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## PHYSICAL CHEMISTRY \_\_\_\_\_ OF SOLUTIONS \_\_\_\_\_

# Chelating Tendencies in the Rows of Polymeric Sorbents and Their Copper(II) and Lead(II) Complexes

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**Abstract**—The physicochemical properties of chelating polymer sorbents (CPSs), derivatives of poly(styrene-2-hydroxy- $\langle 1-azo-1' \rangle$ -2'-hydroxybenzene), are studied with respect to copper and lead ions. The following sorption parameters are determined: the optimum acidity, temperature, and duration; the sorption capacity of the sorbent (SCS); and stability constants of polychelates. Quantitative correlations are found between the dissociation constants (p $K'_a$ ) of the analytical functional group (AFG) of the sorbent, and the pH<sub>50</sub> of chelation of the

tested metals; between  $pK'_a$  and the stability of the complexes ( $\log \beta$ ); and between  $pK'_a$  and the charge of the oxygen atom of the complexing group (z); these correlations are intended for use in elucidating the effect of the structural features and acid-base properties of the AFG on the chemisorption parameters of copper(II) and lead(II). These correlations predict the physical-chemical properties of sorbents and the sorption parameters of trace elements for preconcentrating and separating them from biological, natural, and technical objects

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Global pollution of the biosphere with inorganic compounds is a result of the industrial and agricultural activity of mankind. Heavy-metal pollution of water, soil, and foodstuffs is most dangerous. Copper and lead are classified as toxic elements. Their high abundance in nature, toxicity, migration ability, and cumulating ability necessitate the strict control of their level in nature to maintain it far below their maximum permissible concentrations [1].

In this context, the preconcetration, separation, and determination of these elements are very topical. The use of chelating polymer sorbents (CPSs) for these purposes opens wide possibilities for researchers, namely the individual and group separation of elements with canceling matrix effects and providing high preconcentration coefficient. A distinctive feature of the CPSs is the existence of chemically reactive groups in their polymer matrix, which react with metal ions in solution forming chelates. The properties of the sorbents are mostly dictated by the structure and physical–chemical properties of analytical functional groups (AFGs) in the matrix [2].

Here, we discuss the results of our study of the complexing (chemisorption) of copper(II) and lead(II) by CPSs that are derivatives of polystyrene-2-hydroxy- $\langle 1$ azo-1' $\rangle$ -2'-hydroxybenzene. We also find correlation relations between the structure and properties of AFGs and the physicochemical parameters of chemisorption of the trace elements studied. Studying and comparing parameters such as the acid-base ionization constants of the AFGs ( $pK'_a$ ), the pH<sub>50</sub> of chelation of the metal cations studied, the charge of the oxygen atom of the complexing group (*z*), and the stability constants of the resulting complexes ( $\log \beta$ ), we derive the following correlation relations:  $pK'_a - pH_{50}$ ,  $pK'_a - \log \beta$ , and  $pK'_a - z$ .

These correlation provide a theoretical basis for synthesizing, choosing, and using CPSs with optimum physical-chemical and sorption properties for use in polychelate chemistry and the separation and preconcentration of the trace elements studied.

#### **EXPERIMENTAL**

Stock solutions of the metals with the concentration equal to 1 mg/mL were prepared by dissolving an aliquot of a high-purity-grade metal in hydrochloric acid as in work [3]. Working solutions were prepared by diluting the stock solutions.

Chelating polymer sorbents were synthesized in the Central Chemical Laboratory of the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry and purified by known methods to reagent-grade purity. The AFG concentration  $\psi$  was monitored through ultimate analysis for the key atoms and through determining the sorption capacity of the sorbent (SCS) [2]. Before use, spherical pellets of the

sorbent were pounded with an agate mortar, and screened through a 200-mesh (0.074-mm) screen.

The solution pH was adjusted with weak HCl or a sodium acetate solution and was measured on an I-500 Ionomer pH-meter accurate to  $\pm 0.05$ . The trace-element concentration in test solutions was determined by inversion voltammetry on an Ecotest-VA instrument.

