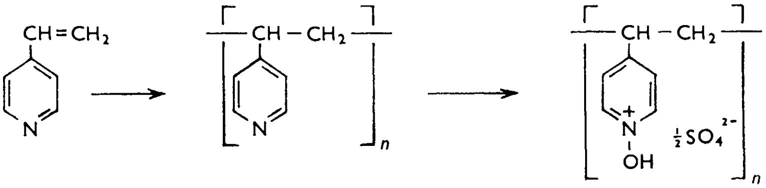
296. *Poly-(1-hydroxy-4-vinylpyridinium) Anion-exchangers.*

By A. Heller, Y. Marcus, and I. Eliezer.

Cross-linked poly-(1-hydroxy-4-vinylpyridinium) ion-exchangers have been prepared, in an attempt to utilize the specificity that *N*-oxides show to heavy metals, and to uranium in particular. However, the polymers obtained behaved as ordinary anion-exchangers, somewhat less basic than Dowex 2. The main advantage of the new exchanger is its high exchange rate.

Recent work has indicated that *N*-oxides tend to form complexes with cations of transition elements and especially with the uranyl cation.[1-4] These complexes are not extractable into common organic solvents, and some of them are fairly soluble in water. It was expected that *N*-oxide polymers would bind cations selectively by complex-formation. However, the quaternary *N*-hydroxides obtained were hydrated and exhibited properties of anion exchangers.

Polymerization of vinylpyridines in aqueous emulsion and subsequent oxidation with



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[1] Heller, *Bull. Res. Council Israel*, 1960, **9**, *A*, 245.
[2] Heller, *Bull. Res. Council Israel*, 1961, **10**, *A*, 7.
[3] Carlin, *J. Amer. Chem. Soc.*, 1961, **83**, 3773.
[4] Quagliano, Fujita, Franz, Phillips, Walensley, and Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770.

a peroxide was found to be rapid and convenient. The cross-linking agent was *p*-divinylbenzene, which was co-polymerized with the vinylpyridine.

Several organic and inorganic peroxides have been successfully applied for the oxidation of the pyridine to the pyridine *N*-oxide. We chose ammonium persulphate. This method is convenient since the two stages of the process are carried out in the same vessel, the ammonium persulphate serving both as a catalyst for the polymerization and as oxidant.

EXPERIMENTAL

Preparation of the Polymer.—A typical polymerization was carried out as follows (in other experiments the amount of cross-linking agent was varied [5]). To iron(II) sulphate (0·5 g.) in water (500 ml.) freshly distilled 4-vinylpyridine (250 g.), a 50% solution (50 g.) of *p*-divinylbenzene in ethylvinylbenzene and Aerosol OT (1·0 g.) were added. The mixture was emulsified by stirring. A 10 ml. portion of aqueous ammonium persulphate (600 g. in 2·5 l.) was added and the mixture heated to 80° under a double water-condenser to avoid escape of the monomer. When the vigorous exothermic reaction subsided, the mixture was stirred for 1 hr. at 80—85° to complete polymerization. Glacial acetic acid (175 ml.) was added and the lumps were broken by stirring. The rest of the ammonium persulphate solution was then run in at a rate that maintained the temperature at 80—84° without external heating or cooling. After the mixture had been left overnight, a saturated solution of ammonium persulphate (75 g.) was added and the mixture then stirred for 4 hr. at 80°. The polymer was allowed to settle and the aqueous solution decanted. The polymer was washed with water (4 × 2 l.) and air-dried; the yield of polymer was almost quantitative (Found: C, 55·6; H, 5·5; N, 7·1. Calc. for $C_{14}H_{16}N_2O_6S$: C, 55·2; H, 5·3; N, 7·1%).

Determination of Selectivity Coefficients.—Selectivity coefficients were determined in batch experiments. 0·1—0·5M-solutions (20 ml.) of sodium salts of various anions (see Table) were equilibrated with weighed amounts of air-dried resin by shaking overnight. When a resin initially in the chloride form was used, both resin and solution were analyzed for chloride by the Mohr method. The other anion was determined by difference from the measured capacity of the resin and the known total concentration of the solution. When a resin initially in the nitrate form was used, the anion was determined by Mohr's method in the case of bromide, and with eosin as indicator in the case of iodide and thiocyanate. The selectivity coefficients determined are concentration quotients. Account was taken of the change in the concentration of the solutions due to water absorbed by the resin.

