A STUDY OF THE DEPENDENCE OF THE KOVÁTS RETENTION INDEX ON THE TEMPERATURE OF ANALYSIS ON STATIONARY PHASES OF DIFFERENT POLARITY

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SUMMARY

The dependence of Kováts retention indices on the temperature of GC analysis is not always regular. In some chromatographic systems this dependence is characterized by a readily perceptible minimum [1–3]. To monitor this type of relationship a set of test compounds was selected from among the aldehydes, ketones, and alkylbenzenes and their gas chromatographic behaviour was studied on stationary phases of different polarity and over a wide range of working temperatures. For some systems we observed a minimum on the plot of I against T_c. This minimum was not only observed, it was also computationally confirmed by use of the equation $I = A + B/T_c + C\ln T_c$, where A, B, and C are terms of the equation with physicochemical significance [2,4–6]. On the basis of this equation we were also able to evaluate two thermodynamic magnitudes, the activation enthalpy, $\Delta H^{\neq}$, and the chemical potential of the partitioning of one methylene group between the two phases of the chromatographic system, $\Delta\mu_{p(CH2)}$, for all the analytes investigated.

INTRODUCTION

One of the earliest relationships describing the dependence of the Kováts retention index, I, on the temperature of chromatographic analysis, T_c, was an empirical relationship of the Antoine type [7–9]:

$$I = a + \frac{b}{T_c + c} \tag{1}$$

(where *a*, *b*, and *c* are the equation constants). Although this relationship applies reasonably well to non-polar analytes on polar stationary phases in narrow intervals of temperature, it does not explain the deviation from regularity first observed by Engewald [1].

In most of the examples described in the literature, the dependence of the Kováts retention index on isothermal column temperature can be represented by a straight-line plot [3,7,8,10–15], even if more detailed studies reveal some lack of regularity. Apart from the nature of the chromatographic system, this apparent linearity can result from using an incorrectly selected range of measurement temperatures (i.e. one which is a too narrow or which is sampled too rarely).

From the numerous experiments reported it is unquestionable that for non-polar analytes chromatographed on non-polar stationary phases the dependence of the retention index on temperature is linear, or at least almost linear [7,8,15], whereas for polar analytes chromatographed on non-polar stationary phases a minimum is observed in the plots [1–3,5]. The nuances of this non-regularity are very well described by the equation:

$$I = A + \frac{B}{T_c} + C \ln T_c \qquad (2)$$

where *A*, *B*, and *C* are, in the first instance, the equation constants. Eq. (2) is the first equation which can be used both to predict this minimum and to calculate its position. It is, in the other words, the first relationship which provides non-empirical support of experimental results.

Here, however, a small digression is necessary. It is evident that the Antoine-type relationship can also be viewed as containing the first two terms of the Taylor expansion:

$$y = a + \frac{b}{x} + c \ln x + dx + ... \qquad (3)$$

If we expand this expression by adding the third Taylor term *c*ln*x*, then we obtain the model given by Eq. (2). Three terms of this expansion fully suffice to reproduce exactly the shape of the plot of *I* against T_c for chromatographic systems.

The final form of Eq. (2) can be achieved in two different ways, i.e. by use of 'kinetic' and 'thermodynamic' models. The 'kinetic' model proposed by Kowalska has been thoroughly derived elsewhere [4]. It is founded on kinetic concepts (transition state theory, theory of phase transfer, and the Eyring equation) and on thermodynamic premises also.

The equation constants A, B, and C have a strict physicochemical meaning and, therefore, two of the constants only are sufficient to calculate the so-called activation enthalpy $\Delta H^{\neq}$ and for estimation of another thermodynamic quantity, the chemical potential of partitioning of one methylene group between the stationary and mobile phases, $\Delta\mu_{p(CH2)}$. On the basis of other work [2,5,6] one can conclude that the established model is correct and that the thermodynamic values derived from this model are quite probable and, therefore, easily accepted.

