

SELECTIVE ION EXCHANGERS WITH ISONITROSOACETAMIDE FUNCTIONAL GROUPS. II.* PROPERTIES AND APPLICATION

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Selective ion exchangers with isonitrosoacetamide functional groups ($-\text{NH}\cdot\text{CO}\cdot\text{CH}=\text{NOH}$) attached to a polycondensate of *m*-aminophenol with formaldehyde (I) or to a styrene-divinylbenzene copolymer (II) were evaluated from a static and a dynamic point of view. The two types of ion exchanger have proved to have practically identical properties, given by the reactivity of isonitrosoacetanilide. The high selectivity of the ion exchangers for Pd^{2+} was utilized to separate palladium in its dilute solutions from an excess of ordinary metals and silver.

The two selective cation exchangers with isonitrosoacetamide functional groups ($-\text{NH}\cdot\text{CO}\cdot\text{CH}=\text{NOH}$), prepared¹ on the basis of a polycondensate (type I) and a copolymer (type II), have been evaluated statically and dynamically. Judging by the properties of isonitrosoacetanilide as an analytical reagent^{2,3}, a selective ion exchanger with these functional groups can be assumed to adsorb a number of different cations under different conditions, and particularly the cation Pd^{2+} , which should be adsorbed even in acid media.

The objective of this work was to determine the principal characteristics of these ion exchangers, *viz.* the titration curves, exchange capacities, selectivity coefficients, distribution coefficients, and the adsorption and the desorption isoplanes. The two types of ion exchanger are compared mutually and with the "monomer" (isonitrosoacetanilide). The most marked differences in the sorption of certain cations can be made use of in practice.

EXPERIMENTAL AND RESULTS

All the chemicals were of analytical grade purity. The majority of cations in the individual solutions were determined chelatometrically⁴ (Hg^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Ca^{2+} , Mn^{2+} and Mg^{2+}), silver was determined by titration with thiocyanate⁵ or gravimetrically in the form of chloride⁶, iron and aluminium were determined by precipitation with ammonia⁷, uranium was determined gravimetrically with the aid of isatine β -oxime⁸, palladium gravimetrically with dimethylglyoxim⁹; low concentrations of palladium were determined photometrically with *p*-nitrosodimethylaniline¹⁰.

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pH was measured with an Acidimeter EK (Druopta, Prague). The titration curves were determined statically in a volume of 100 ml; the amount of the wet ion exchanger corresponded to a dry weight of 0.5 g, the additions of NaOH were 0 to 30 ml of 0.1M-NaOH at $I = 0.1$. The mixture was left standing for 7 days with occasional stirring; pH was then measured and plotted vs the quantity of NaOH added.

The exchange capacities C (mmol/g of dry weight) for selected cations were also determined by a batch procedure in the presence of substances adjusting the medium for the sorption. The weight of the wet ion exchanger corresponded to 0.5 g of the dry resin; prior to the adsorption the solution contained 1 mmol of the cations in 100 ml. After 24 h the concentration of the non-adsorbed ions was determined, the ion exchanger was regenerated direct in the flask, washed with water and employed again.

To determine the distribution coefficients K_D we chose a ratio of $5 \cdot 10^{-2}$ mmol cations/0.5 g of the dry exchanger; this ratio was also used with the chelate-forming ion exchanger Dowex A-1 (see^{11,12}). Further procedure was the same as in the determination of the ion-exchange capacities. The values of K_D were calculated from the equation $K_D = (c_i/c) (V/m)$, where c_i and c denote the number of mmol of the cations bound to the ion exchanger and remaining in the solution, respectively, V is volume in ml, and m the weight of the dry ion exchanger in g.

The selectivity coefficients, K_S , were determined for type II only, in the same way as the exchange capacities. A mixture of two kinds of cations in different ratios, in a total quantity of 1 mmol/0.5 g of the dry weight, was adsorbed from a medium of dilute nitric acid. The value of K_S was calculated from the equation

$$K_S \frac{A}{B} \downarrow = \frac{(x_A)_i \cdot (x_B)_s}{(x_B)_i \cdot (x_A)_s}, \quad (1)$$

where x are the mole fractions of the cations bound to the ion exchanger (i) and remaining in the solution (s) after 24 h adsorption.