The sorption parameters—time ( $\tau$ , min), temperature (T, °C), and optimum acidity (pH<sub>opt</sub>)—were studied as described in work [4]. Solutions 25 mL in volume containing 25 µg of a metal and 25 mg of a sorbent were used in experiments. The pH<sub>50</sub> of sorption was determined graphically from R (%)–pH plots, where Ris the degree of sorption. The SCS was determined as the amount of the metal (in mg) sorbed by 1 g of the sorbent under the optimum sorption parameters.

The number of protons replaced from the AFG during the sorption of copper(II) and lead(II), n, was determined by the procedure developed for CPSs [2].

The stability constants of complexes of CPSs with tested ions were determined potentiometrically at  $20 \pm 2^{\circ}$ C [5].

### **RESULTS AND DISCUSSION**

The tested sorbents were brown spherical pellets insoluble in water, acids, alkalis, and organic solvents.

The structural formula of a fragment of the sorbent is



where X and Y are substituents (H, SO<sub>3</sub>H, NO<sub>2</sub>, Cl, or COOH).

The AFG in this class of sorbents is the o,o'-dihydroxyazo group. The ionization constants of the AFG of sorbents were determined elsewhere [6].

The table lists the physicochemical and analytical parameters of the sorption of trace copper(II) and lead(II) by CPSs.

All test metals are quite rapidly (in 10–30 min) are sorbed at room temperature ( $20 \pm 2^{\circ}$ C). A rise in temperature to 60°C makes the sorption time 5–10 min shorter, but brings about a significant degradation of the chelates. The SCSs for the test sorbents fall in the range of 17.62–25.80 mg of copper(II) or lead(II) per gram of the sorbent.

The numbers of the protons displaced upon sorption imply that the AFGs are involved in complexing. After matching of the pH and degree of extraction (R, %), *n* was found graphically from the slope of the

Parameters of sorbents and	l chemisorption of copper(II)	and lead(II) by CPSs	. Determination con	ditions: $T = 20 \pm 2^{\circ}C$	$C, \mu = 1,$
and $R = 98 - 100\%$ ( $n = 5$ , $R$	P = 0.95)				

Sorbent no.	Sorbent	М	p <i>K</i> ' <sub>a</sub> [6]	Charge on the O atom, z	pH <sub>pt</sub>	pH <sub>50</sub>	SCS <sub>M</sub> , mg/g	τ, min	logβ	n
1 Polystyrene-2	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	8.30	-0.227	3.5-5.5	2.5	17.62	25	8.2	1
	hydroxybenzene	Pb			5.5-7.4	2.1	19.85	30	8.1	1
2 Polystyrene-2-h	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	0.10	-0.226	3.1-5.0	1.9	21.05	25	8.0	1
	hydroxy-5'-chlorobenzene	Pb	8.10		5.7–7.1	1.9	21.22	25	7.9	1
3 Polystyrene-2-h hydroxy-5'-sulf	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	7 75	-0.223	2.5-5.5	1.5	23.20	20	7.5	1
	hydroxy-5'-sulfobenezene	Pb	1.15 -		5.3–7.7	1.7	20.70	25	7.5	1
4	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	7.50	-0.221	2.9–5.1	1.3	25.15	10	7.3	1
	hydroxy-5'-nitrobenzene	Pb	7.50		5.5–7.5	1.4	21.67	15	7.2	1
5 Polystyrene-2-hy	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	7.00	-0.224	3.7–5.4	1.8	20.82	30	7.7	1
	hydroxy-3'-sulfo-5'-chlorobenzene	Pb	7.90		5.0-7.3	1.9	25.10	25	7.6	1
6	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	7 70	0.000	2.8-5.1	1.5	22.68	20	7.5	1
	hydroxy-3',5'-disulfobenzene	Pb	7.70	-0.222	6.0-8.0	1.5	25.80	25	7.4	1
7 Polystyrene-2-	Polystyrene-2-hydroxy-(1-azo-1')-2'-	Cu	5.40 -0.220	0.000	3.0–5.3	1.1	27.76	10	7.2	1
	hydroxy-3'-sulfo-5'-nitrobenzene	Pb		5.3–7.7	1.4	25.40	15	7.1	1	
8 Polystyrene-2-h	Polystyrene-2-hydroxy-<(1-azo-1')-2'-	Cu	7.30 –	-0.218	2.7-5.3	1.1	29.40	15	7.1	1
	hydroxy-3',5'-dinitrobenzene	Pb			5.3-7.0	1.2	25.65	15	6.9	1
9 Polystyrene-2	Polystyrene-2-hydroxy-<(1-azo-1')-2'-	Cu	8.20	-0.221	3.8–5.6	1.8	19.13	25	8.1	1
	hydroxy-3'-carboxy-5'-sulfobenzene	Pb			5.3–7.0	2.2	20.57	30	8.0	1