The 'thermodynamic' approach is based on the Kirchhoff Law. It enables calculation of the aforementioned magnitude $\Delta\mu_{p(CH2)}$, although agreement with data taken from literature [6] is not satisfactory.

EXPERIMENTAL

To check the shape of the plot representing the retention index as a function of temperature, we first had to select several polar (aldehydes and *n*-alkyl ketones) and non-polar analytes (simple alkylbenzenes). All these test solutes were chromatographed using the same working conditions, i.e. at isothermal temperatures in the range 313 to 423 K at 10 K intervals. Analysis was performed on three stationary phases (DB-1, DB-5, and DB-Wax; J&W Scientific, Folsom, CA, USA) differing in polarity although with identical film thickness (1 μm) and geometric dimensions (30 m × 0.32 mm i.d.). The polarities of the stationary phases on the McReynolds scale were: 217 (DB-1), 323 (DB-5), and 2188 (DB-Wax).

All the reagents used in this experiment (including the *n*-alkanes used as reference compounds) were gas chromatographic standards (Poly-Science Corporation, Niles, IL, USA). Experiments were performed with a Fisons Instruments (Rodano/Milano, Italy) GC 8000 Series capillary gas chromatograph. Cold on-column injection and flame ionization detection were used; the carrier gas was helium.

The mean values of the retention indices from the three series of measurements for the three different stationary phases in the temperature range from 313 to 423K are given in Table I.

RESULTS AND DISCUSSION

Table II contains numerical values of the constants from Eq. (2), statistical data, and numerical values of T_{min} (corresponding to the minimum on the plot of I against T_c), both predicted by use of Eq. (2) and measured

Table I

The mean numerical values of I for the analytes investigated on three stationary phases of different polarity (T_c = 313–423K)

Analyte	T_c [K]											
	313	323	333	343	353	363	373	383	393	403	413	423
DB-1												
Butanal	571.50	570.91	568.78	569.15	571.57	573.77	575.99	578.18	580.49	583.70	587.66	588.95
Pentan-2-al	675.36	674.28	674.91	675.32	675.72	676.77	677.72	678.55	678.68	680.44	682.23	686.31
Butanone	575.92	574.45	572.75	572.34	571.45	572.61	572.88	573.87	575.19	576.69	578.90	581.30
Pentan-2-one	667.09	666.82	666.11	665.42	666.63	667.23	668.17	668.33	669.68	670.44	672.02	674.86
Hexan-2-one	767.07	766.66	765.86	766.82	767.68	768.37	768.70	769.32	769.68	771.05	772.24	774.21
Benzene	649.89	651.77	653.93	656.09	658.35	660.36	663.60	664.40	666.96	670.44	672.02	674.86
Toluene	751.72	753.79	756.18	758.31	760.55	763.41	765.53	767.08	769.68	773.08	774.96	777.86
DB-5												
Butanal	627.05	624.13	621.39	615.44	618.79	621.98	628.73	632.95	634.24	637.36	638.34	640.74
Pentan-2-al	700.44	698.24	699.75	700.64	701.70	702.48	704.71	705.68	707.08	710.42	713.43	717.73
Butanone	603.27	602.14	601.20	599.13	596.14	598.30	601.92	602.60	603.82	605.54	607.50	609.91
Pentan-2-one	693.14	692.22	691.63	691.20	690.53	691.40	691.57	691.79	692.92	694.09	696.34	697.44
Hexan-2-one	788.05	787.01	787.84	789.11	789.29	789.92	790.50	791.67	792.39	793.70	795.42	797.53
Benzene	666.03	667.42	669.56	671.74	673.50	675.70	677.75	680.27	681.27	683.59	685.29	687.79
Toluene	767.72	770.81	772.35	774.88	776.58	779.16	781.85	784.33	787.46	790.83	793.44	797.35
DB-Wax												
Butanal	803.22	816.90	823.91	854.46	867.47	874.62	891.30	911.46	931.96	947.71	955.82	980.84
Pentan-2-al	938.03	947.44	968.42	983.35	993.55	1007.15	1019.81	1031.58	1043.68	1064.46	1078.94	1087.98
Butanone	917.39	922.33	925.59	928.27	931.34	935.77	940.31	943.44	946.71	949.95	955.82	959.15
Pentan-2-one	1003.89	1005.72	1007.52	1009.73	1011.09	1012.78	1014.87	1016.30	1018.39	1020.31	1022.25	1023.72
Benzene	947.77	953.66	963.67	971.57	980.53	989.54	998.62	1007.64	1017.28	1028.37	1036.54	1045.90
Toluene	1043.09	1049.50	1057.61	1068.53	1076.25	1084.20	1094.22	1101.89	1111.38	1121.12	1132.30	1142.74

