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Study by scanning electron microscope of phosphorylated polyethylene resins

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A study of surface area using specific resins for uranium from phosphorylated polyethylene has been made. A positive correlation between maximum capacities of the resins and surface area was found. The crosslinked resins with polyols present the best maximum capacities and high adsorption capacities. This is in agreement with the electron micrographs which give information about the adsorption process.

Keywords Polymer matrix; ion-exchanger; phosphonate resins; crosslinked; maximum capacities; adsorption

INTRODUCTION

Phosphorylated organic compounds, by virtue of the electron donating phosphoryl oxygen, have the strongest complexing properties for salts such as uranyl nitrate and lithium chloride.

In order to facilitate manipulation and the subsequent recovery of the complexing phosphoryl ligands it is desirable that they be incorporated into an insoluble polymer matrix with the hope that they would still retain their complexing properties and selectivity, while having physical properties similar to conventional ion-exchangers[1]. Judging from the behaviour of monomeric phosphoryl compounds[2] it is likely that non-ionic polymers of the phosphine type would have sufficiently enhanced complexing strengths to permit high adsorption of metallic salts from aqueous systems.

Resins of the sample phosphonate type ($R-PO(OH)_2$, R = resin) are clearly more selective for the uranyl ion than for resins containing aminophosphonate or aminocarboxylate functional units. Resins having monoacetic functional units of the former type such as the polymerized allyl phosphonate, are much more selective than those containing diacidic functional units such as the polystyrene methylene phosphonates and they later show a high affinity for alkaline earths which makes elution more difficult[3].

The phosphorylated polyethylene resins, crosslinked with diamines and diols, effectively retain uranium as UO_2^{2+}. Thus, they show a higher capacity and selectivity towards Fe(III) and Re(VII)[4] than the commercially used Amberlite IRA-400.

Here we report on surface area and morphological studies by scanning electron microscopy. Phosphorylated polyethylene (PE-4) was crosslinked with ethylenediamine (PE-9), ethyleneglycol (PE-17), diethyleneglycol (PE-18) and triethyleneglycol (PE-17), respectively.

EXPERIMENTAL

Determination of maximum capacities

A 250 ml beaker containing dry resin (1.0 g) and uranyl acetate pentahydrated aqueous solution (100 ml) (equivalent to 4 g of uranium per litre) was placed in a thermostatically controlled bath at 25°C. The mixture was agitated for 2 h at 200 cycles per minute. The aqueous solution was separated by decanting and washed several times with water. This process was repeated twice using the same resin, and using a uranium solution (100 ml) of the same initial concentration. Uranium was analysed by spectrophotometry[5] and the uranium fixed in the resin is determined from the difference.

Determination of surface area

The surface areas of the different resins were determined by the adsorption of a solute from liquid phase method, using an aqueous solution of ammonium chloride at 20°C a transverse section in the ammonium chloride molecule of 31 $(Å)^2$ was considered[6]. The amount of nitrogen was determined by using the Kjeldahl method[7].

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Electron micrographs

The surface of the resin was coated with gold for 3 min to obtain a 150 Å thickness using an Edwards S 150 sputter coater. The electron micrographs were obtained by using a scanning electron microscope, ETEC Autoscan U-1 Model.

Table 1 Maximum capacity and surface area for resin studied

Resins	Maximum capacity (meq uranium g dry resin)	Surface area (m^2)
PE-4	4.8	45
PE-9	2.7	28
PE-17	9.5	88
PE-18	9.6	97
PE-19	4.8	40

RESULTS AND DISCUSSION

The correlation between the maximum capacity and the surface area of the tested resins is shown in *Table 1*. Morphological studies were then carried out by observing the electron micrographs.

The PE-4 resin showed some large holes and after charging with uranium the size of the holes decreases considerably (see *Figures 1* and *2*). This is in agreement with the surface area which is 45 m^2 in the uncharged resin.

The charged, as well as the uncharged PE-9 resin show similar morphology. This is consistent with the low capacity of retention for uranium and the low surface area shown by the resin (see *Figures 3* and *4*).

