

CHROM. 17,166

PREDICTION OF RETENTION DATA BY USING PARAMETERS OF INTERMOLECULAR INTERACTION

II. APPLICATION OF THE MODEL TO GAS-LIQUID CHROMATOGRAPHIC SYSTEMS

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(First received June 10th, 1984; revised manuscript received August 23rd, 1984)

SUMMARY

In this work, we attempt to predict specific retention volumes in gas-liquid chromatographic systems by using the interaction energy parameters D and ϕ , suggested in a previous paper. The investigations have been carried out for 27 polar solutes on the OV-101, OV-17 and oxidipropionitrile stationary phases. The applicability of the parameters D and ϕ for solving practical prediction problems is demonstrated.

INTRODUCTION

In a previous work¹ we investigated the retention behaviour of polar solutes in gas-liquid chromatographic (GLC) systems using IR spectroscopic frequency shifts. In order to obtain better correlations for medium polar solutes and stationary liquid phases the IR frequency shifts have been combined with a calculated interaction parameter incorporating the dispersion forces². The aim of the present paper is to predict retention data by means of the interaction parameters D and ϕ , suggested in the first part of this work³. For this purpose, we derived a semi-empirical relationship connecting these parameters with retention data.

FUNDAMENTALS

Provided the solute concentrations in the stationary (liquid) and mobile (gas) phases are in equilibrium, we can write

$$\Delta G_s^0 = \mu_{iS}^0 - \mu_{iM}^0 = -RT \ln \frac{a_{iS}}{a_{iM}} \quad (1)$$

where ΔG_s^0 is the standard molar Gibbs function of sorption of solute in the stationary liquid, μ_{is}^0 and μ_{im}^0 are the standard chemical potentials of the solute in the stationary liquid and in the mobile phase, respectively, a_{is} and a_{im} are the equilibrium activities of the solute in the stationary liquid and in the mobile phase, respectively, T is the absolute temperature of the system, and R is the molar perfect-gas constant.

To obtain a meaningful relationship between the solute specific retention volume in a given GLC-system and the standard molar Gibbs function of sorption, it is necessary to specify the standard states for the solute in both phases^{4,5}. We have chosen the pure solute in a hypothetical state of infinite dilution in the stationary liquid phase at the temperature and pressure of the system as the solute standard state in the liquid phase, and the pure solute in a hypothetical state of an ideal gas at a standard pressure p^0 and at the temperature of the system as the solute standard state in the mobile phase. With this choice of the standard states and assuming that the actual gaseous phase behaves practically ideal, we can write eqn. 1 as

$$\Delta G_s^0 = -RT \ln \left(V_g \frac{M_1 \cdot p^0}{R \cdot 273.16} \right) \quad (2)$$

where V_g is the specific retention volume defined as recommended⁶.

Starting from these suppositions, we found the relation between retention data and the calculated interaction parameters in the following way:

(1) The specific retention volume V_g is connected with the standard molar enthalpy of sorption of solute in the stationary liquid ΔH_s^0 (see eqn. 2) by the relationship

$$\log V_g = - \frac{\Delta H_s^0}{2.303 RT} + C \quad (3)$$

where C , a constant, is given by

$$C = \frac{\Delta S_s^0}{2.303 R} - \log \frac{M_1 \cdot p^0}{R \cdot 273.16}$$

where ΔS_s^0 is the standard molar entropy of sorption of solute in the stationary liquid, M_1 is the molar mass of the stationary liquid, and p^0 is the gas-phase standard pressure chosen.

(2) Further it may be written:

$$\log V_g = - \frac{\Delta H_s^D + \Delta H_s^{Ass}}{2.303 RT} + C \quad (4)$$

where ΔH_s^D and ΔH_s^{Ass} are the contributions to the total values of ΔH_s^0 due to the dispersion and association forces, respectively.

(3) If our interaction parameters D and φ (see ref. 3) are proportional to the above enthalpy values

$$D \approx \Delta H_s^D \quad (5)$$

and

$$\varphi \approx \Delta H_s^{\text{Ass}} \quad (6)$$

we obtain the semi-empirical equation

$$\log V_g = A_0 + A_1 \cdot \varphi + A_2 \cdot D \quad (7)$$

where A_0 , A_1 and A_2 are empirical constants. Eqn. 7 is used for the prediction of retention data.

