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Interrelation of Swelling and Selectivity of Ion-Exchange Resins. I. Determination of Swelling of Sulfonic Resins in Water

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Abstract

The volume of wet ES 28 and C 25 sulfonic ion exchange resin beads was determined by pycnometry for the H^+, Na^+, and K^+ fo.ms in water, and the relative volume variations were determined by precisely measuring the variations of the bed height in columns when the resins were converted from one ionic form to another. A straightforward correlation was found for the ES 28 resin for which the packing factor β remains sufficiently constant with double-sieved, sufficiently homogeneously dispersed beads. The variations of β have to be taken into account for C 25.

INTRODUCTION

Ion exchangers have been approximated by several independent models (*1*). In order to predict their selectivity, they can be tested, for example, by the Rice and Harris model (*2*) in which the selectivity is determined by the differences in the stability of the ion-pairs between the functional group and the counterion, and the swelling is a consequence of the resulting electrostatic forces. The selectivity should be then quantitatively reflected by the variations of the volume $\bar{V}_R$ of the resin beads containing one equivalent of utilizable capacity C_M', including the matrix and the swelling water or solution.

In this report we first deal with the problems involved in determining the absolute value of $\bar{V}_R$ or its relative variations when the ionic form of the resin or the external concentration of the solution is changed.

This study can also be justified by the importance of the calculation of the heights of the theoretical plate in analytical or industrial applications of the packing factor β, or of the variations in the height of the column during the exchange.

Pycnometric Determinations

The absolute value of $\bar{V}_R$ can be obtained by several techniques including the photographing of spherical beads and the pycnometric determination of bead volumes. When the equilibrium solution is not water, a water-immiscible solvent is necessary in the pycnometer unless the resin content of all the diffusible species (anions, cations, and water) is independently determined.

A good part of the difficulty lies in obtaining a correct wet sample because of the excess water or solution retained by the beads or the film adhering to them.

It is also hard to evaluate the error which this film contributes to the measurement. Only repetitive, well-standardized measurements can give significant and well-reproducible results. For these and other reasons we have limited the pycnometric (absolute) determinations to resins in equilibrium with water $(\bar{V}_R)_{c=0}$. Using all the precautions described in the Experimental section, this was done for the different monovalent ionic forms of the resins to give $(\bar{V}_R)_{c=0}$ values related to the water content (T), the utilizable capacity (C_M') (meq/g), and the density ($\bar{\mu}_R$) (cm^3/g) of the resin phase:

$$(\bar{V}_R)_{c=0} = \frac{10^3(1 + T)}{\bar{\mu}_R C_M'} \tag{1}$$

By choosing the hydrogen form in contact with pure water as a reference state represented by $(\bar{V}_R)_0$, the different $(\bar{V}_R)_{c=0}/(\bar{V}_R)_0$ ratios calculated represent the relative variations of the swelling when the resin is changed in water from an ionic form to another form.

The Bed Height in a Calibrated Column

Independently, and as shown in this report, the relative variations in swelling can also be determined without separating the beads from the water by measuring with a cathetometer the variations of the height (h) of a bed of calibrated spherical beads of total capacity c' enclosed in a cylindrical column of constant cross-section S. h and $\bar{V}_R$ are linked by the relation

$$\bar{V}_R = \frac{(1 - 0.01\beta)hS}{10^{-3}c'} \tag{2}$$

In the simplest case, if H_0 is the bed height in the hydrogen form, h is the bed height in another form, and if the packing coefficient β remains constant, we obtain

$$h/H_0 = (\bar{V}_R)_{c=0}/(\bar{V}_R)_0 \tag{3}$$

Confrontation of the Two Techniques

By comparing the pycnometric and column measurements, one can come to a conclusion on the utilizability of the column technique, which ordinarily is used only qualitatively.

EXPERIMENTAL

Characteristics of the Samples Used

The ion exchangers chosen for these tests were two samples of sulfonic resins. They are both commercial and have chemically similar matrices (polystyrene framework cross-linked with divinylbenzene). One of them, Duolite C 25 resin, has a nominal degree of cross-linking of about 5%; the other, Duolite ES 28 experimental resin, has a nominal degree of cross-linking of 8% and is prepared by low temperature chlorosulfonation.

The resins were both submitted to a series of exchange cycles in different ionic forms in order to remove impurities.

