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PREDICTION OF RETENTION DATA BY USING PARAMETERS OF INTERMOLECULAR INTERACTION

I. A MODEL FOR CALCULATION OF NON-POLAR AND POLAR INTERACTION PARAMETERS

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SUMMARY

Two interaction energy parameters, D and φ , characterizing the interaction between solute and stationary phase in gas-liquid chromatography have been suggested. In the calculation of these parameters, molecular values like atomic group refractions, dipole moments and Van der Waals radii have been used. Moreover, it has been attempted to consider mutual orientations of the interacting molecules.

INTRODUCTION

The prediction of retention data is one of the main tasks in the study of chromatographic processes as well as in the methodical development and analytical application of chromatography. James and Martin¹ already started these investigations with a useful increment system for homologous fatty acids in gas-liquid chromatography (GLC). Since then, besides chromatographic increment systems, many relationships between retention data and substance properties and methods of statistical thermodynamics have been published to describe and predict the chromatographic retention.

Increment methods are mostly based on Kováts retention index system² and the Rohrschneider^{3,4} and McReynolds⁵ constants. Fundamental contributions to the incremental description of the gas chromatographic retention of linear, branched and cyclic hydrocarbons and their derivatives were made by Schomburg⁶, Takačs⁷, Haken *et al.*⁸ and Engewald *et al.*⁹. Recently, more complex polar molecules are included in the increment system investigations, such as aromatic esters⁸, polar substituted benzenes¹⁰ or nitrated polycyclic aromatic hydrocarbons¹¹. The deviation from linearity of additivity of group contributions, mainly of the first species of a homologous series, is now taken into consideration by means of the non-linear relationships proposed by Golovnya and Grigoryeva¹². Many authors have published empirical and semi-empirical rules and relationships between retention data and physical properties

of the solute or stationary liquid molecules, such as molecular weight, carbon number, boiling temperature, vapour pressure, molecular refraction, parachor, dipole moment, average molecular radii and dielectrical constants (for references see ref. 13). The meaning of the solubility parameter in GLC is described by Rohrschneider⁴. Relationships between infrared spectroscopic solvent effect (frequency shifts) and retention data are described and reviewed by Ecknig¹³. He has combined the IR-frequency shift with the average molecular polarizability in an empirical multiparameter relationship. Later, the parameter corresponding to the dispersion forces has been calculated on basis of the London concept¹⁴. Martire¹⁵ used NMR chemical shifts to describe GLC partition coefficients. Recently, besides connectivity indices¹⁶⁻¹⁸, the Van der Waals volumes^{17,18} and the average molecular polarizability¹⁹, some quantum chemically calculated molecular energy parameters were successfully correlated to retention data for aromatic hydrocarbons²⁰ and polar species such as aliphatic esters²¹.

Methods of statistical thermodynamics have also been used for prediction of retention data²²⁻³¹. The "solution of groups" model has been successfully applied for calculating limiting activity coefficients at infinite dilution²⁹⁻³¹. Kiselev and coworkers carried out molecular statistical calculations for the adsorption of complex hydrocarbon molecules on the flat surface of graphitized thermal carbon black³²⁻³⁴. Recently these calculations could be successfully extended from hydrocarbons to oxygen-containing polar molecules³⁴.

The methodical development of the procedures for prediction of retention data shows that polar solute and liquid phase molecules are increasingly taken into consideration. However, for polar chromatographic systems the approximation used in the calculation of retention data is limited by difficulties arising, for example, from the understanding of the contributions by polar groups to the dispersion forces and from the dependence of orientation and induction forces on the intermolecular angles between the interacting groups.

In this paper we attempt to calculate the parameters D and φ , for non-polar and polar interaction respectively, on the basis of a simplified geometric model. D is calculated using the London concept^{14,35} which includes the interacting contributions of polar groups. φ is calculated according to the concepts of Keesom³⁶ and Debye³⁷, taking into account energetically preferred intermolecular orientation angles. The structure of the solution is considered on basis of the lattice model taking into consideration the four nearest neighbours.

The molecules are divided in atomic groups suitable for calculation procedure described. Therefore, groups are formed which permit the calculation of the dipole interaction, considering the specific orientation angle of the interacting groups.

