ON THE STRUCTURE OF ION-EXCHANGE RESINS

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Introduction

The ideal case of an ion-exchange resin is that of a homogene-
ous isotropically-swelling gel with a regular distribution of
charged functional groups throughout the particle. For convenience,
the particle geometry should be spherical, since this requires only
one parameter for its definition, and of course each particle should
have the same radius. The charged groups should each have a single
counterion, and the Donnan membrane effect should permit virtually
no invasion of external electrolyte. When considering the exchange
of ions in such a system, both the original counterion and the ion
for which it exchanges should be of the same size, hydration, and
valency, and should have identical diffusion coefficients both in
the external solution, and inside the homogeneous gel phase. Again
for convenience we should wish the resin to show no preference for
one ion rather than the other.

Life, however, is not like that! (47)

Since the validity of a number of the assumptions which are
made in simplifying kinetic expressions are dependent on structure,
the second part of this presentation is concerned with the non-
ideality of real materials.

Crosslinking and Entanglement

To ensure that the resin is insoluble in the solutions it is
designed to treat, the polymeric chains bearing the charged func-
tional groups must form part of a three-dimensional network. This
can be assured by polyfunctional condensation reactions, as in the

Table VI

Some Crosslinking Monomers

DIVINYLBENZENE
ETHYLENEGLYCOL DIMETHACRYLATE
TRIMETHYLOLPROPANE TRIMETHACRYLATE
DIVINYL KETONE
METHYLENE BIS-ACRYLAMIDE
DIVINYL PYRIDINE
ETHYLENE GLYCOL DIVINYL ETHER
DI-ISOPROPENYL BENZENE
TRIALLYLAMINE
TRIALLYLPHOSPHATE
TRIVINYLBENZENE
DIVINYLSULFONE
VINYL ACRYLATE
PENTAERYTHRITOL TRIACRYLATE
TETRAETHYLENE GLYCOL DIMETHACRYLATE

phenolic resins, by addition copolymerization of bifunctional mono-
mers such as styrene or acrylates with tetra- or higher-functional
comonomers (see Table VI), and by post-polymerization reactions of
various types such as those already described.

The swelling of crosslinked networks has been studied for many
years, and it is well-known that while crosslinks restrain swelling,
the nature and extent of crosslinkage and the state of the network
at its original formation all influence the effectiveness of this
restraint (48).

Conventionally, a crosslinked polystyrene network has for long
been represented as a two-dimensional structural formula of the type
shown in Figure 6 (49). Topologically speaking this is a 4-connected
plane net. Obviously a more reasonable representation would be a
4-connected three-dimensional net, corresponding to the tetrahedral
carbon atoms, in fact a diamond-like structure. This however is
still an idealized structure because the network is not created but
grown, and while it is growing parts of the network can grow through
and interpenetrate the earlier-formed parts. The end result is a
multiply-connected system of considerable complexity.

This network entanglement can be deliberately enhanced, as in
the interpenetrating network materials (50), known nowadays as IPN's
(51), or reduced by polymerization in the presence of an inert,
swelling, diluent (52). In conventional materials, viscoelastic
measurements on unmodified styrene-divinylbenzene copolymers have
given values for the effective intra-crosslink chain length which
are much less than those calculated from the divinylbenzene content
(53). Table VII gives a summary of the results, in which the theor-
etical values of M_c are calculated assuming that only 50% of the
divinylbenzene is effective as a crosslinker, (in line with published
estimates by Gordon & Roe (54), Haward & Simpson (55) and Dusek
(56)). This is a very rapid increase, analogous to the increase
with N of the number of entanglement isomers in linked catenanes
with N rings (Table VIII).

