Unified equation between Kováts indices on different stationary phases for select types of compounds

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Abstract

For homologous series and their branched-chain isomers, in plots of retention indices of one phase vs. those of another phase of different selectivity, the scattered data points form a series of parallel cluster lines, on which isomers containing the same carbon numbers are always located, and compounds with different numbers of methylene groups are found on different lines. The so-called isomer cluster phenomena have been observed for a variety of monofunctional and some multi-functional compounds. A retention equation to describe the new retention phenomena was derived based on the assumption of a constant molar volume of a solute when the intermolecular interactions take place on different stationary phases. Also, the equation can readily be applied to predict retention indices from one phase to others. Over 1000 retention indices on various stationary phases have been predicted with relative higher accuracy, and parts of the results are presented in this paper.

Keywords: Retention indices; Cluster phenomena; Isomer cluster phenomena; Structure–retention relationships

1. Introduction

The quantitative correlation of chromatographic retention parameters with molecular structures and physico-chemical properties is an intensively investigated area. Numerous investigators have attempted to correlate and predict retention indices of diverse compounds, such as odor-active compounds, olefins, drugs, polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins, using some molecular structural information and descriptors [1–8], and attempts have been made to retrieve molecular structure information from retention indices [9]. The correlation and prediction of the retention values of a variety of compounds by using physico-chemical parameters have also been frequently studied [10,11] and many studies have been included in reviews [12–15].

The Kováts retention index is probably the most accurate retention parameter in chromatography. However, most of the methods used to calculate retention indices usually result in predictions with lower precision than the experimental retention data. No realistic scheme for accurate prediction is available, although many attempts have been made. Concerning the complexity of the molecular interactions between solutes and stationary phases, especially differences in molecular orientations and interaction

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distances, it is difficult to describe the behavior of intermolecular interactions quantitatively. To predict accurate retention indices, we must utilize experimental data with the same precision.

Kováts retention indices have been obtained for thousands of compounds on many stationary phases [16–19]. It is a large resource of accurate data which can be applied to predict the retentions of the compounds for variety of stationary phases.

The main aim of this paper is to demonstrate a new relationship between Kováts indices determined on different stationary phases. The correlation equation can be used very simply to predict Kováts indices of selected types of compounds on various stationary phases of different selectivity with relative high accuracy.

2. Isomer cluster phenomena

On plotting Kováts retention indices (I) of homologous compounds on two stationary phases of different selectivity, we can observe isomer cluster phenomena, in which isomers containing the same number of carbon atoms are located on one of the parallel lines. Thus compounds with different numbers of methylene groups are divided into a series of clusters. Fig. 1 is a plot of the Kováts indices of squalane (SQ) vs. benzylbiphenyl (BBP) for 25 paraffins [20,21] containing 5–7 carbon atoms. Three isomer clusters form three lines with an average deviation of 2.1 retention index units (i.u.). Fig. 2 is a plot of I(SE-30) vs. I(PEG 20M) for 41 aromatics [22]; the isomer cluster phenomenon is evident.

Retention indices of aliphatic esters on fourteen stationary phases of different polarities were determined by Ashes and Haken [23]. Figs. 3 and 4 are plots according to the retention data on three phases, SE-30, DC-710 and Silar 5CP. The dispersions of average deviations among these stationary phases are about 3 i.u. for these compounds. It has been shown that the isomer cluster phenomenon occurs with many types of compounds on a variety of stationary phases.
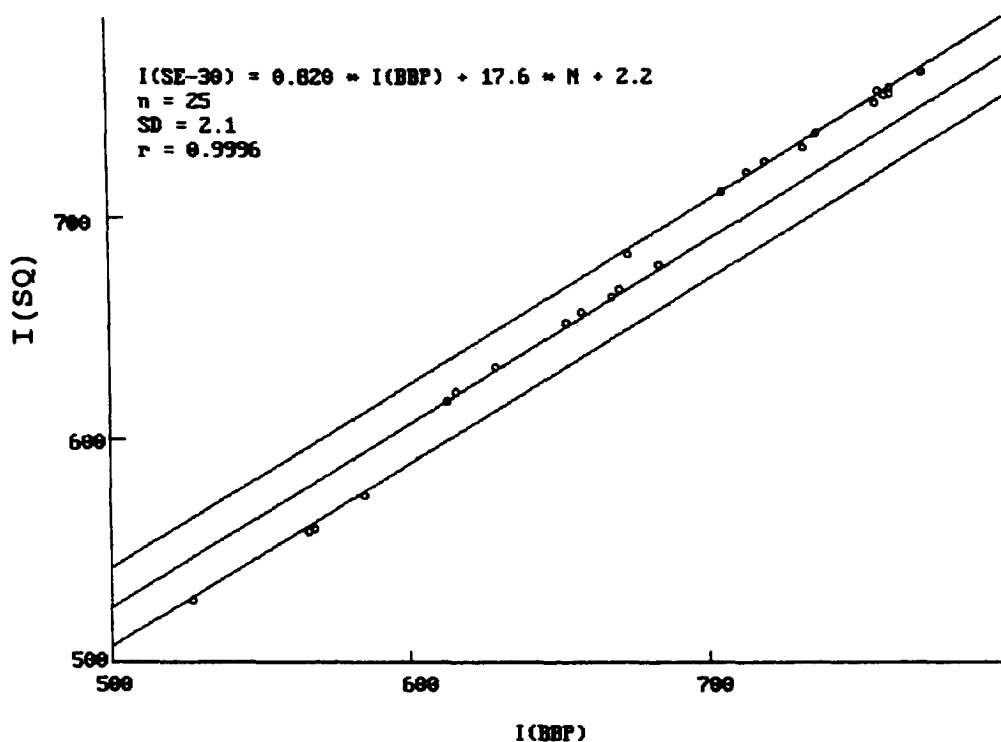

Fig. 1. Plot of Kováts indices (I) on squalane (SQ) vs. benzylbiphenyl (BBP) for 25 paraffins containing 5–7 carbon atoms.

