

Determination of sorbent polarity and selectivity by linear regression of retention indices

OLEG G. LARIONOV*, VICTOR V. PETRENKO and NATALIA P. PLATONOVA

Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Leninskii Prospekt 31, 117915 Moscow (U.S.S.R.)

ABSTRACT

A regression equation for the description of retention indices through molecular parameters of sorbates is proposed. Electron polarizability, dipole moment, molar volume, the molecular connectivity indices of first order and electron-acceptor and electron-donor energetic constants were chosen as descriptors. The regression coefficients obtained relate to the ability of a surface to effect some sorbate-sorbent interactions. The validity of the expression was shown for a wide range of sorbent polarity. A high significance of the steric factor $G = {}^1\chi/V_m$ was revealed. A set of test sorbates was specified for routine determinations of sorbent polarity.

INTRODUCTION

Sorbate-sorbent interactions (SSI) play an important role in sorbate retention in gas chromatography and define both the total polarity and the selectivity of a sorbent. Some recent studies were devoted to the elucidation of the influence of different SSIs on substance retention in gas-liquid chromatography (GLC) [1–5]. As the ability to effect all SSIs relates to the molecular structure of a sorbate and its physico-chemical characteristics, attempts have been made to express the retention of a sorbate through its molecular parameters [6–12]. Also, the determination of stationary phase selectivity by its ability to enter into SSIs was carried out [13,14].

In previous work [15], we demonstrated the scope of the determination of sorbent abilities to undergo some SSIs by multiple linear regression for adsorption energies. This paper deals with the same method applied to retention indices.

The following expression was advanced for the adsorption energy of a sorbate, and includes dispersion, orientation, electron-acceptor and electron-donor terms:

$$-\Delta U = K_1\alpha G + K_2(2\mu^2/3kT + \alpha G) + K_3W_a + K_4W_d + K_5 \quad (1)$$

where α is the polarizability of the sorbate molecule, μ its dipole moment and W_a and W_d its electron-acceptor and electron-donor constants [16]. The coefficients K_1 – K_4 are proportional to the physico-chemical adsorbent characteristics involved in the expressions for each type of SSI. Accordingly, knowing the values of these coefficients

would allow us to estimate an adsorbent's ability to effect certain SSI quantitatively. The applicability of eqn. 1 was tested with a set of 30 sorbates for three adsorbents of different polarity. However, Kováts retention indices are a more convenient and a more readily available source of information on chromatographic properties of adsorbents than adsorption energies. Thus our final aim was the adoption of retention indices as original data for evaluating an adsorbent's ability for different intermolecular interactions.

From the well known thermodynamic expressions [17]

$$\Delta F_{\text{ads.}} = \Delta U_{\text{ads.}} - T\Delta S_{\text{ads.}} \quad (2)$$

$$\Delta F_{\text{ads.}} = -RT(\ln V_s - 1) \quad (3)$$

and the expression for retention indices (RI):

$$RI = (100/b)(\ln V_s - a) \quad (4)$$

where a and b are the intercept and the slope for the retention equation for n -alkanes, one may obtain the following expression:

$$RI = D(-\Delta U_{\text{ads.}}) + DT(\Delta S_{\text{ads.}}) + DRT(1 - a) \quad (5)$$

where $D = 100/bRT$.

Eqn. 1 may be used as an expression for $-\Delta U_{\text{ads.}}$ in eqn. 5 but the expression for $\Delta S_{\text{ads.}}$ through molecular parameters is a more complex problem. However, if there is a correlation between $\Delta U_{\text{ads.}}$ and $\Delta S_{\text{ads.}}$ on an adsorbent (as is the case for many adsorbents), it becomes possible to neglect the second, high correlating term, in regression analysis, in which event the expression for RI will have the following form:

$$RI = K_1 D \alpha G + K_2 D (2\mu^2/3kT + \alpha G) + K_3 DW_a + K_4 DW_d + K_5 \quad (6)$$

Eqn. 6 is applicable for multiple linear regression also, in which event desired values of the coefficients K_i for a sorbent may be obtained by using the molecular parameters for the sorbates and their retention indices on the sorbent. The non-equivalence of RI units for various adsorbents is accounted for by the constant D . For two adsorbents with similar values of RI and different values of b the coefficients K_i will differ.

