

CHROMSYMP. 787

PRINCIPLE OF NON-ADDITIVITY FOR SORPTION ENERGY AND ITS APPLICATION IN CHROMATOGRAPHY

R. V. GOLOVNYA

A. N. Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Ul. Vavilova 28, Moscow (U.S.S.R.)

SUMMARY

An earlier suggested universal equation describing the deviation from linearity of the relationship between retention parameters and increasing homologue number was applied to the calculation of retention parameters of different homologous series, including pseudo-homologous series, using gas chromatography (GC) with packed and capillary columns, gas–solid chromatography, GC on ion exchangers, high-performance and thin-layer chromatography and dissolution of members of homologous series in water–solvent two-phase systems. The accuracy of the calculated parameters is sufficient for the identification of all homologues, including the first members.

INTRODUCTION

Thermodynamic studies of the gas chromatographic (GC) behaviour of homologous series of organic compounds are carried out systematically. The sorption properties of sample substances determined chromatographically may provide sufficient information for the identification of members of homologous series. This implies the use of retention parameters that are proportional to the free sorption energy. Two such parameters exist in chromatography: the specific retention volume, V_g , and the retention index, I .

It is well known that non-linear changes in $\log V_g$ with the increasing homologue number m occur in any homologous series R_mX of aliphatic compounds, including n -alkanes. A particularly pronounced deviation is observed for the first members of the series.

Thermodynamic research showed the absence of constant values of the energy contribution per methylene unit in n -alkanes. The behaviour of n -alkanes on any stationary phase is described by a hyperbolic equation¹.

A more complex dependence of the energy contribution per methylene unit is observed in homologous series R_mX with functional group X. Changes in the methylene unit energy with a propagating alkyl chain do not obey the hyperbolic law, but are more complex¹. Moreover, in contrast to n -alkanes, the energy contribution for the primary methylene group in the R_mX series is always smaller than that for the second and the third CH_2 groups. These results show the need for careful application

of the homomorphic factor, which is based on the assumption of a complete analogy of the GC behaviour of *n*-alkanes and homologous series with functional group X. The results allow us to postulate two reasons for the violation of the additivity principle for energy contributions to the free sorption energy of members of homologous series¹. The energy of the Van der Waals interactions between the stationary phase and a sample molecule having the functional group bonded directly to the methyl group is always lower than the energy of interaction of a molecule having more than four methylene units between CH₃ and X groups.

Another type of violation will occur for substances containing two adjacent methyl groups as substituents. Such molecules do show deviations from additivity owing to the increasing energy of the Van der Waals interactions. This is the reason for the energy increase in *n*-alkanes with a decrease in the number of methylene groups in a homologue. One can also observe this effect, for example, with *o*-xylene, 1,2-dimethylcyclopentane and 1,2-dimethylcyclohexane, with 2,3- or 3,4-dimethylhexane and with dimethyl-substituted heterocyclic compounds².

Based on the thermodynamic representation of the GC separation process, we obtained a uniform equation to describe accurately the dependence of the retention parameters and the free partial energy of sorption on the sequential number *m* of a homologue in any homologous series^{1,3}:

$$Z = \alpha + \beta m + \gamma \cdot \frac{\log m}{m} + \frac{\xi}{(m-2)^2 + 0.1} \quad (1)$$

$$\Delta G = -2.3RT \left\{ \left[\alpha + \beta m + \gamma \cdot \frac{\log m}{m} + \frac{\xi}{(m-2)^2 + 0.1} \right] + \log \left(\frac{T\rho}{273} \right) \right\} \quad (2)$$

where *Z* is the retention parameter [*I*, log *V_g*, *R_F*, log *K*, log *BR* (ref. 22)], *T* is the analysis temperature (K), *ρ* is the density of the stationary phase at the temperature of analysis, *R* is the universal gas constant and *α*, *β*, *γ* and *ξ* are coefficients that depend on the conditions of the GC analysis and on the of the functional group of the series.

Eqn. 1 describes the violation of the linearity principle of additivity of energy contributions in series of aliphatic compounds. In this paper new results confirming the universal nature of eqn. 1 describing the first type of violation of the additivity principle of the energy contributions were obtained.