However, the PE-17 resin shows a large difference

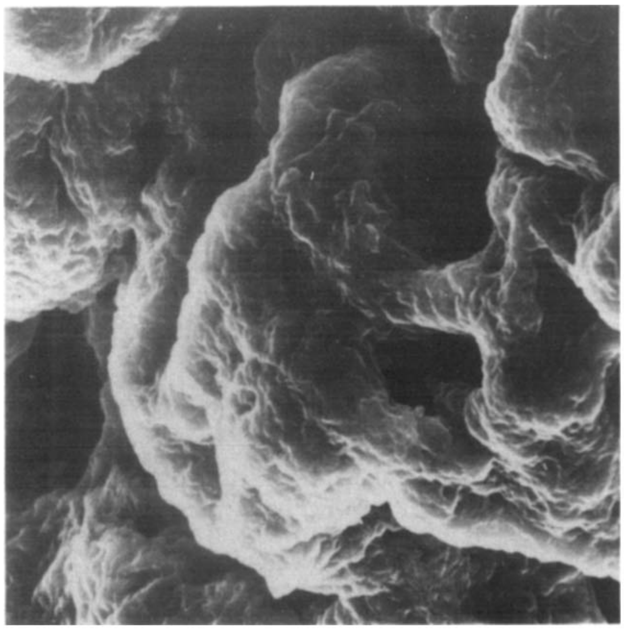

Figure 1 Electron micrographs of the resin PE-4 unloaded (1000X)

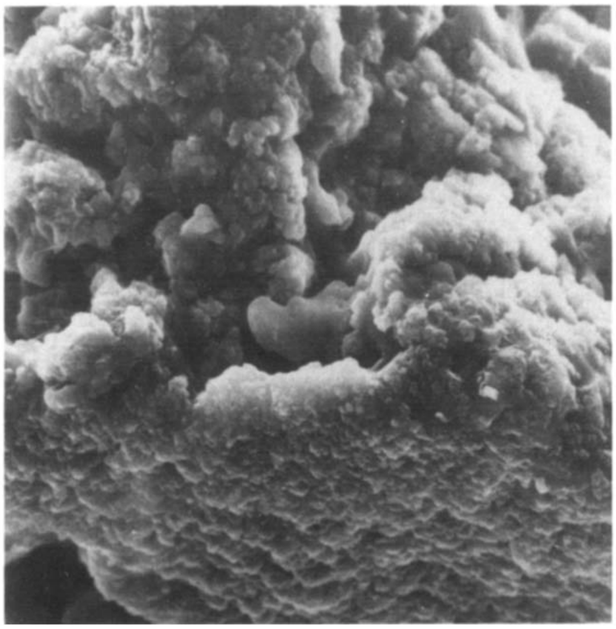

Figure 3 Electron micrographs of the resin PE-9 unloaded (1000 X)

Figure 2 Electron micrographs of the resin PE-4 loaded with uranium (1000 X)

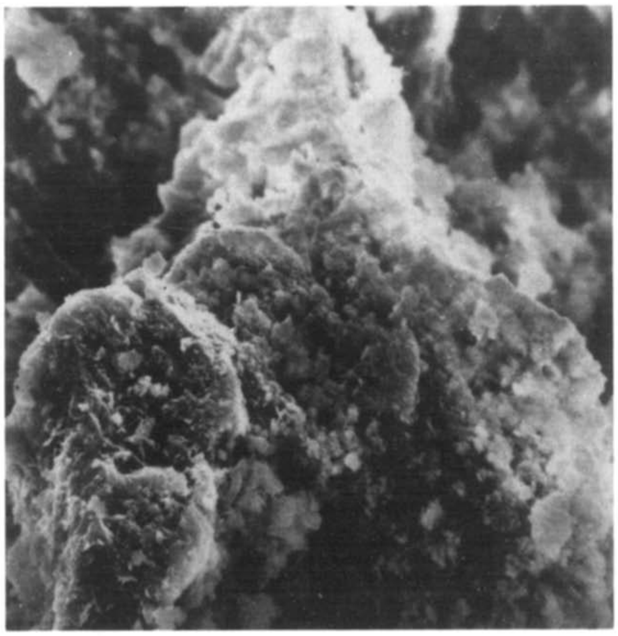

Figure 4 Electron micrographs of the resin PE-9 loaded with uranium (1000 X)

between the porous size of the uncharged resin and that of resin charged with uranium. The charged resin showed a more uniform surface and a surface area of 88 m^2 which can be related to its large retention capacity for uranium (see *Figures 5* and *6*).

The PE-18 resin shows a smooth surface with almost no holes. They look like amorphous overlapped plates. The PE-18 resin with uranium showed a large increase in the porous size and a different morphology. This is in agreement with the large swelling capacity that this resin exhibits when in contact with a uranyl acetate solution. It has a similar surface area to the PE-17 resin which relates greatly to the maximum capacity (see *Figures 7* and *8*).

