Inverse gas chromatography: the use of Laffort solubility factors and topological indices in structure–polarity relationships

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ABSTRACT

Inverse gas chromatography was used in the physico-chemical characterization of 1,3-bis[ω-alkoxyoligo(oxyethylene)]-2-propanols Laffort solubility factors were examined as polarity measures and topological indices as structural parameters Relationships between Laffort solubility factors and polarity index were examined It was found that Laffort solubility factor O and factor E may be usesd as polarity measures Topological indices were used as structural parameters in polarity–structure relationships, which were evaluated and are discussed A higher discriminating power of the Balaban index and Wiener number was found in comparison with the valence connectivity indices

INTRODUCTION

Numerous efforts have been made to characterize properly liquid stationary phases used in gas chromatography [1–5] The term "stationary phases" is used here both for commercial liquid phases and the large group of organic (polymeric and non-polymeric) compounds examined by the procedures of inverse gas chromatography [6–8] The solubility parameter, defined as the square root of cohesive energy density [9–12], seems to be a powerful tool in the description of intermolecular solute–solvent interactions However, the lack of physico-chemical data for most liquid phases owing to their low vapour pressure has limited the use of solubility parameters in the characterization of organic compounds

An interesting attempt to overcome these difficulties is the use of Laffort's solubility factors [13,14]

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Laffort and Patte [14] described a procedure for their determination and found close relationships between solubility factors and solubility parameters for solutes used in the chromatographic process They expressed the retention indices of carefully selected standard solutes according to the following equation

$$I_i = \alpha_i A + \omega_i O + \varepsilon_i E + \pi_i P + \beta_i B + 100 \qquad (1)$$

where I_i denotes the retention index of solutes i as measured on a given stationary phase, α_i and β_i are solubility factors of solute i and A, O, E, P and B are Laffort solubility factors for the examined liquid phase

The physical meaning of solute solubility factors is as follows α is an apolar factor proportional to the molar volume of solute at the boiling point, ω is an orientation factor proportional to dipole moments for simple molecules, ε is an electron factor, π is a proton donor factor, also called acidity factor, and β is a basicity factor proportional to the ability to accept protons [14]

The physico-chemical interpretation of solubility

factors A, O, E, P and B remained unclear Recently, Voelkel and Janas [15] described an attempt to use of Laffort solubility factors in the characterization of some thioethylene derivatives They indicated the existence of statistically significant relationships between some of the Laffort factors and the differences in retention indices for McReynolds probes (e g , $\Delta I_{benzene}$ vs factor E and $\Delta I_{2-pentanone}$ vs factor O)

The polarity parameters, thermodynamic functions of solution and dispersive interactions parameters for 1,3-bis[ω-alkoxyoligo(oxyethylene)]-2-propanols of general formula

$$R(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_mR$$
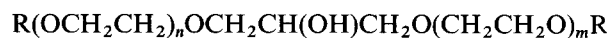
where $R,R' = C_4H_9$, C_6H_{13}, C_8H_{17}, $R = R'$ or $R \neq R'$, $n,m = 0$–3, $n = m$ or $n \neq m$, were published earlier [16,17] Variations in R and R' alkyl groups and in n and m cause significant differences in the properties of examined compounds [16–18]

The polarity index, PI, was proposed by Huebner [19] to characterize surface-active agents examined by gas–liquid chromatography and is calculated from the experimental relationship

$$PI = 100 \log(C - 4\ 7) + 60 \qquad (2)$$

where C is an apparent carbon number equal to the number of carbon atoms in a hypothetical n-alkane having the same retention time as a polar solute (alcohol)

Thermodynamic functions of solution, i e , partial molal Gibbs free energy of solution for a methylene group, $\Delta G_s^m(CH_2)$, or functional group FG, ΔG_s^m (FG), were introduced by Risby and co-workers [20–23] and were used to characterize liquid stationary phases [23] and also surfactants and extractants [16–18] The criterion A developed by Ševčik and Lowentap [24] and the partial molar excess Gibbs free energy of solution per methylene group, ΔG^E (CH$_2$) [25], parameters of dispersive interactions, were used in the characterization of surfactants and extractants [17,26] Poole and Poole [27] suggested the usefulness of criterion A and $\Delta G^E(CH_2)$ as solvent strength parameters