The adsorption and the desorption isoplanes were determined in columns (inner diameter 1 cm, height 30 cm) packed with 15 ml of the swollen ion exchanger (V_i), corresponding to 5 g of the dry material. The column of the ion exchanger was first washed with the acid from which the adsorption proceeded, the concentration of the acid being the same as in the adsorption of the cations. The specific loading, s , was defined as the ratio of the eluate volume in ml/h to the volume of the swollen exchanger in ml. In most experiments s equalled 5, which corresponded to a flow rate of 1.25 ml/min. The contents of the cations were determined in 25 ml fractions of the eluate. The useful capacity, C_u (mmol/g of the dry exchanger), was calculated from the quantity of the cations bound to the column of the exchanger at the moment when the cations appeared in the eluate. After equilibration of the cation concentrations in the applied solution (c_0) and in the eluate (c) the column was washed with an eluting solution till the cations were no longer present in the eluate. The courses of the adsorption and the desorption isoplanes are illustrated graphically.

Static Evaluation of the Ion Exchangers

Titration curves. The titration curve of a resin of the polycondensate type I (Fig. 1) resembles the titration curves of phenolic ion exchangers, described (e.g.) by Griessbach¹³, and indicates a very weak acidity of the functional groups.

The titration curve of a cation exchanger of type II is also shown in Fig. 1, where it is compared with the titration curve of isonitrosoacetanilide, determined by potentiometric titration in 50% ethanol. Comparison of the curve in Fig. 1 was difficult

in calculating the equivalents of the resin; for this reason curve 3 has been shifted along the axis of abscissae. From the calculation for an elementary unit of the resin, II, $C_{10}H_{10}N_2O_2$ (190.2), the theoretical exchange capacity should be 5.26 mval/g of the dry exchanger. The content of nitrogen is not a safe basis for the calculation since it is impossible to distinguish between the isonitrosoacetamide nitrogen and the nitrogen of unreacted amino groups. If the content of nitrogen (found: 11.57%, calculated: 14.75% N) is taken as a basis for a rough estimate the found content of nitrogen is merely 78.5% of the theoretical one and corresponds to a capacity of 4.13 mval/g of the dry exchanger. The capacity for metallic ions is also dependent on the nature of the cations and on their excess in respect to the exchanger. With a solution containing a great excess of Cu^{2+} ions (10 mmol/g of the dry exchanger) before adsorption from the medium of an acetate buffer, pH 5.6, the static capacity C

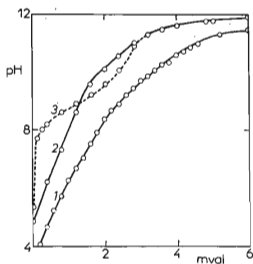


FIG. 1

Titration Curves of Ion Exchangers I (1) and II (2). Comparison with the Titration Curve of Isonitrosoacetanilide (3)

The solution was 1M in $NaNO_3$ and 0.1M in NaOH, $I = 0.1$; mval denotes the milliequivalents of NaOH per gram of the dry exchanger or per 438 mg of isonitrosoacetanilide.

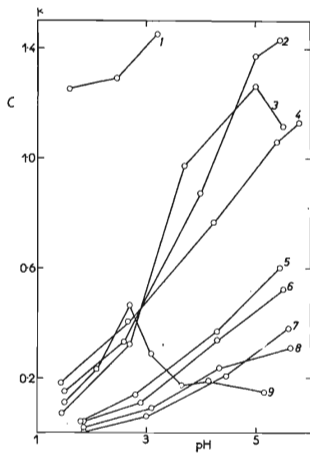


Fig. 2

Exchange Capacity of Ion Exchanger I as a Function of pH for Metallic Ions

C Exchange capacity in mmol/g of the dry exchanger; 1 Hg^{2+} , 2 Cu^{2+} , 3 UO_2^{2+} , 4 Ag^+ , 5 Ni^{2+} , 6 Co^{2+} , 7 Mn^{2+} , 8 Mg^{2+} , 9 Fe^{3+} .

was found to be 5.0 mval/g of the dry exchanger. The total dynamic capacity for Pd^{2+} ions from 1M- HNO_3 was 4.9 mval/g of the dry exchanger. These values, obtained for different cations and different media, are very close and give some idea about the utilization of the resin.

