) method.

One must emphasize that at the other four temperatures the statistical data again indicated the possibility of using these models for prediction of the analyte retention. For the medium-polarity stationary phase (DB-Wax), however, the statistical data obtained are somewhat less accurate and some of the equations can have low statistical validity (particularly at the highest temperatures). It must thus be accepted that the statistical

characteristics of the models enable differentiation – although in a rather limited way – among stationary phases of different polarity.

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 of the chemical potential of partitioning of one methylene group between the phases of the chromatographic system, $\Delta \mu_{p(CH2)}$. The next three tables (Tables IV–VI) show the numerical values obtained for ΔH_{vap} for the analytes studied, both determined by use of the relationships verified in this paper and taken from literature.

Table IV

Numerical values of the enthalpy of vaporization, ΔH_{vap}, calculated by use of Models I and III–VIII for the investigated analytes, and data taken from the literature. The stationary phase was DB-1 ($T_c = 323$ K)

| Analyte | ΔH_{vap} (kJ mol^{-1}) | | | | | | | | | | |
| | Data calculated from the model | | | | | | | Data taken from the literature | | | |
	I	III	IV	V	VI	VII	VIII	(a)	(b)	(c)	(d)
Propanal	33.50	37.91		17.59	13.47	22.81	19.97	22.93	26.87	–	27.24
Butanal	36.47	40.38		21.79	17.43	28.25	25.83	27.24	30.73	–	29.67
Pentanal	39.19	42.69		25.70	21.23	33.32	31.46	31.71	35.81	–	31.88
Hexanal	42.11	44.89		29.67	25.06	38.47	37.13	36.30	38.22	33.44	34.26
Heptanal	44.52	47.24	40.34	33.74	29.05	43.75	43.06	40.67	43.05	38.39	36.21
Octanal	*46.08*	*49.57*		*37.70*	*32.88*	*48.89*	*48.73*	45.19	50.22	–	37.49
Nonanal	*47.86*	*51.89*		*41.62*	*36.75*	*53.97*	*54.46*	–	–	–	38.93
i-Butanal	35.01	39.71		22.06	17.35	28.60	25.72	26.11	29.19	–	28.48
i-Pentanal	38.14	41.81		26.12	21.28	33.87	31.54	29.30	33.96	–	31.03

(a) $-\Delta H_{sol}$, HP-1, $T = 323–383$ K [19]; (b) ΔH_{sol}, PDMS, $T = 298$ K [20]; (c) $-\Delta H_{sol}$, SE-30 [1]; (d) Approximate values (independent of the stationary phase) calculated by use of Trouton's Rule. Italics denote extrapolated data obtained from the dependence of calculated ΔH_{vap} values on the number of carbon atoms in a molecule

From even preliminary comparison it is apparent there is good correlation between the calculated data and those taken from other sources. Data taken from literature are, in a sense, scattered, because they originate from different references and were derived by use of different methods and stationary phases similar to those used in our experiment, although not identical. Similarly, the working temperatures cited in the literature

Table V

Numerical values of the enthalpy of vaporization, ΔH_{vap}, calculated by use of Models I and III–VIII for the investigated analytes, and data taken from the literature. The stationary phase was DB-5 (T_c = 323 K)

Analyte	ΔH_{vap} (kJ mol^{-1})									
	Data calculated from the model							Data taken from the literature		
	I	III	IV	V	VI	VII	VIII	(a)	(b)	(c)
Propanal	34.18	39.47		23.79	18.56	25.11	22.84			27.24
Butanal	37.22	41.92		29.46	24.00	31.11	29.54	33.68	33.18	29.67
Pentanal	40.00	43.57		34.75	29.24	36.69	35.99	38.79	38.28	31.88
Hexanal	42.98	46.09		40.12	34.51	42.36	42.48			34.26
Heptanal	45.43	48.46	32.03	45.62	40.02	48.17	49.25	47.70	48.66	36.21
Octanal	*47.03*	*50.55*		*50.98*	*45.29*	*53.83*	*55.74*	44.30	53.80	37.49
Nonanal	*48.84*	*52.76*		*56.28*	*50.62*	*59.42*	*62.30*	53.30	58.91	38.93
i-Butanal	35.73	40.23		29.83	23.90	31.50	29.42	31.51	32.26	28.48
i-Pentanal	38.93	42.80		35.32	29.32	37.29	36.08			31.03

(a) ΔH_{vap} (298 K) [8]; (b) ΔH_{vap}, DB-5MS (T = 313–353 K) [8]; (c) Approximate values (independent of the stationary phase) calculated by use of Trouton's Rule. Italics denote extrapolated data obtained from the dependence of calculated ΔH_{vap} values on the number of carbon atoms in a molecule