EXPERIMENTAL

The retention volumes of 27 polar solutes (see Table I) have been measured on stationary phases of different polarities [*i.e.* OV-101, OV-17 and oxidipropionitrile (ODPN)] using a Hewlett-Packard Model 5830 A gas chromatograph. The measurements were carried out under the following experimental conditions: column 2 m

TABLE I

DISPERSION PARAMETERS D

Compound number	Solute	$D \cdot 10^{-45} (\text{mol}^{-2})$		
		Stationary phase		
		OV-101	OV-17	Oxidipropionitrile
1	Acetonitrile	67.61	59.21	73.35
2	Propionitrile	79.74	69.90	86.19
3	Methanol	37.22	32.77	39.67
4	Ethanol	49.35	43.46	52.51
5	1-Propanol	61.48	54.15	65.35
6	2-Propanol	64.36	56.70	68.40
7	1-Butanol	73.61	64.84	78.19
8	1-Pentanol	85.74	75.53	91.03
9	<i>n</i> -Propyl chloride	79.12	69.64	84.29
10	<i>n</i> -Butyl chloride	91.25	80.33	97.13
11	<i>n</i> -Ethyl bromide	72.41	63.81	76.79
12	<i>n</i> -Propyl bromide	84.54	74.50	89.63
13	<i>n</i> -Butyl bromide	96.67	85.19	102.47
14	Amyl bromide	108.80	95.88	115.31
15	Ethyl iodide	78.22	69.08	82.31
16	<i>n</i> -Propyl iodide	90.35	79.77	95.15
17	<i>n</i> -Butyl iodide	102.48	90.46	107.99
18	Acetone	69.11	60.63	74.50
19	Methyl ethyl ketone	81.24	71.32	87.34
20	Methyl propyl ketone	93.37	82.01	100.18
21	Methyl amyl ketone	117.63	103.39	125.86
22	Nitromethane	77.60	67.73	85.14
23	Nitroethane	89.73	78.42	97.98
24	1-Nitropropane	101.86	89.11	110.82
25	2-Nitropropane	104.74	91.66	113.87
26	1-Nitrobutane	113.99	99.80	123.66
27	1-Nitropentane	126.12	110.49	136.50

TABLE II
ASSOCIATION PARAMETERS φ

<i>Solutes</i>	φ (D^2/nm^3) <i>stationary phase</i> <i>oxidipropionitrile</i>	$\varphi \cdot 10^{-25}$ ($D^2/mol\ nm^3$) <i>stationary phase</i> <i>OV-17</i>
Nitriles	621.0	2.536
<i>n</i> -Alcohols	506.1	0.5754
<i>sec.</i> -Alcohols	389.3*	0.4426*
Chloroalkanes	252.8	0.4259
Bromoalkanes	234.2	0.3108
Iodoalkanes	198.9	0.2970
Ketones	437.0	1.505
<i>n</i> -Nitroalkanes	747.0	2.751
<i>sec.</i> -Nitroalkanes	574.6*	2.116*

* IR spectroscopical frequency shifts⁶ suggest that *iso*-compounds, in comparison to *n*-compounds, exert 1.3 times weaker association forces on the stationary phase. Considering this experimental fact, we reduced the calculated φ values to the quotient 1.3 in the case of *iso*-compounds studied.

\times 2.5 mm I.D.; support, Inerton (AW, DMCS), 0.125–0.160 mm, 10% support coating; column temperature, 40°C; flow velocity, 23 ml/min; carrier gas, nitrogen; sample size: 0.2 μ l, pure solute. The sample size chosen for this measurements permitted the measurement of the retention data in a concentration-independent region⁷.

The constitution of the silicones OV-101 and OV-17 has been studied by means of NMR spectroscopy⁸ in order to know the exact group composition of the silicones. ODPN has been purified by five-fold vacuum distillation.

RESULTS AND DISCUSSION

In order to predict retention data according to our model, it is necessary to choose systems in which one type of intermolecular interaction between the solute and stationary phase predominates. Thus, it is expected that in systems containing OV-101, OV-17 and ODPN as stationary phases, dispersion-, induction- and orientation forces predominate, respectively.

