CHROM. 10,421

Note

The dependence of the swelling of ion-exchange resins on their crosslinking

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(Received July 5th, 1977)

The swelling of ion-exchange resins is a factor of prime importance in determining their selectivity and their behaviour in a chromatographic column. It depends on many factors, including the nature of the solvent, the presence or absence of an electrolyte in the solution, and its nature and concentration, the nature of the fixed and counter ions, the nature of the resin skeleton and the degree of crosslinking. For a given type of resin (given skeleton and fixed ion) and solvent (water) and in the absence of electrolyte, the swelling depends on the nature of the counter ion and on the degree of crosslinking. It was found in many studies[1–10] that, for a given counter ion, the swelling exhibits an approximately linear relation with the reciprocal of the nominal crosslinking, X, expressed as the percentage of divinylbenzene in the polystyrene-based resins. An expression which holds remarkably well is

$$\bar{n}_w = a + \frac{b(100 + X)}{X} \tag{1}$$

where $\bar{n}_w$ is the number of moles of water per equivalent of resin in the swollen state, and a and b are constants. At low degrees of crosslinking, $(100+X)/X$ is not very different from $100/X$. In eqn. 1, the constant a expresses the amount of "bound" water, due to hydration of the ions, while b expresses the amount of "free" water. The present paper attempts to throw light on the dependence of term b on the crosslinking.

Intuitively, it could have been thought that the swelling by "free" water should depend on the available volume and hence on the third power of some linear dimension of the resin structure, which, in turn, depends inversely on the crosslinking. Instead, we shall show why the dependence should be on $(100+X)/X$, *i.e.*, practically on the inverse first power of the crosslinking. Since the swelling of anion exchangers[6,10] having different crosslinkings has not been studied as extensively as that of cation exchangers[1–5,7–9], some new experimental results are also reported.

EXPERIMENTAL

A commercial polystyrene–methylene–trimethylammonium type anion exchanger (Cl⁻) (Dowex 1; Fluka, Buchs, Switzerland) (50–100 mesh), nominally of $X = 1, 2, 4, 8, 10$ and 16% divinylbenzene crosslinking, was employed. The resin was conditioned by alternate washing with hydrochloric acid and sodium hydroxide, or water and ethanol, in order to remove impurities, fines and low-molecular-weight fragments. The resin was dried in a desiccator in the presence of phosphorus pentoxide at a vacuum of 300 Pa for 2 days. Further drying for 4 days at a vacuum of 10^{-3} Pa caused a loss of weight of $0.097 \pm 0.009\%$ only, and was not considered necessary. Some samples of the resin were dried to constant weight in a vacuum oven at 130°. These samples showed a lower water regain than the others, possibly because of some irreversible changes in the resin. The capacity, in equiv./kg of dry resin (Cl⁻), was determined for 10-g samples by replacing the chloride by perchlorate, and potentiometric titration of chloride with silver nitrate. The accuracy was $\pm 4\%$ for resins having $X = 1$ or 2, $\pm 2\%$ $X = 4$ and $\pm 0.5\%$ for $X = 8, 10$ or 16. For the measurement of swelling, a weighed portion of dry resin was equilibrated at room temperature, $23 \pm 1°$, with water, separated by the centrifugation method[2,11] (5700 rpm for 15 min) and weighed.

RESULTS

The swellings of the resins are shown in Table I. The data may be expressed in terms of eqn. 1, with $a = 7.2 \pm 0.8$ mol/equiv. and $b = 0.42 \pm 0.03$ mol/equiv. Some literature data for a polystyrene sulphonate resin (H⁺) (ref. 5) and a Dowex 1 resin (Cl⁻) (ref. 10) are shown in Fig. 1. The constants a and b for these and other results from the literature are shown in Table II. Since the methods and resins utilized by different workers varied widely, there is little point in comparing the actual values of these constants. What is emphasized is that the data conform to eqn. 1, with a relative standard deviation not exceeding, in most cases, 5%.

TABLE I

THE SWELLING OF DOWEX 1 (Cl⁻) AT DIFFERENT CROSSLINKINGS

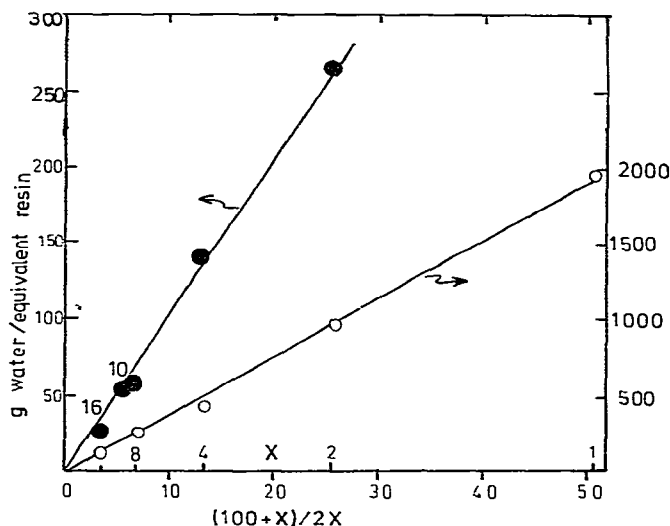| X	Chain length*	$\bar{C}$ (equiv./kg)	$\bar{n}_w$ (mol/equiv.)	
			Vacuum-dried resin	Oven-dried resin
1	50.5	4.54	70.0	49.8
2	25.5	4.34	27.9	27.2
4	13.0	4.13	19.75	17.70
8	6.76	3.83	13.35	12.50
10	5.49	3.10	11.40	11.85
16	3.62	2.25	8.20	6.65

* In ethylene units, see Discussion.

