Homologous Increments of Gas Chromatographic Retention Indices as Characteristic of Organic Compounds Polarity

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Abstract—Properties of homologous increments of gas chromatographic retention indices have been examined, $i_{RI} = RI - 100\,int(M/14)$, where M is molecular weight and RI is retention index. Comparing to the characteristics of other organic substances (normal boiling points, permittivity, dipole moments, retention indices and their differences for standard polar and nonpolar phases, indices of boiling points, molecular masses, molar refractions, and their differences), it has been shown that the i_{RI} value can be used as an additional characteristic of polarity.

Keywords: organic compounds, criteria of polarity, gas chromatographic retention indices, homologous increments of retention indices

The term "polarity" is widely used in organic chemistry and chromatography. One cannot help noticing its various meanings: this term is applied for characterization of chemical bonds, molecules, their fragments, chemical substances, types of molecular interactions, solvents, chromatographic stationary phases, etc. [1]. Pauling has suggested the most determinative definition of the chemical bonds polarity, due to asymmetric distribution of electron density between the atoms of different electronegativity [2]. Speaking of more complex molecular interactions, their polarity can be estimated from different physico-chemical parameters of both molecules and substance. The diversity of micro- and macroscopic properties which might be used for the said purposes leads to objective ambiguity of the polarity characteristics.

Dipole moment (μ, 1 D = 3.336×10^{-30} C m) and permittivity (ε, dimensionless value) are commonly used characteristics of polarity in organic chemistry [3, 4]. Comparison of these parameters for the same compounds illustrates the contradiction of the "polarity" term. For example, ethylene glycol is more polar than acetone according to the value of ε, but less polar according to the dipole moment values. At the same time, acetic acid which is considered among strongly polar solvents according to its elutive power in high-performance liquid chromatography [5] seems much less polar than both acetone and ethylene glycol according to the values of ε and μ (Table 1).

Different physico-chemical values can be used as measures of polarity, for example, hydrophobic factor (log P), logarithm of the distribution coefficient in a heterogeneous 1-octanol–water system [6, 7]. Referring to the above example, ethylene glycol is found to be the most polar compound, while acetone is the least polar one according to this criteria, considering that both are hydrophilic (log P < 0). The log P value often determines the order of elution in reverse-phase HPLC.

The use of gas chromatographic retention parameters allows characterization of the analytes polarity by the difference between retention indices (ΔRI) for standard polar and nonpolar phases [8, 9]:

$$\Delta RI = RI_{polar} - RI_{nonpolar}. \tag{1}$$

In contrast to other criteria mentioned above, the latter one is applicable to individual compounds as well as homologous series, after averaging the ΔRI values of several members of the corresponding series. Besides this, the ΔRI values can also serve as parameters for individual and group (assignment to the

Table 1. The values of dipole moment, permittivity, hydrophobic factor, ΔRI, Δ_{TM}, and $\Delta_{T\text{-}MRD}$ for acetone, acetic acid, and ethylene glycol[a]

Compound	ε	μ, D	$\log P$	ΔRI	Δ_{TM}	$\Delta_{T\text{-}MRD}$
Acetone	20.8±0.4	2.8±0.1	−0.16	348	168	241
Ethylene glycol	38.5±2.0	2.2±0.1	−1.36	880	677	840
Acetic acid	6.2±0.1	1.6±0.2	−0.25±0.04	790	364	544

[a] The accuracy of the reported mean values corresponds to standard deviation of several reference values.

corresponding homologous series) identification of analytes, on top of characterizing the polarity.

The recently proposed approach to characterize an organic substance polarity is based on the calculation and comparison of the indices of its normal boiling temperature (I_T), molar mass (I_M), and molar refractivity (I_{MRD}), determined by analogy with chromatographic retention indices [1]. The general equation for calculation of the index $I_A(x)$ for property A is as follows:

$$I_A(x) = I_n + (I_{n+1} - I_n)\,[(A_x - A_n)/(A_{n+1} - A_n)], \qquad (2)$$

where A_x, A_n, and A_{n+1} are the values of property A of the studied compound and the reference components (n-alkanes with n and $n+1$ carbon atoms in its molecule), such that $A_n < A_x < A_{n+1}$; $I_n = 100n$ and $I_{n+1} = 100(n+1)$ being the threshold values of the index for the reference n-alkanes.

