A Note on the Characterization of the Network Structure of the Ion-exchange Resin

By Manabu SENŌ and Takeo YAMABE

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The ion-exchange resin is a crosslinked polyelectrolyte,* and the degree of crosslinking is usually designated in terms of the nominal content (weight percent) of divinylbenzene in the monomer mixture. It may be very desirable to describe the degree of crosslinking by a well-defined parameter based on the structural analysis, because it is one of the most important factors in determining the ion-exchange behavior of the resin. It is the purpose of this paper to propose a parameter, M_c, the mean molecular weight per crosslinked unit, for the characterization of the network structure of the ion-exchange resin, and to provide some information on the pore size of the resin.

The degree of crosslinking has a most remarkable effect on the swelling behavior of the resin. Unfortunately, the theory of the swelling of the network of the polyelectrolyte is not established, in spite of great efforts.[1] On the other hand, the theory of the swelling of the neutral crosslinked polymer has been demonstrated by Flory[2] and many experimental investigations have proved its validity. The final expression is:

$$-[\ln(1-v_{2m})+v_{2m}+\chi_1 v_{2m}^2] = (v_1/\bar{v}M_c)(1-2M_c/M)(v_{2m}^{1/3}-v_{2m}/2)$$

where v_{2m}, the volume fraction of the solute at the swelling equilibrium; χ_1, a parameter expressing the first-neighbor-interaction free energy, divided by kT, for the solvent with a polymer; v_1 the molar volume of the solvent; $\bar{v}$, the specific volume of polymer, and M, the molecular weight of a structural unit. The volume ratio of swelling, q_v, is defined by;

$$q_v = 1/v_{2m}$$
$$=(\text{swollen volume})/(\text{unswollen volume})$$
$$=1+\frac{\rho_2}{\rho_1}q_w-\frac{\rho_2}{\rho_1}$$

where ρ_1 is the density of the pure solvent, ρ_2. is the density of the polymer in a solution**, and q_w is the weight ratio of the swelling.

Therefore, a characteristic parameter, M_c, of the polymer network can be obtained by the

* Most of the ion-exchange resin available commercially is prepared by the sulfonation or by the chloromethylation, followed by the amination, of the base resin of poly(styrene-divinylbenzene).

1) A. Katchalsky and I. Michaell, *J. Polymer Sci.*, **15**, 69 (1955).

2) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, New York (1953), p. 576.

** This is calculated from the density, ρ_{12}, of a polymer solution by:

$$\rho_2=(1/q_w\rho_1\rho_{12})/\{\rho_1-\rho_{12}(1-1/q_w)\}$$

TABLE I. STRUCTURAL CHARACTERIZATION OF MATRICES OF ION-EXCHANGE RESINS

DVB nominal wt.%	Weight ratio of swelling q_w	Volume ratio of swelling q_v	M_c	n	d, Å
0.05	13.9	15.5	81800	786	6460
0.1	8.8	9.7	35500	341	1070
0.5	4.9	5.37	10200	98	315
1.0	4.1	4.36	5000	48.4	160
2.0	3.05	3.30	2630	25.3	89
4.0	2.25	2.45	1350	13.1	51.3
6.0	1.84	1.93	722	6.96	32.2
8.0	1.70	1.79	432	4.15	23.5
10.0	1.58	1.65	324	3.11	20.3
15.0	1.42	1.47	210	2.02	16.9
20.0	1.34	1.38	165	1.57	15.5

measurement of the swelling ratio of the uncharged matrix of the resin. This is a useful parameter for the theoretical consideration of the ion-exchange behavior, if the introduction of the ion-exchange groups into the resin matrix does not have any appreciable effect on the crosslinked structure of the resin.

The experimental procedure is as follows. The copolymer of styrene and divinylbenzene was prepared with benzoyl peroxide as a catalyst, by the block polymerization in the closed tubes. After purification by means of complete drying in vacuo, the polymer was cut into cylindrical rods, about 5 mm. high and 8 mm. in diameter. The weight ratio of the swelling in toluene was measured by weighing of the rods in dry and swelling-equilibrium states.

The results are shown in Table I. This value agrees well with that cited by Kressman and Millar.[3] From this, the volume ratio of the swelling and the mean molecular weight per crosslinked unit are obtained by the use of the above equations. For this, the following figures are used:

$$\rho_1=0.8716, \quad \rho_2=0.978 \ (20°C)$$

$$\bar{v}=0.952, \quad v_1=105.6, \quad \chi_1=0.38^{4)}$$

The results obtained are shown in Table I. In the same table, the mean number of styrene units per crosslinked unit, n, and the mean (maximum) pore diameter in a full-expanded state, $d=\sqrt{2}\,(2.2n+7.5)$, are also given. The latter value is in accord with Grubhofer's estimation[5] by means of a structural model consideration.

The commercial ion-exchange resins of the nominal 8% divinylbenzene are considered to have the mean available pore size of 30 Å.[6] This value is larger than the present value of 24 Å. This disagreement is probable due to the fact that the usually accepted value is based on the observations of large-ion exchange, dye adsorption and so on; therefore, the larger pores are overcounted than the smaller ones.

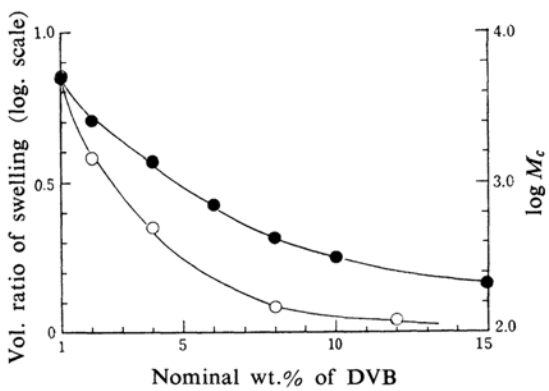

Fig. 1. The volume ratio of the swelling of ion-exchange resins (Dowex 50W, Na-form) in pure water and log M_c–DVB nominal content diagram.
-○- q_v of Dowex 50W, 20°C
-●- log M_c–DVB content

In Fig. 1, the volume ratio of the swelling of the commercially available ion-exchange resin (Dowex 50W, Na-form) in pure water[7] is shown. The ion-exchange resin with a completely dissociated counterion is in a fairly extended state. The details of this will be discussed in a separate paper.

The Institute of Industrial Science
The University of Tokyo
Azabu, Tokyo

3) T. R. E. Kressman and J. R. Millar, *Chem. & Ind.*, **1961**, 1833.
4) C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 677 (1950).
5) N. Grubhofer, *Makromol. Chem.*, **30**, 96 (1959).
6) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York (1962), p. 132.
7) M. Senō and T. Yamabe, unpublished; C. Calmon, *Anal. Chem.*, **24**, 1456 (1952); **25**, 490 (1953).