Sorption of Aromatic Compounds on Macroporous Anion Exchangers Based on Polyacrylamide: Relation Between Structure and Sorption Behavior

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SYNOPSIS

The sorption of phenol, p-toluenesulfonic acid (p-TSA), Na-p-toluenesulfonate (Na-p-TS), 1,2-dihydroxy-3,5-benzene disulfonic acid disodium salt (Tiron), and 3-hydroxy-4(sulfonaphthylazo)-5,7-naphthalenedisulfonic acid trisodium salt (Ponceau 4R) on the macroporous anion exchangers with acrylamide structural units (weak and strong basic anion exchangers) and on the ion exchangers with amidoxime groups were studied. The maximum specific sorption of p-TSA was almost identical with the total exchange capacity for both the weak and strong basic anion exchangers. The sorption of Na-p-TS is strongly related to the functional group structure of the anion exchangers, being significant on the strong basic anion exchangers. The maximum specific sorption of Tiron was higher than the total exchange capacity of the strong basic anion exchangers because it is mainly dependent on the ionic exchange properties. The morphological characteristics influenced only the establishment rate of the sorption equilibrium. The sorption of Ponceau 4R, which has the highest molecular weight, is important on the strong basic anion exchangers with high permanent porosity. The sorption of the organic anions is also dependent on the number of the sulfonic groups. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Organic pollutants (dyestuffs, organic anions, detergents, phenols, antibiotics, and so on) usually present in the industrial waste waters, should be removed even at low concentrations due to their high toxicity. Many researches dealt with the ability of polymer sorbents,[1-5] or ion exchangers[6-11] to remove these organic compounds. The anion exchangers derived from styrene-divinylbenzene (St-DVB) copolymers occupy a special place among the ion exchangers used in this field.[6,8,9] The macroporous anion exchangers allow the penetration of large molecules inside their network as well as an easier elution during the regeneration process. The investigations proved that the adsorption capacity is dependent not only on the number and the type of functional groups, but also on the chemical and physical structure of the macroporous matrix, and on the structure of the organic compound. The se-

lectivities for organic anions increase as the number of aromatic rings in the organic ion increases.[6]

The study of dyestuff adsorption and desorption is important both from the ecological point of view and for analytical purposes.[2,7,11]

The aim of this study was the synthesis of some macroporous anion exchangers with acrylamide structural units substituted with different functional groups, their characterization from the morphological and functional point of view, and the test of the adsorption properties for some organic compounds. Macroporous copolymers of acrylonitrile and divinylbenzene [P(AN-co-DVB)], synthesized in the presence either of toluene or of 2-ethyl-1-hexanol (2EH) as diluent, were used as precursors for these ion exchangers.

EXPERIMENTAL

Materials

Acrylonitrile (AN), technical grade, was distilled at 760 mmHg and the 76–77°C fraction was used. DVB, technical grade (50.25% DVB, 30.87% ethylstyrene,

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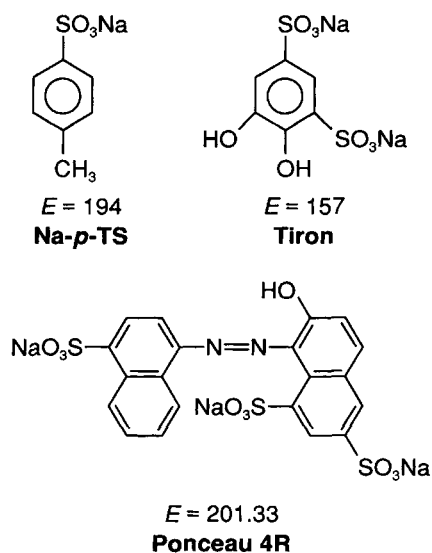
Scheme 1 The structure of aromatic compounds used as models for organic pollutants.

ESt, and 18.32% inert compounds, by gas chromatography), was distilled at 3 mmHg before use. After distillation the composition of DVB was 43.33% DVB, 35.52% ESt, 21.16% inert compounds.

2-Ethyl-1-hexanol (2-EH), technical grade, was distilled at 183.5°C and 760 mmHg before use. Toluene and dimethylformamide (DMF) were analytical grade reagents and were used without further purification.