A major effect of crosslinking (or its equivalent) on the
functionalized matrix is of course on the internal average molality
of the active groups. This is illustrated in Table IX which shows
the total ion exchange capacity (in equivalents per litre of bed
volume) of typical polystyrene sulfonate resins as a function of
their divinylbenzene content. It affects a number of other proper-
ties which are related to mass transfer and kinetics of exchange,
such as the diffusion coefficients of ions in the resin phase (57)
and the extent of electrolyte invasion (58), as well as the equil-
ibrium properties which are involved in determining the extent of
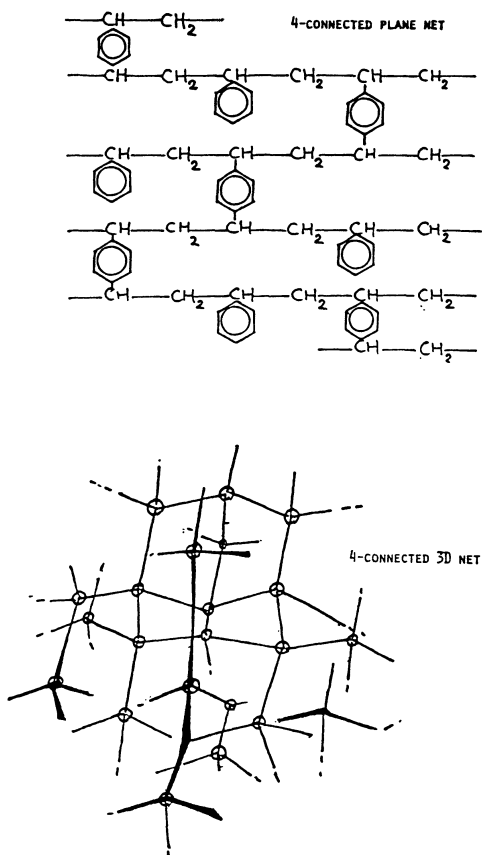exchange in limited-bath kinetic measurements (see Table X).

Figure 6

4-CONNECTED PLANE NET

4-CONNECTED 3D NET

Table VII

Contribution of Entanglement to Crosslinking

% DVB	Intra-crosslink mol. wt. (M_c)		Extra Crosslinking (as % DVB) Due to Entanglement
	Theoretical	from Elasticity	
1	12,900	10,500	0.2
2	6,500	4,500	0.9
4	3,200	1,800	3.1
7	1,800	800	8.8
10	1,400	600	13.3
15	790	230	36.5

Table VIII

Entanglement Isomers of Linked Catenanes with N Rings

N	1	2	3	4	5	6
Entanglement Isomers	---	1	2	6	19	68

Table IX

Moisture Retention & Wet Volume Capacity

(Figures are for fully-substituted RSO_3H resins
in the hydrogen-ion form)

DVB %	WR (G/G)	S.W.R. (G/MEQ)	WET VOLUME CAPACITY (EQUIV./LITER)
1	10.5	1.90	0.31
2	3.6	0.680	0.78
5	1.5	0.275	1.60
10	0.83	0.155	2.26
15	0.60	0.115	2.67
25	0.38	0.078	2.99

Table X

Physicochemical Properties of Crosslinked Sodium
Polystyrene Sulfonate Resins as a Function of
Divinylbenzene Content

DVB %	ELECTROLYTE INVASION $\tilde{M}/M$ @ 0.1 M (REF. 58)	SELECTIVITY COEFFS. K_H^{Na} @ $\bar{X} = 0.5$ (REF. 60)	SELF-DIFFUSION COEFFS. $10^7 \bar{D}_{Na}$ * (SEE FOOTNOTE)
1	0.027	~ 1	---
2	0.018	1.10	~ 22
5	0.008	1.55	~ 15
10	0.002	1.94	` ~ 8
15	0.0006	2.13	~ 3.5
25	VERY SMALL	2.40	~ 1

NOTE: THE ISOTOPIC SELF DIFFUSION COEFFICIENTS
ARE ESTIMATES BASED ON THE WORK OF BOYD
& SOLDANO, MODIFIED TO TAKE INTO ACCOUNT
LATER CRITICISM (59), AND ADJUSTED ON THE
BASIS OF INTER-DIFFUSION COEFFICIENTS
REPORTED BY MILLAR ET AL. (60).

Some early work on polystyrene sulfonate resins with deliberately enhanced entanglement (50) indicated that not all these properties were affected to the same extent. Thus, the selectivity coefficients were markedly increased and ionic diffusion rates appeared to be higher than appropriate to a conventional resin with the reduced swelling achieved in the IPN by using a second interpenetrating network (60).

The reverse effect, reduction in entanglement for a given amount of crosslinker, is observed when the copolymerization occurs in the presence of an inert diluent which solvates the polymer, such as toluene. Here, for moderate amounts of crosslinker and not too exaggerated dilutions, electrolyte invasion was enhanced, selectivity coefficients reduced, and diffusion coefficients increased in comparison with those of a conventional material of the same divinylbenzene content (61). They were essentially similar to those of a resin of the same average internal molality.

