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Model for the mixed ion-exclusion–adsorption retention mechanism in ion-exclusion chromatography☆

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ABSTRACT

The model elaborated in a previous paper for the retention mechanism in ion-exclusion chromatography was generalized to include adsorption of the solute. The computer modelling of the column performance by the Craig method was used in the case of an unbuffered mobile phase. The retention process in the case of a sufficiently buffered mobile phase turned out to be governed by a linear partition isotherm and can be described globally by simple equations. The adsorption constants of several compounds were calculated from the data available in the literature.

INTRODUCTION

Ion-exclusion chromatography (IEC) is an efficient method for the separation of partially ionized species [1–12]. The ion-exclusion mechanism of solute retention is based on the phenomenon that neutral molecules penetrate the ion-exchange resin while the counter ions with respect to the exchanged ion are repulsed or, in other words, excluded from it [1]. Therefore, by this mechanism acidic compounds can be separated on cation-exchange resins and basic compounds on anion-exchange resins. This is the opposite situation to ion-exchange chromatography, where an anion-exchange resin is used to separate anions and a cation-exchange resin to separate cations.

Tanaka *et al.* [13] have shown for a cation-exchange resin that the dependence of the distribution coefficient, K_d, on the pK_a values of various acidic compounds is analogous to the dependence of K_d on the logarithm of the molecular mass in size-exclusion chromatography. They interpreted this as evidence for an ion-exclusion mechanism of acidic solutes separated on a cation-exchange resin.

A more quantitative description of these findings was attempted in a previous paper [14], where the following equation was derived:

$$K_d = \frac{1 + 2c/K_a - \sqrt{1 + 8c/K_a}}{2c/K_a - 2} \quad (1)$$

This equation expresses the distribution coefficient as a function of the solute acidic dissociation constant and the solute concentration at the peak maximum, c.

Eqn. 1 is inconvenient from the analytical point of view because the solute concentration at the peak maxium is not easy to determine and one would prefer the analytical solute concentration instead [14]. Also, the simplifications involved in eqn. 1 are not generally justifiable [15].

The improved approach in ref. 15 removes the inconvenience and some of the simplifications. The price to pay for the improvements is that the

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distribution coefficient can only be evaluated numerically from a non-linear set of equations as an implicit function of the parameters characterizing the system. In general, the solution of the equations cannot be obtained as explicit expressions in a closed form. The equations describe the partitioning of an amount of the solute between specified amounts of the mobile and the stationary phases. The set of equations can be applied locally to a small fragment of the column (corresponding to a theoretical plate) or globally to the peak volume of the solute. The global approach is unjustified for a non-linear partition isotherm. Then the local approach can be conveniently applied in the computer simulation using the Craig method.

Ion exclusion can seldom be considered as the sole retention mechanism even on an ion-exclusion resin [16,17]. Ion-exclusion chromatography, like other chromatographic techniques, is classified according to the primary mechanism of solute retention. The primary mechanism is the coulombic repulsion between the solute ions and the dissociated groups of the resin. However, the fact that there are secondary retention mechanisms is well known. This is especially true for neutral, large molecules, which include aromatic and long-chain aliphatic compounds [18]. Non-ionized solutes cannot be ion excluded and other interactions of the solute with the stationary phase [16–18] have to be considered. The completely non-ionized solutes are just a limiting case for the weakest electrolytes where these interactions co-exist with the ion-exclusion mechanism. Referring to the interactions causing an increase in the solute retention as compared with the ion-exclusion mechanism, we shall tentatively use the term adsorption. We should like to avoid speculation on the nature of this adsorption and focus attention on a tentative phenomenological description instead. It is worth noting, however, that the hydrophobic nature of this interaction for long-chain aliphatic compounds finds support in the literature [18,19]. It has also been found [18] that aromatic compounds are characterized by especially large adsorption, probably caused by their π-electron interaction with the network of the polystyrene–divinylbenzene resin.

The retention of partially ionized organic compounds with a mixed ion-exclusion–adsorption mechanism is expected to be involved in most practical applications of ion-exclusion chromatography. Therefore, in this paper we attempt to include adsorption phenomena in the framework of the models devised initially to describe a pure ion-exclusion mechanism.