I(SE-30) = 0.586 * I(PEG 20M) + 41.0 * N + 105.5
n = 41
SD = 4.2
r = 0.9993

I (SE-30)

1100

1000

900

800

700

600

900   1000   1100   1200   1300   1400

I(PEG 20M)

Fig. 2. Plot of *I* (SE-30) vs. *I* (PES 20M) for 41 aromatics.

I(SE-30) = 0.799 * I(DC-710)+ 17.6 * N - 25.3
n = 63
SD = 2.1
r = 0.9999

I (SE-30)

1100

1000

900

800

700

600

700   800   900   1000   1100   1200

I(DC-710)

Fig. 3. Plot of *I* (SE-30) vs. *I* (DC-710).

I(SE-30) = 0.611 * I(Silar 5CP) + 37.7 * N - 109.6
n = 63
SD = 3.3
r = 0.9998

Fig. 4. Plot of I (SE-30) vs. I (Silar 5 CP).
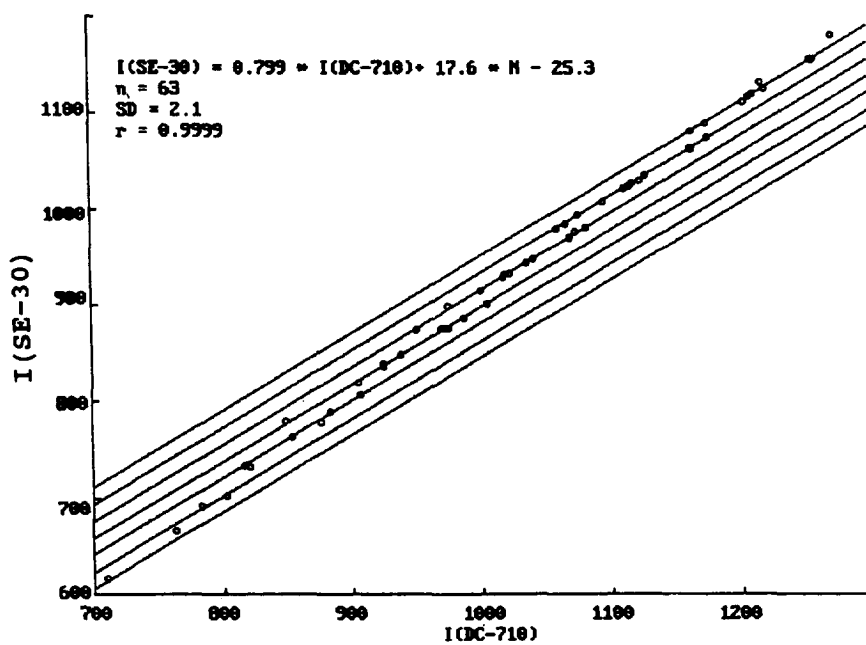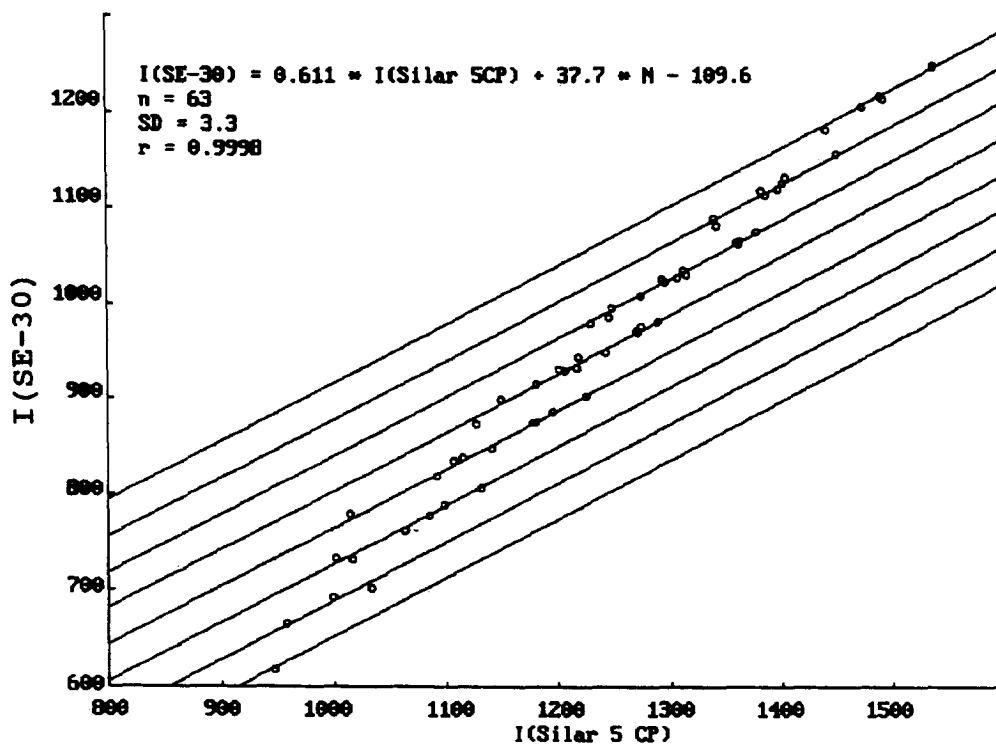
Fig. 5 is a plot of Kováts indices for odor-active alcohol compounds [1]. In this case, the majority of the compounds are followed the retention rule. A few compounds, (1) 2-methyl-2-propanol, (2) 3-methyl-3-pentanol, (3) 2-methyl-3-pentanol, (4) 3-methyl-2-pentanol and (5) 3-ethyl-3-pentanol, deviate from linearity, perhaps because the adjacent substituent group influences the hydrogen bonding interaction.

However, if two phases are structurally similar, all clusters of isomers approach each other, and may overlap as a single line. Fig. 6 shows plots of retention indices on DB-1 vs. DB-5 for 84 paraffins, 36 naphthenes and 17 aromatics [24]. In this case, the isomer cluster phenomenon also occurs, but it plays an insignificant role, compound types/functional groups being the main factors affecting the retention difference. Typical plots of retention indices for compounds of different types on OV-1 vs. SE-54 [16] are shown in Fig. 7.