N,N-Dimethyl-1,3-diaminopropane (DMDAP), technical grade, was distilled at low pressure before use. Benzyl chloride (BC), analytical grade reagent, was distilled at low pressure before use.

p-Toluenesulfonic acid (p-TSA); 1,1-dihydroxy-3,5-benzene disulfonic acid disodium salt (Tiron); and phenol, analytical grade reagents, were used without further purification. 3-Hydroxy-4(4-sulfonaphthylazo)-5,7-naphthalenedisulfonic acid trisodium salt (Ponceau 4R), commercial product with NaCl 40%, was used as received. The solution concentration was calculated taking into account the amount of the dye only.

The structural formulae of the aromatic compounds studied in this work are included in Scheme 1.

Na-p-toluenesulfonate (Na-p-TS) was obtained by neutralization of methanolic p-TSA by methanolic NaOH followed by recrystallization from methanol.

Methods

The syntheses of macroporous copolymers P(AN-co-DVB) were performed as before.[12] All copolymers

were extracted with DMF until PAN homopolymer was totally removed. After separation from DMF the copolymers were washed with methanol and then vacuum dried at 50°C, for 48 h.

The aminolysis–hydrolysis reaction of the nitrile groups with DMDAP was performed at 115°C for 15 h. The molar ratio of the cyano group DMDAP H₂O was 1 : 6 : 4. The anion exchanger beads were separated from the reaction medium by filtration and washing with distilled water to neutral pH, thus obtaining weak basic anion exchangers (WB).

The main reactions that take place in the synthesis of ion exchangers used in this work are presented in Scheme 2.

In order to obtain strong basic anion exchangers (SB), the ion exchangers with tertiary amine groups were washed many times with methanol and then dried at 50°C for 48 h. The reaction of the tertiary amine groups with BC was carried out in DMF as reaction medium at 60°C for 8 h. The molar ratio of the amino group/BC was of 1 : 2. After the separation of the reaction medium, the anion exchanger beads were washed with methanol to remove BC and then with distilled water.

The synthesis of the ion exchangers with amidoxime groups (AAO) was performed with a methanolic solution of hydroxylamine (HA) at 80°C for 2 h. The molar ratio of HA : CN was 2 : 1.

The anion exchangers were conditioned by alternate conversions to hydroxide and chloride forms with 4% NaOH and 4% HCl aqueous solutions. The WB as free base and the SB in chloride form were washed with distilled water until the complete removal of free OH⁻ and free Cl⁻ ions. The anion exchange capacity of the anion exchangers was deter-

Scheme 2
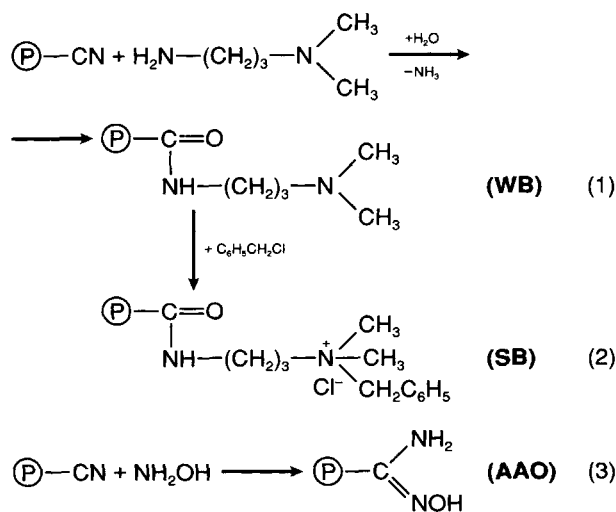
mined as before.[12] In order to test the adsorption properties, the samples were dried at room temperature for 5 days. The moisture content was determined by vacuum drying of samples at 40°C until constant weight was reached.

For the morphological characterization, the anion exchanger samples were rinsed several times with anhydrous ethanol. After filtration, the samples were left in isopropanol for 24 h. Finally they were rinsed 3–4 times with anhydrous methanol and dried in air at room temperature for 24 h. Then the samples were vacuum dried at 40°C for about 7 days. The solvent regain indexes (methanol and DMF for macroporous copolymers and water for anion exchangers) were determined by centrifuging the samples at 500 × g after immersion for 48 h in the appropriate solvent.

The apparent density (ρ_{ap}) was mercury pycnometer determined at 10^{-4} Torr and the specific density (ρ_{sp}) was measured in n-heptane.

