Sorption of Organic Compounds on Strong Basic Macroporous Anion Exchangers

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Synopsis

The behavior of various strong basic type II macroporous anion exchangers against the sorption of some organic acid alkaline salts as follows: natrium benzoate, natrium benzenesulfonate, potassium α-naphthylacetate, natrium β-naphthalenesulfonate, and natrium anthraquinone-2-sulfonate was established. The values of the sorption capacities depend on the morphology of anion exchanger network, the type and the size of organic anion, as well as the type of anion exchanger.

INTRODUCTION

In addition to their exchange properties, ion exchangers can be used as adsorbents owing to the pore structure of their networks.

Gel-type ion exchangers have the capability to remove organic compounds from solutions according to their porosity and the molecular weight of the substance, but elution during the regeneration is quite difficult and incomplete. On one hand, the macroporous-type anion exchangers allow large molecules of organic substances to penetrate inside their network, and on the other hand, to be easily eluted during regeneration.

The so-called "scavenger resins," a special type of anion exchange resins are used in: (1) the treatment of surface water to remove organic pollutants; and (2) the decolorization of various solutions of organic products such as sugar, glycerol, and gelatine.

Generally speaking, "scavenger" resins have a low ion exchange capacity but high adsorption.

The macroporous ion exchangers used in the demineralization systems work simultaneously as both ion exchangers and as scavenger resins.

Reports of many investigations refer to the sorption of the various organic substances; humic, fulvic, xanthic, lignosulfonic and fatty acids, detergents, phenols, quaternary ammonium salts, antibiotics, and so on by ion exchangers.[1-14]

Our studies deal with the aspects of the sorption of alkaline salts of some organic acids such as: natrium benzoate (NaB), natrium benzenesulfonate (NaBS), potassium α-naphthylacetate (KNA), natrium β-naphthalenesulfonate (NaNS),and natrium anthraquinone-2-sulfonate (NaAQS) on different anion exchangers used in the water demineralization processes.

Previously we studied the sorption of the above-mentioned organic compounds on several type I strong basic macroporous anion exchangers. In the

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present report the authors have intended to study the peculiarities of the sorption on type II strong basic macroporous anion exchangers.

It is well-known that such anion exchangers have higher operating capacity and improved regeneration efficiency than type I anion exchangers.

The anion exchangers used in this study were prepared using styrene-divinylbenzene (St-DVB) macroporous copolymers with various porosities.

EXPERIMENTAL

Materials

Synthesis of macroporous St-DVB copolymers was carried out by radical suspension copolymerization. DVB technical grade (55.44% DVB, 33.38% ethylstyrene, and 11.18% nonpolymerizable compounds) was used in all experiments.

The experimental parameters used during the copolymerization process as well as the other characteristics of the copolymers are given in Table I.

The amounts of DVB and the volumes of diluents were limited by technical reasons (in order to obtain anion exchangers with high physical stability and exchange capacity). The diluent removal was carried out by extraction with methanol.

The chloromethylated copolymers were prepared by reaction of the copolymers with chloromethyl methyl ether (CMME) in the presence of anhydrous $ZnCl_2$ (copolymer : CMME : $ZnCl_2$ molar ratio 1 : 6 : 0.5) at 50°C for 8 h.

The anion exchangers were obtained by reaction of chloromethylated copolymers with a 20% aqueous solution of amines such as: N,N-dimethyl-2-hydroxyethylamine or trimethylamine (1 : 2 —CH_2Cl : amine molar ratio) at 50°C for 8 h.

The organic compounds used in the sorption studies were of A.R. grade or synthesized and purified in laboratory.

Methods

Samples of anion exchangers were conditioned by alternate conversions to hydroxide and chloride forms with 4% aqueous NaOH or HCl solution. After the last conversion to the chloride form, the resins were washed with deionized water until complete removal of chloride ions. All samples were dried at room temperature for 5 days. The moisture content was determined as follows: 1–2 g of each sample were dried in vacuum at 40°C until the constant weight was reached. The total exchange capacity of resins was determined by the elution of Cl^- anions with 4% Na_2SO_4 aqueous solution after which the chloride ions were potentiometrically determined with 0.02 N $AgNO_3$ aqueous solution.

