Styrene Furfural-Based Weak-Base Anion Exchanger

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Synopsis

A weak-base anion-exchange resin based on Styrene-furfural polymer has been prepared and characterized. A suitable composition to the repeating unit in the polymer has been proposed and supported by experimental evidences.

INTRODUCTION

Synthesis and characterization of cation exchange resins (sulfonic and phosphonic) based on styrene and furfural polymer have been reported in the literature.[1-3] However, details of anion exchange resins based on the same polymer have not been reported so far, and this paper describes the synthesis and characterization of a weak-base anion exchanger.

EXPERIMENTAL

Chloromethylation of Styrene Furfural Polymer

To 10 g of (−20 + 40 BSS) styrene furfural(1:1)polymer (1) in a two-necked round-bottom flask, about 50 ml chlorodimethyl ether was added, and the polymer was allowed to swell for 12 hr at room temperature. Anhydrous aluminium chloride, 10 g, was dissolved in 50 ml freshly distilled chlorodimethyl ether and added slowly to the flask cooled with ice water. Then the contents were mildly stirred for 24 hr at room temperature (~25°C). The polymer granules were then filtered, washed with 1:1 aqueous dioxane containing 10% v/v concentrated hydrochloric acid, and finally with distilled water till free of chloride. The chloromethylated granules were packed in a glass column provided with a sintered disc support, and commercial acetone was passed to remove any trapped chlorodimethyl ether and confirmed by colorless effluent. The granules were then dried at 60°C for about 3 hr and stored.

Estimation of Chlorine in the Chloromethylated Polymer

Dry chloromethylated polymer, 0.2 g, was digested with about 6 ml of chemically pure pyridine for 2 hr on a water bath, and the contents were then acidified with 25 ml of 1:1 glacial acetic acid and 6 ml of 1:1 nitric acid. The chloride content in the solution was estimated by Volhard's method.[4] A blank experiment was similarly carried out.

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Amination

Chloromethylated polymer (7.5% chlorine), 10 g, were swollen in 1:1 dioxane–water mixture for 12 hr and 50 ml diethylamine was added. The contents were kept mildly agitated for 12 hr at room temperature (~25°C). The granules were then filtered, washed with water, followed by 10% HCl, and finally with deionized water till free of chloride.

Conditioning

The aminated resin was conditioned to the free base form or amine hydrochloride form by following Kunin's standard procedure.[5]

Estimation of Nitrogen

The percentage of nitrogen in the aminated product was estimated by the Kjeldahl's method (4, page 256).

Capacity and Moisture

The ion exchange capacity and moisture content of the resin were determined by Kunin's method.[5]

pH Titration Curve

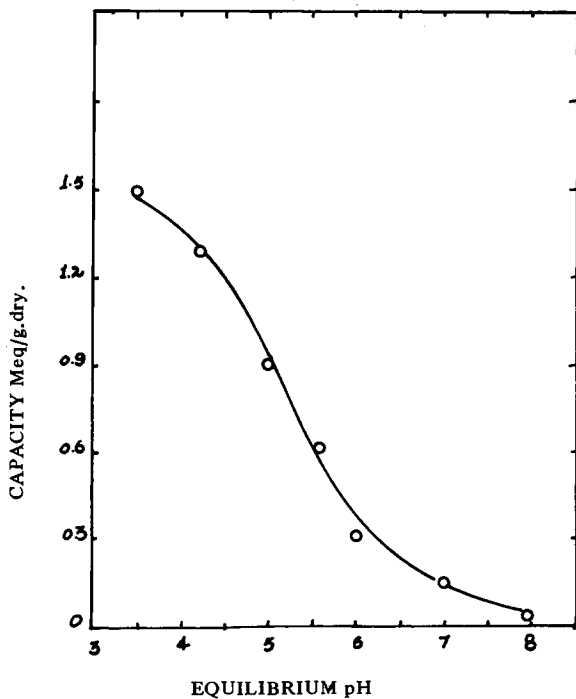The pH titration study was carried out by the standard procedure.[5]
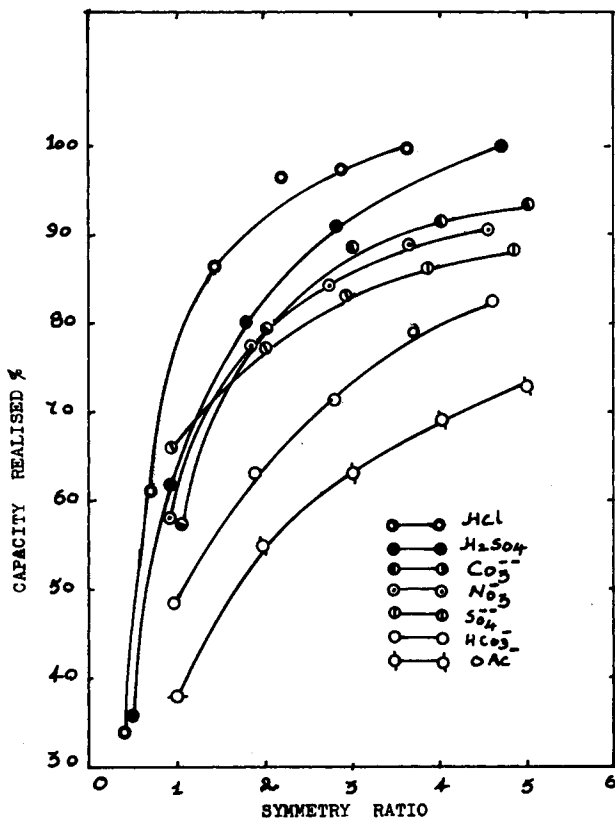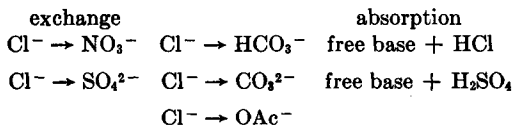

