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Note

Sorption properties of carboxylic cation exchangers toward some basic antibiotics

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Carboxylic acid resins are widely used for the separation of basic antibiotics having amino groups. The success of this application depends on the appropriate choice of the resin. Thus, the porous structure of the adsorbent (resin) must match the size of the adsorbate. If this condition is not fulfilled, low yields of separated antibiotics and short lifetimes of the resin activity due to irreversible adsorption are obtained.

In this paper several commercial resins and our own products are compared with reference to the sorption and desorption of streptomycin, viomycin and polymyxin E.

EXPERIMENTAL

Streptomycin (MW 581.6), viomycin (MW 685.7) and polymyxin E (MW 1145.5) were products of Polfa (Warsaw, Poland). Carboxylic resins were obtained from Rohm & Haas, Philadelphia, Pa., U.S.A. (Amberlite), Zerolit Ltd., Isleworth, Great Britain, (Zerolit), Diamond Shamrock, Cleveland, Ohio, U.S.A. (Duolite) and Chemie-Kombinat Bitterfeld, Bitterfeld, G.D.R. (Wofatit). The other samples used were described elsewhere[1]. The resins and their properties are listed in Table I.

The adsorption experiments were performed with resins (Na^+) packed in thermostated columns (100 × 1.3 cm) by upward flow. Aqueous solutions containing fixed amounts of the antibiotics as their sulphates were introduced into the column. The amounts were chosen on the basis of preliminary experiments: *ca.* 350 mg of streptomycin or viomycin and *ca.* 150 mg of polymyxin E per cm^3 of resin bed. The concentrations of the solutions were *ca.* 10,000 U/cm^3 for streptomycin and viomycin (*ca.* 10 mg/cm^3) and *ca.* 50,000 units/cm^3 for polymycin E (*ca.* 3 mg/cm^3).

The flow-rate was 0.1 ml/min. The column was rinsed with deionized water, then for desorption with 0.5 *N* aqueous H_2SO_4 solution, applied downward (1:1 water–methanol 0.5 *N* H_2SO_4 solution in the case of polymyxin E). The flow-rate was 0.01 ml/mln and the elution was stopped when the acid concentration in the effluent

TABLE I

PROPERTIES OF CARBOXYLIC ACID RESINS

AA = Acrylic acid; MA = methacrylic acid; DVB = divinylbenzene.

Resin	*Chemical structure*	*Ion-exchange capacity*		*Water content (%)*		*Increase of volume on neutralization $H^+ \rightarrow Na^+$ (%)*
		mequiv./g	*mequiv./ml*	H^+	Na^+	
Amberlite IRC-84	acrylic	10.5	3.5	46		65
Zerolit 226	MA + DVB	9.5	3.7			
Zerolit 236	acrylic		4.2			
Duolite CC-3	AA + DVB		4.5	50		90
Wofatit CP	AA + DVB	10.0	3.5	55		55
KDMT-521	MA + DVB*	9.3	2.6	60	72	44
KDAT-522	AA + DVB*	7.7	2.4	54	69	52
KDMO-512	MA + DVB**	9.2	3.0	54	68	47
KDAO-515	AA + DVB**	10.7	2.8	71	81	34
KDM-51	MA + DVB	9.1	2.9	45	69	77

* Resin prepared directly from monomers (5% of DVB) with an aromatic diluent.

** Resin prepared with an aliphatic diluent.

was constant. At the end, the resins were rinsed with deionized water. All column experiments were performed at 15°.

The sorption capacity was calculated as the fraction of the original amount of antibiotic adsorbed by the resin, and the desorption efficiency as the fraction of the adsorbed amount which was eluted, both values being expressed in wt.-%.

Streptomycin and viomycin were determined colorimetrically[2,3] and polymyxin E was determined biologically[4].

