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DETERMINATION OF THE PORE SIZE DISTRIBUTION, BY EXCLUSION CHROMATOGRAPHY, OF ION-EXCHANGE POLYMERS WHICH SWELL IN WATER

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SUMMARY

It is shown experimentally that the partial exclusion of sugars and dextrans from the pores of a cation-exchange resin with a given counter ion is, if the eluent is 0.2 *M* sodium sulphate in deionized water, a consequence of the geometry of these standard samples alone. A method is described for determining the pore size distribution of polystyrene-based cation exchangers in aqueous systems by exclusion chromatography. A given standard sample *i* can penetrate pores of a solid with diameters smaller than $\varnothing_i$ ("exclusion value"). Some $\varnothing$-values are tabulated for standard samples as determined experimentally. Pore size distributions of cation exchangers, as measured by the exclusion chromatographic method, are described. In some applications the available pore volume of a swellable cation exchanger is of interest. This is of course, among others, a function of the counter ion, because the available pore volume for sugars and dextrans is codetermined by the solvent shell of the counter ion (Gibbs–Donnan equation). With the method described above this influence can be determined by experiments in aqueous systems. It is demonstrated that an interaction takes place between poly(ethylene glycol)s and polystyrene-based cation-exchange resins with water as the eluent. High-performance liquid chromatographic separations of amino acids and similar compounds on silica and on polystyrene-based cation exchangers are discussed.

INTRODUCTION

The morphological properties of rigid solids having pore diameters ranging from 10 to 4000 Å can be conviently determined by exclusion chromatography (EC)[1–3]. The principles and boundary conditions of the EC method for the determination of the structural data of porous rigid solids have been described in detail[2]. The pore structures of *in situ* coated stationary phases[4] and of chemically bonded stationary phases[5] have also been determined by this EC method. The mean pore diameters, $\varnothing_m$, are very similar if they are determined by classical methods (*i.e.*, nitrogen capillary condensation (*e.g.*, ref. 6) or mercury porosity[7] or by the EC

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method. Experience has shown that, for a given solid, capillary condensation, mercury porosimetry and the EC method yield similar $\varnothing_m$ values, but increasingly broad pore size distributions. This is due to the different boundary conditions and to the wall effect in EC and has been discussed elsewhere[8]. A simple and rapid method for determining only the mean pore diameters has also been described[9]. Thus, it has been shown experimentally, that in EC the h values of a homologous series *versus* the relative molecular mass of the samples and the pore size distribution of the rigid solid determined by EC exhibit the same maximum.

The permanent porosity of "semi-rigid" gels can be determined by all of the methods discussed above. The pore structure of non-rigid solids, however, is a function of the swelling medium employed. Pore size distributions of such gels, obtained by classical methods, obviously reflect the method of sample preparation required and bear no relation to the pore size distribution when swollen in a fluid medium.

It has been shown that the exclusion method is also suitable for determining the morphological properties of swellable solids[10]. The normal standard samples (phenylalkanes and polystyrenes) are insoluble in water and in other polar eluents. The pore size distribution of swellable polymers, especially of ion exchangers, in water is of some interest. This problem is discussed in this paper.

EXCLUSION CHROMATOGRAPHIC METHOD

The principles and boundary conditions of the EC method for the determination of the structural data of porous solids have been described elsewhere[2,10]. EC calibration graphs (*i.e.*, the elution volumes as a function of the relative molecular masses of the sample) can be used to calculate the mean pore diameters and pore size distributions of solids, if one assigns $\varnothing$ (Å) to the standard samples used for calibration, where $\varnothing_i$ defines the smallest pore diameter that is accessible to a given sample of relative molecular mass M_i. The total pore volume, $V_{p,total}$, of a solid is defined as the difference between the elution volume of the smallest inert standard sample and that of the greates standard. The sum of the residues R of a given pore diameter $\varnothing_i$ is defined as the fraction of total pore volume, $V_{p\ total}$, formed by all the pores with a diameter greater than $\varnothing_i$. Usually it is assumed that the elution volume V_e in EC can be described by the equation

