

EFFECT OF THE WAY OF FIXING 8-HYDROXYQUINOLINE TO GLYCIDYL METHACRYLATE GEL ON THE PROPERTIES OF THE RESULTING CHELATING ION EXCHANGER

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The practical sorption capacity, rate of establishment of the sorption equilibrium, pH-dependence of the distribution coefficient of Cu^{2+} ions, sorption isotherm, and stability of the ion exchanger were determined and mutually compared for two different ways of fixation of 8-hydroxyquinoline to glycidyl methacrylate gel (G-gel). The effect of the ion exchanger particle size on some of its properties was also investigated. In the ion exchanger obtained by direct fixation of copper(II) 5-(4-hydroxyphenylazo)-8-quinolate, the modified reagent retains a steric arrangement suitable for chelation.

Chelating ion exchangers are being studied mainly with a view to improving their sorption properties. Of importance, particularly for their application in analytical chemistry, are a rapid establishment of the sorption equilibrium and high values of the distribution coefficients^{1,2}.

Chelating ion exchangers are prepared to an increasing extent from polyacrylate gels². A suitable matrix for the fixation of reagent, from the reactivity point of view, is the glycidyl methacrylate gel (G-gel) containing free epoxy groups. Two ways of fixation of 8-hydroxyquinoline to G-gel were studied by us previously³: a direct fixation of the suitably modified reagent, or its copper(II) complex, and a three-stage, indirect fixation consisting in a stepwise modification of the matrix and coupling of the reagent to the diazotized G-gel in the third step of synthesis. The effects of the reagent modification and catalysis (for the direct fixation) and of the gel modification (for the indirect fixation) on the capacities of the exchangers obtained were examined. The direct fixation of copper(II) 5-(4-hydroxyphenylazo)-8-quinolate in pyridine appeared to suit best from the point of view of the practical sorption capacity; the capacity of the ion exchanger obtained by indirect fixation of 8-hydroxyquinoline involving immobilization of 1,4-diaminobenzene in the first step was also utilizable.

The properties of chelating ion exchangers depend primarily on the kind of the reagent fixed (selectivity) and on the kind of the matrix used (kinetic properties). Fixation of the reagent in a chelate form may also have a significant effect; this way of fixation has not been so far studied.

In the present paper, the properties of the new chelating ion exchangers with 8-hydroxyquinoline bonded to G-gel are compared with a view to elucidating the effect of fixation of a copper(II) complex of the reagent on the selectivity, rate of sorption equilibrium establishment, and ion exchanger stability.

EXPERIMENTAL

The direct fixation of copper(II) 5-(4-hydroxyphenylazo)-8-quinolinate in pyridine and the indirect fixation of the reagent with immobilization of 1,4-diaminobenzene in the first step of synthesis were performed by described procedures³. Prior to analytical properties testing, the samples were twice suspended shortly in 1 M-HCl.

All the properties of the chelating ion exchangers were examined *via* sorption of Cu^{2+} ions. The static determination of the practical sorption capacity was performed by 24 h sorption from 20 ml of 0.01 M- CuCl_2 solution in acetate buffer of pH 4.6. The sorbed ions were eluted with 10 ml of 1 M-HCl. The residual concentration of Cu^{2+} ions in the solution and the amount of ions eluted from the ion exchanger were determined colorimetrically³.

The rate of establishment of the sorption equilibrium was determined by monitoring the decrease in the residual concentration of Cu^{2+} ions in the solution, sampled from the slurry through a glass frit⁴. The sorption isotherm was measured in acetate buffer (pH 4.6) at 25°C; the exchanger suspension in a solution of Cu^{2+} ions was agitated for 2 h. The distribution coefficients of Cu^{2+} ions were determined in dilute hydrochloric acid solutions and in buffer solutions after Clark and Lubs and Kolthoff and Vleeschhouwer (ionic strength 0.1).

The chemical stability was tested by repeated sorption-desorption cycling and by 24 h or 48 h action of 1 M to 5 M-HCl; the practical sorption capacity was measured dynamically (each fifth sorption-desorption cycle) or statically.

RESULTS AND DISCUSSION

Previously³ the synthesis of the chelating ion exchanger was optimized with a view to attaining the maximum capacity. With new samples of the ion exchanger prepared by direct fixation the dynamically established practical sorption capacity was never attained, the difference, however, is insignificant with respect to the experimental error. A survey of the practical sorption capacities of the ion exchangers prepared both by direct and by indirect fixation, for two different particle size values, is given in Table I. The values obtained by the dynamic and static methods differ only slightly, which gives evidence of good kinetic properties of the ion exchanger and an easy accessibility to the free functional analytical groups. Ion exchangers of larger particles contained more bonded molecules of reagent and also exhibited higher capacities. Although the difference is rather small, the effect seems to be of general validity because it has been also observed on Spheron-oxine ion exchanger⁵ and on glycidyl methacrylate ion exchanger with bonded ethylenediamine⁶. The capacity increase with respect to the smaller-size ion exchanger is more pronounced for the sample obtained by direct fixation of the copper(II) chelate.