As an estimate from Fig. 1 the value of pK of isonitrosoacetanilide is 9. The titration curve of an exchanger of type II is rather difficult to evaluate. It resembles the titration curves of ion exchangers with slightly acid functional groups¹³; its shape is different from that of the titration curve of isonitrosoacetanilide. If we consider a capacity of 5.0 mval/g of the dry exchanger II the pK value of the isonitrosoacetamide group read off from Fig. 1 equals 10.

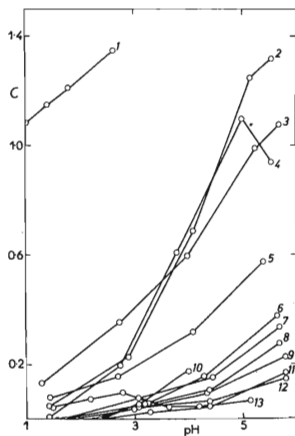


FIG. 3
Exchange Capacity of Ion Exchanger II as a Function of pH for Metallic Ions

C Exchange capacity in mmol/g of the dry exchanger; 1 Hg^{2+} , 2 Cu^{2+} , 3 Ag^+ , 4 UO_2^{2+} , 5 Pb^{2+} , 6 Ni^{2+} , 7 Zn^{2+} , 8 Co^{2+} , 9 Ca^{2+} , 10 Al^{3+} , 11 Mn^{2+} , 12 Mg^{2+} , 13 Fe^{3+} .

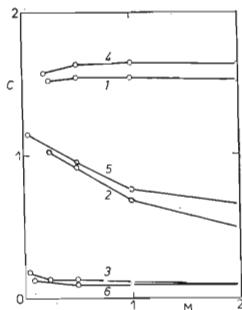


FIG. 4
Exchange Capacities of Ion Exchangers I and II in Relation to Acidity for Pd^{2+} , Ag^+ and Hg^{2+}

1, 2, 3 Ion exchanger I, 4, 5, 6 ion exchanger II; 1 Pd^{2+} , 2 Pd^{2+} , 3 Ag^+ , 4 Pd^{2+} , 5 Hg^{2+} , 6 Ag^+ . Curve 2 refers to the medium of HCl , the others to HNO_3 ; C exchange capacity in mmol per g of the dry exchanger, M molarity of the acid.

The exchange capacities. With both types of ion exchanger the exchange capacities were determined for the cations Hg^{2+} , Cu^{2+} , UO_2^{2+} , Ag^+ , Ni^{2+} , Co^{2+} , Mn^{2+} , Mg^{2+} and Fe^{3+} , with type II in addition for Pb^{2+} , Zn^{2+} , Ca^{2+} and Al^{3+} ; the medium employed was an acetate buffer, dilute acetic acid, or a mineral acid. The results are given in Fig. 2 (type I) and Fig. 3 (type II).

Comparison reveals that the polymeric type II has lower and more pH-dependent capacities. However, the sorption order of the cations is the same with the two types. The considerable adsorption of mercuric ions from a mildly acid medium suggests that the reactivity of functional groups correspond to the reactivity of isonitrosoacetanilide, since this agent in an acetate solution reacts preferentially with mercuric ions².

From the determined exchange capacities it is possible to deduce the following affinity order for either type of ion exchanger in an acid or mildly acid medium: $\text{Pd}^{2+} \gg \text{Hg}^{2+} \gg \text{UO}_2^{2+} \cong \text{Cu}^{2+} \gg \text{Ag}^+ \gg \text{Pb}^{2+} > \text{Fe}^{3+}, \text{Al}^{3+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} \cong \text{Mg}^{2+}$.

With ion exchanger II, stable even in alkaline media, we have also determined the capacities for eight kinds of cations forming ammo complexes. In the medium of an ammoniacal buffer, pH 10.2, the most adsorbed metal was copper ($C = 1.55 \text{ mmol/g}$ of the dry exchanger), the least adsorption was observed with palladium ($C = 0.49$).