The PE-19 resin shows a small diameter porous surface. The charged resin shows a decrease in the porous size, similar to that in the PE-14 resin (see *Figures 9* and *10*).

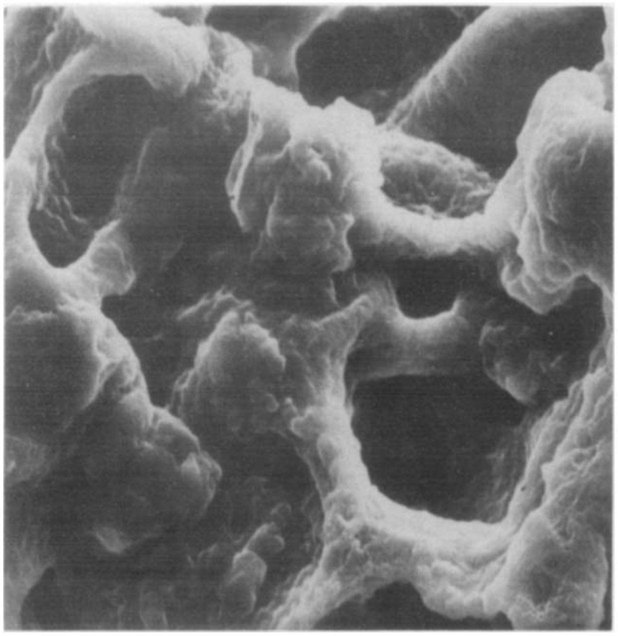

Figure 5 Electron micrographs of the resin PE-17 unloaded (1000 X)

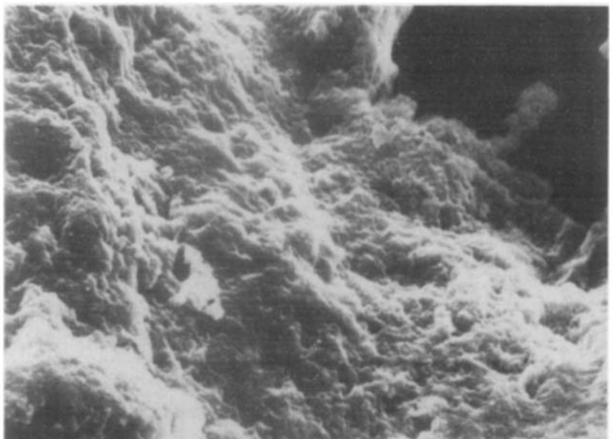

Figure 6 Electron micrographs of the resin PE-17 loaded with uranium (1000 X)

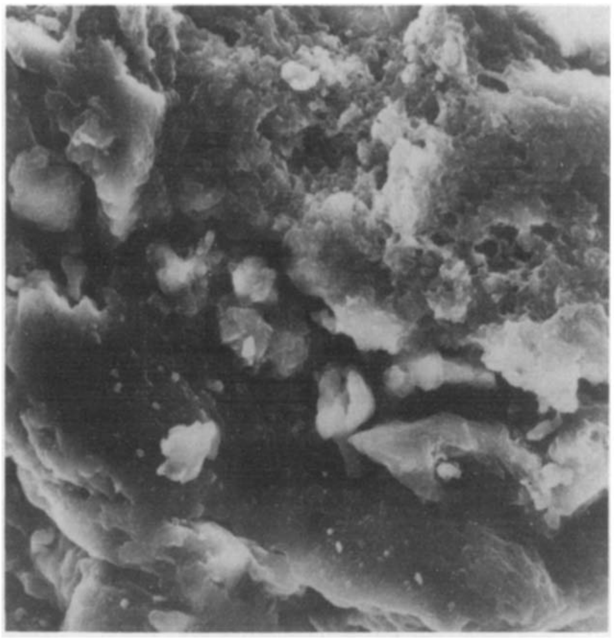

Figure 7 Electron micrographs of the resin PE-18 unloaded (1000 X)

