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GENERAL CONTRIBUTION TO THE THEORY OF RETENTION INDEX SYSTEMS IN GAS-LIQUID CHROMATOGRAPHY

IV. PRE-CALCULATION OF INTERACTION FACTORS ON MIXED STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY BY COMPUTER

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SUMMARY

In earlier work, it was shown that gas chromatographic interactions can be characterized not only by the differences in retention indices, but also by quotients of the indices. This paper shows the practical application of Rohrschneider's concept based on quotients with the help of the McReynolds system for mixed stationary phases. Examples are given of the pre-calculation of retention indices on mixed stationary phases.

INTRODUCTION

It is well known that the prediction of retention data is of great importance in gas-liquid chromatography from both theoretical and practical stand points, and many workers have dealt with various aspects of this problem. As the results that have been achieved were summarized recently¹, we omit here any survey or evaluation of previous work. Only one topic is dealt with, namely the prediction of interaction factors for mixed phases.

Extension of our equation for predicting retention indices with mixed stationary phases is considered. The practical importance of mixed stationary phases is very great, as various workers have made considerable efforts to produce standard apolar and polar stationary phases. In this field, Kováts *et al.*² have obtained significant results.

THEORETICAL

As described in a previous paper³, the following two relationships can be written:

$$I = \pi I_m \quad (1)$$

and

$$I_x^p = I_x^{sq} \sum_{i=1}^5 f_i s_i \quad (2)$$

where

I = retention index, in index units (i.u.);

π = interaction factor;

I_m = molecular index contribution (i.u.);

x = symbol for unknown substance;

i = serial number of standards;

f_i = polarity factor:

$$f_i = \frac{I_i^p}{I_i^{sq}} \quad (3)$$

s_i = substance-specific factor: $\sum_{i=1}^5 s_i \approx 1.000$.

From eqns. 1 and 2, we can write

$$\pi_x^p(T) = \pi_x^{sq}(T) \sum_{i=1}^5 \left(\frac{\pi^p}{\pi^{sq}} \right)_i s_i \quad (4)$$

where T = column temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$; constant).

Considering that s_i is, under isothermal conditions, independent of the stationary phase and depends only on the quality of the substance examined and the standard substances used, eqn. 4 is suitable for the prediction of interaction factors on mixed stationary phases:

$$\pi_x^m(T) = \pi_x^{sq} \sum_{i=1}^5 \left(\frac{\pi^m}{\pi^{sq}} \right)_i s_i \quad (5)$$

(T = constant), where m represents the mixed stationary phase.

Based on the papers by Rohrschneider⁴ and McReynolds⁵, the choice of the standard substances, the errors of the prediction calculations, etc., were examined by means of a computer. It has been stated that an approximate calculation does not depend on the quality of the five standard substances chosen (this is the optimum number of the standard substances, although that for a rough approximation three standards are satisfactory); the approximate calculation is dependent only on the magnitude of the errors made when determining the retention data for the standards³.

It has been proved that any phase can act as a standard stationary phase³. These relationships and statements are also valid for mixed stationary phases, for which excellent results were obtained.

RESULTS

As an example, the calculation of the interaction factor of toluene is shown for

Apiezon L as stationary phase at 100.0° using the original five standard substances of Rohrschneider⁴:

$$\begin{aligned} \pi_{\text{toluene}}^{\text{APL}}(100.0^\circ) &= \pi_{\text{toluene}}^{\text{sq}}(100.0^\circ) \cdot \sum_{i=1}^5 f_i s_i = 4.00 [(1.049307 \cdot 0.957878) + \\ &+ (1.101563 \cdot 0.313725) + (1.047081 \cdot 0.173300) - (1.105033 \cdot 0.361882) - \\ &- (1.079137 \cdot 0.085840)] = 4.16 \end{aligned} \quad (6)$$

I_m for toluene is 189.25 i.u., then

$$I_{\text{toluene}}^{\text{APL}}(100.0^\circ) = 4.16 \cdot 189.25 = 787.3 \text{ i.u.} \quad (7)$$

There was perfect agreement between the calculated and measured values.

TABLE I

VALUES OF POLARITY FACTORS AT 120.0° FOR FIVE STANDARD SUBSTANCES

Standard substances: f_1 = pentanone; f_2 = nitropropane; f_3 = pyridine; f_4 = 2-methyl-2-pentanol; f_5 = 1-iodobutane.