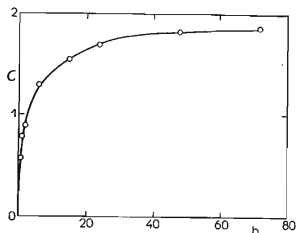


FIG. 5

Time Dependence of the Adsorption of Pd^{2+} on Ion Exchanger II from the Medium of 1M-HNO_3

C Exchange capacity in mmol per g of the dry exchanger.

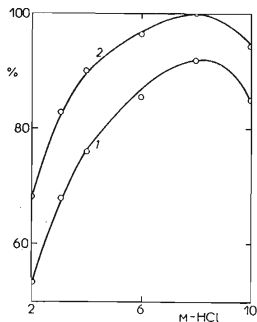


FIG. 6

Static Desorption (%) of Pd from Ion Exchanger II as a Function of HCl Concentration

1 Desorption after the first 100 ml portion of HCl, 2 total desorption after the second 100 ml portion of HCl.

The values found with the remaining six kinds of cations are too close to permit mutual separation.

Desorption of the majority of different cations, carried out in flasks after withdrawing the solution from which the adsorption had proceeded, was quantitative even by the action of 0.2M-HCl. The liberation of silver, effected by nitric acid, was more difficult, quantitative desorption did not occur up to a concentration of 1–2M-HNO₃. Desorption of mercury was incomplete with both types of ion exchanger. Although different procedures were tried out, the recovered mercury never amounted to more than 35%.

Special attention was paid to the sorption of palladium in acid solutions since in this medium Pd²⁺ was reported³ to form a precipitate with isonitrosoacetanilide. We have determined the exchange capacities for palladium in relation to concentration of nitric acid and compared these with the capacities for silver (Fig. 4). The adsorption of palladium to exchangers of either type is high (1.6 mmol/g of the dry exchanger) and independent of concentration of HNO₃ within the investigated range (0.15 to 2M). Silver, by contrast, is adsorbed to a slight extent only (0.1 mmol/g of the dry exchanger). The difference between the sorption of palladium and silver is considerable and suggests the possibility of separation. Similar results were obtained in the medium of perchloric acid.

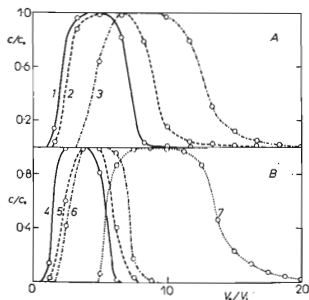


FIG. 7

The Adsorption and Desorption Isoplanes of Pb²⁺ (1 and 5), Cu²⁺ (2 and 6), Ag⁺ (3 and 7) and Ni²⁺ (4) in 1M-HNO₃ on Ion Exchangers I (A) and II (B)

c/c_0 Concentration ratio of the cations in the eluate (c) and in the applied solution (c_0); V_e/V_i volume ratio of the eluate to the ion exchanger in the column.

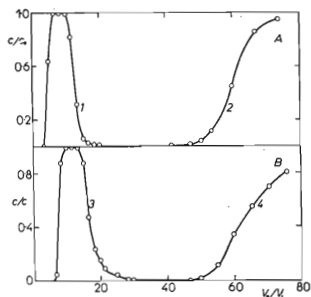


FIG. 8

The Adsorption Isoplane of Pd²⁺ (2 and 4) Compared to the Adsorption and Desorption Isoplanes of Ag⁺ (1 and 3) on Ion Exchangers I (A) and II (B)

c/c_0 Concentration ratio of the cations in the eluate (c) and in the applied solution (c_0); V_e/V_i volume ratio of the eluate to the ion exchanger in the column.

The ion exchanger of type II has been investigated for the time dependence of the adsorption of palladium from 1M-HNO₃. The adsorption (a batch procedure) was discontinued at selected intervals and the determined capacities were plotted *vs* the time of adsorption (Fig. 5). The curve shows that the adsorption is very slow. This slowness indicates that the mechanism of the binding may be different from that operative in the ordinary ion exchange.