The ratio (2) allows transformation of any dimensional property of an organic substance into its dimensionless equivalent and, hence, their comparison. The indices of properties mentioned above have been directly applied in gas chromatography for identification purposes [10–12], whereas the differences $\Delta_{TM} = (I_T - I_M)$ and $\Delta_{T\text{-}MRD} = (I_T - I_{MRD})$ have been suggested to be used as a criteria to elucidate the necessity of derivatization of polar compounds for gas chromatographic analysis [13]. If the $\Delta_{TM} < 400$ and $\Delta_{T\text{-}MRD} < 600$ inequalities are held, than the polar analytes should not be necessarily derivatized for the analysis, but if $\Delta_{TM} > 600$ and $\Delta_{T\text{-}MRD} > 800$, the derivatization is required. If necessary, the $I_T \gg I_M$ condition (an indication of strongly polar compounds) may be considered as an additional criterion of chromatographic signal asymmetry for such analytes on nonpolar stationary phases [14].

It is interesting to note that the latter three criteria are in better coincidence than the earlier mentioned ones. According to the values of ΔRI, Δ_{TM}, and $\Delta_{T\text{-}MRD}$,

the polarity of the above discussed substances is increased in the acetone < acetic acid < ethylene glycol series (Table 1).

Thus, most of the polarity criteria are also applicable for other purposes, including the refinement of gas chromatography identification results, prediction of the elution order, and decision on the necessity of derivatization. The total number of currently recognized polarity criteria exceeds 150, as estimated in report [15]. Besides, each of the known methods of polarity estimation has its own advantages and disadvantages. The absence of a common criterion of polarity explains the existence of "robust" methods, for example, "ranking of different functional groups according to boiling points" [16].

Determination of different characteristics of polarity has its own special features. For example, measurement of ε and μ values is impossible without isolating the pure substance. Quantification of the $\log P$ value requires the use of laborous spectral or chromatographic methods. Determination of the ΔRI value demands the use of two columns with stationary phases of different polarity; moreover, in the case of complex mixtures it requires the matching of the components signals in both chromatograms, which is a sophisticated issue. Calculation of I_T, I_M, and I_{MRD} indices requires the data on normal boiling points and also (for the estimation of molar refractivity) on the relative density and refraction index. Evidently, the polarity parameters computable without additional experiments or the use of reference data are preferable for practical purposes. Considering the wide use of chromato–mass spectrometry, it is rational to verify the efficiency of characteristics based on simultaneously determined mass-spectrometric (molecular mass) and chromatographic parameters (retention indices). Such characteristics are known – homologous increments of additive properties, but they have not been considered polarity criteria. This study aimed to study homologous increments of gas-chromatographic retention

indices as the measure of polarity of organic substances, supplementing the earlier known methods.

Homologous increments of gas chromatographic retention indices. One of the approaches of data interpretation well-known in the field of organic mass spectrometry assumes the representation of mass numbers of molecular and fragmented ions in fragments as tetradecimal numbers. This relates the principles of interpretation of mass spectrometry data with such taxonomic category of organic compounds as homologous formed with the homologous difference CH_2, its mass number being 14. This is equivalent to the $M = 14x + y$ equation or (written in symbolics of number theory) to the following expressions [17, 18]:

– the ion mass numbers (m/z) and parameters y (and vise versa) are congruent modulo 14: $m/z \equiv y(\mathrm{mod}14)$, $y \equiv m/z(\mathrm{mod}14)$;

– $0 \leq y \leq 13$ is a remainder of the division of (m/z) by 14;

– if the value of y refers to the mass number of molecular ions (M), it defines the number of the homologous group of the considered compounds, y_M;

– (x) integer quotient of division of (m/z) by 14, $x = \mathrm{int}(M/14)$ or $x = (M - y)/14$;

If A is an organic compound property which can be estimated using additive schemes, the following equation is used for the calculation of homologous increment of this property (i_A) [18]:

$$i_A = A - x\Delta A(CH_2), \qquad (3)$$

where $\Delta A(CH_2)$ is the increment of the property A for the homologous difference CH_2.