CALCULATION OF THE NON-POLAR PARAMETER D

The parameter D is a measure of the energy of dispersion forces acting between solute and stationary phase molecules. D has been calculated by the equation

$$D = \sum_{i=1}^m \sum_{j=1}^n D_{ij} \cdot K_i \cdot W_j \quad (1)$$

summing the interaction contributions D_{ij} of all of the interacting groups i and j of

the solute and the stationary phase molecules, respectively, corrected by introducing the shielding factor K_i and the contact point concentration W_j . The number of interacting atomic groups i and j are given by m and n , respectively, D_{ij} is calculated by

$$D_{ij} = \frac{R_i \cdot R_j}{r_{ij}^6} \quad (2)$$

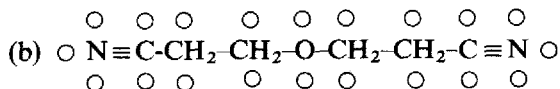
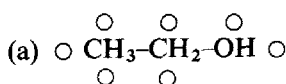
and describes the dispersion interaction between two interacting atomic groups i and j . Eqn. 2 was given by Korol^{38,39} who applied the London concept on non-polar GLC systems. The distance r_{ij} between interacting groups is the sum of their Van der Waals radii. R_i and R_j are the atomic group refractions.

K_i and K_j , defined as the number of contact points of an atomic group, are the number of sites on which the molecule is able to interact with neighbouring molecules. The number of contact points is determined by statistical thermodynamics, assuming that each atomic group can interact with the four nearest neighbours. Nearest neighbours may be atoms or atomic groups of the interacting molecules as well as chemically bonded atomic groups of the molecular groups considered. Consequently, the value of K_i or K_j is 4 if interacting groups are not shielded, and 0 in case of total shielding. Increasing the number of nearest neighbours did not improve the precision of the retention data calculated.

W_j is the concentration of contact points belonging to the atomic group j in the stationary phase molecules defined by

$$W_j = \frac{\Sigma K_j}{K_{\text{total}}} \quad (3)$$

ΣK_j is the number of all interacting contact points of atomic group j . K_{total} is the total number of contact points of all different atomic groups contained in the stationary phase molecules. The calculation procedure of the parameter D for ethanol-oxidipropionitrile dispersion interaction is given in Table I. The contact points (O) of the interacting molecules ethanol and oxidipropionitrile are schematically illustrated by (a) and (b), respectively



As atomic groups we consider either single atoms, such as $\equiv\text{C}$, $\text{N}\equiv$ and $-\text{O}-$, or groups consisting of an atom chemically bonded with hydrogen, such as $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{OH}$. Because of the small diameter of the hydrogen atom and of the short bond length between hydrogen and other atoms these groups are considered to be spherical, similar to single atoms.

TABLE I
CALCULATION SCHEME OF THE PARAMETER D FOR THE DISPERSION INTERACTION ETHANOL-OXIDIPROPIONITRILE

$$D = \sum_{i=1}^m \sum_{j=1}^n D_{ij} \cdot K_i \cdot W_j = 51.86 \cdot 10^{-45} \text{ mol}^{-2} \quad (m = 3; n = 4).$$

Interaction, $i \dots j$	r_i (nm)	r_j (nm)	R_i (ml/mol)	R_j (ml/mol)	K_i	K_j	K_{total}	W_j	$D_{ij} \cdot 10^{-45}$ (mol ⁻²)	$D_{ij} \cdot K_i \cdot W_j \cdot 10^{-45}$ (mol ⁻²)	$\sum_{j=1}^n D_{ij} \cdot K_i \cdot W_j \cdot 10^{-45}$ (mol ⁻²)
CH ₃ ... N	0.2	0.15	5.718	3.118	3	6		0.3	9.699	8.729	23.54
CH ₃ ... C	0.2	0.165	5.718	3.617	3	4		0.2	8.747	5.248	
CH ₃ ... CH ₂	0.2	0.2	5.718	4.618	3	8		0.4	6.447	7.736	
CH ₃ ... O	0.2	0.14	5.718	1.642	3	2		0.1	6.081	1.824	
CH ₂ ... N	0.2	0.15	4.618	3.118	2	6		0.3	7.833	4.700	12.67
CH ₂ ... C	0.2	0.165	4.618	3.617	2	4	20	0.2	7.064	2.826	
CH ₂ ... CH ₂	0.2	0.2	4.618	4.618	2	8		0.4	5.207	4.166	
CH ₂ ... O	0.2	0.14	4.618	1.642	2	2		0.1	4.912	0.982	
OH ... N	0.178	0.15	2.652	3.118	3	6		0.3	6.573	5.916	15.65
OH ... C	0.178	0.165	2.652	3.617	3	4		0.2	5.831	3.499	
OH ... CH ₂	0.178	0.2	2.652	4.618	3	8		0.4	4.156	4.987	
OH ... O	0.178	0.14	2.652	1.642	3	2		0.1	4.171	1.251	

