

# Preparation and properties of ion-exchange resin possessing complexing group based on $\alpha$ -amino acid bound to hydroxyethylmethacrylate gel

<sup>a</sup>V. HADRABOVÁ, <sup>b</sup>J. ČOUPEK, and <sup>a</sup>J. MAJER

<sup>a</sup>Department of Analytical Chemistry, Faculty of Pharmacy,  
Komenský University, CS-832 32 Bratislava

<sup>b</sup>Laboratorní přístroje, CS-162 03 Prague

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This paper deals with the preparation of ion-exchange resin possessing complexing group. That was gained by modification of the fundamental material Separon HEMA, to the side chains of which the  $\alpha$ -amino acid lysine was introduced. Simultaneously its properties are studied, which results in determination of distribution coefficients for three cations Cu(II), Ni(II), and Zn(II) in dependence on pH.

Работа посвящена приготовлению ионообменников с комплексообразующей группой посредством модификации исходного материала Сепарон ГЕМА введением  $\alpha$ -аминокислоты лизина в боковые цепи. Одновременно изучаются его свойства и определяются коэффициенты разделения для трех распространенных катионов Cu(II), Ni(II) и Zn(II) в зависимости от pH среды.

The heterogeneous macroporous gel obtainable by copolymerization of 2-hydroxyethylmethacrylate with ethylenedimethacrylate is produced by Lachema, Brno (named Spheron) and also by Laboratorní přístroje, Prague (named Separon HEMA). The fundamental skeleton may be modified by introduction of the end epoxide groups. This modification gives the possibility to react it with a great number of other compounds [1, 2].

There were studied properties of Spheron, which was modified by various compounds as ethylenediamine [3], salicylidenediamine [4], 2-hydroxyethylamine, ethylamine, diethylamine [5], 8-hydroxyquinoline [6, 7] and by salicylic acid [8]. The latter two of these ion-exchange resins possessing complexing group were tested from the point of view of their capacities for some usual divalent and trivalent cations [6]. The dependence of affinity of individual cations to ion-exchange resin on pH has been also studied.

The aim of this work was to prepare modified gel with properties of ionex possessing complexing group to be usable for extractions or chromatographical separations of some metal ions. For this purpose the following arrangement of groups was selected — the carboxyl group and primary amino group in  $\alpha$  position, which would enable formation of stable five-membered chelate rings. Basing on chemical properties, the  $\alpha$ -amino acid lysine was selected for introduction of such an arrangement of functional groups to the skeleton of gel matrix.

## Experimental

The following reagents were used in this work: Separon H-300,  $E_{\max} = 125\text{--}200\ \mu\text{m}$ , Laboratorní přístroje, Prague; L-lysine pure, Fluka A.G., Buchs SG Switzerland; monochloroacetic acid, anal. grade, Lachema, Brno; 85 % formic acid, Lachema, Brno; succinic acid, pure, Lachema, Brno; 5,5-diethylbarbituric acid SPOFA;  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , anal. grade,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , anal. grade, and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , anal. grade, Lachema, Brno.

Potentiometric titrations as well as the pH measurements were performed with universal pH-meter (Radelkis, Hungary), the equilibria in ionex were attained with the aid of the table shaking apparatus Meas Autocentrum, Prague, the concentrations of metal ions were determined by atomic absorption spectrometry performed on AAS 1 (Zeiss, Jena).

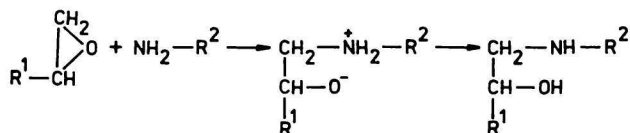
Condensation of lysine to the end oxiran rings of gel matrix was performed in ethanolic solution of NaOH ( $c = 10^{-3}\ \text{mol l}^{-1}$ ) at laboratory temperature. Amount of lysine bonded was determined by alkalimetric potentiometric titration with NaOH solution of  $c = 0.1\ \text{mol l}^{-1}$ .

The separation equilibria in the system containing modified Separon HEMA and solution of particular cations were determined by the static method. In order to determine the dependence of separation equilibria on pH there was used a system of buffer solutions prepared from organic acids and their sodium salts: monochloroacetic acid—sodium monochloroacetate (pH 2.5—3.5), formic acid—sodium formate (pH 4.0), succinic acid—sodium succinate (pH 4.5—6.5), and 5,5-diethylbarbituric acid—sodium 5,5-diethylbarbiturate (pH 7.5—8.5). The ionic strength of all buffer solutions was adjusted using NaCl to a constant value of  $I = 0.1\ \text{mol l}^{-1}$ . Amount of the chelated cations was determined after elution of individual charges of ion exchanger with diluted HCl ( $c = 0.2\ \text{mol l}^{-1}$ ) by atomic absorption spectrometry using the calibration curve method.