**Fig. 1.** Correlation between the acid–base properties  $(p K'_a)$  of the AFGs of sorbents and the pH<sub>50</sub> for sorption of (a) copper and (b) lead for sorbents 1–9.

 $\log R (100 - R)$  versus pH plot. In the test systems, one proton is replaced for copper and zinc.

A match between the  $pH_{50}$  of sorption for copper and lead and the acid–base properties ( $pK'_a$ ) of the AFG implies that there are correlation relations between these quantities (Fig. 1); the correlations are described by the following linear equations:

for the copper–sorbent system,  $pH_{50} = (pK'_a - 5.8)$ 0.75 (r = 0.9696);

for the lead-sorbent system,  $pH_{50} = (pK'_a - 5.95)$ 1.19 (r = 0.9723).

The quantitative relation between the  $pK'_a$  of the AFG and the  $pH_{50}$  of sorption verifies the direct involvement of the 2'-hydroxy group of the AFG of the test sorbents in chelation.

From the structure of the AFG introduced preparatively into the polymer matrix, the numbers of the protons replaced upon sorption, and the quantitative relation between the  $pK'_a$  of the AFG and the  $pH_{50}$  of sorption, we suggest that the most likely structure of the resulting chelate complex is



where  $\bullet$  denotes a metal ion (Cu<sup>2+</sup> or Pb<sup>2+</sup>).

This structure of the complex suggests that the metal cation forms a valence bond with a phenyl oxygen atom, a coordination bond with the azo nitrogen atom, and another coordination bond with the oxygen atom of the phenyl group that remains undissociated under the sorption conditions ( $pK_{OH} = 9.08-9.80$ ;  $pH_{opt} 2.5-8.0$ ). The net positive charge of the cation is balanced by the anions in the solution.

Comparing the ionization constants of the AFGs with the stability constants and the charge of the oxygen atom of the complexing group, we found correlation relations between these parameters (Figs. 2, 3). Mathematically, these correlations are described by the following linear equations:

for the copper–sorbent system,  $pK'_a = 0.97 \log \beta + 6.25 (r = 0.9922);$ 

for the lead-sorbent system,  $pK'_a = 0.84 \log \beta + 6.95 (r = 0.9957)$ .

The  $pK'_a - z$  correlation is based on the linear correlation between the acid–base properties of the AFG and the electron charge induced by the substituent in the *para* on the reactive site and neighboring atoms; the latter is revealed by quantum-chemical computations using Hyper Chem Release 7.01 for Windows software.

From the correlation between the acid–base properties of the AFG and the charge of the oxygen atom of the complexing group, it follows that the substituent is in the effective position in which the electron density is redistributed along the conjugated chain to the oxygen atom of the AFG; ultimately, this is manifested as a change in the acid–base properties of the AFG.