The surface area was determined by nitrogen adsorption at the N_2 boiling temperature by the Haul–Dümbgen method,[13,14] on a Ströhlein Area Meter apparatus. The mean pore radius was calculated using the following equation:

$$\bar{r}_p = \frac{2 V_p}{S_{BET}} \times 10^3 \quad (nm)$$

(cylindrical shape of pores was assumed) were:

$$V_p = \frac{1}{\rho_{ap}} - \frac{1}{\rho_{sp}}, \quad \text{pore total volume, } cm^3/g.$$

The sorption of organic compounds was performed as follows: about 1 g anion exchanger was introduced into each of a series of flasks fitted with stirrers. Measured volumes of an aqueous solution of organic compounds with known concentration were added to each flask. The volume of solution was taken so that the amount of organic compound exceeded by 10–15% the exchange capacity of the resin. At known time intervals liquid samples were taken from vessels and the concentrations of organic compound retained by the anion exchanger resin was calculated as the difference between the initial amount of organic compound and that determined in the liquid layer after contact with the resin. Specific adsorption (x/m) was then calculated as the meq number of organic compound retained on 1 g of dried resin and plotted versus time. The concentrations of the organic compounds in solution were determined spectrophotometrically using a SPE-

Table I Morphological Characteristics of Macroporous Copolymers of Acrylonitrile (AN) and Divinylbenzene (DVB)

Sample	DVB (wt %)	AN (wt % Calc.)	Diluent	F_v^a (mL/mL)	Third Comonomer[b] Name	Third Comonomer[b] wt %	Methanol Uptake (g/g)	DMF Uptake (g/g)	Apparent Density (g/mL)	Porosity[c] (%)	Surface Area (m²/g)	Mean Pore Radius (Å)
100	15	72.7	2-EH	0.45	—	—	1.2628	2.4420	0.4613	58.44	36.80	688.52
101	15	67.7	2-EH	0.45	EA	5	1.1905	2.4117	0.4754	57.17	21.92	1097.20
102	15	62.7	2-EH	0.45	EA	10	1.1713	2.2917	0.4831	56.47	22.23	1051.80
103	15	67.7	2-EH	0.45	St	5	1.2300	2.2705	0.4690	57.75	30.58	805.28
104	15	72.7	Toluene	0.45	—	—	0.9539	2.0593	0.5589	49.65	42.39	419.12
105	15	72.7	Toluene	0.40	—	—	1.0989	1.9185	0.5929	46.58	46.41	338.59
106	15	72.7	Toluene	0.50	—	—	1.2307	2.5333	0.5480	50.63	50.76	364.03
U9	20	67.7	Toluene	0.47	—	—	—	—	0.5360	51.71	74.29	259.72

[a] $F_v = V_{diluent}/V_{monomers} + V_{diluent}$; F_v, volume fraction of diluent; 2-EH, 2-ethyl-1-hexanol.
[b] EA, Ethyl acrylate; St, Styrene.
[c] Porosity = $[1 - (\rho_{ap}/\rho_{sp})] \times 100$ where ρ_{sp} = specific density measured in n-heptane, average value = 1.110 g/mL.

Table II   Functional Characteristics of Weak (WB) and Strong (SB) Basic Anion Exchangers

Sample No.	Functional Group	Ionic Form	Total Exchange Capacity meq/mL	meq/g	Water Uptake (g/g)
100 WB	$-(CH_2)_3-N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	OH^-	0.573	2.63	1.6538
100 SB	$-(CH_2)_3-N^+\genfrac{}{}{0pt}{}{}{}-CH_3$, CH_3, $CH_2C_6H_5$	Cl^-	0.4105	1.7617	1.6925
102 WB	$-(CH_2)_3-N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	OH^-	0.490	2.348	1.6105
103 WB	$-(CH_2)_3-N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	OH^-	0.488	2.109	1.5377
103 SB	$-(CH_2)_3-N^+-CH_3$, CH_3, $CH_2C_6H_5$	Cl^-	0.336	1.484	1.4936
105 WB	$-(CH_2)_3-N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	OH^-	0.756	3.032	1.4367
105 SB	$-(CH_2)_3-N^+-CH_3$, CH_3, $CH_2C_6H_5$	Cl^-	0.494	2.073	1.6510
104 WB	$-(CH_2)_3-N\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$	OH^-	0.735	2.990	1.3125
104 SB	$-(CH_2)_3-N^+-CH_3$, CH_3, $CH_2C_6H_5$	Cl^-	0.553	2.041	1.4714

Table II (*Continued*)

Sample No.	Functional Group	Ionic Form	Total Exchange Capacity		Water Uptake (g/g)
			meq/mL	meq/g	
106 WB	—(CH$_2$)$_3$—N（CH$_3$ / \ CH$_3$）	OH$^-$	0.588	2.976	1.6200
106 SB	—(CH$_2$)$_3$—N$^+$—CH$_3$（CH$_3$ / \ CH$_2$C$_6$H$_5$）	Cl$^-$	0.532	1.883	1.2428
AAO 10^a	—C（NH$_2$ / \\ NOH）	—	1.012	3.710	1.4527

Sample numbers from Table I.
^{a} From U$_9$ copolymer (Table I).