Similar attempts can be found in the recent literature [20,21], but the different volumes of the stationary and the mobile phases were not taken into account and also the predictions of the models were applied to dicarboxylic acids. In our option, dicarboxylic acids are an unfortunate choice for a test of a model for an ion-exclusion mechanism owing to the additional complications in their retention mechanism such as size-exclusion and shielding effects [18].

THEORY

Model formulation

The chromatographic column will be considered as a uniform, homogeneous mixture of the eluent and the support. The mobile phase flow-rate is assumed to be constant and also uniformly distributed within the column.

The ion-exclusion mechanism is ruled by the Donnan membrane equilibrium as described previously [14,15]. The partitioning of the solute due to this mechanism takes place between the stationary and mobile phases. Both phases contain solvents with identical physico-chemical parameters, including dielectric constants. The stationary phase is regarded as a solution of resin functional groups immobilized by the resin network. The immobilized functional groups cannot enter the mobile phase. We shall also assume that the resin functional groups are completely dissociated and their concentration is much higher than that of the solute. These are reasonable assumptions for typical analytical conditions. As found previously [15], they make the parameters describing the chromatographic peak independent of the resin functional group concentration and their dissociation constant.

Under the above assumptions, only undissociated forms of the solutes exist in the stationary phase and can be adsorbed from there into

what we call the adsorption volume. The existence of an adsorption phase filling the adsorption volume is postulated. A linear isotherm is assumed to govern the adsorption mechanism. The adsorption volume, the stationary phase volume and the mobile phase volume are assumed to add up to the geometrical volume of the column. The stationary phase and the mobile phase volumes are identified with the inner and the dead column volumes, respectively.

The equilibration after the repartitioning of the analyte solute is assumed to be fast enough to be able to neglect kinetic effects, diffusion, temperature changes and other non-equilibrium effects.

A buffered mobile phase is also considered in the case of complete buffer dissociation and its concentration is much higher than that of the solute compound.

Equations describing the system

The assumptions outlined above lead to a set of equations analogous to eqns. 2–10 in ref. [15] for the case of a pure aqueous mobile phase. The first equation in the set expresses the thermodynamic equilibrium condition for the case of solute concentrations low enough to substitute concentrations for activities:

$$[H^+]_M[R^-]_M[HR]_M = [H^+]_S[R^-]_S[HR]_S \quad (2)$$

The definition of the acidic dissociation constant is

$$K_a = [H^+]_M[R^-]_M/[HR]_M \quad (3)$$

The mobile and stationary phases are characterized by equal concentrations of the neutral form of the solute:

$$[HR]_M = [HR]_S \quad (4)$$

The mobile and stationary phases are electrically neutral. It follows that

$$[H^+]_M = [R^-]_M \quad (5)$$

$$[H^+]_S = [F^-]_S + [R^-]_S \quad (6)$$

As the resin functional groups are completely dissociated, their concentration in the stationary phase can be expressed as follows:

$$c_f = [F^-]_S \quad (7)$$

The mass conservation equation for the amount m of the acidic compound on a theoretical plate distributed in the mobile, the stationary and the adsorption phase volumes is

$$m = ([R^-]_M + [HR]_M)v_M + ([R^-]_S + [HR]_S)v_S + [HR]_A v_A \quad (8)$$

From now on we shall assume that $[R^-]_S = 0$, which follows from the already assumed excess of functional group concentration with respect to the concentration of the solute.

The neutral form of the solute is assumed to be partitioned between the stationary and the adsorption phases according to the Nernstian law or, equivalently, according to the linear Henry isotherm. This is expressed as

$$[HR]_A = K_H[HR]_S \quad (9)$$

where K_H is a constant.

Solution method

Eqns. 2–9, after some algebra, yield the following set of equations:

$$[R^-]_M = \frac{\sqrt{[K_a^2V_M^2 + 4K_am(V_M + V_S + K_HV_A)]}}{2(V_M + V_S + K_HV_A)} \quad (10)$$

$$[HR]_M = [R^-]_M^2/K_a \quad (11)$$

$$[HR]_A = K_H[HR]_M \quad (12)$$

The above equations express the three concentrations $[R^-]_M$, $[HR]_M$ and $[HR]_A$ as functions of the parameters K_a, m, V_M, V_S and the product K_HV_A in an explicit form. Eqn. 11 is analogous to the set of eqns. 19–21 in ref. 15. The set of equations in ref. 15 cannot be solved in so simple a way and require a time-consuming recurrent numerical procedure to calculate $[R^-]_M$ as an implicit function of the parameters. The closed form of eqn. 10 yields a significant time decrease in the computer simulation described below and it is based on the assumption that $[R^-]_S = 0$, which is reasonable under analytical conditions.