Fig. 1. pH Titration curve.

Fig. 2. Exchange/absorption curves.

Acid Absorption and Exchange Studies

Various exchange reactions were studied by equilibrating the resin in the chloride form with the appropriate solutions for 24 hr (a time found to be sufficient for attainment of equilibrium). The ratio of solid to liquid phase was kept constant at 1 g of resin for each 50 ml of solution. The extent of reaction was varied through a change in the concentration of the solution added. The concentration of the initial solution was varied from 0.005 to $0.1N$. The exchange reactions were followed by analysis of the Cl^- ion released by the resin into the solution. Acid absorption was followed by estimating the reduction in acidity. The following systems were studied:

exchange		absorption
$Cl^- \rightarrow NO_3^-$	$Cl^- \rightarrow HCO_3^-$	free base $+$ HCl
$Cl^- \rightarrow SO_4^{2-}$	$Cl^- \rightarrow CO_3^{2-}$	free base $+$ H_2SO_4
	$Cl^- \rightarrow OAc^-$	

RESULTS AND DISCUSSION

Table I contains the data on the percentage of chlorine, nitrogen, capacity and moisture content of the samples studied. The theoretical values of nitrogen and capacity as calculated on the basis of —SF— as the repeating unit in the

TABLE I
Chlorine, Nitrogen, Capacity, and Moisture Content of the Samples

| | Theoretical | | |
	a	b	Observed
Chlorine, %	14.29	7.5	—
Nitrogen, %	4.36	1.83	1.82
Capacity, meq/g dry	3.11	1.46	1.4–1.5
Moisture content, %			15–17

polymer are given under (a) in Table I, where —SF— represents a 1:1 mole ratio addition polymer of styrene and furfural. The theoretical nitrogen and capacity calculated on the basis of the observed chlorine content of 7.5% is given under (b) in Table I. The values obtained for nitrogen content and capacity agree with values under (b).

A perusal of the pH titration curve (Fig. 1) reveals that the resin exhibits typical weak base characteristics as other styrene divinylbenzene-based counterparts.

Kunin and Meyers[6] have reported a systematic study on the fundamental properties of certain anion exchangers. Properties studied and reported here such as anion exchange and acid absorption are on similar lines. The results of the exchange and absorption studies are graphically plotted (Fig. 2) according to the method of Jenny.[7] The percentage exchange/absorption is plotted against symmetry ratio. The symmetry ratio is defined as the ratio of equivalents of anion added as soluble electrolyte and the equivalents added as the exchangeable anion. This method of presentation permits one to compare the relative exchange potentials of the various anions.

An examination of Figure 2 reveals that the relative affinities for anions follow the sequence $CO_3^{2-} > NO_3^- > SO_4^{2-} > HCO_3^- > OAc^-$ for the Cl^- form of the resin. The free base form has shown more affinity toward HCl over H_2SO_4. Thus, the anion exchanger prepared can be used for the uptake of anions, and its operational efficiency increases with lowering the pH of the solution to be treated.

References

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