This should be recalled when comparing the early work of Pepper and his colleagues, or that of Gregor and others, with later publications. In the manufacture of commercial DVB, the divinylbenzene isomers are obtained as a mixture with their precursors in the original feedstock, and are separated by fractional distillation. Over the years, the techniques have improved to the extent that normal commercial DVB today contains 55-60% of divinylbenzene isomers the remainder consisting almost entirely of the corresponding ethylstyrenes, while concentrates of up to 88% divinylbenzene isomers are regularly available. In the late forties, however, the crosslinker content was only 25-35% and the ethylstyrene content was similar. The remainder in those days was mainly the original diethylbenzene feedstock, in quite significant amounts. Thus the higher DVB content materials of those days were in fact solvent-modified, with the resultant physicochemical differences already described.

Pores and Heterogeneity

Arising from the work on solvent-modification, which had already been used empirically by Clarke for ion-exchange membranes (62), and by Mikes (63) for ion-exchange resins, it was found that with high crosslinker contents and substantial dilution the solvent-free matrix was opalescent in appearance and demonstrably porous in character (61). The existence in the gel phase of micropores has generally been accepted, and recent work by Freeman & Schram using inverse gel permeation chromatography (64) has given a measure of the micropore structure in the THF-swollen DVB-crosslinked polystyrene matrix. Their figures are interesting to compare with average pore diameters calculated by Grubhofer (65) for the water-swollen sulfonates (Table XI).

Table XI

Average Swollen Pore Diameters (Å)

DVB %	HC Matrix (Ref. 64)	Sulfonated Copolymer (Ref. 65)
1	77	343
2	54	151
4	37	58
8	14	30
16	13	15

In the macroporous copolymers there is a much wider range of pore sizes and the existence of pores of 10,000 Ångstroms diameter, or larger, has been demonstrated by electron-micrography and mercury porosimetry in a number of instances. These pores, unlike the gel porosity, persist in the unswollen state. They are usually continuously interconnected, and can accommodate liquids which would not normally be taken up by the resin, making it possible to carry out exchange in non-aqueous liquids at rates not achievable in conventional materials. The porosity also cushions the material against damage by osmotic shock, and permits extensive electrolyte invasion which facilitates exchange in partly-ionized resins. Most weakly-basic resins at the present time are synthesized on macroporous matrices.

The pore structure (and indeed the surrounding gel structure) of a macroporous resin is critically dependent on a number of factors. We have already seen that for solvating diluents crosslinker content and dilution are very important. The nature of the diluent itself is also a determining factor. In order to achieve a macroporous product, phase separation must occur during the formation of the matrix. If this is achieved by the use of a poorly-solvating or non-solvating diluent (66), phase separation occurs early on, and a high crosslinker content is not essential. In the ultimate case where the diluent is polymeric (67), phase separation is very early and the pore sizes achieved are large.

The characteristics of the three classic types of macroporous matrices are summed up in Table XII. An excellent early review on synthesis and structure of macroporous styrene-divinylbenzene copolymers is given by Seidl, Malinsky, Dusek and Heitz (68).

More recently, the need to tailor matrices to obtain optimum performance has occasioned a great deal of work, most of which is proprietary and published only in patent form, on the judicious blending of SOL and NONSOL porogens to achieve special results. The most recent and most comprehensive of the patent disclosures on the subject of mixed porogens (69) are those from Asahi (70).

The solvents used as components of the mixed porogen are divided into three groups:

    i)   solvents for all homopolymers of the monomers used
   ii)   non-solvents for all homopolymers of the monomers used
  iii)   solvents for some, non-solvents for other of the
           homopolymers of the monomers used.

(In the case of polyvinyl monomers, "good swellant" is understood to replace the term "solvent".)