CALCULATION OF THE POLAR PARAMETER φ

The parameter φ is a measure of the energy of association interaction given by the sum of the intermolecular interactions (dipole-dipole, induction, H-bonding, charge transfer), caused by polar functional groups^{40,41}.

We have selected chromatographic systems (solutes and liquid phases) where either dipole-dipole (φ_{or}) or induction forces (φ_{ind}) gives the most important contribution to the association forces. In our model, the H-bonding contribution is considered to be a dipole-dipole interaction and π -systems are regarded to contribute to the induction forces.

φ_{or} and φ_{ind} have been calculated by the equation

$$\varphi = \sum_{\mu=1}^{m'} \sum_{\nu=1}^{n'} \varphi_{ij}^{\mu\nu} \cdot K_{\mu} \cdot W_{\nu} \quad (4)$$

where μ and ν are termed contact segments belonging to the polar atomic groups i and j chosen on basis of the following three principles:

(1) Each atom may have four nearest neighbours (interacting or chemically bonded groups).

(2) Orientations of the interacting polar groups providing minimum potential energy are preferred.

(3) In order to achieve the minimum potential energy (maximum interaction energy), all of the contact segments of the solute will interact with the stationary phase molecule, provided that it is not hindered sterically.

The first principle is considered in the determination of K_{μ} and W_{ν} . The second principle is the basis for the calculation of orientation angles and the distance r_{ij} .

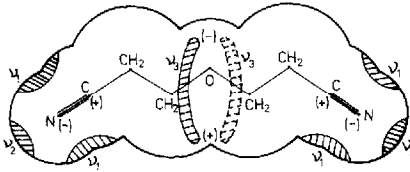
The contact segment is defined as that part of the molecular surface area, where the polar groups may contact during the intermolecular interaction. For each interacting dipole, a maximum of four nearest neighbours have been taken into account (comparable to the contact points). However, the contact segments are determined regarding the mutual orientations between the interacting groups. In Fig. 1 the contact segments of the ethanol-oxidipropionitrile interaction are demonstrated.

$\varphi_{ij}^{\mu\nu}$ is the energy parameter of the orientation interaction (φ_{ij}^{or}) or induction interaction (φ_{ij}^{ind}) between the polar groups i and j on the contact segments μ and ν ; K_{μ} is the number of contact segments μ , which are characterized by equal interaction energy, W_{ν} is defined by

$$W_{\nu} = \frac{\Sigma \nu}{\nu_{total}} \quad (5)$$

where $\Sigma \nu$ is the sum of energetically equal contact segments. ν_{total} is given by the total sum of all contact segments of the stationary phase molecule which are geometrically able to interact with the corresponding contact segments μ of the solute molecule.

Oxidipropionitrile (stationary phase)



Ethanol (solute)

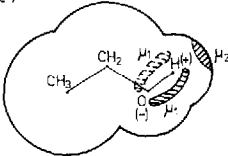


Fig. 1. The most probable arrangement of contact segments (shaded areas) on the molecular surfaces of oxidipropionitrile and ethanol for the interaction between these molecules.

