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Minimum in the temperature dependence of the Kováts retention indices of nitroalkanes and alkanenitriles on an apolar phase

Miklós Görgényi[a],*, Károly Héberger[b]

[a]*Department of Physical Chemistry, University of Szeged, P.O. Box 105, H-6701 Szeged, Hungary*
[b]*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary*

Abstract

The Kováts retention indices (I) of 1-nitroalkanes and alkanenitriles were determined on polydimethylsiloxane and Innowax (polyethylene glycol) columns in a wide temperature range. The temperature dependence of the retention indices exhibits a definite minimum for the early members of the homologous series. The position of the minimum shifts to lower temperatures with increasing carbon atom number of the solute. The thermodynamic explanation of an extreme in the I vs. T function is the higher solvation heat capacities of nitroalkanes and alkanenitriles relative to those of the reference n-alkanes, owing to the deviation from the ideal state in the solution. A novel equation was derived which describes the minimum in the I vs. T function, too.
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1. Introduction

The Kováts retention index I is a useful tool for the identification of a compound in gas chromatography. As these indices are not sensitive to the GC conditions (in contrast with the simple retention time), I can be appropriately reproduced in various laboratories by using modern capillary columns.

I is rarely available in a wide range of temperature, so some kind of extrapolation is necessary to provide I at the necessary temperature.

Ettre and Billeb [1] suggested a nonlinear equation for the temperature dependence of I:

$$I \propto \frac{aT + b}{cT + d} \tag{1}$$

*Corresponding author. Tel.: +36-62-544-628; fax: +36-62-544-652.
E-mail address: gorgenyi@chem.u-szeged.hu (M. Görgényi).

where a, b, c and d are empirical constants.

They found that hydrocarbons (except toluene) exhibit linear behavior in an extended temperature range on squalane and even on a polar polyethylene glycol (PEG) phase. Therefore, a linear equation can be used in a shorter temperature range (Eq. (2)):

$$I = a + bT \tag{2}$$

which is widely used for the prediction of I in a narrow temperature range. The linear model is frequently used and recommended [2–4]. Nevertheless, the assumption of linearity must be treated with caution.

The temperature gradient (the first temperature derivative of I) is equal to parameter b in the linear equation. The dI/dT values depend on the structure of the solute and the stationary phase. This can be utilized for identification purposes [2,5,6].

Eq. (1) is a hyperbolic one. The constants a, b, c

and d characterize the interactions of the solute with the stationary phase. Takács et al. derived an Antoine-type equation for the temperature dependence of I [7]:

$$I = A + \frac{B}{T + C} \tag{3}$$

In most cases, the hyperbola section in the temperature interval used in GC can be considered nearly linear, but in some cases (columns with polar stationary phases) nonlinearity is observed [7–9].

Tudor and Moldovan made a thorough study of the temperature dependence of Kováts indices. Two types of hyperbola exist in GC practice: a concave increasing I vs. T ($B < 0$) and a convex decreasing I vs. T ($B > 0$) curve [10]. They did not report cases where the curve is concave, but I decreases with T as in the present investigations.

To the best of our knowledge the only evidence for a minimum in I is observed by Hennig and Engewald for some selected C_{10} hydroxy compounds on a HP-5 column [11]. The minimum has been explained on the assumption of interfacial effects. The effect of a change in film thickness (below 0.5 μm) on I seems to support this assumption. The contribution of interfacial adsorption to the retention of C_{10} hydroxy compounds may be supported, for example, by the significant surface effect in the case of 1-heptanol on squalane at 80.8 °C [12]. It is still not clear why the adsorption should result in a minimum in the temperature dependence of I.

Interfacial adsorption is generally observed for n-alkanes on polar stationary phases [12–17] or for some polar compounds on apolar phases [12,18,19].

The constants in Eq. (3) were calculated for the C_{10} hydroxy compounds exhibiting a minimum or with an almost linear I vs. T relationship [10]. The main differences were observed in the constant B in Eq. (3) for the compounds with a minimum (low $B < 0$) as compared to *cis*-verbenol and *trans*-pinocarveol (high $B < 0$), which furnish almost linear I vs. T relationships. The Antoine fit of Engewald's compounds results in hyperbola constants with high error [10]. Accordingly, it is not surprising that the minimum behavior cannot be described by a hyperbola.