Numerical modelling of column performance with unbuffered mobile phase

We use the Craig method in a fashion fully analogous to that in our previous paper [15]. The Craig method turns out to yield improved results with respect to K_d values as compared with the global approach [15]. It also yields correct predictions with regard to the peak shape [15]. We use it in the case of an unbuffered mobile phase when the non-linear partition isotherm invalidates the use of the global approach.

Let us briefly recall that in this method the partitioning of the solute is calculated using eqns. 10–12 for a small fragment of the column corresponding to a theoretical plate. The portion of the mobile phase at the plate is then "moved" to the next plate, simulating the passage of the solute. The mass conservation balance requires that the amount of solute at the plate is composed of what remains in the stationary and the adsorption phases plus what is brought by the incoming portion of the mobile phase. The solute amount is then repartitioned again, closing the cycle. The procedure implies that the equation

$$m(i, j) = ([R^-]_M^{(i-1,j-1)} + [HR]_M^{(i-1,j-1)})v_M + [HR]_S^{(i-1,j)}v_S + [HR]_A^{(i-1,j)}v_A \quad (13)$$

is solved at the ith time step and the jth plate with the following initial and boundary conditions:

$$[HR]_S^{(0,j)} = [HR]_A^{(0,j)} = [HR]_M^{(0,j)} = [R^-]_M^{(0,j)} = 0 \quad \text{for } i = 1, \ldots, N \quad (14)$$

$$([R^-]_M^{(i,0)} + [HR]_M^{(i,0)}) = c_i \quad \text{for } i = 1, \ldots, V_i/v_m \quad (15)$$

$$([R^-]_M^{(i,0)} + [HR]_M^{(i,0)}) = 0 \quad \text{for } i > V_i/v_m \quad (16)$$

Buffered mobile phase

The consideration of the buffered mobile phase in our previous paper [15] led to considerable complication of the equations. However, the buffered mobile phase turns out to be particularly interesting and simple to analyse when the buffer concentration is much higher than that of the solute. Then eqn. 3 assumes the form

$$K_a = c_b[R^-]_M/[HR]_M \quad (17)$$

where c_b is the buffer concentration. This leads to the linear distribution isotherm and the distribution coefficient K_d is given by

$$K_d = \frac{[HR]_S V_S + [HR]_A V_A}{([HR]_M + [R^-]_M)V_M} = \frac{V_S + K_H V_A}{(1 + K_a/c_b)V_S} \quad (18)$$

When there is no adsorption ($K_H V_A = 0$) then the above equation assumes a simpler form:

$$K_d = \frac{c_b}{c_b + K_a} \quad (19)$$

It is worth noting that the peak shape remains unchanged during elution when the partition isotherm is linear, as in the considered case of excess of buffer with respect to the solute compound in IEC. The peak migrates down the column with the effective velocity U_a lower than the mobile phase velocity u:

$$U_a = u/(1 + V_S/V_M + K_H V_A/V_M + K_a/c_b) \quad (20)$$

RESULTS

Assessment of assumed simplifications

As mentioned in the previous section, the simple form of eqn. 11 used in the simulations is due to the assumed excess of dissociated resin functional groups when the dissociated form of the acid is practically excluded from the resin: $[R^-]_S = 0$. Mathematically, eqn. 11 is strict in the limit of infinite functional group concentration ($c_f \to \infty$) with an arbitrary non-vanishing dissociation constant for the groups ($K_f > 0$).

In order to assess the practical validity of the discussed assumption, computer simulations were performed for several pK_a values of the acidic solute excluding adsorption. The results are presented in the form of simulated peak profiles in Fig. 1. The simulated peak profiles are almost identical with those obtained previously [15] for the same set of pK_a values and for finite, reasonable values of c_f and K_f (see Fig. 9 in ref.