G-gel, as a hydrophilic macroporous matrix, favours a rapid equilibrium establish-

ment. This is evidenced by the time dependences of sorption of Cu^{2+} ions for a 10 to 15% capacity saturation and for a complete saturation of the ion exchangers (Fig. 1a,b). With a low degree of saturation, the equilibrium establishes rapidly (the amount of Cu^{2+} ions is sorbed on the ion exchanger of the smaller grain size within 4 min). On the saturated ion exchanger the equilibrium establishes considerably more slowly, particularly because of the slow completion of the saturation. This is illustrated by the time in which the equilibrium establishes on the ion exchanger

TABLE I

Effect of the particle size on the practical sorption capacities of the chelating ion exchangers prepared

Grain size μm	Fixation	$Q_g(\text{N})$ mmol g^{-1}	$Q_a^{\text{dyn}}(\text{Cu}^{2+})$ mmol g^{-1}	$Q_a^{\text{st}}(\text{Cu}^{2+})$ mmol g^{-1}
65–130	direct	0.72	0.16	0.17
150–250	direct	0.85	0.18	0.21
65–130	indirect	0.85 ^a	0.18	0.19
150–250	indirect	1.07 ^a	0.19	0.21

^a Value obtained by calculation.

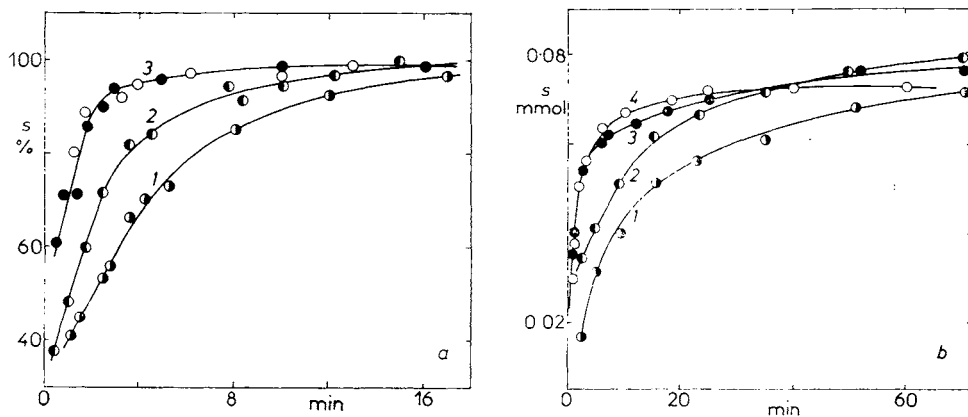


FIG. 1

Time dependence of sorption of Cu^{2+} ions on the chelating ion exchangers prepared by direct (\circ , \bullet) and indirect (\odot , \bullet) fixation. a 10–15% saturation, b saturation of approximately 0.5 g of ion exchanger; grain size (μm): 1, 2 150–250, 3, 4 65–130

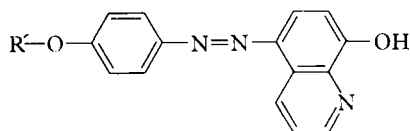
prepared by indirect fixation ($t_{100} = 53$ min) in comparison with the time of half capacity saturation for this ion exchanger ($t_{1/2} = 0.8$ min). The slower equilibrium establishment for the saturated ion exchanger concerns the poorly accessible functional analytical groups inside the gel particles, whereas for a low degree of saturation the major process is the "diffusion into film" (ref.⁷) towards the readily accessible functional analytical groups, promoted by the hydrophilic nature of the matrix.

In agreement with the increasing resistance against mass transport with increasing particle size, the sorption equilibrium on the coarser ion exchanger established more slowly (Fig. 1*a,b*); on a sample with 2–3 times larger particles, the time required for the equilibrium to establish was approximately two times longer for the direct fixation of the copper(II) chelate and 3–4 times longer for the indirect fixation. These relations were independent of the degree of the ion exchanger saturation, which indicates that the functional analytical groups are distributed in a similar manner in the particles of different size.