Both C 25 and ES 28 resin samples studied were formed of spherical beads with size distributions ranging from 0.4 to 1.0 mm in diameter in the hydrogen form.

First Sieving: In Hydrogen Form in Water (State I). The largest fraction corresponded with our calibrated sieves to beads varying from 0.63 to 0.80 mm in diameter. This is the fraction that we used in the following.

Second Sieving: In K^+ Form in 3 M *KCl (State II).* The conversion from State I to State II corresponds to a deswelling of 23.2% for the ES 28 and of 29% for the C 25 resin. A second sieving of the same fraction with the same sieve previously used eliminates the smallest beads of the fraction, thus giving, upon returning to State I, the limiting diameters 0.68 to 0.80 mm for ES 28 and 0.71 to 0.80 mm for C 25.

Pycnometric Determination of $\bar{V}_R$

$\bar{V}_R$ was calculated from Eq. (1).

The wet sample was obtained by a technique that has already been used by Bourgeois (*3*) in our laboratory and that can be reproduced with only a 1 % error. In order to separate the resin beads from the equilibrium solution, the mixture is introduced in to a high porosity sintered glass filter funnel covered by a damp cloth and placed on a vacuum filter vial connected to a mercury manometer and a pump. When suction is established the pressure in the vial quickly attains a constant value (15 to 20 mm of mercury) and then increases abruptly. We believe that this pressure increase corresponds to the elimination of the supernatant and the intergranular liquid, so a sample of wet resin is taken *at the beginning of the pressure increase.* The damp cloth wets the air circulating between the beads after the pressure increase, and thus avoids evaporation of the swelling water if the air is too dry. The wet sample obtained in this way is then weighed (m_w), dried in a vacuum oven for 2 days and weighed again (m_d), and T is calculated using $T = m_w/m_d$. The dry weight can also be obtained by the very reproducible "isotherm drying" under gas flow (*4*).

The density of the resin phase $\bar{\mu}_R$ is determined in a specific gravity bottle at 25°C from a sample of wet resin taken during the drying process.

The capacity is determined by the usual titration method.

Determination of the Relative Variations in $\bar{V}_R$

Measurement of the Height of the Resin Bed h. The column used is a glass one, closed at the bottom by a high-porosity sintered glass in order not to slow down the liquid which circulates at about 200 cm^3/hr. A siphon device is used to maintain the level of the liquid in the column. For practical reasons (resin quantity) we use columns of about 2 cm in diameter (a large one, of course, in comparison with that of the resin beads). We introduce enough resin so $H_0 \neq 150$ mm and thus reduce the relative uncertainty in the measurements of h. These are performed with a cathetometer at the interface between the supernatant liquid and the resin bed. They are carried out at ambient temperature.

Determination of the Packing Coefficient at Zero External Concentration. Let v be the volume of the resin bed of height h, cross-section S, and $\bar{v}_R$ the volume of the corresponding resin phase of density $\bar{\mu}_R$ and total wet weight m_s. β is linked to these variables by

$$\beta = (1 - \bar{v}_R/v)100 = (1 - (m_s/\bar{\mu}_R)/hS)100 \qquad (4)$$

RESULTS

With heterogeneously dispersed (unsieved) resin beads (diameters between 0.4 and 1 mm), the column technique has shown poor reliability. Hysteresis cycles, which depend on successive ionic forms and the solution concentration, have been observed.

With double-sieved ES 28 samples (0.68 to 0.80 mm bead diameter), h values could be reproduced systematically to within less than 0.5 mm for all ionic forms, and the ratio h/H_0 is independent of the geometrical characteristics of the resin bed (Table 1). Small hysteresis cycles have been always observed with double-sieved C 25 samples.

