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NOTE

Separation of Germanium from Ethylene Glycol Distillates by *N*-Methylglucamine Resin

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INTRODUCTION

Germanium compounds have been widely used as polycondensation catalysts in the manufacture of polyesters (*1*). The reaction proceeds with successive distillation of ethylene glycol (EG) from the reaction mixture. In this process, about 50–75% of the germanium fed appears in the EG distillates along with water, diethylene glycol, low-molecular weight polyesters, etc. This loss and the high cost of germanium have provided incentive for developing a method to separate and recover germanium from the EG distillates. However, the small amount of work devoted to this purpose is recognized only in the patent literature (*2–5*).

We have found that germanium is selectively adsorbed on the chelating resin containing the 1-deoxy-1-(methylamino)-D-glucitol groups, *N*-methylglucamine resin, from neutral and alkaline aqueous solutions (*6*). The present note describes the possibility of the application of the same resin to the separation of germanium from EG distillates produced in commercial polyester plants.

EXPERIMENTAL

The *N*-methylglucamine resin $R—CH_2—N(CH_3)—C_6H_8(OH)_5$, Diaion CRB 02, was obtained from Mitsubishi Chemicals, Japan. Unless otherwise stated, all the experiments were carried out by using the resin (20–100 mesh) in the hydroxide form. The total adsorption capacity of this resin was found by the acid adsorption method to be 2.15 meq/g dried resin.

The crude EG distillate was obtained from the commercial plant for the manufacture of polyesters. The suspended solids were removed from the crude distillate by filtration, and we used this filtrate as the sample solution throughout the experiments. The concentration of germanium in the sample solution was determined to be 8.90 m*M*/L and that of water was 11.4 wt%. No germanium was detected in the suspended solids by x-ray fluorescence analysis. The aqueous germanium solution (Ge 8.90 m*M*/L, pH 8.0) was employed as a reference in all the experiments. This solution was prepared by dissolving hexagonal germanium dioxide (99.999%, Rare Metallic, Japan) in dilute sodium hydroxide solution. The other reagents used were all analytical grade.

The adsorption rate of germanium on the resin was determined by the batch method. About 0.2 g of dried resin (35–40°C, 3 h, 1 torr) and 25 mL of the sample solution were shaken mechanically in a water bath at 25°C. The amount of germanium adsorbed on the resin was calculated from the difference between the germanium concentrations in the solution before and after contact with the resin. Column experiments were performed with a fixed-bed column packed with 5 mL resin beads (7 mm ϕ × 140 mmH). The concentration of germanium in the solution was determined by using an inductively coupled plasma atomic emission spectrometer (Model SPS 1200AR, Seiko Instruments, Japan).

RESULTS AND DISCUSSION

Adsorption Rate of Germanium

Figure 1 shows the effect of shaking time on germanium adsorption from the sample and aqueous solutions. For comparison, the resin in the chloride form was employed for the sample solution. Relatively slow rates were observed for germanium adsorption from the sample solution on the resins in either form. In these cases the adsorption of germanium was initially fast but gradually became slower with time and reached equilibrium after 48 h. In contrast, the adsorption equilibrium in the aqueous germanium solution was attained within 5 h. Such a decrease in the adsorption rate of germanium in the sample solution seems to be attributable to the very slow intraparticle diffusion rate of germanium, probably caused by the high kinematic viscosity of the sample solution (10.7 cSt, 25°C).

The amount of germanium adsorbed at equilibrium in the sample solution was found to be about 0.96 m*M*/g dried resin in the hydroxide form. This datum is exactly comparable to that obtained from the aqueous germanium solution with the same resin. On the other hand, the resin in the chloride form had a lower value of 0.76 m*M*/g dried resin. Based on this fact, we used the resin in the hydroxide form for the column system discussed below.

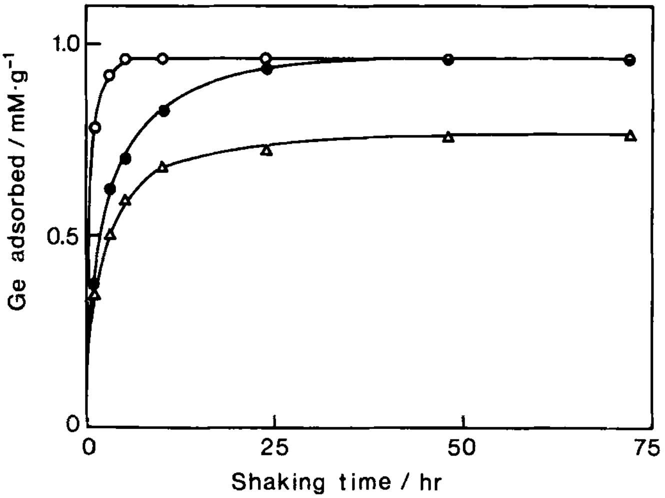

FIG. 1. The rate of adsorption of germanium in the sample and aqueous solutions on the resin in the different forms. (○) Germanium adsorbed from the aqueous solution on the resin in the hydroxide form; (●) germanium adsorbed from the sample solution on the resin in the hydroxide form; (△) germanium adsorbed from the sample solution on the resin in the chloride form.

