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Effect of Film Thickness on the Retention Index of Nitro and Cyano Compounds. Interpretation of the Logarithmic Equation

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Abstract

Recently, a minimum was observed on the temperature dependence of retention indices in case of polar solutes chromatographed on apolar stationary phases. Physical significance is attributed to the equation constants describing the minimum. The equation constants are explained using a thermodynamic and a kinetic approach. Statistical properties of the models for different film thicknesses are compared. Chemical potential for one methylene unit is calculated in different ways for various film thicknesses and compared with literature values. The activation enthalpy attributed to the solvation process decreases as the carbon atom number (molecular mass) of the compounds decreases. The activation enthalpies for cyanoalkanes are always higher than those for the respective nitroalkanes. The interpretation of the equation constants does not change if the film thickness of the stationary phase increases (it is varied). This fact eliminates adsorption on the surface of the column wall from the possible causes responsible for the minimum on the retention index versus temperature curve.

Introduction

The temperature dependence of the Kováts retention indices has been debated for a long time. Finally, the scientific community has agreed that the temperature dependence could be given with a simple linear equation and for a wide temperature range with an Antoine-type hyperbolic equation (1). Tudor reinvestigated the temperature dependence of the retention indices and examined linear (2) and hyperbolic (3) equations, as well as their interconnection (4). An extremum was observed in the temperature dependence if polar compounds were chromatographed on apolar columns (5–7). Recently, explanation has also been given for the new equation describing the observed minimum (8,9):

$$I = A + B/T + C\ln T \qquad \text{Eq. 1}$$

In this work, we extend the validity range of the explanation for the equation constants (parameters of regression A, B, and C) to the highly polar compounds nitro- and cyanoalkanes. Moreover, we intend to study the effect of film thickness on the retention phenomenon.

Experimental

The physicochemical interpretation of the relationship between the isothermal column temperature and the retention index (I), which shows a minimum, has already been given earlier (8,9). Herewith, it is not expedient to recapitulate the entire train of thoughts. Only the most important parts are summarized.

The first explanation of the minimum in the I versus T empirical relationship can be denoted as "thermodynamic". The Kováts retention index for the ith solute ($I_{(i)}$) can be given using the thermodynamic expressions (7,9–11):

$$I_{(i)}/100 = \Delta\mu_{(i)}/\Delta\mu_{CH2} \qquad \text{Eq. 2}$$

where $\Delta\mu_{(i)}$ is the chemical potential of partitioning of the ith solute between the mobile and the stationary phase and $\Delta\mu_{pCH2}$ is the analogous chemical potential of partitioning for one methylene group of an n-alkane. The chemical potential depends on the temperature. However, as a first approximation, a mean value $\Delta\mu_{pCH2}$ can be used for the given range of temperatures. Moreover, $\Delta\mu_{pCH2}$ denotes the average value and its definition is as follows:

$$\Delta\mu_{CH2} = -RT_{mean}\ln K_{CH2} \qquad \text{Eq. 3}$$

where R is the gas constant, T_{mean} is the average of the temperature range, and K_{CH2} is the partition constant for one methylene

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unit. Then, using Kirchoff's law to express the temperature dependence of the thermodynamic quantities ΔH (enthalpy of solvation) and ΔS (entropy of solvation), we receive the following constants for equation 1:

$$A = 100T_{mean}(\Delta\Delta C_p - \Delta\Delta S^o + \Delta\Delta C_p \ln T_o)/\Delta\mu_{CH2} \qquad \text{Eq. 4}$$

$$B = 100T_{mean}(\Delta\Delta H^o - \Delta\Delta C_p T_o)/\Delta\mu_{CH2} \qquad \text{Eq. 5}$$

$$C = -100T_{mean}\Delta\Delta C_p/\Delta\mu_{CH2} \qquad \text{Eq. 6}$$

where $\Delta\Delta C_p$ is the difference between the molar heat capacity of solution of solute *i* and the molar heat capacity of solution of the *n*-alkane eluted before the solute, $\Delta\Delta S^o$ is the difference between the entropy of solution of solute *i* and the entropy of solution of the *n*-alkane eluted before the solute, and $\Delta\Delta H^o$ is the difference between the enthalpy of solution of solute *i*, and the enthalpy of solution of the *n*-alkane eluted before the solute. T_o means the reference temperature; superscript "o" means the standard values. It should be mentioned that Snijders et al. have already calculated enthalpy and entropy terms (12) from retention indices using a simplified equation missing the logarithmic temperature term in equation 1.