EXPERIMENTAL

Generation of descriptors

The physico-chemical and topological parameters for the sorbate molecules were obtained in the following way. Polarizability, α , was calculated from the Lorentz-Lorenz equation:

$$\alpha = \frac{3}{4\pi L} \cdot V_m \cdot \frac{(n^2 - 1)}{(n^2 + 2)} \quad (7)$$

where V_m is the molar volume and n is the refractive index. Dipole moments were taken from ref. 18. The constants W_d and W_a for the gas phase were calculated from the data presented in ref. 16. For molecules with two electron-donor atoms (dioxane, nitroalkanes), W_d values were multiplied by 2. Thermodynamic W_d values for alcohols and ethers are very close. However, the accessibility of the oxygen atom in dialkyl ethers is much lower than in the corresponding alcohols, so the W_d values for ethers were divided by 2.

To take steric effects into account, some topological descriptors [19] were also involved. The molecular connectivity indices (MCI) of the first order were calculated from the expression:

$${}^1\chi = \sum^n (\delta_i \delta_j)^{-1/2} \quad (8)$$

where n is the number of valence bonds in a molecule and δ_i and δ_j are the atom number of valences directed to the adjoining non-hydrogen (*e.g.*, C, O, N) atoms. For cyclic molecules an allowance for a ring equal to 0.5 was subtracted from the values of ${}^1\chi$. For example, for the calculation of ${}^1\chi$ value for acetone:

$${}^1\chi = (1 \times 4)^{-1/2} + (4 \times 2)^{-1/2} + (4 \times 2)^{-1/2} + (4 \times 1)^{-1/2} = 1.707$$

The steric factor G was calculated as the ratio ${}^1\chi/V_m$ and was then normalized to the maximum magnitude, so the G factor ranges in value from 0.63 (CCl_4) to 1.00 (CH_3NO_2). This factor seems to reflect the degree of engagement of a molecule with a surface. Hence we may assume that the product αG has the meaning of the "effective polarizability" of a molecule for adsorption on a surface. Fig. 1 illustrates this phenomenon for adsorption of non-polar alkanes on completely non-polar hydrogen treated thermally graphitized carbon black (HT GTCB) when eqn. 6 reduces to

$$RI = K_1 D \alpha G + K_5 \quad (9)$$

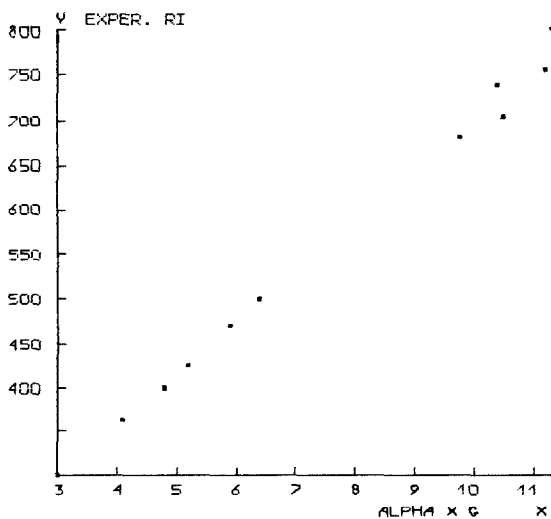


Fig. 1. Experimental RI values vs. αG on HT GTCB at 150°C .

The *RI* values of linear and branched butanes, pentanes and octanes [20] show a good linear dependence on their αG values, while alkanes with the same α values (or number of carbon atoms) have different retention indices.

Twenty sorbates with various structure and their molecular descriptors are listed in Table I. The descriptors of other molecules are available as supplementary material.