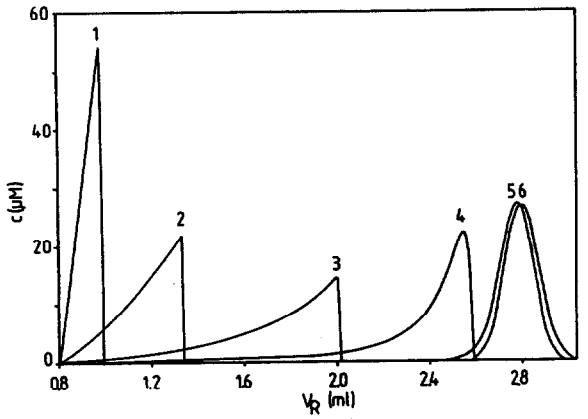

Fig. 1. Simulated chromatographic peaks of acidic compounds in an unbuffered mobile phase. The pK_a values of the compounds represented by peaks 1, 2, 3, 4, 5 and 6 are 3, 4, 5, 6, 8 and 12 respectively. The values of the other parameters are $c_i = 10^{-3}$ M, $V_M = 800$ μl, $V_S = 2000$ μl, $V_i = 5$ μl, $N = 1000$ and $K_H = 0$.

15). The assumption is therefore valid under working chromatographic conditions.

The validity of eqn. 20 can be assessed in a similar way for the dependences of the distribution coefficient on the acid dissociation constant and on the buffer concentration. These dependences are presented in Figs. 2 and 3, respectively. Again, it is worth noting that although based on a very simple, easy to use equation, the results in Figs. 2 and 3 are close to the analogous results obtained previously using a more general and therefore unduly complicated approach (see Figs. 4 and 8 in ref. 15).

Adsorption evaluation

Having shown the practical validity of the assumptions used when deriving eqns. 10 and 19, let us consider how they could be applied in chromatographic data evaluation. From eqn. 10, it follows that the solute retention depends on the product $K_H V_A$. The product can be resolved into the factors on the basis of some extra assumption such as additivity: $V_M + V_S + V_A = V$, where $V = \pi d_c^2 l_c$ is the geometrical volume of the column cavity calculated from its dimensions, *i.e.*, the inner column diameter d_c and the column length l_c.

An example of the dependence of V_R on $K_H V_A$ is presented in Fig. 4 for the pK_a value as for

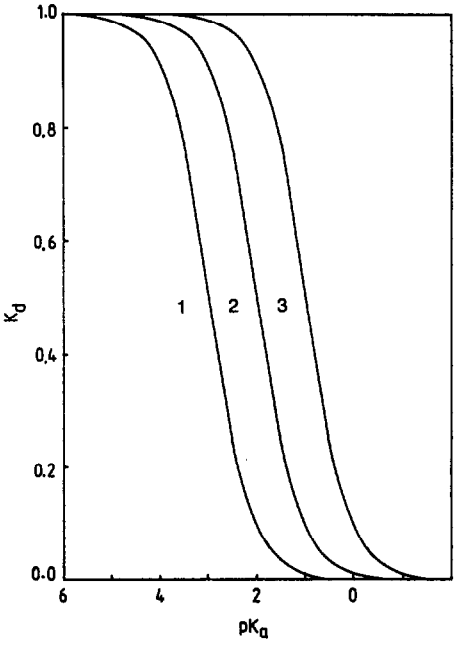

Fig. 2. Distribution coefficient K_d as a function of the solute pK_a value for the following mobile phase buffer concentrations: (1) $c_b = 10^{-3}$ M, (2) $c_b = 10^{-2}$ M and (3) $c_b = 10^{-1}$ M.