It has been shown that topological indices can be used as structural parameters [28–33] These parameters were developed for saturated hydrocarbons, but the procedures proposed by Balaban [34] and Barysz *et al* [35] made them useful for describing the

structures for all groups of compounds Topological indices are sensitive to the length of the alkyl chain, the length of the oxyethylene and thioethylene chain and the presence of different heteroatoms Hence they could be used to characterize the structure of organic compounds However, the discriminating power of any topological index may be limited to an examined group of compounds It has been shown [36] that for the group of oligooxyethylene derivatives of alcohols, thioalcohols and alkylamines the best retention–structure correlations were obtained when the valence molecular connectivity indices were used as structural parameters The relationships which use the Balaban index I_B and $W(G)$ were characterized by only moderate statistical characteristics

The aim of this paper is to discuss the usefulness of Laffort's solubility factors in the characterization of examined compounds used as GC stationary phases Parameters to be used in physico-chemical characterization should be sensitive to any changes in the structure of examined substances It is of interest to check whether solubility factors obey such a condition Topological indices generally change with increase in the number of exethylene units in the oligooxyethylene chain Do they indicate the changes in the distribution of oxyethylene units in two oligooxyethylene chains?

EXPERIMENTAL

Thirty pure model 1,3-bis[ω-alkoxyoligo(oxyethylene)]-2-propanols were used as liquid stationary phases in a GC column The method of synthesis, some physico-chemical data and the conditions of chromatographic measurements were described previously [16,17]

Retention data collected earlier were used to calculate solubility factors according to Laffort's idea following the procedure described by Voelkel and Janas [15] Topological parameters were calculated according to the procedure of Barysz *et al* [35], which has been used in earlier papers [36,37]

RESULTS AND DISCUSSION

The examined compounds were divided into three groups according to the differences in the alkyl groups, viz , (i) $R = R' = C_4H_9$, (ii) $R = R' = C_6H_{13}$,

TABLE I

LAFFORT SOLUBILITY FACTORS FOR $Bu(EO)_nCH_2-CH(OH)CH_2(OE)_mOBu$

Formula		Solubility factors					Polarity index[a]
n	m	A	O	E	P	B	
0	0	—	—	—	—	—	92 3
	1	203	214	238	259	339	96 2
	2	210	221	252	272	394	99 5
	3	196	195	254	253	525	103 2
	4	194	244	268	289	399	105 7
1	1	207	209	243	269	399	98 9
	2	206	251	259	295	305	102 9
	3	195	201	262	208	503	105 4
	4	213	198	264	264	521	107 7
2	2	205	166	256	230	624	104 5
	3	193	192	269	245	598	107 5
	4	205	243	281	295	429	108 9
3	3	198	237	278	282	468	109 1
	4	201	253	284	297	425	110 0

[a] 70°C, ethanol as polar solute Taken from ref 16

and (iii) $R \neq R'$ and R or $R' = C_4H_9$, C_6H_{13}, C_8H_{17} The estimated Laffort solubility factors for these three groups of oxyethylates are presented in Tables I–III Polarity indices at 70°C (ethanol as a polar solute) taken from refs 16 and 17 are also given for comparison The polarity index has been

TABLE II

LAFFORT SOLUBILITY FACTORS FOR $Hex(EO)_nCH_2-CH(OH)CH_2(OE)_mOHex$

Formula		Solubility factors					Polarity index[a]
n	m	A	O	E	P	B	
0	0	202	169	219	216	384	82 9
	1	194	137	225	199	545	89 4
	2	194	284	246	271	288	92 5
	3	193	232	260	268	306	95 4
1	1	198	229	244	275	278	93 6
	2	197	206	248	257	392	96 2
	3	192	213	255	264	416	99 1
2	2	182	150	255	168	639	100 2
3	3	189	246	271	282	364	103 1

[a] 70°C, ethanol as polar solute Taken from ref 16

discussed as a polarity parameter for a large group of surface-active agents and extractants [38–41] The term "polarity of liquid stationary phases" has often been used and discussed, but is often misunderstood According Poole and to Poole [5,27], solvent strength (polarity) could be defined as the capacity to enter into various solute–solvent interactions, whereas solvent selectivity is a measure of relative capacity of a solvent for a particular solute–solvent interaction