EXPERIMENTAL

Retention indices of nitrogen-containing compounds were determined on a Biokhrom-1 gas chromatograph with a flame ionization detector using helium of highest purity as the carrier gas. The injection and the detector oven temperatures were maintained at 150°C. Nitrogen-containing compounds were analysed under isothermal conditions at 110°C. Glass capillary columns containing Apiezon LH + KF (30 m × 0.25 mm I.D.) and PEG-40M + KF (40 m × 0.27 mm I.D.) were used for separation.

The mixtures of substances to be analysed were prepared by dissolving 20 μl of each of the compounds in 1 ml of pentane. The volume of sample injected was 0.2–0.3 μl.

Experimental retention parameters of the other compounds were taken from the papers cited in Tables II–IX and used for calculations.

RESULTS AND DISCUSSION

The application of the universal eqn. 1 to describe the chromatographic behaviour of different homologous series, including pseudo-homologous series, was examined. The universal equation has the following advantages: it provides the possibility of describing the chromatographic behaviour of all homologues, including the first member of a series, for the first time; it allows the behaviour of all homologous series to be described, including those never described before by any known equations; and the accuracy of the prediction of retention parameters is higher than that obtained with previous equations.

The universal equation allows the calculation of the main parameters of homologues with high accuracy in GC with packed and capillary columns, gas–solid chromatography, GC on ion exchangers, high-performance (HPLC) and thin-layer chromatography (TLC) and dissolution of homologues in water–solvent two-phase systems.

Gas chromatography

The accuracy of the prediction of retention indices for two series of amines analysed on glass capillary columns with hydrogenated Apiezon L and PEG-40M at 110°C is demonstrated in Table I. These series of amines did not obey any previously suggested equations.

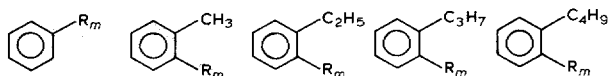
TABLE I

GC WITH CAPILARY COLUMNS: COMPARISON OF EXPERIMENTAL AND CALCULATED RETENTION INDICES OF ORGANIC COMPOUNDS ON APIEZON LH + KF AND PEG-40M + KF

The data were obtained by Svetlova *et al.*⁵.

Compound	I^{Ap} (80°C)		I^{PEG} (110°C)	
	Exptl.	Calc. by eqn. 1	Exptl.	Calc. by eqn. 1
Methyl-di- <i>n</i> -propylamine	757	757	837	837
Ethyl-di- <i>n</i> -propylamine	838	838	895	895
Propyl-di- <i>n</i> -propylamine	917	916	962	961
Butyl-di- <i>n</i> -propylamine	1004	1005	1047	1047
Pentyl-di- <i>n</i> -propylamine	1094	1094	1135	1134
Methylisobutylamine	674	674	803	803
Ethylisobutylamine	719	718	841	841
Propylisobutylamine	812	812	918	917
Butylisobutylamine	911	910	1014	1015
Pentylisobutylamine	1009	1008	1115	1115
Hexylisobutylamine	1107	1107	1214	1214

We investigated the applicability of the universal eqn. 1 to the calculation of the retention parameters of isomeric alkylbenzenes of the following series³:



which, according to Soják *et al.*⁶ cannot be described by a linear equation when analysed on capillary columns with either polar or non-polar stationary phases. The data in Table II show that retention indices calculated by eqn. 1 are in good agreement with the experimental values. Retention indices can be predicted using eqn. 1 with an accuracy sufficient for identification purposes.

A study of the applicability of eqn. 1 to the calculation of the retention indices of organic compounds in GC with packed and capillary columns was carried out for more than 70 homologous series of N-, S- and O-containing substances of different classes. The $\log V_g$ values of the compounds were calculated^{1,4,7,8} on ten stationary phases of different polarity at 80–160°C for organic compounds with the functional groups $R_m\text{OH}$, $\text{CH}_3\text{C(O)R}_m$, HC(O)OR_m , $\text{C}_2\text{H}_5\text{C(O)OR}_m$, $\text{CH}_3\text{C(O)OR}_m$, $\text{C}_3\text{H}_7\text{C(O)OR}_m$ and HC(O)R_m , and were compared with the experimental data⁹.