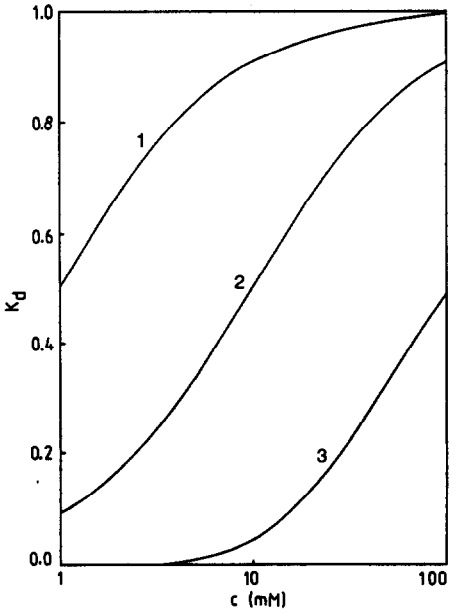

Fig. 3. Distribution coefficient K_d as a function of the buffer concentration for the following solute K_a values: (1) 10^{-3} M, (2) 10^{-2} M and (3) 10^{-1} M.

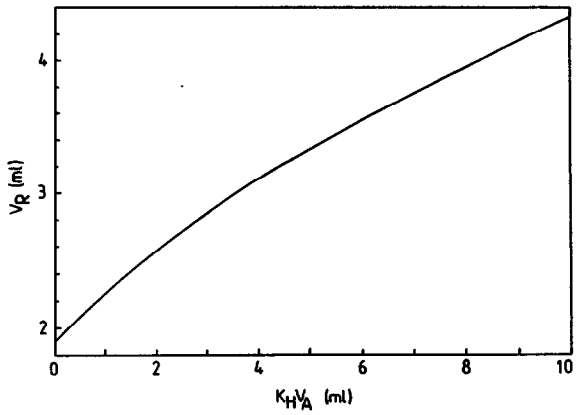

Fig. 4. Retention volume V_R as a function of the solute adsorption strength K_HV_A. $pK_a = 4.48$ is selected as for valeric acid. Other conditions as in Fig. 1.

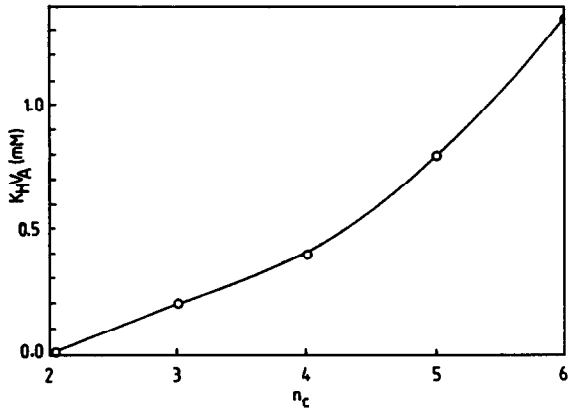

Fig. 5. Adsorption strength as expressed by K_HV_A for a number of aliphatic acids as a function of the number of carbon atoms n_c in the acid chain.

valeric acid. The dependence can be used conversely to determine the K_HV_A product from the experimentally determined retention volume V_R.

Table I presents adsorption constants calculated on the basis of our data [14] for a number of aliphatic acids using the Craig method. The retention volumes based on the calculations and obtained experimentally are also given in Table I. The data indicate an increase in adsorption with increasing chain length. This is illustrated in Fig. 5, where the adsorption strength as measured by K_HV_A is plotted as a function of the chain length. This behaviour of the aliphatic acids has been confirmed recently [18,19,22].

The results for the peak shapes presented in Fig. 6 indicate that the significant increase in the

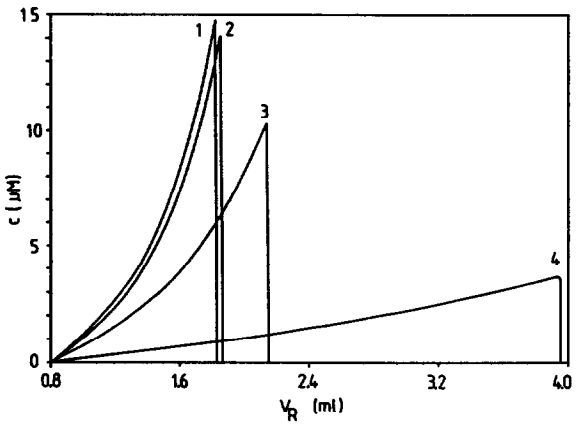

Fig. 6. Simulated peak shapes for K_HV_A values of (1) 0, (2) 10^{-7}, (3) 10^{-6} and (4) 10^{-5} ml. The pK_a value is 4.76; other conditions as in Fig. 1.