The isomer cluster phenomenon characterizes both stationary phases and solute type. It can be used to compare the selectivity of stationary phases and it can also be applied for other purposes. The prediction of the Kováts indices of various stationary phases from those on known phases is one of the useful applications. Therefore, a prediction equation was derived and utilized for this purpose, as discussed in the following sections.

3. Unified equation

Concerning the isomer cluster phenomenon, there must exist some unvariable characteristics for selected types of compounds when they interact with molecules of different stationary phases. It has been shown that the molar volume is constant for a specified type compound. Based on this assumption, Eq. 1 was derived (see Appendix) as follows [25]:

$$I = AI' + BN + C \qquad (1)$$
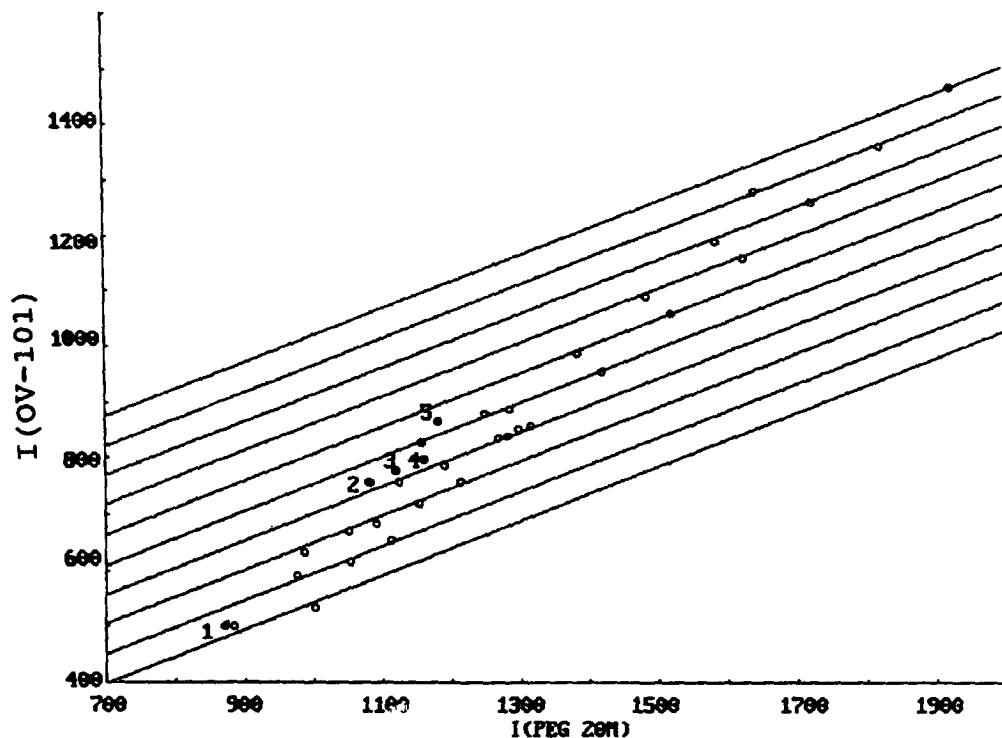
Fig. 5. Plot of I (OV-101) vs. I (PES 20M) for odor-active alcohol compounds.

where A, B and C are constants for a specified type of compound, I' is the retention index of a known phase and N is the carbon number in the carbon chain and branched carbon chain(s).

A, B and C are related to a number of parameters that can be used to account for the above retention behaviors. A is the slope of the linear plot and is determined by the relative

Fig. 6. Plot of I (DB-1) vs. I (DB-5) for 84 paraffins, 36 naphthenes and 17 aromatics.

Fig. 7. Plot of I (OV-1) vs. I (SE-54) for different types of compounds.

interaction energy of a methylene group on two stationary phases (see Appendix). B is mainly determined by the difference in relative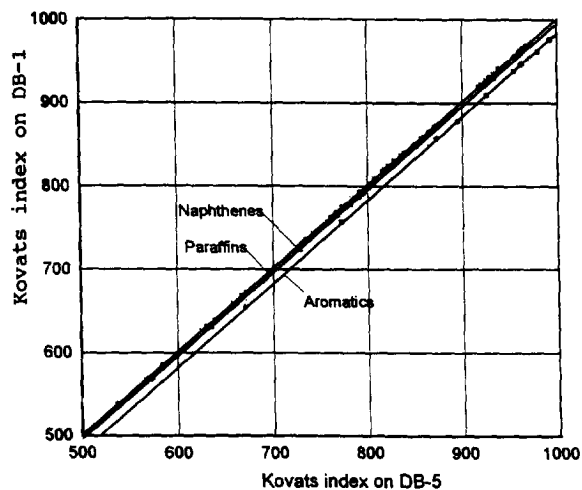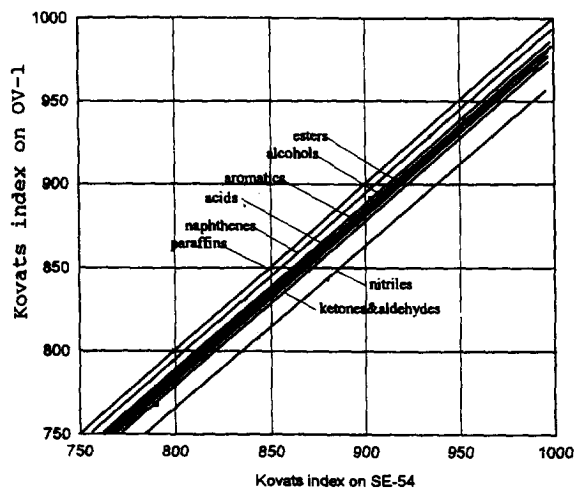 inter-molecular interaction distances of the carbon chain on two phases for a given type of compound. C is determined mainly by the properties of functional group(s) of the given type of compound, which include the interaction differences of dispersive, dipole–induced-dipole and hydrogen bonding interactions between two stationary phases. Therefore, one type of compound shares one set of coefficients in Eq. 1.