The sorption of organic substances was performed as follows: 1 g anion exchanger was introduced in a thermostatted flask at 25°C fitted with a stirrer. Then, measured volumes of aqueous solution of organic compound with known concentration were added to each flask. At specific intervals, the aliquot parts of solution were removed and the chloride ions and organic anions contents were determined. The amounts of adsorbed organic anions on anion exchangers were calculated as the difference between the initial amount

TABLE I
Parameters of the Copolymerization Processes and Some Characteristics of Macroporous Copolymers

Sample	DVB (%)	Diluent		ρ_{ap} g/cm^3	Pore volume mL/g	Regains, g/g	
		Type	Amount (f_o)[a]			Toluene	Cyclohexane
10 L	10	n-Heptane	0.40	0.3700	1.768	2.7807	2.2007
14 L	10	2-EHA[b]	0.40	0.8580	0.220	1.0880	0.3220
15 L	10	Gasoline[c]	0.40	0.9790	0.078	2.3600	0.1070
18 L	15	Gasoline[c]	0.40	0.5836	0.579	2.0226	1.0390
21 L	20	Gasoline[c]	0.40	0.5370	0.773	1.9809	1.5922
29 L	10	n-Heptane	0.55	0.7529	0.393	1.6341	0.9739
31 L	10	Gasoline[c]	0.55	0.9883	0.077	1.2462	0.0915

[a] Volume fraction.
[b] 2-Ethylhexanol.
[c] b.p. 110–130°C.

of organic compound and that determined on aliquot part after contact with resin. From the results the sorption capacity (x/m) as the mEq number of adsorbed organic compound on 1 g of vacuum dried resin was calculated. The values of x/m were plotted versus time.

The concentrations of solutions of organic compounds were determined spectrophotometrically using a Unicam SP-800 UV spectrophotometer. The following wavelengths were used (standard 1 cm quartz cell): 224.5 nm (NaB); 282.5 nm (KNA); 263.0 nm (NaBS); 320.5 nm (NaNS); and 330.5 nm (NaAQS).

RESULTS AND DISCUSSION

Table II gives the values of the total exchange capacities and water regains of anion exchangers used in this study.

TABLE II
Total Exchange Capacities and Water Regains of Anion Exchangers

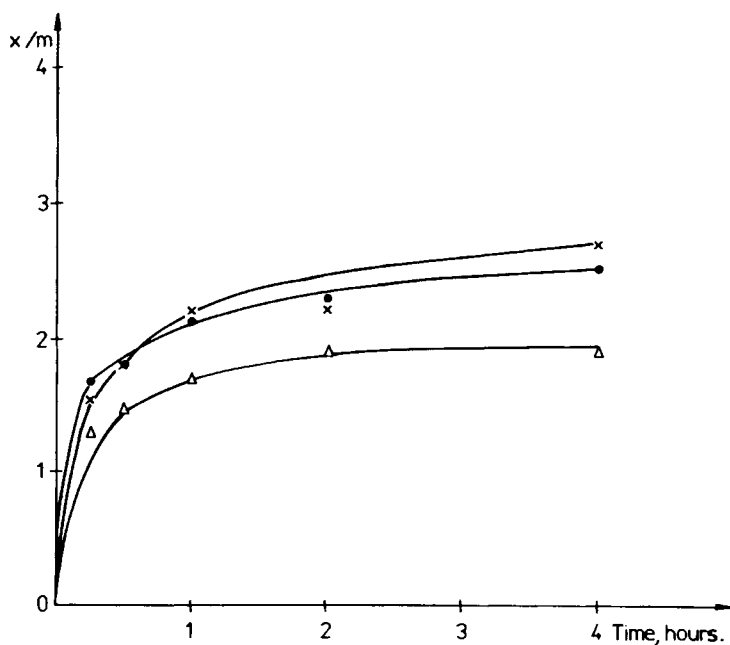| Sample	Total exchange capacity, mEq/g	Water regain, g/g
10 L type I	3.18	3.1123
10 L type II	3.10	1.2849
14 L type II	3.33	0.8473
15 L type I	3.19	2.0653
15 L type II	3.10	0.9777
18 L type II	2.91	0.8488
21 L type II	2.40	1.0967
29 L type II	3.32	0.8593
31 L type II	3.11	0.9190