We recently observed a minimum in the I vs. T graph for the early members of the homologous series of aliphatic ketones and aldehydes [20]. Accordingly, we assumed the existence of a minimum for the retention of highly polar compounds on an apolar phase. 1-Nitroalkanes and alkanenitriles may provide good models for this purpose. One of our aims is to find a thermodynamic explanation for the appearance of a minimum, and to establish what structural changes occur in the stationary solution.

2. Experimental

The C_3–C_6 1-nitroalkanes, propanenitrile, pentanenitrile and undecane were purchased from Aldrich, nitromethane, nitroethane and acetonitrile were from Reanal (Hungary), while the C_6–C_{10} n-alkanes and butanenitrile were from Fluka in purum or purissimum quality. The retention measurements were performed with a 5890 Hewlett-Packard Series II gas chromatograph equipped with a flame ionization detection (FID) system. The data were evaluated with a HP 3365 ChemStation. The carrier gas was nitrogen. The fused-silica open tubular column, with an inner diameter of 0.32 mm and 100% polydimethylsiloxane (PDMS) as stationary phase, has the following dimensions: 50 m HP-1 (Hewlett-Packard, USA), film thickness $d_f = 1.05$ μm, 30 m RTX-1 (Restek, USA), $d_f = 0.5$ μm and 30 m HP-1 (Agilent, USA), $d_f = 3$ μm. The 30 m HP-Innowax (cross-linked polyethylene glycol) column has a $d_f = 0.5$ μm. The retention indices were determined from three repetitions at each temperature.

3. Theory

3.1. Derivation of the thermodynamic form of I including the solvation heat capacity, ΔC_p

The thermodynamic form of I is given by Eq. (4), according to earlier suggestions [6] and assuming that the standard enthalpy and entropy of solvation (ΔH° and ΔS°) are temperature-independent quantities:

$$I = 100 \frac{(\Delta H_x^\circ - \Delta H_z^\circ) + T(\Delta S_z^\circ - \Delta S_x^\circ)}{(\Delta H_{z+1}^\circ - \Delta H_z^\circ) + T(\Delta S_z^\circ - \Delta S_{z+1}^\circ)} + 100z \tag{4}$$

where x is the solute eluting between the n-alkanes with carbon numbers z and $z+1$. Even the differences in ΔH° and ΔS° were assumed to be constant. Eq. (4) can be converted to Eq. (3) [6].

We regard ΔH° and ΔS° as temperature-dependent, and ΔC_p as a temperature-independent quantity (Eqs. (5) and (6))

$$\Delta H_T = \Delta H_{T_o} + \Delta C_p (T - T_o) \tag{5}$$

$$\Delta S_T = \Delta S_{T_o} + \Delta C_p \ln \frac{T}{T_o} \tag{6}$$

After substitution of these equations in Eq. (4) and rearrangement, we obtain

$$I_x = 100 \frac{a - T(b + \Delta\Delta C_{p,x-z} \ln T)}{c - T(d + \Delta\Delta C_{p,(z+1)-z} \ln T)} + 100z \tag{7}$$

where a, b, c and d are constants:

$$a = \Delta\Delta H_{T_{o,x-z}} - T_o \Delta\Delta C_{p,x-z} \tag{8}$$

$$b = \Delta\Delta S_{T_{o,x-z}} - \Delta\Delta C_{p,x-z} \ln(eT_o) \tag{9}$$

$$c = \Delta\Delta H_{T_{o,(z+1)-z}} - T_o \Delta\Delta C_{p,(z+1)-z} \tag{10}$$

$$d = \Delta\Delta S_{T_{o,(z+1)-z}} - \Delta\Delta C_{p,(z+1)-z} \ln(eT_o) \tag{11}$$

As an example for the meaning of the symbols, $\Delta\Delta H^\circ_{(z+1)-z} = \Delta H^\circ_{(z+1)} - \Delta H_z$ is the standard solvation enthalpy difference of the n-alkanes with carbon numbers $z+1$ and z.

4. Results

The I values of the 1-nitroalkanes and alkylnitriles at different temperatures and stationary-phase film thicknesses are shown in Tables 1–3, while some representative I vs. T relationships are presented in Figs. 1–5.

