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NEW SELECTIVE PYRAZOLE-CONTAINING SORBENTS FOR CHROMATOGRAPHY OF NOBLE METALS

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SUMMARY

New selective pyrazole-containing sorbents were obtained by copolymerization of N-vinyl-3(5)-methylpyrazole with divinyl monomers and by amination of chloromethylated copolymers of styrene and divinylbenzene by 3(5)-methylpyrazole.

The amination conditions were determined by the model reaction between 3(5)-methylpyrazole and benzyl chloride in the presence of bases.

The chemical and thermal stability of both types of sorbent were determined.

The synthesized sorbents possess high sorptional capacities with respect to the platinum family metals, gold and silver.

INTRODUCTION

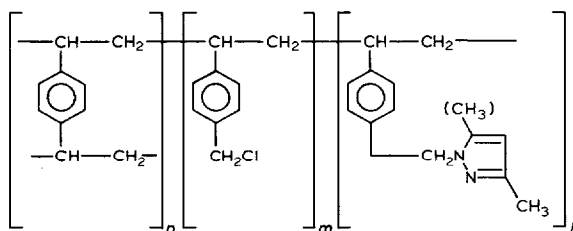
For chromatographic analysis of noble metals and their sorption from spent industrial solutions and sewages, anionites with high and low basicities, such as AV-17 and AN-18, are now used which have suitable kinetic and mechanical properties. However, these sorbents have rather poor selectivities, therefore their applications are very restricted and new highly selective sorbents are required.

In order to solve this problem we have used 3(5)-methylpyrazole (MPz) and its vinyl derivatives. Heterocyclic ligands such as pyrazole and its derivatives have been investigated in detail. Many of them, and in particular MPz, produce stable complexes with cations such as those of Mg, Fe, Co, Ni, Zn, Hg, As, Ag, Au and the platinum metals. At the same time, polymer sorbents containing pyrazole rings exhibit high selectivity only towards platinum metals, gold and silver^{1,2}.

At present, there are two ways to synthesize pyrazole-containing sorbents: (i) copolymerization of N-vinyl-3(5)-methylpyrazole (N-VMP) with divinylbenzene (DVB) or with ethylene glycol dimethylacrylate (DMEG)³, the corresponding products being referred to a SVPD and SVPE; (ii) amination of chloromethylated copolymers of styrene and divinylbenzene having different porosities with MPz^{1,2,4}.

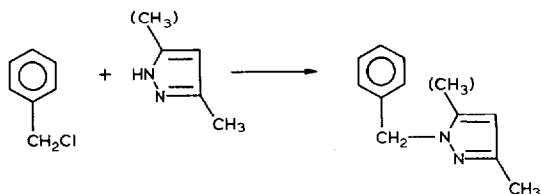
Use of the first method gave several sorbents whose sorption capacity with respect to 0.1 M silver nitrate markedly decreases (from 4.2 to 1.2 mg-equiv./g) with increasing content of divinyl monomers in the initial mixture. The sorption capacity is also affected by the isomer composition of N-VMP, *viz.*, decreasing with increasing content of the 5-isomer.

The second method yielded sorbents possessing the following structure



where $m = 12\text{--}30$, $l = 10\text{--}80$ mol %, $n = 100 - (m + l)\%$. However, the amination by MPz is relatively slow and the considerable amount of residual chloromethyl groups in the resulting sorbent reduces its hydrophilic properties and has a deleterious effect on the sorption process.

In order to improve the sorption properties and to increase the conversion yield of amination of chloromethylated MPz copolymers, we have studied the reaction between MPz and benzyl chloride, where the latter acts as a model of the active structural fragment of the styrene–divinylbenzene copolymer. The reaction was performed at $80\text{--}100^\circ\text{C}$ under various conditions: with stoichiometric proportions of the reagents, in the absence and in the presence of excess of MPz and in the presence of bases such as carbonates and hydroxides of alkali metals which effectively remove hydrogen chloride from the reaction zone:



The conversion yield of the N-alkylation reaction (Table I) and the quantitative relations of N-substituted pyrazole isomers were measured using ^1H NMR spectroscopy.

The molar ratio of N-substituted pyrazole isomers, 3-isomer:5-isomer, was 1:2 in the presence of a base and 1:3 without a base. Since under the conditions involved only one nitrogen atom is alkylated regardless of the reagent concentrations, the presence of a base sharply augments the alkylation rate and affects the isomer composition of N-alkylated MPz derivatives.

The highest conversion yield was observed when using potassium hydroxide or sodium hydroxide as a base, at a level of 0.25–1.0 mol per mol of CH_2Cl groups (see Table II), while other bases do not markedly influence the process.