experimentally. Table III gives thermodynamic values of $\Delta H^{\neq}$ and $\Delta\mu_{p(CH2)}$ for each individual chromatographic system (both derived from our model and taken from the literature). Low-polarity and polar analytes were investigated, and stationary phases of different polarity. For all three columns, however, the stationary phase film thickness was identical (1 μm), eliminating the impact of different film thicknesses on retention.

From comparison of the Kováts retention indices obtained (Table I) it is apparent that occasionally the numerical values of I do not change regularly with increasing column temperature. This is apparent for polar oxo compounds chromatographed on the low-polarity stationary phases DB-1 and DB-5 (Fig. 1). Study of the behaviour of the same compounds on the medium polarity stationary phase (i.e. DB-Wax) reveals, however, no minimum in the plots. Similarly, no minimum is observed for the low-polarity alkylbenzenes chromatographed on any of the stationary phases used.

Table II

Terms B and C of the equation $I = A + B/T_c + C\ln T_c$ with the respective errors, regression data (r: regression coefficient, F: the value of the Fischer–Snedecor test, in each case for the confidence level $p < 0.0000$, s: the standard error of estimation; for each analyte the number of measurements, n, = 36), and the calculated and experimental values of the temperature minimum (T_{min}) for each individual set of analytes

Analyte	$B \pm s_B$	$C \pm s_C$	r	F	s	T_{min} [K] Calc.[*]	T_{min} [K] Expt.[**]
DB-1							
Butanal	228328 ± 13514	694.38 ± 37.21	0.9922	1046.20	0.8822	329	332
Pentan-2-al	120144 ± 11536	362.82 ± 31.77	0.9772	348.97	0.7531	331	328
Butanone	204718 ± 4081	581.22 ± 11.24	0.9959	1991.60	0.2664	352	353
Pentan-2-one	120853 ± 7502	356.20 ± 20.66	0.9841	506.07	0.4897	339	340
Hexan-2-one	77944 ± 6719	237.68 ± 18.50	0.9844	517.86	0.4386	328	327
Benzene	51497 ± 6989	224.39 ± 19.24	0.9984	5298.60	0.4562	229	–
Toluene	50961 ± 5416	226.34 ± 14.91	0.9991	9562.41	0.3536	225	–
DB-5							
Butanal	348202 ± 48370	1024.60 ± 133.19	0.9247	97.38	3.1575	340	340
Pentan-2-al	188556 ± 11782	575.15 ± 32.44	0.9918	990.71	0.7691	328	327
Butanone	243697 ± 18522	694.62 ± 51.00	0.9494	150.70	1.2091	351	349
Pentan-2-one	130892 ± 6454	372.76 ± 17.77	0.9773	351.32	0.4216	351	356
Hexan-2-one	82711 ± 6844	258.53 ± 18.85	0.9904	843.91	0.4468	320	320
Benzene	26757 ± 4982	146.25 ± 13.72	0.9990	8013.04	0.3252	183	–
Toluene	101754 ± 6597	375.17 ± 18.64	0.9990	7961.04	0.4306	271	–
DB-Wax							
Butanal	322989 ± 70404	1476.68 ± 193.86	0.9969	2636.31	4.5958	219	–
Pentan-2-al	170716 ± 44791	972.30 ± 123.33	0.9983	4746.24	2.9238	176	–
Butanone	79468 ± 10829	354.47 ± 29.82	0.9986	5948.07	0.7069	224	–
Pentan-2-one	24941 ± 3993	134.71 ± 10.99	0.9992	10333.10	0.2606	185	–
Benzene	206792 ± 10103	900.36 ± 27.82	0.9998	40716.20	0.6595	230	–
Toluene	231345 ± 15242	966.49 ± 41.97	0.9995	17759.17	0.9949	239	–