The parameters D and φ , calculated for the respective interactions, are shown in Tables I and II. As expected, the dispersion parameters are reflecting the contri-

TABLE III
EMPIRICAL COEFFICIENTS (A_0 , A_1 AND A_2) OF EQN. 7 AND THE RESPECTIVE CORRELATION COEFFICIENTS r

<i>Stationary phase</i>	A_0	A_1	A_2 (mol^2)	r
OV-101	0.1919	—	$2.439 \cdot 10^{-47}$	0.880
OV-17	0.1442	$4.708 \cdot 10^{-27}$ ($mol\ nm^3/D^2$)	$3.087 \cdot 10^{-47}$	0.901
Oxidipropionitrile	0.6186	$2.731 \cdot 10^{-3}$ (nm^3/D^2)	$0.9553 \cdot 10^{-47}$	0.899

bution of the different alkyl chain lengths to the intermolecular interactions and, therefore, to retention data, while the association parameters are the same for all the species of a homologous series. By correlating these parameters with the retention data measured, the coefficients of eqn. 7 (listed in Table III) were determined. These coefficients were used to predict the $\log V_g$ values of all the solutes on the stationary phases studied. The correlation coefficients are rather different from 1. The precision is sufficient for the correct prediction of the retention sequence of the "unknown" polar substances I-V in the chromatograms, but not for precalculation of the absolute retention volumes.

The predicted ODPN values are compared graphically with the measured values in Fig. 1a. This figure shows the majority of the points to be near to the ideal 45° correlation. Moreover, in most cases, correct retention sequence of the individual substance pairs was predicted. From 27 solutes investigated, 351 substance pairs may be combined, and only for 25 substance pairs the retention sequence was predicted incorrectly, *i.e.*, the prediction of the retention sequence was successful in 93% of all the cases⁸. Similar results were obtained with OV-101 and OV-17.

The average deviation of the calculated retention data from the measured ones was 6.7%, which is commensurate with the results of Rohrschneider⁹ (6%), Mar-

