Macroreticular Phenolic Cationites

N. L. N. Sarma[a]; Padma Vasudevan[a]

[a] Department of Chemistry, Indian Institute of Technology, New Delhi, India

PLEASE SCROLL DOWN FOR ARTICLE

Macroreticular Phenolic Cationites

N. L. N. SARMA and PADMA VASUDEVAN

Department of Chemistry
Indian Institute of Technology
New Delhi 110 029, India

ABSTRACT

Macroreticular cation exchangers can be prepared by polymeriz-
ing sulfonated phenols with formaldehyde under acidic conditions.
The resins are highly porous with large surface areas. Their
properties compare well with those based on styrene and
divinylbenzene copolymers.

INTRODUCTION

It is well known that macroreticular ion exchangers have some
advantages due to their characteristic porous structure permitting
operation under severe physical and chemical stresses. Most of
the resins of this type reported in the literature [1] are based on
styrene-divinylbenzene (DVB) copolymers which are hydrophobic,
in addition to macroreticular hydrophilic resins derived from hydroxy-
alkylmethyl acrylates [2] and others. Although ionites based on
phenol-formaldehydes are one of the earliest known ion exchangers,
not much work is available on the porosity of such resins. Vasudevan
et al. [3] reported preparation of macroreticular structures based
on phenol-formaldehydes condensed with highly porous materials
such as sulfonated coals. During the course of these investigations,

it was found that not only the composites but also the pure resins were porous. It was of interest to extend these investigations and establish the optimum conditions under which macroreticularity is obtained in the phenolics. In this paper the preparation and properties of such resins are reported.

EXPERIMENTAL

Preparation of Phenol-Formaldehyde Resins

Sample P-I was prepared by sulfonating 10 g of phenol (BDH reagent) with 12.5 ml of concentrated sulfuric acid (specific gravity 1.82), heating on a water bath for 1 hr, and polymerizing with 11.0 ml of 37% formalin (BDH reagent). The contents were heated for 6 hr, and the resinous mass was washed free of acid and cured at 70°C for several hours. Sample P-II was prepared in the same way as P-I but with addition of 5 g more of unsulfonated phenol along with formaldehyde before polymerizing. Sample P-III was prepared by neutralizing phenolsulfonic acid by addition of NaOH solution till the mixture was at pH ~ 8 and finally polymerizing with formaldehyde. Sample P-IV was prepared in the same way as P-III but with addition of 5 g of unsulfonated phenol in excess before adding alkali to the phenolsulfonic acid. The composite cationite SP was prepared by diluting phenol-sulfonic acid with 25 ml of water to keep the spent acid concentration at 13 $\underline{N}$ and treating with 5 g of sawdust. The mixture was finally polymerized with formalin.

Characterization of the Samples

The same particle size distribution was obtained by sieving. The scientific weight capacity of the samples was determined by pH titrations and the degree of swelling by the gravimetric method. Infrared spectra were recorded on a Hilger-Watts H 800-03 spectrophotometer by scanning over the range 700-4000 cm^{-1} for samples with KBr as pellets. The thermograms of the resins were obtained by heating in a Stanton thermobalance.

Porosity Studies

The pore structure of the resins was examined by electron micrography. Pore volumes were determined by mercury porosimetry by using an Aminco porosimeter.

TABLE 1. Physical and Chemical Characteristics of the Ion Exchangers

Sample	Gravimetric swelling (%)	Density, (g/cc)		Capacity (meq/g)	DTG Peaks for all samples (°C)
		Apparent	Real		
P-I	200-250	0.78	1.43	1.8	130 (Dehydration)
P-II	50-150	1.35	1.60	2.0	325 (Desulfonation)
P-III	100-150	1.27	1.54	1.7	
P-IV	100-150	1.40	1.58	1.6	460, 550-75
SP	100-150	0.97	1.68	1.8	(Oxidative degradation)

Surface Area Measurements

Surface areas were determined by the BET-N_2 adsorption method at liquid nitrogen temperature and also by studying the adsorption (λ = 400 nm) of p-nitrophenol (PNP) from benzene solutions by using a Hilger-Watts SP-500 spectrophotometer.

RESULTS AND DISCUSSION

The important physical and chemical characteristics of the resins are shown in Table 1.

The particle diameters lie in the range 100-1000 μm. Comparison of the apparent and real densities indicate that the mass is porous. The swelling in water, of the order of 100-300% by weight may be attributed to water adsorption in the pores. However, the volumetric swelling is not high, indicating that the pores are of the nongel type. It may be noted that sample P-I polymerized under acidic conditions has the lowest density.

The results of investigations by mercury porosimeter and the surface area measurements by BET and PNP methods are given in Table 2. Figure 1 is a representative electromicrograph at a magnification of 40,000. It is observed that while all four resins have a total pore volume greater than 0.1 cm^3/g, P-I samples prepared under acidic conditions have the highest pore volume (0.6 cm^3/g). The pore radii of the samples are in the range of 10^2-10^4 Å.