Anyway, the empirical "polarity index" has been successfully used to characterize the properties of surface-active agents and surfactants [36–41] Strong correlations existing between the polarity index, PI, and HLB number, well known in surfactant physico-chemistry or HLB (calculated from PI) and extraction rate of copper [42–45], have been reported The HLB (hydrophile–lipophile balance) number is the ratio of the effective molecular masses of the hydrophilic groups to the sum of the molecular masses of the lipophilic (hydrophobic) groups in the surfactant molecule [46] For non-ionic surfactants the HLB number is between 1 and 20 Compounds with $HLB > 10$ are hydrophilic and exhibit a high affinity for the aqueous phase, and those with $HLB < 10$ are hydrophobic Hence the HLB number characterizes different properties of organic molecules containing both polar and non-polar groups As an example, surface-active agents with $HLB = 1$–6 will stabilize water-in-oil emulsions, whereas more hydrophilic compounds with
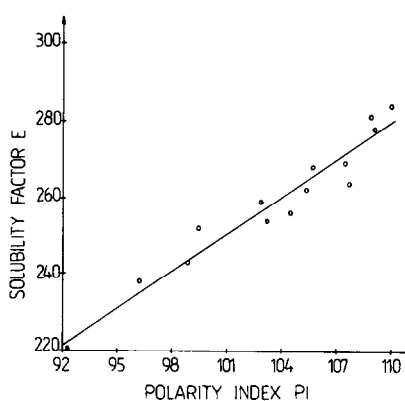

Fig 1 Laffort solubility factor E vs polarity index (ethanol as polar agent) relationship for 1,3-bis[ω-alkoxyoligo(oxyethylene)]-2-propanols

TABLE III

LAFFORT SOLUBILITY FACTORS FOR $R(EO)_nCH_2CH(OH)CH_2(OE)_mOR'$

Formula				Solubility factors					Polarity index[a]
R	R'	n	m	A	O	E	P	B	
C_8H_{17}	C_8H_{17}	0	0	194	148	215	197	401	74 4
		0	1	192	165	225	214	397	81 8
		0	2	191	151	232	208	495	86 2
C_8H_{17}	C_4H_9	0	0	188	323	248	321	−94	81 9
		0	1	196	318	253	327	−50	88 6
		1	1	213	201	235	257	309	90 0
C_6H_{13}	C_4H_9	0	1	202	183	229	236	407	92 6

[a] 70°C, ethanol as polar solute Taken from ref 16

HLB = 8–18 tend to stabilize oil-in-water emulsions

For the group of 1,3-bis[butoxyoligo(oxyethylene)]-2-propanols, the best relationship with polarity index has been found for the solubility factor E (Fig 1) It is statistically significant the correlation coefficient $R = 0\ 9695$ and the F ratio $= 187\ 97$ The same relationship for the second group of compounds examined is as follows

$$E = 9\ 2064 + 2\ 5107PI \tag{3}$$

where E = solubility factor and PI = polarity index, with $R = 0\ 9316$ and $F = 45\ 99$

Both correlations are statistically valid, but several deviations from the straight line in Fig 1 suggest that the examined parameters, at least in some instances, behave differently with the structural changes of oxyethylates There are four structural elemets that could influence the properties of our compounds (i) the length of alkyl groups R and R', (ii) the number of oxyethylene units (n,m) in oligooxyethylene chains, (iii) asymmetry in R and R', (iv) asymmetry of two oxyethylene units The variations of the discussed polarity and topological parameters caused by the changes in the above-mentioned structural elements are presented in Table IV The deviations from the straight line in Fig 1 are the result of different sensitivities of the factor E and polarity index PI on changing the asymmetry in both alkyl chains and oligooxyethylene chains The polarity index decreases with increasing asymmetry in R and R' but with decreasing asymmetry in

TABLE IV

VARIATION OF POLARITY INDEX, LAFFORT SOLUBILITY FACTOR E AND TOPOLOGICAL INDICES WITH CHANGES IN THE STRUCTURE OF THE EXAMINED COMPOUNDS