Let us consider the homologous increments of retention indices (i_{RI}) as an example of parameters i_A [19]. Since the increment RI for homologous difference is 100 (the difference between the indices of the two sequential homologs), Eq. (4) is held.

$$i_{RI} = RI - 100x. \qquad (4)$$

In other words, the i_{RI} value is equal to the difference of the directly measured retention index of the analyte and the value of RI corresponding to the hypothetical n-alkane with $x = \mathrm{int}(M/14)$. Therefore, they represent combined chromato–mass-spectrometric parameters and possess the properties of differential analytical characteristics [20]; at the same time, they serve as the characteristic of organic substances

Table 2. Illustration of dependency of homologous increments of gas chromatographic retention indices $i_{RI\text{-}nonpolar}$ on the number of carbon skeleton branching of molecules (Z)

Isoalkane	$Z = 1$		Isoalkane	$Z = 2$	
	RI	i_{RI}		RI	i_{RI}
2-MeC$_5$	569	−31	2,2-Me$_2$C$_4$	537	−63
3-MeC$_6$	676	−24	2,4-Me$_2$C$_5$	631	−69
4-MeC$_7$	767	−33	2,5-Me$_2$C$_6$	732	−68
3-EtC$_7$	871	−29	4-Et-2-MeC$_6$	827	−73
4-MeC$_8$	865	−35	2,2-Me$_2$C$_7$	818	−82
5-MeC$_9$	961	−39	3,6-Me$_2$C$_8$	936	−64
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .
Average		−32±5	Average		−70±7

polarity. Besides this, the use of statistically processed i_{RI} data for homologous series appears efficient for the estimation of molecular masses of compounds for which molecular ions signal is not detected in the electron ionization mass spectra [21].

Similarly to the ΔRI mentioned above, the homologous increments i_A are applicable to individual substances as well as to homologous series (by averaging the data for individual homologs). Secondly, the RI values used for the homologous increment calculation might be determined using stationary phases of different polarity. The retention indices on standard nonpolar polydimethylsiloxane (RI$_{nonpolar}$) and standard polar polyethylene glycol stationary phases (RI$_{polar}$) are of great interest [22]. Correspondingly, it is possible to obtain at least two sets of values: $i_{RI\text{-}nonpolar}$ and $i_{RI\text{-}polar}$. Considering the expressions (1) and (4), these parameters are related as follows: $\Delta RI = i_{RI\text{-}polar} - i_{RI\text{-}nonpolar}$, the indices corresponding either to an individual substance or to a homologous series. However, since nonpolar phases are used much more often, the values of $i_{RI\text{-}nonpolar}$ are the most useful for practical purposes.

Another feature of homologous increments (similarly to the retention indices) is the dependence on the number of carbon chain branches of the homological molecules. This can be exemplified by the data for the simplest isoalkanes given in Table 2. Normal boiling points exhibit a similar trend.

Homologous increments of retention indices as a polarity characteristic. There is no formal limitations

Table 3. Physico-chemical parameters of organic compounds selected for the comparison of different criteria of polarity estimation