Retention indices were calculated by eqn. 1^{1,3,8} for homologous series with the following groups: $-\text{OH}$, HC(O)- , $\text{CH}_3\text{C(O)-}$, HC(O)CH=CH- , $\text{R}'\text{C(O)O-}$ (where $\text{R}' = \text{H}$, CH_3 , $n\text{-C}_6\text{H}_{11}$), $(\text{CH}_3)_2\text{CHC(O)O-}$, $(\text{CH}_3)_2\text{CHCH}_2\text{C(O)O-}$, $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{-C(O)O-}$, $n\text{-C}_3\text{H}_7\text{CH}(\text{CH}_3)\text{C(O)O-}$, $(\text{C}_2\text{H}_5)_2\text{CHC(O)O-}$ and

TABLE II

CAPILLARY CHROMATOGRAPHY: RETENTION INDICES, EXPERIMENTAL AND CALCULATED BY EQN. 1 FOR ALKYL BENZENES ON SQUALANE AND ACETYL *n*-BUTYL CITRATE (ABC) AT 95°C

Compound	Retention index on			
	Squalane		ABC	
	Exptl. ⁶	Calc.	Exptl. ⁶	Calc.
2-Methylbutylbenzene	1140.3	1140.3	1274.9	1274.9
2-Ethylbutylbenzene	1207.9	1207.9	1343.1	1343.1
2-Propylbutylbenzene	1279.0	1279.3	1412.2	1411.8
1,2-Dibutylbenzene	1369.7	1370.0	1502.2	1501.9
2-Pentylbutylbenzene	1460.6	1462.0	1591.9	1593.6
2-Hexylbutylbenzene	1555.1	1554.2	1686.5	1685.4
Methylbenzene	755.4	755.5	876.6	876.5
Ethylbenzene	845.7	845.6	963.7	963.9
<i>n</i> -Propylbenzene	933.6	934.1	1063.9	1061.6
<i>n</i> -Butylbenzene	1031.8	1033.8	1162.2	1161.1
<i>n</i> -Hexylbenzene	1230.0	1228.0	1359.3	1360.6
<i>n</i> -Heptylbenzene	1329.0	1327.7	1459.5	1460.2
<i>n</i> -Octylbenzene	1427.8	1427.3	1559.7	1559.8
<i>n</i> -Nonylbenzene	1526.6	1527.2	1660.0	1559.2
<i>n</i> -Decylbenzene	1625.3	1626.8	1759.5	1758.6

$-C(O)OR'$ (where $R' = C_2H_5, n-C_4H_9, n-C_6H_{13}$). Experimental data on packed columns were taken from refs. 9–11.

Retention indices of the homologous series $R_mC(O)H$, $R_mC(O)OCH_3$ and $R_mC(O)OR$, where $R' = C_2H_5-C_6H_{13}$, were also calculated using eqn. 1 on the capillary columns. The calculated values^{3,5} are in a good agreement with the experimental data^{5,12}.

The coefficients of eqn. 1 were calculated for homologous series of N-containing compounds also: $R'NH-$ (where $R' = H, CH_3, n-C_5H_{11}$), $(CH_3)_2CHNH-$, $C_2H_5(CH_3)HN-$, $(CH_3)_2CH(CH_2)_2NH-$, $(CH_3)_3CNH-$, $R'NHC(CH_3)HNH-$, (where $R' = CH_3-n-C_3H_7$), $(R'_2)_2N-$ (where $R' = CH_3-n-C_5H_{11}$), cyclohexyl-*n*-alkylamine and *N-n*-alkylpiperidine for three stationary phases (Apiezon L + KOH, Triton X-305 + Na_3PO_4 and Carbowax 1000 + Na_3PO_4) at $100^\circ C$ ^{3,5,13–15}. Retention indices were calculated with high accuracy.