RESULTS AND DISCUSSION

The results of the experiments are shown in Fig. 1. The antibiotics of relatively low molecular weight (*i.e.*, streptomycin and viomycin) were reasonable adsorbed on most samples. The exception was KDM 51, which differed from the other carboxylic acids by its low swelling capacity. The elution was easier for streptomycin than for viomycin in agreement with their MW values. Shaded parts of Fig. 1 represent the amount of antibiotic which remained in the resin bed after elution. The heights of these areas correspond to values calculated as:

(100 — desorption efficiency) · sorption capacity

The resin which greatly shrinks upon $Na^+ \rightarrow H^+$ exchange (*cf.*, Table I) showed comparatively low desorption efficiency because the adsorbate was physically enclosed in the matrix during the elution with acid. The antibiotic with a higher MW value, polymyxin E, had a different adsorption on the individual samples compared with the streptomycin and viomycin, since transport of the adsorbate through the swollen gel became significant. It was found that the heterogeneity of the polymer was very important in this case. The samples with macroporous structure, *i.e.*, Amberlite IRC-84,

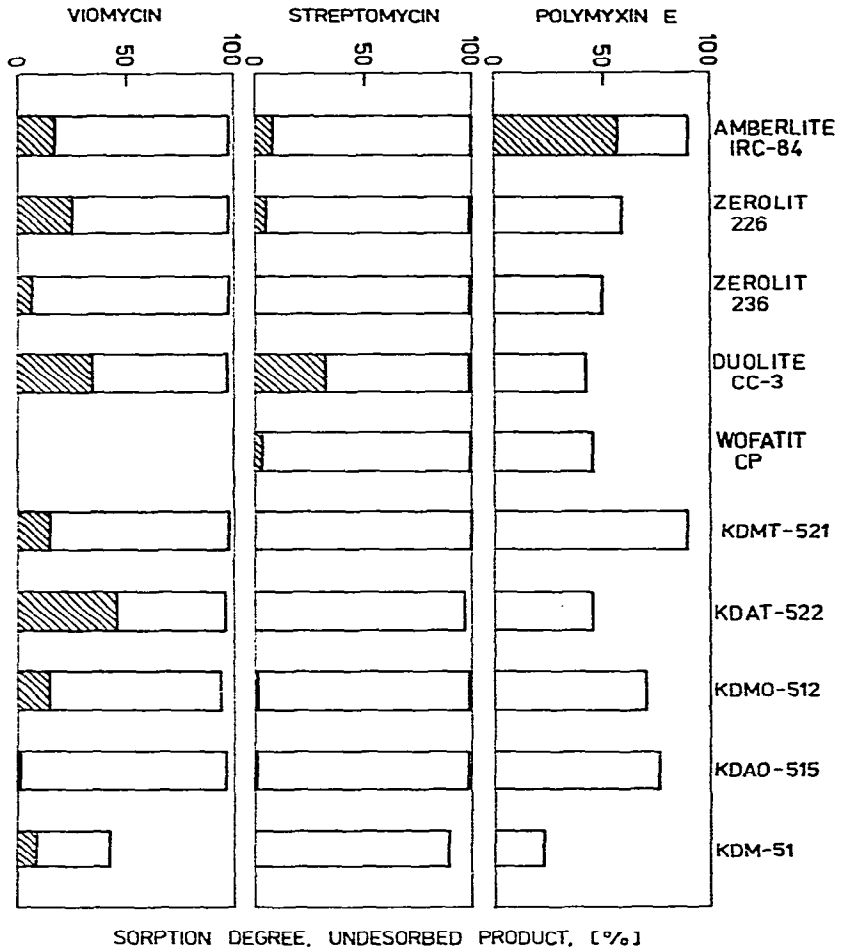

Fig. 1. Sorption and desorption properties of carboxylic cation exchangers toward antibiotics. The heights of the unshaded areas correspond to the sorption capacity of the resins and represent the percent of antibiotic which was sorbed by the resin; the shaded parts correspond to the amount of the antibiotic which remained in the resin after elution (see text).

KDMT-521, KDAT-522, KDMO-512 and KDAO-515, showed much better efficiencies than the other polymers.

The results support the structural model of carboxylic resin prepared by copolymerization of (meth)acrylic acid and divinylbenzene presented elsewhere[1]. This model postulates that a porous carboxylic acid resin is composed of a rigid skeleton, which prevents shrinkage, and a relatively loosely crosslinked gel available for the transport of large molecules.

REFERENCES

1 H. Galina and B. N. Kolarz, *J. Appl. Polym. Sci.*, 23 (1979) 3017; 24 (1979) 891, 901.
2 M. Samogyi, *J. Biol. Chem.*, 160 (1945) 61.
3 S. Ochab and B. Borowiecka, *Chem. Anal. (Warsaw)*, 8 (1963) 99.
4 *U.S. Pharmacopeia XIX*, Mack Publishing Co., Easton, Pa., 1975, p. 390.