[*] Values calculated by use of Eq. (4)
[**] Experimental values

The minimum is usually observed in the lower regions of the working temperature, possibly because of the relatively low molecular weight of an analyte. No correlation was, however, observed between the temperature at which the minimum occurred and the boiling point of a given analyte, and no correlation was established between increasing stationary phase polarity (and, automatically, its changing chemical structure also) and a shift in a defined direction of the minimum in the plot of I against T_c. It was, on the other hand, established that on the stationary phases for which a minimum was observed, and for a given class of analytes

Table III

Experimental values of the enthalpy of activation, $\Delta H^{\neq}$ and of the chemical potential of partitioning of one methylene group, $\Delta\mu_{p(CH2)}$, and values taken from the literature. Numerical values of $\Delta H^{\neq}$ corresponding to I–T_c plots with no minimum are marked in italics

Analyte	$\Delta H^{\neq}$		$\Delta\mu_{p(CH2)}$								
	Expt.	Lit. data	Expt.	Lit. data							
DB-1											
Butanal	–2734	–2410 (a)	–441	–3789 (b)							
Pentan-2-al	–2753	–2384 (a)	–843	–3020 (b)							
Butanone	–2928	–2741 (a)	–526	–3360 (b)	1964 (c)	–1860 (d)	–1952 (e)	–1937 (f)	1987 (g)	1859 (h)	2009 (i)
Pentan-2-one	–2821	–2634 (a)	–858	–3141 (b)							
Hexan-2-one	–2726	–2591 (a)	–1287	–2606 (b)							
Benzene	*–1908*	No data available	–	No data available							
Toluene	*–1872*		–								
DB-5											
Butanal	–2825		–299								
Pentan-2-al	–2726		–532								
Butanone	–2917	No data available	–440	2034 (j)	1780 (k)	–1916 (l)	1935 (m)	1916–2032 (n)			
Pentan-2-one	–2919		–821								
Hexan-2-one	–2660		–1183								
Benzene	*–1521*		–								
Toluene	*–2255*		–								
DB-Wax											
Butanal	*–1818*		–207								
Pentan-2-al	*–1460*		–315								
Butanone	*–1864*	No data available	–863	1619 (o)	–1860 (p)	–1674 (q)	1364–1674 (r)				
Pentan-2-one	*–1539*		–2271								
Benzene	*–1910*		–								
Toluene	*–1990*		–								

(a) HP-1, $T = 293$–343, and 363–383°C; values calculated from the kinetic equation using the terms B and C [5]; (b) HP-1, $T = 293$–343 and 363–383°C; values calculated from the kinetic equation using the term C [5]; (c) OV-101, $T = 368$ K; calculated values [16]; (d) OV-101, $T = 393.2$ K [17]; (e) PDMS, $T = 393.2$ K [17]; (f) SE-30, $T = 394.6$ K [18]; (g) SE-30, $T = 383.15$ K [19]; (h) OV-101, $T = 383.15$ K [19]; (i) OV-1, $T = 383.15$ K [19]; (j) OV-3, $T = 368$ K; calculated values [16]; (k) SE-54, $T = 368$ K; calculated values [16]; (l) OV-3, $T = 394.6$ K [18]; (m) SE-52, $T = 383.15$ K [19]; (n) OV-3, $T = 383.15$ K [19]; (o) Carbowax 20M, $T = 368$ K; calculated values [16]; (p) Carbowax 20M, $T = 393.2$ K [17]; (q) Carbowax 20M, $T = 394.6$ K [18]; (r) PEG 20M, $T = 333.15$ K [19]