CORD M42 spectrophotometer. The following wavelengths were used (standard 1 cm quartz cell): 261.5 nm (*p*-TSA and Na-*p*-TS); 291.5 nm (Tiron); 516 nm (Ponceau 4R); 269.5 nm (phenol).

RESULTS AND DISCUSSION

The morphological characteristics of various P(AN-*co*-DVB) copolymers are presented in Table I. The influence of the composition of the monomer mixture on the solvent uptakes, surface area, and mean pore radius can be seen from Table I. The introduction of the third comonomer (ethyl acrylate or St) led to a decrease of the surface area and a corresponding increase of the mean pore radius. The porosity and the mean pore radius are smaller when the copolymers were prepared with toluene as diluent comparative with copolymers prepared in the presence of 2EH at the same cross-linking degree (samples 100 and 104, Table I).

These differences might be explained by the thermodynamic quality of the diluents (i.e., the cohesive energy density of diluents and monomers) versus PAN or aromatic macromolecular chains. So, toluene is a "bad solvent" for PAN chains, and 2EH is a bad solvent both for PAN and aromatic macromolecular chains.

The aminolysis–hydrolysis reaction of the nitrile groups contained in P(AN-*co*-DVB) copolymers with *N,N*-dialkylaminoalkylamines in the presence of water could constitute a way to form WB with tertiary amine groups.[12] The tertiary amine groups can be transformed in ammonium quaternary salt groups by the reaction with alkyl halide according to Scheme 2.

The ion exchange characteristics of the WB and SB are included in Table II. The anion exchangers with the same cross-linking degree and different dilutions have similar total exchange capacities for the same diluent (104, 105, and 106 SB). However, the volumic exchange capacity decreases along with the increase of the dilution. The resins synthesized in the presence of toluene have a total exchange capacity higher than the resins prepared in the presence of 2EH for the same cross-linking degree. This difference could be explained by a better access of reactants to the nitrile groups in the case of the more flexible structures (when toluene was used as diluent).

The influence of the diluent and of the chemical transformations on the morphological characteristics of the anion exchangers can be followed in Table III.

In order to test the sorption properties of these ion exchangers the following organic compounds

Table III Morphological Characteristics of Some Anion Exchangers

Sample	Apparent Density (g/mL)	Specific Density (g/mL)	Porosity[a] (%)	V_p[b] (mL/g)	S_{sp} (m²/g)	Mean Pore Radius (Å)
100 WB	0.6021	1.0301	41.55	0.690	22.19	622
100 SB	0.7290	1.0424	30.06	0.412	8.26	998.6
103 WB	0.5451	1.0672	48.92	0.897	24.00	747.5
103 SB	0.7100	1.0810	34.32	0.483	14.61	661.7
104 WB	1.0285	1.0224	—	—	< 1.0	—
104 SB	0.9971	1.0540	5.39	0.054	10.38	104.3
106 WB	0.6313	1.0301	38.71	0.613	22.53	544.4
106 SB	0.7935	1.0425	23.88	0.301	12.48	482.4
AAO 10	0.6071	1.105	54.94	0.7422	45.00	329.8

Sample numbers and functional group from Table II.
[a] Porosity = $[1 - (\rho_{ap}/\rho_{sp})] \times 100$.
[b] Pore volume, $V_p, = (1/\rho_{ap}) - (1/\rho_{sp})$.

were used: p-TSA, Na-p-TS, two sulfonic dyes [different both by the molecular weight and by the number of sulfonic groups (Tiron and Ponceau 4R)] and phenol.

The results obtained for the sorption test of p-TSA are presented in Figure 1. The sorption depends mainly on the total exchange capacity of resins. The maximum specific adsorption of p-TSA was almost identical with the total exchange capacity for all the resins tested in our study.

The sorption equilibrium is quickly achieved in the case of 103 WB and 103 SB. We assume that the great permanent porosity of the matrix and a greater concentration of the aromatic unit content, given by the presence of St units, favor the sorption process.