Fig. 1. Sorption of natrium banzenesulfonate on anion exchangers: ($\triangle$) 21 L; ($\bullet$) 18 L; ($\times$) 15 L.
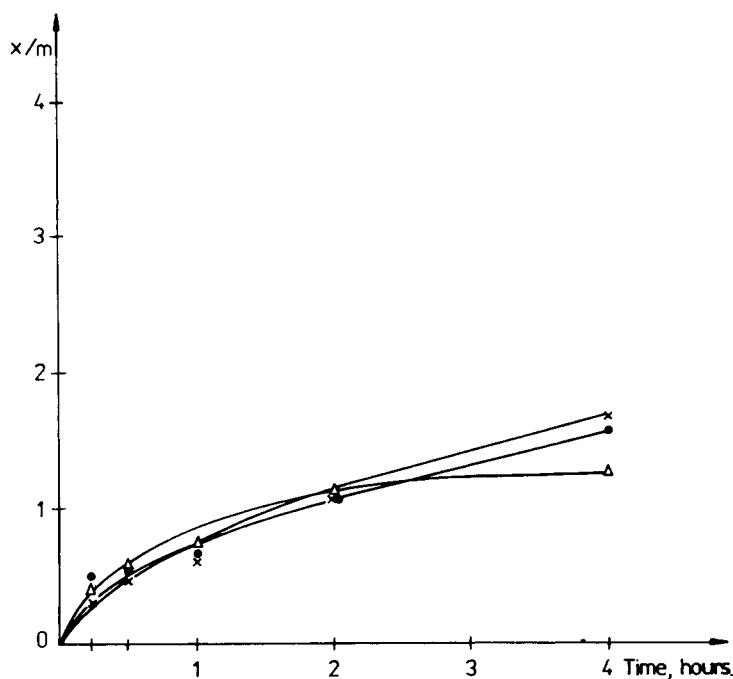
Fig. 2. Sorption of natrium anthraquinone-2-sulfonate on anion exchangers: ($\triangle$) 21 L; ($\bullet$) 18 L; ($\times$) 15 L.

From Table II the anion exchangers, except resin 21 L, have virtually identical total exchange capacities. Type I anion exchangers have also considerably greater water regains than type II anion exchangers. Water regain depends on the value of ion exchange capacity and the porosity and flexibility of the network. In our case, the second and third characteristics determine the water regain; the ion exchange capacities are approximately equal.

The behaviors of resins 15 L, 18 L, and 21 L during the sorption process of the NaBS and NaAQS compounds are compared in Figures 1 and 2.

The starting copolymers of the three anion exchangers mentioned above were performed using the same kind and amounts of diluent (gasoline, $f_v =$ 0.40) but with various DVB percents.

The samples of NaBS and NaAQS are the sulfonic compounds with, respectively, the smallest and largest molar volume.

From the experimental results presented in the figures we note that

1. All resins have lower values for the sorption capacity of NaAQS compound by comparison with NaBS compound and the sorption rate is faster for the latter.
2. The highest crosslinked anion exchanger (21 L) has the poorest sorption power of the two anions, though its parent copolymer has the largest porosity. Resins 15 L and 18 L have very close values of x/m.
3. Resin 21 L reaches a constant value for x/m during the first 4 h of the sorption process. However, afterward the 15 L and 18 L samples show increased sorption capacity. The larger increase is observed in the case of NaAQS compounds.
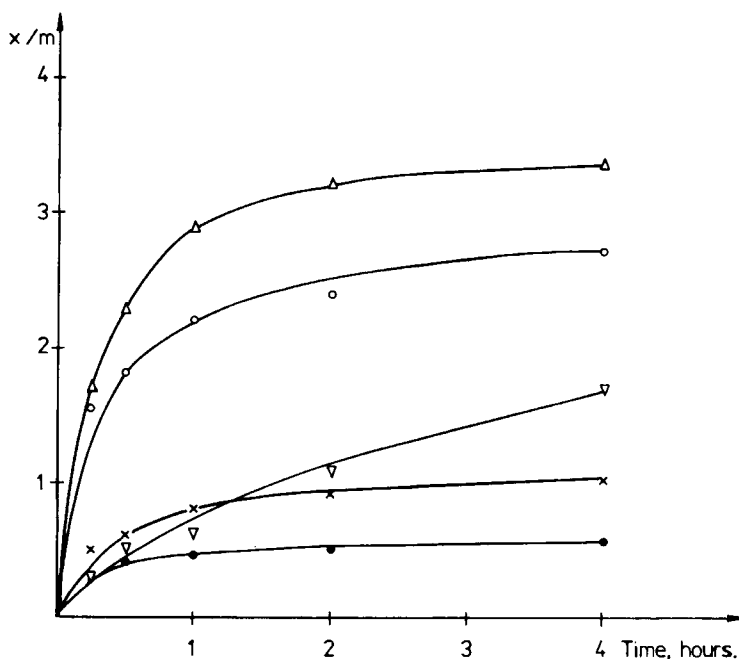
Fig. 3. Sorption on 15 L anion exchanger of: (●) NaB; (×) KNA; (▽) NaAQS; (○) NaBS; (△) NaNS.