The calculation of the energy parameter $\varphi_{ij}^{\mu\nu}$

The orientation forces acting between two polar atomic groups i and j on the contact segments μ and ν are calculated by the formula of Keesom^{3,6}:

$$\varphi_{ij}^{or} = - \frac{\mu_i \cdot \mu_j}{r_{ij}^3} \cdot [-2 \cos \theta_i \cdot \cos \theta_j + \sin \theta_i \cdot \sin \theta_j + \cos (\Phi_i - \Phi_j)] \quad (6)$$

In practice, eqn. 6 is simplified by neglecting the third term, because the interaction energy has a maximum only in the case of a planar orientation between the dipoles. The orientation angles and distances are defined as it is illustrated in Fig. 2. μ_i and μ_j are the dipole moments of the groups i and j , respectively.

$$\varphi_{ij}^{or} = - \frac{\mu_i \cdot \mu_j}{r_{ij}^3} \cdot [-2 \cos \theta_i \cdot \cos \theta_j + \sin \theta_i \cdot \sin \theta_j \cdot \cos (\Phi_i - \Phi_j)]$$

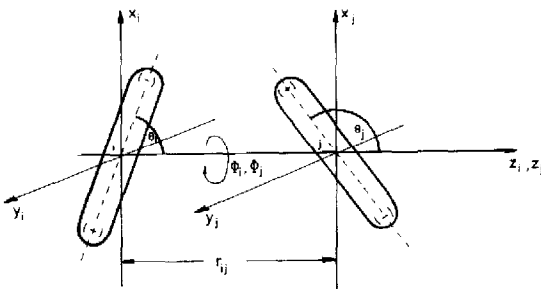


Fig. 2. Interaction energy of the two dipoles i and j between the polar interacting groups i and j . θ_i , θ_j , Φ_i , Φ_j = orientation angles, μ_i , μ_j = dipole moments of the groups i and j , r_{ij} = distance between the geometrical centers.

The induction forces are calculated by the formula of Debye³⁷:

$$\varphi_{ij}^{\text{ind}} = - \frac{\mu_i^2 \cdot \alpha_j \cdot (3 \cos \theta_i + 1)}{2 r_{ij}^6} \quad (7)$$

where α_j is the group polarizability of the interacting group j .

The orientation angles θ_i and θ_j and the distance r_{ij} have been calculated on basis of the Van der Waals radii R of the interacting two-atomic groups consisting of the atoms 1 and 2 using the geometrical model shown in Fig. 3. θ_i is the angle between the line a , connecting the geometrical centers of the interacting dipole groups, and the line d , being the symmetry axis of these groups. θ_j is the angle between line a and b . The distance r_{ij} between these geometrical centers depends on the orientation of the interacting groups influenced by the sterical structure of the interacting molecules and on the Van der Waals radii R_{i1} , R_{i2} , R_{j1} and R_{j2} of their atoms.

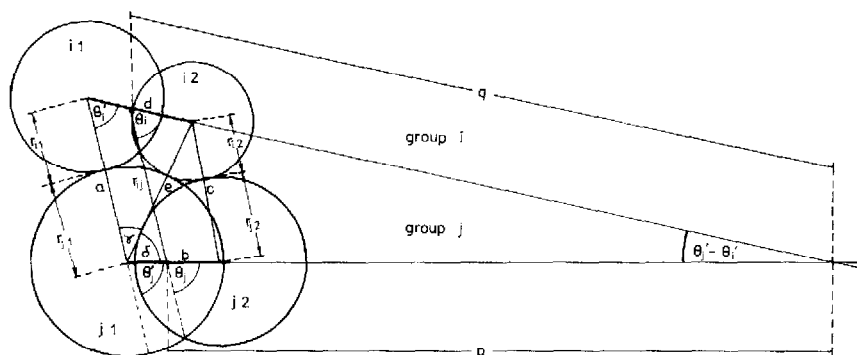


Fig. 3. Geometrical model for calculation of the distance r_{ij} and the angles of mutual orientations θ_i and θ_j between two dipole groups i and j . (Calculation scheme given in ref. 41.)

The influence of the orientation angles θ_{ij} and the distance r_{ij} on the energy of the dipole-dipole interaction are shown in Table II for interacting CN- and CH₂Cl-groups. Obviously, the highest interaction energy will be obtained if the interacting dipole groups are arranged nearly parallel (planar). Consequently, in GLC systems, parallel orientations should be preferred because they are energetically favoured. Calculations performed for other polar functional groups studied here lead to the same result.