Empirically, retention phenomena such as Kováts indices for selected types of compounds, as shown above, can be quantitatively correlated using two variates, the retention index and the number of carbon atoms. Hence Eq. 1 can also be obtained by the intercorrelation method.

Table 1 gives the coefficients for some mono-multi-functional compounds between OV-1 and SE-54 phases. Generally, there is no great difference in A on the two stationary phases OV-1 (dimethylpolysiloxane) and SE-54 (5% phenyl–95% dimethyl polysiloxane) owing to the similar compositions, whereas B and C are different for various types of compounds owing to the differ-

Table 1
Coefficients of Eq. 1 for various types of compounds between OV-1 and SE-54 phases at 60°C

Compound type	A	B	C
Aromatic	0.986	0.53	26.91
RCOOH	1.038	−4.10	−1.31
RCN	1.066	−5.80	11.41
RNH$_2$; R$_2$NH	1.054	−5.57	3.97
NR$_3$	0.989	1.00	11.83
RCl	1.015	−1.42	11.67
RBr	1.013	−1.79	1.02
RI	1.003	−2.00	18.91
>C=O	1.072	−6.68	6.88
ROH	1.020	−1.69	2.94
RCOOR′	1.037	−3.08	6.92
Alkenol	1.028	−2.64	11.30
Amino alcohol	1.029	−2.28	11.98
BrRBr	1.074	−8.24	−4.87

The data are recalculated from Ref. [16].

Table 2
Coefficients of Eq. 1 for aliphatic esters between SE-30 and other phases at 150°C

Phase	A	B	C
OV-7	0.839	12.8	−1.8
DC-710	0.799	17.6	−25.3
OV-25	0.749	25.5	−68.2
100% Ph	0.697	30.4	−76.1
DC-230	0.918	3.61	31.0
DC-530	0.863	11.4	−4.2
XE-60	0.712	25.3	−78.6
XF-1150	0.658	37.3	−170.3
OV-225	0.671	29.5	−69.9
Silar 5CP	0.611	37.7	−109.6
QF-1	0.882	7.6	−177.0

The data are recalculated from Ref. [23].

ent functional groups. The results are in accord with the plots in Fig. 7.

Table 2 lists the coefficients of Eq. 1 for aliphatic ester compounds between SE-30 and eleven other phases of different polarity. In these cases, the values of A, B and C vary greatly owing to the differences in phase properties and compositions. In spite of the complexity of inter-molecular interactions, Eq. 1 is apparently valid, and deviations from linearity for most compounds are within the limits that can be achieved in different laboratories.

4. Prediction of Kováts retention index

To predict Kováts indices, the initial step is to obtain the three coefficients A, B and C in Eq. 1. Either regression analysis or calculation using the retention indices of three compounds on two stationary phases can be applied. In selecting the three compounds, at least one of them must be different in carbon number. Taking Kováts indices on OV-1 as the known data and to predict retention indices on SE-54, values $A = 1.020$, $B = −1.69$ and $C = 2.94$ for alcohols (as listed in Table 1), are calculated using the retention indices of three compounds, 1-butanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol, respective-

Table 3
Comparison of predicted and observed retention indices for alcohols, ketones and esters