Table I. Statistical Properties of the Fit for the Model I = A + B/T + ClnT for Different Film Thicknesses

	*A**	*B**	*C**	*T*mean	*R*†	*F*†	*S*†
d_f = 0.5 µm							
Nitromethane	–831.3	70230	198.2	343.15	0.99687	635.7	0.1062
Nitroethane	–796.2	66120	209.5	343.15	0.99905	2096	0.07864
1-Nitropropane	–769.5	64510	220.8	343.15	0.99987	15000	0.05603
1-Nitrobutane	–862.4	71610	250.2	348.15	0.99987	13950	0.06786
1-Nitropentane	–809.4	73180	257.7	348.15	1.00000	657000	0.01057
1-Nitrohexane	–676.7	70170	253.7	348.15	0.99974	6673	0.11530
Acetonitrile	–806.6	64230	184.0	338.15	0.997074	595.6	0.08323
Propanenitrile	–573.2	54580	164.3	338.15	0.991821	211.3	0.08237
Butanenitrile	–622.1	58570	186.9	338.15	0.999666	5229.4	0.03594
Pentanenitrile	–743.8	67660	220.8	338.15	0.999525	3678.7	0.06348
d_f = 1.05 µm							
Nitromethane	–753.1	66490	186.3	343.15	0.990980	218.8	0.1860
Nitroethane	–802.7	66790	209.9	343.15	0.998912	1835	0.07733
1-Nitropropane	–537.2	53310	186.3	343.15	0.997187	708.0	0.2431
1-Nitrobutane	–851.7	71410	248.1	348.15	0.999881	14690	0.06374
1-Nitropentane	–712.3	67930	243.3	348.15	0.999955	393206	0.04383
1-Nitrohexane	–254.4	48210	192.0	348.15	0.997307	647.2	0.3823
Acetonitrile	–422.2	45620	127.1	343.15	0.997725	876.1	0.06784
Propanenitrile	–441.3	48060	144.6	343.15	0.996369	547.8	0.06024
Butanenitrile	–420.6	48390	157.1	343.15	0.997832	919.6	0.1111
Pentanenitrile	–374.2	48690	166.5	343.15	0.999741	7732.8	0.05863
d_f = 3.0 µm							
Nitromethane	–618.1	59410	166.6	343.15	0.999202	2504	0.04865
Nitroethane	–655.5	58970	188.5	343.15	0.999569	4639	0.05176
1-Nitropropane	–645.3	58120	202.3	343.15	0.999840	12530	0.06156
1-Nitrobutane	–642.4	60230	217.8	353.15	0.999311	2175	0.1545
1-Nitropentane	–689.8	66430	240.1	348.15	0.999909	19180	0.06427
Acetonitrile	–657.5	57620	161.4	378.15	0.993375	560.4	0.1921
Propanenitrile	–562.3	53580	162.5	378.15	0.999096	4144	0.1243
Butanenitrile	–600.2	56780	183.5	378.15	0.999684	11870	0.1183
Pentanenitrile	–619.0	60330	202.6	378.15	0.999779	16970	0.1280

* *A*, *B*, and *C* are fitted parameters in the model suggested in reference 9: $I = A + B/T + C\ln T$.

† *R*, *F*, and *S* are multiple correlation coefficients, Fisher statistics, and residual error, respectively.

The other explanation of the temperature dependence of retention indices is based on kinetic considerations. Therefore, it is called the kinetic explanation. The solution/vaporization process can be described with a quasi-kinetic equation between the solute in the mobile (m) and the stationary (s) phase. Assuming rate constants for this process, we may use Transition State Theory to give the temperature dependence of the reaction rate constant by the Eyring-Polanyi equation. Applying the Bronsted relation in its simplest form, we arrive to the physical meanings for the constants *A*, *B*, and *C* in equation 1 (8,9):

$$A = -100\mathrm{R}T_{mean}[\ln(\mathbf{k}/\varepsilon\mathbf{h}) + \Delta S^{\ddagger}/\mathrm{R}]/\Delta\mu_{CH2} \qquad \text{Eq. 7}$$

$$B = 100T_{mean}\Delta H^{\ddagger}/\Delta\mu_{CH2}, \qquad \text{Eq. 8}$$

$$C = -100RT_{mean}/\Delta\mu_{CH2} \qquad \text{Eq. 9}$$

The parameter *A* contains the Boltzman (**k**), Plack (**h**), and Broensted (ε) constants and the activation entropy ($\Delta S^{\ddagger}$). As the latter two remain unknown, no physically meaningful magnitude can be calculated from equation 7. The activation enthalpy ($\Delta H^{\ddagger}$) can be determined from equation 8, as the mean value of $\Delta\mu_{pCH2}$ can be calculated from the constant *C*. The ratio between *B* and *C* provides the activation enthalpy of solution.