The induction interaction energy between a nitrile group and a phenyl ring has been calculated using a similar geometrical model. The energetically favoured orientation is a nearly parallel orientation between the ring plane and the symmetry axis of the nitrile group shown in Table III.

As shown in Table II, unfavourable sterically hindered orientations lead to smaller interaction energies (example 4 and 6) or to repulsion effects (example 5).

Using these results we derived the most probable arrangements of the contact segments for all of the molecules studied.

TABLE II

ENERGY PARAMETERS ϕ_{ij}^{or} OF THE INTERACTION BETWEEN A NITRILE GROUP AND A CH₂-Cl GROUP AT DIFFERENT ORIENTATIONS θ_i AND θ_j

Number	Interaction	$-2 \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j$	r_{ij} (nm)	ϕ_{ij}^{or} (D^2/nm^3)
1		0.998	0.345	170.5
2		0.585	0.352	94.1
3		0.707	0.400	77.5
4		≈ 0	0.432	0
5		-2	Repulsion	
6			Orientations are sterically hindered by chemically bonded neighbouring atoms	

TABLE III

ENERGY PARAMETERS ϕ_{ij}^{ind} OF THE INTERACTION BETWEEN A NITRILE GROUP AND A PHENYL RING AT DIFFERENT ORIENTATIONS θ_i

Interaction	$3 \cos \theta_i + 1$	R (ml/mol)	r_{ij} (nm)	$ \phi_{ij}^{ind} \left(\frac{D^2}{\text{mol nm}^3} \right) \cdot 10^{-24}$
	1.388	29.93	0.359	126.8
	4.000	14.94	0.387	115.3
	4.000	29.93	0.463	78.8
	1.000	14.94	0.491	6.91

TABLE IV
 CALCULATION SCHEME OF THE PARAMETER φ FOR THE ASSOCIATION INTERACTION ETHANOL-OXIDIPROPIONITRILE

$$\varphi = \sum_{\mu=1}^{m'} \sum_{\nu=1}^{n'} \varphi_{ij}^{\mu\nu} \cdot K_{\mu} \cdot W_{\nu} = 506 D^2 \text{ nm}^{-3} \quad (m' = 2, n' = 3).$$

Interaction $i \dots j$	Dipole moment (D)		r_{ij} (nm)	$\frac{-2 \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j}{\sin \theta_i \sin \theta_j}$	$\varphi_{ij}^{\mu\nu}$ (D^2/nm^3)	K_{μ}	W_{ν}	$\varphi_{ij}^{\mu\nu} \cdot K_{\mu} \cdot W_{\nu}$ (D^2/nm^3)	$\sum_{\nu=1}^{n'} \varphi_{ij}^{\mu\nu} \cdot K_{\mu} \cdot W_{\nu}$ (D^2/nm^3)
	i	j							
$\mu_1 \dots \nu_1$	1.5	3.6	0.290	0.971	215	2	0.667	287	328
$\mu_1 \dots \nu_2$	—	—	—	0	0	—	—	0	
$\mu_1 \dots \nu_3$	1.5	0.987	0.299	1.110	61.5	2	0.333	41	
$\mu_2 \dots \nu_1$	—	—	—	0	0	—	—	0	178
$\mu_2 \dots \nu_2$	1.5	3.6	0.393	2	178	1	1	178	
$\mu_2 \dots \nu_3$	—	—	—	0	0	—	—	0	

According to the third principle, in addition to the two interactions ($\mu_1 \dots v_1$) (see Fig. 1) giving a maximum interaction energy and being possible from the geometrical viewpoint, a third interaction ($\mu_2 \dots v_2$) must be taken into the account. The calculation of the parameter φ for this case is demonstrated in Table IV.

CONCLUSION

For GLC systems the interaction energy parameters D and φ are complex values, depending on contributions of all non-polar and polar atomic groups. In order to calculate the parameter φ , representing polar interaction forces, the mutual positions of the interacting molecules must be known. These positions have been chosen so, that they correspond to maximum interaction energy.

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