

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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Patente de Invención ☒ Patente de Modelo de Utilidad ☐
Vía Nacional ☐
Vía PCT (fase nacional) ☒ Cap. I ☐ Cap. II ☒

No. Sol. Internacional: PCT/AU2007/001409
Fecha de Presentación Internacional: 2007-09-21.

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

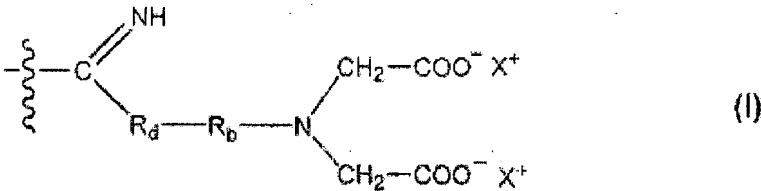
1. Documentos estudiados

Descripción:	Folios 28-65	2009-03-26
Reivindicaciones:	Folios 66-75	2009-03-26
	Folios 84-93	2009-05-28
	Folios 96-105	2009-07-15
Prioridad: AU 2006905249	Folio 1	2006-09-21

2. Objeto de la invención

Título de la solicitud: Una resina de intercambio iónico y un proceso para su uso.
Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención se refiere a una resina que es un copolímero de un poliestireno y un polímero no estirénico, en donde el polímero no estirénico incluye la subunidad de formula (I):



El problema técnico planteado en la presente solicitud de patente radica en la necesidad de diseñar una resina de intercambio iónico que sea utilizable en procesos de resina en pulpa en términos comerciales y que sea capaz de adsorber preferiblemente metales valiosos y al mismo tiempo tener una resistencia hidromecánica apropiada y una buena durabilidad, de modo tal, que se pueda utilizar repetidamente en los equipos de procesamiento de pulpa. Para solucionar ese problema técnico la presente solicitud plantea una resina que es un copolímero de un poliestireno y un polímero no estirénico, en donde el polímero no estirénico incluye la subunidad de fórmula (I).

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C08L 25/12.

3. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486), y su contenido técnico corresponde con el de la prioridad reivindicada.

4. De la solicitud de Patente

Reivindicaciones (artículo 30 D 486)

El capítulo reivindicatorio se considera una generalidad que no se encuentra soportada en la descripción y que no permite definir específicamente el objeto y el alcance de la invención. El capítulo reivindicatorio no es conciso. El solicitante debe limitar el alcance de su invención y definir específicamente la resina de interés que a su vez debe estar enteramente soportada en la descripción.

En este sentido sírvase retirar frases y expresiones tales como "*polímero no estirénico, grupo enlazante divalente, al menos, aproximadamente, es menor, menos del, por debajo, adición del agente alcalino a la fase líquida antes o durante el paso de adsorción*" dado que son imprecisas y no permiten definir el objeto ni el alcance de la invención específicamente.

Asimismo se llama la atención del solicitante frente a las reivindicaciones 14 y 15, las cuales no son claras y no definen específicamente el sustituyente de poliestireno. El solicitante debe presentar de forma clara y específica la estructura de la resina de interés. Ahora bien, sírvase definir y aclarar las estructuras N y S dado que pueden generar confusión pues no es claro si se trata de la misma estructura o no.

Igualmente se requiere al solicitante en términos de claridad frente al significado del radical NR en por ejemplo la reivindicación 1. En ninguna parte de la reivindicación se aclara el significado de R. Sírvase corregir.

Por último, no encuentra evidencia técnica suficiente para suponer que la generalización reclamada pueda tener el mismo comportamiento que muestra la particularidad ensayada. El solicitante deberá limitar el alcance de la invención y definir la resina y el método de interés.

En consecuencia, el capítulo reivindicatorio no cumple con el requisito de concisión, claridad y sustento en la descripción de acuerdo al art. 30 de la Decisión 486.

Descripción (artículo 28)

La descripción resulta ser insuficiente para el amplio alcance que tiene el capítulo reivindicatorio. Se le recuerda al solicitante que la descripción debe ser una divulgación suficiente y adecuada para la materia que se está reclamando, pero el alcance de la misma va mucho más allá de aquella materia que se encuentra enteramente soportada en la descripción. En ese sentido, esta Oficina considera que no se encuentra suficiente soporte técnico en la descripción para reclamar una extrapolación tan amplia a partir de estudios tan puntuales. El solicitante debe limitar el alcance del capítulo reivindicatorio.

Por lo tanto, la descripción no cumplió con el requisito de claridad y/o divulgación completa de acuerdo al art. 28 de la Decisión 486 y el art. 22 del Tratado PCT.

5. Determinación del Estado de la Técnica

Considerando que la fecha de la prioridad de la solicitud internacional PCT es 2006-09-21, se realizó la búsqueda en el estado de la técnica y se encontraron los documentos relacionados a continuación, que pueden afectar la patentabilidad del objeto de la presente solicitud:

Nº	Documento	Título	Fecha de publicación
D1	WO2004098775	A resin and process for extracting non-ferrous metals	2004-11-18
D2	XP008108672	Organic ion exchangers as beads. Synthesis, characterization and applications Polymers for advanced technologies, 20080801 WILEY & SONS, BOGNOR REGIS, GB - ISSN 1042-7147	2006-08-09

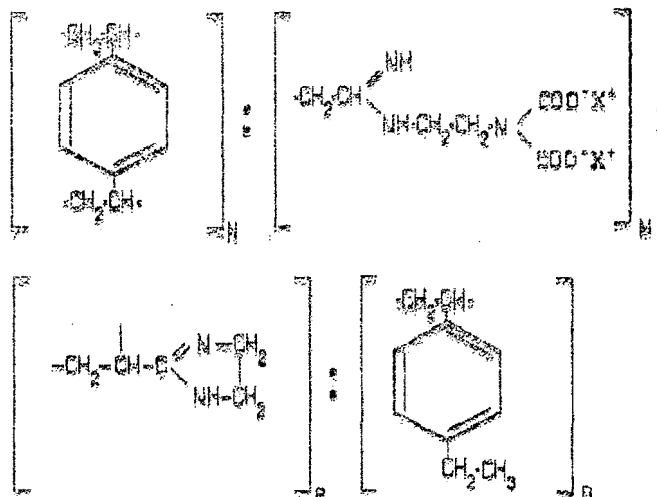
El solicitante podrá consultar el documento citado en la siguiente URL:

D1

http://worldwide.espacenet.com/publicationDetails/biblio?DB=EPODOC&II=0&ND=4&adjacent=true&locale=en_EP&FT=D&date=20041118&CC=WO&NR=2004098775A1&KC=A1

D2: anexo al expediente

El documento D1 hace referencia a una resina de intercambio iónico adecuada para la hidroextracción de metales no ferrosos a partir de materia prima como pulpas, entre otras, que tiene la estructura:

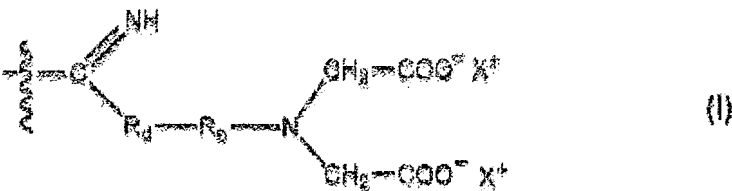


El documento D2 hace referencia a la preparación de intercambiadores aniónicos basados en subunidades de N,N-dietil-2-hidroxi-etil bencilamonio cloruro y a la preparación de intercambiadores aniónicos con grupos de amina primaria por la reacción de aminólisis-hidrólisis con grupos 1,2-diaminoetano del nitrilo, contenidos en algunos copolímeros porosos de acrilonitrilo-divinilbenceno, seguido por la carboximetilación de los grupos de amina primaria para preparar iones quelantes intercambiadores.