Compound	I_{OV-1} (exp.)	I_{SE-54} (exp.)	I_{SE-54} (pred.)	ΔI	Compound	I_{OV-1} (exp.)	I_{SE-54} (exp.)	I_{SE-54} (pred.)	ΔI
Formic acid, propyl ester	605.79	623.60	622.78	-0.82	Propionic acid, methyl ester	615.21	630.43	632.54	2.09
Acetic acid, isopropyl ester	646.54	661.78	661.99	0.21	Isobutyric acid, methyl ester	670.97	686.58	687.31	0.73
Formic acid, isobutyl ester	673.40	689.84	689.83	-0.01	Propionic acid, ethyl ester	694.19	711.16	711.38	0.22
Acetic acid, propyl ester	696.34	713.63	713.63	0.00	Butyric acid, methyl ester	705.61	722.96	723.22	0.26
Formic acid, butyl ester	707.64	725.53	725.32	-0.21	Acetic acid, isobutyl ester	757.65	774.13	774.13	0.00
Isovaleric acid, methyl ester	761.30	777.34	777.92	0.58	Butyric acid, ethyl ester	784.04	800.00	801.48	1.48
Propionic acid, propyl ester	792.58	809.79	810.34	0.45	Acetic acid, butyl ester	796.18	814.16	814.07	-0.09
Isovaleric acid, ethyl ester	838.35	854.28	854.75	0.47	Propionic acid, isobutyl ester	852.83	869.02	869.76	0.74
Butyric acid, propyl ester	881.53	898.88	899.51	0.63	Propionic acid, butyl ester	891.40	909.12	909.74	0.62
Acetic acid, pentyl ester	896.36	914.88	914.88	0.00	Isobutyric acid, isobutyl ester	900.00	915.56	915.62	0.06
Hexanoic acid, methyl ester	907.01	925.46	925.92	0.46	Isobutyric acid, butyl ester	938.55	954.26	955.02	0.76
Butyric acid, isobutyl ester	940.26	956.57	957.36	0.79	Acetic acid, 2-ethylbutyl ester	956.99	974.66	974.70	0.04
Butyric acid, butyl ester	979.36	997.07	997.88	0.81	Hexanoic acid, ethyl ester	982.90	1000.00	1001.55	1.55
Isovaleraldehyde	636.32	657.70	655.62	-2.08	3-Methyl-2-butanone	640.92	661.44	660.55	-0.89
2-Pentanone	666.34	687.79	687.79	0.00	3-Pentanone	676.41	700.00	698.58	-1.42
3,3-Dimethyl-2-butanone	693.05	711.58	709.79	-1.79	4-Methyl-2-pentanone	721.24	741.61	740.00	-1.61
2-Methyl-3-pentanone	733.02	752.40	752.62	0.22	3-Methyl-2-pentanone	734.75	754.92	754.48	-0.44
2-Methylvaleraldehyde	742.38	762.95	762.65	-0.30	3-Hexanone	764.84	785.88	786.72	0.84
2-Hexanone	767.93	790.03	790.03	0.00	2,4-Dimethyl-3-pentanone	779.01	795.28	795.29	0.01
5-Methyl-3-hexanone	816.74	835.88	835.72	-0.16	2-Methyl-3-hexanone	819.95	838.42	839.16	0.74
5-Methyl-2-hexanone	836.53	858.37	856.92	-1.45	4-Heptanone	853.35	873.44	874.95	1.51
3-Heptanone	865.79	886.89	888.28	1.39	2-Heptanone	868.70	891.01	891.40	-0.39
2,2,4-Tetramethyl-3-pentanone	900.00	914.09	911.70	-2.39	2-Ethylhexanal	934.65	954.71	955.45	0.74
2,6-Dimethyl-4-heptanone	954.66	970.95	970.27	-0.68	2,2-Dimethyl-3-heptanone	964.66	980.56	980.99	0.43
2-Octanone	968.77	991.27	992.01	0.74	Isobutyl alcohol	611.31	626.00	626.21	0.21
2-Methyl-2-butanol	626.20	640.33	639.71	-0.62	1-Butanol	646.48	662.08	662.08	0.00
2,2-Dimethyl-1-propanol	657.34	670.46	671.47	1.01	3-Methyl-2-butanol	666.02	680.26	680.32	0.06
2-Pentanol	682.66	700.00	697.29	-2.71	3-Pentanol	684.21	700.00	698.88	-1.18
2,3-Dimethyl-2-butanol	715.26	729.44	728.86	-0.58	2-Methyl-2-pentanol	717.57	731.39	731.21	-0.18
3-Methyl-1-butanol	719.03	734.39	734.39	0.00	4-Methyl-2-Pentanol	744.14	758.42	758.31	-0.11
1-Pentanol	750.40	766.59	766.38	-0.21	2-Methyl-3-pentanol	757.96	772.28	772.41	0.13
2,4-Dimethyl-2-pentanol	775.91	789.03	789.03	0.00	3,3-Dimethyl-1-butanol	778.77	763.63	763.63	0.00
3-Hexanol	780.36	795.07	795.25	0.18	2,2-Dimethyl-3-pentanol	805.63	818.97	819.34	0.37
2-Methyl-2-hexanol	817.33	831.38	831.27	-0.09	2-Methyl-1-pentanol	818.35	833.58	834.00	0.42
2,4-Dimethyl-3-pentanol	821.18	834.49	835.20	0.71	4-Methyl-1-pentanol	821.19	836.97	836.89	-0.08
2,3-Dimethyl-3-pentanol	823.66	838.69	837.73	-0.96	2-Ethyl-1-butanol	825.94	841.00	841.74	0.74
3-Methyl-3-hexanol	826.62	841.11	840.75	-0.36	3-Methyl-1-pentanol	828.82	845.00	844.67	-0.33
5-Methyl-3-hexanol	838.15	852.08	852.51	0.43	3-Ethyl-3-pentanol	843.09	858.19	857.54	-0.61
1-Hexanol	852.96	869.44	869.29	-0.15	2,2-Dimethyl-1-pentanol	867.57	881.00	882.51	1.51
4-Heptanol	875.42	890.00	890.52	0.52	2,2,4-Trimethyl-3-pentanol	881.49	894.07	895.02	0.95
3,5-Dimethyl-3-hexanol	883.13	896.48	896.70	0.22	2-Heptanol	885.57	900.00	900.87	0.87
2-Methyl-2-heptanol	916.43	930.38	930.66	0.28	2,2,4-Trimethyl-1-pentanol	930	943	944	1
5-Methyl-3-heptanol	943.58	957.88	958.34	0.46	6-Methyl-2-heptanol	951.10	965	966	1
4-Ethyl-3-hexanol	953.26	967.63	968.25	0.62	1-Heptanol	955.05	971.73	971.73	0.00
2-Ethyl-4-methyl-1-pentanol	972	986	987	1	4-Octanol	975.50	990.22	990.90	0.68
3-Octanol	981.97	996.71	997.47	0.76	3,6-Dimethyl-3-heptanol	986.60	1000.00	1000.54	0.54

Retention indices are taken from Ref. [16].

ly. Coefficients for esters are calculated by using isobutyl formate, propyl acetate and isobutyl acetate and those for ketones using 2-pentanone, 2-hexanone and 2,4-dimethyl-3-pentanone. The average prediction error for 43 alcohols, 26 esters and 23 aldehydes and ketones is 0.63 i.u., which precision is almost the same as achieved experimentally. A comparison of predicted and experimental retention indices is given in Table 3. Kováts indices of 137 hydrocarbons between DB-1 and DB-5 phases [24], as shown in Fig. 6, were calculated in the same way (results not presented) and similar precisions were obtained.

As an additional verification of the results, Kováts indices of other monofunctional compounds of different types were predicted by using the coefficients listed in Table 1 and compared with experimental data. Identical accuracy was observed.

A large difference in phase polarities may result in extra prediction errors. Nevertheless, for most compounds, the prediction deviations are still within a few index units. The determination of Kováts indices on polar phases may also result in differences of a few index units [26]. Since stationary phases differ in structure, the orientations of molecular interactions would be differ-

ent, and this effect may result in deviations from linearity for some specific structural types of compounds.

Table 4 gives a comparison of the predicted and experimental Kováts indices on Carbowax 20M for primary alcohols and ketones. Since the structure of Carbowax 20M (polyethylene glycol) is different from that of OV-1 (dimethylpolysiloxane), predicted errors for 3,3-dimethyl-1-butanol and 2,4-dimethyl-3-pentanone are observed. This is probably due to the adjacent methyl groups hindering interactions of functional groups.

Table 5 gives a list of predicted and experimental data for the paraffins shown in Fig. 1. Hundreds of prediction data for aliphatic esters on stationary phases of different polarity have been obtained (not presented here), most of them being within a few index units. Aromatic compounds can also be predicted by Eq. 1, despite the structure (polarity) difference with respect to aliphatic isomers. Table 6 lists the retention indices and predicted results for 41 aromatics on two phases with a large polarity difference.