All of these aspects demonstrated that the diffusion phenomenon is the rate-determining state in the sorption process. The larger size of NaAQS compound relative to NaBS determines a slower diffusion of the first molecule in the St-DVB network.

We assume that the diffusion phenomenon which takes place during the sorption process of organic molecules in anion exchange resins is a gel and pore diffusion, which play a combined role. The use of more porous anion exchangers might eliminate a few or all aspects of the sorption process of the two compounds on the three resins.

To show evidence of the influence of the organic molecule structures on their sorption process, the behavior of resin 15 L to sorption of the five organic molecules was determined. The results are plotted in Figure 3.

Figure 3 indicates that the arylsulfonic anions are adsorbed better than arylcarboxylic anions because the first anions belong to the stronger acids. The values of x/m in the series of arylcarboxylic anions follow the order KNA > NaB and in the series of arylsulfonic anions the order is NaNS > NaBS > NaAQS during the first 4 h of contact time between the solutions and the resins.

It is well known that the sorption of organic anions can take place by normal ion-exchange process and by different types of molecular forces between the St-DVB network and the adsorbed molecules and between the adsorbed molecules.

The magnitude of these forces becomes increasingly important as the number of atoms in the adsorbed molecule increases and also as the aromatic character of the molecule increases.
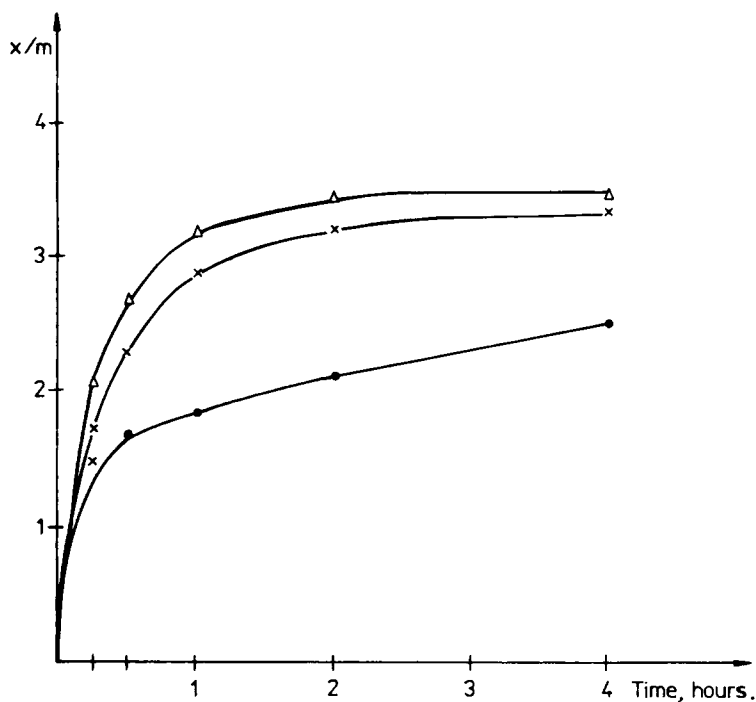
Fig. 4.   Sorption of natrium naphthalenesulfonate on anion exchangers: (●) 14 L; (×) 15 L; (△) 10 L.

Taking into account the above, the following range concerning the adsorption of sulfonated compounds is possible: NaAQS > NaNS > NaBS. However, the major role of these compounds on the sorption of organic molecules has the morphology of an anion exchanger network, which allows access of adsorbed molecules. In our situation the swollen network of the anion exchange resin 15 L gives an easier access of NaNS molecules in comparison with NaAQS.