Structural element	Polarity index, PI	Laffort solubility factor, E	Balaban index, I_B	Wiener number, $W(G)$	Connectivity index, $^1\chi^v$
No of carbon atoms in alkyl group(s)	↓[a]	↓	↓	↑	↑
No of EO units in m (n = constant)	↑	↑	↑	↑	↑
Asymmetry in R and R'	↓	↑	↓	↑	No change
Asymmetry	↑	↓	↓	↑	No change

[a] The arrows ↑ and ↓ indicate an increase or decrease of a given parameter with a rising change of structural parameter

TABLE V

TOPOLOGICAL INDICES FOR $Bu(EO)_n CH_2 CH(OH) CH_2 (OE)_m OBu$

Formula		Topological parameter				
n	m	I_B	$W(G)$	$^1\chi^v$	$^2\chi^v$	$^3\chi^v$
0	0	3 4567	373 625	5 6436	3 5108	2 0340
	1	3 5312	667 000	6 7210	4 1231	2 4060
	2	2 5663	1087 875	7 7983	4 7355	2 7780
	3	3 5882	1658 750	8 8757	5 3479	3 1501
	4	3 6025	2402 125	9 9530	5 9602	3 5221
1	1	3 5967	1081 875	7 7983	4 7354	2 7780
	2	3 6256	1646 750	8 8757	5 3479	3 1501
	3	3 6425	2384 125	9 9530	5 9602	3 5221
	4	3 6512	3316 500	11 0304	6 5726	3 8941
2	2	3 6550	2378 125	9 9530	5 9602	3 5221
	3	3 6708	3304 500	11 0304	6 5726	3 8941
	4	3 6797	4448 375	12 1077	7 1850	4 2661
3	3	3 6859	4442 375	12 1077	7 1850	4 2661
	4	3 6958	5820 258	13 1851	7 7974	4 6381

oligooxyethylene chains Factor E, in contrast to PI, is highest for compounds with strong asymmetry of alkyl groups and having equal oligooxyethylene chains Hence the discussed physico-chemical parameters are not completely equivalent

Topological parameters calculated for the examined oxyethylates are presented in Table V–VII To examine the sensitivity of topological indices to structural changes, several data have been extracted and are shown in Tables VIII and IX The Balaban index decreases with increasing number of carbon atoms in alkyl chains, but increases with increasing length of oligooxyethylene chains Asymmetry of any structural element causes a decrease in this topological index The Wiener number always increases when all the discussed structural elements

TABLE VI

TOPOLOGICAL INDICES FOR $HexO(EO)_n CH_2 CH(OH) CH_2 (OE)_m OBu$

Formula		Topological parameter				
n	m	I_B	$W(G)$	$^1\chi^v$	$^2\chi^v$	$^3\chi^v$
0	0	3 4102	826 625	7 6436	4 9250	3 0340
	1	3 4880	1299 000	8 7210	5 5373	3 4060
	2	3 5328	1928 875	9 7983	6 1497	3 7780
	3	6 5646	2738 750	10 8757	6 1497	3 7780
1	1	3 5512	1922 875	9 7983	6 1493	3 7780
	2	3 5880	2726 750	10 8759	6 7621	4 1501
	3	3 6105	3733 125	11 9530	7 3745	4 5221
2	2	3 6192	3727 125	11 9530	7 3745	4 5221
3	3	3 6610	6419 375	14 1077	8 5992	5 2661

TABLE VII

TOPOLOGICAL INDICES FOR $R(EO)_nCH_2CH(OH)CH_2(OE)_mOR'$

Formula				Topological parameter				
R	R'	n	m	I_B	$W(G)$	$^1\chi^v$	$^2\chi^v$	$^3\chi^v$
C_8H_{17}	C_8H_{17}	0	0	3 3705	1551 625	9 6436	6 3392	4 0340
		0	1	3 4464	2247 000	10 7210	6 9516	4 4060
		0	2	3 4965	3129 750	11 7983	7 5639	4 7780
C_8H_{17}	C_4H_9	0	0	3 3643	934 625	7 6436	4 9250	3 0340
		0	1	3 4680	1305 000	8 7210	5 5373	3 4060
		1	1	3 5236	1934 875	9 7983	6 1497	3 7780
C_6H_{13}	C_4H_9	0	1	3 5100	948 000	7 7210	4 8302	2 9060