Some obvious characteristics of the I vs. T relations can be summarized as follows:

(a) the temperature dependence of I exhibits a well-defined minimum for the early members of the homologous series of 1-nitroalkanes and al-

kanenitriles in the investigated temperature range on the PDMS column (Figs. 1 and 2);

(b) the minimum shifts to lower temperatures with increasing alkyl chain length. To demonstrate this behavior in one diagram, the dependent variables were calculated from the difference of the retention indices and their average values in the given temperature range (Fig. 3);

(c) the minimum in the I vs. T relationship can be observed for C_1–C_5 alkanenitriles at around 20 °C (Table 2), even for pentanenitrile, while for 1-nitroalkanes containing more than three carbon atoms (Table 1, Fig. 5), the extreme value in I lies outside the experimental temperature range;

(d) I increases slightly with decreasing stationary film thickness. I_{min} is more sensitive to the film thickness only below 1 μm (Figs. 4 and 5);

(e) there is no minimum on the polar Innowax column, or any indication that a minimum exists for the 1-nitroalkanes near the temperature range used (Table 3);

(f) a minimum cannot be observed for higher members of the homologous series *in the temperature range used*. If we fit the curves with the adequate minimum-containing equation [20]

$$I = A' + B'/T + C' \ln T \tag{12}$$

where A', B' and C' are empirical constants, the following minima are obtained (PDMS column, $d_f = 0.5$ mm): $T_{min} = 355.5$ (nitromethane); $T_{min} = 315.6$ (nitroethane); $T_{min} = 286.2$ (1-nitropropane); $T_{min} = 275.6$ (1-nitrobutane); $T_{min} = 272.0$ (1-nitropentane); $T_{min} = 261.0$ (1-nitrohexane), all in Kelvin. We may safely conclude that the minimum shifts outside the temperature window of the measurements.

The observations that nitromethane does not display significant adsorption [21] under GC conditions and that only a slight adsorption was observed for 1-nitropropane on squalane [14,15] do not support the idea that the minimum is due to adsorption. The absence of the minimum on the Innowax column makes it improbable that the wall of the capillary tube exerts a significant effect on the retention index, i.e. the surface has no effect on the existence of the minimum above a stationary film thickness of 0.5 μm.

Table 1
Average values of Kováts retention indices of 1-nitroalkanes on a PDMS column with different film thicknesses, d_f[a]

t (°C)	d_f	Nitromethane	Nitroethane	1-Nitropropane	1-Nitrobutane	1-Nitropentane	1-Nitrohexane
20	0.5	534.30	619.20	704.88			
	1.05	532.36	617.38	702.58			
	3.0	531.15	616.27	702.10			
30	0.5	532.97	618.96	705.15	803.42	904.76	1004.5
	1.05	530.84	616.69	703.04	801.26	902.07	1001.2
	3.0	530.05	615.97	702.42		901.45	
40	0.5	532.00	618.79	705.52	804.18	905.43	1005.7
	1.05	529.99	616.62	703.37	801.69	902.88	1003.5
	3.0	529.26	615.90	702.92	801.32	902.40	
50	0.5	531.36	618.82	706.10	804.92	906.31	1006.6
	1.05	529.36	616.52	704.14	802.56	903.74	1004.4
	3.0	528.66	616.07	703.52	802.43	903.31	
60	0.5	530.78	618.98	706.76	805.87	907.34	1007.7
	1.05	528.89	616.86	704.63	803.56	904.83	1005.8
	3.0	528.15	616.25	704.26	803.51	904.49	
70	0.5	530.58	619.35	707.61	806.98	908.56	1009.1
	1.05	528.53	617.17	705.68	804.49	906.18	1006.6
	3.0	527.88	616.67	705.13	804.40	905.73	
80	0.5	530.38	619.93	708.65	808.25	909.94	1010.5
	1.05	528.40	617.67	706.55	805.73	907.54	1008.4
	3.0	527.75	617.22	706.13	805.74	907.12	
90	0.5	530.51	620.61	709.81	809.65	911.44	1012.2
	1.05	528.30	618.28	707.51	807.11	909.00	1010.0
	3.0	526.13	617.81	707.16	807.39	908.61	
100	0.5	530.84	621.56	711.08	811.13	913.03	1014.0
	1.05	528.51	619.09	708.09	808.56	910.55	1011.7
	3.0	527.85	618.58	708.43	808.56	910.36	
110	0.5	531.21	622.48	712.33	812.74	914.73	1015.8
	1.05	529.23	620.05	709.99	810.15	912.27	1013.6
	3.0	528.16	619.51	709.77	810.11	911.95	
120	0.5	531.31	623.37	713.85	814.57	916.51	1017.6
	1.05	528.98	620.88	711.34	811.84	914.08	1015.4
	3.0	528.60	620.51	711.18	811.95	913.83	

[a] d_f in μm.