The packing coefficient β (Table 2) of double-sieved ES 28 resin is shown to be nearly constant within the limits of accuracy (1 to 2%) of v and $\bar{\mu}_R$ determinations. For the less cross-linked C 25 resin, there are increases

TABLE 1

Reproducibility of h Measurements for a Double-Sieved ES 28 Resin Sample for Different States in Water and as a Function of the Geometrical Characteristics of the Resin Bed

Series No.:	1		2		3	
Cross-section S of the column (cm^2):	3.12		3.15		3.06	
Ionic form	h (mm)	h/H_0	h (mm)	h/H_0	h (mm)	h/H_0
H^+	153	1	100.5	1	66	1
Na^+	140	0.91_5	91	0.90_5	59.5	0.90_2
K^+	133	0.86_9	87	0.86_6	57	0.86_3

TABLE 2

Determination of the Packing Coefficient β Relative to Double-Sieved Samples of C 25 and ES 28 Resins for Different Monovalent Ionic Forms at Zero External Concentration

Resin	Ionic form	v (cm^3)	v_R (cm^3)	β
C 25	H^+	10.7	7.30	31.8
	Na^+	9.4	6.17	34.3
	K^+	12.1	7.57	37.4
ES 28	H^+	11.4	7.58	33.5
	Li^+	12.6	8.40	33.3
	Na^+	9.7	6.42	33.7
	K^+	13.0	8.80	32.3
	NH_4^+	11.9	7.94	33.2

TABLE 3

Comparison of the Pycnometric Method and the Bed Height Determination for C 25 and ES 28 Resins at Zero External Concentration and for Different Monovalent Ionic Forms

Resin:	C 25			ES 28			
Ionic form:	H^+	Na^+	K^+	H^+	Li^+	Na^+	K^+
Pycnometric method							
C_M' (meq/g)	5.10	4.58	4.27	5.00	4.86	4.51	4.21
T	1.78_0	1.37_0	1.05_5	1.23_6	1.16_4	0.97_3	0.81_9
μ_R (g/cm^3)	1.11_0	1.21_1	1.26_0	1.19_2	1.20_6	1.26_1	1.28_4
$(\bar{V}_R)_{c=0}$ (cm^3)[a]	473	428	384	375	370	347	338
Bed height							
$h_{c=0}$ (mm)	168	156	146	153	152	140	133
$(\bar{V}_R)_{c=0}$ (cm^3)[b]	481	431	384	379	378	346	336
$(\bar{V}_R/h)_{c=0}$ (cm^2)[c]	28.2	27.4	26.4	24.5	24.4	24.8	25.4

[a] $(\bar{V}_R)_{c=0}$ was calculated using Eq. (1).

[b] $(\bar{V}_R)_{c=0}$ was calculated using Eq. (2).

[c] $(\bar{V}_R/h)_{c=0}$ is the ratio between $(\bar{V}_R)_{c=0}$ taken from the pycnometric method and h, the bed height of a constant amount of resin in the specified forms; modifications of this ratio reflect those of the value.

when the swelling decreases, but all values remain between the limits of 30.4 and 39.6 reported by Manalo (*5*) for a series of commercial resins; for ES 28 they also remain very close to the theoretical value of beds constituted with spherical beads.

In Table 3 the pycnometric and bed-height determinations in water are given and compared to a few ionic forms of the resins. For ES 28 resin there is a practically constant ratio between $(\bar{V}_R)_{c=0}$ (pycnometric method) and h, and thus Eq. (3) can also be used as a fairly good approximation. For C 25 resin, because of the variations of β (Table 2), Eq. (2) should be used. This difference is probably due to anisotropic deformations of the less cross-linked C 25 resin.

CONCLUSIONS

Swelling determinations carried out on C 25 and ES 28 resins have enabled us to establish good conditions under which the bed height technique can be applied without corrections (Eq. 3). The resin sample should fulfill the following criteria (satisfied by ES 28):

1. Be used in spherical bead form. Although we have not studied different cases, the spherical form of the beads surely allows more homogeneous packing.

2. ***Be homogeneously dispersed.*** For fairly large-sized resin beads (0.1 to 1 mm), the double-sieving technique, which is dependent on the swelling properties of the ion-exchanger resin, suffices.

3. *Present isotropic swelling deformations of the beads.* That is, have a constant packing factor. This criterion depends on the nature of the beads.

Anisotropic swelling deformation of the matrix can modify the packing of the column, and the corresponding corrections are no longer negligible (use of Eq. 2). The measurements of h obtained with C 25 resin show that this phenomenon also introduces an additional error in these values. Thus it seems possible to use the absolute uncertainty of h to detect deformations in the matrix.

For a resin sample that satisfies the first two conditions and provides h measurements that can be reproduced with good precision, this technique can be considered as quantitative. It was used to study the swelling variations of sulfonic and carboxylic resins (*6*, *7*).

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