$$V_e = V_z + K V_p \tag{1}$$

where V_z is the interstitial volume. The numerical values of R and K are, of course, identical. All three "calibration" graphs (*i.e.*, V_e *vs.* M, R *vs.* $\varnothing$ and K *vs.* $\varnothing$) describe the pore structure of the solid stationary phase; their shapes are very similar and are interpreted as integral pore size distribution curves. Experience has shown that the pore size distribution of many rigid solids and swellable polymers can best be illustrated by a log-normal distribution curve. Consequently, these "calibration" graphs are usually plotted with V_e *vs.* log M, R *vs.* log $\varnothing$ and K *vs.* log $\varnothing$ axes.

EXPERIMENTAL AND RESULTS

Morphological properties of solids having average particle sizes up to 250 μm can be determined by the EC method. If the particle sizes are "large" the equipment

TABLE I

AVERAGE PARTICLE SIZES (d_p) OF SILICA AND CATION-EXCHANGE RESIN STATIONARY PHASES

*Type**	*Phase*	*Producer or distributor*	d_p (μm)
a	SiO_2 Kugelgel	Dynamit-Nobel (Troisdorf, G.F.R.)	10
a	Mikro H	Home-made	15
a	Nr-80-3-U	Prof. Dr. K. Unger (University of Mainz)	9
a	H-90-7	Home-made	7
a	Si 200	Merck (Darmstadt, G.F.R.)	10
a	Si 500	Merck	10
a	Si 1000	Merck	10
b	Lewatit SPC 108/H	Bayer (Leverkusen, G.F.R.)	20
b	HC-X-7	Hamilton (Bonduz, Switzerland)	25

* a = Silica; b = cation-exchange resin.

can be simple, because the pressure drop over the column is small. As shown in Table I, the average particle size, d_p, of the stationary phases (solids) used in the following experiments was smaller than 25 μm, and consequently a typical high-performance liquid chromatographic (HPLC) apparatus was used. The following components were set up in series: a pump with a constant flow-rate (M 6000; Waters Assoc., Milford, MA, U.S.A.), a sample injector (U6K; Waters Assoc.), a stainless-steel separation column with a drilled-out[11] internal diameter of 4.2 mm and a length of 20–45 cm, a UV detector[11] of our own design (254 ± 10 nm, cell volume 8 μl) and/or a differential refractometer detector (R 401; Waters Assoc.).

All measurements were carried out at room temperature.

The silica columns were packed by a modified viscosity method[12].

The strongly acidic cation-exchange resin ($-SO_3H$) was regenerated with 1 *N* hydrochloric acid, washed to neutrality with 1 *N* sodium chloride solution and flushed for 1 h with deionized water. For maximum swelling it was stored for 24 h in deionized water. A slurry of 3 g of ion-exchange resin in 40 ml of water was packed into the column in the usual way. The packing pressure never exceeded 10 bars if Lewatil SPC 108/H was packed. Care was taken to prevent the columns from running dry.

Water-soluble standard samples

For the calibration graph the following samples were chosen: ribose, xylose, lactose, raffinose (Merck, Darmstadt, G.F.R.), stachyose (Südzücker, Offstein, G.F.R.) and dextrans (Pharmacia, Uppsala, Sweden). In the following a dextran with a weight-average molecular weight, for example, of 40,000 will be described as T-40. The hold-up volume of a column, with water as eluent, was always measured with D_2O, *i.e.*, it was assumed that D_2O is the smallest inert sample.

In the following, the total pore volume, V_p, of a solid will be defined as the difference between the elution volumes of D_2O ($\varnothing$ = 3.5 Å) and T-2000 ($\varnothing$ = 1500 Å). The defined total pore volume of microporous solids (*i.e.*, $\varnothing$ < 20 Å) can be an

extremely sensitive function of the arbitrarily chosen smallest inert sample. The elution volume of T-2000 was defined as the interstitial volume, V_z.