Table VI

Numerical values of the vaporization enthalpy, ΔH_{vap}, calculated by use of Models I and III–VIII for the investigated analytes, and data taken from the literature. The stationary phase was DB-Wax (T_c = 323 K)

Analyte	ΔH_{vap} (kJ mol^{-1})										
	Data calculated from the model							Data taken from the literature			
	I	III	IV	V	VI	VII	VIII	(a)	(b)	(c)	(d)
Propanal	33.24	42.75		20.74	16.75	25.45	26.44	28.62			27.24
Butanal	36.19	44.53		25.68	21.66	31.52	34.20	31.14	30.22		29.67
Pentanal	38.89	46.92		30.30	26.39	37.18	41.66	34.05	35.53		31.88
Hexanal	41.79	49.03		34.97	31.14	42.92	49.17	37.74	39.79	35.55	34.26
Heptanal	44.17	51.14	39.28	39.77	36.11	48.81	57.01	41.42	44.06	38.81	36.21
Octanal	*45.73*	*53.26*		*44.44*	*40.87*	*54.54*	64.52	45.15	48.61		37.49
Nonanal	*47.49*	*55.39*		*49.06*	*45.68*	*60.21*	*72.12*		52.63		38.93
i-Butanal	34.74	44.85		26.00	21.57	31.91	34.06	28.91			28.48
i-Pentanal	37.85	45.84		30.79	26.45	37.79	41.77	31.98			31.03

(a) $-\Delta H_{sol}$, HP-Innowax, T = 323–383 K [19]; (b) $-\Delta H_{sol}$, Carbowax 1540 [21]; (c) $-\Delta H_{sol}$, PEG-20 000 [1]; (d) Approximate values (independent of the stationary phase) calculated by use of Trouton's Rule. Italics denote extrapolated data obtained from the dependence of calculated ΔH_{vap} values on the number of carbon atoms in a molecule.

are not the same as those employed in our experiment. Owing to a widely accepted assumption that thermodynamic magnitudes are stable over a relatively wide range of temperatures, however, we can use data taken from other sources for comparison with our own. The comparison very much favors the results derived with aid of the models investigated in this paper. The last columns in Tables IV–VI contain identical values of ΔH_{vap}, calculated by use of Trouton's universal rule, which couples the magnitude of ΔH_{vap} with the boiling point of a given substance, T_B ($85 = \Delta H_{vap}/T_B$). Because of the approximate nature of Trouton's rule, the results obtained should be treated 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 with aid of the relationships I–VIII is certainly affected by, e.g., the discrepancy between the temperatures at which the chromatograms were obtained and the temperature of measurement of the physicochemical data used in our models (e.g. refraction index, density, molar volume, and molar refraction), which is usually 20°C (293 K). The lowest measurement temperature in our gas chromatographic experiment was 323 K and with increasing measurement temperatures computational discrepancies also increase, because the non-chromatographic properties appearing in the equations largely depend on the aforementioned physicochemical values.

For all eight equations numerical values of ΔH_{vap} can be derived from both fitting terms shown in Table I. Usually, however, one term gives clearly superior results. Usually the greater the number of individual physical properties involved in a given term, the better the agreement between the numerical value of ΔH_{vap} derived from our experiment and data taken from the literature. Models I and II are an exception to this rule. For these the excessive complexity of A makes its use for our purpose practically impossible. The only consistent difference between terms in the pairs of suitable terms from the other models is the measurement temperature, T_c, which seems to have a decisive effect (except for model III) on agreement between computed data and those taken from the literature.

Incidentally, for each of the eight models discussed better results were always obtained by use of B. For this reason, in Tables II and III numerical values of B only are given, and further used for calculation of the numerical values of ΔH_{vap} shown in Tables IV–VI. In these three

tables we introduced results for the two additional analytes – octanal and nonanal – which had not been investigated experimentally, because of their excessively high boiling points. Instead, the respective ΔH_{vap} values for these two analytes were extrapolated from the linear dependence of this magnitude on the number of carbon atoms for the homologous series of compounds; these data are given in italics.

If we consider the numerical values obtained for ΔH_{vap} with sufficient care we will discover that more satisfactory results have been obtained from use of the low-polarity stationary phases (i.e. from DB-1 and DB-5) than from the medium-polarity phase DB-Wax. Particularly good results could be obtained by use of Models V, VII, and VIII, and also Model I. The relatively large number of physicochemical properties in term B for all these models enables more precise description of the chromatographic system considered and hence secures greater adequacy of the results obtained. It cannot be denied, however, that an equally rich physicochemical background underlies Model VI and that despite this most of the thermodynamic results derived from this model are much too low; this might be because of either incorrect selection of the measurement points or a mutual relationship among the variables of this model.