Table XII

Characteristics of Macroporous Matrices

POROGEN TYPE	MINIMUM CROSSLINKER REQUIREMENT	TYPICAL SIZE OF MACROPORES	STRUCTURE OF GEL FRACTION
SOL (SOLVATING DILUENT)	REL. HIGH	$\sim$ 200 Å	DISENTANGLED < NORMAL CROSSLINKING
NONSOL (POORLY SOLVATING DILUENT)	LOW-MEDIUM	$\sim$ 500 Å	ENTANGLED > NORMAL CROSSLINKING
POL (POLYMERIC DILUENT)	VERY LOW	$\sim$ 1500 Å	NORMAL CROSSLINKING

The mixed porogen (here termed a modifier) is made up of a number of solvents chosen from among the three groups. Five types of modifier can be distinguished, the simplest of which is a single solvent from group iii. Addition of group ii solvents results in an increase in pore diameter, while addition of group i solvents reduces pore size. A mixture of group i and group ii solvents gives a wide variation in pore structure as the i:ii ratio is varied, but the finest control is obtained by using an appropriately chosen mixture of solvents from group iii.

Clearly much depends on the types of monomers being copolymerized. Unlike the classic DVB/Styrene copolymers which are of low polarity and whose components all have very similar solubility parameters (8.8-9.1), the choice in the case of polar co-polymers is often much more difficult.

Six examples of types of polar monomer mixes are given. In each case at least one crosslinker, one polar monomer, and one comonomer (whose polarity range is that from butadiene to 2-vinyl-pyridine) are involved. Table XIII lists the (approximate) values of solubility parameter for these, and the Examples concerned. For each of these Examples I-VI suitable solvents are given, and Table XIV indicates these solvents with approximate values of solubility parameter and the groups into which they fall for each Example.

The type of porosity can thus be adjusted for any given copolymer. However, the pore volume is dependent on the volume of modifier and in the Asahi patents the amount of modifier appropriate to a given crosslinking is defined, curiously, in terms of the square root of the % crosslinking. The scope of the patent is given, in the usual manner, by bracketing, giving first a range within which the invention will work, secondly a preferred range, and thirdly a recommended range. The percentage by weight of modifier (D) referred to the total weight of monomers is given as a function of the percentage by weight of crosslinking agent (X) on the same basis by the following relations:

$$\text{typical} \qquad 7\sqrt{X} \leq D \leq 500\sqrt{X}$$

$$\text{preferred} \qquad 20\sqrt{X} \leq D \leq 200\sqrt{X}$$

$$\text{recommended} \qquad 34\sqrt{X} \leq D \leq 150\sqrt{X}$$

It can be seen that there is a fairly wide scope for variation, and that at least in the S/DVB case the recommended limits cover most of the useable range for NONSOL-modified materials.

The large range of polarities and porosities which may be required, and the empirical nature of "solubility parameters" for insoluble polymers, make it difficult to sum this information up

Table XIII

Examples of Polar Monomer Mixtures
from Asahi Patents

Crosslinker[a-f]	Polar Monomer	Comonomer	δ
divinylbenzene		1:3 butadiene[a,c,d]	8.3
			8.9
		ethylstyrene[a,b,c,d,e,f]	~9
		styrene[a,b,c,d,e,f]	9.1
	methacrylonitrile[a]		9.3
	methacrylonitrile[a]	methyl methacrylate[a,c,d,e,f]	9.5
ethylene glycol dimethacrylate	acrylonitrile[a]	methyl acrylate[a,c,f]	~10
	N-vinylcarbazole[b]		10.7
			12.5
divinylpyridine	c ———2-methyl-5-vinyl pyridine——— a,d		~13
			13.1
	c ———2-vinyl pyridine——— a,d,f		13.5
	4-vinyl pyridine[d]		13.5
	2-vinylimidazole[d]		14
	2-methyl-N-vinyl imidazole		14
	acrylamide[e]		14.5
	N-vinylpyrrolidone[f]		15

a) Example III   d) Example I
b) Example IV   e) Example VI (ethylene bis-acrylamide can also be included among x-linkers)
c) Example II   f) Example V