TABLE I
VALUES OF CHOSEN DESCRIPTORS FOR 20 SUBSTANCES

No. Sorbate	α (\AA^3)	μ^2 (D^2)	W_a (kJ/mol) ^{1/2}	W_d (kJ/mol) ^{1/2}	<i>G</i>
1 Hexane	11.85	0	0	0	0.67
2 Heptane	13.7	0	0	0	0.70
3 Octane	15.53	0	0	0	0.73
4 Nonane	17.38	0	0	0	0.75
5 Benzene	10.38	0	0	4.5	0.85
6 Ethanol	5.09	2.8	0.933	11.7	0.74
7 <i>n</i> -Propanol	6.95	2.8	0.923	11.8	0.77
8 <i>n</i> -Butanol	8.78	2.7	0.922	11.8	0.80
9 Isobutanol	8.81	2.6	0.907	11.9	0.74
10 <i>tert.</i> -Butanol	8.93	2.4	0.859	12.1	0.64
11 Methyl ethyl ketone	8.20	7.7	0	10.4	0.76
12 Acetone	6.35	8.0	0	10.6	0.70
13 Nitromethane	4.94	12.0	0	12.2	1.00
14 Nitroethane	6.74	12.8	0	12.8	0.97
15 2-Nitropropane	8.55	13.9	0	13.4	0.90
16 1-Nitropropane	8.57	13.7	0	12.8	0.95
17 Ethyl acetate	8.80	3.1	0	9.2	0.86
18 Acetonitrile	4.38	15.5	0	9.4	0.79
19 Dioxane	8.60	0.2	0	22.7	0.89
20 Pyridine	9.53	4.8	0	20.7	0.94

The data set

RI values for the following sorbents were taken as initial data for regression analyses: commercial Porapaks and Chromosorb Century Series, Polysorb N and its three modifications, copolymers of divinylbenzene (DVB) and glycidyl methacrylate (GMA) together with its three modifications, barium sulphate and graphitized thermal carbon black (GTCB). The structures of the sorbents and literature references are given in Table II. Also, a copolymer of epithiopropyl methacrylate (ETPMA) and ethylene dimethacrylate (EDMA) modified by ethylenediamine (EDA) (GS-EDA) [21] was studied. Further, this sorbent was modified by adsorption of Ni(II) ions on its surface. *RI* values for these two sorbents were measured at 150°C. A Tswett 530 chromatograph equipped with a flame ionization detector and with helium as carrier gas was used.

Ref. 22 was used as a mathematical basis for the multiple linear regression method. A BASIC program with matrix statements was written for an Iskra 226 personal computer. The correlation coefficient *R* was used in order to ascertain the validity of the regression expression.

TABLE II
SORBENTS INVESTIGATED

Name	Polymer matrix	Modification agent (or functional groups)	<i>R</i> / ref.
GTCB			23
Porapak Q	DVB-EVB		24
Porapak QS	DVB-EVB		24
Porapak S	DVB-EVB	Vinylpyridine	25
Porapak P	DVB-EVB	Styrene	25
Porapak R	DVB-EVB	Vinylpyrrolidone	25
Porapak N	DVB-EVB	Vinylpyrrolidone	25
Porapak T	DVB-EVB	Ethylene dimethacrylate	25
Chromosorb 102	DVB-styrene		26
Chromosorb 101	DVB-styrene		26
Chromosorb 105	DVB-styrene		26
Chromosorb 104	DVB-acrylonitrile		26
DVB-GMA	DVB-GMA		27
DVB-GMA '1	DVB-GMA	-CH(OH)CH ₂ OH	27
DVB-GMA '2	DVB-GMA	-CH(OH)CH ₂ N ⁺ (CH ₂ CH ₂ OH) ₃ OH ⁻	27
DVB-GMA '3	DVB-GMA	-CH(OH)CH ₂ NHC(CH ₂ OH) ₃	27
Polysorb N	DVB-2,5-methylvinylpyridine	-CH ₃	27
Polysorb N '1	As above	-CH ₂ OH	27
Polysorb N '2	As above	-COOH	27
Polysorb N '3	As above	-CH ₃ ; N _{pyr} = O	27
GS-EDA	EDMA-ETPMA	-CH(SH)CH ₂ NH(CH ₂) ₂ NH ₂	
GS-EDA-Ni	EDMA-ETPMA	As above + Ni ²⁺	
BaSO ₄			28

