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Attempts to use Laffort's solubility factors as polarity parameters for organic compounds in inverse gas chromatography

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ABSTRACT

Solubility factors were applied to characterize organic compounds used as the stationary phase in a gas chromatographic column. A procedure for their determination is proposed and the physico-chemical meaning is discussed. Relationships between solubility factors and appropriate retention index increments ΔI_i for McReynolds solutes are presented. The influence of the structure of thioethylene derivatives on the parameters examined is discussed.

INTRODUCTION

Rohrschneider [1,2] expressed the polarity of the stationary phase as a polynomial, where the variables represent increments prescribed for different solute–solvent intermolecular interactions. Hartkopf *et al.* [3,4] discussed the validity of *a priori* selected standard solutes and indicated some contradictions existing in the Rohrschneider–McReynolds system. They showed, by means of solubility parameters, that each standard solute will act in different types of intermolecular interactions, not only the selected ones. Laffort and co-workers [5,6] introduced semi-empirical solubility factors calculated from retention data for standard solutes measured on five selected stationary phases of different polarity. They assumed that the retention index (I_i) of a given solute could be expressed as

$$I_i = \alpha A + \omega O + \varepsilon E + \pi P + \beta B + 100 \quad (1)$$

where α, ω, ε, π and β represent the properties of a solute i and A, O, E, P and B are solubility factors that characterize the stationary phase.

Patte *et al.* [6] described the physico-chemical meaning of the solute parameters as follows: α = apolar factor, ω = orientation factor proportional to the dipole moment, ε = electron factor, π = proton donor factor or acidity factor and β = proton acceptor factor or basicity factor. However, they discussed only one

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solvent solubility factor. They indicated the existence of a relationship between factor E and the density of the stationary phase at its boiling point.

The physico-chemical characteristics of liquid stationary phases in gas chromatography (GC) are far from completely known. We have applied inverse GC for the characterization of non-ionic surface-active agent and metal extractants [7–12]. Different polarity parameters have been used, including retention indices for polar standards [7–12], dispersive force parameters [10], thermodynamic parameters [9–12] and parameters that represent electrical intermolecular interactions [8]. The proposal of Laffort and co-workers offers the possibility of describing more completely the properties of stationary phases.

The formal similarity of Rohrschneider's equation and eqn. 1 induced us to search for relationships between McReynolds "constants" and solvent solubility factors determined for various stationary phases.

EXPERIMENTAL

Eight thioalkanes of the general formula $RSCH_2CH_2S(CH_2)_nSCH_2CH_2SR$, where R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$ and n = 2, 3, 4, 5 and 6 were used as stationary phases. These compounds were synthesized by the group of Professor Beger at the Mining Academy, Freiberg (Germany), and kindly donated for our investigation.

The chromatographic conditions were as follows: column, 1 m × 3 mm I.D.; column temperature, isothermal at 90°C; column packing, 25% (w/w) surfactant on Celite (80–120 mesh); carrier gas, helium; flow-rate, 40 ml/min; detector, flame ionization; gas chromatograph, Chrom 5 (Kovo, Czechoslovakia); non-polar standards, C_5–C_9, n-alkanes; polar agents, McReynolds solutes, *i.e.*, 1-butanol, 2-pentanone, benzene, pyridine and 1-nitropropane, and additionally methanol, ethanol, propanol and 2-butanone were used.

Retention indices of the polar solutes were measured for all the stationary phases examined. Solubility factors for the solutes were taken from ref. 6. We measured the Kováts retention indices of nine selected solutes on each stationary phase. For any stationary phase compound j we have the general form of eqn. 1:

$$I_{ij} - 100 = \alpha_i A_j + \omega_i O_j + \varepsilon_i E_j + \pi_i P_j + \beta_i B_j \quad (2)$$

where I_{ij} denotes the retention index of the solute i as measured on stationary phase j; α_i–β_i are solubility factors for solute i and A_j–B_j are Laffort solubility factors for stationary phase j. In our case, i = 1–9 and j = 1–8.

For one stationary phase, we have a series of nine equations in the form

$$I_i - 100 = \alpha_i A + \omega_i O + \varepsilon_i E + \pi_i P + \beta_i B \quad (3)$$

where α_i–β_i have the same meaning as in eqn. 2 and I_i is the retention index of solute i. It is possible to solve this set of equations if we have $i \geqslant 5$ retention data (I_i) for different solutes. We calculated Laffort's solubility factors by the use of eqn. 2 separately for each stationary phase (j = 1–8), *i.e.*, we used the form of eqn. 3. The solubility factors are given in Table II.