Model III, on the other hand, furnishes results which are too high. This might be because of the relatively higher error of this approach, because of computation of ΔH_{vap} from another thermodynamic magnitude, $\Delta \mu_{p(CH2)}$, which will be discussed later.

Tables IV–VI contain no results derived from Model II. From this model we can only obtain mean values of the enthalpy of vaporization, one and the same value 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 B values derived from Model II are contrast so strikingly with analogous results from all the other models that they were disregarded without futile discussion. From Model IV one can also obtain mean ΔH_{vap} values, this time with positive signs and also the correct order of magnitude, but again they were identical for all the analytes considered and consequently could be regarded as a rough approximation only.

For the medium-polarity stationary phase (DB-Wax) the general trend of somewhat different performance of the individual models is again repeated, but with a tendency to furnish less accurate ΔH_{vap} values. Use of the medium-polarity stationary phase in conjunction with Model VIII furnishes numerical values of ΔH_{vap} which are too high, even though this

model performs really well in conjunction with the low-polarity stationary phases.

To summarize, if we view our models on the basis of the resulting thermodynamic values differences among the polarities of the stationary phases used become more distinct than if we merely compare statistical data for these models. For the less polar stationary phases significantly better agreement is obtained between thermodynamic data derived from our models and those originating from literature. This is understandable, because on the low-polarity stationary phases unwanted intermolecular interactions (which are not taken into account by the models) are absent. With increasing stationary phase polarity, the more probable become specific interactions which evidently worsen the results.

At the remaining working temperatures, the general pattern of the regularities observed is the same as at the lowest temperature, i.e. results from the low-polarity stationary phases are relatively better than those from the medium-polarity phase. Increasing the temperature of the experiment increases the differences between the numerical values of ΔH_{vap} calculated from the tested models and those taken from the literature. Although we lack comparative (i.e. reference) data valid for higher temperatures, we still can notice 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 which include large numbers of physicochemical properties decrease quite violently at higher temperatures. In contrast, models for which the fitting terms are rather simple (physicochemically) do not lead to similar breakdown and predicted values can even increase with increasing temperature. This is most probably because the column temperature present in the fitting term increasingly predominates the other properties therein. Again this observation confirms the correctness of our choice of 323 K as the most representative temperature for the experiment.

As already mentioned, in Models III and IV we must first calculate the magnitude $\Delta\mu_{\text{p(CH2)}}$, known as the chemical potential of the partitioning of one methylene group, CH_2, to be able to calculate ΔH_{vap}. The most handy way of determining the numerical value of $\Delta\mu_{\text{p(CH2)}}$ is to use term B from Model III. These results and the respective statistical information are given in Table VII. High correlation coefficients, r, (certainly better for the low-polarity phases than for the medium-polarity phase), high numerical values of the F-test, and relatively low standard errors, s, (s refers to the Kováts index, its numerical value is of the order 10^2–10^3) give evidence of

the high statistical validity of the model equations, which makes them suitable for determination of $\Delta\mu_{p(CH2)}$.

Table VII

Fitting terms B for Model III (including their errors) and regression data (n – number of measurements, r – correlation coefficient, F – Fischer–Snedecor test value with the confidence level $p < 0.0000$ in each individual case, s – the standard estimation error) 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	3.77 ± 0.06	21	0.9977	4056.6	9.3589
348	4.03 ± 0.08	24	0.9952	2280.7	16.6913
373	4.24 ± 0.07	30	0.9961	3567.5	20.2511
398	4.55 ± 0.08	36	0.9949	3333.8	29.2009
423	4.68 ± 0.09	36	0.9930	2414.2	35.3134
DB-5					
323	3.68 ± 0.07	21	0.9966	2794.1	11.0147
348	3.67 ± 0.07	21	0.9966	2805.1	10.9656
373	4.24 ± 0.08	30	0.9952	2887.2	22.4725
398	4.63 ± 0.10	36	0.9925	2232.9	36.3054
423	4.61 ± 0.10	36	0.9923	2171.2	36.6415
DB-Wax					
323	4.13 ± 0.05	15	0.9991	7583.9	5.0579
348	3.70 ± 0.10	24	0.9918	1332.3	20.0816
373	4.16 ± 0.09	24	0.9949	2134.3	19.7295
398	4.18 ± 0.08	24	0.9955	2426.7	18.6197
423	4.73 ± 0.12	36	0.9896	1604.3	43.7804

A selection of the $\Delta\mu_{p(CH2)}$ data calculated by use of Model III and data taken from literature are listed in Table VIII, this time for all five working temperatures employed in our experiment. In the same way as for ΔH_{vap}, reference values of $\Delta\mu_{p(CH2)}$ again originate from a variety of different sources, refer to similar, but not identical, stationary phases and temperatures, and were also derived for different methyl group-containing compounds. Some numerical values taken from literature are positive whereas others are negative; this reveals the somewhat arbitrary nature of the assumption of thermodynamic equilibrium in gas chromatography as a result of the vaporization $\leftrightarrow$ solution process, as a deliberate substitute for analyte partitioning between the stationary and mobile phases.