Compound	M	bp, °C	$RI_{nonpolar}$	RI_{polar}	ΔRI	ε	μ, D	$i_{RI-nonpolar}$	$i_{RI-polar}$	Δ_{T-M}	Δ_{T-MRD}
Acetonitrile	41	81.6	460	1002	542	37	3.9	160	702	189	276
Ethanol	46	78.3	452	926	474	24.6	1.7	152	626	322	404
1,3-Butadiene	54	–4.4	389	497	108	2.1	0	89	197	33	-34
Acetone	58	56.1	472	820	348	20.7	2.9	72	420	168	241
Propylamine	59	48	510	798	288	5.3	1.2	110	398	134	168
N-Methylformamide	59	182	722	1629	907	182	3.8	322	1229	**632**	759
Acetic acid	60	118	638	1428	790	6.2	1.7	238	1028	364	544
Ethylenediamine	60	117	620	1205	585	14	1.9	220	805	360	428
Nitromethane	61	101	531	1152	621	36	3.5	131	752	290	488
Ethylene glycol	62	197	726	1606	880	38	2.3	326	1206	**677**	**840**
Pyrrole	67	130	716	1516	800	8.3	1.8	316	1116	271	444
Cyclopentene	68	44.2	555	700	145	2.1	0.2	155	300	57	91
Furan	68	31.5	497	794	297	2.9	0.7	97	394	27	146
Butyronitrile	69	117	642	1108	466	21	3.6	78	407	295	382
Isobuturonitrile	69	103	595	1015	420	20.6	4.3	195	615	240	326
1-Pentene	70	30.0	488	530	42	2.1	0.5	–12	30	8	+6
2-Butanone	72	79.6	578	907	329	18.5	2.8	78	407	141	242
Tetrahydrofuran	72	65.7	619	875	256	7.6	1.7	119	375	100	215
N,N-Dimethylformamide	73	152.3	738	1325	588	38	3.8	238	825	400	524
Diethylamine	73	56.2	548	710	162	3.7	1.0	48	210	62	92
1-Butanol	74	117.6	658	1141	483	17.5	1.7	158	641	262	345
Diethyl ether	74	34.5	485	626	141	4.3	1.2	–15	126	–7	69
Nitroethane	75	114	623	1172	549	28	3.6	123	672	241	440
Methyl cellosolve	76	124.5	623	1177	554	16	2.1	123	677	274	436
Benzene	78	80.1	657	978	321	2.3	0	157	478	99	124
1-Chloropropane	78	46.2	531	739	208	8.1	2.0	31	239	–11	135
Dimethyl sulfoxide	78	189	790	1569	779	47	4.0	290	1069	530	686
Pyridine	79	115.5	731	1214	483	12.4	2.2	342	714	218	295
2-Chloroethanol	80	128.7	633	1373	740	25.4	1.8	133	873	256	479
Thiophene	84	84.2	651	1031	380	2.7	0.6	51	431	73	183
Dichloromethane	84	40	515	935	420	9.0	1.6	–85	335	–79	210
n-Hexane	86	68.7	600	600	0	1.9	0.1	0	0	+9	+10
Morpholine	87	128.9	788	1271	483	7.4	5.0	188	671	207	353

Table 3. (Contd.)

