

Synthesis and Characterization of Styrene–Divinylbenzene Loaded with Di(2-ethylhexyl)phosphonic Acid. I. Influence of Diluent Mixture on the Porous Structure of the Copolymer

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ABSTRACT: Styrene–divinylbenzene copolymers were synthesized in the presence of di(2-ethylhexyl)phosphonic acid (EHEHPA) to be applied in the separation of rare earths by extraction chromatography. The copolymers were prepared by suspension polymerization in the presence of pure EHEHPA or in a mixture with isooctane, heptane, or toluene. The composition of the diluent mixture employed in the synthesis was varied. The apparent density, fixed pore volume, and surface area of the copolymers were determined. The content of EHEHPA retained in the copolymer beads was also determined, and it was found to be independent of the porous structure of the copolymer matrix. That content was only dependent on the amount of EHEHPA present in the diluent mixture. The toluene/EHEHPA mixtures produced the copolymers with the best properties required for extraction chromatography supports. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 781–787, 1998

Key words: styrene–divinylbenzene copolymers; chelating agent; extraction chromatography; di(2-ethylhexyl)phosphonic acid

INTRODUCTION

The rare earths' separation has been widely studied due to the great number of applications of these elements in many sectors of industry. The separation of some adjacent pairs of rare earths is still very difficult because the chemical properties of these elements are very similar.¹

Solvent extraction and ion exchange are the most used methods for rare earths' separation, but in recent years, extraction chromatography has deserved special attention, because this technique combines the high selectivity of solvent extraction

with the efficiency of column chromatography in the separation of metal ions in aqueous solution.^{2,3}

In this method, an inert sorbent loaded with a liquid chelating agent is used as a chromatographic packing material. The chelating agents used are the same employed in solvent extraction, such as di(2-ethylhexyl)phosphoric acid (DEHPA) and tri-*n*-octylphosphine oxide (TOPO). Di(2-ethylhexyl)phosphonic acid (EHEHPA) has shown a good performance in the separation of rare earths, due to its higher separation factor for two adjacent lanthanides in comparison with other chelating agents.^{4–6} Porous styrene–divinylbenzene (Sty–DVB) copolymers obtained by suspension polymerization are the most used sorbents in extraction chromatography, due to the possibility of controlling their morphology during the synthesis.⁷

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The immobilization of the chelating agent or extractant in the polymer matrix can be performed by two methods: The first one consists of swelling the polymer beads in the liquid extractant or in a mixture of it with an inert solvent that will be eliminated from the beads at the end of the swelling process. The good performance of this method depends on the extractant's affinity for the polymer, which, generally, is very low. So, the poor immobilization of the extractant leads to its elimination during the separation process. The second method of immobilization involves the impregnation of the extractant during the synthesis of the polymer beads. In this case, the chelating agent acts as a nonsolvating diluent to the Sty-DVB copolymer, forming macroporous structures.^{3,7,8}

The presence of a nonsolvating diluent during the polymerization causes phase separation on the copolymer structure, resulting in a macroporous material. This material is formed by agglomerates of microspheres linked together by the reaction of residual monomers at the end of the polymerization process; the channels between these agglomerates constitute the copolymer macropores.⁹ When the chelating agent is present in the polymerization system, the agglomerates are impregnated during their formation, which results in a better distribution of the extractant over the polymer matrix.

However, these chelating agents are polar molecules with a low affinity for the Sty-DVB copolymer, producing structures with large pores and low surface areas. These copolymers have low mechanical resistance and, consequently, they are not adequate to be used in chromatographic columns. This problem can be solved by mixing suitable diluents with the chelating agent. The synergistic mixture offers the possibility of producing copolymers with diversified porous structures.^{10,11}

In this work, we studied the synthesis of Sty-DVB copolymers in the presence of EHEHPA. The porous structure of the copolymer was varied by using different inert diluents mixed with the chelating agent. The influence of these mixtures on the porous structure of the copolymer is discussed in this article.

EXPERIMENTAL

Materials

Styrene was washed with a 5 wt % aqueous NaOH solution to remove the inhibitor, followed by washing with water until neutralization. The monomers,

Sty and DVB, were distilled under reduced pressure. The initiator 2,2'-azobisisobutyronitrile was recrystallized from methanol. The diluents isooctane, heptane, and toluene were used as received. The DVB content was fixed at 30% molar in relation to Sty and the monomers' dilution degree was fixed at 100% in relation to the volume of the monomer mixture. Mixtures of EHEHPA with isooctane, heptane, or toluene were used as diluents in the proportions shown in Table I. Poly(vinyl alcohol) (PVA) was used as a suspension agent, and NaCl, as a salting-out agent. Both were used at 5% w/v in relation to the volume of the aqueous phase. The volume relation between aqueous and organic phases was fixed at 4 : 1.