6. Examen de patentabilidad (artículo 14 D486)

Nivel Inventivo (artículo 18 D486)

La solicitud de patente en estudio presenta en la reivindicación 1 una resina la cual es un copolímero de un poliestireno y un polímero no estirénico, en donde el polímero no estirénico incluye la siguiente subunidad contentiva de acetato:

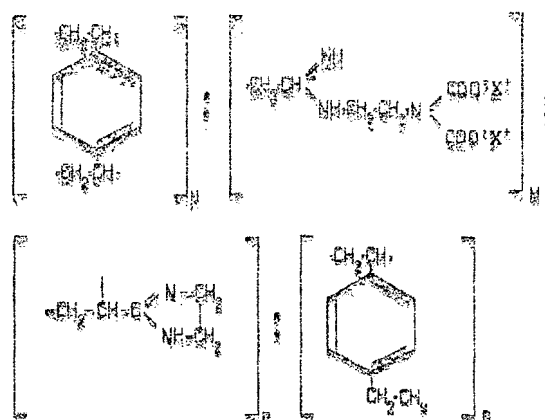


En donde R_b es un grupo enlazante divalente; R_d es NH, NR, O ó ausente.

Comparación de las características técnicas esenciales, con las del Estado de la Técnica:

Características esenciales	D1	D5
una resina la cual es un copolímero de un poliestireno y un polímero no estirénico,	una resina la cual es un copolímero de un poliestireno y un polímero no estirénico,	intercambiadores iónicos estireno-divinilbenceno que incluyen
en donde el polímero no estirénico incluye la siguiente subunidad contentiva de acetato:	en donde el polímero no estirénico incluye la siguiente subunidad:	Chemical structure of styrene-divinylbenzene ion exchange resin showing a benzene ring connected to a polymer chain with a quaternary ammonium group.
Chemical structure (I) showing a polymer chain with a wavy line on the left connected to a carbon atom. This carbon is double-bonded to an NH group and single-bonded to an R_d group. The R_d group is connected to an R_b group, which is then connected to a nitrogen atom. The nitrogen atom is bonded to two CH₂-COO⁻ X⁺ groups.	Chemical structure of a polymer chain with a wavy line on the left connected to a carbon atom. This carbon is double-bonded to an NH group and single-bonded to a CH₂ group. The CH₂ group is connected to a nitrogen atom, which is bonded to two CH₂-COO⁻ X⁺ groups.	

El documento D2 se consideran el estado de la técnica cercano a la invención definida en la reivindicación 1 porque divulga a una resina de intercambio iónico adecuada para la hidroextracción de metales no ferrosos a partir de materia prima como pulpas, entre otras, que tiene la estructura:



Específicamente, la resina de intercambio iónico de D1 es útil en procesos hidrometalúrgicos para la extracción de metales no ferrosos a partir de materia primas, tal como pulpas. Dicha resina puede ser utilizada para extraer metales no ferrosos como níquel, cobalto y cobre.

La resina divulgada en el documento D1 es especialmente estable en el proceso de extracción de metales no ferrosos, ofreciendo igualmente una alta selectividad de los mismos.

La resina del documento D1 difiere de la resina de esta invención en el radical derivado de acetato en el sustituyente de fórmula (I) tal como lo muestra la tabla anterior.

No obstante, dicha diferencia no parece provocar ningún efecto técnico inesperado o sorprendente dado que se sigue obteniendo una resina de intercambio iónico útil para procesos de extracción de metales no ferrosos (Ni y Co) desde pulpas, que son especialmente estables y selectivas.

De este modo, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así: ¿cómo modificar la resina del documento D1 para obtener una resina de intercambio iónico alternativa?

Sin embargo, la inclusión de un radical acetato en resinas de intercambio iónico basadas en copolímeros de estireno ya se había sugerido desde el documento D2 el cual presenta una sustitución de acetato en la amina terciaria de una resina análoga. Por lo tanto dicha modificación sería obvia para una persona medianamente versada en la materia. Y dado que la solicitud no presenta ninguna evidencia técnica que se pueda interpretar como un salto cualitativo en la técnica en términos de alguna mejora frente a la resina conocida desde D1, se concluye que la resina de interés es una alternativa evidente a partir del estado del arte citado que no provoca ningún efecto inesperado o sorprendente y carece de nivel inventivo. Análogamente el proceso de la reivindicación 31 tampoco tiene nivel inventivo.

7. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	WO2004098775	1-45	Nivel Inventivo
D2	XP008108572	1-45	Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento o si a pesar de la respuesta, subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.



JOSE LUIS SALAZAR LÓPEZ

Director de Nuevas Creaciones (C)

El anterior requerimiento fue notificado por fijación en lista, de fecha

28 AGO. 2012

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0729

Organic ion exchangers as beads. Synthesis, characterization and applications[†]

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Two less explored strategies in the preparation of porous organic ion exchangers in bead form are presented in this paper: the preparation of macroporous strong base anion exchangers with *N,N*-diethyl-2-hydroxyethyl benzylammonium chloride units, a less explored chloromethylation reagent of the styrene-divinylbenzene copolymers being used, and the preparation of anion exchangers with primary amine groups by the aminolysis-hydrolysis reaction with 1,2-diaminoethane of the nitrile groups, contained in some porous copolymers of acrylonitrile-divinylbenzene, followed by the carboxymethylation of the primary amine groups to prepare chelating ion exchangers. The influence of porogen nature, monomers dilution and crosslinking degree on the properties of the ion exchangers was examined. Structural characterization, functionalization-morphology correlations, the ion exchange properties, and potential applications for the ion exchangers thus prepared have been discussed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: macroporous anion exchangers; porogen; ion exchangers; synthesis; monomers

INTRODUCTION

Organic ion exchangers in bead form are still the most widely utilized materials in the purification, concentration and separation processes of inorganic and organic ions in many fields of science and industry.^{1–10} Common ionic functional groups are strong acid, weak acid, strong base and weak base; amphoteric ion exchangers, containing both base and acid functional groups, are effective in the separation of both anions and cations, and chelating ion exchangers bind mainly cations by stronger bonds than the electrostatic ones. Their synthesis is performed either by the copolymerization of monomers containing preformed ionic or ionizable groups, or by polymer analogous reactions on non-ionic crosslinked copolymers. In these investigations, some synthetic weak and strong anion exchangers have been obtained by polymer-analogous reactions performed on either porous styrene-divinylbenzene (S-DVB) copolymers^{11,12} or porous acrylonitrile-DVB (AN-DVB) copolymers.^{13,14}