increasing the length of the carbon chain of the analytes (i.e. increasing their molecular weight) induces a shift of the minimum in the I–T_c plot towards lower temperatures (Fig. 2). Because of the limited number of test solutes
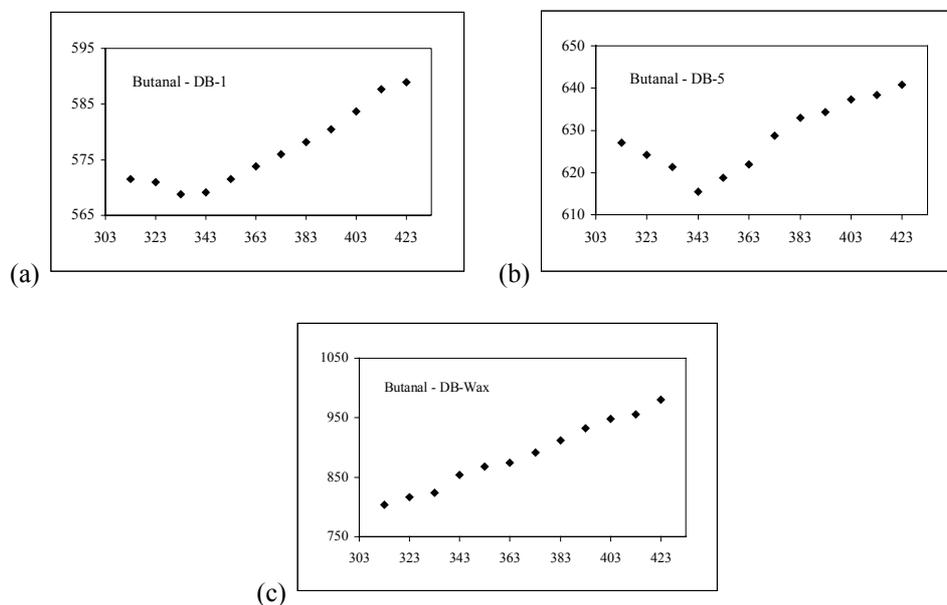
Fig. 1

Graphical representation of the dependence of the Kováts retention index on isothermal column temperature for butanal analysed on three stationary phases of different polarity (typical example). (a) DB-1 (McReynolds polarity, Σ, = 217); (b) DB-5 (Σ = 323); (c) DB-Wax (Σ = 2188)

so far investigated, this statement should be taken as an observation only and not as a conclusion.

The numerical value of the temperature at the minimum on the I–T_c plot can be calculated by fitting terms B and C of Eq. (2):

$$T_{min} = \frac{B}{C} \tag{4}$$

where T_{min} is the temperature of the gas chromatographic analysis at which the numerical value of the retention index is lowest for a given analyte, under the working conditions used. Computed values of T_{min} usually agreed well with experimental values, as is shown by the data in Table II and by the figures.