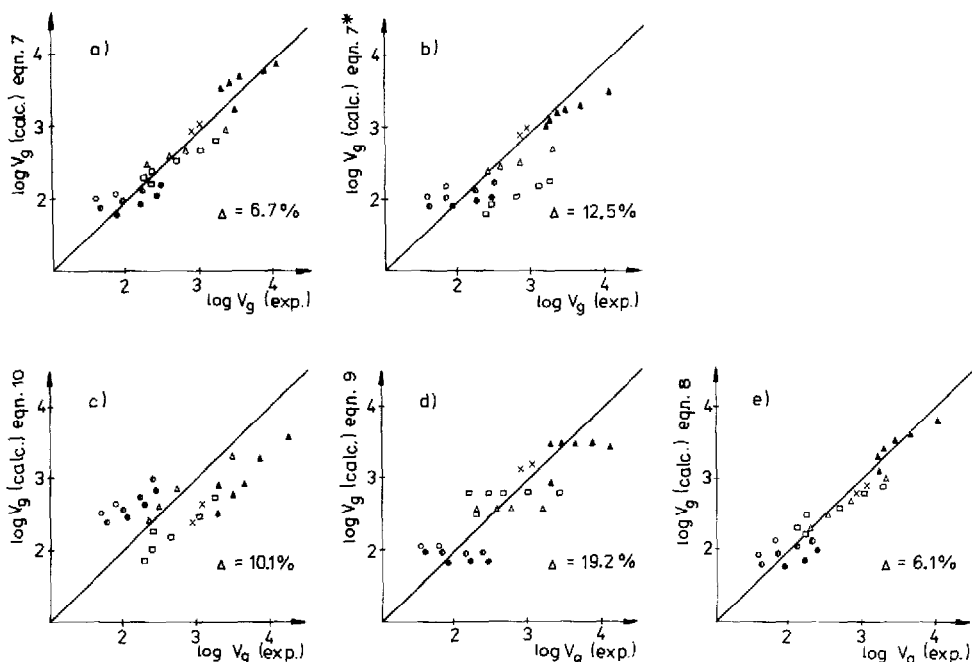


Fig. 1. Correlations between experimental and calculated retention data on oxidipropionitrile. a, According to eqn. 7; b, according to eqn. 7 with φ_{ij}^{or} calculated according to $\varphi_{ij}^{or} = -\frac{2}{3kT} \cdot \frac{\mu_i^2 \cdot \mu_j^2}{r_{ij}^6}$; c, according to eqn. 10; d, according to eqn. 9; e, according to eqn. 8. Δ = average deviation of the calculated retention values. Symbols: nitrites = x, alcohols = □, chloroalkanes = ○, bromoalkanes = ●, iodoalkanes = ●, ketones = △, nitroalkanes = ▲.

tire¹⁰ (5%) and Gassiot et al.¹¹ (3%) when using solutes of one substance class only.

For different types of compound, our model undoubtedly is only a rough approximation of the real conditions in GLC-systems. However, it may be suitable for the prediction of retention data reflecting some particular retention-determining properties of the system. In order to examine our model in this sense, we studied the effect of the calculated association and dispersion interaction contributions, specific orientations and the experimentally determined standard entropy of sorption, ΔS_s^0 , on the accuracy of the prediction of retention data. For this purpose, the $\log V_g$ values were calculated according to four different approaches deviating from our model:

(1) In addition to our model, the standard entropy of sorption, ΔS_s^0 , determined from the temperature dependence of the specific retention volume, was included in the calculation according to

$$\log V_g = A_0 + A_1 \cdot \varphi + A_2 \cdot D + A_3 \cdot \Delta S_s^0 \quad (8)$$

(2) Specific orientations between the interacting molecules were neglected.

(3) Dispersion interactions were neglected, and the retention data were evaluated according to

$$\log V_g = A_0 + A_1 \cdot \varphi \quad (9)$$

(4) Dispersion interactions only were considered, neglecting association forces:

$$\log V_g = A_0 + A_2 \cdot D \quad (10)$$

In Fig. 1b-e, the results of each of the calculations obtained for ODPN are correlated with the experimental $\log V_g$ values. A comparison of these diagrams with the correlation obtained from our model (Fig. 1a) leads to the following conclusions:

(a) The agreement between calculated and experimental values may be significantly improved if specific orientations between the interacting molecules are considered (Fig. 1b).

TABLE IV

EXPERIMENTAL AND CALCULATED RETENTION TIMES t_R ON PHENYL METHYL SILICONE GUM OV-17 (SEE FIG. 2)

Peak number in Fig. 2	Solute	t_R (min)	
		Experimental	Calculated according to eqn. 7
4	Ethanol	2.81	2.31
I	Propionaldehyde	4.69	5.25
II	Diethylamine	6.18	14.6
2	Propionitrile	15.15	15.53
III	Dichloroethane	20.91	21.96
IV	Amyl chloride	35.64	54.25
V	Amyl bromide	80.88	75.68
26	1-Nitrobutane	159.8	129.7

TABLE V

EXPERIMENTAL AND CALCULATED RETENTION TIMES t_R ON OXIDIPROPIONITRILE (ODPN) (SEE FIG. 3)

Peak number in Fig. 3	Solute	t_R (min)	
		Experimental	Calculated according to eqn. 7
15	Ethyl iodide	0.55	0.55
I	Propionaldehyde	8.88	5.55
IV	Amyl chloride	9.62	11.74
4	Ethanol	14.85	16.21
19	Methyl ethyl ketone	23.28	22.40
III	Dichloroethane	31.05	39.43
2	Propionitrile	63.76	68.60
23	Nitroethane	145.5	195.2

(b) The estimation of retention data according to the suggested model (*i.e.* by considering both association and dispersion forces) is much more accurate compared to a calculation in which only one type of interaction is considered (fig. 1c and d).

(c) The consideration of the entropy of sorption does not improve the accuracy of the prediction significantly (Fig. 1e).