Figure 4 presents the sorption of NaNS compound on resins 10 L, 14 L, and 15 L. The starting copolymers of these resins were obtained with the same DVB and diluent amounts but with various types of diluents (see Table I). The sorption follows the order 10 L > 15 L ≫ 14 L. This order does not follow the porosity values of the three copolymers as 10 L > 14 L > 15 L (Table I). This discrepancy is a consequence of the anion exchange resin morphological structure.

Figure 5 gives the electron micrographs of samples 10 L, 14 L, and 15 L. It can be seen that the network of the gasoline-modified copolymer (15 L) has smaller pores sizes and less compact polymer areas than the samples 10 L and 14 L. The heptane-modified copolymer (10 L) has the highest porosity.

These aspects show once more that both the gel porosity and the macroporosity could play a combined role during the sorption of the organic compound on the anion exchangers. But, the molecular size of the organic compounds is rather important.

It is also known that the physicochemical characteristics and amounts of the diluent used in the copolymerization process determine the porosity of the
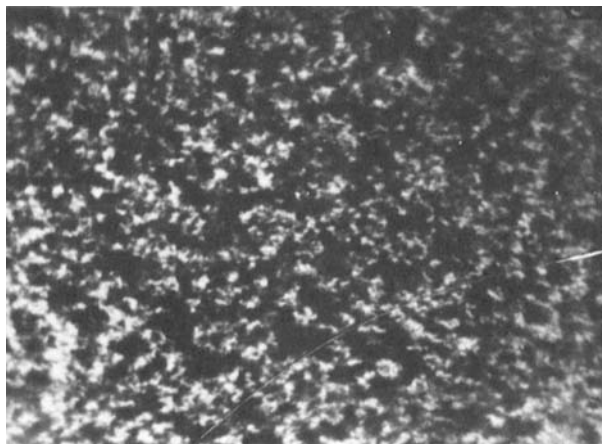
(a)
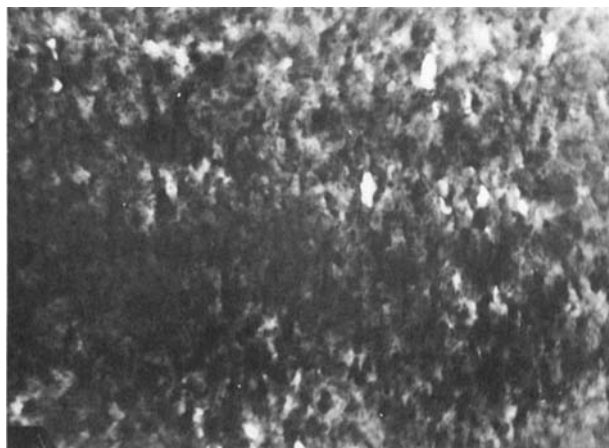
(b)

Fig. 5. Electron microscope images of: (a) copolymer 10 L ($\times$12,500); (b) copolymer 14 L ($\times$12,500); and (c) copolymer 15 L ($\times$12,500).

copolymers. Consequently we have synthesized modified copolymers in the presence of various amounts of n-heptane (samples to 10 L and 29 L) or gasoline (samples 15 L and 31 L; see Table I) which were subsequently transformed into anion exchangers.

The behaviors of the four anion exchangers against NaNS molecule sorption are presented in Figure 6. One can see from this figure that the obtained macroporous copolymers with smaller volume of the diluents led to the anion exchangers which had lower sorption capacities. Greater differences occur in the case of anion exchangers 10 L and 29 L sorption performed from heptane-modified copolymers.

We also would like to present the influence of the anion exchanger type on the sorption of organic molecules. With respect to this we performed type I and type II anion exchangers on base of copolymers 10 L and 15 L. For these
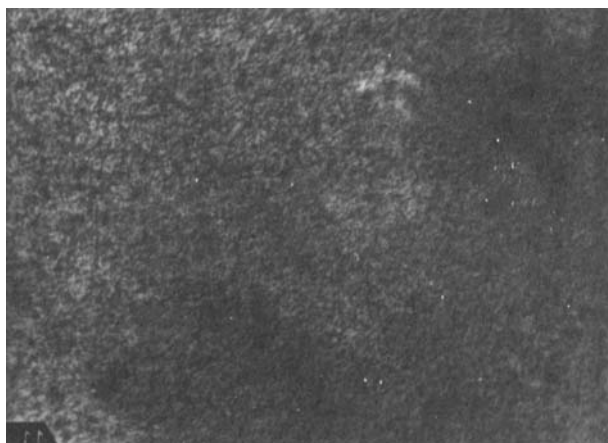
(c)

Fig. 5. (*Continued from the previous page.*)

resins, the sorption capacities versus the NaNS and KNA compounds were determined. The results are presented in Figure 7.