McReynolds code number	Stationary phase	Polarity factor				
		f_1	f_2	f_3	f_4	f_5
2226	Hexatriacontane	0.99522	1.00153	1.01574	1.00000	1.01223
2063	Nujol	1.00319	1.00920	1.01574	1.00290	0.99878
2298	Mineral oil	1.00478	1.01074	1.01860	1.00435	1.01345
2270	Liquid paraffin	1.00319	1.01074	1.01860	1.00290	1.01467
2277	Convoil-20	1.01276	1.02607	1.03004	1.01449	1.01834
2128	Apiezon M	1.02392	1.04601	1.05722	1.01739	1.03912
2127	Apiezon L	1.02392	1.04908	1.06009	1.01884	1.04279
2013	Apiezon L (treated)	1.02552	1.04755	1.06152	1.01884	1.03912
2082	Polybutene-32	1.03828	1.06442	1.05722	1.02609	1.02934
2033	Montan wax	1.02233	1.03221	1.06724	1.03043	1.01956
2081	Polybutene-128	1.03987	1.06288	1.06009	1.02029	1.03545
2012	Apiezon L	1.03030	1.05675	1.06724	1.02319	1.04401
2318	DC-330	1.06699	1.09356	0.90844	1.04493	1.00000
2066	SF-96	1.06699	1.09356	0.90987	1.04493	1.00000
2195	Apiezon J	1.04306	1.07515	1.08154	1.03333	1.05134
2077	SE-30	1.07018	1.09816	1.05866	1.04493	1.00367
2101	DC-11	1.07656	1.10583	1.08011	1.05217	1.00367
2316	DC-510	1.09569	1.13650	1.08154	1.06087	1.01956
2078	SE-52	1.10367	1.15031	1.09585	1.06377	1.02812
2314	DC-556	1.12759	1.18098	1.11302	1.07681	1.03912
2186	Butyl stearate	1.10367	1.17178	1.10157	1.12319	1.04523
2204	OV-3	1.12919	1.19018	1.12589	1.07971	1.04768
2100	Beeswax	1.09729	1.13497	1.17454	1.12464	1.05012
2144	Fluorolube-HG1200	1.18182	1.22086	1.16881	1.09855	1.01467
2194	Apiezon H	1.12919	1.23159	1.18455	1.06667	1.06479
2171	Butoxyethylstearate	1.13238	1.20859	1.13877	1.14783	1.05990
2080	Halocarbon wax	1.18501	1.21933	1.17597	1.10145	1.01956
2123	OV-7	1.17703	1.26227	1.18312	1.11159	1.08313
2120	DC-550	1.18660	1.27301	1.19313	1.11739	1.09046
2323	Apiezon W	1.15708	1.23773	1.22031	1.13043	1.11369

As a further example, the calculation of the retention index of *n*-propanol is shown for a mixed stationary phase consisting of 2% SE-30 + 6% PEG-20M. The s_i values of *n*-propanol, using Rohrschneider's original standard substances, are as follows:

$$\begin{aligned} s_1 &= 0.044869 \\ s_2 &= 0.069656 \\ s_3 &= 0.475062 \\ s_4 &= 0.422686 \\ s_5 &= -0.009240 \\ \hline \sum_{i=1}^5 s_i &= 1.003033 \end{aligned}$$

The closeness of the sum of the s_i values to 1.000 indicates to the accuracy of the approximation. The retention index of *n*-propanol at 100.0° for the mixed stationary phase is

$$I_{n\text{-propanol}}^{2\% \text{ SE-30} + 6\% \text{ PEG-20M}}(100.0^\circ) = 485.0 \left[\left(\frac{834.2}{649.0} \cdot 0.044867 \right) + \right]$$

TABLE II

SUBSTANCE-SPECIFIC FACTORS OF DIFFERENT MODEL COMPOUNDS ACCORDING TO ROHRSCHEIDER⁴ AT 100.0° FOR GAS CHROMATOGRAPHIC STATIONARY PHASE