TABLE I

EXPERIMENTALLY DETERMINED RETENTION VOLUMES, $V_R^{exp.}$ [14], COMPARED WITH THOSE CALCULATED ASSUMING A PURE ION-EXCLUSION MECHANISM, $V_R^{calc.}$, AND THE ADSORPTION STRENGTH AS EXPRESSED BY K_HV_A CALCULATED USING CRAIG METHOD FOR SOME VOLATILE FATTY ACIDS

Acid	pK_a	$V_R^{exp.}$ (ml)	$V_R^{calc.}$ (ml)	K_HV_A (ml)
Acetic	4.76	1.51	1.51	0.0
Propionic	4.87	1.66	1.59	$2.0 \cdot 10^{-7}$
Butyric	4.81	1.66	1.55	$3.0 \cdot 10^{-7}$
Valeric	4.84	1.84	1.57	$8.0 \cdot 10^{-7}$
Caproic	4.88	2.09	1.60	$13.5 \cdot 10^{-7}$

TABLE II

ADSORPTION STRENGTH AS MEASURED BY $K_H V_A$ CALCULATED FROM THE DATA IN REF. 3 FOR SOME ALIPHATIC ALCOHOLS

Alcohol	$K_H V_A \times 10^3$ (ml)	Alcohol	$K_H V_A \times 10^3$ (ml)
Methanol	0.0	*n*-Butanol	57.0
Ethanol	3.6	*sec.*-Butanol	28.3
n-Propanol	15.0	*tert.*-Butanol	11.9
Isopropanol	8.16		

retention volume due to the strong adsorption coincides with an increased asymmetry of the peak shape. This effect has also been observed experimentally [17,23].

Analogous calculations were performed for the homologous series of aliphatic alcohols on the basis of the experimental data from ref. 3. Table II gives the estimated products $K_H V_A$. They turned out to be identical with those calculated using eqn. 18. The simulated peak shapes are presented in Fig. 7. Again, good agreement with the experimental data is found.

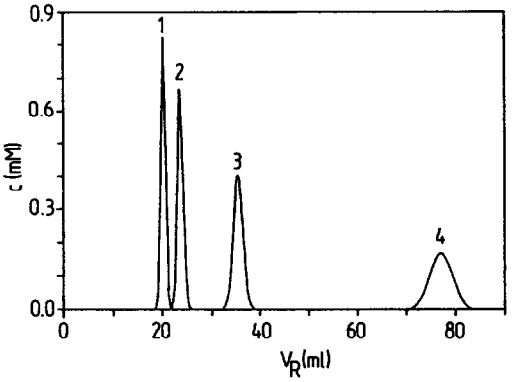

Fig. 7. Simulated chromatographic peaks of alcohols: (1) methanol; (2) ethanol; (3) propanol; (4) butanol. The chromatographic parameters are those given in ref. 3.

Tables III and IV give the experimental and calculated retention volumes and adsorption constants K_H based on recently collected data for a number of aromatic acids and amines, respectively, in buffered mobile phases [18,22]. The calculations of retention volumes and adsorption constants were based on eqns. 18 and 19. Aromatic compounds are characterized by very strong adsorption and it is the adsorption that governs the retention mechanism for these compounds rather than ion exclusion on ion-exchange resins.

CONCLUSIONS

Adsorption, although considered a secondary mechanism in ion-exclusion chromatography, in many instances plays the dominant role in the retention of the solutes. The retention mechanism of weakly dissociated organic compounds on an ion-exclusion resin has to be interpreted as a combination of ion exclusion and adsorption on the resin network. The adsorption contributes little to the retention of ions. However, it has a large effect on the retention of weakly ionized solutes. To describe this effect the model presented in this paper can be applied.