This figures shows that approximately equal values of x/m were obtained in the case of the sorption of KNA by the four anion exchange resins. There are greater differences in the case of NaNS molecule. The type II anion
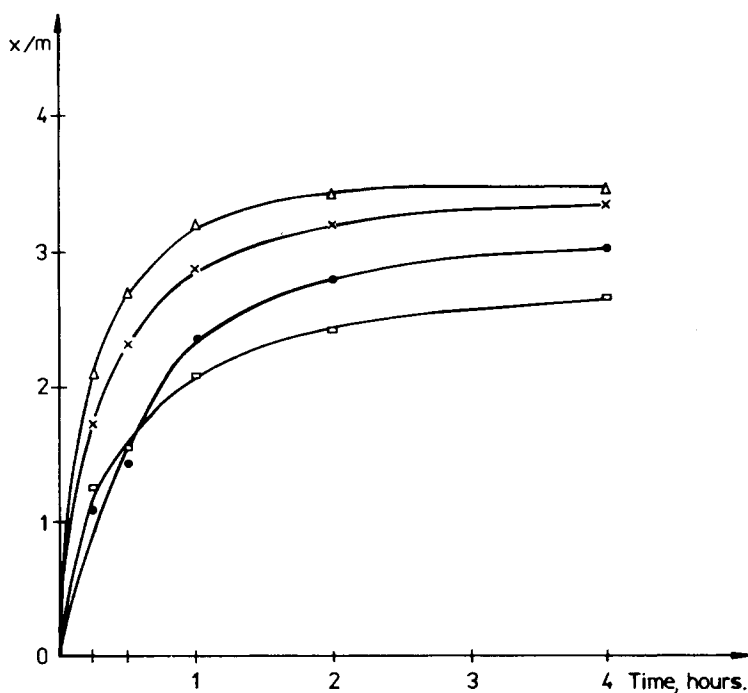

Fig. 6. Sorption of natrium naphthalenesulfonate on anion exchangers: (□) 29 L; (●) 31 L; (×) 15 L; (△) 10 L.
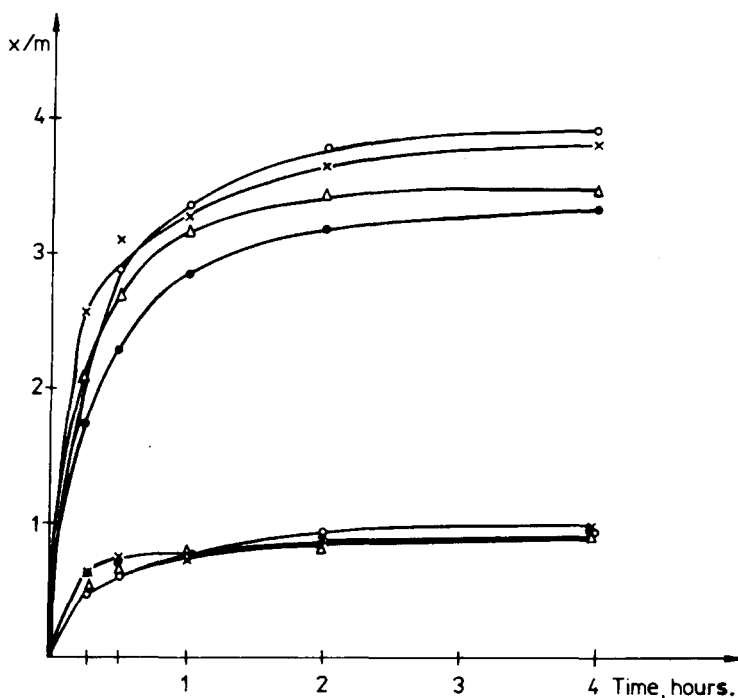
Fig. 7. Sorption of potassium α-naphthylacetate and of natrium naphthalenesulfonate on anion exchangers: (○) type I 15 L; (×) type I 10 L; (△) type II 10 L; (●) type II 15 L.

exchangers have lower sorption capacities than type I. The same behavior is evident for water regains.