The results obtained for the adsorption trials of Na-p-TS are presented in Figure 2. The SBs have a significant sorption capacity although the maximum specific adsorption is lower than the total ex-
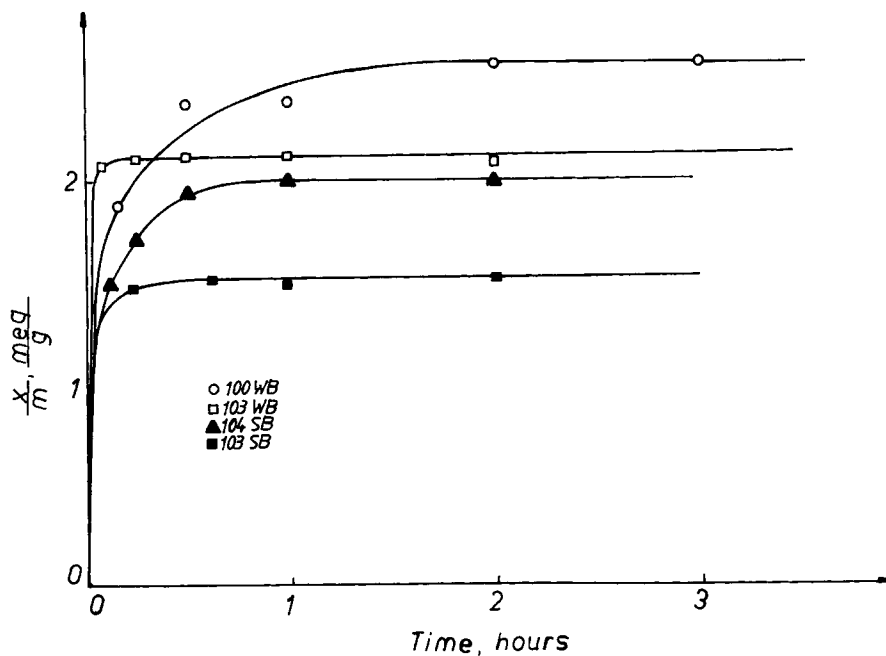

o 100 WB
□ 103 WB
▲ 104 SB
■ 103 SB

Figure 1 Sorption of p-TSA on anion exchangers.
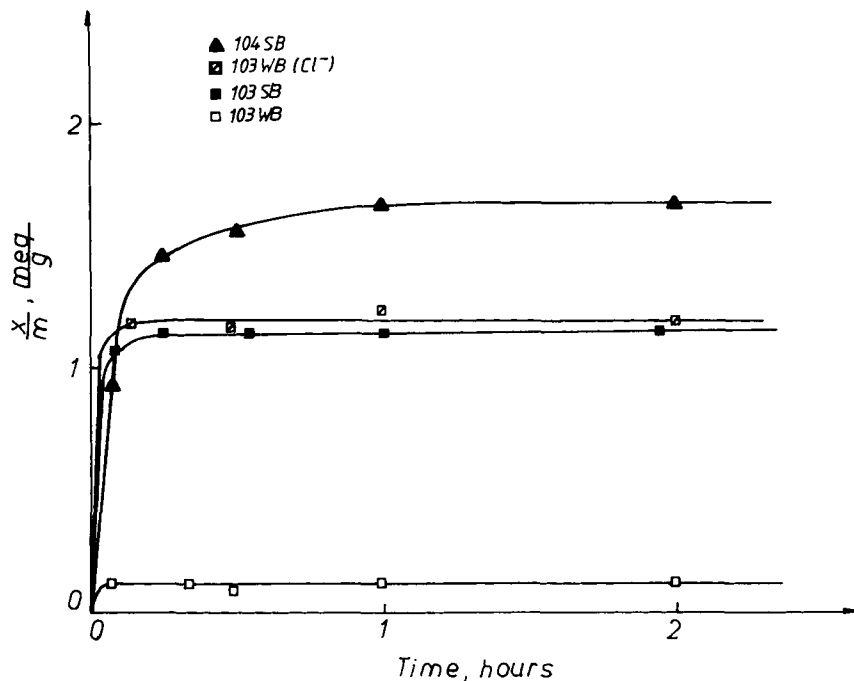
Figure 2   Sorption of Na-p-TS on anion exchangers.