The usefulness of the correlation (eqn. 7) for the prediction of the retention sequence shall be demonstrated for the stationary phases OV-17 and ODPN and eight polar solutes. Although in some cases the calculated retention times apparently

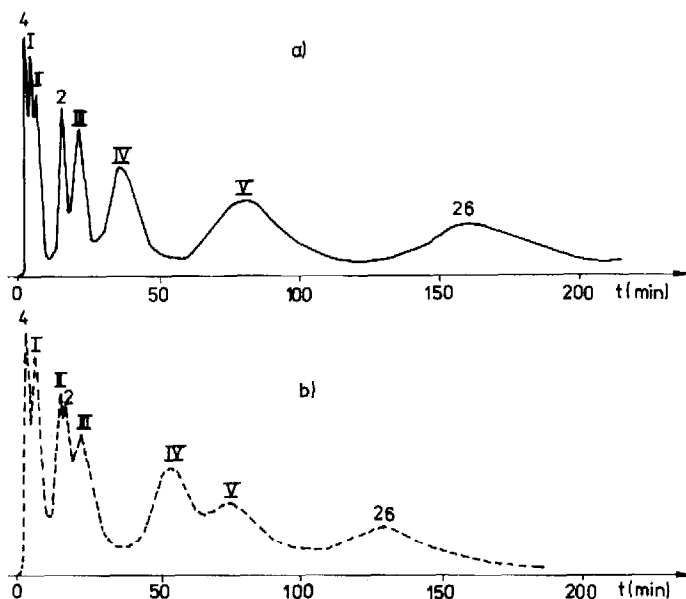


Fig. 2. Comparison between an experimental and a constructed chromatogram (stationary phase: OV-17). a, Experimental chromatogram; b, constructed chromatogram (retention times according to Table IV; peak widths according to experimental values).

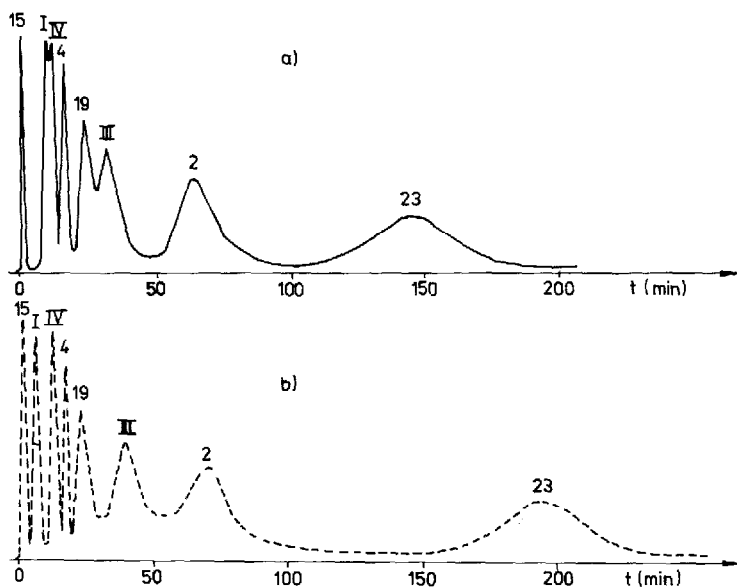


Fig. 3. Comparison between an experimental and a constructed chromatogram (stationary phase: oxidipropionitrile). a, Experimental chromatogram; b, constructed chromatogram (retention times see Table V; peak width according to experimental values).

deviate from the experimental values (Tables IV and V), the predicted retention sequence agrees with the experimental one for all the solutes under study. Moreover, it is remarkable that the retention sequence of prionaldehyde (I), diethylamine (II), dichloroethane (III), amyl chloride (IV) and amyl bromide (V) [*i.e.* solutes of which the retention data have not been considered in the determination of the empirical coefficients A_0 , A_1 and A_2 (eqn. 7)] were predicted correctly too.

To illustrate the usefulness of the results, the chromatograms in the Figs. 2 and 3 obtained experimentally are compared with the chromatograms based on the calculated retention times listed in the Tables IV and V.

CONCLUSION

The suggested model³ provides a semi-empirical estimation of retention data and yield a correct prediction of the retention sequence for 93% of all the solute pairs investigated. The results show that the estimation of the specific orientations between the interacting molecules, and the separation of intermolecular forces into contributions due to association and dispersion forces, significantly improve the accuracy of retention data prediction in GLC systems. However, our model may fail with systems, in which the difference between the individual $\log V_g$ values are smaller than 7% of the values measured.

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