"increase" Valence molecular connectivity indices are less useful as they are not sensitive to asymmetry of the examined compounds This is also shown in Table IV In any case, physico-chemical and topological parameters change in the same way with changes in structural elements

Let us consider derivatives having $R = R' = C_4H_9$ In this instance, one can omit the influence of this element In relationships of PI vs I_B, PI vs $W(G)$, E vs I_B and E vs $W(G)$, changes of only two structural elements (i e , length of oligooxyethylene chains and their asymmetry) cause similar behaviour of both physico-chemical and topological parameters As an examole, both the polarity index and Balaban index increase with increasing number of oxyethylene units and decrease with increasing asymmetry of the alkyl group However, asymmetry of oligooxyethylene chains causes an increase in PI whereas the Balaban index decreases the PI vs I_B relationship is given in Fig 2 Significant deviations from a straight line can be seen although the correlation coefficient $(R) = 0 9524$ and $F = 117 26$ A similar situation is observed for the relationship between polarity index and Wiener number, $W(G)$ In this instance much better fits to the multiplicative model

$$PI = aI_B^b, \quad R = 0 9938, \quad F = 965 9$$

are presented in Fig 3a The same results were obtained for hexoxy derivatives (Fig 3b)

A similar situation is observed for relationships between the Laffort solubility factor E and both topological indices The linear relationship for E vs $W(G)$ (Fig 4) is characterized by $R = 0 9124$, $F = 59 6$, but also in this instance deviations from the straight line are considerable Much better statistical relationships were obtained for multiplicative models for both butoxy and hexoxy derivatives (Fig 5a, $R = 0 9729$, $F = 212 7$, Fig 5b, $R = 0 9529$, $F = 69 2$) The regression of factor E on the Balaban index was characterized by R values well below 0 9

TABLE VIII

EFFECT OF COMPOUND ASYMMETRY ON TOPOLOGICAL INDICES FOR $R(EO)_nCH_2CH(OH)CH_2(OE)_mOR'$

n	m	$R = R' = C_6H_{13}$			$R = C_8H_{17}$, $R' = C_4H_9$		
		I_B	$W(G)$	$^1\chi^v$	I_B	$W(G)$	$^1\chi^v$
0	4	3 4102	826 625	7 6436	3 3643	834 625	7 6436
0	1	3 4880	1299 000	8 7210	3 4680	1305 000	8 7210
1	1	3 5512	1922 875	9 7983	3 5236	1934 875	9 7983

TABLE IX

EFFECT OF ASYMMETRY IN DISTRIBUTION OF OXY-ETHYLENE UNITS FOR $BuO(EO)_nCH_2CH(OH)CH_2(OE)_mOBu$

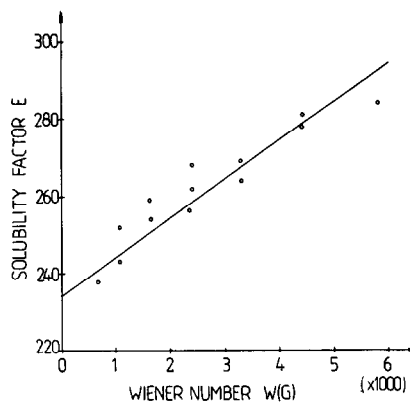| n	m	Topological parameter		
		I_B	$W(G)$	$^1\chi^v$
0	4	3 6025	2402 125	9 9530
1	3	3 6425	2384 125	9 9530
2	2	3 6550	2378 125	9 9530

Fig 4 Linear relationship between solubility factor E and Wiener number $W(G)$ for 1,3-bis[ω-butoxyoligo(oxyethylene)]-2-propanols

Fig 2 Linear relationship between polarity index (PI) and Balaban index (I_B)