A special concern has been lately focused on the preparation of macroporous strong base anion exchangers (SBAEs) effective in the enrichment process of ²³⁵U by chemical exchange in the U(IV)–U(VI) system.^{15,16} A high permanent porosity, a good stability of the resin in HCl with

concentrations up to 8 N, a thermal resistance up to 150 °C at least and a high mechanical strength are requested for this purpose. Connected with this direction, the adsorption properties of the SBAE for the uranyl chlorocomplex ions have been investigated. In previous work, the preparation of some macroporous S-DVB copolymers by employing 2-ethyl-1-hexanol (2EH) as a porogen, at a high dilution of monomers ($D \geq 0.55$), and their subsequent transformation in macroporous SBAEs with a mean pore radius higher than 50 nm and a good thermal and mechanical stability.¹² These resins showed a moderate adsorption capacity for the uranyl chlorocomplex ions, because of a low ion exchange capacity correlated with their very high pore volume. Therefore, in the present study, the characteristics of the starting macroporous S-DVB copolymers synthesized in the presence of *n*-butyl alcohol (nBA) as porogen and those of the SBAEs derived therein will be correlated to identify the possibilities to improve the adsorption capacity for uranyl chlorocomplex ions. The solubility parameters, δ_1 , of 2EH and nBA, were compared first, their values being 19.4 (MPa)^{1/2} and 23.3 (MPa)^{1/2}, respectively.¹⁷ The values of $(\delta_1 - \delta_2)^2$, where $\delta_2 = 18.60$ (MPa)^{1/2},¹⁷ corresponds to the S-DVB copolymer, which gave information about the solvating power of a certain solvent for a polymer,¹⁷ are 0.64 and 22.09, respectively. The higher value of $(\delta_1 - \delta_2)^2$ is expected to determine a higher porosity at a lower monomer dilution, when nBA is used as a porogen.¹⁸ Paraformaldehyde (CH₂O)_n/trimethylchlorosilane (TMCS) in the presence of FeCl₃ as catalyst, in CHCl₃ as a reaction medium was used for

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the chloromethylation of macroporous S-DVB copolymers. This reagent has been utilized first for the chloromethylation of linear polymers¹⁹ and recently for some macroporous S-DVB copolymers prepared in the presence of 2EH as porogen.¹² Macroporous SBAE with diethyl 2-hydroxyethyl benzylammonium groups were obtained by the amination of the chloromethylated S-DVB copolymers with diethyl 2-hydroxyethylamine (DEHEA).

Among the weak base anion exchangers (WBAEs), those bearing primary amine groups are of a great interest due to their high reactivity, which offer a good chance for various post-derivatization reactions. However, ion exchangers with primary amine groups are difficult to obtain by chemical reactions on S-DVB copolymers. Hofmann degradation of the amide groups contained in a crosslinked copolymer of acrylamide (AA), according to the method employed by Tanaka and Senju for the preparation of poly(vinylamine) from polyacrylamide,²⁰ has been already used to prepare WBAEs with vinylamine units.²¹ WBAEs with aminoethylacrylamide units were generated in this study by the aminolysis-hydrolysis reaction with 1,2-diaminoethane (EDA) of the nitrile groups, contained in some porous AN-DVB copolymers, according to the method previously established for polyacrylonitrile (PAN)²² and applied by others.²³ A large number of studies about the synthesis and characterization of the selective chelating ion exchangers with wide applicability in the removal of toxic metal and complex ions from industrial effluents, as well as in metal ion recovery processes, were lately achieved.^{4-7,9} Therefore, anion exchangers with primary amine groups were further post derivatized by a carboxymethylation process with $\text{ClCH}_2\text{COONa}$ (NaMCA) to prepare porous chelating ion exchangers (CIEs) with iminodiacetic functional groups.

Fourier transform infrared (FT-IR) spectroscopy, solvent uptakes, morphological characterization in the dry state and ion exchange capacity measurements were used in order to obtain deeper information on the structural changes which occur by the chemical reactions on the earlier mentioned copolymers. The adsorption capacity for uranyl chlorocomplex ions of the SBAEs, and for Cu^{2+} of the CIEs was also examined.

EXPERIMENTAL

Materials

Styrene, technical grade (99% purity) was distilled at 400 Pa before use. DVB, technical grade (54.5% *o*-DVB, *m*-DVB, *p*-DVB, 36.2% ethylstyrene and 9.3% inert compounds, by gas chromatography) was distilled at 400 Pa before use. Benzoyl peroxide (BPO) was employed as a radical polymerization initiator for all copolymers after two times recrystallization from methanol. Toluene and nBA used as porogens were reagent grade and used as received. 2EH technical grade was distilled at 183.5 °C and 101.3×10^3 Pa. Gasoline with a distillation range, $t_f = 110\text{--}130^\circ\text{C}$, at 101.3×10^3 Pa was used as received. $(\text{CH}_2\text{O})_n$, technical grade, was used as received. FeCl_3 and TMCS from Fluka Chemical Co. (Buchs, Switzerland) were used without further purification. Chloroform, distilled at normal pressure after washing three times with water and drying for 48 hr on Na_2SO_4 , was used as solvent. DEHEA, purchased from Fluka Chemical Co.

(Buchs, Switzerland), was distilled at 400 Pa before use. Acrylonitrile, technical grade, was distilled at $76\text{--}77^\circ\text{C}$, 101.3×10^3 Pa. EDA was distilled at 125°C , 101.3×10^3 Pa before use. NaMCA was prepared by the reaction between the monochloroacetic acid and NaOH in ethanol.

Methods

Macroporous S-DVB copolymers, as finely divided beads with diameters within the range $90\text{--}200\ \mu\text{m}$, were prepared by the suspension polymerization method. The organic phase was added in a volume ratio of 1:2.5 to the aqueous phase which contained 0.2% ammonium salt of styrene-maleic acid copolymer, 0.2% food grade gelatine and 2% NaCl, prepared in a four-necked reaction reactor (1000 ml) fitted with a mechanical stirrer, condenser and thermometer. The stirrer speed was kept at around 320 rpm in order to obtain at least 90% beads with diameter within the range $90\text{--}200\ \mu\text{m}$. The polymerization was allowed to proceed at 60, 80 and 85°C for 1, 10 and 3 hr, respectively. Afterwards, the copolymer beads were filtered and sieved under water, and finally washed with warm water to remove the dispersing agents. The removal of porogen was performed by static methanol extraction as previously shown in the literature.¹² Nominal crosslinking degree of copolymers was taken as the DVB content in the monomers mixture. Dilution of the monomer mixture, D , was calculated as the ratio between the volume of porogen (V_P) and the volume of the whole organic phase ($V_m + V_P$), $[D = V_P / (V_m + V_P)]$.