RESULTS AND DISCUSSION

To verify the validity of eqn. 6 the set of 20 sorbates (Table I) was processed using slightly polar Porapak P, Porapak T (medium polarity) and GS-EDA as a polar sorbent with electron-acceptor groups. The structures of the sorbates in the data set differ significantly, so the descriptors of eqn. 6 were uncorrelated. The correlation matrix is shown in Table III.

The scatter plots for moderately polar and polar sorbents are given in Figs. 2 and 3. The regression coefficients with standard deviations, their Student *t*-values and *R* values for the three sorbents are given in Table IV. For each sorbent the correlations

TABLE III
CORRELATION MATRIX FOR DESCRIPTORS USED IN EQN. 6 (*N* = 20)

	αG	μ^2	W_a	W_d
αG	1.00	-0.476	-0.386	-0.444
μ^2		1.000	-0.277	0.284
W_a			1.000	0.214
W_d				1.000

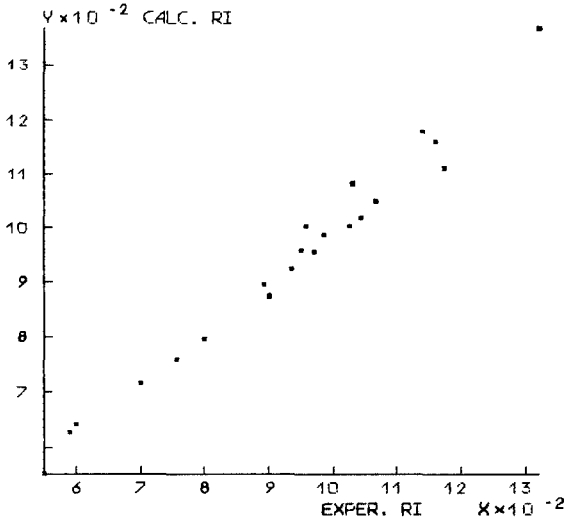


Fig. 2. Calculated vs. experimental RI values on Porapak P at 175°C.

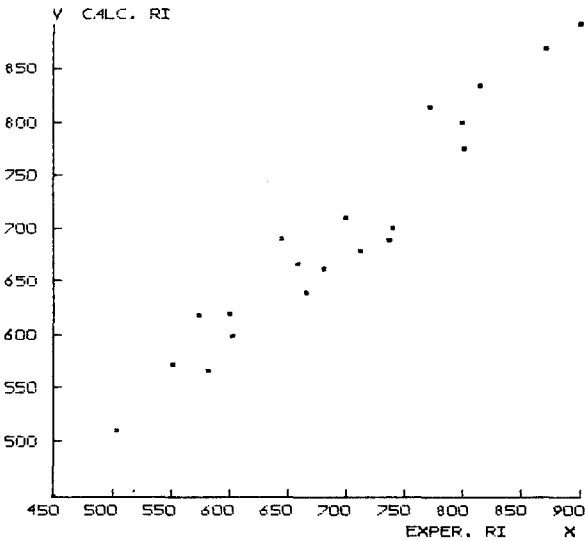


Fig. 3. Calculated vs. experimental RI values on GS-EDA sorbent at 150°C.

between regression coefficients show the same behaviour and the term K_5 is highly correlated with K_1 . The correlation matrix for GS-EDA is shown in Table V.