Fig. 1. The swelling, in grams of water per equivalent of dry resin, of a polystyrene sulphonate cation exchanger (H⁺) (○) and a polystyrene methylene trimethylammonium anion exchanger (Cl⁻) (●) as a function of the crosslinking X.

TABLE II

RELATION OF SWELLING TO CROSSLINKING; THE PARAMETERS OF EQN. 1 AND THE STANDARD DEVIATION OF THE FIT, σ

Ionic form	a	b	σ (%)	Ref.	Ionic form	a	b	σ(%)	Ref.
H⁺R⁻	1.0	1.02	4.4	3	R⁺F⁻	4.6	0.31	4.8	6
	0.0	1.02	3.0	5	R⁺Cl⁻	4.2	0.23	6.8	6
	0.7	0.86	2.8	7		0.0	0.55	4.0	10
	3.4	0.60	3.3	8		7.2	0.42	2.4	this work
	0.8	0.84	3.2	9					
Li⁺R⁻	11.2	0.91	4.0	1	R⁺Br⁻	3.4	0.14	4.6	6
	1.5	0.68	2.5	8	R⁺I⁻	2.9	0.04	5.2	6
	0.8	0.71	3.5	9					
Na⁺R⁻	0.6	0.64	3.3	7					
	2.9	0.52	4.8	8					
	1.2	0.63	6.3	9					
K⁺R⁻	11.0	0.88	4.2	1					
	0.5	0.62	3.4	7					
	0.8	0.56	3.7	9					
NH₄⁺R⁻	10.7	0.79	6.0	1					
Cs⁺R⁻	0.7	0.51	4.7	7					
	0.7	0.51	4.8	9					

DISCUSSION

We will now show how geometrical considerations lead to eqn. 1. Consider Fig. 2, which shows three groups of styrene and p-divinylbenzene polymerizing into three parallel, crosslinked chains. Each chain starting from $100 - X$ styrene units and X divinylbenzene units donates X ethylene groups to neighbouring chains (this does
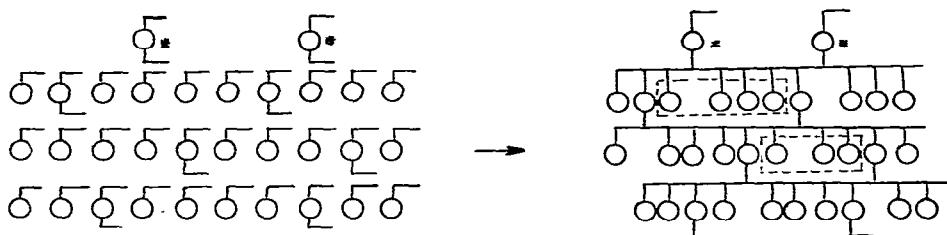
Fig. 2. Schematic picture of the polymerization of styrene containing 20% divinylbenzene (the exchange groups are not shown) to form three chains. The regions enclosed in dashed lines constitute the pores, limited by crosslinking bridges. The divinylbenzene groups marked with asterisks, contributing bridging units, belong to a fourth chain.

not affect its length), but also receives X ethylene groups from its neighbours, so that the chain consists of $100 - X + X + X = 100 + X$ ethylene groups, and has $2X$ bridges to other chains. The number of units between two junctions to such bridges is $(100 + X)/2X$ (see Table I), and is, thus, approximately inversely proportional to the nominal crosslinking. (The fact that, on average, one p-ethylstyrene molecule replaces a styrene molecule for each p-divinylbenzene molecule present does not change this picture.)

When such a polymer swells, the increase in dimensions cannot occur along the crosslinking bridges, since in this direction the swelling of one pore will interfere with that of its neighbour, so that the swelling is, essentially, two-dimensional only. The swelling thus produces a layer of water of a constant mean thickness t. A simple pore of dimension d along a chain will then provide a swelling volume of td^2. If this pore is divided into n sections because of junctions to other chains, the swelling volume will be n times $t(d/n)^2$ or td^2/n. Therefore, for a length $d = (100 + X)e$ equalling that of $100 + X$ ethylene groups of length e, divided into $2X$ sections, the pore volume becomes $te^2(100 + X)^2/2X$. This volume contains $100 + X$ benzene rings, hence also this number of functional groups, so that the pore volume per equivalent of resin is $N_A te^2(100 + X)/2X$, where N_A is Avogadro's number. Dividing by the molar volume of water v_w^0 yields

$$\bar{n}_w \text{ (pores)} = (N_A te^2/2v_w^0)(100 + X)/X = b(100 + X)/X \tag{2}$$

the number of moles of "free" water per equivalent of resin. This has the correct functional dependence on the crosslinking X, when compared with the empirical eqn. 1. The parameter b is seen to equal $N_A te^2/2v_w^0$. The molar volume of liquid water can be utilized in this expression, since the "free" water in the pores is not subject to electrostriction. (The parameter a should take account of this, together with the solvation). Since the dimension e of an ethylene group is known ($ca.$ 0.25 nm), the thickness t of the water layer is given by:

$$t = (2v_w^0/N_A e^2)b \approx 1.0\, b \text{ nm} \tag{3}$$

A comparison with the values of b in Table II shows this to be the right order of magnitude for t.

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