A mixture of commercial $(\text{CH}_2\text{O})_n$ and TMCS in an equimolar ratio, as chloromethylation agent, and FeCl_3 , as catalyst, were used for the chloromethylation reaction in CHCl_3 as a reaction medium, at 50°C . Chloromethylated copolymers (CMC) were separated from the reaction mixture, washed three times with methanol, two times with water/methanol (1:1, v/v) and finally with methanol. CMC samples were dried at 40°C for 48 hr and then characterized by total chlorine content, Schöniger method, and morphological characteristics, as will be described later. Synthesis of SBAEs was performed by the reaction of the CMC samples with DEHEA in water *N,N*-dimethylformamide (DMF) as a reaction medium at 60°C , at an amine/Cl ratio of 2:1, for 10 hr. Afterwards, the anion exchanger samples were separated by filtration from the reaction mixture, washed two times with water and then quantitatively collected and kept under water.

AN-DVB copolymers were prepared in the presence of three porogens: gasoline with $t_f = 110\text{--}130^\circ\text{C}$, toluene and 2EH by a suspension polymerization method, as follows: ratio between the aqueous phase to organic phase was 2:1; temperature regime was 2 hr at 60°C , 3 hr at 70°C and 5 hr at 85°C . The copolymer fraction with bead sizes in the range $0.35\text{--}1.00\ \text{mm}$ was selected, porogen was removed by extraction with methanol and PAN likely to be formed in this monomer mixture was removed with DMF, 24 hr. Finally, the AN-DVB beads were washed with methanol and dried at room temperature, 24 hr and in vacuum at 50°C , 48 hr. Anion exchangers with primary amine groups were obtained by the aminolysis-hydrolysis reaction of the nitrile groups with EDA, 8 hr at $118\text{--}120^\circ\text{C}$, at a molar ratio nitrile/EDA/ H_2O of 1:10:2. The excess of EDA was removed by distillation,

filtration and finally washing the beads with distilled water up to the neutral pH. To prepare a CIE with iminodiacetate groups, the ion exchangers with primary amine groups were reacted with NaMCA, in aqueous medium, at 70 °C and a pH 7.5–8.0, with NaI as catalyst.

The anion exchange capacity was determined as previously shown after the regeneration of the anion exchanger with NaOH 1 mol/l.¹³ Determination of cation exchange capacity was performed as it has been previously shown.²⁴ For the structural and morphological characterization in the dry state, the anion exchangers were usually rinsed several times with anhydrous ethanol and then left in *iso*-propyl alcohol for 24 hr. Finally, the beads were rinsed three times with anhydrous methanol, dried in air at room temperature for 24 hr and at 40 °C under reduced pressure for 3 days.

The FT-IR spectra were recorded on a DIGILAB spectrometer Scimitar Series, USA, resolution of 4 cm⁻¹, using KBr pellets. The solvents uptake coefficients were determined by centrifuging samples at 500 g after an immersion for 48 hr in the appropriate solvent. The apparent density (ρ_{ap}) was determined using a mercury pycnometer at 1.333 × 10⁻² Pa. The real density (ρ_r) was measured in *n*-heptane. The specific surface area (S_{sp}) was determined by the nitrogen adsorption at the boiling temperature of liquid nitrogen, by the Haul-Dümbgen method on a Ströhlein Area Meter apparatus. The average pore radius was calculated using the following equation, cylindrical shape of pores being assumed:

$$r_p = (2V_p/S_{sp}) \times 10^3 \text{ (nm)} \quad (1)$$

where $V_p = (1/\rho_{ap}) - (1/\rho_r)$, pore total volume (in cm³/g).

Sorption capacity for the uranyl chlorocomplex ions was performed as previously shown.^{12,25} Study of the metal ion retention properties of the chelating ion exchangers was done using batch equilibrium procedure. Thus, aqueous metal ion solutions (100 ml) with different concentrations were treated with about 2.0 g of ion exchangers at room temperature. The metal ion solution was CuSO₄ · 5H₂O with different concentrations. The pH of the metal-ion solution was adjusted before equilibration over a range of 3 to 6 with a citrate-phosphate buffer solution. The resin was filtered off, and the concentration of the metal ion remaining in the filtrate was measured by UV-vis spectroscopy at 775 nm (that was the maximum absorption wavelength of CuSO₄). UV-vis

spectroscopy was performed on a UV-vis Specord M42 Carl Zeiss Jena, Germany.

The concentration of metal ion bound was calculated with eqn (2)²⁶:

$$\text{Metal ion bound} = [(S_0 - S)V]/(W \times 1000) \quad (2)$$

where S_0 and S are the concentrations of the metal ion in aqueous solution (in mg/l) before and after the interaction with chelating resin, respectively, V is the volume of the aqueous phase (in ml) and W is the amount of the dry resin (in g).

RESULTS AND DISCUSSION

Macroporous strong base anion exchangers with *N,N*-diethyl 2-hydroxyethyl benzylammonium functional groups

Morphological characteristics, pore volume, V_p , specific surface area, S_{sp} , and mean pore radius, r_p , of some macroporous S-DVB copolymers, synthesized in the presence of nBA as porogen were collected and the results are shown in Table 1.

As Table 1 shows, at the same crosslinking degree, the pore volume, V_p , increased, with the increase in dilution. The specific surface area, S_{sp} , decreased and the mean pore radius, r_p , increased with the increase in dilution. At a constant dilution, the pore volume, V_p , increased, the surface area, S_{sp} , increased too, and the average pore radius, r_p , decreased with the increase of the nominal crosslinking degree, as expected. The earlier mentioned copolymers were used in the preparation of some SBAEs, the first step being the chloromethylation with (CH₂O)_n/TMCS in the presence of FeCl₃ as catalyst, first at a molar ratio of 1:8:8:0.5, styrene/(CH₂O)_n/TMCS/FeCl₃, in CHCl₃ as a reaction medium, as has been described in detail elsewhere.¹²

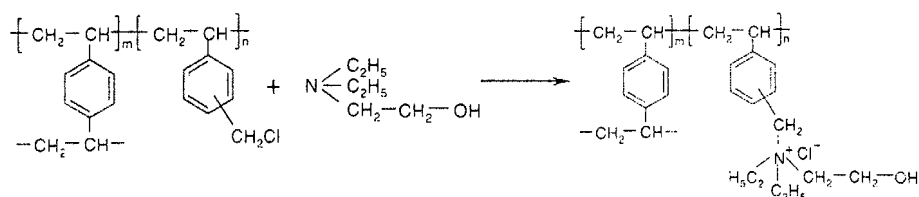
Table 1 shows that some morphological changes occur in the chloromethylation process. Thus, the pore volume, V_p , decreased, the specific surface area, S_{sp} , increased and the mean pore radius, r_p , decreased, and all these changes show that further crosslinks were generated most probably by the self-alkylation reaction as a side reaction.¹² To optimize the chloromethylation process with this new chloromethylation agent, some further investigations were necessary.²⁷ Thus, it was observed that the decrease of the catalyst content has a

Table 1. Morphological characteristics of the starting S-DVB matrix and the corresponding SBAE

DVB/dilution	Transformation stage	V_p (ml/g ¹)	S_{sp} (m ² /g ¹)	r_p (nm)
8:0.44	Starting copolymer	1.035	23.5	88.1
	CMC ^a	0.814	78	20.8
	SBAE	1.03	26.1	79
8:0.44	Starting copolymer	1.035	23.5	88.1
	CMC ^b	0.956	42.8	48.9
	SBAE	1.164	26.75	87
8:0.48	Starting copolymer	1.3472	13.5	199.6
	SBAE	1.2514	7.3	343
10:0.44	Starting copolymer	1.1707	41.1	56.9
	CMC	0.5451	52	20.9
	SBAE	1.1316	40.2	56.3

^a FeCl₃/styrene = 0.5:1, molar ratio.