Choice of eluent

If the stationary phase is a cation-exchange resin, it is well known[13,14] that dextrans with high molecular weights are excluded from a given portion of the pore volume not only because of their geometry, but also because of the Donnan potential effect (carboxylic groups in the dextrans). Further, the dextrans tend to associate in water. This effect and the electrostratic exclusion can be minimized by the addition of inorganic salts such as sodium sulphate[13–15].

In the following it will be demonstrated that the standard samples are not adsorbed on the cation-exchange resins if the eluent is properly chosen because, if a sample is adsorbed or excluded owing to electrical fields, then its elution volume will be a function of the ionic strength of the mobile phase.

In order to alter the elution power, either sodium sulphate or acetonitrile was added to water. As shown in Table II, the elution volumes of sugars are practically constant if the concentration of sodium sulphate in deionized water is increased up to 0.3 *M*. On the other hand for dextrans a minimum concentration of 0.2 *M* sodium sulphate is required to avoid changes in their retentions. It was shown by experiments that dextran molecules will be adsorbed on the organic matrix of the ion-exchange resin if the concentration of sodium sulphate in water is 1 *M* or higher.

On the other hand, the elution volumes of the sugars and dextrans remained unchanged, to a first approximation, if the concentration of acetonitrile in water was lower than 10% (v/v), as shown in Table III. If the concentration of acetonitrile was increased to 30%, the elution volumes increased by 20% or more.

In subsequent work 0.2 *M* sodium sulphate solution was always used as the eluent when the stationary phase was a cation-exchange resin. With this system the peak symmetries were acceptable, as shown for some sugars in Fig. 1.

Calibration table for the water-soluble standard samples

The mean pore diameters of the silicas given in Table I vary between 12 Å (SiO_2 Kugelgel) and 1000 Å (Si 1000). The hydrodynamic permeability of these rigid

TABLE II

ELUTION VOLUMES OF DEXTRANS AND SUGARS AS A FUNCTION OF THE CONCENTRATION OF SODIUM SULPHATE IN WATER

Stationary phase: Lewatit SPC 108/H. L = 45 cm; I.D. = 4.0 mm; V_c = 5.54 cm^3; F = 1 cm^3/min.

Sample	V_e (cm^3)			
	M^* = 0	M = 0.1	M = 0.2	M = 0.3
T-40	2.88	3.02	3.14	3.11
T-10	3.14	3.23	3.36	3.30
Lactose	3.84	3.89	3.91	3.85
Xylose	4.12	4.12	4.21	4.22

* M = molarity of sodium sulphate in water.

TABLE III

ELUTION VOLUMES OF DEXTRANS AND SUGARS AS A FUNCTION OF THE ACETONITRILE CONCENTRATION IN WATER

Column geometry similar to and stationary phase identical with that in Table II.

Sample	V_e *(cm³)*		
	0% (v/v)	*5% (v/v)*	*10% (v/v)*
T-500	2.59	2.59	2.55
T-70	2.71	2.71	2.71
T-40	2.80	2.81	2.78
T-10	3.13	3.12	3.10
Raffinose	3.67	3.67	3.60
Lactose	3.82	3.82	3.78
Xylose	4.10	4.10	4.13

solids is constant if measured in methylene chloride or water as eluent. Therefore, it is not likely that their pore structure changes with these eluents.

The integral pore size distributions of different silicas were determined with methylene chloride as the eluent and polystyrene and phenylalkane standards[2,3]. These values are marked with crosses in Figs. 2 and 3.

The column filled with methylene chloride eluent was then flushed with methanol and deionized water and equilibrated with 0.2 *M* sodium sulphate in deionized water.