The release of palladium from the ion exchangers is rather difficult and has therefore been studied in detail. Of the tested acids, solutions of chelate-forming agents and their mixtures with organic solvents the best eluting agent has proved to be 8M-HCl. This concentration, however, is too high for the polycondensate ion exchanger (type I) and its prolonged action affects the structure of the resin. To avoid this damage the exchanger was repeatedly exposed to 6M-HCl. With the resistant skeleton of the type II exchanger even concd. hydrochloric acid could be employed. The results of repeated static desorption of palladium in relation to concentration of HCl are given in Fig. 6.

TABLE I
Distribution Coefficients, K_D , for Ag⁺ and Pd²⁺ in Relation to Concentration of HNO₃

M-HNO ₃	K_D		M-HNO ₃	K_D	
	Ag ⁺	Pd ²⁺		Ag ⁺	Pd ²⁺
	Type I		Type II		
1	40	12 500	0.1	70	2 700
			0.5	60	2 900
			1	60	3 100
			2	40	3 800

TABLE II
Selectivity Coefficients, K_S , for Pd²⁺-Ag⁺ Mixtures in 1M-HNO₃ and Ion Exchanger II

n_{Pd}/n_{Ag}^a	$x_{Pd^{2+}}^b$		$K_S^{Pd^{2+}/Ag^+}$
	solution	exchanger	
9 : 1	0.654	0.994	92
7 : 3	0.298	0.982	128
1 : 1	0.130	0.954	140
3 : 7	0.049	0.906	190
1 : 9	0.005	0.743	523

^a Molar ratio before sorption, ^b mole fraction of Pd²⁺ in an equilibrium mixture.

The distribution coefficients. The determined values of K_D for Ag^+ and Pd^{2+} in dilute HNO_3 are listed in Table I. They prove a high selectivity of the ion exchangers, especially of type I, for Pd^{2+} in solutions of dilute acids.

The selectivity coefficients. The values of K_S were determined with type II for mixtures of Pd^{2+} and Ag^+ in 1M- HNO_3 (Table II). The selectivity for Pd^{2+} is high and increases with the decreasing concentration of Pd^{2+} .

Dynamic Evaluation of the Ion Exchangers

The sorption and desorption isoplanes of cations possibly accompanying Pd^{2+} (Cu^{2+} , Pb^{2+} , Ni^{2+} and Ag^+) are shown in Fig. 7. A 0.01M solution of cations (c_0) in 1M- HNO_3 was applied onto the column at $s = 5$. The first cations leaving the column were Ni^{2+} , Pb^{2+} and Cu^{2+} , the Ag^+ ions appeared later. With the two types of ion exchanger the order of elution is the same; in the case of the polymeric type II the curves are steeper. With the exception of Ag^+ , the last traces of the cations are eluted more easily from type II. The sorptions of Pd^{2+} and Ag^{2+} under the same conditions are compared in Fig. 8. The useful capacity for palladium is high (1.25 and 1.88 mmol per g of the dry exchangers I and II, respectively). The slopes of the curves show the possibility of separating palladium from silver and ordinary metals. The desorption data for palladium are given in Table III. According to the static experiments, 6M-HCl can be recommended for the type I exchanger, and higher concentrations of HCl, possibly in a mixture with acetone, for type II. From the analytical point of view type I is rather inconvenient because elution is too slow.

TABLE III
Desorption of Pd(%) from Columns of Selective Ion Exchangers
 V_e/V_i denotes the volume ratio of the eluate to the ion exchanger.