The ratio of B to C can also be regarded as providing evidence that curves will lack a minimum, because the numerical value of this ratio occurs outside the range of working temperatures employed and lacks credibility (because in such circumstances the computed T_{min} values have
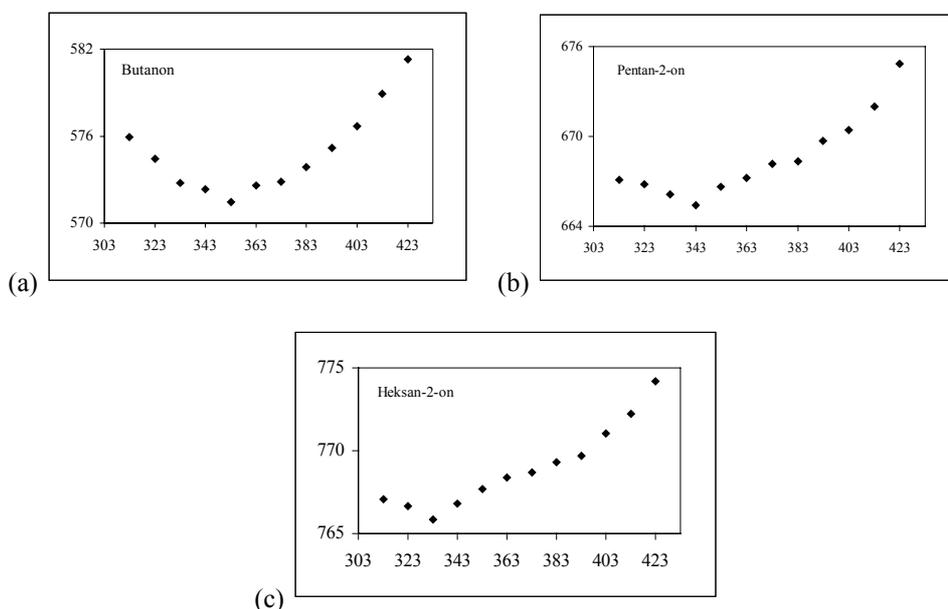
Fig. 2

Shift of the minimum value, T_{min}, for analytes from the same class of compounds, on the stationary phase DB-1 (typical example). (a) butanone; (b) pentan-2-one; (c) hexan-2-one

negative values in degrees Celsius). Some hint about the presence or absence of the minimum is encoded in the statistical data (Table II). Very high values of the correlation coefficient r and of the F-test (as observed for all the analytes on the stationary phase DB-Wax and for benzene and toluene on the other stationary phases) are indicative of linearity of the I–T_c plot and, hence, the lack of a minimum also.

The same terms which enable determination of T_{min} can also be used for calculation of the enthalpy of activation, $\Delta H^{\neq}$. Because:

$$B = \frac{100}{\ln K_{p(CH_2)}} \left(-\frac{\Delta H^{\neq}}{R} \right) \tag{5}$$

and

$$C = \frac{100}{\ln K_{p(CH_2)}} \tag{6}$$

(where R is the universal gas constant, 8.314 J mol^{-1} K^{-1}, and $K_{p(CH2)}$ is the constant for partitioning of one methylene group between the two phases

of the chromatographic system), after the transformations needed we obtain the relationship:

$$\Delta H^{\neq} = -\frac{B}{C}R = -T_{min}R \qquad (7)$$

This enthalpy is always negative, because the terms B and C always have the same sign. The numerical values of $\Delta H^{\neq}$ obtained on the stationary phase DB-1 correspond very well with data from the literature [5]. Because of the lack of similar results from other stationary phases, further comparison with literature results is, however, barely possible. It seems, however, that the numerical values of $\Delta H^{\neq}$ obtained on another low-polarity stationary phase (i.e. on DB-5) are highly probable and also acceptable. The range of magnitude, -2.5 to -3 kJ mol^{-1}, can be compared with the energies of weak intermolecular interactions (and with those for phase transfer, assumed in transition state theory, TST [4]); occurrence of any chemical reaction is excluded, because the energy involved would be at least an order of magnitude higher. This general outcome leads to the conclusion that the chromatographic process, which in the 'kinetic' approach is depicted as a series of equilibria of the vaporization $\leftrightarrow$ solution type, is a purely physical process.

The magnitude of $\Delta H^{\neq}$ depends on temperature and, more precisely, on the temperature, at which the minimum is obtained (Eq. 7). It seems correct to conclude that with the systems for which there is no such minimum, this magnitude lacks its original meaning. The respective $\Delta H^{\neq}$ values appear in italics in Table III and their absolute values are perceptibly lower than for the systems comprising a polar analyte and a low-polarity stationary phase. This difference might be indicative of the lack of an energy maximum in the course of phase transfer in TST (if we assume the validity of the TST approach [4]), which is equivalent to lack of formation of a transition complex in adsorption and/or desorption of the analyte molecule on the interface between the two phases. The enthalpy of activation ($\Delta H^{\neq}$) can be described as the heat of adsorption and/or desorption at temperature T_{min}. Its negative sign suggests an exothermic process with an equilibrium shifted towards solution, whereas $\Delta H^{\neq}$ can be regarded as the heat of adsorption of the molecule on the surface of the stationary phase from the gas phase.