The elution volumes of D_2O, sugars and dextrans were measured and their K (or R) values were calculated with the help of eqn. 1. These K values, determined on different silicas, were then plotted to give the calibration graph for the corresponding

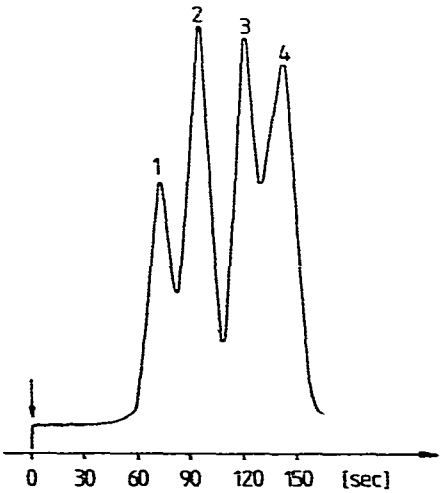

Fig. 1. Separation of sugars. Eluent: 0.2 *M* Na_2SO_4 in water. F = 1 cm³/min. Stationary phase: HC-X-7 cation-exchange resin (d_p = 25 μm). L = 25 cm; I.D. 4.1 mm; V_c = 3.35 ml, V_p = 0.42 cm³/cm³ empty column volume. Packing pressure: 400 bar. Hold-up (D_2O): 166 sec. Refractive index detector. Samples: 1, stachyose; 2, lactose; 3, xylose; 4, ribose.

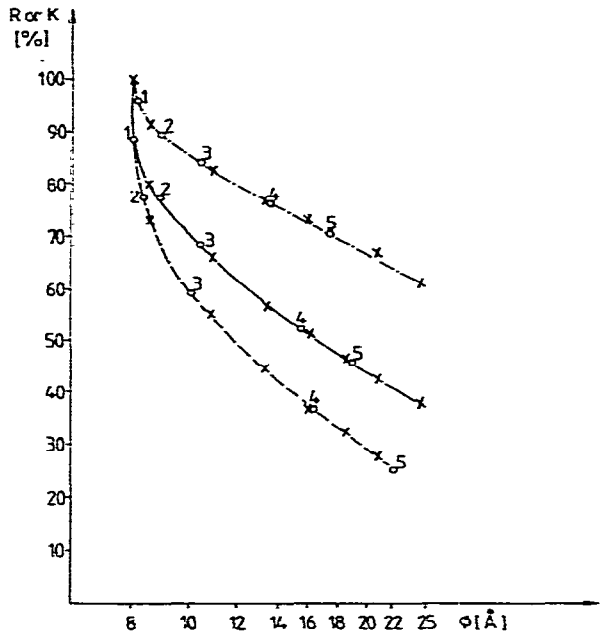

Fig. 2. Semi-logarithmic integral pore size distribution of microporous silicas and the $\varnothing$ values for water-soluble standard samples. Stationary phases: –·–·–, Mikro H silica; ——, SiO_2 Kugelgel silica; – – –, Nr-80-3-U silica. Samples: ×, phenylalkane standards (in CH_2Cl_2 eluent); 1, ribose (the eluent here and in the following is 0.2 *M* Na_2SO_4 in deionized water); 2, xylose; 3, lactose; 4, raffinose; 5, stachyose.