V_e/V_i	Type I 6M-HCl	Type II		
		12M-HCl + acetone (1 : 1)	8M-HCl	10M-HCl
5	75.2	94.23	95.16	97.15
10	82.3	97.29	97.76	98.88
15	87.7	98.98	98.50	99.22
20	90.7	99.93	99.09	99.45
25	93.8	100.00	99.53	99.64
30	95.2	—	99.79	99.79
35	95.8	—	99.94	99.90
40	96.3	—	100.00	99.97
45	96.5	—	—	100.00

TABLE IV
Separation of Pd from High Contents of Other Cations on Ion Exchanger II

Cation	mg	Given Pd ²⁺ mg	Found Pd mg	Difference %
Ni ²⁺	125			
Cu ²⁺	125	10.73	10.81	+0.74
Fe ³⁺	125			
Ni ²⁺	250			
Cu ²⁺	250	21.46	21.46	±0.0
Fe ³⁺	250			
Pb ²⁺	250	10.73	10.78	+0.47
Pb ²⁺	500	21.46	21.37	-0.42
Ag ⁺	500	10.73	10.81	+0.74
Ag ⁺	1 000	21.46	21.71	+1.16

Like in the static regeneration, desorption from type II cannot be enhanced by increasing the concentration of HCl above 8M. The addition of acetone is rewarding for the elution itself, but brings about difficulties in the evaluation of the eluate. Elution with 8M-HCl seems to be the most advantageous.

Application of Selective Ion Exchangers

Type I. It has been ascertained that low concentrations of palladium can be adsorbed from a relatively concentrated, acid solution of AgNO₃.

Onto a column of $V_i = 15$ ml was applied a solution which was 0.2M in AgNO₃ (21.6 g Ag/l), 0.5M (3%) in HNO₃ and 0.001M in Pd(NO₃)₂ (0.106 g Pd/l) at $s = 10$. Palladium appeared in the eluate after 2960 ml of the solution had passed through; this corresponds to a useful capacity of 0.59 mmol Pd/g of the dry exchanger. The Ag⁺ ions were washed out with 1M-HNO₃, the bulk of palladium ions was then desorbed with 6M-HCl. With 300 ml of 6M-HCl there was recovered about 90% of the adsorbed palladium. The ion exchanger has also been tested for the recovery of palladium from the washings left after palladium plating. A model solution of metal ammine-complexes, containing 26 mg Pd²⁺/l, 30 mg Cu²⁺/l, (NH₄)₂SO₄ and NH₃, was brought onto a column (inner diameter 5 mm) with the ion exchanger ($V_i = 3$ ml of the exchanger, corresponding to 1 g of the dry material). At $s = 10$ there had passed 3135 and 3150 ml of the model solution before palladium appeared in the eluate. The column was then washed with 10 ml of 0.25M-HNO₃, the ion exchanger was regenerated by a very slow passage of 30 ml of 6M-HCl ($s = 2$), then it was washed with 10 ml of water. There was obtained 72 and 71 mg of Pd, *i.e.* about 89%. Another 30-ml fraction of 6M-HCl contained 6 mg of Pd²⁺.

The procedure might be useful for concentrating very dilute acid solutions of palladium containing high concentrations of ordinary metals and silver. Even with an incomplete desorption there remains the possibility of repeated use and the rest of the metal could be obtained by combustion of the exchanger.

Type II. The exchanger was employed for separation of palladium from analysed mixtures.

Small columns (inner diameter 5 mm, height 15 cm) were packed with the swollen exchanger (0.5 g of the dry resin). The volume of the exchanger was $V_1 = 2$ ml. The columns were washed with 1M-HNO₃, then solutions of Pd²⁺ and other cations were allowed to pass through. The accompanying cations in rather high concentrations were Cu²⁺, Ni²⁺, Fe³⁺ and Pb²⁺ or Ag⁺. The acidity of the solution was adjusted to 1M-HNO₃. Since the amount of the exchanger was five times greater than that necessary for the given content of Pd²⁺ to be sorbed the flow rate through the column was higher (1 ml/min, which corresponds to $s = 30$). After passage of the analysed mixture the column was washed with 50 ml of 1M-HNO₃ (25V₁) and palladium was desorbed with 100 ml of 8M-HCl (50V₁). The desorption proceeded at a very low flow rate (10 ml/h, $s = 5$), preferably overnight. The results are given in Table IV.

The sorption and the desorption of palladium were quantitative and the ion exchanger has proved to be usable for the separation of palladium from much higher quantities of ordinary metals and silver. The ion exchanger has a constant volume. The stability of the functional group is good since after 10 working cycles no change in capacity was observed.

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