Let us reconsider Table IV For all 30 compounds examined, i e , taking into account also the changes in alkyl groups, the most statistically significant correlations should be obtained for the polarity index and Balaban index In this instance three or four arrows are in the same direction, indicating that the influence of structural elements on PI an I_B is similar
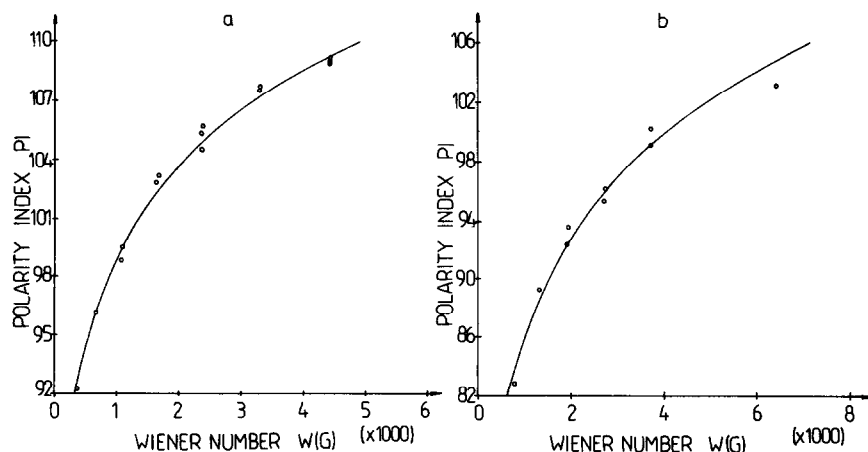

Fig 3 Relationship between polarity index PI and Wiener number $W(G)$ for (a) 1,3-bis[ω-butoxyoligo(oxyethylene)]-2-propanols and (b) 1,3-bis[ω-hexoxyoligo(oxyethylene)]-2-propanols
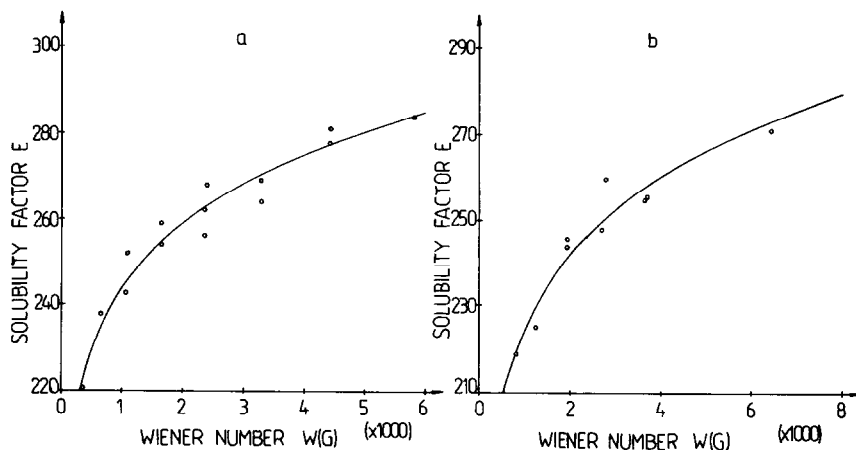
Fig 5 Relationship between Laffort's solubility factor E and Wiener number $W(G)$ for (a) 1,3-bis[ω-butoxyoligo(oxyethylene)]-2-propanols and (b) 1,3-bis[ω-hexoxyoligo(oxyethylene)]-2-propanols

CONCLUSIONS

It has been shown that Laffort's solubility parameters could be determined by the technique of inverse GC The direction of change of some of them (factors E and O) is generally similar to that of the polarity index, an accepted measure of surfactant polarity The most important difference is the opposite influence of the asymmetry of structural fragments on these two groups of physico-chemical parameters However, factors E and O could be used as polarity parameters

The examined topological parameters are generally sensitive to changes in the structure of compounds with the exception of valence molecular connectivity indices, which do not distinguish between symmetric and asymmetric homologues This means that the Balaban index and Wiener number exhibit a higher discrimination power, i e , lower degeneracy in comparison with valence connectivity indices

There is not complete agreement between the changes in physico-chemical and topological parameters caused by the changes in structural fragments (Table IV) However, several statistically satisfactory relationships were derived for polarity index and Wiener number $W(G)$ or Balaban index I_B, and also for factor E and $W(G)$

Topological indices are sensitive and useful measures of the structure of organic compounds They could be used in the examination of the influence of structure on, e g , polarity parameters, such as polarity index and Laffort's solubility factor E

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