Compound	M	bp °C	$RI_{nonpolar}$	RI_{polar}	ΔRI	ε	μ, D	$i_{RI\text{-}nonpolar}$	$i_{RI\text{-}polar}$	$\Delta_{T\text{-}M}$	$\Delta_{T\text{-}MRD}$
Ethyl isothiocyanate	87	132	736	1265	529	19.7	3.3	136	665	220	317
Methyl *tert*-butyl ether	88	55.2	567	692	125	4.5	1.4	−33	92	−49	30
Butyric acid	88	163	824	1639	815	2.9	0.9	224	1039	342	524
Ethyl acetate	88	77.1	602	893	291	6.0	1.8	2	293	18	196
1,4-Dioxane	88	101.3	702	1083	381	2.2	0.4	103	483	98	292
1-Butanethiol	90	98	705	909	204	4.9	1.5	105	309	78	141
Toluene	92	110.6	760	1050	290	2.4	0.4	160	450	106	125
1-Chlorobutane	92	78.4	637	845	208	7.4	2.0	37	245	−10	133
Aniline	93	184	958	1751	793	7.0	1.5	358	1151	399	436
Phenol	94	181.8	971	1973	1002	10	1.4	371	1373	381	483
Dimethylsulfone	94	236	852	1903	1051	46	4.5	252	1303	**647**	909
Furfurol	96	161.7	810	1449	639	42	3.6	210	849	271	448
Cyclohexanone	98	155.6	873	1305	432	18.3	2.9	273	705	236	368
1,2-Dichloroethane	98	83.5	632	1068	436	10.4	1.8	−68	368	−38	247
2,2,2-Trifluoroethanol	100	73.6	441	1175	734	27	2.5	−259	475	−82	381
Triethylamine	101	89.4	677	774	97	2.4	0.8	−23	74	−31	−4
Diisopropyl ether	102	68.5	598	665	67	3.9	1.4	−102	−35	−105	−30
Propyl acetate	102	101.5	692	980	288	6.3	1.8	−8	280	−1	177
Acetic anhydride	102	140	706	1227	521	20.7	2.9	6	527	148	425
Propylene carbonate	102	241.7	929	1827	898	65	5.0	229	1127	**623**	**917**
Styrene	104	145.2	879	1260	381	2.4	0.2	179	560	154	143
Benzaldehyde	106	179	942	1530	588	17.6	2.9	242	830	281	378
Diethylene glycol	106	245	941	1958	1017	30	2.3	241	1258	**613**	**851**
Anisole	108	154	902	1349	947	4.3	1.3	202	649	158	252
Chlorobenzene	112	131.7	839	1244	405	5.6	1.6	39	444	40	202
2,2,4-Trimethylpentane	114	99.2	691	692	+1	1.9	0	−109	−108	−97	−97
Ethyl butyrate	116	121.6	780	1037	257	5.1	1.7	−20	237	−22	159
Tetramethyl carbamide	116	177	956	1450	494	23.4	3.4	156	650	200	367
Chloroform	118	61.2	609	1018	409	4.8	1.1	−191	219	−254	169
N,N-Dimethylaniline	121	193	1065	1660	595	5.0	1.6	265	860	242	257
Nitrobenzene	123	210.8	1062	1683	621	34.8	4.2	262	883	313	514
Benzyl chloride	126	179.3	986	1484	498	6.7	1.9	86	584	380	200
Quinoline	129	237	1224	1921	697	9.0	2.2	324	1021	402	452

[a] The values of $\Delta_{T\text{-}M} = (I_T − I_M)$ and $\Delta_{T\text{-}MRD} = (I_T − I_{MRD})$, exceeding 600 and 800, respectively, are given in bold as a criterion of unsatisfactory chromatografic characteristics of the substance on standard nonpolar stationary phases and the necessity of derivatization.

on the use of the i_{RI} values as additional characteristic of organic molecules polarity, based on chromato–mass-spectrometric parameters. However, their basic chemometric analysis seems reasonable for the comparison with other properties applied for the said purpose.

Table 3 shows the values of different properties of $N = 66$ simple organic substances, used as polarity references. The compounds are sorted in the order of ascending molecular masses (M), from 41 to 129 Da. Normal boiling points (°C) are required for the calculation of boiling temperature indices (I_T) using the equation (2). The values of I_{MRD} correspond to molar refractivity calculated from the reference data on relative density (d_4^{20}) and refraction index (n_D^{20}) (not shown in Table 3). For each considered compound, its dielectric constant and dipole moment are also given. The listed chromatographic parameters include the retention indices on standard polar and nonpolar stationary phases, their difference, and homological increment of the indices for polar and nonpolar phases considered in this study. For clarity, values of I_T, I_M, and I_{MRD} are omitted; but their differences Δ_{T-M} and Δ_{T-MRD} are given. In accordance with the earlier obtained estimations [1], the values of hydrophobic factors log P, hardly correlating with other polarity characteristics, are not included in the list of considered parameters.