^b FeCl₃/styrene = 0.1:1, molar ratio.



Scheme 1.

positive influence, reducing the impact of the chloromethylation step on the morphological characteristics of the starting S-DVB copolymer. The influence of the FeCl_3 /styrene molar ratio on the morphology of the chloromethylated copolymer can be seen in Table 1, where two samples of CMC derived from the copolymer with 8% DVB and $D = 0.44 \text{ ml/ml}$ and functionalized with 0.5:1 and 0.1:1 FeCl_3 /styrene molar ratio are included. A lower S_{sp} and a higher r_p are observed for the lower catalyst/styrene molar ratio. Therefore, in the preparation of the SBAE a molar ratio of 0.1:1, FeCl_3 /styrene was used.

SBAEs were prepared by the reaction of CMC with DEHA, according to Scheme 1.

A particular aspect of the SBAE included in Table 1 is that the morphological characteristics, V_p , S_{sp} , and r_p , of the final resins are comparable with those of the starting S-DVB copolymers.

Functional characteristics of some SBAEs, as a function of the nominal DVB content, are presented in Table 2. The values of the ion exchange capacities are in good agreement with the high porosity of these anion exchangers, a higher ion exchange capacity being observed when the DVB content of the starting copolymer was lower. Table 2 includes also a SBAE sample prepared in the presence of 2EH as porogen,¹² and a commercial anion exchanger having a swelling porosity,²⁵ for comparison.

Table 2 shows that at a lower ion exchange capacity, correlated with a higher permanent porosity, a lower amount of uranium was adsorbed. As Table 2 shows, even if the ion exchange capacity of the resin Dowex Marathon is much higher than that of the macroporous SBAE derived from the copolymer prepared with nBA as porogen, the difference between the adsorption capacity values of uranium is not so high. This shows that both the permanent porosity and the structure of the functional groups must have a contribution. A study on the influence of the functional group and of the temperature on the adsorption capacity of uranium will be presented in a forthcoming article.

Weak base anion exchangers with 2-aminoethylacrylamide units and chelating resins derived therein

Solvent regain for some AN-DVB copolymers prepared in the presence of gasoline with t_f 110–130 °C as porogen, at a constant monomer dilution, $D = 0.15 \text{ ml/ml}$, were plotted in Fig. 1. The influence of the monomer dilution on the solvent regains, at a constant crosslinking degree, 10% DVB, when toluene and 2EH were used as porogens, can be observed in Fig. 2.

As Fig. 1 shows, the AN-DVB copolymer, with the highest content in AN (6% DVB), has the highest values of solvent regain, for both solvents (cyclohexane and toluene). These results were explained by the higher swelling in DMF of the copolymers with a lower content in DVB. The good solvent (DMF), used in the extraction step of the soluble PAN from the AN-DVB copolymer, was replaced from copolymer with methanol, which is a non-solvent for both the PAN sequences and the aromatic components. Thus, the swelling porosity

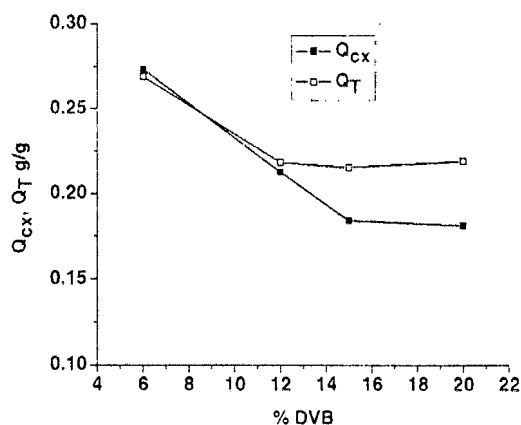


Figure 1. Solvent regains as a function of DVB content of the AN-DVB copolymers prepared in the presence of gasoline with $t_f = 110$ –130 °C as porogen, at a dilution of monomers of 0.15 ml/ml: cyclohexane, Q_{CX} , and toluene, Q_T .

Table 2. Functional characteristics of the SBAEs

SBAE based on S-DVB copolymer, DVB/dilution/porogen	Ion exchange capacity		Uranium sorption capacity (mg U/g of dry resin) ^b	Pore volume (ml/g)
	(meq/ml)	(meq/g)		
10:0.55:2EH	0.325	1.424	31.90	1.39
8:0.44:nBA	0.61	1.75	161.6	1.164
10:0.44:nBA	0.552	1.51	—	1.131
Dowex Marathon ^a	1.1	—	194.32	Swelling porosity

^aIncluded for comparison.

^bAccording to refs. 12 and 25.

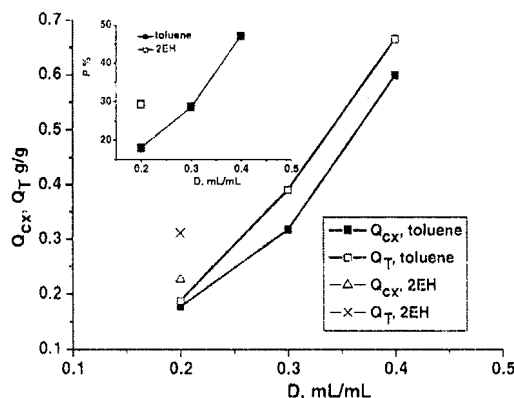


Figure 2. Solvent regains as a function of the monomer dilution of the AN-DVB copolymers prepared in the presence of toluene and 2EH as porogens, at a nominal crosslinking degree of 10% DVB: cyclohexane, Q_{CX} , and toluene, Q_T . The inset: porosity of the same AN-DVB copolymers.

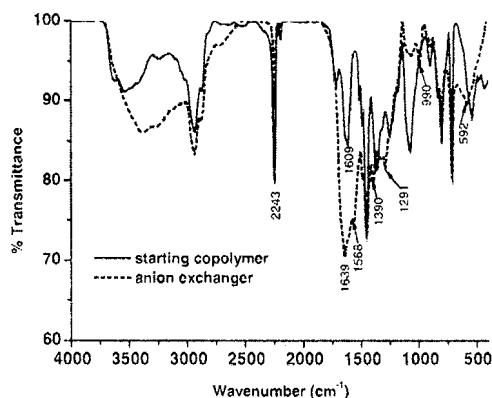


Figure 3. FT-IR spectra of the WBAE comparative with the starting copolymer with a nominal crosslinking degree of 12% DVB and a monomer dilution of 0.15 mL/mL, gasoline as porogen.

was completely preserved.¹¹ After about 12% DVB, the swelling porosity had a lower contribution. The higher values of Q_T compared with Q_{CX} at higher crosslinking degree, are explained by the increase of toluene affinity for the copolymers with a higher content in aromatic components.