Compound	Substance-specific factors					Σs_i
	s_1	s_2	s_3	s_4	s_5	
2,4-Dimethylpentane	0.686587	-1.980136	1.375029	0.892681	0.026183	1.000344
2-Ethylhexene-1	0.759267	-1.900532	1.102218	0.996753	0.041830	0.999926
Cyclohexane	1.030491	-1.508764	0.583512	0.774533	0.124701	1.004473
Toluene	0.957878	0.313725	0.173300	-0.361882	-0.085840	0.997181
Styrene	1.020207	0.724409	0.000569	-0.618494	-0.129609	0.997082
Phenylacetylene	0.945232	-0.447209	-0.014495	0.550535	-0.038894	0.995169
Acetone	-0.299755	-0.090141	0.835675	0.275182	0.278998	0.999959
Propionaldehyde	0.074208	0.261979	0.680431	-0.047713	0.024498	0.993403
Crotonaldehyde	0.276623	0.445900	0.458587	-0.166058	-0.008380	1.006672
<i>n</i> -Butyl acetate	0.177331	-2.196349	1.330376	1.528989	0.155906	0.996253
Acetonitrile	0.204035	0.452159	-0.518815	0.752911	0.119395	1.009685
Nitroethane	0.073153	0.478315	0.433010	0.100860	-0.082549	1.002789
Dioxan	0.334029	-0.161374	0.567546	0.146231	0.117415	1.003847
Di- <i>n</i> -butyl ether	0.593533	-2.183045	1.233308	1.241994	0.111645	0.997435
Thiophen	1.048596	0.334112	-0.226222	-0.117673	-0.039992	0.998821
Trichloromethane	1.039087	0.343899	-0.344669	0.062531	-0.109092	0.991756
Tetrachloromethane	1.081700	-0.941170	0.216941	0.063126	0.015411	1.004149
Methyl iodide	1.342160	1.041551	-0.714803	-0.613731	-0.051318	1.003859
Ethyl bromide	0.913829	0.261395	0.039691	-0.154207	-0.063369	0.997339
Difluorotetrachloroethane	0.676964	-2.767883	0.989986	1.950613	0.149426	1.004623
<i>n</i> -Propanol ^a	0.044867	0.069656	0.475068	0.422702	-0.009240	1.003033
Isopropanol	-0.132591	0.679591	0.659740	-0.132476	-0.073808	1.000456
Allyl alcohol	0.133901	-0.412692	0.123288	1.139601	0.020455	1.004553
<i>tert</i> -Butanol	-0.206439	1.780854	1.023257	-1.319603	-0.288772	0.989297
Cyclopentanol	0.375640	-0.069293	0.422138	0.253892	0.024423	1.006800

$$\left(\frac{780.8}{384.0} \cdot 0.069636 \right) + \left(\frac{780.8}{531.0} \cdot 0.475068 \right) + \left(\frac{992.0}{457.0} \cdot 0.422702 \right) - \left(\frac{1053.7}{695.0} \cdot 0.009240 \right) = 873.7 \text{ i.u.} \quad (8)$$

The measured value was 867.8 i.u., the difference being -5.9 i.u.

The primary importance of predictions by using eqn. 5 is that a great amount of the published data measured on homogenous stationary phases can be used, thus facilitating practical gas chromatography. We wish to study the temperature dependence of the s_i values in order to extend the applicability of eqn. 5.

The polarity factors necessary for the calculations are given in Table I.

TABLE III

COMPARISON OF MEASURED⁵ AND CALCULATED RETENTION INDICES FOR *n*-BUTANOL AT 120.0° ON DIFFERENT STATIONARY PHASES

McReynolds code number	Stationary phase	$I_{\text{measured}} - I_{\text{calculated}} (\text{i.u.})$
2226	Hexatriacontane	-4.9
2063	Nujol	-3.7
2298	Mineral oil	-4.4
2270	Liquid paraffin	-2.5
2128	Apiezon M	+0.2
2127	Apiezon L	-1.4
2013	Apiezon L (treated)	+0.5
2082	Polybutene-32	-2.7
2081	Polybutene-128	+1.8
2012	Apiezon L	+0.5
2318	DC-330	-1.1
2066	SF-96	+0.7
2195	Apiezon J	-0.5
2077	SE-30	+0.8
2316	DC-510	-0.7
2078	SE-52	+3.2
2314	DC-556	-1.6
2204	OV-3	+3.2
2100	Beeswax	-14.4
2144	Fluorolube HG-1200	-34.1
2171	Butoxyethyl stearate	-8.5
2080	Halocarbon wax	-31.4
2123	OV-7	+2.5
2120	DC-550	+1.9
2323	Apiezon W	+11.0
2179	Dinonyl sebacate	-15.8
2061	DC-703	+0.7
2056	Diisodecyl adipate	-15.3
2169	Ditridecyl phthalate	-10.0
2149	Bis(2-ethylhexyl)tetra- chlorophthalate	-16.8
2310	DEG stearate	-11.7
2313	Octyl decyl adipate	-15.2
2250	Dilauryl phthalate	-12.2
2170	Diisooctyl adipate	-17.8
2024	TMP tripelargonate	-14.8

Substance-specific factors for different model compounds according to Rohrschneider⁴ at 100.0° for stationary phases are given in Table II.

In Table III, the results predicted by using various combinations of McReynolds' standards are compared with the measured data.

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