Copolymer Synthesis

Sty-DVB copolymer beads were synthesized by suspension polymerization at 70°C during 24 h in a 1-L three-necked round-bottomed flask fitted with a condenser, a stopper, and a mechanical stirrer. The aqueous phase was prepared by dissolving PVA and NaCl in water and the organic phase was constituted of the monomers, the diluent mixture, and the initiator. The aqueous phase was added to the flask followed by the organic phase under stirring at room temperature. Ten minutes later, heating was started.

Purification of the Copolymer Beads

At the end of the polymerization, the obtained beads were vacuum-filtered and washed repeated times with water by stirring each time for 30 min at 50°C until the water became transparent, in order to assure the total removal of PVA, NaCl, the diluents, and the excess of unreacted monomers. The beads were sieved and a 150–200 mesh fraction was separated. This fraction was purified with ethanol to remove the monomers and diluents from the pores of the beads following the same procedure described for the washing with water. The beads were finally filtered, washed with methanol, and dried at 60°C for 48 h.

Characterization

The apparent density (d_{ap}) of the copolymer was determined by the graduated cylinder method, a modification of the ASTM 1895 method. The fixed pore volume (V_{fp}) was determined by water-uptake measurements¹² and the surface area was obtained from a N₂ adsorption measurement fol-

Table I Characteristics of Copolymers Synthesized in the Presence of EHEHPA

Diluent System	Composition of Diluent System (% v/v)	d_{ap} (g/cm ³)	V_{fp} (cm ³ /g)	S (m ² /g)	EHEHPA Content (% w/w)
EHEHPA	100	0.26	1.19	43	52
Isooctane/EHEHPA	100/0	0.34	0.64	66	—
	80/20	0.30	0.89	0.76	17
	50/50	0.29	1.05	58	35
	20/80	0.27	1.16	46	47
Heptane/EHEHPA	100/0	0.42	0.32	56	—
	80/20	0.33	0.76	87	18
	50/50	0.30	0.95	87	35
	20/80	0.28	1.11	48	47.5
Toluene/EHEHPA	100/0	0.62	0	^a	—
	80/20	0.61	0	^a	16.5
	60/40	0.54	0.15	49	26
	50/50	0.37	0.60	114	33
	20/80	0.31	0.94	76	43

d_{ap} , apparent density; V_{fp} , fixed pore volume; S , surface area.

^a Not measurable by BET method.

lowing the BET method (ASAP 2010, Micromeritics).

The content of EHEHPA retained in the copolymer network was determined using the 100–140 mesh fraction that was not purified with ethanol. The beads were only dried for 48 h at 60°C. A determined amount of the copolymer (around 0.5 g) was weighed and extracted by stirring during 30 min at 50°C with 25 mL of ethanol in an Erlenmeyer flask. Then, the extracted EHEHPA was titrated with a 0.1N NaOH aqueous solution using phenolftalein as an indicator. The EHEHPA content was expressed as weight-to-weight ratio.

RESULTS AND DISCUSSION

Table II presents the Hildebrand solubility parameters of the Sty–DVB copolymer and diluents used in this work. That physical constant for the chelating agent EHEHPA was not found in the literature, but we may suppose that its value is higher than that of the copolymer. This hypothesis is based on the polar structure of EHEHPA.

According to the Hildebrand solubility parameter theory, when the difference between the solubility parameters of the polymerization diluent and of the copolymer is higher than 3.0, $|\delta_1 - \delta_2| > 3$ (MPa)^{1/2}, the diluent is considered to have a low thermodynamical affinity for the copolymer.