change capacity. On the other hand, the WBs (103 WB for example), with free tertiary amine groups, show a weak sorption capacity, while the same anion exchangers in Cl^- form had a sorption capacity about 10 times higher. This is proof for a sorption by the ion exchange process only.
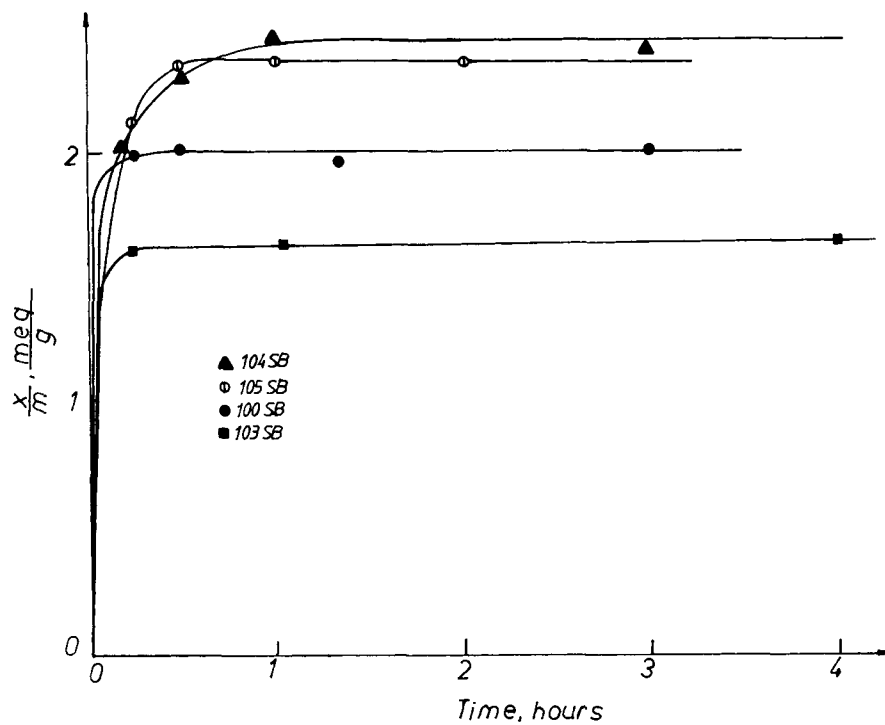

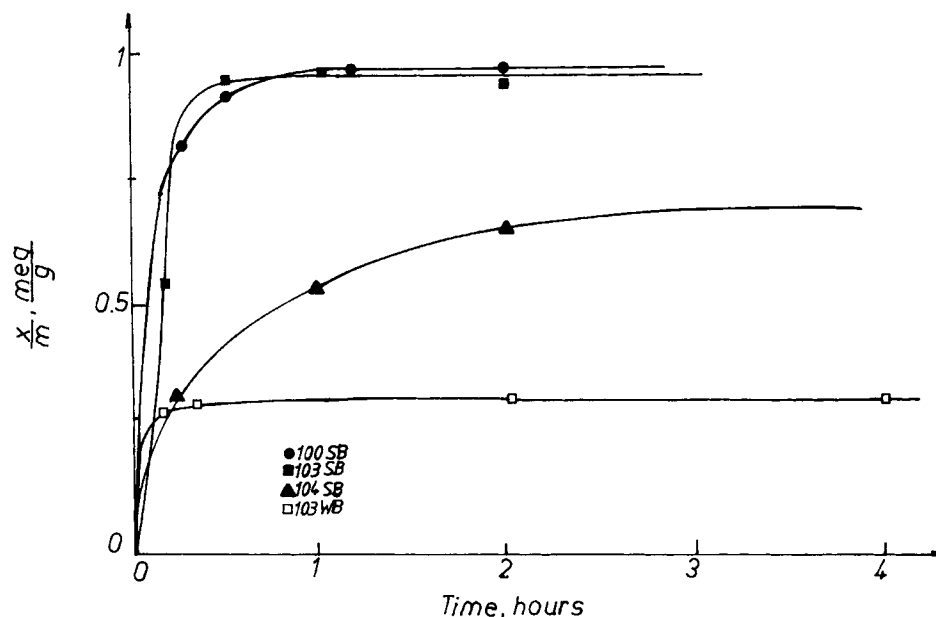**Figure 3**   Sorption of Tiron on strong basic anion exchangers.

Figure 4   Sorption of Ponceau 4R on anion exchangers.

The sorption trials of Tiron were made only on the SBs because the basic pH appearing in contact with the WB resins caused changes in the dye structure (Fig. 3). The degree of Tiron sorption is related mainly to the ion exchange capacity of the resins, but we assume that the structure of Tiron may also play an important role in the adsorption mechanism.