Comparison of selectivity coefficients of 8% cross-linked resins.

Anion	Poly-(1-hydroxy-4-vinylpyridinium)			Dowex 1 *		Dowex 2 *		Dowex 2 †	
A	X_{RA} [a]	C_t [b]	K_{Cl}^A [c]	X_{RA} [d]	K_{Cl}^A	X_{RA} [d]	K_{Cl}^A	X_{RA} [d]	K_{Cl}^A
F	0·4 [d]	0·2—0·3	0·3	0·23	0·09	0·26	0·13	0·10—0·85	0·1—0·06
Cl	—	—	1	—	1	—	1	—	1
Br	0·5—0·6 [e]	0·1—0·3	2·2 [f]	0·60	2·8	0·52	2·3	0·12—0·78	2·9
NO_3	0·5—0·9 [d]	0·1—0·5	2·2	0·62	3·8	0·64	3·3	0·22—0·92	2·9
I	0·5—0·7 [e]	0·1—0·2	7·3 [f]	0·73	8·7	0·73	7·3	0·12—0·93	34—13
CNS	0·7—0·8 [e]	0·1—0·3	11 [f]	—	—	0·7—0·8 ‡	10 ‡	0·02—0·95	0·3—18
Salicylate	0·6—0·8 [d]	0·1—0·2	13	0·82	32	0·84	28	—	—
ClO_4	>0·7 [d]	0·1—0·3	20	0·95 §	37 §	>0·7 ‡	35 †	0·26—0·96	4—28

[a] X_{RA} = fraction of resin in the form of anion A. [b] C_t = total molar salt concentration in solution. [c] $K_{Cl}^A = [A]_r[Cl]_s/[Cl]_r[A]_s$. [d] Resin initially in chloride form. [e] Resin initially in nitrate form. [f] Calc. from $K_{Cl}^A = K_{NO_3}^A K_{Cl}^{NO_3}$.

* Wheaton and Bauman, *Ind. Eng. Chem.*, 1951, **43**, 1088. † Gregor, Belle, and Marcus, *J. Amer. Chem. Soc.*, 1955, **77**, 2713. ‡ Freeman, Coryell, and Yellin, Prog. Rep. Lab. Nucl. Sci., M.I.T., May 31st, 1958. § Eliezer and Marcus, Research Laboratories, Semi-Annual Report, July—Dec. 1960, I.A.E.C. Report No. IA-620 (1961).

RESULTS AND DISCUSSION

Stability of the Exchanger.—Dry poly-(1-hydroxy-4-vinylpyridinium) salts are stable up to 100°, but their neutral aqueous solutions release gases above 70°. Acid solutions are stable up to 90°.

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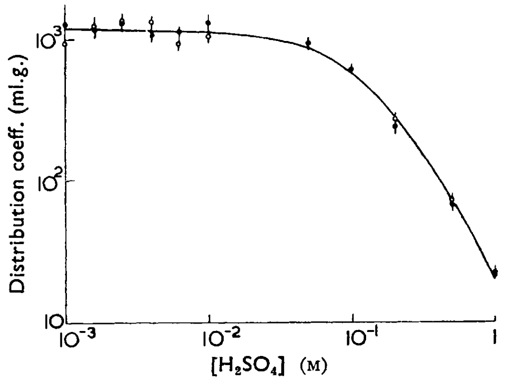
[5] Heller, Israel Patent 14,445/1960.

Hydration and Swelling.—The pure polymer salts are water-soluble. Cross-linking by *p*-divinylbenzene strongly reduces the solubility in water. Polymers containing 2·5%, 5%, 7·5%, and 10% of cross-linking (on a molar basis) were prepared. The 2·5% and the 5% cross-linked polymers swelled too much to be useful as ion-exchangers. The 7·5% cross-linked polymer was suitable for anion-exchange but the 10% polymer was brittle.