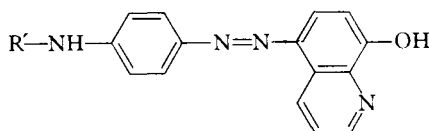
The difference in the rate of establishment of the sorption equilibrium on the ion exchangers prepared by the two different procedures was quite marked in the case of the coarser exchangers; on the ion exchanger prepared by direct fixation of the copper(II) chelate at a 15% degree of saturation the equilibrium established about two times faster than on the ion exchanger obtained by the indirect fixation (Fig. 1*a*). With the saturated ion exchangers the difference was somewhat higher (Fig. 1*b*). The higher resistance against mass transport in the bulkier particles along with the "diffusion into gel" results in greater demonstration of a different steric accessibility of the functional analytical groups in the ion exchangers prepared by the two procedures. The results show that the functional analytical groups in the ion exchanger prepared by direct fixation of copper(II) chelate are in a more suitable arrangement; in the ion exchanger prepared by indirect fixation, the unreacted intermediates cause a steric hindrance to the accessibility to the functional analytical groups.

The selectivity of chelating ion exchangers with bonded 8-hydroxyquinoline is well known⁸. Therefore, only the selectivity changes associated with the way of fixing the reagent to the matrix are studied. The selectivity was characterized by the dependence of the distribution coefficients of Cu^{2+} ions (D_g) on pH (Fig. 2). The differences in the D_g values for the ion exchangers prepared by direct fixation of the chelate (structure *I*) and by indirect fixation (structure *II*) at the same pH are a consequence of the different modification of the reagent. The $\text{R}'\text{—NH—}$ group provides the functional analytical group with electrons more easily (by means of delocalization) than the $\text{R}'\text{—O—}$ group, thereby lowering the deprotonation constant ($K_{\text{dp}} = \beta_2 K_1^2 K_2^2$) and thus increasing the pH value at which complexes are formed. As a consequence, the ion exchanger prepared by direct chelate fixation exhibits higher D_g values. The higher coordination by ligands about the central ion also contributes to the increase in D_g . The slope of the pH-dependence of $\log D_g$ at low degrees of saturation (15%) is about 2 for the exchanger prepared by direct fixation

of the copper(II) complex, which corresponds to a composition of ML_2 . For the ion exchanger prepared by the indirect fixation the slope is about 1.8, which indicates that ML type complexes also form even at so low degrees of saturation. This again documents the more convenient arrangement of the functional analytical groups in the formed ion exchanger.



I



II

At higher degrees of saturation, the expected decrease in D_g , associated with the increasing proportion of ML type complexes and increasing distortion energy in the complex formation, was observed. In accordance with this, the differences between

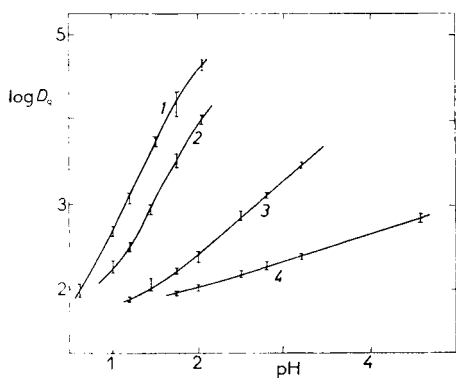


FIG. 2

Dependence of distribution coefficients of Cu^{2+} ions on pH for the ion exchangers prepared by direct (1, 3) and indirect (2, 4) fixation. Degree of saturation (%): 1, 2 10–15, 3 80, 4 65

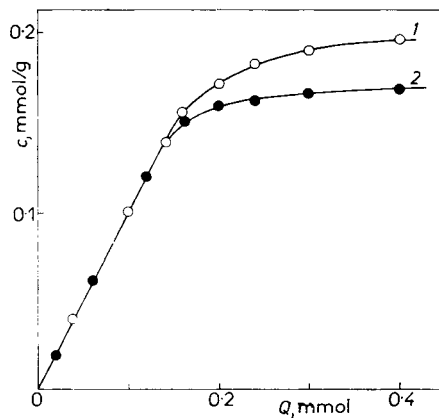


FIG. 3

Sorption isotherms of Cu^{2+} ions at pH 4.6 for ion exchangers prepared by indirect (1) and direct (2) fixation; c is the concentration of Cu^{2+} ions in the ion exchanger, Q is the amount of Cu^{2+} ions in solution

the D_g values for the ion exchangers prepared by the two different procedures were still higher (Fig. 2). For the ion exchanger prepared by direct fixation the slope of the linear segment of the $\log D_g$ vs pH plot decreased, at an 80% degree of saturation, to a value of approximately 1; hence, the copper(II) ions are bonded predominantly in ML type complexes. For the ion exchanger prepared by indirect fixation the corresponding value is very low, indicating a nonselective sorption caused by amino groups or phenolic groups as products of the incomplete conversion in the intermediate steps. Adsorption on the exchanger surface is also conceivable.