Figure 2 shows higher solvent regains (Q_{CX} and Q_T) of the AN-DVB copolymers with 10% DVB when 2EH has been used as a porogen comparative with toluene, at the same dilution of monomers. This shows a higher solvating power of toluene than of 2EH, because of the presence of DVB and ethylstyrene as comonomers in this matrix. These results are supported by the porosity values (the inset of Fig. 2).

WBAEs with primary amine groups were prepared by the reaction of AN-DVB copolymers with EDA, in the presence of water, according to Scheme 2.

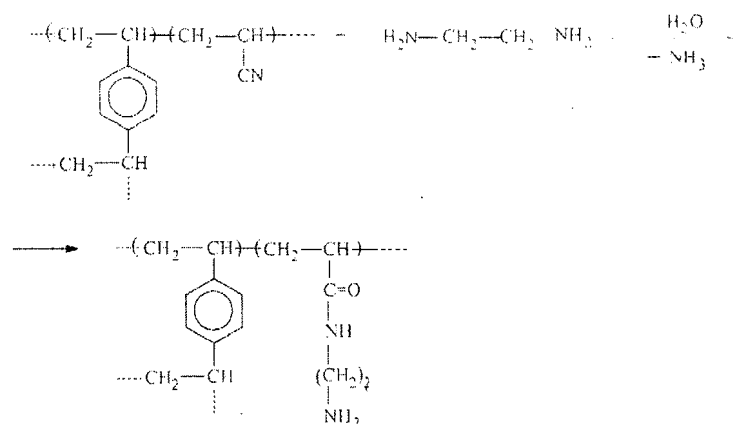
The first information about the transformation of the nitrile groups into 2-aminoethylacrylamide groups were supplied by FT-IR spectra. As Fig. 3 shows, the characteristic band of the nitrile groups from 2243 cm^{-1} diminished, but it is still present after 8 hr of reaction with EDA of the AN-DVB

copolymer with 12% crosslinking degree. The new bands at 1639 , 1568 and 1291 cm^{-1} have been assigned as follows: the stretching vibrations of the C=O bond (amide I band), the deformation vibrations of the N-H bond (amide II band), the O-C-N bond (amide III band), respectively.

After 10 hr of reaction the ion exchange capacity slightly increased, but the characteristic band of the nitrile groups was still present.

Anion exchange capacities, both volumetric (C_{ev}) and gravimetric (C_{eg}), as a function of the starting copolymer structure, are plotted in Fig. 4.

Gravimetric ion exchange capacity, C_{eg} , is correlated with the content of ionic groups in the dry state of the anion exchanger, which intimately depend on the AN content in the starting copolymer. As Fig. 4 shows, C_{eg} continuously decreased with decreasing AN content. However, C_{ev} also depends on the content of ionic groups, but furthermore is correlated with the ability of the anion exchanger to be swollen in water, usually slightly increasing with the increase of the crosslinking degree. The values of C_{eg} in Fig. 4 show a slight increase with the increase of DVB from



Scheme 2.

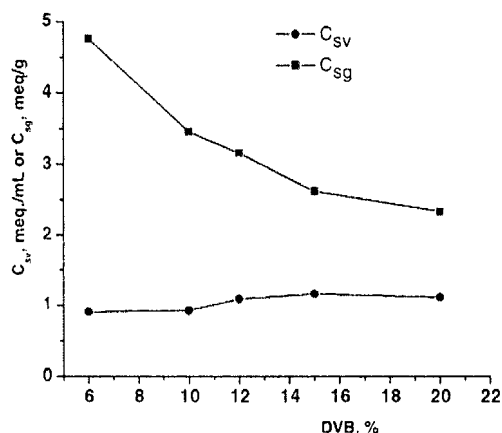


Figure 4. Ion exchange capacities of the WBAEs derived from AN-DVB as a function of DVB content; gasoline with $t_1 = 110\text{--}130^\circ\text{C}$ was the porogen, at a monomer dilution of 0.15 ml/ml.

6 to 12% and a plateau up to 20% of DVB after that, and thus confirming our expectations.

As Fig. 5 shows, the trend of the porosity, indicated first by the solvent regain of the starting copolymers prepared in the presence of gasoline as porogen (Fig. 1), was confirmed by the porosity values as a function of the nominal crosslinking degree, an abrupt decrease being observed with the increase

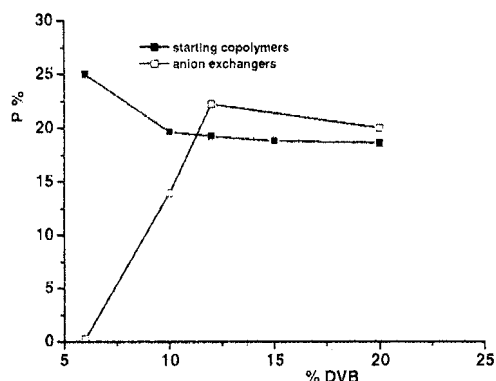


Figure 5. Porosity of the WBAEs derived from AN-DVB as a function of DVB content; gasoline with $t_1 = 110\text{--}130^\circ\text{C}$ was the porogen, at a monomer dilution of 0.15 ml/ml comparative with the starting copolymer.

of DVB content from 6 to 10% and a monotonous, but slight decrease, after that.

A different behavior was observed for the corresponding WBAE. The absence of a permanent porosity for the anion exchanger derived from the copolymer with 6% DVB can be observed, followed by a fast increase up to about 12% DVB and a slight decrease after that. The anion exchanger samples used for the determination of porosity have been dried by heating the samples at 105°C , up to a constant weight. Water is a good solvent for the anion exchangers and therefore a collapse of their structure occurred at a low content of the crosslinker. Such anion exchangers seem to become permanently porous only after 12% of DVB.

To obtain CIEs with iminodiacetic groups, the post-derivatization of the primary amine groups by the reaction with NaMCA was performed in the present study, according to Scheme 3.