Taking the wide range of RI values (about 500 i.u.), the simplicity of eqn. 6 and the different structures of the sorbates into account, one may consider the R values as fairly high and the deviations from experimental RI values as fairly small. It should be noted that exclusion of the steric factor G from eqn. 6 decreases R for the three sorbents

TABLE IV

REGRESSION COEFFICIENTS K_i WITH THEIR STANDARD ERROR AND STUDENT'S t -VALUES ON THREE SORBENTS

Parameter	Porapak P		Porapak T		GS-EDA	
	K_i	t	K_i	t	K_i	t
K_1	120 ± 9	13.0	132 ± 9	14.9	109 ± 9	11.4
K_2	16 ± 4	4.5	28 ± 3	8.3	37 ± 4	9.0
K_3	3 ± 6	0.5	25 ± 6	4.3	39 ± 7	5.7
K_4	17 ± 3	6.3	17 ± 3	6.6	66 ± 4	16.3
K_5	181 ± 42	4.1	208 ± 35	5.7	259 ± 38	6.3
s (i.u.)	29.9 (3.8%)		24.5 (3.4%)		34.4 (3.6%)	
R	0.970		0.972		0.985	

to 0.891, 0.890 and 0.973, respectively. Hence the presence of G significantly increases the validity of eqn. 6 with an unchanged number of regression coefficients.

Comparing K values from Table IV it can be seen that the polar Porapak T, as compared with Porapak P, relates to increasing the ability to effect orientation SSI (K_2 increases from 16 to 28) and electron-donor ability of the sorbent surface (K_3 increases from 3 to 25), whereas the electron-acceptor ability (K_4) remains the same. This is in accordance with expectations given the presence of $-C(O)O-$ groups on the more polar polymer surface due to modification by ethylene dimethacrylate. For the GS-EDA sorbent low values of K_1 and abrupt increases for K_2 – K_4 values were observed. This is in accord with the presence on the surface of hardly polarizable amino groups with appreciable dipole moments and electron-donor properties and with electron-acceptor properties of the $-SH$ group. Hence apparently the K values are in agreement with the sorbent's expected abilities to effect SSI.

The following conclusions were made after subsequent analyses for various sorbents with a changed sorbate set, number of sorbates in a set and alternate descriptors (Balaban indices, $^2\chi$, donor number). Small variations of the sorbate set have no appreciable affect on K values except when substances with high descriptor magnitudes (pyridine, W_d ; alcohols, W_a ; nitroalkanes and nitriles, μ^2) are excluded. Perceptible regression standard deviations and standard errors in coefficients the K_i are obviously connected with two sources: a rough approximation of the real SSI by

TABLE V

CORRELATION BETWEEN THE REGRESSION COEFFICIENTS FOR GS-EDA SORBENT

	K_1	K_2	K_3	K_4	K_5
K_1	1.00	0.454	0.499	0.201	-0.939
K_2		1.000	0.567	-0.395	-0.472
K_3			1.000	-0.320	-0.494
K_4				1.000	-0.383
K_5					1.000

eqn. 6 and with the inadequacy of the chosen descriptors to characterize the behaviour of some sorbate molecules. The latter is concerned especially with μ , W_d and ${}^1\chi$. We have used the dipole moments which characterize the whole molecule whereas for adsorption obviously the dipole moments of individual bonds ($=C=O$, $-C\equiv N$) are more important. Equilibrium thermodynamic values of W_d from ref. 16 do not include differences in the spatial accessibility of donor atoms in various molecules (compare alcohols with dialkyl ethers) and different degrees of availability of the same functional group with carbon chains of various length (compare methanol with butanol). Some allowances for W_d were made from the start of the study (see Experimental). In general, the steric factor G describes the degree of engagement of a molecule with a surface fairly well. For example, G values for molecules with different structures are as follows: *n*-butanol 0.80, isobutanol 0.74, *tert.*-butanol 0.64, planar pyridine 0.94 and *n*-hexane 0.67. For molecules with similar structures the G values are as follows: di-*n*-butyl ether 0.79, *n*-nonane 0.75, *tert.*-butanol 0.64 and carbon tetrachloride 0.63. Some problems arise because of the cyclic structure of molecules, or the presence of triple bonds or heteroatoms from atoms of higher atomic number (Cl, Br, I, S) in a molecule. The wide confidence interval for K_3 relates to the narrow ranges of the values of W_a used.