RESULTS AND DISCUSSION

It is obvious that an increase in the hydrocarbon part of the molecule will decrease the polarity of a compound. The compound's polarity could be expressed, *e.g.*, by polarity indices commonly used for the characterization of surfactants (Table I) [7–12]. Solubility factors *O*, *E* and *P* decrease with increase in the number of carbon atoms in the stationary phase, as shown as an example for factor *O* in Fig. 1. Phase 3 does not fit this relationship, probably owing to experimental error. The influence of the methylene group in the central hydrocarbon chain is much weaker than those in the alkyl side-group. The central methylene groups are screened by thioethylene units and their influence on estimated parameters is relatively smaller. For example, each methylene units decreases factor *O* by 13.78 i.u., compared with 12.89 i.u. for the those in the alkyl side-chain.

Similar relationships exist between the sum of the first five McReynolds solutes, $\sum_{i=1}^{5} \Delta I_i$, and the number of carbon atoms (Fig. 2). This supports the idea that solubility factors could be discussed as polarity parameters in the characterization of organic compounds. They are sensitive to changes in the structure of stationary phases. However, the question of their physico-chemical meaning remains open. The density of the stationary phase discussed by Patte *et al.* [6] as the quantity which may be correlated with factor *E* is not the most important property of a stationary phase. Possibly the solvent solubility factors are the only invariable mathematical parameters in multivariate equations. The solvent solubility factor *E* is highly correlated with ΔI_{Bz} for benzene (Table II, Fig. 3). The value of ΔI_{Bz} is used for the description of intermolecular interactions caused mainly by the presence of π-electrons. It means that the factor *E* could characterize the ability of a stationary phase to take part in such interactions. Rohrschneider chose 2-butanone for the description of dipole orientation forces while McReynolds [13] introduced the higher homologue 2-pentanone. However, Hartkopf *et al.* [3,4] showed that a ketone as a polar standard does not

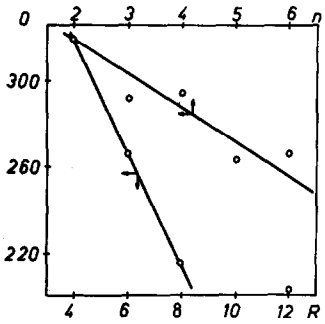
TABLE I

RETENTION AND POLARITY PARAMETERS FOR EXAMINED COMPOUNDS AT 90°C

No.	Stationary phase		ΔI^b					Polarity index		Criterion *A*
	R[a]	*n*[a]	Bz	MPK	Bu	Py	Np	CH_3OH	C_2H_5OH	
1	C_6	2	118	149	192	180	212	518	567	2.240
2	C_8	2	81	136	175	164	189	614	562	2.261
3	C_{12}	2	68	114	163	135	149	501	545	2.297
4	C_4	2	135	183	228	200	244	557	621	2.100
5	C_4	3	119	180	223	200	243	553	613	2.110
6	C_4	4	129	174	224	200	243	550	607	2.116
7	C_4	5	113	168	215	200	231	549	602	2.130
8	C_4	6	112	165	212	199	226	547	597	2.141

[a] In the general formula $RSCH_2CH_2S(CH_2)_nSCH_2CH_2SR$.

[b] ΔI = difference in Kováts retention indices as measured on a given stationary phase and on squalane at 90°C. Bz = benzene; MPK = 2-pentanone; Bu = 1-butanol; Py = pyridine; Np = 1-nitropropane.



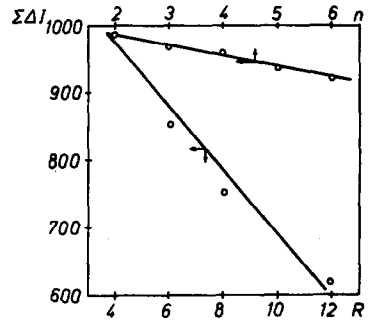


Fig. 1. Influence of the number of carbon atoms in the central (n, upper horizontal axis) and peripheral (R, lower horizontal axis) hydrocarbon chains on the solubility factor O for the examined compounds.

Fig. 2. Influence of the number of carbon atoms in the central (n, upper horizontal axis) and peripheral (R, lower horizontal axis) hydrocarbon chains on the sum of the first five McReynolds solutes, $\Sigma\Delta I_i$, for the examined compounds.

properly and selectively characterize this type of interaction. The correlation coefficient for the relationship ΔI_{MPK} *vs.* factor O is relatively high (Fig. 4). We can discuss factor O as a dipole orientation factor bearing in mind the limitations of 2-pentanone as a standard.