The absence of T_{min} should not be perceived as indicative of the complete absence of the adsorption/desorption process, but indicative of a process with a far less pronounced energetic effect. Significant energetic

effects are observed only when polar analytes are chromatographed on low-polarity stationary phases.

Considering the experimental values of $\Delta H^{\neq}$ it seems justified to expect that within one and the same class of compounds these values ought to grow with increasing carbon chain length. Because of errors inherent in the determination of terms B and C of Eq. (2), the expected regularity is, however, occasionally perturbed. Another observation focuses on oxo analytes. With ketones, the numerical values of $\Delta H^{\neq}$ are always lower than for the analogous aldehydes. Good confirmation of these observations and intuitions is also furnished by results in the literature [2,5,6]. From the experimental data it is, however, impossible to deduce any obvious correlation between stationary phase polarity (or structure) on the one hand and numerical values of T_{min} or $\Delta H^{\neq}$ on the other.

Another thermodynamic property which can be determined by use of Eq. (2) is, $\Delta \mu_{p(CH2)}$, the chemical potential of partitioning of one methylene group between the two phases of the chromatographic system. This can be obtained from term C of Eq. (6), discussed earlier. Because:

$$\Delta \mu_{p(CH_2)} = -RT \ln K_{p(CH_2)} \qquad (8)$$

it is apparent that:

$$\Delta \mu_{p(CH_2)} = -\frac{100 R \overline{T}}{C} \qquad (9)$$

where $\overline{T}$ is the mean temperature of the range of temperatures applied (368 K in the experiment discussed in this paper).

It must, unfortunately, be admitted that by use of this approach numerical values of $\Delta \mu_{p(CH2)}$ can be estimated semi-quantitatively only, because of a considerable evaluation error. Apart from very few exceptions the results obtained are significantly lower than values found in the literature (see Table III).

Among data taken from the literature (Table III) we find both negative and the positive values of $\Delta \mu_{p(CH2)}$. This incoherence is evidence of arbitrary assumptions made by different authors in the physical description of the vaporization ↔ solution equilibrium.

Our experimental results are indicative of negative $\Delta \mu_{p(CH2)}$ values, i.e. to the process of achieving thermodynamic equilibrium by dissolution. This observation is in agreement with the negative values of the enthalpy of activation ($\Delta H^{\neq}$), which imply the same conclusion.

CONCLUSIONS

The 'kinetic' model which describes the temperature dependence of Kováts retention index seems correct physicochemically and thermodynamically. It is, moreover, a general model which unequivocally reveals the minimum on the plot of I against T_c and enables its simple prediction ($T_{min} = B/C$). The minima on the aforementioned plots of I against T_c occur exclusively for polar analytes chromatographed on low-polarity stationary phases. No similar effect has ever been observed for polar analytes chromatographed on polar stationary phases, or for low-polarity analytes chromatographed on stationary phases of any polarity.

The 'kinetic' model enables satisfactory description of the phenomenon studied, as confirmed by the respective numerical values of statistical data. This model enables determination of the enthalpy of activation, which can possibly be understood as the heat of adsorption/desorption at the temperature T_{min} for systems comprising a polar analyte and a low-polarity stationary phase. The rather insignificant value of $\Delta H^{\neq}$ unequivocally indicates that in the chromatographic processes investigated in our experiment the processes occurring are exclusively physical (and not chemical). The negative values of both $\Delta H^{\neq}$ and $\Delta \mu_{p(CH2)}$ unequivocally indicate that in our experiment the equilibrium of the vaporization $\leftrightarrow$ solution process was shifted towards solution.

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