Table XIV

Classification of Porogens or "Modifiers" from Asahi Patents

Solvent	Polarity	I	II	III	IV	V	VI	δ
hexanes	---	ii	ii	ii	ii	ii		∿ 7
didodecyl phthalate	small							7.2
heptanes	---	?	ii	ii	?	ii		7.5
octanes	---	ii	ii	ii	ii	ii		7-7.5
decanes	---	ii	?	ii	?	ii		7.5-8
dioctyl phthalate	small							7.9
cyclohexane	---	ii	ii	ii		ii		8
di-isopropyl ketone	+					iii		8
ethyl benzoate	+	iii	i	iii				8.2
ethyl propionate	+	iii	i				iii	8.4
methyl isobutyl ketone	+	iii		[iii]	iii			8.4
benzonitrile	(+)	i	i					8.4
butyl acetates	+	iii					iii	8.3-8.5
n-butyl propionate	+	iii		iii		iii		8.8
xylenes	---	iii	i	iii	i		iii	8.8
ethylbenzenes	---	iii		iii	i	iii	iii	8.8
toluene	---	iii	i	iii	i	iii	iii	8.9
methyl propionate	+			iii	iii			8.9
dibutyl adipate	+	iii		iii				8.9
ethyl acetate	+	iii		iii	iii	iii		9.1
benzene	---	iii	i	iii		iii	iii	9.2
chloroform	(+)				i			9.3
methyl ethyl ketone	+	iii	i	[iii]	iii			9.3
tetralin	---	iii			i	iii	iii	9.5
chlorobenzene	(+)	iii	i					9.5
tetrachloroethane	(+)	i			i			9.7
2-nitropropane	(+)	i	i	[iii]				9.9
cyclohexanone	+	i	i	[iii]				9.9
tetrahydrofuran	+				i			9.9
o-dichlorobenzene	(+)	iii	i		i			10
dioxan	+				i			10
diethyl phthalate	+	iii		iii				10
amyl alcohols	+	iii	iii	ii				10-11
octanols	+	iii	iii	ii	ii			∿ 10.5
n-butyronitrile	(+)			[iii]				10.5
methyl benzoate	+	iii	i	iii			iii	10.5
acetophenone	+	i						10.6
propionitrile	(+)			[iii]				10.7
pyridine	+							10.7
dimethyl phthalate	+	iii	i					10.7
butanols	+	iii	iii					10.5-11.5
hexanols	+	iii	iii	ii	ii			∿ 10.7
nitroethane	(+)	i		[iii]				11.1
cyclohexanol	+	iii	iii	ii	ii			11.4
benzyl alcohol	+	i						12.1
nitromethane	(+)							12.7

( ) = poor hydrogen bonding   [ ] = in acrylonitrile copolymers only

more concisely.

Pore Size Measurements

Up until now we have used the concept of porosity as though everyone were familiar with it (which they usually are) and understood it (which they frequently do not). Dictionary definitions of porosity are usually cyclic and unhelpful. If one uses the term "porosity" to mean a local absence of matrix, the state of having holes in the medium, then it becomes as unquantifiable as "friability" or "happiness". What is often referred to as the porosity of a solid material is the percentage (or fraction) of voids within the porous solid. This can be defined by the apparent density, if the normal matrix density is known.

Thus, a silicate glass with density 2.8 g/mL when foamed to 80% porosity will give a product every mL of which will contain 0.2 mL or 0.56 g of glass, and 0.8 mL of air. The apparent density will be 0.56, and provided the porosity is closed, i.e. liquids cannot enter, the product will float on water.

If the pores are open and interconnected, the water will penetrate and the material will behave as a composite with an average density of 1.36, sinking in the water. To calculate the apparent density, out of water, you would have to take the external volume, and the net weight, and correct for the amount of water held internally.

With macroporous organic sorbents or ion exchange resins, the situation is complicated by the swelling of the matrix. Unlike the foamed glass in the previous example, where a hole is a hole is a hole, a hole in an elastic matrix will increase in size as its boundaries increase. If the swelling of the polymer is isotropic, a volume change of x% in the polymer implies a corresponding volume change in the pore, and usually this is so for the materials we have been considering.

Unfortunately, electron micrographic, mercury porosimetric and BET/N_2 adsorption techniques, which have found widespread application to the measurement of pore-size distribution in macroporous organic polymers, require dry out-gassed samples of the polymer in question. In consequence neither give an adequate description of the porosity of the sample under normal operating conditions. Indeed, unless appropriate precautions are taken in the preparation of the dry out-gassed samples, the figures obtained even on these are open to considerable criticism (71), and may indeed be meaningless.

One method which permits measurement of surface areas in swollen resins is the sorption of p-nitrophenol (PNP) from aqueous

or organic solution, introduced some twenty years ago by Giles and
Nakhwa (72), and used by Fang and Golownia on macroporous organic
polymer matrices (73). Some comparisons of BET/N_2 and PNP figures
were given in a recent review (74). The method is apparently little
used, probably because it is not easy to automate.