The range of several properties given in Table 3 is limited, for example, parameters such as ε, μ, $RI_{nonpolar}$, RI_{polar}, ΔRI, I_T, I_M, and I_{MRD} cannot be negative. As far as the Δ_{T-M} and Δ_{T-MRD} differences and the $i_{RI-nonpolar}$ and $i_{RI-polar}$ increments are concerned, formally there are no limitations on them, and they can be either positive or negative. This feature might complicate the estimation of polarity using the mentioned parameters. For example, 13 compounds from Table 3 considered the most nonpolar according to the $i_{RI-nonpolar} \leq 0$ criteria include obviously polar alcohol, 2,2,2-trifluoroethanol ($i_{RI-nonpolar} = -259$). The reason for such abnormally weak chromatographic retention of fluorinated compounds is the low polarizability of fluorine leading to much lower retention parameters in comparison with the nonfluorinated analogs; however, this feature should not be related to the term "polarity". The mentioned inconsequence can be easily overcome using the homologous increments of RI on polar stationary phases. In this case the, most nonpolar compounds of these listed in Table 3 are expectedly n-hexane ($i_{RI-polar} = 0$), diisopropyl ether (–35), and 2,2,4-trimethylpentane (–108). 13 compounds possess

the values of $i_{RI-polar} \geq 1000$ (the highest ones, of 1303 and 1373, correspond to dimethylsulfone and phenol), yet some of then exhibit low values of ε and μ. This is also related to the effect of molecular polarizability on the chromatographic retention. The examples above illustrate the objective inequivalence of different systems of polarity characterization.

In general, comparison of data obtained for the individual compounds (for example, such as listed in Table 3), is poorly informative for the overall assessment of the properties of homologous increments of retention indices in comparison with other polarity characteristics. To do so, it is necessary to compare entire datasets for the considered compounds. To determine the extent of their similarity, one should compare the correlation coefficients (R) for different datasets. This transformation is among the basic operations of the principal component analysis method [1, 23]. More comprehensive chemometric data analysis, like given in [1], can be omitted in the considered case.

The matrix of cross-correlation coefficients for the dataset given in Table 2 has the dimension of 11×11 (Table 4). Since this matrix is symmetrical with respect to the diagonal elements equal to unity, we can further consider a reduced dataset of R values containing only 55 values. 15 values of R exceed 0.8 (shown in bold), which corresponds to good correlation of the considered combinations of datasets. For 16 datasets, the values of R do not exceed 0.5, which should be interpreted as absence of cross-correlation, and they can be excluded from further consideration. In addition, the number of R values exceeding 0.8 is given in Table 4 for each dataset.

Let us begin the analysis with the correlation coefficients for parameters ε and μ. Remarkably, they exhibit the best cross-correlation ($R = 0.802$), while for other combinations of the parameters the highest R (0.784) is observed for the ε–Δ_{T-MRD} pair. The retention indices for standard nonpolar phases ($RI_{nonpolar}$) possess similar properties, and the R values exceed 0.8 only for the combinations with the retention indices for standard polar phases (RI_{polar}) and normal boiling points (bp). The values of RI_{polar} are correlated with five other characteristics: bp, $RI_{nonpolar}$, ΔRI, $i_{RI-npolar}$ and Δ_{T-MRD}. Thus, the polarity criteria show the examples of satisfactory correlation with other parameters as well as the examples of their discrepancy. The latter example is molecular mass (M) which is not correlated with any other value listed in

Table 4. Matrix of correlation coefficients for the datasets of physico-chemical characteristics of the compounds[a]