The hydration of the nitrate, chloride, and sulphate of the 7·5% cross-linked poly-(1-hydroxy-4-vinylpyridinium) resin was measured by the gain in weight after equilibration with water of the dry resin (dried to constant weight at 14 mm. over magnesium perchlorate) and centrifugation. The gain was 130% for the chloride, 200% for the nitrate, and 280% for the sulphate. With air-dried resin, the gain was 50% for the chloride and 100% for the nitrate. There is thus a large volume change in different ionic forms. This would be a disadvantage for column operations.

Capacity.—The capacity of the 7·5% cross-linked resin in the chloride form, dried for 24 hr. at 100°/14 mm. over phosphorus pentoxide, was determined by equilibration with an excess of a 0·5M-sulphate solution. It was found to be 5·2 mequiv./g., to be compared with the calculated value of 5·6 mequiv./g. The air-dried resin had a capacity of 1·9—2·1 mequiv./g. in the chloride form and 2·5—2·7 mequiv./g. in the nitrate form.



The distribution of uranium(VI) between poly-(1-hydroxy-4-vinylpyridinium sulphate) and dilute sulphuric acid solutions.

Exchange Kinetics.—The self-diffusion of bromide in the resin was determined by bringing the resin bromide, loaded with radioactive bromide, into contact with a solution of non-radioactive bromide.

For particles of average diameter 2 mm., the rate of increase of radioactivity in the solution was of the first order, with a half-time of 0·73 min. These measurements gave a calculated [6] self-diffusion coefficient of bromide in the resin of 6×10^{-6} cm.^{2} sec.$^{-1}$. This exceptionally high value indicates that the resin has considerable porosity. Further, it seems likely that the *N*-hydroxy-groups and the polar nature of the resin greatly facilitate the exchange of the anions between the resin and the aqueous phase.

Absorption and Separation of the Anionic Complexes.—Cobalt(II), nickel(II), iron(III), copper(II), and zinc(II) were separated after absorption on the resin by elution with decreasing concentrations of hydrochloric acid.[7] Nickel was eluted by concentrated acid, cobalt by 8N-, copper(II) by 3N-, and iron(III) by 1·5N-hydrochloric acid; zinc was removed by using finally 0·1N-perchloric acid.

The distribution of the sulphate complexes of the uranyl ion between the resin and dilute sulphuric acid solutions is shown in the Figure. In spite of the observed tendency of uranium(VI) to form complexes with *N*-oxides,[1,2] it was not absorbed on the resin from dilute hydrochloric or nitric acid.

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[6] Boyd and Soldano, *J. Amer. Chem. Soc.*, 1953, **75**, 6091.

[7] Kraus and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1460.

Selectivity.—The selectivity of the resin was measured for a series of univalent anions chosen so as to permit comparison with selectivity data available for other resins. For this purpose a resin with 8% of cross-linking was convenient (see Table). Variation of the pH of the solutions used between 3 and 7 did not affect the results.

The Table shows that the order of selectivity is almost the same for all three resins; however, a contraction of the scale is observed on going from Dowex 1 to Dowex 2 to the present resin. This is probably due to a difference in basicity: Dowex 2 is not as strong a base as Dowex 1, and the present resin is apparently somewhat less strong still, but all three can by classified as strongly basic exchangers.

Conclusions.—The resin, unlike the free *N*-oxide,[1,2,3] did not yield stable co-ordination compounds with transition metals or uranium. This might be due to the impossibility of forming suitably directed covalent bonds with two adjacent planar aromatic *N*-hydroxy- or *N*-oxide groups.

Comparison with other anion-exchange resins indicates that the poly-(1-hydroxy-4-vinylpyridinium) resins have a very high water uptake and a high rate of exchange. Its capacity, although higher for the completely dried material, which has a low equivalent weight, is similar, in the swollen state, to that of other resins. It has the disadvantage of lower basicity (becoming unstable above pH 10) and of smaller selectivity towards anions. The smaller selectivity may be due to its larger water content at similar nominal cross-linking and hence a larger effective dielectric constant.[8]

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DEPARTMENT OF RADIOCHEMISTRY, ISRAEL ATOMIC ENERGY COMMISSION LABORATORIES,
SOREQ RESEARCH ESTABLISHMENT, REHOVOTH, ISRAEL. [*Received, August 8th,* 1962.]

[8] Maydan, Ph.D. Thesis, Hebrew University, Jerusalem, 1962.