TABLE 2. Porosity and Surface Areas of the Ion Exchangers

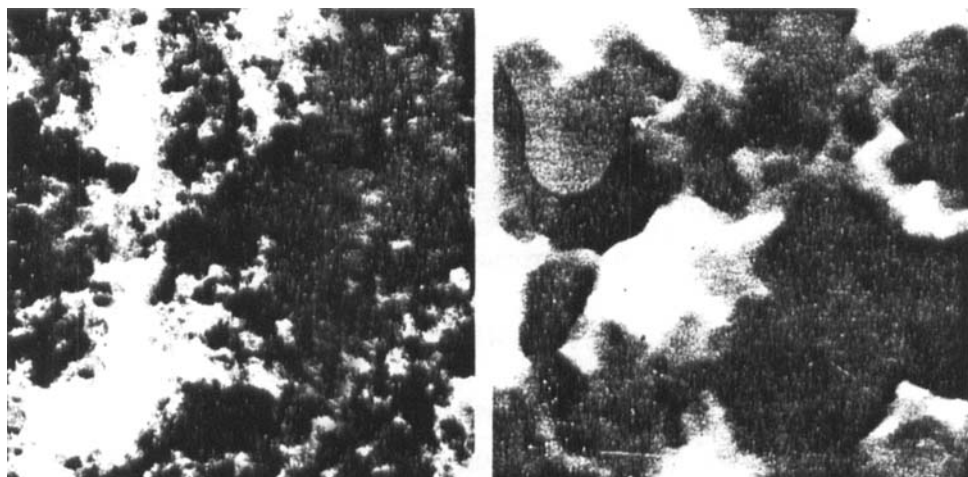| Sample	Total pore volume (cm^3/g)	Total porosity (%)	Surface area (m^2/g)	
			PNP method	BET method
P-I	0.58	45	126	92
P-II	0.12	16	71	15
P-III	0.14	17	41	16
P-IV	0.08	11	41	4
SP	0.44	43	-	-

FIG. 1. Electron micrographs of (a) sample P-I and (b) sample P-III. ×40,000.

Figure 2 is a representative BET plot for sample P-I. The measured surface areas for the samples are in the range of 1-100 m^2/g. Once again, the surface areas are in the order P-I > P-II > P-III > P-IV. Surface areas were also calculated by PNP adsorption on the hydrogen form of the resin, assuming surface occupancy of one molecule to be 52.5 $\mathring{A}^2$. Considering the approximations involved, these data (40-130 m^2/g) match very well the areas obtained by the BET method. Thus,
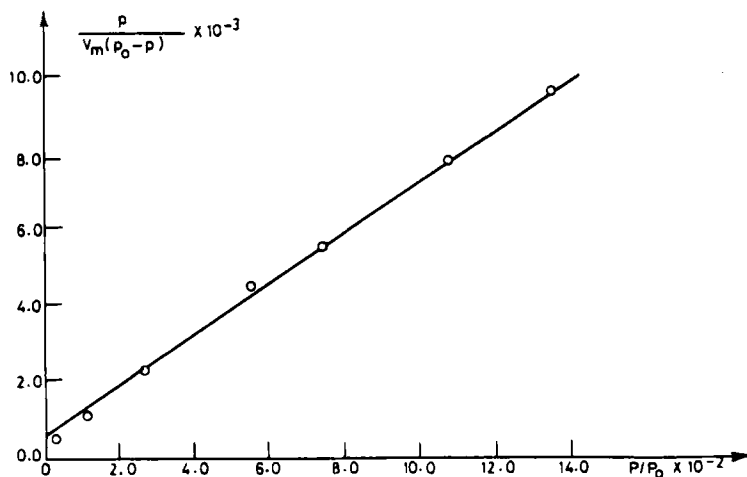
FIG. 2. BET plot for sample P-I.

for rough computations, it seems possible to use the PNP adsorption method as an index of sample surface areas. Giles et al. [4] also concluded that the technique is suitable for surface area measurements on ion-exchange resins with medium size pores.

CONCLUSIONS

Macroreticular structures can be obtained from phenol-formaldehydes having surface areas of the order of 50-100 m^2/g and total pore volumes as high as 0.6 cm^3/g. The pore diameters are in the range 10^2-10^4 Å. These values are comparable with the commercial macroreticular resins based on styrene-DVB copolymers. The porosity is found to be maximum if the resin is prepared with approximately equimolar quantities of sulfonated phenol and formaldehyde and if the polymerization is done in a highly acidic medium.

ACKNOWLEDGMENTS

REFERENCES

[1] R. Kunin, Ion Exchange in the Process Industries, Society of
     Chemical Industry, London, 1970.
[2] O. Mikes, P. Strop, I. Zbrozek, and J. Couper, J. Chromatogr.,
     119, 339 (1976).
[3] P. Vasudevan, S. Nanda, M. Singh, and N. L. N. Sarma, J. Polym.
     Sci., 16, 2545 (1978).
[4] C. H. Giles and A. P. D'Silva, Trans. Faraday Soc., 65, 1943
     (1969).