Parameter	M	bp, °C	$RI_{nonpolar}$	RI_{polar}	ΔRI	ε[b]	μ	$i_{RI\text{-}nonpolar}$	$i_{RI\text{-}polar}$	$\Delta_{T\text{-}M}$	$\Delta_{T\text{-}MRD}$	Number of values of R, exceeding 0.8
M	1	0.470	0.718	0.357	0.068	–0.107	–0.031	–0.139	–0.018	–0.130	–0.051	0
bp, °C	0.470	1	**0.876**[b]	**0.939**	0.777	0.529	0.505	0.666	**0.808**	0.793	0.772	3
$RI_{nonpolar}$	0.718	**0.876**	1	**0.801**	0.515	0.160	0.241	0.568	0.569	0.498	0.418	2
RI_{polar}	0.357	**0.939**	**0.801**	1	**0.907**	0.501	0.484	0.701	**0.922**	0.796	**0.831**	5
ΔRI	0.068	0.777	0.515	**0.907**	1	0.588	0.511	0.639	**0.939**	0.798	**0.896**	3
ε	–0.107	0.529	0.160	0.501	0.588	1	**0.802**	0.340	0.578	0.665	0.784	1
μ	–0.031	0.505	0.241	0.484	0.511	**0.802**	1	0.340	0.509	0.552	0.663	1
$i_{RI\text{-}nonpolar}$	–0.139	0.666	0.568	0.701	0.639	0.340	0.340	1	**0.828**	**0.820**	0.626	2
$i_{RI\text{-}polar}$	–0.018	**0.808**	0.569	**0.922**	**0.939**	0.578	0.509	**0.828**	1	**0.895**	**0.900**	6
$\Delta_{T\text{-}M}$	–0.130	0.793	0.498	0.796	0.798	0.665	0.552	**0.820**	**0.895**	1	**0.890**	3
$\Delta_{T\text{-}MRD}$	–0.051	0.772	0.418	**0.831**	**0.896**	0.784	0.663	0.626	**0.900**	**0.890**	1	4

[a] The values of R exceeding 0.8 are put in bold. [b] The abnormally high value of ε (182 for N-methylformamide) is excluded.

Table 4 (the highest value of $R = 0.718$ is found for $RI_{nonpolaar}$.

This discussion aims to consider the properties of homologous increments of retention indices which can be determined using both nonpolar and polar phases. In comparison with other polarity characteristics, the values of $i_{RI\text{-}nonpolar}$ are rather unique, since they are satisfactorily correlated only with its analogs for polar phases ($i_{RI\text{-}polar}$, $R = 0.828$) and the earlier given [1, 13] differences of indices of boiling points and molecular masses ($\Delta_{T\text{-}M}$, $R = 0.820$). At the same time, their polar analog $i_{RI\text{-}polar}$ is correlated with the values of six other criteria [bp (0.808), RI_{polar} (0.922), ΔRI (0.939), $i_{RI\text{-}nonpolar}$ (0.828), $\Delta_{T\text{-}M}$ (0.895), and $\Delta_{T\text{-}MRD}$ (0.900)]. It should be noted that determination of homologous increments is much simpler in comparison with other polarity characteristics, since it is based on the use of simultaneously determined mass spectrometry and chromatography data. Furthermore, considering the preferential use of the columns with nonpolar stationary phases in modern chromatography, the application of $i_{RI\text{-}nonpolar}$ seem advantageous; this parameter can be related to the number of branchings in the molecule main chain.

The simplest criteria to verify the obtained estimations of the correlation coefficients is the recalculation for a smaller (generally, another) dataset. For example, reducing Table 3 to $N' = 20$ objects leads to different values of R, yet preserving the general trend.

Some correlation coefficients given in Table 4 are of 0.8–0.9 which gives an impression of possibility of recalculation between the polarity characteristics using corresponding linear regression equations. In fact, this procedure cannot be recommended due to low accuracy of the results. The differences between indices of boiling point (I_T) and molar refractions (I_{MRD}) are linear with homologous increments of gas-chromatographic retention indices on polar phases ($i_{RI\text{-}polar}$). The parameters of the linear regression equation are as follows: $a = 0.57\pm0.03$, $b = -21\pm24$. Despite high value of the correlation coefficient $R = 0.900$, the value of the dispersion S_0 (average accuracy of obtained results) is 100, which is inappropriate for practical usage. Therefore, the transformation between the polarity parameters is not accurate, and they should be used independently.