The maximum adsorption capacity was higher than the total exchange capacity for all the studied resins. The sorption equilibrium was also achieved quickly in the case of the anion exchangers with high permanent porosity (103 and 100 SB). However, the anion exchangers with the highest exchange capacity had the highest maximum specific adsorption. That means the sorption capacity for this dye is related more to the ionic exchange properties and less to the morphological characteristics. The maximum specific adsorption higher than the total exchange capacity could be explained by the presence of two sulfonic groups in the Tiron structure as well as by hydrophobic interactions that could take place between the molecules of Tiron.

The results obtained for the sorption of Ponceau 4R were included in Figure 4. The sorption of this dye depended both on the chemical structure of the functional groups of the resin and on its porosity. The total exchange capacity is less important in this case. The anion exchanger 104 SB, although having the highest exchange capacity among the SBs, showed the smallest sorption capacity. The sorption equilibrium is quickly reached when the resins have

a great porosity (100 and 103 SB). The influence of the sulfonic group number of the organic compounds on the maximum specific adsorption of the anion exchangers was resumed in Figure 5.

The maximum specific adsorption of Ponceau 4R on the WBs with free tertiary amine groups (103 WB) was much smaller than on the SBs with similar morphological characteristics (103 and 100 SB), but higher than for Na-p-TS. That means the sorption capacity of Ponceau 4R depends not only on the functional group structure but also on the number of sulfonic and aromatic groups of the dye. Although Ponceau 4R has a molecular weight much higher than Na-p-TS, the sorption of the former is higher than of the latter.

The synthesis of resins with high sorption capacity for Ponceau 4R (100 and 103 SB) was performed with 2EH as diluent, the mean pore radius of these resins being much higher than that of the resins obtained in the presence of toluene.

The adsorption capacity of the SBs (100 and 104 SB) for phenol is almost identical with their total exchange capacity, while that of the WBs (100 and 104 WB) is lower than their total exchange capacity (Fig. 6). The achievement of the sorption equilibrium depends on the anion exchanger porosity. As in the case of the other organic compounds, the sorption equilibrium is quickly reached in the case of the macroporous anion exchangers (100 WB and 100 SB). The results obtained for phenol proved a sorption capacity lower in the case of WBs compared
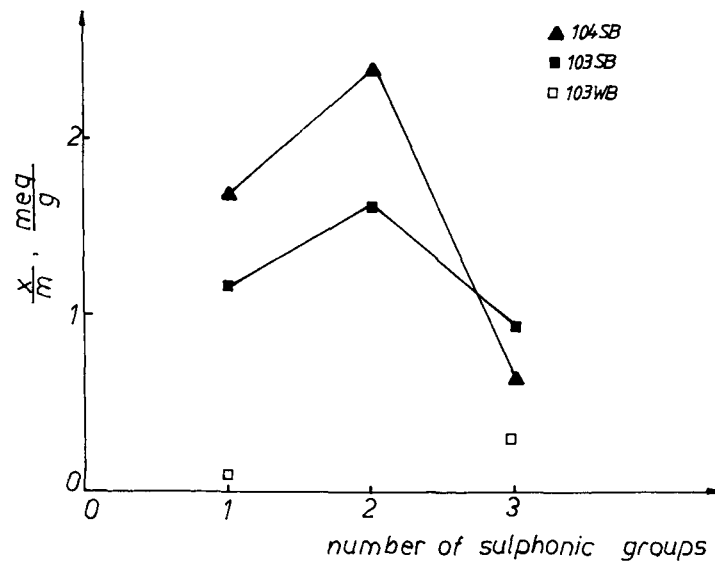
Figure 5   Influence of sulfonic group number of aromatic compounds on the sorption on anion exchangers: (1) sulfonic groups, Na-*p*-TS; (2) sulfonic groups, Tiron; (3) sulfonic groups, Ponceau 4R.

with the sorption results of *p*-TSA. These results led us to the conclusion that the sorption of the organic compounds with acid properties on the anion exchangers depends mainly on the strength of the organic anion.