In that case, a higher degree of phase separation will occur during the copolymerization process, resulting in highly entangled polymeric chains which will precipitate in the form of microspheres. When precipitation takes place in the presence of a bad solvent for the copolymer [$|\delta_1 - \delta_2| > 3$ (MPa)^{1/2}], the drops of the diluent diminishes the compactness of the microspheres, producing structures with large pores and, consequently, with low apparent density.^{9,14} Table II shows that isooctane is the diluent with the lowest affinity for the copolymer. The values of the apparent density for the copolymers synthesized with pure EHEHPA, isooctane, heptane, and toluene increased in that order [Fig. 1(a)], indicating that EHEHPA forms the more porous structure, i.e., it

Table II Hildebrand Solubility Parameters (δ) of the Diluents Used in the Copolymer Synthesis¹³

Diluent	δ (MPa) ^{1/2}	$ \delta_1 - \delta_2 $ (MPa) ^{1/2}
EHEHPA	?	?
Toluene	18.2	0.4
Heptane	15.1	3.5
Isooctane	14.1	4.5

δ_1 , δ of Sty–DVB copolymer equal to 18.6 (MPa)^{1/2}; δ_2 , δ of diluent.

is the worst solvent for the copolymer. This behavior is illustrated in Figure 2, where electron micrographs show resins with different porous structures. The values of pore volumes increased in the order toluene < heptane < isooctane < EHEHPA, duplicating when one changes the diluent from one to the next in the line [Fig. 1(b)]. However, the surface area had no significant changes [Fig. 1(c)]. Based on eq. (1),¹⁵ which shows the relation between pore volume and surface area, we can suggest that, probably, an accentuated increase in pore diameter has occurred with the decrease of the diluent solvating power:

$$\bar{D} \text{ is the } 4 \times 10^4 V_{p,f}/S \quad (1)$$

where \bar{D} is the average pore diameter (\AA), $V_{p,f}$ is the fixed pore volume (cm^3/g), and S is the surface area (m^2/g).

When a mixture of diluents is used, the solubility parameter of the mixture (δ_m) can be calculated by the equation of Small (2)¹⁶:

$$\delta_m = (x_1 V_1 \delta_1 + x_2 V_2 \delta_2)/(x_1 V_1 + x_2 V_2) \quad (2)$$

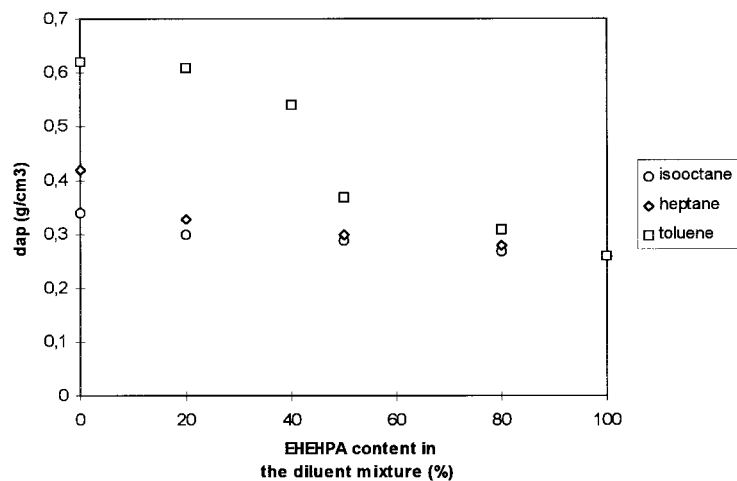
where x_1 and x_2 are the molar fractions of the diluents 1 and 2; V_1 and V_2 , the molar volume of the diluents 1 and 2; and δ_1 and δ_2 , the solubility parameter of the diluents 1 and 2, respectively. According to eq. (2), in a determined composition of the mixture, the resulting solubility parameter may assume the same value as that of the copolymer, producing a mixture with a better solvating power than that of the pure diluents. Generally, that effect, named cossolvency, is observed when the δ value of the copolymer is between the δ values of the diluents. This cossolvency effect produces polymer structures with lower pore volumes and areas than those of the structures produced with the pure agents. However, the cossolvency cannot be predicted only by the solubility parameter of the diluent mixture; it is also influenced by the structure of diluent molecules and by the interactions of the diluent molecules with themselves.¹⁰

Based on these facts, a cossolvency effect may be expected with the use of isooctane or heptane mixtures with EHEHPA, but that was not observed in this work. The macroporosity increased with increase of the EHEHPA proportions in the diluent mixture, as shown in Figure 1 (a,b). For high contents of EHEHPA (80% in diluent mixture), the copolymers obtained presented the same characteristics of the one obtained with pure