4.1. How is the minimum behavior reflected in the thermodynamic functions?

ΔH and ΔC_p were determined from the retention factor k by the parameter estimation method described in Refs. [22,23]. ΔS^o was determined from Eq. (13) and from the van't Hoff equation:

$$K = \beta k \tag{13}$$

where β is the phase ratio. The calculated thermodynamic quantities are listed in Table 4.

The standard solvation enthalpies at 298.15 K are not sensitive to change in the film thickness, but slight increases in ΔC_p and ΔS can be observed for thick films.

The ΔC_p of solvation of *n*-alkanes increases linearly with the number of CH_2 groups in the molecule (with the molecular size in the apolar solvent) [24]. The additivity rule is also valid in aqueous solution [25,26]. However, this is not unambiguous for the early members of the homologous series of 1-nitroalkanes and alkanenitriles: ΔC_p remains approximately constant within the experimental error and increases slightly for the higher members (Table 4).

The difference in the solvation heat capacity between 1-nitroalkane and the reference *n*-alkane

Table 2
Average values of Kováts retention indices of alkanenitriles on a PDMS column with different film thicknesses, d_f^a

t (°C)	d_f^a	Acetonitrile	Propanenitrile	Butanenitrile	Pentanenitrile
20	0.5	457.95	546.43	639.31	741.10
	1.05	455.48	544.09	636.68	737.93
	3.0	455.45	543.13	635.94	737.27
30	0.5	456.94	545.79	639.02	741.10
	1.05	454.63	543.58	636.56	738.07
	3.0	454.52	542.69	635.87	737.44
40	0.5	456.24	545.38	638.95	740.99
	1.05	454.05	543.13	636.54	738.42
	3.0	453.90	542.41	635.97	737.79
50	0.5	455.64	545.11	639.03	741.27
	1.05	453.52	543.00	636.73	738.78
	3.0	453.32	542.29	636.14	738.24
60	0.5	455.24	545.11	639.25	741.73
	1.05	453.15	542.97	637.04	739.41
	3.0	452.92	542.32	636.54	738.84
70	0.5	455.10	545.21	639.64	742.32
	1.05	452.87	542.97	637.39	739.96
	3.0	452.71	542.38	636.93	739.50
80	0.5	454.91	545.26	640.15	743.04
	1.05	452.67	543.13	637.89	740.67
	3.0	452.50	542.60	637.50	740.32
90	0.5	455.09	545.75	640.80	743.93
	1.05	452.73	543.55	638.64	741.65
	3.0	452.35	542.90	638.14	741.21
100	0.5	455.52	546.29	641.64	744.98
	1.05	452.74	543.78	638.96	742.52
	3.0	452.53	543.33	638.86	742.19
110	0.5	455.85	546.59	642.45	746.12
	1.05	453.06	544.25	640.03	743.53
	3.0	452.72	543.83	639.74	743.33
120	1.05	453.31	544.91	640.92	744.66
	3.0	452.90	544.44	640.72	744.50
130	3.0	453.18	545.05	641.67	745.75
140	3.0	453.70	545.79	642.74	747.03
150	3.0	454.45	546.65	643.90	748.48
160	3.0	455.25	547.65	645.19	749.97
170	3.0	455.74	548.60	646.43	751.52
180	3.0	456.69	549.63	647.77	753.12
190	3.0	457.67	550.72	649.23	754.80

[a] d_f in μm.