As expected from the theoretical considerations, Eq. 1 is also adaptable for compounds with multi-functional groups if the substituted posi-

Table 4
Comparison of predicted and observed retention indices for primary alcohols and 3-ketones on Carbowax 20M

Compound	I_{OV-1} (exp.)	I_{CW} (exp.)	I_{CW} (pred.)	ΔI
Isobutyl alcohol	611.31	1088.67	1089.52	0.85
1-Butanol	646.48	1142.64	1142.64	0.00
2,2-Dimethyl-1-propanol	657.34	1105.94	1107.55	1.61
3-Methyl-1-butanol	719.03	1205.70	1200.72	−4.98
1-Pentanol	750.40	1251.00	1248.10	−2.90
3,3-Dimethyl-1-butanol	778.77	1255.81	1239.70	−16.11
2-Methyl-1-pentanol	818.85	1300.00	1299.95	−0.05
1-Heptanol	955.05	1453.83	1453.83	0.00
2-Methyl-3-pentanone	733.02	1000.00	1003.25	3.25
3-Hexanone	764.84	1053.43	1053.43	0.00
2,4-Dimethyl-3-pentanone	779.01	1000.00	1015.30	15.30
5-Methyl-3-hexanone	816.74	1078.31	1074.81	−3.50
2-Methyl-3-heexanone	819.95	1071.62	1079.87	8.25
3-Heptanone	865.79	1152.16	1152.16	0.00
2,2,4,4-Tetramethyl-3-pentanone	900.00	1085.16	1085.16	0.00
2,2-Dimethyl-3-heptanone	964.66	1178.63	1187.14	8.51

Data from Ref. [16]. $A = 1.510$, $B = -51.49$, $C = 372.19$ for alcohols; $A = 1.577$, $B = -60.48$, $C = 210.06$ for ketones.

Table 5
Comparison of predicted and the experimental Kováts indices on benzylbiphenyl liquid phase for paraffins at 78.5°C ($A = 1.20$, $B = -21$, $C = 5$)

Compound	I_{SQ} (exp.)[a]	I_{BBP} (exp.)[b]	I_{BBP} (pred.)	ΔI
2,2-Dimethylbutane	539.0	527	527	0
2,3-Dimethylbutane	569.8	566	564	-2
2-Methylpentane	570.7	568	565	-3
3-Methylpentane	586.2	585	583	-2
2,2-Dimethylpentane	628.0	613	613	0
2,4-Dimethylpentane	632.0	616	618	2
2,2,3-Trimethylbutane	643.3	629	631	2
3,3-Dimethylpentane	662.8	653	655	2
2-Methylhexane	667.8	658	661	3
2,3-Dimethylpentane	674.8	668	669	1
3-Methylhexane	678.2	671	673	2
2-Ethylpentane	689.2	684	686	2
2,2,4-Trimethylpentane	693.5	674	673	-1
2,2-Dimethylhexane	721.3	705	707	2
2,5-Dimethylhexane	730.7	714	718	4
2,4-Dimethylhexane	735.1	720	723	3
2,2,3-Trimethylpentane	741.4	733	731	-2
3,3-Dimethylhexane	747.6	737	738	1
2,3,3-Trimethylpentane	764.8	760	759	-1
2-Methyl, 3-ethylpentane	765.5	762	760	-2
2,3-Dimethlhexane	761.4	757	755	-2
2-Methylheptane	766.3	758	761	3
4-Methylheptane	768.2	762	763	1
3,4-Dimethylhexane	774.7	773	771	-2
3-Ethylhexane	775.7	773	772	-1

[a] Data from Ref. [20].
[b] Data from Ref. [21].

tions and the number of substitutent functional groups are of the same. Table 7 presents some predicted data for these compounds with multifunctional groups. Table 7 also lists some positional isomers of dibromoalkanes. 1,2-Dibromobutane is an exception, perhaps owing to the interaction of the two bromo groups.

Acknowledgements

Appendix

Derivation of Eq. 1

According to the statistical thermodynamic treatment in high-performance liquid chromatography by Lu and co-workers [27–30], the chemical potential of solute A in pure liquid phase B (for a pure phase, $\partial N_{B\,i}^l / \partial N_A^l = 0$) is

$$\mu_A^l = RT\left\{ -\ln N_A^l - \frac{\chi_A^l}{kT} + \frac{V_A^l}{V_B^l} + \ln V_l + \ln\left[\left(\frac{2\pi m_A kT}{h^2} \right)^{3/2} j_A^l \right] \right\}$$

(A1)

Table 6
Kováts indices of 41 aromatics on PEG 20M and SE-30 and predicted values using Eq. 1

