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Abstract

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RADIATION-CHEMICAL SYNTHESIS OF NEW ION-EXCHANGE SORBENTS OF MINERAL-ORGANIC NATURE

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The ion-exchange sorbents of mineral origin currently used (oxides, hydroxides, and salts of metals, aluminosilicates, silica gels, permutites, bentonites, glauconites, zeolites, etc.) possess a developed specific surface area, the ability for chemical and molecular sorption and for the sorption of colloidal particles, often amphoteric ion-exchange properties, and increased radiation and thermal stability (2). As a rule, they swell only slightly in aqueous solutions, and ion exchange takes place mainly on the surface of the sorbent, so that the kinetics of exchange is not complicated by processes associated with diffusion of ions in the phase of the sorbent itself, as is the case for most ion-exchange sorbents of organic origin. On the other hand, synthetic organic ion-exchange resins (1) surpass inorganic sorbents in such important characteristics as capacity, basicity or acidity, and chemical stability; they have better hydrodynamic characteristics. It is of interest to obtain ion exchangers in which the advantages of sorbents of both types would be combined. In some cases this goal can apparently be achieved by modifying the surface of mineral sorbents through the chemical attachment of organic radicals to it (3). We have attempted to solve the stated problem by a fundamentally new route—by combining inorganic sorbent carriers with organic polymers bearing functional groups.

In formulating this investigation we proceeded from the results of earlier studies, in which the fundamental possibility had been shown of obtaining mineral-organic products by methods of graft polymerization initiated either mechanochemically (during grinding of mineral bodies in the presence of liquid monomers) (4) or radiation-chemically (by irradiating mineral powders in the presence of vapors of vinyl monomers) (5). In both cases, active centers are generated on the surface of the mineral substance; these centers initiate the chain process of polymerization, so that the growing polymer chains become chemically bound to the surface of the substrate.

To initiate graft polymerization on inorganic sorbents we chose the radiation method, since it makes it possible to carry out the process without disrupting the structure of the sorbent and independently of its initial dispersity; moreover, in vapor-phase graft radiation polymerization the homopolymer (i.e., polymer not chemically bound to the substrate and removable by solvents) is formed only in relatively small amounts.

The mineral sorbent was first pumped down to a residual pressure of 10^{-5} mm Hg. Irradiation was carried out with X-rays (dose rate 50-100 rad/sec, integral dose $5 \cdot 10^6$ rad) at a temperature of 90°; the vapor pressure of the monomer in the reaction vessel was, in the case of styrene, about 30 mm Hg, and in the case of acrylic acid, 25 mm Hg.

On the basis of the system white carbon black (consisting mainly of SiO_2)—styrene, a mineral-organic product was obtained containing 21 wt.% grafted polystyrene (relative to the weighed amount of carbon black taken). Molecu-

molecular weight of the grafted polystyrene was $4 \cdot 10^5$.* The grafted polystyrene was subjected to sulfonation by treatment with sulfuric acid in the presence of silver sulfate at 60° (^{6,7}). After washing with distilled water until the wash waters were neutral, the physicochemical parameters of the sorbent obtained were determined. The potentiometric titration curve is shown in Fig. 1, 1. It has the form typical of a sorbent with strongly acidic groups. The total static exchange capacity (t.s.e.), determined in 0.1 N NaOH, was 1.4 mg-equiv/g. The t.s.e. of pure SiO_2 in 0.1 N NaOH was 0.7 mg-equiv/g; moreover, in this case it is necessary to take into account the possibility of dissolution of SiO_2 in NaOH with formation of sodium silicate, and therefore the t.s.e. of pure SiO_2, equal to 0.7 mg-equiv/g, may be somewhat overestimated. The t.s.e. of white carbon black with grafted onto it, but not sulfonated, polystyrene was 0.5 mg-equiv/g.

Thus, the functional groups $-SO_3H$ account for approximately 0.9 mg-equiv/g, which corresponds to sulfonation of the grafted polystyrene by $\sim 40\%$, assuming that theoretically one sulfo group should correspond to each benzene ring. By changing the conditions, it is apparently possible to increase the degree of sulfonation of the polymer.