The sorption trials of some organic compounds on the ion exchanger with amidoxime groups led to the results presented in Figure 7. As expected, the sorption of Ponceau 4R is small; this is due to both the much smaller mean pore radius than that of the
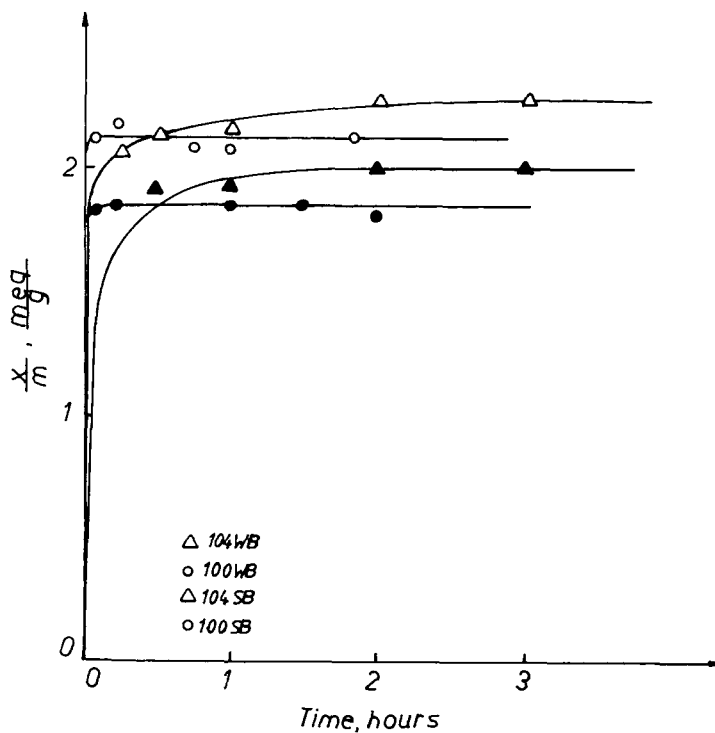

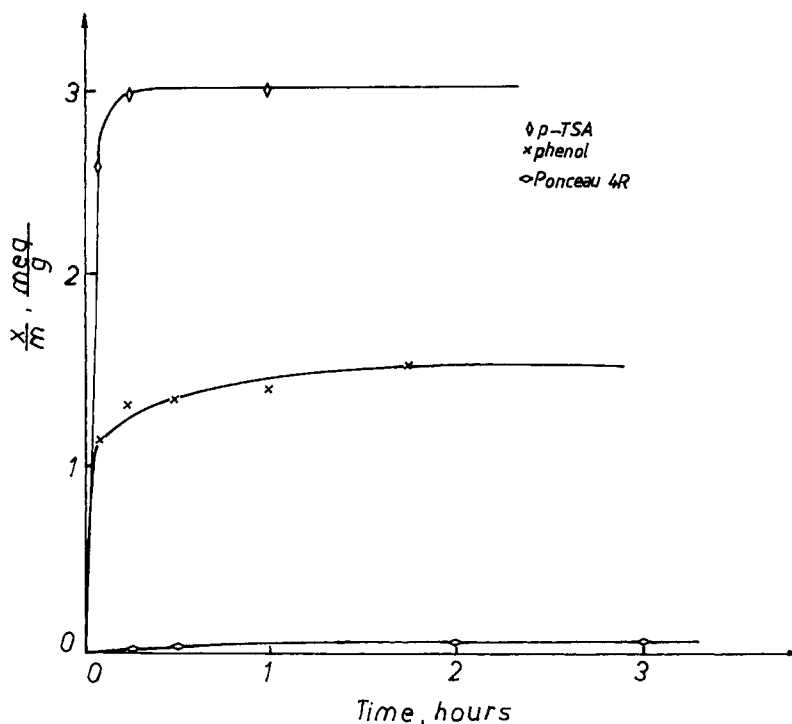**Figure 6**   Sorption of phenol on anion exchangers.

Figure 7   Sorption on anion exchanger, AA0-10.

anion exchangers with a cross-linking degree of 15% DVB and the structure of the functional groups.

CONCLUSIONS

The study of the sorption properties of the acrylic anion exchangers obtained by chemical reactions of the nitrile groups in macroporous P(AN-co-DVB) copolymers revealed some main aspects:

1. the maximum sorption activity is related to the functional group structure, the morphological characteristics of the resin, as well as the structure of the organic compound;

2. the sorption of small molecules is higher on the resins with expanded structure and the sorption of large compounds (Ponceau 4R) is better on the resins with high permanent porosity;

3. the establishment rate of the sorption equilibrium is mainly dependent on the porosity of the ion exchanger, even in the case of the small molecules; it seems the diffusion has a significant role in all these trials.

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