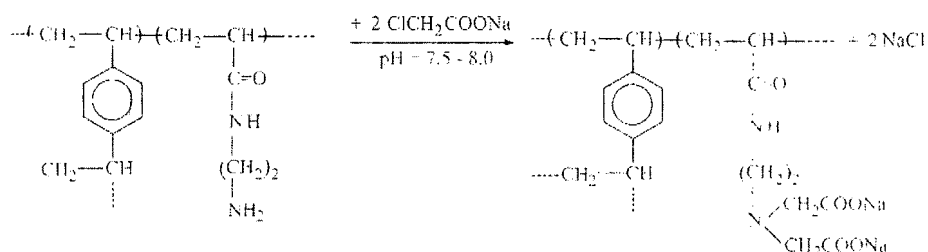
To monitor the progress of the nucleophilic substitution reaction, the ratio between the ionic chlorine content found at a given moment, and the theoretical value expected for a complete transformation of the primary amine groups into tertiary amine groups (Scheme 3) was followed, this being considered the transformation degree (α). In Fig. 6 is plotted the transformation degree (α) of the primary amine groups into iminodiacetic groups, as a function of the reaction duration (hr), anion exchanger based on the copolymer with 12% DVB and gasoline as porogen, at a monomer dilution of 0.15 ml/ml. By using NaI as a catalyst, the reaction was complete in about 9 hr, because an interhalogen exchange occurred in this case.

The FT-IR spectra of the WBAE with primary amine groups and the corresponding CIE are shown in Fig. 7. Besides the characteristic bands of the secondary amide (1640 , 1291 cm^{-1}), the new bands at 1452 and 1394 cm^{-1} , assigned to carboxylic groups, were observed in the FT-IR spectra of the CIE.

Metal complexation capacities of two CIEs, whose characteristics are presented in Table 3, are illustrated in Fig. 8 as a function of the initial concentration of CuSO_4 .

A monotonous increase of Cu^{2+} retention was observed for the resin with the higher ion exchange capacity and a lower porosity. However, the adsorption capacity of the resin with the higher porosity (CIE2, Table 3) was less dependent on the initial concentration of the metal solution, but increased significantly after 48 hr (results not shown here).

The inset of Fig. 8 shows that the adsorption results obtained with the resin CIE1 obey the Freundlich isotherm.



Scheme 3.

116

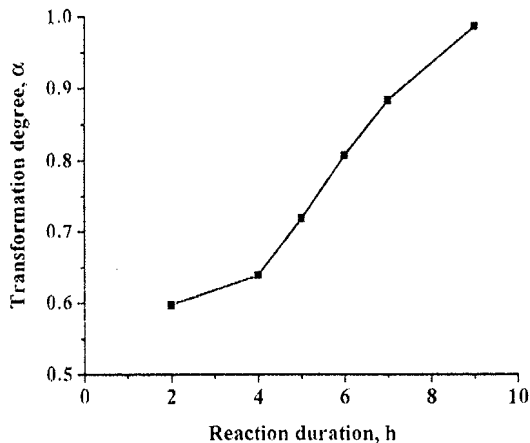


Figure 6. Transformation degree of the primary amine groups into iminodiacetic groups: starting copolymer: with 12% DVB and a dilution of 0.15 ml/ml, gasoline with $t_f = 110\text{--}130^\circ\text{C}$ was the porogen.

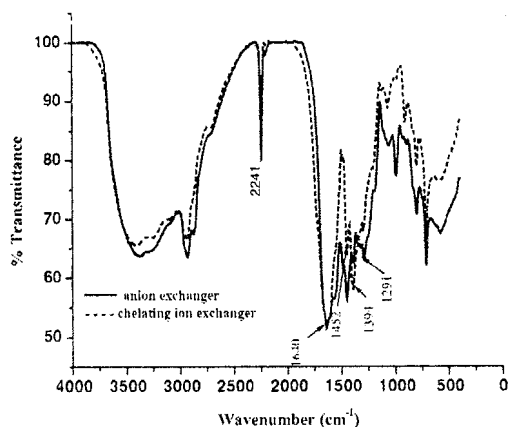


Figure 7. FT-IR spectra of the anion exchanger with primary amine groups prepared by the aminolysis-hydrolysis of the AN-DVB copolymer with 12% DVB and a dilution of 0.15 ml/ml, gasoline with $t_f = 110\text{--}130^\circ\text{C}$ as porogen (—), and of the corresponding chelating ion exchanger (---).

eqn (3):

$$\log q_e = \log k_f + (1/n) \log C_e \quad (3)$$

where q_e , the amount of metal adsorbed at equilibrium (in mg/g), k_f and n are Freundlich constants and C_e is the equilibrium concentration (in mg/l).

The Cu^{2+} retention continuously decreased with the increase of pH from 3 to 6 for both CIE resins, as Fig. 9 shows. It seems that the optimum adsorption pH of Cu^{2+} is located between 2.0 and 3.0.

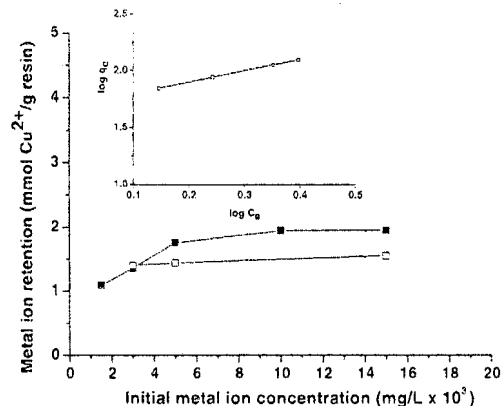


Figure 8. Cu^{2+} retention as a function of the structure of the CIE and the initial concentration of the metal solution. The inset: Freundlich isotherm for the CIE with 12% DVB and a monomer dilution of 0.15 ml/ml.

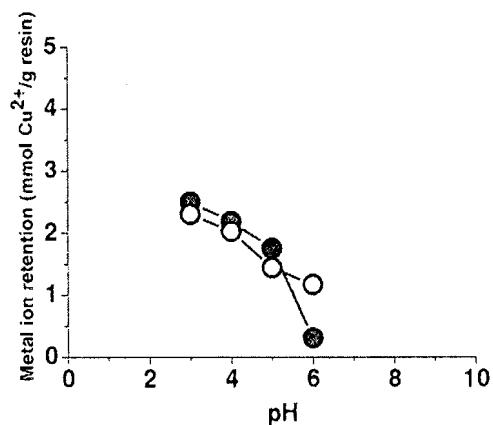


Figure 9. The influence of the solution pH on the Cu^{2+} retention at an initial Cu^{2+} concentration of 5×10^{-3} mg/l.

CONCLUSIONS

The synthesis and characterization of some porous ion exchangers, by less used strategies, were examined in this work as follows:

- SBAEs with *N,N*-diethyl 2-hydroxyethyl vinylbenzylammonium chloride units and a mean pore radius in the range 50–80 nm were prepared by the chloromethylation of the macroporous S-DVB copolymers, obtained in the presence of nBA as porogen, with a less used chloromethylation agent, $(\text{CH}_2\text{O})_n/(\text{TMCS})$, in the presence of FeCl_3 as catalyst, followed by the amination with DEHEA;
- WBAEs with 2-aminoethylacrylamide units were obtained by the aminolysis-hydrolysis reaction of the nitrile groups

Table 3. Characteristics of the CIEs

Sample	DVB (%)	Porogen	D (ml/ml)	P (%)	C_{gv} (meq/ml)	C_{sg} (meq/g)	Q_w (g/g)
CIE1	12	Gasoline, $t_f = 110\text{--}130^\circ\text{C}$	0.15	15	1.87	4.97	0.755
CIE2	15	Toluene	0.47	35	1.106	2.907	—

contained in AN-DVB copolymers prepared in the presence of three porogens (toluene, gasoline and 2EH) with different solubility parameters;

- CIEs with iminodiacetic groups were generated by the carboxymethylation of the primary amine groups with NaMCA, in the presence of NaI.
- sorption capacity of Cu^{2+} of the CIE was influenced by the porosity of the resin and the solution pH.