Compound	I (PEG 20M)[a]	N	I (SE-30)[a]	I (pred.)	ΔI
Benzene	954.5	0	657.1	664.8	7.7
Toluene	1049.5	1	759.9	761.5	1.6
Ethylbenzene	1131.9	2	851.4	850.8	−0.6
m-Xylene	1145.3	2	859.6	858.6	−1.0
p-Xylene	1138.9	2	860.8	854.9	−5.9
o-Xylene	1185.7	2	882.2	882.3	0.1
n-Propylbenzene	1210.1	3	941.8	937.6	−4.2
Isopropylbenzene	1176.9	3	911.3	918.1	6.8
1-Methyl-3-ethylbenzene	1224.9	3	949.0	946.3	−2.7
1-Methyl-4-ethylbenzene	1223.4	3	950.6	954.4	−5.2
1-Methyl-2-ethylbenzene	1258.4	3	964.6	965.9	1.3
1,3,5-Trimethylbenzene	1242.2	3	956.2	956.4	0.2
1,2,4-Trimethylbenzene	1277.6	3	977.5	977.1	−0.4
1,2,3-Trimethylbenzene	1325.4	3	1006.0	1005.2	−0.8
n-Butylbenzene	1309.1	4	1039.6	1036.6	−3.0
Isobutylbenzene	1241.3	4	994.3	996.9	2.6
1-Methyl-3-isopropylbenzene	1266.5	4	1006.6	1011.6	5.0
1-Methyl-4-isopropylbenzene	1268.8	4	1009.5	1013.0	3.5
1-Methyl-2-isopropylbenzene	1276.4	4	1020.6	1017.4	−3.2
1,3-Diethylbenzene	1297.3	4	1034.8	1029.7	−5.1
1-Methyl-3-propylbenzene	1301.0	4	1034.8	1031.9	−2.9
1-Methyl-4-propylbenzene	1301.0	4	1038.1	1031.9	−6.2
1,4-Diethylbenzene	1305.2	4	1040.0	1034.3	−5.7
1,2-Diethylbenzene	1324.0	4	1043.5	1045.3	1.8
1,3-Dimethyl-5-ethylbenzene	1319.8	4	1042.6	1042.9	0.3
1-Methyl-2-propylbenzene	1327.7	4	1048.3	1047.5	−0.8
1,4-Dimethyl-2-ethylbenzene	1343.5	4	1059.0	1056.8	−2.2
1,3-Dimethyl-4-ethylbenzene	1350.0	4	1061.7	1060.6	−1.1
1,2-Dimethyl-4-ethylbenzene	1357.2	4	1066.1	1064.8	−1.3
1,3-Dimethyl-2-ethylbenzene	1372.1	4	1069.6	1073.5	3.9
1,2-Dimethyl-3-ethylbenzene	1394.8	4	1083.5	1086.8	3.3
1,2,4,5-Tetramethylbenzene	1406.8	4	1096.4	1093.9	−2.5
1,2,3,5-Tetramethylbenzene	1416.5	4	1099.5	1099.5	0.0
1,2,3,4-Tetramethylbenzene	1461.6	4	1127.5	1126.0	−1.5
n-Pentylbenzene	1404.3	5	1140.5	1133.4	−7.1
1,3-Dimethyl-5-propylbenzene	1406.2	5	1126.0	1134.5	8.5
1,4-Dimethyl-2-propylbenzene	1415.0	5	1140.0	1139.7	−0.3
1,3-Dimethyl-4-propylbenzene	1429.0	5	1143.7	1147.9	4.2
1,2-Dimethyl-4-propylbenzene	1435.8	5	1149.5	1151.8	2.3
1,3-Dimethyl-2-propylbenzene	1451.6	5	1152.2	1161.1	8.9
1,2-dimethyl-3-propylbenzene	1458.6	5	1166.5	1165.2	−1.3

[a] Kováts indices from Ref. [22].

where the superscript l denotes a parameter in the liquid phase and g in the gas phase, h is Planck's constant, j_A^l is the internal partition function of solute A, k is Boltzmann's constant, m_A is the mass on the solute, N_A^l is the number of solutes in the liquid phase, R is the gas constant, T is absolute temperature, V_A^l and V_B^l are the molar volumes for the solute and solvent, respectively, V_l is the volume of liquid phase and χ_A^l is the interaction energy between the solute and solvent. The chemical potential for solute A in the gas phase is

Table 7
Comparisons of predicted and observed retention indices for different types of multi-functional group compounds

Compound	I_{OV-1} (exp.)	I_{SE-54} (exp.)	I_{SE-54} (pred.)	ΔI
3-Buten-1-ol	618.91	636.98	636.98	0.00
2-Methyl-2-propen-1-ol	629.11	646.35	647.46	1.12
2-Buten-1-ol	649	666	668	2
2-Methyl-4-penten-2-ol	694.62	710.28	709.53	−0.75
3-Methyl-3-buten-1-ol	713.62	731.70	731.70	0.00
4-Methyl-1-penten-3-ol	740.10	754.41	756.28	1.87
4-Penten-1-ol	735.81	754.51	754.51	0.00
2-Methyl-1-penten-3-ol	763.67	778.54	780.51	1.97
2,3-Dimethyl-4-penten-2-ol	781.91	797.12	796.61	−0.51
1-Hepten-4-ol	850.88	867.35	867.52	0.17
2-Amino-1-butanol	804.30	830.50	830.50	0.00
3-Amino-1-propanol	775.50	807.76	803.23	−4.53
2-Amino-2-methyl-1-propanol	730.84	754.91	754.91	0.00
2-Aminoethanol	644.27	670.38	670.38	0.00
2-Methylaminoethanol	700.00	725.82	725.44	−0.38
1,4-Dibromobutane	1062.81	1100.00	1103.52	3.52
1,4-Dibromopentane	1110.37	1146.36	1146.36	0.00
1,5-Dibromepentane	1175.86	1216.69	1216.69	0.00
1,2-Dibromobutane	1200.00	1238.01	1250.85	12.84
1,6-Dimromohexane	1280.17	1320.70	1320.46	0.24
1,7-Dibromoheptane	1384.14	1423.89	1423.89	0.00
1,8-Dibromooctane	1486.28	1524.99	1525.32	0.34
1,9-Dibromononane	1587.93	–	1626.25	–

Data from Ref. [16]. $A = 1.028$, $B = -2.64$, $C = 11.30$ for alkenols; $A = 1.029$, $B = -2.28$, $C = 11.98$ for amino-alcohols; $A = 1.074$, $B = -8.24$, $C = -4.87$ for dibromoalkanes.