The correlation between the  $pK'_a$  of the sorbents studied, except for the carboxysulfo-substituted sorbent, and the charge of the oxygen atom of the complexing group is

$$z = 0.25 \, \mathrm{pK'_a} - 0.213$$

or  $pK'_a = (z + 0.213)/0.25 (r = 0.9743).$ 

These correlations quantitatively predict, proceeding from  $pK'_a$ , the  $pH_{50}$  of sorption and the strength of complexes formed by ions with this group of sorbents.

For example, let us have no a sorbent bearing an arsono group AsO<sub>3</sub>H<sub>2</sub>. The tabulated Hammett constant  $\sigma_n$  for this substituent is 0.460 [2]. The correlation relation between  $\sigma_n$  and pK'<sub>a</sub> for mono- and disubstituted



**Fig. 2.** Correlation between the acid–base properties  $(p K'_a)$  of the AFGs of sorbents and the stability constants  $(\log \beta)$  of the complexes formed with (a) copper and (b) lead ions for sorbents 1–9.

sorbents was derived previously:  $pK'_a = 8.29 - 0.29\sigma_n$ , and  $pK'_a = 8.11 - 0.38\sigma_{n+o}$  [7]. We can use these correlation relations to calculate  $pK'_a$  for the given model monosubstituted sorbent:

 $pK'_a = 8.29 - (0.29 \times 0.46) = 8.16.$ 

Next, substituting this value to the correlation equation, we calculate  $pH_{50}$  and  $\log\beta$  as follows:

for copper, 
$$pH_{50} = (8.16 - 5.8)/0.75 = 3.15$$
,  
 $\log \beta = (8.16 - 6.25)/0.97 = 1.97$ ;  
for lead,  $pH_{50} = (8.16 - 5.95)/1.19 = 1.86$ ,  
 $\log \beta = (8.16 - 6.95)/0.84 = 1.44$ .



**Fig. 3.** Correlation between the acid–base properties  $(pK'_a)$  of the AFGs of sorbents and the charge of the oxygen atom of the complexing group for sorbents 1–8.

Thus, the calculations show that the predicted sorbent is not superior to the existing one in its  $pH_{50}$  of sorption (the pH shift is 0.76 (Cu) and 1.95 (Pb)), and its synthesis for subsequent use in the development of a new preconcentration method is impertinent in view of the unavailability of the precursor.

#### REFERENCES

- 1. V. F. Protasov, *Ecology, Health, and Environmental Protection in Russia* (Finansy i Statistika, Moscow, 2001) [in Russian].
- N. N. Basargin, Yu. G. Rozovskii, V. A. Golosnitskaya, et al., Correlations and Prediction of the Analytical Properties of Chelating Polymer Sorbents and Their Complexes with Chemical Elements (Nauka, Moscow, 1986) [in Russian].
- 3. P. P. Korostelev, Solution Preparation for Chemical Analysis (Izd-vo AN SSSR, Moscow, 1962) [in Russian].
- N. N. Basargin, Yu. G. Rozovskii, V. A. Golosnitskaya, et al., Organic Reagents and Chelating Sorbents in Mineral Analysis (Nauka, Moscow, 1980) [in Russian].
- K. M. Saldadze and V. D. Kopylova-Valova, *Complexing* Ion Exchangers (Complexites) (Khimiya, Moscow, 1980) [in Russian].
- N. N. Basargin, E. R. Oskotskaya, O. E. Simakova, and E. A. Dorofeeva, *Application of Poly(azostyrene) Sor*bents with o,o'-Dihydroxyazo Group in Environmental Analysis for Be, Cd, Sc, Y, Co, and Ni: Theory and Practice (OGU, Nauka, IGEM RAN, Izd-vo OOO Kartush, Orel, 2006) [in Russian].
- N. N. Basargin, E. R. Oskotskaya, and A. V. Chebrova, Zh. Fiz. Khim. **80** (12), 2260 (2006) [Russ. J. Phys. Chem. **80** (12), 2016 (2006)].