Table VIII

Numerical values of the chemical potential of the partitioning of one methylene group between the stationary and mobile phases, $\Delta\mu_{p(CH2)}$, calculated by use of Model III and taken from the literature

$\Delta\mu_{p(CH2)}$ (J mol^{-1})									
Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
T_c = 323 K		T_c = 348 K		T_c = 373 K		T_c = 398 K		T_c = 423 K	
DB-1									
2257	2282 (a) −2363 (b) −2594 (c) 2591 (d)	2111	2112 (a) −2221 (b) −2388 (c) 2385 (d)	2003	1964 (a) −2079 (b) −2182 (c) 2178 (d) 1987 (e) 2009 (f) 1859 (g)	1868	1722 (a) −1937 (b) −1976 (c) 1972 (d) −1937 (h) −1860 (i) −1952 (j)	1815	1555 (a) −1795 (b) −1771 (c) 1765 (d)
DB-5									
2311	2399 (k) 1913 (l)	2317	2152 (k) 1839 (l)	2006	1978 (k) 1765 (l) 1935 (m) 2032 (n)	1835	1821 (k) 1691 (l) −1916 (o)	1844	1636 (k) 1661 (l)
DB-Wax									
2058	1897 (p) −2035 (q)	2295	1725 (p) −1919 (q)	2044	1607 (p) −1793 (q) 1639 (r)	2031	1448 (p) −1672 (q) 1674 (s) −1674 (t) −1816 (u)	1796	1263 (p) −1550 (q) 1364 (r)

(a) OV-101 [4]; (b) OV-101, on the basis of Ref. [10]; (c) PDMS, on the basis of Ref. [10]; (d) PDMS, on the basis of Ref. [15]; (e) SE-30, T = 383.15 K [16]; (f) OV-1, T = 383.15 K [16]; (g) OV-101, T = 383.15 K [16]; (h) SE-30, T = 394.6 K [18]; (i) OV-101, T = 393.2 K [9]; (j) PDMS, T = 393.2 K [9]; (k) OV-3 [4]; (l) SE-54 [4]; (m) SE-52, T = 383.15 K [16]; (n) OV-3, T = 383.15 K [16]; (o) OV-3, T = 394.6 K [18]; (p) Carbo-wax 20M [4]; (q) Superox 20M, on the basis of Ref. [10]; (r) PEG-20M, [16]; (s) PEG-20M, T = 394.6 K [16]; (t) Carbowax 20M, T = 394.6 K [18]; (u) Carbowax 20M, T = 393.2 K [9]

The numerical values of $\Delta\mu_{p(CH2)}$ calculated from our experimental data are all positive, which agrees well with the positive ΔH_{vap} values and most probably confirms a shift in thermodynamic equilibrium of the analyte partitioning between the two phases towards vaporization. One $\Delta\mu_{p(CH2)}$ value only is given for each temperature; this is, of course, the mean value calculated for one CH$_2$ group, irrespective of the analyte itself and of the position of the group in the structure of the analyte.

Excellent correlation was again observed between computed and the reference values obtained on the low-polarity stationary phases whereas correlation was worse for the medium-polarity phase (the respective numerical values were slightly too high). This phenomenon is obviously a consequence of intermolecular interactions between the stationary phase and the analytes. If we focus on one stationary phase only we will notice a general trend of decreasing $\Delta\mu_{p(CH2)}$ values with increasing working temperature, implying easier (i.e. less energetic) transfer of the methylene group from one phase to another. Numerical values of $\Delta\mu_{p(CH2)}$, calculated from term A of Model III are all too high.

CONCLUSIONS

All the models tested in this study are characterized by high statistical performance and can therefore be used for prediction of the retention of the investigated analytes in capillary gas chromatography, and also for derivation of the two thermodynamic properties molar enthalpy of vaporization, ΔH_{vap}, and chemical potential of the partitioning of one methylene group, $\Delta\mu_{p(CH2)}$. Computed numerical values of these thermodynamic properties proved very comparable with data taken from literature. It became clear that these models provided better thermodynamic results if the terms used for calculation contained physicochemical properties characteristic of the analytes considered.

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

Gas chromatography is highly suitable for use as a convenient alternative measurement technique for acquisition of thermodynamic data.

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