The experiments were completed as described elsewhere (7). The retention index values listed in reference 7 were used for the calculations. The original manuscript (7) contained a misprint in case of nitromethane at 90°C and at 3.0-µm film thickness. The correct value is 527.78 index units (i.u.). An apolar dimethyl polysiloxane column was used to obtain a well-defined minimum as a function of the temperature of the retention indices (9).

Results and Discussion

The equation constants of the logarithmic model: $I = A + B/T + C\ln T$ and the quality of fits are summarized in Table I for different stationary phase film thicknesses. The statistical fits are highly significant in all cases. Generally, the temperature dependence of the retention indices can be described with a 0.1–0.2-i.u. precision. The precision of the fits increases as the number of carbon atoms in a molecule increases. Cyanoalkanes can better be described, except for the film thickness d_f = 3.0 µm, but this can be accidental.

The two approaches (thermodynamic and

kinetic) allow calculation of some thermodynamic magnitudes. As $\Delta\Delta H^o$, $\Delta\Delta C_p$, and $\Delta\Delta S^o$ are known via independent ways (7), $\Delta\mu_{CH2}$ can be determined using equations 4–6 and 9. Moreover, the chemical potential for one methylene unit is known from the literature for different temperatures (10,11).

Chemical potentials for one methylene unit and activation enthalpies of solution calculated from equations 4–6 and 9 are summarized in Table II. Columns two to four in Table II list the $\Delta\mu_{CH2}$ values. They show a strong dependence of the carbon atom number. Although the deviations are quite large, there is no doubt that the $\Delta\mu_{CH2}$ values are dispersed around the true value. The large dispersion is understandable, as the thermodynamic magnitudes ($\Delta\Delta H^o$, $\Delta\Delta C_p$, and $\Delta\Delta S^o$) were derived using different approaches having their own uncertainties. Moreover, the subtractions enhance the error. Equations 4–6 contain these thermodynamic magnitudes in different combinations. Therefore, their error levels are also different. Moreover, the coupling (correlation) of constants *A*, *B*, and *C* deteriorates the exact determination of $\Delta\mu_{CH2}$ in the case of an individual cyano or nitro compound. The average of more numerous determinations, however, provides a more realistic value. Probably, several assumptions cannot be considered as valid (e.g., temperature dependence of $\Delta\mu_{CH2}$ cannot be neglected during the calculations and the equality of $\Delta\mu_{CH2}$ and $\Delta\mu_{CH3}$ is also not true rigidly). If we compare the $\Delta\mu_{CH2}$ values in Table II with the recalculated values for the same temperature taken from literature [$d_f = 0.5$ µm, $T_{mean} = 342.6$ K, $\Delta\mu_{CH2} = 2104$ J/mol; $d_f = 1.05$ µm, $T_{mean} = 344.6$ K, $\Delta\mu_{CH2} = 2098$ J/mol; $d_f = 3.0$ µm, $T_{mean} = 360.4$ K, $\Delta\mu_{CH2} = 2044$ J/mol; all calculated from the values of *b* (slopes of *n*-alkane retention values)] (10,11), then we may conclude that the $\Delta\mu_{CH2}$ values determined via equations 4–6 are close to the literature values. The thermodynamic explanation suggests a possibility to calculate thermodynamic magnitudes ($\Delta\Delta H^o$, $\Delta\Delta C_p$, and $\Delta\Delta S^o$) (back-

Table II. Chemical Potential of Solution for One Methylene Unit and the Activation Enthalpy of Solution for Different Film Thicknesses (d_f)