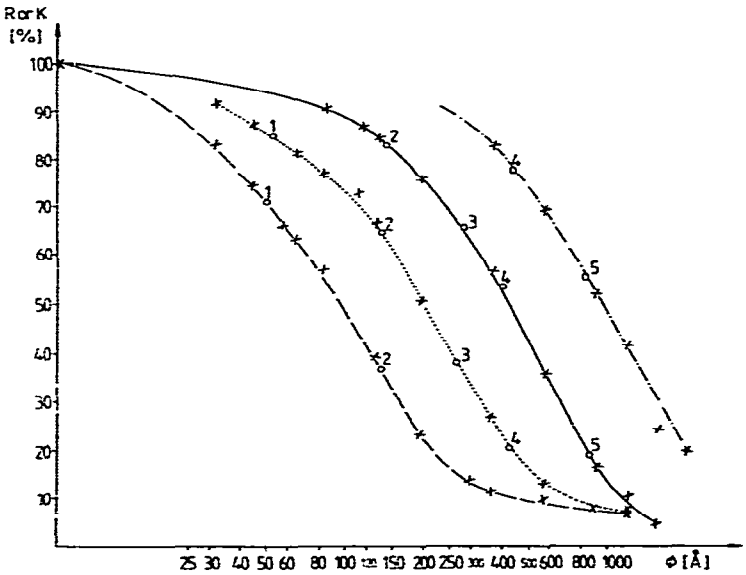

Fig. 3. Pore size distribution of silicas. Stationary phases: – – –, H-90-7 silica; ...., Si 200 silica; ——, Si 500 silica; –·–·–, Si 1000 silica. Samples: ×, polystyrene standards (in CH_2Cl_2 eluent); 1, T-4 (the eluent here and in the following is 0.2 *M* Na_2SO_4 in deionized water); 2, T-10; 3, T-40; 4, T-70; 5, T-500; 6, T-2000. F = 1 ml/min.

TABLE IV

Ø VALUES OF THE WATER SOLUBLE STANDARD SAMPLES

Eluent: 0.2 *M* Na_2SO_4 in deionized water.

Sample	$Ø_{average}$ (Å)	Ø (Å)	*Solid phase**
D_2O	3.5	—	—
Ribose	8	8.0	a
		8.1	b
Xylose	9	9	a
		9	b
		8.5	c
Lactose	10.5	10.5	a
		10.5	b
		10	c
Raffinose	15	15.5	a
		13.5	b
		16.0	c
Stachyose	19	18.5	a
		17.2	b
		22.0	c
T-4	51	50.5	d
		52.5	e
T-10	140	138	d
		138	e
		143	f
T-40	270	266	e
		275	f
T-70	415	427	e
		389	f
		427	g
T-500	830	841	f
		813	g
T-2000	1500	1500	g

* a, SiO_2 Kugelgel; b, Mikro H; c, Nr-80-U; d, H-90-7; e, Si 200; f, Si 500; g, Si 1000.

silica, as shown in Figs. 2 and 3. If the random condition of the pore size distribution measurements with EC are fulfilled, then the Ø values of a given sugar or dextran, as calculated from the calibration graphs of different silicas, must be very similar.

As shown in Table IV, the scatter of the Ø values of a given water-soluble standard sample is less than ±5% (mostly less than 3%) except for raffinose and stachyose. In the third column in Table IV, the Ø values are given as calculated from the calibration graph for a given silica (column 4). The average calibration values as given in the second column in Table IV, will be used to determine the pore size distribution of solids with water-soluble standard samples.

For D_2O it was arbitrarily assumed that its "diameter" is its Ø-value (3.5 Å). This approach is open to discussion. The Ø values of ribose, xylose and lactose are similar (8–10.5 Å). They are used together only if the slope of the pore size distribution curve of a solid is steep in this region. Unfortunately only one standard sample (T-4) was found in the Ø region between 19 and 140 Å.

Coil diameter of some polymers and their ∅ values

Polystyrenes dissolved in a "good" solvent (*i.e.*, methylene chloride) may be regarded as random coils. As was previously found[2], the rotational coil diameters of polystyrenes must be about 2.5 times smaller than the diameters of the pores in the solid (*i.e.*, ∅ values) to allow the polymer unhindered access to the pores (*i.e.*, to enable "instantaneous equilibrium" to be achieved).