Homologous series of the following S-containing compounds were examined: $R'S-$ (where $R' = H, CH_3-n-C_6H_{13}$), $R'S_2$ (where $R' = CH_3-n-C_5H_{11}$), $(CH_3)_2CHS-$, $(CH_3)_2CHCH_2S-$, $(CH_3)_2CH-$, $(CH_2)_2S-$, $(CH_3)_3CS_2-$, C_6H_5S- , $CH_2=CHS-$, $CH_2=CHCH_2S-$, $CH\equiv CCH_2S-$, $R'C(O)S-$ (where $R' = CH_3-n-C_3H_7$), $(CH_3)_3CS-$, $(CH_3)_2CHS_2-$, $(CH_3)_3CCH_2S_2-$, $(CH_3)_2CHC(CH_3)HS-$ and $C_2H_5C(CH_3)HS-$.

The coefficients of the retention parameters were calculated for four stationary phases, Apiezon M, Triton X-305, OV-17 and Carbowax 1000, at $130^\circ C$ ^{3,7,8}. Experimental data were presented elsewhere¹⁶. The relative error in determining retention indices using eqn. 1 did not exceed 1%. Such an accuracy of prediction of retention indices for polar branched homologous series has been achieved for the first time (see Table I).

If the principle of non-additive changes in Van der Waals interaction energy is of a general nature, this effect should be true not only for gas-liquid chromatography on packed and capillary columns, but also for other variants of chromatography.

Ion exchangers

Tests of the universal nature of eqn. 1 showed that it describes the behaviour of the homologues in GC on ion exchangers with good accuracy. The coefficients of

TABLE III

GC ON ION EXCHANGERS: COEFFICIENTS OF EQN. 1 FOR CALCULATION OF RETENTION INDICES OF *n*-ALKANOLS ON MACROPOROUS METHACRYLATE ION EXCHANGERS

Experimental retention indices were taken from ref. 17.

<i>Ion exchanger</i>	α	β	γ	ξ	<i>Standard deviation</i>
H ⁺	405.4	96.3	48.3	-1.9	0.001
Na ⁺	465.4	82.3	-178.1	-6.3	0.001
Rb ⁺	431.5	72.8	-467.7	-4.8	0.005
Cs ⁺	363.3	153.0	911.1	4.1	0.001
Li ⁺	369.3	149.7	364.0	7.6	0.003

TABLE IV

ION-EXCHANGE CHROMATOGRAPHY: EXPERIMENTAL AND CALCULATED RETENTION INDICES OF *n*-ALKANOLS FOR Li⁺ ION EXCHANGER

Homologue	Retention index		
	Calculated by eqn. in ref. 17*	Experimental from ref. 17	Calculated by eqn. 1
Methanol	702	526	526
Ethanol	732	615	615
<i>n</i> -Propanol	761	688	688
<i>n</i> -Butanol	787	840	840

$$* I = I_{\alpha} + I_{\mu} + I_{Cp} + I_R^{17}.$$

eqn. 1 for the calculation of retention indices for *n*-alkanols analysed on macroporous methacrylate ion exchangers with H⁺, Na⁺, Rb⁺, Cs⁺ and Li⁺ ions are given in Table III. For calculation of the coefficients, experimental values of the retention indices were taken from ref. 17. That standard deviation of the calculated retention indices from the experimental values is not more than 0.005. Retention indices of *n*-alkanols for the Li⁺ ion exchanger calculated using the linear equation suggested by Hradil *et al.*¹⁷ and eqn. 1 are given in Table IV. The values calculated using eqn.

TABLE V

REVERSED-PHASE LIQUID CHROMATOGRAPHY: EXPERIMENTAL AND CALCULATED CAPACITY FACTORS, *k'*, OF HOMOLOGUES OF BROMOPHENACYL ESTERS OF SATURATED CARBOXYLIC ACIDS

Mobile phase water-solvent	Homologue number (<i>m</i>)	Capacity factor (<i>k'</i>)		
		Calculated by eqn. in ref. 18	Experimental from ref. 18	Calculated by eqn. 1
0.7% methanol	1	0.90	0.93	0.93
	2	1.40	1.38	1.40
	3	2.17	2.16	2.17
	4	3.37	3.54	3.52
	5	5.22	5.71	5.73
0.5% 1,4-dioxane	1	2.17	2.30	2.30
	2	3.89	4.11	4.11
	3	6.97	7.48	7.48
	4	12.48	13.52	13.53
	5	22.36	24.50	24.49
0.6% acetonitrile	1	1.11	1.00	1.00
	2	1.59	1.53	1.53
	3	2.30	2.27	2.26
	4	3.31	3.33	3.34
	5	4.77	4.93	4.92
Standard deviation		1.22-0.26		0.02-0.01

1 and the experimental values from ref. 17 were identical, but retention indices calculated by the Hradil equation differed from the experimental values by up to 176 i.u. (for ethanol). The advantages of eqn. 1 for the calculation of retention parameters are obvious.