	$\Delta\mu_{pCH2}$*	$\Delta\mu_{pCH2}$†	$\Delta\mu_{pCH2}$‡	$\Delta\mu_{pCH2}$§	$\Delta H^{‡}$**
$d_f = 0.5$ µm					
Nitromethane	–4817	–3566	–2891	–1439	2946
Nitroethane	–2930	–2047	–1622	–1362	2624
1-Nitropropane	–1979	–1059	–1041	–1292	2429
1-Nitrobutane	–850.5	–287.6	–473.1	–1157	2379
1-Nitropentane	–609.7	–125.2	–324.2	–1123	2361
1-Nitrohexane	–960.9	–228.8	–425.4	–1141	2299
Acetonitrile	–5231	–4538	–3252	–1528	2901
Propanenitrile	–5916	–4203	–2943	–1711	2762
Butanenitrile	–4691	–3271	–2244	–1504	2606
Pentanenitrile	–3910	–2807	–1899	–1273	2548
Average	–3189	–2213	–1711	–1353	2586
$d_f = 1.05$ µm					
Nitromethane	–10140	–6576	–5912	–1531	2967
Nitroethane	–7701	-5001	–4284	–1359	2646
1-Nitropropane	–3462	–1491	–1511	1532	2380
1-Nitrobutane	91.88	313.3	0	–1167	2394
1-Nitropentane	–1694	–645.8	–768.4	–1190	2321
1-Nitrohexane	–9938	–1952	–2020	–1508	2088
Acetonitrile	–8099	–5633	–3752	–2244	2984
Propanenitrile	–6427	–4183	–2777	–1973	2764
Butanenitrile	–4279	–2809	–1617	–1816	2562
Pentanenitrile	–5273	–3340	–1628	–1713	2431
Average	–5692	–3132	–2427	–1603.3	2554
$d_f = 0.5$ µm					
Nitromethane	–6360	–4061	–3377	–1712	2965
Nitroethane	–3591	–2243	–1821	–1514	2602
1-Nitropropane	–1878	–832.2	–915.9	–1410	2389
1-Nitrobutane	2099	1515	843.2	–1348	2299
1-Nitropentane	–1156	–298.8	–536.4	–1205	2300
Acetonitrile	–5579	–4367	–2976	–1948	2969
Propanenitrile	–5153	–3858	–2514	–1935	2742
Butanenitrile	–3990	–2903	–1854	–1713	2571
Pentanenitrile	–3390	–2441	–1475	–1552	2476
Average	–3222	–2166	–1625	–1593	
2590					

* Calculated from equation 4 and using $\Delta\Delta C_p$ and $\Delta\Delta S^o$ from the literature (9): $T_o = 298$ K.

† Calculated from equation 5 and using $\Delta\Delta C_p$ and $\Delta\Delta H^o$ from the literature (9): $T_o = 298$ K.

‡ Calculated from equation 6 and using $\Delta\Delta C_p$ from the literature (9).

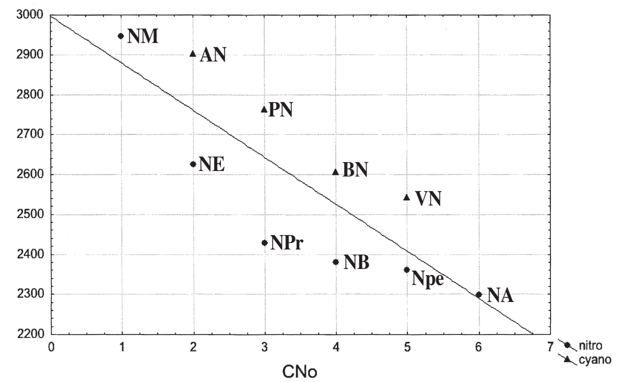

Figure 1. Activation enthalpy of solutions for nitroalkanes (•) and cyanoalkanes (•) against the carbon atom number (data of Table II) at 0.5-µm film thickness. Notations: nitromethane (NM), nitroethane (NE), 1-nitropropane (NPr), 1-nitrobutane (NB), 1-nitropentane (Npe), 1-nitrohexane (NH), acetonitrile (AN), propanenitrile (PN), butanenitrile (BN), and pentanenitrile (VN).

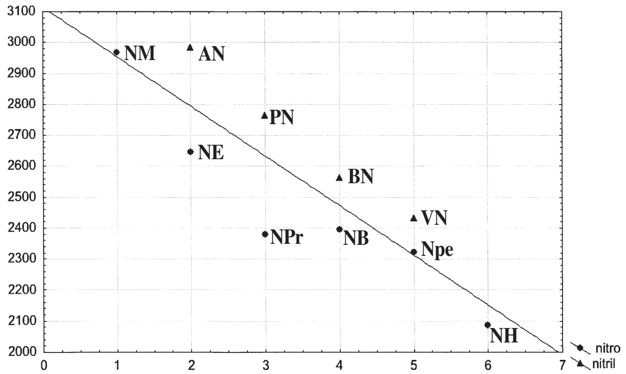

Figure 2. Activation enthalpy of solutions for nitroalkanes (▲) and cyanoalkanes (▲) against the carbon atom number (data of Table II) at 1.05-µm film thickness. Notations as in Figure 1.