Kuga[16] tabulated the molecular weights and hydrodynamic ratio of equivalent spheres (r) of some polymers. The $\varnothing/r$ ratio dextrans (as given in Table IV in this paper and in Table II in ref. 16) vary for the dextrans between 2.5 (for T-500) and 3.2 (for T-70). This factor is in tolerable agreement with 2.5 as given for polystyrenes in methylene chloride[2]. However, Kuga[16] accepts, without detailed experimental argument, the simple assumption that the diameter of the smallest permeable pore ("exclusion value", ∅...) is equal to the hydrodynamic diameter ($2r$). This assumption does not seem likely, because of the experimental conditions and because of the known kinetics in a column packed with porous material.

The probability that a polymer can enter a pore, if its hydrodynamic diameter is identical with the pore "diameter", is small if a high-speed equilibration is required.

Other water-soluble standard samples

Kuga[16] proposes oligo(ethylene glycol)s (OEG) and poly(ethylene glycol)s (PEG) as standard samples. As has been shown[14,17], and as is summarized in Table V, there is unfortunately an interaction between these samples and the cation-exchange resins. If 10% (v/v) of acetonitrile is dissolved in deionized water then the elution volumes decrease, compared with water. This is probably a consequence of hydrophobic interactions between the samples and the matrix of the ion-exchange resin (reversed-phase mechanism). As will be shown, the average (*i.e.*, the most probable) pore size of HC-X-7 cation-exchange resin is around 10 Å. The decrease in the elution volumes is small if acetonitrile is added to water and the sample is PEG 500 or

TABLE V

ELUTION VOLUMES OF OLIGO(ETHYLENE GLYCOL)S AND POLY(ETHYLENE GLYCOL)S AS A FUNCTION OF THE ACETONITRILE AND SODIUM SULPHATE CONCENTRATIONS IN WATER

Stationary phase: HC-X-7. L = 25 cm; I.D. = 4.1 mm; V_c = 3.35 cm^3; F = 1 cm^3/min.

Sample	V_e (cm^3)		
	10% CH_3CN	*H_2O*	*0.2 M Na_2SO_4*
EG	2.38	2.45	2.55
DiEG	2.18	2.35	2.65
TriEG	2.04	2.31	2.61
PEG 200	1.94	2.18	2.61
PEG 300	1.47	1.84	–
PEG 400	1.27	1.51	–
PEG 600	1.11	1.14	–
PEG 1000	1.04	1.07	
PEG 40,000	1.04	1.07	

larger, because these molecules are more or less excluded. On the other hand, the elution volumes increase if the eluent is 0.2 *M* sodium sulphate in water. In this system PEG 1000 and PEG 40,000 are irreversibly adsorbed. The elution volumes for PEG 300, 400 and 600 were not measured. Because of these interactions between the OEG and PEG samples and the ion-exchange resins these samples are not proposed as standard samples and are not included in Table IV.

We did not measured the interactions between poly(ethylene oxide)s and polystyrene resins as proposed by Kuga[16]. In the absence of such interactions they could be standard samples for pore size distribution with water as the eluent and would extend the calibration values given in Table IV.

Pore size distribution of ion exchangers

Fig. 4 shows the integral pore size distribution of the cation-exchange resin Hamilton HCX-7 (Na^+). The sample T-4 ($\varnothing$ = 51 Å) is excluded. It may be that molecules with $\varnothing > 19$ Å but definitely smaller than 51 Å are also excluded. As can be seen in Fig. 4, the most probable pore diameter is around 9 Å and more than 75% of the total pore volume belongs to pores with a pore diameter smaller than 10.5 Å. The differential pore size distribution of this phase is extremely narrow. The pore volume of this cation-exchange resin, as calculated from the elution volumes of D_2O and T-2000, is high (0.55 cm^3/cm^3, empty column volume). This stationary phase can be packed using pressures of up to 700 bar.