It is well established that germanic acid, $Ge(OH)_4$, forms strong complexes with many polyhydroxy compounds (7). Such a complex formation between $Ge(OH)_4$ and hydroxy groups in the resin is considered to contribute to the adsorption of germanium in the EG distillate on the *N*-methylglucamine resin. Further details on the adsorption mechanisms and the germanium species present in the EG distillates are under investigation.

Column System

Batch experiments indicated that the adsorption rate for germanium in the sample solution is not sufficiently rapid, but the amount of germanium adsorbed at equilibrium is comparable to that obtained from the aqueous germanium solution. This fact gave us incentive to attempt a continuous separation of germanium from the sample solution by conducting column experiments. Figure 2 shows the breakthrough curves for germanium obtained with the sample solution at the influent rates of 2 and 4 bed volumes per hour (BV/h), together with the curve of the aqueous germanium solution at an influent rate of 2 BV/h. As the rate increased from 2 to 4 BV/h, the breakthrough points of germanium in the sample solution decreased from 12 to 7 bed volumes. These were significantly smaller than the value of 36 bed volumes obtained with aqueous germanium solution under the

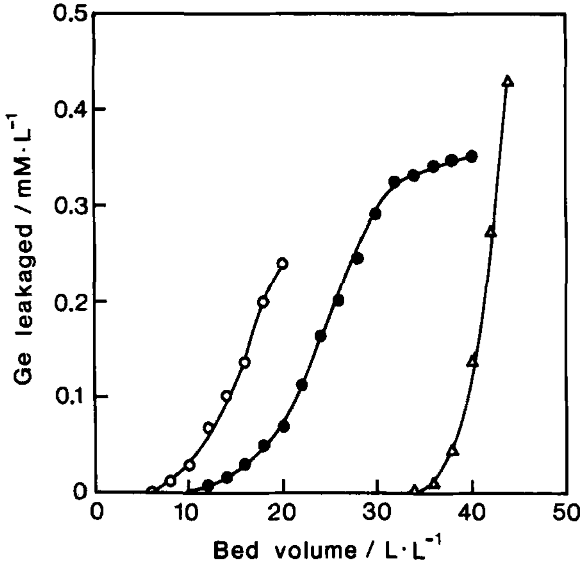

FIG. 2. Breakthrough curves for germanium in 5 mL resin bed (7 mm ϕ × 140 mmH). (○) Sample solution loaded at the influent rate of 4 bed volumes per hour (BV/h); (●) sample solution loaded at 2 BV/h; (△) aqueous solution loaded at 2 BV/h.

same column conditions. Such a rapid leakage of germanium may be caused, as noted earlier, by the very slow intraparticle diffusion rate of germanium in the high viscosity sample. From these results, we were forced to apply an influent rate of 2 BV/h to the sample solution.

The germanium adsorbed on the resin was eluted quantitatively by dilute hydrochloric acid. After 2 bed volumes, most of germanium was eluted in the next 4 bed volumes of 1 *M* hydrochloric acid. An influent rate of 10 BV/h was suitable for elution and the subsequent regeneration steps. The regeneration of the resin column was performed with 4 bed volumes of 1 *M* sodium hydroxide solution. This regeneration step was applied to the column experiments because the resin in the hydroxide form exhibited higher capacities for germanium than those of the resin in the chloride form (Fig. 1). The recycle of adsorption, elution, and regeneration steps was repeated 10 times to check the reproducibility of the column system by loading 10 bed volumes of the sample solution on the same resin bed in each cycle. Complete separation and a considerable concentration effect of germanium could be achieved in the effluents collected in each cycle. From these facts it is concluded that the commercially available *N*-methylglucamine resin has proved to be useful for selective separation of germanium from the EG distillates when using a continuous column system.

Germanium may be recovered from the collected effluents by such conventional methods as $GeCl_4$ distillation (*5*), solvent extraction (*8*), and tannin precipitation (*9*).

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