For many of sorbents studied, aryl compounds (benzene, toluene) show high deviations, both positive and negative, from experimental RI values. This, perhaps, relates to the inadequate description of the molecules by the factor G and to disregarded interactions of the aromatic electron ring with sorbent polymer chains. For all sorbents very low predicted RI values were obtained for small molecules of chloro-substituted alkanes, especially for chloroform and methylene chloride. This clearly relates to the incorrect description of the molecules by the factor G .

In spite of the difficulties discussed for most sorbates, a satisfactory prediction of RI values was observed. The K_i values obtained conformed with the physico-chemical nature of the surface functional groups.

For practical application of the method to comparisons of sorbent surface properties, it is necessary to fulfil the following conditions. For every sorbent the test set of sorbates must be the same. The requirements for the sorbates included in test set are as follows: (1) all kinds of SSI included in eqn. 6 must be represented; (2) the magnitude of the descriptors should have as wide a range as possible; (3) the descriptors must be uncorrelated; (4) the chromatographic behaviour of the sorbates should be adequately described by all of the chosen molecular parameters; (5) a small number set is more convenient for routine analysis and collection of reference RI values; and (6) all the substances should be commonly used in chromatographic practice.

Nine sorbates conforming to these conditions were selected: hexane, nonane, ethanol, *n*-propanol, *n*-butanol, acetone, methyl ethyl ketone, nitromethane and pyridine. Their descriptor correlation matrix is shown in Table VI. The test set RI values were processed for 23 sorbents. The results are given in Table VII. It should be noted that for barium sulphate the K values were evaluated approximately because of the low R value arising from the extremely high polarity of this ionic sorbent. Calculated contributions of each term in eqn. 6 for Parapak QS, Chromosorb 104 and the GS-EDA sorbent are given in Table VIII. Examination of the various types of SSI contributions shows that they are comparable. Hence it is a very rough approximation to apply their RI values as representative of one kind of SSI.

TABLE VI

CORRELATION MATRIX FOR DESCRIPTORS USED IN EQN. 6 ($N = 9$)

	αG	μ^2	W_a	W_d
αG	1.00	-0.544	-0.393	-0.438
μ^2		1.000	-0.325	0.505
W_a			1.000	0.220
W_d				1.000

For evaluation of the overall sorbent polarity, summarizing of "specific" coefficients K_2 - K_4 normalized to their maximum values was carried out:

$$P = (K_2/95 + K_3/122 + K_4/92) \cdot 100 \quad (10)$$

Calculated P values are given in Table VII. It is worth remarking that the overall polarity masks the variations of individual K values and correlates with Rohrschneider's polarity calculated through the sum of five net RI values (see Table IX).

For non-polar GTCB all "specific" K values are equal to zero. Porapak show

TABLE VII

THE COEFFICIENTS K_i AND R VALUES FOR REGRESSION ANALYSES WITH TEST SET OF SORBATES ($N = 9$)

Sorbent	K_1	K_2	K_3	K_4	K_5	R	P
GTCB	108	0	0	0	67	0.991	0
Porapak Q	130	16	14	-1	154	0.995	29
Porapak QS	158	19	14	0	120	0.999	32
Porapak S	182	29	33	-1	111	0.997	58
Porapak P	138	29	16	16	89	0.999	61
Porapak R	175	30	38	-1	120	0.999	63
Porapak N	180	40	35	3	127	0.999	74
Porapak T	156	52	42	11	102	0.999	101
Chromosorb 102	144	17	11	1	146	0.999	28
Chromosorb 101	125	26	14	13	104	0.999	53
Chromosorb 105	177	27	27	3	98	0.999	53
Chromosorb 104	132	69	43	21	94	0.999	131
DVB-GMA	118	56	50	14	139	0.998	115
DVB-GMA '1	110	43	48	24	119	0.999	111
DVB-GMA '2	105	48	55	33	128	0.997	131
DVB-GMA '3	117	46	56	35	126	0.998	132
Polysorb N	104	18	36	40	1	0.986	93
Polysorb N '1	112	30	43	44	41	0.988	115
Polysorb N '2	83	54	63	32	160	0.997	144
Polysorb N '3	117	95	122	38	38	0.993	240
GS-EDA	132	59	68	58	150	0.996	181
GS-EDA-Ni	145	36	52	92	138	0.999	181
BaSO ₄	83	147	203	102	443	0.960	432