Characterization of polarity of several homologous series. One can characterize any compounds

Table 5. Average values of homologous increment of retention indices $i_{RI-nonpolar}$ (± standard deviation) for selected series of organic compounds with the number of branchings $Z = 1$ and $Z = 2$

Series	y_M	$i_{RI} \pm s_{RI}$ ($Z = 0$)	$i_{RI} \pm s_{RI}$ ($Z = 1$)
Tetraalkoxysilanes	12	–594±62	not available
Trialkyl phosphates	0	–256±45	not available
Trialkyl phosphites	12	–235±52	–258±25
Alkylnitrites	5	–113±6	–143±17
Alkanes	2	0	–32±5
Alkylnitrates	7	7±8	–50±12
Nitroalkanes	5	13±9	–24[a]
Dialkyl phosphonates	12	29±9	–4±10

[a] A single value is given without standard deviation.

and any homologous series using homologous increments [18]. However, to illustrate their practical application it is rational to choose several series characterized recently, for example, dialkyl phosphonates $(RO)_2PH=O$ [24] and trialkyl phosphonates $(RO)_3P$ [21, 25]. Theirs mass spectra and gas chromatographic retention indices have been reported in [21, 24, 25], and the averaged homologous increments $i_{RI-nonpolar}$ calculated from the M and RI values are given in Table 5.

For each series, two datasets of $i_{RI-nonpolar}$ are given in Table 5: one for the homologs containing only n-alkyl substituents ($Z = 0$), and another for the homologs with a single branching in the carbon chain ($Z = 1$). The variations of the given values are symbate. The data for several additional series, namely alkanes (reference series), trialkyl phosphates $(RO)_3P=O$, alkylnitrites ($RON=O$), alkylnitrates ($RONO_2$), nitroalkanes (RNO_2), and tetraalkyloxysilanes $[(RO)_4Si]$ are also given for comparison. The retention indices data have been extracted from [22].

Comparison of given data have revealed that several compounds containing a nitro group, one of the most polar functional groups in organic molecules, are actually rather nonpolar. This is the reason why alkylnitrates have been recommended as derivatives of aliphatic alcohols for the determination by the method of vapor-phase gas chromatography [26]. However, the polarity of alkylnitrates and nitroalkanes is insignificantly higher than that of alkylnitrites and is close to

the value for alkanes, according to the $i_{RI-nonpolar}$ criterion. For tetraalkoxysilanes, the values of RI are 600 units lower than for n-alkanes with the same value of $x = int(M/14)$. The unusually low values of $i_{RI-nonpolar}$ for have been found for trialkyl phosphites (–235±52), and these for trialkyl phosphates containing the P=O fragment in the molecule are lower than (–256±45). From the series considered, dialkyl phosphonates $(RO)_2PH=O$ are the most polar, with $i_{RI-nonpolar}$ = 29±9. The use of this criterion is preferable for $Z = 0$, because the homologs with n-alkyl part have been characterized much better than the branched ones.

The properties of tributyl phosphate widely used in industry can be mentioned as a confirmation of the accuracy of the polarity estimation using $i_{RI-nonpolar}$. This compound is readily soluble in nonpolar hydrocarbons, since its 15–40% solutions in kerosene are used for extraction of transuranic elements for regeneration of power plant wastes [27, 28]. Dielectric constant of tributyl phosphate is slightly higher (~6.8), than that of acetic acid (6.18±0.05). As follows from Table 5, trialkyl phosphites should exhibit the same properties.

In summary, estimations of polarity of organic substances on the basis of homologous increments of gas chromatographic retention indices can be recommended for the application along with other known parameters.

EXPERIMENTAL

The values of physico-chemical properties of organic substances given in Table 3 were extracted from [29–31] and original publications. Table 3 includes additionally rounded reference data known to the maximal number of significant digits. The values of bp, ε, and μ were given with accuracy of no more than a decimal digit, whereas the averaged retention indices and the derived values ($i_{RI-nonpolar}$, $i_{RI-polar}$, Δ_{T-M}, and Δ_{T-MRD}) (reported without standard deviation) were rounded to integers.

Statistical data processing and calculation of correlation coefficients were performed using Microsoft Excel (version 2007).

CONFLICT OF INTEREST

No conflict of interest was declared by authors.

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