Table 3
Average values of Kováts retention indices of 1-nitroalkanes on polyethylene glycol (HP-Innowax) column

| t (°C)	Nitromethane	Nitroethane	1-Nitropropane	1-Nitrobutane	1-Nitropentane	1-Nitrohexane
50	1178.5	1179.4	1227.2	1310.2	1405.8	1502.5
60	1179.2	1181.3	1230.4	1313.5	1409.6	1506.9
70	1180.6	1183.9	1233.8	1317.5	1414.0	1511.8
80	1182.9	1187.3	1237.8	1322.0	1418.8	1516.8
90	1184.7	1190.2	1241.4	1326.6	1423.2	1521.6
100	1187.8	1194.2	1246.1	1331.2	1428.6	1527.3
110	1188.5	1196.2	1248.4	1333.7	1431.0	1530.5
120	1190.2	1199.2	1251.6	1337.1	1434.5	1533.4
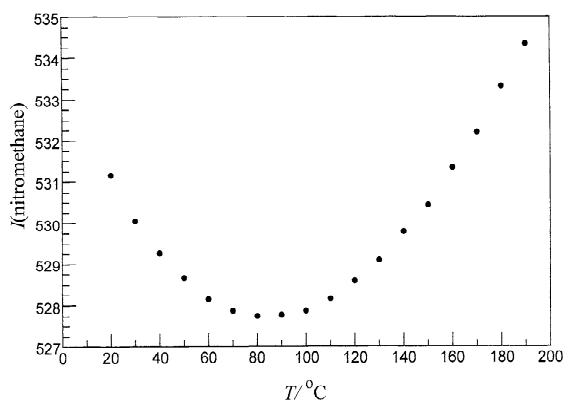
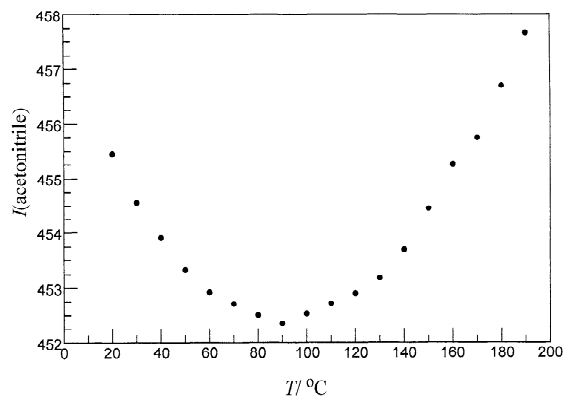Fig. 1. Temperature dependence of the Kováts retention index *I* of nitromethane on a PDMS column. Film thickness, 3 μm.

Fig. 2. Temperature dependence of the retention index of acetonitrile on a PDMS column. Film thickness, 3 μm.
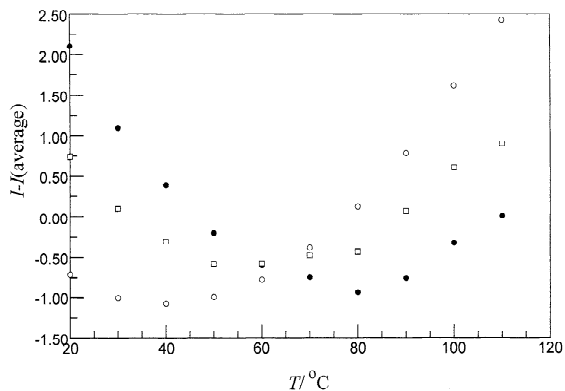

Fig. 3. Shifts in the extreme value of the retention index of alkanenitriles vs. *T* graphs. Acetonitrile ●, propanenitrile □, butanenitrile ○.
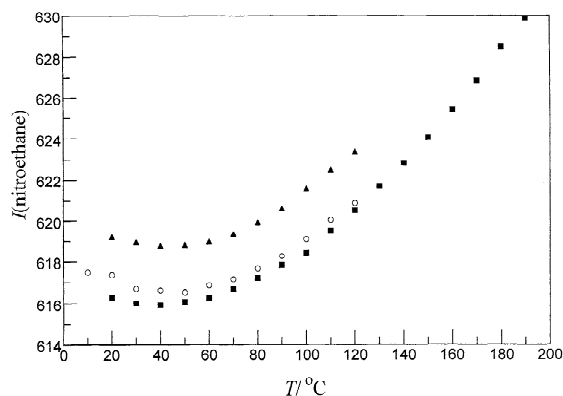