Factors A and B could be correlated with any of the ΔI_i values (Table III). Golovnya and Mišarina [14] indicated that the interactions of methylene groups in the alkyl chain are omitted in the Rohrschneider–McReynolds system. Criterion A [15] defined as

$$\text{criterion } A = \frac{t'_{Rn+1} - t'_{Rn}}{t'_{Rn} - t'_{Rn-1}} \tag{4}$$

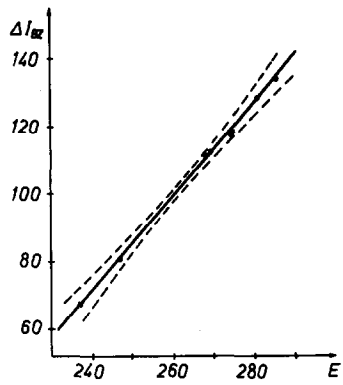
where t'_{Rn+1}, t'_{Rn} and t'_{Rn-1} are adjusted retention times for n-alkanes having $n + 1$, n and $n - 1$ carbon atoms, respectively, was used as a dispersive force parameter for

TABLE II

SOLUBILITY FACTORS

Stationary phase[a]	Solubility factor				
	A	O	E	P	B
1	197	264	274.6	216.1	71.6
2	192.4	214.1	247	175	222.8
3	198.2	204.2	237.3	186.1	179.9
4	197.2	317.8	285.5	261.2	−20.6
5	195.6	290.8	274.4	234.1	71.6
6	198.2	297.2	280.8	244	31.1
7	193.2	262.3	268.9	212.3	151.1
8	195.7	267.6	268	217.7	122.1

[a] See Table I.



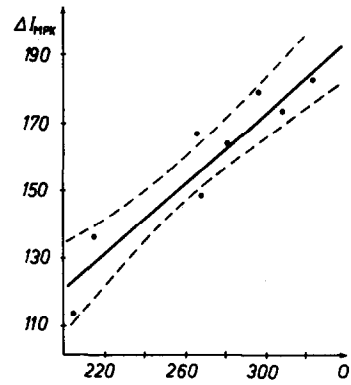


Fig. 3. Relationship between ΔI_{Bz} and solubility factor E (confidence limit for $\alpha = 0.05$).

Fig. 4. Relationship between ΔI_{MPK} and solubility factor O (confidence limit for $\alpha = 0.05$). MPK denotes methyl propyl ketone, *i.e.*, 2-pentanone.

the characterization of apolar interactions. Criterion A was correlated with the solubility factor A, but the correlation coefficient is low (Table III). This means that the solubility factor A could not be considered as interchangeable with the criterion A. Ševčik and Löwentap's criterion A [15] has a different origin to Laffort's factor A.

Relationships between solubility factor P and different ΔI_i values are characterized by very moderate correlation coefficients ($R = 0.9$) and we cannot decide on the best one, *i.e.*, that which has the strongest physico-chemical meaning. The ΔI_i values refer to the behaviour of selected solutes on given liquid phases, while Laffort's solubility factors characterize essentially the properties of the liquid phase. These groups of parameters could be correlated or not, as shown here.

TABLE III

CORRELATION COEFFICIENTS FOR LINEAR RELATIONSHIPS $\Delta I_Y = a + bX$

Y = McReynolds solute; X = solubility factor.

Parameter	*A*	*O*	*E*	*P*	*B*
ΔI_{Bz}	Low	0.9722	0.9990	0.9247	Low
ΔI_{Bu}	Low	0.9480	0.9129	0.8952	Low
ΔI_{MPK}	Low	0.9421	0.9160	0.8698	Low
ΔI_{Np}	Low	0.9252	0.9351	0.8342	Low
ΔI_{Py}	Low	0.8717	0.8943	0.7683	Low
Criterion *A*	Low	−0.8988	−0.8393	−0.8469	0.6879

CONCLUSIONS

Semi-empirical solubility factors could be used in the physico-chemical characterization of organic compounds used as GC stationary phases. It has been shown that

at least two Laffort solubility factors could be correlated with McReynolds constants and therefore they could be considered as a measures of π-electron (E factor) and orientation forces (O factor). For example, the high value of E indicates that a given organic compound could interact with a solute by π-electron forces. The larger the value of the solubility factor, the stronger are the interactions measured by that parameter. Solubility factors decrease with increase in the number of carbon atoms both in the central methylene chain and in alkyl end-groups. Factors E and O decrease with increase in the number of crabon atoms in the central hydrocarbon chains and as in the peripheral groups.

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