For most people, seeing is believing, and there is something
very convincing about an electron micrograph. Since, most ion
exchange chemists are aware of the possibility of artefacts, such
pictures as have been published have survived extensive review.
However, uncertainties arise in mercury porosimetry, and in surface
area and pore size distribution measurements by adsorption methods,
which are not so well appreciated outside the specialized surface
chemistry laboratory. Taking the BET technique first, the most
obvious is that the surface area is measured in terms of an amount
of sorbate, and the amount of sorbate per unit area is not accur-
ately known. The best known of the permanent gases used in the BET
technique is nitrogen, with a molar cross-sectional area of 16.2 Å^2,
and relatively unambiguous isotherms on most surfaces. For many of
the other sorbates, the apparent cross-sectional area A_m is depend-
ent on the system or the sorbent, and wherever possible calibration
should be made against a N_2 value. Krypton is a case in point —
values from 17-22 have been used at various times in various cir-
cumstances, giving a possible variation in surface of ± 13%.
Similar problems arise in sorption from solution; p-nitrophenol has
an A_m value which ranges from about 15 on metal oxides in hydrocar-
bon solvents to 53 in polar solvents on carbon.

Secondly, the sorbate will absorb only when it can approach
the surface, and it will desorb only if it has first adsorbed.
Consequently, the probing of micropores with larger sorbates is
pointless, while restricted porosity or the so-called ink-bottle
pores will give rise to hysteresis effects on the adsorption curve
which require interpretation. In any case, there is evidence that
the Kelvin equation, which is the basis for pore size calculations
based on sorption, becomes invalid at relative pressures below p/p_0
values of ~ 0.2, i.e in the 20 Å range, despite the lack of steric
hindrance to the diffusion of N_2 (with a rotational diameter of
3.2 Å).

With the mercury intrusion technique, the interfacial tension
between the mercury and the polymer surface is the factor which
controls the penetration of mercury at a given pressure. The pres-
sure required (Table XV) is dependent on the radius of the capillary,
and under normal conditions (unwetted surface, clean mercury, open
pore structure) there is a natural limitation of around 20 Å radius,
at which the pressure required is approximately 3600 Kg. cm^{-2}, about
3,500 atmospheres). Pressures as low as 2000 Kg. cm^{-2} can result in
irreversible damage to the pore structure, and if the newer scanning
porosimeters are used there may be uncertainty about what is actually

Table XV

Range of Pore Size Determination

PORE DIA Å	POROSIMETER PRESSURE ($Kg. cm^{-2}$)	BET/N_2 (p/p_o)
20	--	0.16
50	2742	0.57
100	1300	0.78
200	598	0.89
500	253	0.95
1000	112	--
5000	26.4	--
10000	12.7	--

being measured. The ink-bottle pores in a structure, again, give
rise to problems. What is actually measured is a volume penetrated,
and if some pore volume of 1000 Å diameter is only accessible through
a 100 Å orifice, it will register only when 1300 Kg. cm^{-2} pressure
is applied, and will be associated therefore with a 100 Å diameter
pore. It will also not empty when the pressure is reduced, and the
variation in sequential volume/pressure curves shown on a single
sample of Diaion HP 20 (Figure 7) can reflect either retained
mercury in ink-bottle pores or small pore wall breakdown.

Surface areas calculated from mercury porosimetry are dependent
on assumptions of pore geometry, and usually cover the range of pore
size from about 50-100,000 Å diameter, so that pores below 50 Å
which can contribute appreciably to internal surface are neglected.
By that same token, pore volumes derived from the BET adsorption
measurements are indirectly estimated also, and cover a range of
pore size from about 25 Å diameter to about 250 Å above which there
is no condensation. Thus the very large macropores which can con-
tribute significantly to the total volume in an actual pore size
distribution can be omitted from consideration. Clearly, even for
the limited objective of obtaining as full as possible pore size
distributions on dry, unswollen materials, both types of measurement
are essential, and they should only be combined with circumspection
and with consistent geometrical assumptions.