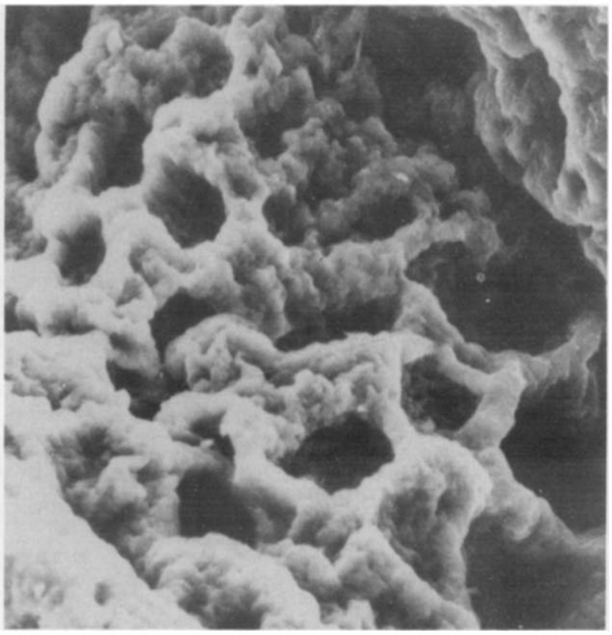

Figure 8 Electron micrographs of the resin PE-18 loaded with uranium (1000 X)

We observe two types of behaviour in these resins. First, the PE-4, PE-9 and PE-19 resins show a decrease in the porous size when they are in contact with uranium and this is in good agreement with the results from the surface area determination. Secondly, the PE-17 and PE-18 resins containing crosslinked hydrophilic groups show an increase in the porous size when they are in contact with the uranium solutions. These phenomena can be explained by assuming that the ether oxygen (e.g. ethyleneglycol, diethyleneglycol) is outside the grain of the resin. Also, it is assumed that the phosphate groups, being more hydrophobic, are on the inside of the resins.

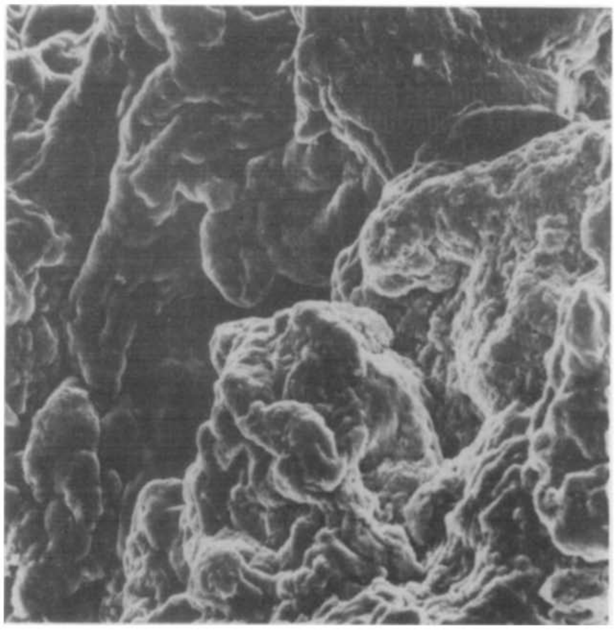

Figure 9 Electron micrographs of the resin PE-19 unloaded (200 X)

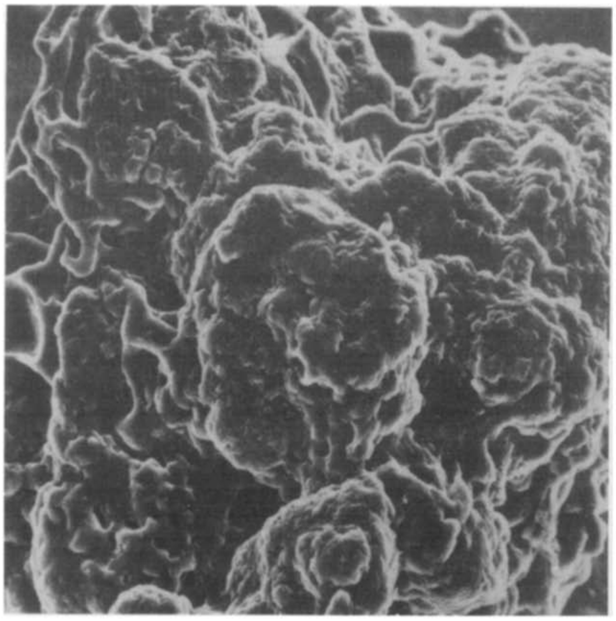

Figure 10 Electron micrographs of the resin PE-19 loaded with uranium (200 X)

Therefore, we assume that the complex between the resin and uranium compress the hydrocarbon chain therefore increasing the porous size.

Thus, the charged resins would not have enough available surface area which accounts for no adsorption of ammonium ion.

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