The above conclusions are borne out by the sorption isotherm of Cu^{2+} ions (Fig. 3). For the ion exchanger prepared by direct fixation of the copper(II) chelate the sorption isotherm exhibits wider linearity region (78% against 67% of practical sorption capacity). The slower completion of saturation for the exchanger prepared by indirect fixation again points to a nonselective sorption. In both cases, though, the linearity range is fairly wide, so that sorption of highly dilute solutions is efficient even on ion exchangers saturated to a high extent.

The practical sorption capacities determined during the ion exchanger cycling or on a long-run action of dilute hydrochloric acid (Tables II and III, respectively)

TABLE II

Chemical stability of the ion exchangers with respect to cycling

Fixation procedure	$Q_a^{\text{dyn}}(\text{Cu}^{2+})$ mmol g^{-1}	$Q_a^{\text{dyn}}(\text{Cu}^{2+})$, mmol g^{-1} , in cycle:			
		5th	10th	15th	20th
Direct	0.18	0.18	0.20	0.20	0.20
Indirect	0.19	0.21	0.21	0.22	0.23

TABLE III

Static practical sorption capacities of the ion exchanger after 24 h and 48 h action of hydrochloric acid. Starting static sorption capacity 0.21 mmol g^{-1} for both exchangers

Fixation procedure	Time of action h	$Q_a^{\text{st}}(\text{Cu}^{2+})$, mmol g^{-1}			
		1M-HCl	2M-HCl	3M-HCl	5M-HCl
Direct	24	0.20	0.21	0.21	0.22
	48	0.23	0.23	0.25	0.24
Indirect	24	0.21	0.23	0.24	0.26
	48	0.23	0.25	0.25	0.26

reflect the hydrolytic stability of the ion exchanger. In both cases the practical sorption capacity increased; the increase was more pronounced (24%) for the exchanger prepared by indirect fixation. The solution obtained by eluting the sorbed metal from the ion exchanger with dilute hydrochloric acid was yellow to yellow-orange in colour. These changes are due to the residual activity of G-gel⁹, which contains some unreacted epoxy groups embedded in the gel even after the reagent fixation. These groups are hydrolyzed by the hydrochloric acid whereupon the gel grows hydrophilic and some fixed functional analytical groups become accessible, and consequently, the capacity of the exchanger increases.

It follows from the comparison of the properties of the chelating ion exchangers prepared by the two procedures that the direct fixation of the chelate to the macroporous gel with relatively large pores (where the steric hindrance during the fixation of the bulky molecules does not lower appreciably the bonded reagent content) is superior to the indirect fixation. The properties of such an ion exchanger confirmed the assumption that the reagent in a chelate form retains its favourable steric arrangement. As compared with the exchanger prepared by indirect fixation, this exchanger exhibits higher distribution coefficients, its selectivity is not impaired by nonselective sorption, two reagent molecules take part in the complexation at low degrees of saturation, its linearity span of the sorption isotherm is wider, and for particles larger than 0.1 mm the sorption equilibrium establishes considerably faster. The low solubility of the chelate in most organic solvents, however, may present a serious obstacle.

For the ion exchangers prepared the sorption equilibrium establishes rapidly both at low and high degrees of saturation, their D_g values are high and the linearity range of their sorption isotherms is wide. Their shortcomings are the comparatively low capacity and poor stability, which, although not limiting their sorption ability, make the ion exchangers unsuitable for analytical use because of the changes occurring in their properties. This poorer stability was also the reason for the higher experimental errors of the capacity determinations³.

REFERENCES

1. Janák K., Janák J.: *Chem. Listy* 75, 465 (1981).
2. Myasoedova G. V., Savvin S. B.: *Zh. Anal. Khim.* 37, 499 (1982).
3. Janák K., Janák J.: *This Journal* 48, 2352 (1983).
4. Janák K.: *Thesis*. Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno 1982.
5. Slovák Z., Toman J.: *Fresenius' Z. Anal. Chem.* 278, 115 (1976).
6. Švec F., Kálal J., Kálalová E., Marek M.: *Angew. Makromol. Chem.* 87, 95 (1980).
7. Burba P., Lieser K. H.: *Fresenius' Z. Anal. Chem.* 279, 17 (1976).
8. Slovák Z., Slováková S., Smrž M.: *Anal. Chim. Acta* 75, 127 (1975).
9. Švec F.: Private communication.

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