$$\mu_A^g = -RT\left\{ -\ln N_A^g + \ln\left[\left(\frac{2\pi m_A kT}{h^2} \right)^{3/2} j_A^g \right] \right. $$
$$\left. + \ln V_0 \right\} \tag{A2}$$

where V_0 is the volume of gas phase and N_A^g is the number of solutes in the gas phase. The chemical potentials in the gas and liquid phases are equal at equilibrium, $\mu_A^l = \mu_A^g$, hence we have

$$\ln k' = \ln \frac{N_A^l}{N_A^g} = -\frac{\chi_A^l}{kT} + \ln \frac{j_A^l}{j_A^g} + \frac{V_A^l}{V_B^l} - \ln \beta \tag{A3}$$

where $\beta = V_0/V_l$ is the phase ratio. The χ_A^l term includes all forms of intermolecule interaction energies, such as dispersive, dipole–induced-dipole and hydrogen bonding, etc. Hence the retention equation for solute A can be further expressed (with the assumption $j_A^l = j_A^g$) as

$$\ln k' = \frac{B_1\alpha_A + B_2\mu_A^2 + B_3 + B_4}{RT} + \frac{V_A^l}{V_B^l} - \ln \beta \tag{A4}$$

where B_1, B_2, B_3 and B_4 are constants expressed as follows:

$$B_1 = N_0 \cdot \frac{z}{r^6} \left(\frac{3}{2} \cdot \frac{\alpha_B I_A I_B}{I_A + I_B} + \mu_B^2 \right)$$

$$B_2 = N_0 \cdot \frac{z}{r^6} \left(\frac{2}{3} \cdot \frac{\mu_B^2}{kT} + \alpha_B \right)$$

$$B_3 = -N_0 \chi_H$$

$$B_4 = -N_0 \chi_0$$

where I_A, α_A, μ_A and I_B, α_B, μ_B denote as the approximate ionization energy, polarizability, dipole moment for solute A and stationary phase B, respectively; N_0 is Avogadro's number. The parameters r and z are the average distance

between solute A and solvent B and the number of solvents around solute A, respectively; χ_H and χ_0 are the energy of hydrogen bonding and the remaining forms of energy, respectively.

The Kováts retention index can be expressed as

$$I = 100\left(n + \frac{\ln k'_A - \ln k'_n}{\ln k'_{n+1} - \ln k'_n}\right) \tag{A5}$$

where n is the carbon number of a paraffin. Substituting the retention values of solute A and normal paraffins in Eq. A5 by Eq. A4, we obtain

$$I = 100n + 100 \times$$

$$\frac{B_1\alpha_A - B_n\alpha_n + B_2\mu_A^2 + B_3 + B_4 + RT\Delta V_A/V_B^l}{B_n\Delta\alpha_{CH_2} + RT\Delta V_{CH_2}/V_B^l} \tag{A6}$$

where $\Delta V_A = V_A^l - V_n^l$ is the molar volume difference between the solute and an n-paraffin, $\Delta\alpha_{CH_2}$ and ΔV_{CH_2} are the molar polarizability and volume of a methylene group, respectively, and B_n is the B_1 constant for an n-paraffin.

ΔV_A is an independent variate of the stationary phase, so we can obtain an expression for ΔV_A from Eq. A6 as

$$\Delta V_A = \frac{V_B^l}{RT}\left[\left(\frac{I}{100} - n\right)(B_n\Delta\alpha_{CH_2} + RT\Delta V_{CH_2}/V_B^l)\right.$$

$$\left. - B_1\alpha_A + B_n\alpha_n - B_2\mu_A^2 - B_3 - B_4\right] \tag{A7}$$

In the same way, we can obtain the expression for ΔV_A for another phase as

$$\Delta V_A = \frac{V_B^{'l}}{RT}\left[\left(\frac{I'}{100} - n\right)(B'_n\Delta\alpha_{CH_2}\right.$$

$$+ RT\Delta V_{CH_2}/V_B^{'l}) - B'_1\alpha_A + B'_n\alpha_n$$

$$\left. - B'_2\mu_A^2 - B'_3 - B'_4\right] \tag{A8}$$

Setting Eq. A7 equal to Eq. A8, we obtain

$$I = \frac{1 + K'}{1 + K}\cdot I' + \frac{100}{1 + K}\left(K\cdot\frac{B_1}{B_n} - K'\cdot\frac{B'_1}{B'_n}\right)N$$

$$+ \frac{100}{1 + K}\left[\left(K\cdot\frac{B_1}{B_n} - K'\cdot\frac{B'_1}{B'_n}\right)\frac{\alpha_0}{\Delta\alpha_{CH_2}}\right.$$

$$+ \left(K\cdot\frac{B_2}{B_n} - K'\cdot\frac{B'_2}{B'_n}\right)\frac{\mu_A^2}{\Delta\alpha_{CH_2}}$$

$$\left. + \left(K\cdot\frac{B_3 + B_4}{B_n} - K'\cdot\frac{B'_3 + B'_4}{B'_n}\right)\frac{1}{\Delta\alpha_{CH_2}}\right] \tag{A9}$$

where $\alpha_0 = \alpha_A - \alpha_n$ is the polarizability of the functional group of solute A, N denotes the carbon number of the molecule skeleton and K and K' are methylene constants on the two phases as follows:

$$K = \frac{B_n\Delta\alpha_{CH_2}V_B^l}{RT\Delta V_{CH_2}}$$

$$K' = \frac{B'_n\Delta\alpha_{CH_2}V_B^{'l}}{RT\Delta V_{CH_2}}$$

The equation for Kováts indices on different phases can be expressed as

$$I = AI' + BN + C \tag{A10}$$

where A, B and C are constants:

$$A = \frac{1 + K'}{1 + K}$$

$$B = \frac{100}{1 + K}\left(K\cdot\frac{B_1}{B_n} - K'\cdot\frac{B'_1}{B'_n}\right)$$

$$C = \frac{100}{1 + K}\left[\left(K\cdot\frac{B_1}{B_n} - K'\cdot\frac{B'_1}{B'_n}\right)\frac{\alpha_0}{\Delta\alpha_{CH_2}}\right.$$

$$+ \left(K\cdot\frac{B_2}{B_n} - K'\cdot\frac{B'_2}{B'_n}\right)\frac{\mu_A^2}{\Delta\alpha_{CH_2}}$$

$$\left. + \left(K\cdot\frac{B_3 + B_4}{B_n} - K'\cdot\frac{B'_3 + B'_4}{B'_n}\right)\frac{1}{\Delta\alpha_{CH_2}}\right]$$

For one class of monofunctional compounds, the difference in the terms α_0 and μ_A and hydrogen bonding are usually very small, so they can share one set of coefficients. For the same class of multi-functional compounds, they can also share the same set of coefficients except for the situa-

tion where extra intramolecular interactions take place between the functional groups.

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