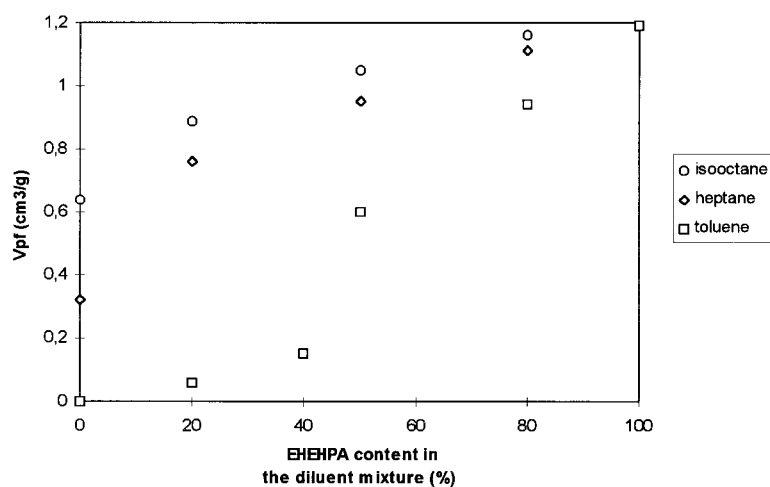
EHEHPA. The other compositions produced copolymers with intermediate characteristics relative to those produced with pure diluents. The addition of EHEHPA decreased the solvating power of isooctane and heptane, probably because these diluents have some degree of affinity with the aliphatic chains of EHEHPA and the resultant interaction is higher than their interaction with the polymer chains. Thus, an increase of phase separation during the copolymer synthesis has probably occurred. A more pronounced decrease in the apparent density and an increase in the fixed pore volume was observed in the heptane mixture when 20% of EHEHPA was used, in comparison with the similar isooctane mixture. Since heptane has a linear structure, its interaction with EHEHPA may be stronger than the interaction of isooctane with EHEHPA, which presents a branched structure that is more difficult to interact. A small amount of EHEHPA caused a more effective decrease in the solvating power of heptane than in that of isooctane, but it was not enough to make the heptane mixtures worse diluents than the isooctane mixtures. For each proportion, the isooctane system produced resins with lower apparent densities and higher fixed pore volumes than did the heptane system.

The copolymers obtained with the toluene/EHEHPA mixtures presented porosity in a dry state only when 40% or higher proportions of EHEHPA were employed in the synthesis [Fig. 1(a,b)]. Toluene is a good solvent for the copolymer and a poorer solvent for EHEHPA than is isooctane or heptane due to its aromatic structure. Thus, it is necessary to use higher amounts of EHEHPA to provoke an effective decrease in the solvent power of toluene. This system produces copolymers with lower pore volumes and higher surface areas in comparison with isooctane or heptane systems, to the proportions of 50 and 80% of EHEHPA (Table I). Probably, a decrease in pore diameter occurred when toluene was used, enhancing the solvating power of the diluent mixture. Even high amounts of EHEHPA are influenced by toluene, which can be observed in the characteristics of the copolymers prepared with 20% toluene/80% EHEHPA and 100% EHEHPA (Table I).

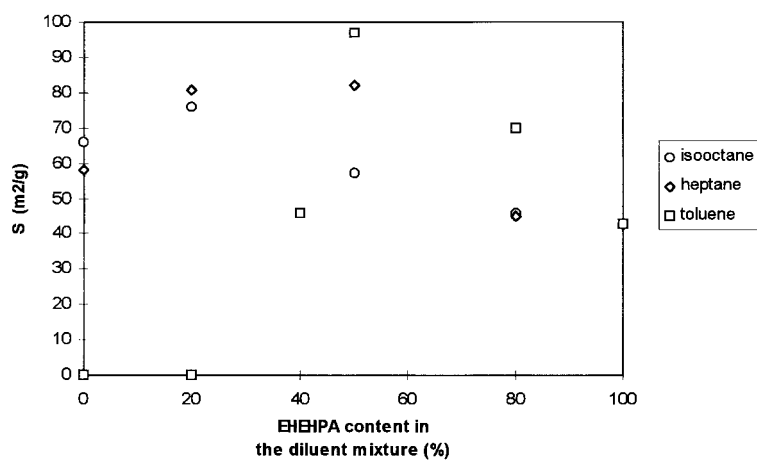
For the same composition of the diluent mixture, the content of EHEHPA in the copolymer matrix was the same for all systems, even for the copolymer prepared with 80% toluene/20% EHEHPA, which presents no porosity in the dry state (Table I). During the extraction of EHEHPA for its quantification, ethanol swelled the gel



(a)



(b)



(c)

Figure 1 Effect of EHEHPA content on (a) apparent density, (b) fixed pore volume, and (c) surface area of Sty-DVB copolymers.