Reversed-phase liquid chromatography (RPLC)

The applicability of eqn. 1 to RPLC is demonstrated in Table V. The capacity factors, k , of homologues of *p*-bromophenacyl esters of saturated carboxylic acids were taken from a paper by Jandera¹⁸, who analysed these substances by RPLC using three different mobile phases: methanol, dioxane and acetonitrile mixed with water. The standard deviation of the capacity factors calculated using eqn. 1 is one to two orders of magnitude lower than that calculated by Jandera's equation¹⁸. The advantages of the application of the universal equation are obvious.

It was interesting to apply the universal equation to describe the behaviour of unusual homologous series and to compare the results with those calculated by a linear equation. An example is given in Table VI. Experimental retention indices of pseudo-homologous series of polysulphanes analysed by reversed-phase HPLC were taken from a paper by Möckel¹⁹. A comparison of the experimental values with those calculated by the linear Möckel equation and by eqn. 1 clearly demonstrates the advantages of our universal equation over the linear equation.

Thin-layer chromatography

In TLC the applicability of eqn. 1 was verified using data on the separation

TABLE VI

REVERSED-PHASE HPLC: EXPERIMENTAL AND CALCULATED RETENTION INDICES OF PSEUDO-HOMOLOGOUS SERIES OF H_2S_n

Chromatographic conditions: 100 × 8 mm I.D. column with Radial-Pak A (5 μm); eluent, methanol at 1 ml/min, 40–50 bar; temperature, 27.9°C; UV detection at 254 nm¹⁹.

<i>Homologue</i>	<i>Retention index</i>		
	<i>Calculated by eqn. in ref. 19</i>	<i>Experimental from ref. 19</i>	<i>Calculated by eqn. 1</i>
H ₂ S ₂	461	455	455
H ₂ S ₃	587	573	578
H ₂ S ₄	712	710	707
H ₂ S ₅	838	842	838
H ₂ S ₆	963	969	968
H ₂ S ₇	1088	1095	1097
H ₂ S ₈	1214	1222	1223
H ₂ S ₉	1339	1347	1348
H ₂ S ₁₀	1465	1471	1471
H ₂ S ₁₁	1590	1593	1593
H ₂ S ₁₂	1715	1714	1714
H ₂ S ₁₃	1841	1835	1835
H ₂ S ₁₄	1966	1955	1955
Standard deviation	7.5		1.9

TABLE VII

THIN-LAYER CHROMATOGRAPHY: COMPARISON OF EXPERIMENTAL AND CALCULATED R_F VALUES FOR n -ALKYL ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

Mobile phase: benzene.

Homologue number (m)	R_F for esters of			
	Acrylic acid		Methacrylic acid	
	Exptl. from ref. 20	Calculated by eqn. 1	Exptl. from ref. 20	Calculated by eqn. 1
2	0.39	0.39	0.43	0.43
3	0.46	0.47	0.51	0.51
4	0.52	0.51	0.54	0.56
5	0.56	0.55	0.63	0.60
6	0.60	0.58	0.65	0.64
7	0.62	0.62	0.68	0.68
8	0.63	0.64	0.71	0.71
9	0.65	0.67	0.73	0.73
10	0.70	0.69	0.75	0.76
12	0.73	0.72	0.79	0.79
14	0.75	0.75	0.80	0.81
16	0.78	0.78	0.83	0.83
18	0.81	0.81	0.84	0.84

n -alkyl esters of acrylic and methacrylic acids on Silufol plates. Experimental data were taken from a paper by Horna *et al.*²⁰. A significant deviation from linearity of the R_F values of methacrylic acid esters was observed. It can be seen from Table VII that all homologues from the second up to the eighteenth can be calculated with high accuracy using eqn. 1. The standard deviation does not exceed 0.01.