REFERENCES

- Alberti G, Casciola M, Constantino U. In *Encyclopedia of Analytical Chemistry*, vol. 4, Townshend A, Worsfold PJ (eds). Academic Press: London, 1995; 2273–2278.
- Fontanals N, Marcé RM, Galà M, Borull F. Preparation and characterization of highly polar polymeric sorbents from styrene-divinylbenzene and vinylpyridine-divinylbenzene for the solid-phase extraction of polar organic pollutants. *J. Polym. Sci., Part A: Polym. Chem. Ed.* 2003; **41**: 1927–1933.
- Liu C, Tang T, Huang B. Preparation of macroporous functionalized polymer beads by a multistep polymerization and their application in zirconocene catalysts for ethylene polymerization. *J. Polym. Sci., Part A: Polym. Chem. Ed.* 2003; **41**: 873–880.
- Denizli A, Sanli N, Garipcan B, Patir S, Alsancak G. Methacryloylamidoglutaric acid incorporated porous poly(methylmethacrylate) beads for heavy-metal removal. *Ind. Eng. Chem. Res.* 2004; **43**: 6095–6101.
- Luca C, Măruță C, Bumia I, Urmenyi AM, Sandu M, Rață D. Acrylic weak-base anion exchangers and their behaviors in the retention process of some heavy-metal cations. *J. Appl. Polym. Sci.* 2005; **97**: 930–938.
- Malik AM, Mukhtar R, Zaidi SAR, Ahmed S, Ajzal Awan M. Ion-exchange properties of 4-vinylpyridine-divinylbenzene based anion exchangers for ferric chloride complex anions. *React. Funct. Polym.* 2002; **51**: 117–120.
- Park I-H, Suh J-M. Preparation and uranyl ion adsorptivity of macroporous chelating resins containing a pair of neighboring amidoxime groups in a monomeric styrene unit. *Angew. Makromol. Chem.* 1996; **239**: 121–132.
- Martel B, Morcellet M. Sorption of aromatic compounds in water using polymer sorbents containing amino groups. *J. Appl. Polym. Sci.* 1994; **51**: 443–451.
- Rivas BL, Jara M, Pereira ED. Preparation and adsorption properties of the chelating resins containing carboxylic, sulfonic and imidazole groups. *J. Appl. Polym. Sci.* 2003; **89**: 2852–2856.
- Badyal JP, Cameron AM, Cameron NR, Oates LJ, Øye G, Steel PG, Davis BG, Coe DM, Cox RA. Comparison of the effect of pore architecture and bead size on the extent of plasmachemical amine functionalization of poly(styrene-co-divinylbenzene) permanently porous resins. *Polymer* 2004; **45**: 2185–2192.
- Dragan S, Csergő D, Manolescu I, Carpov A. 2-Ethyl-1-hexanol as diluent in the synthesis of styrene-divinylbenzene copolymers and anion exchangers. I. Morphological aspects. *React. Polym.* 1987; **5**: 123–131.
- Dragan ES, Avram E, Axente D, Marcu C. Ion exchange resins. III. Functionalization-morphology correlations in the synthesis of some macroporous, strong basic anion exchangers and uranium-sorption properties evaluation. *J. Polym. Sci., Part A: Polym. Chem. Ed.* 2004; **42**: 2451–2461.
- Dragan S, Grigoriu G. Ion exchange resins. I. Anion exchangers with tertiary amine groups on poly(acrylonitrile-co-divinylbenzene) networks. *Angew. Makromol. Chem.* 1992; **200**: 27–36.
- Dragan S, Cristea M, Airinei A, Poinescu Ig, Luca C. Sorption of aromatic compounds on macroporous anion exchangers based on polyacrylamide: relation between structure and sorption properties. *J. Appl. Polym. Sci.* 1995; **55**: 421–430.
- Kawakami F, Okuyama K, Obanawa H, Takeda K. ACEP adsorbent structure and characteristics. *Bull. Res. Lab. Nucl. Reactors* 1992; **1**: 182–185.
- Nomura M, Higuchi N, Fuji Y. Mass dependence of uranium isotope effects in the U(IV)-U(VI) exchange reaction. *J. Am. Chem. Soc.* 1996; **118**: 9127–9130.
- Gardon JL. In *Encyclopedia of Polymer Science and Technology*, vol. 3, Mark HF, Gaylord NG, Bikales NM (eds). Wiley: New York, 1965; 833–842.
- Okay O. Macroporous copolymer networks. *Prog. Polym. Sci.* 2000; **25**: 711–779.
- Avram E. Polymers with pendent functional groups. VI. A comparative study on the chloromethylation of linear polystyrene and polysulphone with paraformaldehyde/ Me_3SiCl . *Polym.-Plast. Technol. Eng.* 2001; **40**: 275–281.
- Tanaka H, Senju R. Preparation of polyvinylamine by the Hofmann degradation of polyacrylamide. *Bull. Chem. Soc. Jpn.* 1976; **49**: 2821–2823.
- Dragan S, Dinu MV, Vlad CD. Ion exchange resins. II. Acrylamide crosslinked copolymers as precursors for some ion exchangers. *J. Appl. Polym. Sci.* 2003; **89**: 2701–2707.
- Dragan S, Barboiu V, Petrariu I, Dima M. Cationic polyelectrolytes. III. Nitrile-groups reaction of macromolecular compounds with *N,N*-dialkylaminoalkylamines. *J. Polym. Sci., Polym. Chem. Ed.* 1981; **19**: 2869–2880.
- Kolarz BN, Wojaczynska M, Herman B. Polyacrylamide sorbents. Synthesis and sorption properties. *React. Polym.* 1989; **11**: 29–35.
- Dragan S, Vlad CD. Functional polymers based on acrylamide crosslinked copolymers. *Macromol. Symp.* 2002; **181**: 47–55.
- Axente D, Marcu C, Dragan ES, Avram E. Adsorption of U(VI) from HCl solutions on anion exchange resins. *Rev. Chim.* 2005; **56**: 825–829.
- El-Hamshary H, El-Garawany M, Assubaie FN, Al-Eed M. Synthesis of poly(acrylamide-co-vinylpyridine) hydrogels and their application in heavy metal removal. *J. Appl. Polym. Sci.* 2003; **89**: 2522–2526.
- Avram E, Dragan ES. Morphological changes induced by the chloromethylation reaction as a function of the chloromethylation conditions with $\text{TMCS} \cdot \text{CH}_2\text{O}$. *React. Funct. Polym.* Submitted for publication.