TABLE VIII

CONTRIBUTIONS OF EACH TERM OF EQN. 6 FOR THREE SORBENTS: (A) PORAPAK QS, (B) CHROMOSORB 104 AND (C) GS-EDA

Sorbate	Sorbent	Rf		Contribution of term number				
		Exptl.	Predicted	1	2	3	4	5
Hexane	A	600	602	482	0	0	0	120
	B	600	594	499	0	0	0	94
	C	600	603	465	0	0	0	138
Ethanol	A	400	409	226	21	40	2	120
	B	690	698	234	97	154	118	94
	C	1007	996	218	47	161	432	138
Methyl ethyl ketone	A	565	557	378	56	0	2	120
	B	850	856	392	265	0	105	94
	C	990	1015	365	128	0	384	138
Nitromethane	A	495	506	297	87	0	2	120
	B	935	932	308	408	0	122	94
	C	1079	1069	286	198	0	447	138
Pyridine	A	695	698	540	35	0	3	120
	B	1025	1024	560	163	0	207	94
	C	1500	1497	521	79	0	759	138

TABLE IX

COMPARISON OF POLARITIES CALCULATED FOR CHROMOSORBS AND PORAPAKS BY EQN. 10 AND ROHRSCHEIDER'S POLARITY [29]

Method	Chromosorb				Porapak				
	102	105	101	104	Q	P	R	N	T
By eqn. 10	28	53	53	131	29	61	63	74	101
Rohrschneider	197	347	555	1831	68	708	331	499	1240

increasing K_2 and K_3 values as the original polymer matrix is modified by vinylpyrrolidone, vinylpyridine and ethylene dimethacrylate. It should be noted that the K values depend both on the type of functional group and on its concentration on the surface, because the "average" molecular characteristics of a surface change with variation in the polymer composition.

For the Chromosorb Century Series, Chromosorb 104 is the most polar sorbent. Its K_3 and especially K_2 values are very high owing to the presence of electron-donor cyano groups [$\mu(\text{CH}_3\text{CN}) = 3.94 \text{ D}$]. Some electron-acceptor ability of the surface may be accounted for by partial positive charges on the carbon atom in the cyano group.

Modified copolymers of DVB and GMA show decreasing K_2 values after destruction of the epoxy ring [$\mu(\text{C}_2\text{H}_2\text{O}) = 1.9 \text{ D}$ and $\mu(\text{C}_2\text{H}_5\text{OH}) = 1.7 \text{ D}$] and

gradually increasing K_4 values as the concentration of OH groups on the surfaces is increased.

Increasing K_2 , K_3 and K_4 values after introducing OH groups onto the original Polysorb N surface were observed. Subsequent conversion of this group into COOH increases K_2 and K_3 significantly but the decrease in K_4 (electron acceptor) may be accounted for by the formation of intermolecular bonds such as $-\text{COOH} \cdots \text{N}$ (pyridine ring). Extremely high values of K_2 and K_3 for the third modification of Polysorb N relate to the high dipole moment and strong electron-donor ability of the $=\text{N}=\text{O}$ bond conjugated with the pyridine ring.

Very high values of K_4 were found for the GS-EDA sorbent with SH and NH groups. Adsorption of Ni(II) ions on this surface leads to an abrupt increase in K_4 owing to the electron-acceptor properties of the ion and to a decrease in K_2 and K_3 owing to the formation of a chelate complex of ethylenediamine with the Ni(II) ion.

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