This situation is explained by the differences between the basicities of the two anion exchangers. It has been shown that the type II resin has a lower basicity.

As shown in the Experimental Section, we determined from aliquot parts the amounts of chloride and organic anions. The obtained results are presented in Table III.

Notice that in all cases the sorption capacities for the organic molecules are higher than the chloride amounts removed from the resin phase. (The values

TABLE III
The Sorption Capacities of NaNS Compound and Chloride Removed Amounts
from Resin Phase at 4 H Time

Sample	Sorption capacity, mEq organic anion/g resin	Chloride removed, mEq Cl$^-$/g resin
10 L type I	3.84	2.66
10 L type II	3.47	2.41
14 L type II	2.52	2.20
15 L type I	3.93	3.16
15 L type II	3.36	2.85
29 L type II	2.67	2.59
31 L type II	3.03	2.24

are given for the first 4 h of the contact between the solutions and resins.) The anion exchangers 10 L (type I and II) present the highest differences between the two values because their macroporosity has the highest values. The various values between sorption capacities and chloride-removed amounts show that the sorption of organic substances on ion exchangers take place by the ion exchange process and by the physical process. The magnitude of the differences between the two processes depends on the morphology of anion exchanger network.

CONCLUSIONS

Experimental results were obtained for the sorption of the alkaline salts of five organic acids from aqueous solutions on several macroporous strong basic anion exchangers (type I and type II).

Sorption can take place by a normal ion exchange process and by a physical process determined by molecular forces.

It was observed that the values of sorption capacities depend on: (1) the morphology and chemical nature of ion exchanger network and (2) the chemical nature and the size of organic anion.

References

1. A. L. Wilson, *J. Appl. Chem.*, **9**, 352 (1959).
2. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J. Chem. Soc.*, 218 (1963).
3. J. R. Millar, D. G. Smith, and T. R. E. Kressman, *J. Chem. Soc.*, 304 (1965).
4. L. V. Dmitrenke and D. K. Hale, *J. Chem. Soc.*, 5570 (1965).
5. R. L. Gustafson and J. A. Lirio, *Ind. Eng. Chem. Prod. Res. and Dev.*, **7**, 116 (1968).
6. F. Martinola and G. Naumann, *Angew. Makromol. Chem.*, **4**, 185 (1968).
7. G. V. Samsonov, E. B. Trostianskaia, and G. E. Elchin, *Ionîi obmen-Sorbţiia organiceskih veşcestv*, Izdatelstvo "Nauka", Leningrad 1969, p. 268.
8. F. Martinola and A. Richter, *International Water Conference*, Western Pennsylvania, 1970.
9. C. Oehme and F. Martinola, *Chem. and Ind.*, **74**, 823 (1973).
10. I. K. Tsitovich and I. I. Sidorova, *Sorbtsiya Khromatogr.*, **103** (1979); *CA* **92**/1980, 117046 k.
11. A. T. Davydov, L. T. Ponirovskaya, N. B. Fadeeva, and V. K. Kozun, *Zh. Prikl. Khim. (Leningrad)*, **53**(5), 1178 (1980).
12. B. S. Brayalovskii, Sh. Sh. Shamanaev, and Yu. V. Anikin, *Zh. Prikl. Khim. (Leningrad)*, **53**(8), 1869 (1980).
13. Ya. I. Korenmann, A. T. Alymova, S. N. Taldykina, N. S. Logunova, and N. S. Kobeleva, *Kolloidn. Zh.*, **43**(3), 455 (1981).
14. N. N. Gavrilova, V. S. Pirogov, A. D. Morozova, Yu. S. Nadezhin, N. N. Kuznetsova, and G. V. Samsenov, *Zh. Prikl. Khim. (Leningrad)*, **54**(5), 1190 (1981).
15. C. Luca, G. Chitanu, I. Petrariu, A. Airinei, and A. Carpov, *Rev. Roum. Chim.*, **23**(11–12), 1635 (1978).