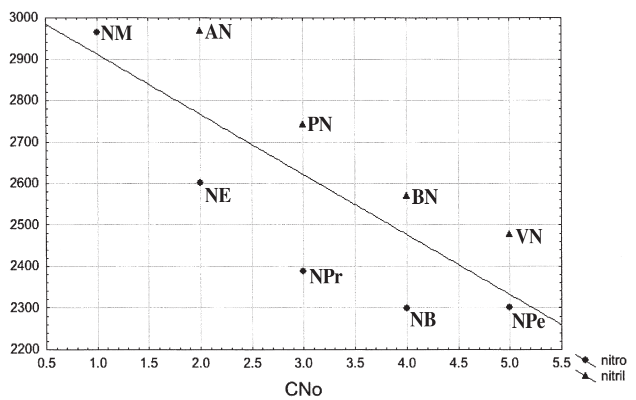

Figure 3. Activation enthalpy of solutions for nitroalkanes (●) and cyanoalkanes (▲) against the carbon atom number (data of Table II) at 3.0-µm film thickness. Notations as in Figure 1.

wards calculation as mentioned), if the $\Delta\mu_{CH2}$ value is known from the literature. However, the errors mentioned and the neglects used will make the thermodynamic magnitudes very uncertain, even if the retention indices were determined precisely. The kinetic explanation provides acceptable $\Delta\mu_{pCH2}$ values, although the absolute values are slightly underestimated compared with the literature values.

It is impossible to compare the activation enthalpy determined in this study with some literature values because, until now, no activation enthalpy was attributed to the solvation process. However, there are some proofs that the determined activation enthalpy is acceptable. A physicochemical process has smaller activation enthalpy than a chemical reaction, and this is just the case here. The equation constants *B* and *C* with an increasing molecular mass do not show any systematic change. Although, $\Delta\Delta H^{\ddagger}$ values were determined from equation constants *B* and *C*, the activation enthalpy changes in one direction in a systematic manner. Some tendencies can be observed independently from the film thickness. These are illustrated in Figures 1–3.

As it can be seen from the figures, the activation enthalpy of solution decreases as the carbon atom number (molecular mass) of the compounds decreases. This can be expected because the solute becomes more and more apolar (similar to the stationary phase) as the carbon chain increases. The activation energies for cyanoalkanes are always higher than those for the respective nitroalkanes. Moreover, the activation enthalpy is a convex function against the carbon atom number for both compound classes. The convex character suggests a limiting value; if the carbon chain is long enough, $\Delta\Delta H^{\ddagger}$ approaches the limit value. [The standards were *n*-alkanes (i.e., the activation enthalpy for *n*-alkanes was per definitionem zero).] The adsorption heat in gas–solid chromatography is at least by one order of magnitude higher than this activation enthalpy (13). The activation enthalpy values fall within the 2000 to 3000 J/mol scope in all three cases. No special differences can be observed with different film thickness. This fact rules out adsorption on the column wall as a possible cause for the minimum.

Hennig and Engewald (5) observed a minimum on the retention index versus temperature curve using alcohols and phenols as the solutes on an apolar stationary phase (HP-5). They explained the minimum with interfacial effects, without any quantitative evaluation. Adsorption seems to be a plausible explanation for causing a minimum, if adsorption plays greater role at smaller temperatures.

There are some indications that adsorption cannot be the dominant effect in formation of the minimum. Poole observed that nitromethane does not display any significant adsorption under gas chromatographic (GC) conditions (14). Similarly, our earlier study reveals that a minimum cannot be observed on the Innowax column (7). It is possible in a polar column that the polar groups of the phase block the active sites on the wall; thus, they have no effects on the sample molecules. On the other hand, if a nonpolar phase is used, the tube's active sites are unblocked, and, therefore, they will affect the sample molecules. The effect presented in Figures 1–3 reveals that less and less activation enthalpy is needed as the carbon atom of the solutes increases; it seems as if an existing structure would be gradually distorted.

The existence of the minimum can also be explained with the increased molar heat capacity of the polar solute compared with that of the *n*-alkane (7). The logarithmic model (equation 1) is analogous to the boiling point dependence of the retention data (15–17), if the isothermal column temperature is substituted with the boiling point of the solute. Temperature dependence of the retention indices can be found in the literature with thermodynamic explanations (18,19).

During derivation of equations 4–6 and 7–9, we took into account that the enthalpy and entropy of solutions are also temperature-dependent. However, we neglected the temperature dependence of the molar heat capacity, which is quite common in the literature, especially within the narrow range of applied temperatures in GC practice. Because of the neglects, the approach presented here can only be considered as an approximation.

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