## Results and discussion

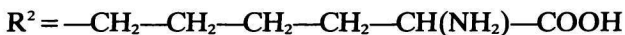
Kellner *et al.* [9] have studied the reactions of oxiran rings on gel matrix using 2,3-epoxypropylpivalate as a model compound. That paper involves the study of kinetics of condensation of carboxyl group in benzene and dimethylformamide medium, respectively, and condensation of amino group with oxiran ring in benzene under catalysis of 4-nitrophenol. The next paper [10] describes the study

of condensation of oxiran ring in the side chains of gel at the same conditions and with the same compounds as in the previous paper. We have worked out a new way of preparation of Separon—lysine, because lysine itself is insoluble in nonpolar solvents (it is soluble in water and poorly in alcohols). In order to condensate the end amino group, we have used an alcoholic medium, as for instance *Cromwell* and *Barker* [11], with a little addition of NaOH. The following course of that reaction is supposed



Scheme 1

where  $\text{R}^1$  = the rest of skeleton of gel matrix



The end amino group (positioned at C-6) is nucleophilic enough to react without a catalyzing agent. The addition of NaOH simultaneously aids to maintain both amino groups in nonprotonated forms. The amount of lysine bonded to gel matrix was determined as amount of protons, which may be released from  $-\text{COOH}$  group in the course of alkalimetric potentiometric titration, and that was expressed in mmole per 1 g of dry ion-exchange resin. Fig. 1 shows the dependence of amount of amino acid bonded to the polymer skeleton on concentration of lysine in the reaction mixture. Further increase of lysine concentration is limited by its solubility in ethanolic medium.

The separation equilibria in the system of Separon—lysine were studied with three cations ( $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Zn}(\text{II})$ ) by the static method. We made an effort to determine such a region of pH, in which the complex of metal ion and  $\alpha$ -amino acid chemically bound to matrix of gel may exist. In order to avoid the competitive reactions, it was necessary to select the systems of organic acids and their sodium salts as the appropriate buffer solutions, which do not form insoluble compounds or complexes with cations under study. Regardless of this it was impossible to buffer the region between pH 6.5—7.5. Also the investigation of upper limit of pH region of the complex formation by the static method for individual cations was restricted because of hydrolysis at higher pH values (Fig. 2).

The time dependence of complex formation of  $\text{Cu}(\text{II})$  in the system Separon—lysine was the following part of experiment. The rate of attaining the equilibrium is, as known, one of the determining factors; which, in general,

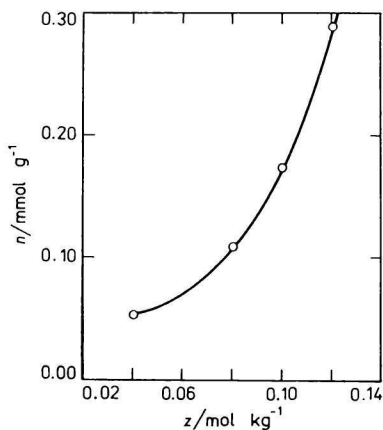


Fig. 1. Dependence of the amount  $n$  of lysine bonded to 1 g of gel on initial composition  $z$  of reaction mixture (in moles of lysine per 1 kg of mixture).

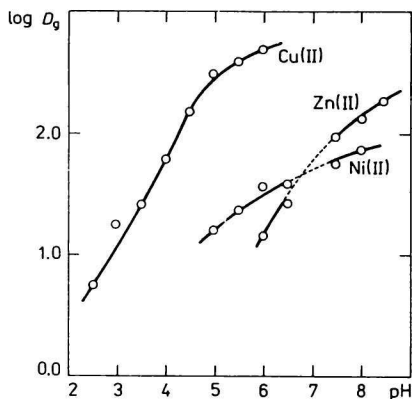


Fig. 2. Dependence of  $\log D_g$  on pH of solution. Determination for Cu(II): system containing 0.1 g of modified Separon HEMA (0.17 mmole of lysine per 1 g) and 10 ml Cu(II) ( $c = 0.016 \text{ mol l}^{-1}$ ). Determination for Ni(II) and Zn(II): system containing 0.1 g of modified Separon HEMA (0.29 mmole of lysine per 1 g) and 10 ml Me(II) ( $c = 0.030 \text{ mol l}^{-1}$ ).

indicates the use of ion-exchange resins with complexing group. If the equilibrium is attained with a time delay, then it is impossible to use such a system and material for chromatographic separations of metal ions, but for extractions in the trace analysis only. For determination of rate of the equilibrium attainment we have used ion-exchange resin swollen in distilled water ahead in order to make all the groups accessible by the same manner (Fig. 3).

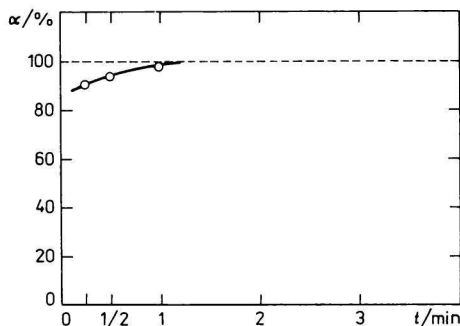


Fig. 3. Time dependence of Cu(II) extraction at pH 5.5: system containing 0.1 g of modified Separon HEMA (0.17 mmole of lysine per 1 g) and 10 ml Cu(II) ( $c = 0.016 \text{ mol l}^{-1}$ ).

From the given results it is obvious that ion-exchange resin would have some very desirable properties, which are provided namely by ease of its preparation and by quick attainment of equilibrium.

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