The computer simulations based on the model yield qualitatively correct peak shapes as in-

TABLE III

EXPERIMENTALLY DETERMINED RETENTION VOLUMES, $V_R^{exp.}$ [18], COMPARED WITH THOSE CALCULATED ASSUMING A PURE ION-EXCLUSION MECHANISM (EQN. 19), $V_R^{calc.}$, AND THE ADSORPTION STRENGTH AS MEASURED BY $K_H V_A$ CALCULATED USING THE GLOBAL APPROACH (EQN. 18) FOR SOME AROMATIC CARBOXYLIC ACIDS

Acid	K_a	$V_R^{exp.}$ (ml)	$V_R^{calc.}$ (ml)	$K_H V_A$ (ml)
Gallic	$3.89 \cdot 10^{-5}$	13.5	12.3	1.3
o-Nitrobenzoic	$6.76 \cdot 10^{-3}$	15.5	4.6	84.0
Acetylsalicylic	$2.69 \cdot 10^{-5}$	23.0	12.4	10.9
Salicylic	$1.00 \cdot 10^{-3}$	43.0	8.0	69.9
m-Nitrobenzoic	$3.24 \cdot 10^{-4}$	70.0	10.4	78.9

TABLE IV

EXPERIMENTALLY DETERMINED RETENTION VOLUMES, $V_R^{exp.}$ [18], COMPARED WITH THOSE CALCULATED ASSUMING A PURE ION-EXCLUSION MECHANISM (EQN. 19), $V_R^{calc.}$, AND THE ADSORPTION STRENGTH AS MEASURED BY $K_H V_A$ CALCULATED USING THE GLOBAL APPROACH (EQN. 18) FOR SOME AROMATIC AMINES

Compound	pK_b	$V_R^{exp.}$ (ml)	$V_R^{calc.}$ (ml)	$K_H V_A$ (ml)
Pyridine	8.75	22.4	13.4	11.4
3-Aminopyridine	8.00	27.4	13.4	17.7
α-Picoline	8.08	33.0	13.4	25.3
4-Aminopyridine	4.89	35.0	13.27	12.2
γ-Picoline	7.92	39.4	13.4	33.0
β-Picoline	8.48	41.8	13.4	35.6
2, 6-Lutidine	7.28	51.4	13.4	48.2
2, 4-Lutidine	7.01	66.4	13.4	67.3
2, 3-Lutidine	7.43	66.9	13.4	68.5
3, 4-Lutidine	7.51	81.8	13.4	86.2
3, 5-Lutidine	7.85	97.1	13.4	106.5
p-Aminoaniline	7.84	19.6	13.4	7.8
o-Aminoaniline	9.51	70.8	13.4	72.3
Aniline	9.39	114.0	13.4	126.8
p-Methylaniline	8.89	200.9	13.4	241.0
o-Methylaniline	9.56	206.7	13.4	241.0
m-Methylaniline	8.30	223.2	13.4	266.3
4, 6-Dimethylaniline	9.11	394.3	13.4	482.0
3, 5-Dimethylaniline	9.11	456.2	13.4	558.1
Benzylamine	4.67	49.1	13.2	46.9
2-Phenylethylbenzylamine	4.16	84.6	12.7	97.6
o-Benzylamine	4.81	87.1	13.2	95.1
p-Benzylamine	4.64	104.9	13.2	119.3

fluenced by the adsorption mechanism. It is worth emphasizing that the simplifications introduced in this paper are justifiable under working chromatographic conditions and lead to very simple equations describing the chromatographic process. They lead to a 20-fold decrease in computing time when applied to the computer simulations described previously [15]. The equations are particularly simple in the case of mobile phases with a sufficiently concentrated buffer where a linear partition isotherm obtains.

SYMBOLS

A as a subscript refers to the adsorption phase
c_b mobile phase buffer concentration
c_f functional group concentration in the support
c_i injected solute concentration
d_c column diameter
HF (F^-) functional group in undissociated (dissociated) form
HR (R^-) acidic solute in undissociated (dissociated) form
K_a solute acid dissociation constant
K_d distribution coefficient
K_f resin functional group dissociation constant
K_H Henry's isotherm adsorption constant
l_c column length
m solute mass on one theoretical plate
N column theoretical plate number
U_a effective linear velocity of the solute compound
u linear velocity of the mobile phase
V column volume
v_A $= V_A/N$
V_A volume of the adsorbed layer on one theoretical plate

V_i	injected solute volume
V_M	column dead volume, column mobile phase volume
v_M	$= V_M/N$
V_R	retention volume
V_S	column inner volume, column stationary phase volume
v_S	$= V_S/N$

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