A test of the universal nature of eqn. 1 was carried out on nine testosterone

TABLE VIII

DISSOLUTION: COMPARISON OF EXPERIMENTAL AND CALCULATED PARTITION COEFFICIENTS FOR n -ALKANOLS IN TWO-PHASIC BINARY SYSTEM (n -OCTANOL-WATER)

Homologue	K		
	Calculated by linear eqn. in ref. 21	Experimental from ref. 21	Calculated by eqn. 1
CH_3OH	-0.08	-0.82	-0.82
$\text{C}_2\text{H}_5\text{OH}$	-0.22	-0.32	-0.32
$\text{C}_3\text{H}_7\text{OH}$	0.31	0.34	0.32
$\text{C}_4\text{H}_9\text{OH}$	0.84	0.88	0.88
$\text{C}_5\text{H}_{11}\text{OH}$	1.37	1.40	1.45
$\text{C}_6\text{H}_{13}\text{OH}$	1.90	2.03	2.01
$\text{C}_7\text{H}_{15}\text{OH}$	2.95	3.15	3.14
Standard deviation			0.02

esters analysed by TLC. The lipophilic character of the testosterone esters was expressed by their chromatographic R_m values²¹. The non-polar stationary phase used was a silica gel G layer impregnated with silicone DC 200. The mobile phases were methanol and acetone. The TLC behaviour of all members of the testosterone series obeyed the following universal equations^{21,22}:

In acetone:

$$R_m = -0.3659 + 0.1472 m + 0.1834 \left(\frac{\log m}{m} \right) - \frac{0.0007}{(m-2)^2 + 0.1}$$

In methanol:

$$R_m = 0.2053 + 0.1986 m + 0.073 \left(\frac{\log m}{m} \right) - \frac{0.0027}{(m-2)^2 + 0.1}$$

It is interesting that the hemolytic activity ($\log BR$) of testosterone derivatives²² also obeys eqn. 1:

$$\log BR = 1.8426 + 0.1284 m + 6.0890 \left(\frac{\log m}{m} \right) - \frac{0.7824}{(m-2)^2 + 0.1}$$

The accuracy of the calculated values of R_m and $\log BR$ is sufficient for identification purposes.

All these results demonstrate the preference for the universal equation, which can be successfully used in TLC in addition to GC and HPLC.

Dissolution

The universal nature of the equation allows one to assume that it can describe not only chromatographic processes, but all processes in which Van der Waals interactions between molecules take place. As an example, we considered the dissolution of organic compounds. Partition coefficients, K , are used to describe the dissolution of organic compounds in water-solvent systems²³. We demonstrated the applicability of eqn. 1 for the calculation of K values of members of homologous series of amines, acids and alkanols in two-phase binary solvent systems. These series, including the first homologue, could not be described earlier by linear equations. Table VIII shows the experimental²¹ partition coefficients for seven homologues of n -alkanols, together with those calculated using eqn. 1 and the linear Rekker equation. It is clear that only eqn. 1 can describe all members with good accuracy. A high accuracy of the K values was obtained for amines and acids dissolved in eight different water-solvent two-phase systems³.

We conclude that the universal equation can be applied successfully to describe the dissolution process of organic substances in homologous series.

Another example of the applicability of the universal equation is given in Table IX. Ten members of homologous series of sodium salts of amino acids were dissolved in a very complex two-phase system containing five or six components²⁴. Components of three such systems are given in the last column of Table IX. As an example we obtained coefficients of the universal equation for three systems. The standard deviations demonstrated the high accuracy of the equation.

In conclusion, we should emphasize that our equation describing deviations from linearity of the dependence of the Van der Waals interaction energy permits one to calculate retention parameters of homologues starting from the first member

TABLE IX

DISSOLUTION OF DNP-NHCH(R_m)COONa IN TWO-PHASE 5-6-COMPONENT SYSTEMS: COEFFICIENTS OF EQN. 1 FOR CALCULATION OF PARTITION COEFFICIENTS (ln K) (*m* = 1-10)

Experimental values of ln K were taken from ref. 24.