As shown in Table II, the sorption capacities of pyrazole-containing sorbents produced in presence of bases are much greater than those of sorbents produced without bases⁴. For example, a sorbent synthesized using the method described¹ with 7.8% of nitrogen has a sorption capacity for Ag of 1.7 mg-equiv./g, while a sorbent

TABLE I
EFFECT OF A BASE ON THE ALKYLATION OF MPz BY BENZYL CHLORIDE

Reaction time (min)	Conversion yield of MPz (%)	K ($l \text{ mol}^{-1} \text{ s}^{-1}$)
<i>Without a base</i>		
20	16	$3 \cdot 10^{-5}$
60	35	$5 \cdot 10^{-5}$
240	50	$2 \cdot 10^{-5}$
<i>In presence of bases</i>		
5	70	$8 \cdot 10^{-3}$
10	85	$4 \cdot 10^{-3}$
240	85	$4 \cdot 10^{-3}$

produced in presence of a base has a capacity of 2.1 mg-equiv./g, the content of pyrazole groups being the same. The sorption capacities of these sorbents seem to depend on their specific structures which in turn are dependent on the syntheses conditions.

In order to obtain quantitative estimates of the structural differences we have calculated the kinetic parameters for thermal decomposition of the sorbents. To do this we have used a relation describing the decomposition activation energy, E , of linear polymers⁵

$$\log R_T = \log A + (E/R)[W_M/T_M^2 R_M] \log W - (1/2.303 T)$$

where W_M , T_M and R_M are the residual mass, temperature and the decomposition rate, respectively, at the point in the differential thermogravimetric curve where the decomposition rate is maximal; A is a statistical factor. The values of E were calculated from:

$$\log R_T = f[(W_M/T_M^2 R_M) \log W - (1/2.303 T)]$$

TABLE II
EFFECT OF THE NATURE OF THE BASE ON THE INTERACTION OF A CHLOROMETHYLATED COPOLYMER WITH MPz AT 80°C

Duration: 2 h.

Base	Moles of base per mol of CH_2Cl groups	Content of N in the sorbent (%)	Sorption capacity for 0.1 M silver nitrate (mg-equiv. Ag/g)
Potassium carbonate	1.0	8.0	1.9
Ammonium hydroxide	2.5	7.6	1.8
Sodium hydroxide	1.0	11.3	2.9
Sodium hydroxide	0.5	11.3	2.9
Sodium hydroxide	0.25	11.3	2.8
Sodium hydroxide*	0.25	7.8	2.1

* Duration: 0.5 h.

The sorbent produced in the presence of sodium hydroxide has $E = 31.5$ kJ/mol, while that produced with use of a protonated form of MPz has $E = 50.0$ kJ/mol. The values of the decomposition activation energy obtained are in good agreement with those of other sorbents with three-dimensional polymer matrices, *e.g.*, ion exchangers with iminodiacetate groups⁶ whose kinetic parameters were calculated⁷.

The difference in the E values of the sorbents is, seemingly, due to the different extents of organization of the three-dimensional polymer matrices, that in the case of amination by a protonated form of MPz being much greater. It is clear that when the amination reaction is rapid in the presence of sodium hydroxide (see Table I), the number of groups participating in the slow solid-phase cross-linking reaction decreases. On the contrary, in the absence of bases, the rate of the cross-linking reaction involving chloromethyl groups becomes comparable with that of the main reaction of the polymer-analogous conversion, the density of the polymer network being increased thereby.

Thus the observed differences in sorption capacities with respect to silver ions are due to the different accessibilities of pyrazole groups in the diversely structured polymer matrices, although the pyrazole group content is the same.

A further improvement in the sorption capacity of pyrazole sorbents for Ag was achieved when MPz was treated (in the presence of sodium hydroxide) with chloromethylated telogenated copolymers (referred to as SPD-d) which contain up to 30% of chlorine. The sorption capacity of such sorbents is 4.0–4.5 mg-equiv./g (for 0.1 *M* silver nitrate).

The thermal stability of N-VMP-based sorbents was studied by thermogravimetry in a nitrogen atmosphere. It was shown that for both types of sorbents the mass losses due to removal of water of hydration are not greater than 5% at 590 K because of the sorbents hydrophobic nature. The decomposition activation energy of the sorbents was calculated using the equation

$$\alpha = 1 - e^{-K_d \tau^n}$$

or in the differential form:

$$\frac{d\alpha}{d\tau} = n K_d^{1/n} (1 - \alpha) [-\ln(1 - \alpha)]^{\frac{n-1}{n}}$$

The values obtained are practically coincident: 30.1 kJ/mol for SVPD, 30.4 kJ/mol for SVPE. The pK_a value for SVPD-5, determined by potentiometric titration according to the Gregor equation, $\text{pH} = pK_a + n \log(\alpha/1 - \alpha)$, is -0.27 for the acid–base equilibrium, *i.e.*, much less than that (2.53) of non-substituted pyrazole. It indicates the very low basicity of nitrogen in the copolymer. This is why the copolymers exhibit no swelling in aqueous solutions, but swelling can be greatly increased by acidifying the solution.