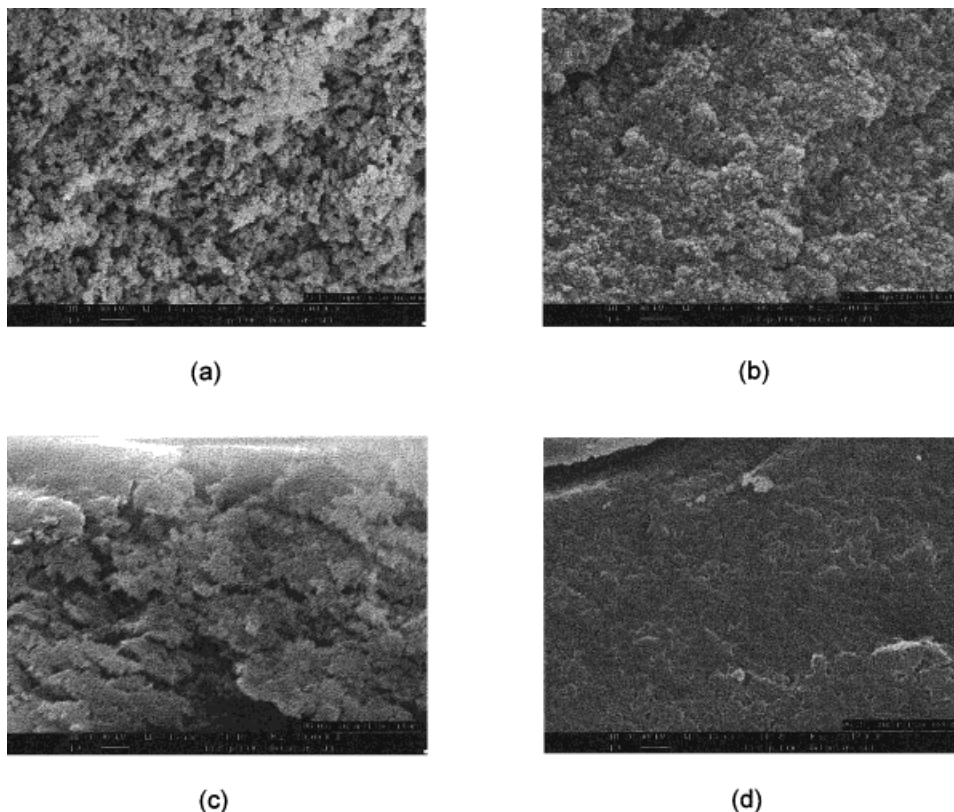


Figure 2 Electron micrographs of the internal surface of resins synthesized in presence of (a) 100% EHEHPA, (b) 100% heptane, (c) 100% isooctane, and (d) 100% toluene (magnification 25,000).

structure and extracted all the EHEHPA that was among the polymer chains. In the macroporous structure, EHEHPA is distributed in the pores and among the agglomerates of the microspheres. The amount of EHEHPA in both structures is the same, but in the gel structure, it is only accessible in the swelling state.

CONCLUSION

The adsorbents used in extraction chromatography should have a high surface area to permit the formation of an extensive layer of the chelating agent over the polymer matrix and should have large pores to make easier the diffusion process of ions through the polymer network. This ideal structure can only be reached by a diluent mixture like toluene/EHEHPA, which combines the properties of a good and a bad solvent, producing structures with intermediate characteristics of those produced with the pure diluents. In this work, a cosolvency effect for the isooctane/EHEHPA and heptane/EHEHPA systems was not observed.

The porous structures obtained by those systems are very similar, presenting very large pores, but the copolymer surface areas are not large enough to produce a homogeneous layer of the complexing agent over the polymer matrix. The content of EHEHPA in the copolymer structure was more dependent on the amount of EHEHPA used in the diluent mixture than on the type of copolymer porous structure formed. However, gel structures do not swell in water, and, consequently, metal ions cannot have contact with the chelating agent present in the whole structure. In a macroporous structure, water is able to diffuse through the macropores, making a more effective contact with the chelating agent.

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