The ion-exchange sorbent obtained practically does not swell in water or in aqueous electrolyte solutions. By the method of radioactive indicators ($Na^{24}, Cl^{36}, Fe^{59}$) it was established that this ion-exchange sorbent, like other mineral-organic sorbents synthesized by us, possesses the ability for molecular sorption and sorption of colloidal particles. The specific surface area of SiO_2 increases somewhat as a result of grafting and sulfonation. Thus, if the specific surface area of SiO_2, measured by the BET method from the adsorption of n-heptane and krypton, was ~ 30 m^2/g, then the specific surface area of the ion exchanger obtained by us was ~ 40 m^2/g. On the basis of coarse-porous silica gel of the KSK grade, by radiation-chemical graft polymerization of styrene followed by sulfonation of the grafted polymer (25 wt.%), a mineral-organic ion-exchange sorbent was obtained with a t.s.e. in 0.1 N NaOH equal to 1.8 mg-equiv/g. The capacity of pure KSK under analogous conditions is 0.5 mg-equiv/g; consequently, the $-SO_3H$ groups account for 1.3 mg-equiv/g, which corresponds to an approximately 70% degree of sulfonation. The potentiometric titration curve of the sorbent obtained has a form analogous to

Fig. 1, 1.

On the basis of the system white carbon black—acrylic acid, a mineral-organic ion-exchange sorbent with functional carboxyl groups was obtained, containing 25 wt.% of grafted polyacrylic acid. The sorbent does not swell in water. The potentiometric titration curve is shown in Fig. 1, 2; the t.s.e. in $0.1\,N$ NaOH proved to be 3 mg-equiv/g. The theoretically calculated capacity with respect to COOH groups is 3.5 mg-equiv/g. The static exchange capacity (s.e.c.) in the exchange of H^+ for Na^+ in a neutral medium (pH 7), determined by the radioactive-indicator method and by potentiometric titration on an autotitrator of W. G. Pye Co. ([8]), proved to be 0.8-1 mg-equiv/g. The sorbent obtained displayed interesting kinetic properties. Thus, the rate of establishment of ion-exchange equilibrium in the exchange of H^+ for Na^+ practically does not change when the concentration of NaCl in solution is varied from $10^{-1}\,N$ to $2 \cdot 10^{-4}\,N$ (Fig. 2), whereas existing ion-exchange resins (for example, KU-2, Dowex-50, Amberlite IR-120, and others) show a sharp dependence of the rate of establishment of ion-exchange equilibrium on the concentration of electrolytes in solution ([8]). Consideration of Fig. 2 shows that if, for concentrations of the order of $10^{-1}N$ there is no great difference in the rate of establishment of ion-exchange equilibrium for the sorbent synthesized by us and, for example, for KU-2, whereas for a concentration of $2 \cdot 10^{-4}N$ this difference is very pronounced. Thus, if on KU-2 under these conditions in the first 10 min only 13% of the equilibrium capacity is realized, then on the sorbent synthesized by us equilibrium is already established by this time.

[Figure 1 and Figure 2]

Fig. 1. Curves of potentiometric titration of the sorbent based on white carbon black and polystyrene (1) and of the sorbent based on white carbon black and polyacrylic acid (2).

Fig. 2. Rate of establishment of ion-exchange equilibrium (pH 7) in the exchange of H^+ ions for Na^+ on: 1 –KU-2 ([NaCl] = 10^{-1} N); 2 –KU-2 ([NaCl] = $2 \cdot 10^{-4}$ N); 3 –sorbent based on white carbon black and polyacrylic acid ([NaCl] = 10^{-1} N); 4 –sorbent based on white carbon black and polyacrylic acid ([NaCl] = $2 \cdot 10^{-4}$ N). (The rate of establishment of ion-exchange equilibrium on white carbon black under these conditions could not be determined because of the very low capacity of the sorbent.)

Thus, the mineral-organic ion-exchange sorbents synthesized by us by a

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* If the formation of an active center on the surface of a grain ($d = 10^{-5}$ cm) is considered as the result of energy transfer to the surface from a layer of effective thickness δ, and the radiation-chemical yield of active centers is taken as $G = 1$, then in our case the value $\delta = 10 \div 30$ Å, which is consistent with the data obtained in studies of energy transfer from a solid to molecules sorbed on its surface in the process of radiolysis.

radiation-chemical route possess, in comparison with existing ion-exchange resins, certain advantages: a) absence of swelling, or very slight swelling; b) a highly developed specific surface and, associated with it, an ability for molecular sorption and for sorption of colloidal particles; c) an increased rate of exchange at low electrolyte concentration in solution and a weak dependence of the exchange rate on the electrolyte concentration.

By changing the conditions for carrying out the reactions of graft polymerization and the introduction of ion-exchange groups, it is apparently possible to increase the capacity of mineral-organic ion-exchange sorbents. At present, investigations are being carried out to obtain new mineral-organic ion-exchange sorbents based on combinations of various inorganic carriers with organic and organoelement polymers containing various functional groups.

In conclusion, we consider it our pleasant duty to express gratitude to K. V. Chmutov, V. L. Tal' roze, S. R. Rafikov, and B. A. Alekseev for discussion of the work.

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Note: Figure translations are in progress. See original paper for figures.