The pore size distribution of another polystyrene-based cation-exchange resin, Lewatit SPC 108/8, is shown in Fig. 5. The distribution is much broader. About 50%

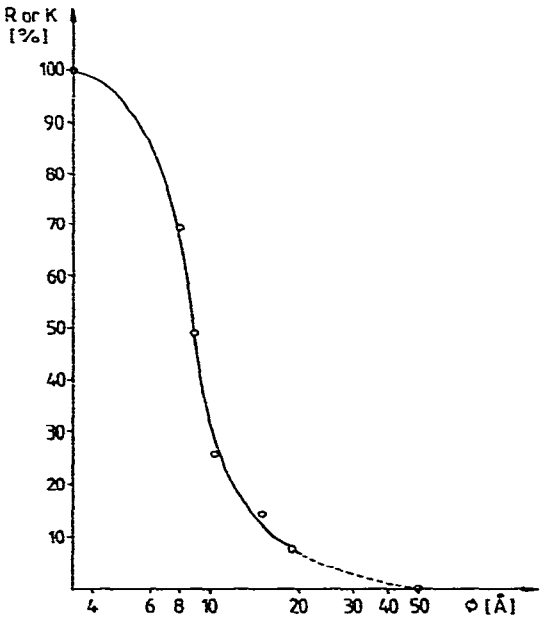

Fig. 4. Integral pore size distribution of the cation-exchange resin Hamilton HC-X-7 (Na^+). Eluent: 0.2 *M* Na_2SO_4 in deionized water. L = 25 cm; I.D. = 4.1 mm; V_p = 0.55 cm^3/cm^3; V_c = 3.35 cm^3; F = 1 ml/min. Packing pressure: 400 bar.

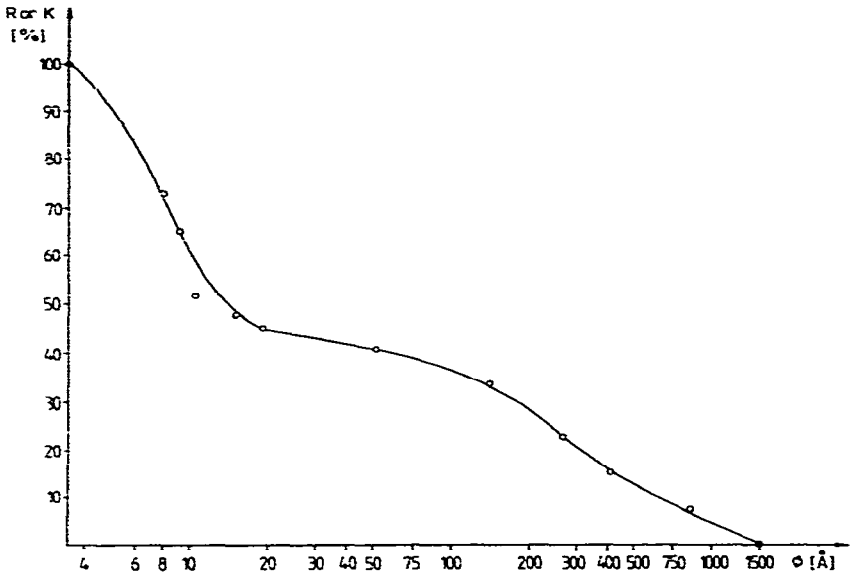

Fig. 5. Pore size distribution of the cation-exchange resin Lewatit SPC 108/8 (Na^+). Eluent: 0.2 *M* Na_2SO_4 in deionized water. L = 45 cm; I.D. = 4 mm; V_p = 0.42 cm^3/cm^3; F = 1 ml/min. Packing pressure: 5 bar.

of the total pore volume is in the micropores with $\varnothing < 10$ Å and about 20% belongs to pores with $\varnothing > 100$ Å. The pore volume is 0.42 cm^3/cm^3. Packing pressures of up to 15 bar are tolerable. The well known fact is again demonstrated that if a substantial proportion of the pores of a polystyrene resin have a diameter greater than about 15 Å, then its pressure stability decreases sharply.