Fig. 4. Temperature dependence of the retention index of nitroethane on columns with different film thicknesses, ■ 3 μm, ○ 1.05 μm, ▲ 0.5 μm.
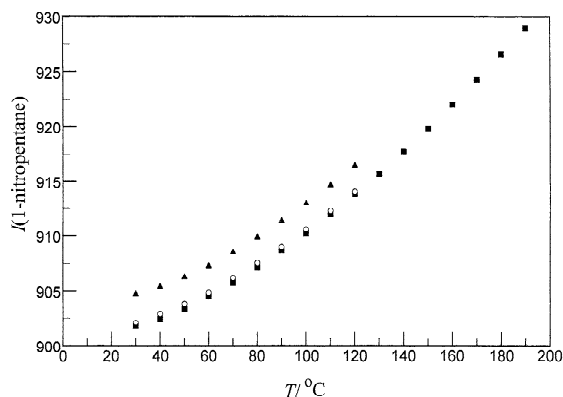

Fig. 5. Temperature dependence of the retention index of 1-nitropentane on columns with different film thicknesses, ■ 3 μm, ○ 1.05 μm, ▲ 0.5 μm.

which elutes closely before it, i.e. $\Delta\Delta C_p = \Delta C_p$(nitroethane)$-\Delta C_p$(*n*-hexane) continuously decreases with increasing alkyl chain length, i.e. the effect of the polar group slowly diminishes. The difference approximates to zero for 1-nitrohexane and decane: $\Delta\Delta C_p \approx 0$ (Table 5).

Some representative C_{10} hydroxy compounds behave similarly: *cis*-verbenol has a similar ΔC_p to that of the preceding *n*-alkane (Table 5). The minimum is outside the temperature range applied for this compound.

Our results show that not only ΔH and ΔS, but even their differences are not always constant in the thermodynamic form of the Kováts retention index

Table 4

Solvation enthalpy, entropy and heat capacity data for 1-nitroalkanes and alkylnitriles on a PDMS stationary phase with different film thicknesses at 298 K[a]

	$d_f = 0.5$ μm			$d_f = 1.05$ μm			$d_f = 3.0$ μm		
	$-\Delta H$[b]	$-\Delta S$	ΔC_p[b]	$-\Delta H$	$-\Delta S$	ΔC_p	$-\Delta H$	$-\Delta S$	ΔC_p
Nitroalkanes									
Nitromethane	27,725±66	52.8	70.8±1.7	28,244±148	54.6	81.3±4.2	−29,526±84	56.9	88.3±2.0
Nitroethane	31,511±67	58.1	75.6±1.7	31,656±131	58.9	81.0±3.7	−32,995±82	61.5	90.5±2.0
1-Nitropropane	35,083±64	62.9	77.5±1.6	34,240±132	60.8	68.5±3.7	−36,633±75	66.5	93.3±1.8
1-Nitrobutane	39,279±83	68.9	79.8±1.8	38,542±149	67.0	66.5±3.6	−40,480±142	71.4	89.8±2.7
1-Nitropentane	43,872±92	75.9	85.3±2.0	43,456±199	75.1	77.2±4.3	−45,426±104	79.6	102.1±2.3
1-Nitrohexane	48,360±87	82.5	90.3±1.9	47,858±190	81.8	88.6±4.1			
Alkylnitriles									
Acetonitrile	25,429±96	45.8	61.4±2.5	23,780±94	46.4	57.8±2.1	−26,043±133	58.3	86.3±3.2
Propanenitrile	29,496±83	51.7	62.0±2.2	27,442±37	51.3	60.9±1.0	−29,854±133	57.4	90.3±3.2
Butanenitrile	33,575±63	57.7	66.9±1.7	31,490±28	57.2	62.2±1.2	−33,967±135	63.6	95.7±3.2
Pentanenitrile	38,189±61	64.6	74.0±1.6	36,752±83	66.1	68.2±3.2	−38,552±141	70.7	102.1±3.3

[a] The thermodynamic data are given in J mol^{-1} and J K^{-1} mol^{-1}, respectively.
[b] Calculated by the parameter estimation method [22,23].