Also studied were the sorptions of sulphuric, hydrochloric and nitric acids and the accompanying adsorption of water by the sorbents. It was shown that when the acid concentrations are not greater than 0.6 g-equiv./l, the sorption curves practically coincide. At higher concentrations, sulphuric acid is absorbed to greater extents than

the other acids. The absorption of water is much more extensive, *viz.*, when the acid concentrations are higher than 0.2 g-equiv./l, 200 mmol/g of water are absorbed from a sulphuric acid solution, 170 mmol/g from a hydrochloric acid solution and 100 mmol/g from a nitric acid solution⁸.

The isotherms for sorption of silver by SVPD-5 from solutions containing different concentrations of nitric acid (the ionic strength due to NO_3^- being constant and equal to 1 M) have two steps in the $C_R = \varphi(P)$ coordinates, each being adequately described by the modified Nikolskii equation:

$$C_R = S - \frac{1}{\bar{K}} \cdot P^{1/2}$$

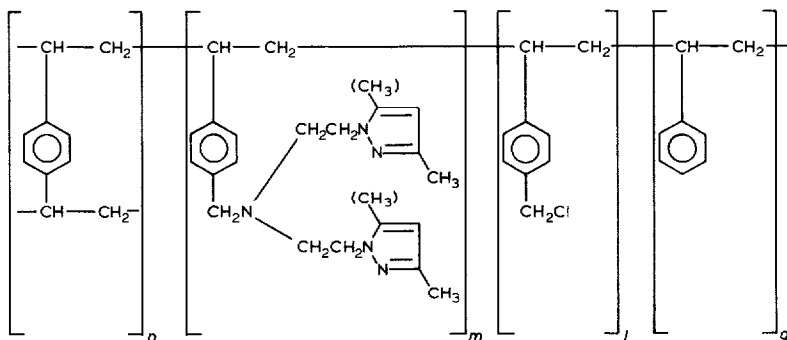
The shape of the isotherms at microconcentrations of Ag indicates that monosolvates of the type $\sim \text{PzAgNO}_3$ are produced. Finally, silver can easily be desorbed from the sorbents by a small amount of 0.5 M ammonium solution.

Of interest is that the sorption capacities of the sorbents depend on the type of pyrazole used initially (N-VMP or MPz). Thus, the SVPD sorbents exhibit more complete extraction of gold, silver and platinum metals from acidic solutions, while the sorbents produced from styrene-DVB copolymers are selective in alkaline and neutral media.

The sorption capacity of SVPD increases with increasing acidity from 0.1 to 1 M but then decreases and for the platinum metals obeys the following sequence: Pd, Os, Pt, Rh. The fact that in some cases the sorption properties of these metals differ markedly can be used for separation purposes.

In order to concentrate microquantities ($0.02\text{--}10 \text{ mg/cm}^3$) of platinum metals (Pd, Pt, Rh, Ir) from 1 M hydrochloric acid for quantitation, the SDP-d sorbents were used. In the presence of up to 50 mg/cm^3 of Cu^{2+} ions, Pd, Pt and Ir are extracted quantitatively, while the sorption of Rh is 78%. When the copper concentration is increased to 100 mg/cm^3 , the sorption of Rh decreases to 56%, hence this sorbent cannot be used for quantitation of Rh.

The sorption of Rh is much greater with sorbents which contain, along with pyrazole groups, amino groups having various basicities. For example, the sorbent with the structural formula⁹



can extract 84% Pd, 96% Pt, 86% Rh and 90% Ir from a 1 M solution of hydrochloric acid containing 100 mg/cm^3 of Cu. The sorption kinetics is thus improved,

and the process of sorptional concentration is more rapid. The noble metals can then be quantitatively desorbed by alkaline solutions of ammonium nitrate or rhodanide.

CONCLUSIONS

New types of highly selective polymer sorbents containing pyrazole rings have been developed for selective sorption of noble metals from diverse solutions. The sorbents were synthesized by suspension copolymerization of N-VMP with divinyl monomers and by amination of chloromethylated copolymers of styrene and divinylbenzene having gel or macroporous structures by NPz in the presence of proto-philic.

Both types of sorbents possess high sorption capacities with respect to platinum metals, gold and silver and are selective. The pyrazole-containing sorbents are chemically and thermally stable.

The optimum pH for sorption of platinum metals as well as the desorption conditions have been determined.

The kinetic characteristics of the sorbents are improved by introducing additional amino groups.

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