Different types of cation exchangers in HPLC

The cation-exchange resin described in Fig. 4 is used as a stationary phase for the separation of amino acids and other ionic compounds. As can be seen from its pore size distribution, only a fraction of its pore volume and its surface area is available for bulky and electrostatically charged molecules. Cation-exchange stationary phases with large pore volumes and with mean pore sizes around 1000 Å can be prepared on silica bases. The integral (solid line) and the differential (broken line) pore size distributions, measured with methylene chloride as eluent and polystyrene standards[2], are shown in Fig. 6. The circles in Fig. 6 indicate the K (or R) values achieved with stachyose and dextran samples and 0.2 *M* sodium sulphate solution as eluent. It is remarkable and typical for this solid, with $\varnothing_m$ = 96 Å, that the total pore volume was very similar whether it was measured with benzene ($\varnothing$ = 8 Å) in methylene chloride eluent or with D_2O ($\varnothing$ = 3.5 Å) in water as the smallest inert sample. Consequently, a large proportion of the total pore volume of this solid is in pores with $\varnothing > 8$ Å. Si 100 silica is a matrix with $-(CH_2)_3-SO_3H$ as the functional group[18]. Its average pore size is 96 Å with a specific surface area of about 300 m^2/g (130 m^2/cm^3) and with a specific pore volume of 0.36 cm^3/cm^3. This phase is pressure-stable up to at least 1000 bar. The ion-exchange capacity of this silica-based ion

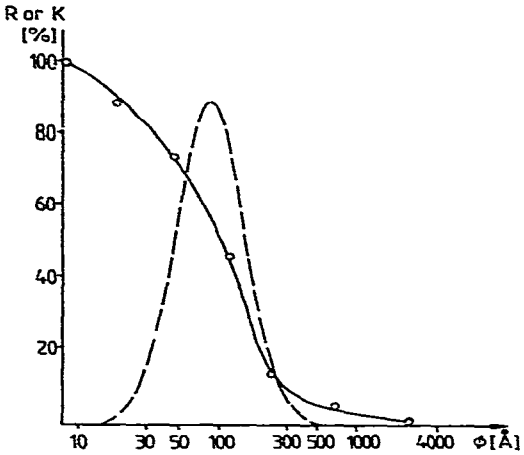

Fig. 6. Differential and integral pore size distribution of a silica-based cation exchanger. Silica base: Si 100 (10 μm). Functional group: propylphenylsulphonic acid. Packing density: 0.44 g/cm^3. Specific surface area: 300 m^2/g. Capacity: 1 mequiv./g (0.44 mequiv./cm^3). L = 25 cm; I.D. = 4.1 mm; V_c = 3.34 cm^3; V_p = 0.36 cm^3/cm^3. Solid line: the eluent is CH_2Cl_2 and the standard samples are benzene and polystyrenes. Circles: the eluent is 0.2 M Na_2SO_4 and the samples are sugar and dextrans.

exchanger is about 1 mequiv./g or 0.44 mequiv./cm^3 (ref. 18). The corresponding values for polystyrene-based cation exchangers used in HPLC are about 4–5 mequiv./g and 1–1.5 mequiv./cm^3, but with an average pore size well under 20 Å.

From the point of view of the accessibility of bulky molecules it would seem that the silica-based exchangers are superior to the polystyrene-based exchangers. On the other hand, it was shown experimentally that separations of ionic species can be effected with silica-based exchangers under identical conditions. However, these separations are only as good as those achieved with the classical polystyrene ion exchangers. Owing to the interactions with the different matrices the selectivities will vary.

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LIST OF SYMBOLS

d_p average particle size
F flow-rate
K distribution coefficient in EC, as defined in eqn. 1
L column length
M relative molecular mass

R sum of residues
r hydrodynamic radius of equivalent sphere
V_c empty column volume
V_e elution volume
V_p total pore volume
V_z interstitial volume
$\varnothing$ pore diameter
$\varnothing_m$ mean pore diameter

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