Table 5

Differences between the heat capacities of solvation of 1-nitroalkanes, alkanenitriles, some C_{10} hydroxy compounds and the reference *n*-alkanes as a function of the carbon number of the alkyl chain. Column: RTX-1, film thickness 0.5 μm

Pairs of compounds	$\Delta\Delta C_p$[a]	Pairs of compounds	$\Delta\Delta C_p$[a]	Pairs of compounds	$\Delta\Delta C_p$[b]
Nitromethane–pentane	16.7	Acetonitrile–butane	17.7	Thymol–dodecane	44.5
Nitroethane–hexane	9.9	Propanenitrile–pentane	14.3	Citronellol–dodecane	16.9
1-Nitropropane–heptane	6.7	Butanenitrile–hexane	12.4	*cis*-Verbenol–undecane	−4.3
1-Nitrobutane–octane	3.4	Pentanenitrile–heptane	12.4		
1-Nitropentane–nonane	2.4				
1-Nitrohexane–decane	−4.4				

[a] At 298.15 K.
[b] At 343.15 K.

(Eq. (4)). The minimum is due to the increased ΔC_p of the polar solute compared to that of the *n*-alkane. Therefore, Eq. (7) is more suitable for a solute with a minimum or for a hyperbolic curve than the Antoine equation. In Table 6, we demonstrate the applicability of Eq. (7). There is some deviation between the experimental and the calculated data, which increases with temperature. The reason for this differ-

ence is probably the temperature dependence of ΔC_p. However, it is obvious that Eq. (7) has an extreme value (Table 6).

From the definition

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P \qquad (14)$$

it follows that, at a given temperature T, ΔC_p is a

Table 6

Comparison of the experimental and calculated (Eq. (7)) I data for nitromethane and nitroethane. Column, RTX-1

t (°C)	20	30	40	50	60	70	80	90	100	110	120
Nitromethane (exp.)	534.3	533.0	532.0	531.4	530.8	530.6	530.4	530.5	530.8	531.2	531.3
Nitromethane (calc.)	534.2	533.4	532.7	532.2	531.9	531.6	531.6	531.7	531.9	532.4	533.1
Nitroethane (exp.)	619.2	619.0	618.8	618.8	619.0	619.4	619.9	620.6	621.6	622.5	623.4
Nitroethane (calc.)	620.1	620.0	620.0	620.1	620.4	620.8	621.4	622.1	623.0	624.0	625.2

measure of the change of entropy with temperature. In GC distribution, the solute is accompanied by an unfavorable entropy contribution, and ΔS is negative (Table 4). This is due to the condensation of the gaseous solute in the liquid state and the accompanying cavity formation in the stationary phase. This entropy decrease is not compensated by the favorable cavity filling.

ΔC_p is positive, which means that $\Delta S_{T_2} - \Delta S_{T_1}$ ($T_2 > T_1$) should also be positive, i.e. ΔS_{T_1} is more negative than ΔS_{T_2}, i.e. with increasing temperature, the entropy term becomes more favorable.

In consequence of certain physico-chemical processes, ΔC_p is higher than expected for the early members of the homologous series (Table 5). For these compounds, therefore, the entropy change varies more strongly than expected from the increase in simple randomization on temperature increase. This process may be due to distortion of a structure existing at lower temperature. As the adsorption is not significant for nitromethane, for instance on an apolar phase (squalane) [21], some other explanation should exist.

When polar compounds (ketones, nitroalkanes, nitriles, etc.) are dissolved in an apolar phase (e.g. alkanes), then, owing to the strong antipathy between the solute and the solvent, the distribution is nonrandom [27–29]. In this case, there is a sharp increase in the excess molar heat capacity near the upper critical solution temperature (UCST) where the solute and the solvent separate [30]. Unfortunately, there are no data for the UCST of PDMS with similar solutes used. The UCST increases with the molar mass of the solvent [31]. As the carbon chain length of the polar solute increases, the characteristic W-shaped curve (C_p^E vs. composition) slowly disappears [32]. These and other observations support our observations.

5. Conclusions

A minimum in the temperature dependence of the retention indices was observed for polar compounds in apolar solvents. This behavior is more pronounced if the difference in polarity between the solute and stationary phase is high. The different features of polar and apolar compounds may result in an increased ΔC_p of the solute and a decreased entropy of solvation compared to the reference *n*-alkane. Consideration of the temperature dependences of ΔH and ΔS leads to an equation (Eq. (7)) which is able to describe the minimum from thermodynamic quantities in the *I* vs. *T* graph.

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