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SYNTHESIS AND PROPERTIES OF SOME SNAKE-CAGE ION-RETARDATION RESINS

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SUMMARY

In certain separation processes, snake-cage amphoteric retardation resins undergo a decrease in chemical stability followed by loss of their separation ability.

A means has been found of preventing this decay by cross-linking the "snake" polymer within the matrix. New ion-exchange resins have been synthesized on this basis and are termed "net-cage" resins. Their most important properties are tabulated.

INTRODUCTION

Snake-cage ion-retardation resins have found industrial applications in many separation processes involving highly concentrated solutions, such as the separation of ionizable, slightly ionizable and non-ionizable organic and inorganic compounds, splitting of complexes and in processing waste water in the Sirotherm Project^{1–3}. The absorbed solutes are displaced from the resin and the resin is regenerated merely by rinsing it with water. A snake-cage resin is a cross-linked polymer system containing a physically constrained mixture of linear polymers^{4,5}. The main separation properties of an amphoteric snake-cage resin depend, above all, on the correct proportion of anionic to cationic sites. Amphoteric snake-cage resins can also act as true ion-exchange resins, but only at certain pH ranges.

Investigations have been performed in order to explain the origin of the deterioration of these resins, which occurs during their working life.

EXPERIMENTAL AND RESULTS

A glass column of 9 cm I.D. and 105 cm height was surrounded with a jacket of warm water and filled with an amphoteric ion-retardation resin based on Wofatit SBW and polyacrylic acid. This arrangement was used in the following separations.

(1) Sodium thiocyanate was separated from sodium thiosulphate in a solution with a total starting concentration of 400–900 g/l. After 40–50 separation cycles, the ion-retardation resin had completely lost its separation abilities.

(2) Calcium maltobionate–calcium bromide, a complex compound, was split in order to obtain a very pure concentrated solution of calcium maltobionate for use

TABLE I

PROPERTIES OF NET-CAGE RESINS BASED ON WOFATIT SBW-X4 AND POLY-(ACRYLIC + *a*% SORBIC) ACID

Test solution: cane sugar + NaCl.

No.	Sorbic acid content, <i>a</i> (%)	Separation ability, $100 \cdot \frac{\Delta V_{max}}{V_T}$	Capacity max., $\frac{V_{soln.}}{V_T}$	Regeneration ability by water, $\frac{V_{water}}{V_T}$	Water content of resin (%)	Swelling volume in saturated NaCl _{aq.} (%)	Comparative swelling half-time in water*
1	0.0	57	136	30.0	41.0	+35	100
2	2.0	62	143	25.0	42.5	+30	110
3	5.0	53	103	16.0	50.5	+30	105
4	10.0	39	88	13.5	58.5	+15	90
5	15.0	31	90	10.5	58.0	+6	88
6	25.0	24	92	9.0	55.6	-4	95
7	50.0	20	97	12.0	52.5	-10	97
8	100.0	16	101	16.5	45.0	-10	100

* 100 represents 28 sec.

in pharmaceutical preparations. Before each following separation cycle, the resin bed was thoroughly rinsed with boiling water so as to effect complete regeneration and to remove any bromide ions present inside the resin. Leakage appeared within 6–8 cycles and increased rapidly, rendering impossible any further cleavage of the complex compound.

(3) The used ion-retardation resins from the above columns were subjected to batchwise saturation with acrylic acid and, by using peroxy polymerization initiators, were polymerized to give amphoteric snake-cage resins. The reconstructed resin beds were used repeatedly in the above separation processes with good results.

TABLE II

PROPERTIES OF NET-CAGE RESINS BASED ON WOFATIT SBW-X4 AND POLY-(ACRYLIC ACID + *a*% DIVINYLBENZENE)

Test solution: cane sugar + NaCl.

No.	Divinylbenzene content in relation to acrylic acid (mole:mole)	Separation ability, $100 \cdot \frac{\Delta V_{max}}{V_T}$	Capacity max., $\frac{V_{soln.}}{V_T}$	Regeneration ability by water, $\frac{V_{water}}{V_T}$	Water content of resin (%)	Swelling volume in saturated NaCl _{aq.} (%)	Comparative swelling half-time in water*
1	0% DVB	57	136	30	41.0	+35	100
2	1:40	59	142	20	38.0	+30	91
3	1:30	53	118	15	36.5	+28	97
4	1:20	47	101	15	37.0	+25	100
5	1:15	44	95	22	37.5	+22	105
6	1:10	41	92	33	37.2	+20	118
7	1:7	38	86	40	36.0	+15	116
8	1:4	25	76	45	33.5	+10	104
9	1:2	16	72	42	32.0	+6	103

* 100 represents 28 sec.

Nevertheless, after the same number of cycles, the resin beds again lost their separation abilities.

New ion-retardation resins have been synthesized in the following way. Basic resins such as Wofatit SBW, Wofatit SBK and Wofatit SBU in the hydroxide form were subjected to successive batchwise neutralization and polymerization using mixtures of acrylic acid and a cross-linking agent (2–33% divinylbenzene, 2–100% sorbic acid and 2–100% muconic acid. In a further series of experiments, acidic resins such as Wofatit KPS and Wofatit CP in the hydrogen form were neutralized using mixtures of monovinylpyridines and 2–100% divinylpyridine or 2–33% divinylbenzene as cross-linking agent. After polymerization and subsequent de-solvation of unpolymerized raw materials, the resins obtained were subjected to detailed investigation, and the results are given in Tables I and II.

The best resins were used in the separation processes described above. After 50 separation cycles, no significant deterioration occurred and no leakage appeared.

DISCUSSION

In certain separation processes, known snake-cage resins undergo a decrease in durability owing to de-solvation of "snake" molecules out of the matrix "cage". The resulting unfavourable relation between cationic and anionic sites can be restored to a satisfactory extent by soaking the used retardation resins with the "snake" monomer and by subsequent polymerization, but the stability of the reconstructed resin is still not adequate. It has been shown that one can obtain stable retardation resins by cross-linking the "snake" polymer. The "snakes" thus form "nets" and so cannot leave the resin "cage".

It was possible to increase the stability of retardation resins by modifying their synthesis route to give a composition with a cross-linked "snake" structure within a cross-linked matrix cage. These new ion-retardation resins do not exhibit the tendency to lose their "snakes" as do the previous products. They show also different selectivities towards many solutes, which can be regulated by changing the degree of "snake" cross-linking. There is a distinct sieve effect in their behaviour.

As the "snakes" are now cross-linked, it is more appropriate to name these products "net-cage" resins. Net-cage resins are produced in Poland under the name "Saturion", and a patent application has been filed describing a method of producing them.

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