Coefficients of eqn. 1				Standard deviation	Components of two-phase system
$\alpha \cdot 10^4$	$\beta \cdot 10^4$	$\gamma \cdot 10^4$	$\xi \cdot 10^4$		
2202	355	1703	90	0.0003	Ficoll-dextran 70-water, Na ₂ HPO ₄ , NaH ₂ PO ₄
782	355	1703	90	0.0003	Ficoll-dextran 70-water, NaCl, Na ₂ HPO ₄ , NaH ₂ PO ₄
-45367	12742	59950	2876	0.0001	<i>n</i> -Octanol-dextran 70-water, NaCl, Na ₂ HPO ₄ , NaH ₂ PO ₄

in gas-liquid, gas-solid and liquid-liquid systems, and the results presented here have demonstrated its universal nature.

REFERENCES

- 1 R. V. Golovnya and D. N. Grigoryeva, *Chromatographia*, 17 (1983) 613.
- 2 R. V. Golovnya and A. L. Samusenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1993.
- 3 R. V. Golovnya and D. N. Grigoryeva, in P. Sandra and W. Bertsch (Editors), *Proceedings of the 6th International Symposium on Capillary Chromatography, Italy, May 1985*, Hüthig, Heidelberg, 1985, p. 715.
- 4 R. V. Golovnya and D. N. Grigoryeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1240.
- 5 N. I. Svetlova, A. L. Samusenko and R. V. Golovnya, in P. Sandra and W. Bertsch (Editors), *Proceedings of the 6th International Symposium on Capillary Chromatography, Italy, May 1985*, Hüthig, Heidelberg, 1985, p. 725.
- 6 L. Soják, J. Jának and J. A. Rijks, *J. Chromatogr.*, 135 (1977) 135.
- 7 R. V. Golovnya, D. N. Grigoryeva and I. L. Zhuravleva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 1825.
- 8 R. V. Golovnya and D. N. Grigoryeva, *Proceedings of the IInd Conference of CMEA Countries*, Slovnaft, Bratislava, 1984, paper 5.5, pp. 1-24 (in Russian).
- 9 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts, Evanston, IL, 1966.
- 10 J. R. Chrétien and J. E. Dubois, *J. Chromatogr.*, 158 (1978) 43.
- 11 V. P. Uraletz and R. V. Golovnya, *Zh. Anal. Khim.*, 33 (1978) 782.
- 12 F. S. Calixto and A. G. Raso, *Chromatographia*, 14 (1981) 143.
- 13 R. V. Golovnya, I. L. Zhuravleva, N. I. Svetlova and D. N. Grigoryeva, *Zh. Anal. Khim.*, 35 (1980) 1976.
- 14 R. V. Golovnya, I. L. Zhuravleva, M. B. Terenina and D. N. Grigoryeva, *Zh. Anal. Khim.*, 36 (1981) 968.
- 15 R. V. Golovnya, I. L. Zhuravleva, A. F. Aerov and D. N. Grigoryeva, *Zh. Anal. Khim.*, 36 (1981) 742.
- 16 V. G. Garbuzov, T. A. Misharina, A. F. Aerov and R. V. Golovnya, *Zh. Anal. Khim.*, 40 (1985) 709.
- 17 J. Hradil, F. Švec, N. M. Gogitidze and T. G. Andronikashvili, *J. Chromatogr.*, 324 (1985) 277.
- 18 P. Jandera, *J. Chromatogr.*, 314 (1984) 13.
- 19 H. J. Möckel, *Fresenius Z. Anal. Chem.*, 318 (1984) 116.
- 20 A. Horna, H. Pechová, A. Tůmová and J. Churáček, *J. Chromatogr.*, 288 (1984) 230.
- 21 G. C. Nijs and R. F. Rekker, *Chim. Ther.*, 5 (1973) 521.
- 22 G. L. Biagi, M. C. Guerra and A. M. Barbaro, *J. Med. Chem.*, 13 (1970) 944.
- 23 R. F. Rekker, *The Hydrophobic Fragmental Constant*, Elsevier, Amsterdam, 1978.
- 24 B. Yu. Zaslavsky, L. M. Miceeva and S. V. Rogozhin, *J. Chromatogr.*, 212 (1981) 13.