From the foregoing discussion, it will be evident that para-
meters like "mean effective pore diameter" are essentially meaning-
less, even as a means of empirical comparision, if the actual dis-
tributions are not already known to be similar. Similar remarks
apply to integrated values like "total surface area" or "pore
volume", even in the rare instances when the measurement techniques
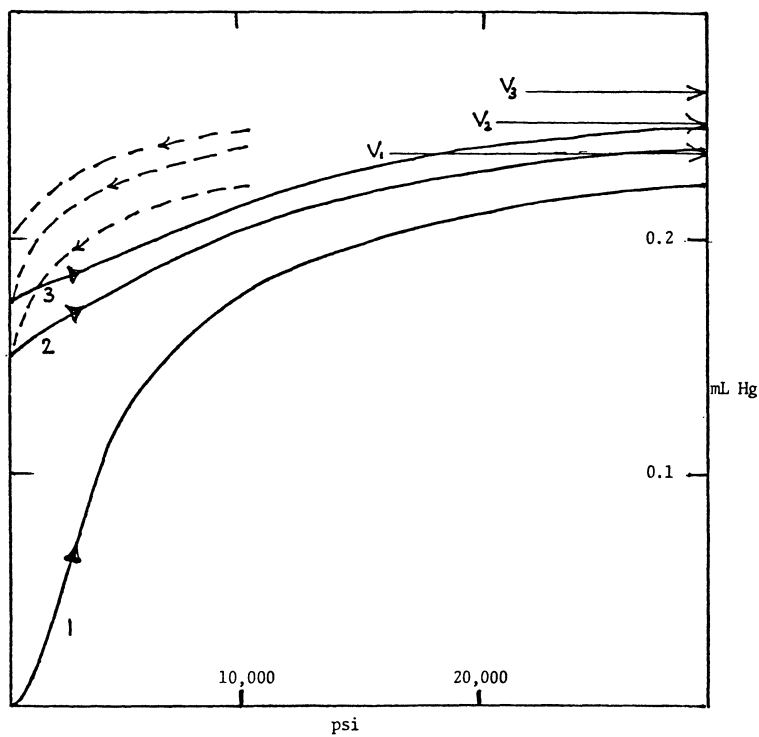are clearly defined.

Effects of Structural Heterogeneity on Mass Transfer and Kinetics

While this will be dealt with in later sections of this
Advanced Study Institute, one or two points should be made in the
light of the ideas presented in this section.

It has already been pointed out that electrolyte invasion into
the macropore regions of macroporous resins is extensive. There is
however a significant difference between invasion in SOL- and NONSOL
modified materials resulting from the difference in detailed struc-
ture, the ratio of internal to external electrolyte concentration
being higher for the NONSOL-modified materials of comparable average
internal molality (66).

It may be assumed that because of the existence of macropores,
the thickness of the unconvected Nernst film, which is (under low
concentration conditions) a limiting factor in the so-called film-

Figure 7. Repeated Hg Scanning Porosimetry on Diaion HP-20

(Sample size, 0.2189 g)

V_1 : 1.10 mL/g

V_2 : 1.19 mL/g

V_3 : 1.23 mL/g

diffusion kinetics (75), is somewhat higher than for corresponding conditions on a conventional gel-type exchanger. Since the stirred film thicknesses are of the order of microns, however, this is unlikely to be more than a second-order effect. The effect in unstirred systems, such as the immobilized biocatalysts discussed by Kasche and Kuhlmann (76), is negligible.

The effect of macroporosity on the titration curves of ion-exchange resins is on the apparent dissociation constant only, and the thermodynamic dissociation constant of the group is essentially unaffected. Some second-order differences may exist as a result of the distribution of charged groups which is demonstrably more heter-ogeneous than in conventional gel resins.

One area where clear-cut differences have been reported is in the diffusion coefficients within the resin for relatively large ions (61b). The physical constraints on self-diffusion within an exchanger involve excluded volume effects, tortuosity and anisotropy of pore structure. The presence of a macropore system in the resin phase will tend to reduce such constraints, and although the measured diffusion coefficients were indeed higher, the major effect was on the Arrhenius activation energies for exchange interdiffusion, which were essentially those for diffusion in free aqueous solution. How-ever, since the large ions in this case were appreciably excluded from the gel region, this may be no more than a reflection of this fact, an artefact of the kinetic theory employed (77).

Much more work is needed to obtain the data which will enable us to understand and quantify the kinetics of ion exchange in such complex systems. In the meantime, let us be on our guard against taking the mathematical consequences of our plausible assumptions as a reflection of what some of us like to regard as the "real world".

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