

ХИМИЧЕСКИЕ НАУКИ

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SORPTION OF Cu^{2+} , Zn^{2+} , Cd^{2+} AND Pb^{2+} -IONS BY DIAION CR-11 AND DUOLITE C-467 CHELATING ION EXCHANGERS

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ABSTRACT

The equilibrium sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} -ions by polyampholytes Diaion CR-11 (with iminodiacetic group, Na^+) and Duolite C-467 (with amino-fosfon group, Na^+), depending on the degree of neutralization of the ionogenic groups, concentrations of solutions and acidity is investigated. Equilibrium and kinetic parameters of sorption processes are defined, thermodynamic quantities are calculated.

АННОТАЦИЯ

Исследована равновесная сорбция ионов Cu^{2+} , Zn^{2+} , Cd^{2+} и Pb^{2+} полиамфолитами Diaion CR-11 (с иминодиуксусной группой, Na^+) и Duolite C-467 (с амино-фосфоновой группой, Na^+), в зависимости от степени нейтрализации ионогенные группы, концентрации растворов и кислотности. Определены равновесные и кинетические параметры сорбционных процессов, рассчитаны термодинамические величины.

Key words: ampholytes, metal-ions, sorption, equilibrium, isotherms, kinetic and thermodynamic quantities

Ключевые слова: амфолиты, ионы металлов, сорбция, равновесие, изотермы, кинетические и термодинамические величины

Introduction

The complexity of cleaning waste water from heavy metal ions and the lack of universal methods are the reason for implementing for this purpose various methods (reagent, electrochemical, membrane, sorption) with their inherent drawbacks. Currently, more attention is paid to sorption processes using polymer sorbents. Therefore, an increase in the sorption selectivity is of current importance. There is sufficient information on the clarity of the calculation of the equilibrium conditions, kinetic properties, thermodynamic parameters of the absorption of iron metal ions with various nature and sorbents of functional groups [1-3]. The study of the equilibrium conditions of the ion exchange results in ultimately leading to the removal of the isotherm equation and of determining the change constant or selectivity coefficient. For this reason, from model solutions connected with increasing of sorption selectivity research is perceived as an actual problem.

The purpose of this work was to study the sorption equilibrium and the rate of its establishment in ionite-inorganic electrolyte systems.

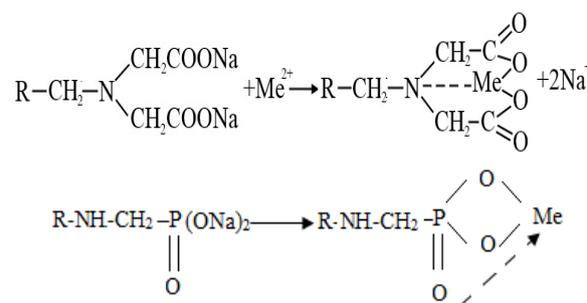
Section Experimental

The polymer matrix of ion exchangers is polystyrene, crosslinked with divinylbenzene, with grafted macroporous aminophosphonic (Duolite C467) and highporous (Diaion CR-11) with iminodiacetic acid functional groups [2]. Sorption of the studied ions was carried out under static conditions on the Na-form of ion exchangers from aqueous solutions of nitrates of these metals of the chemical grade with a pH of 2-8 in the concentration range of 0.5-5.0 $\text{gMe}\cdot\text{l}^{-1}$. The residual concentration of Cu^{2+} ions in equilibrium solutions was determined by the complexometric method with pyridyl-azo-naphtol (PAN), zinc and cadmium ions

with eriochrome black T, and lead ions with xylenol orange [3]. In a series of experiments, the accuracy of the results was controlled by determining the concentration of studied ions at atomic absorption spectrometer Thermo Scientific iCE 3500 AA. The quantity of ions passing to the ionite phase at equilibrium condition has been calculated according to the formula: $A = (C_0 - C_e)V/m$ (Eq. 1).

Results and Discussion

The sorption with Diaion CR-11 and Duolite C 467 polyampholyte are realized due to substitution of Na ions with Me^{2+} and formation of coordinate communication between Me^{2+} ions and N and O atoms, substitution of the sorbents of Me^{2+} ions with H^+ ions of functional groups.



The maximal sorption capacity of these sorbents is 4.40 and 3,50 meq/g according to the above sequence, their matrices are in the form of , macroporous and highporous, their swelling rates are 3,43 and 3,50.

The ion exchange constants in the system of ionite ions of metals were calculated for the case of the exchange of a monovalent ion into a bivalent ion using the well-known formula:

$$K = C_{\text{H(Na)sorbent}}^{1/2} \cdot C_{\text{H(Na)solution}} / C_{\text{H(Na)sorbent}} \cdot C_{\text{solution}}^{1/2} \text{ (Eq. 2)}$$

The calculated ion exchange concentration constants for solutions with an initial concentration of 1,0 g/l of Duolite C467 and Diaion-CR11 ion exchangers are, the amount of metal ions that passes to the sorbent phase has been higher than $K > 1$. In experiments with relatively high concentrations ($> 2.00 \text{ g Me}^{2+} \cdot \text{L}^{-1}$), high values of K are obtained from the calculations. Such changes of the values of K have an impact on the values of genuine energy and enthalpy. The acidity of the initial and equilibrium solutions was measured with by Akvilon pH meter-pH 430 meter.

The kinetics of sorption of ions was studied by the method of limited volume. The values of effective diffusion coefficients are calculated from the equation proposed by Q. Boyd and colleagues [4]. The magnitude of the entropy of activation was calculated from the equation proposed by R.M. Barrer et al. [5]:

$D_0 = d^2(ekT/h) \cdot \exp(\Delta S^* / R)$ (Eq. 3). Where d is the diffusion path (ion hopping distance), equal to 0.5 nm. The entropy factors $\lambda^2 \cdot \exp(\Delta S / R)$ are calculated according to the method proposed by S.Gleston using the formula [6]:

$$D = e\lambda^2 kT / h \cdot \exp(\Delta S^* / R) \cdot \exp(-E_{akt} / RT)$$

(Eq. 4). The groups of the basic nature of ion exchangers are responsible for the formation of a coordination bond during the sorption of the studied ions at $\text{pH} > 2$. Groups of acidic nature, depending on the pH of the solution, partially or completely dissociate and are responsible for the sorption of metal ions as a result of ionic interaction. At low pH values, the phosphoric acid and carboxyl groups of ion exchangers are slightly dissociated, and therefore, competing sorption between metal ions and hydrogen ions for functional groups of ion exchangers is observed. With the pH solubility constant stability of the ionic zinc complexes, the cadmium and the swollen with the functional groups of sorbents rise, while in the ionic media they are degenerated. High values of the stability constants of copper ion complexes with functional groups of the studied ion exchangers compared with similar values for zinc, cadmium and lead ions in the pH 3-5 range contribute to the extraction of copper ions in this pH range. During sorption with Diaion CR-11 ion exchanger, the maximum values of the distribution coefficient P at an initial concentration of $0,5 \text{ g Me} \cdot \text{l}^{-1}$ for Cu^{2+} ions are $1.62 \cdot 10^3$, for Zn^{2+} - $0.6 \cdot 10^3$, for Cd^{2+} - $0.48 \cdot 10^3$ and for Pb^{2+} - $0.94 \cdot 10^3 \text{ cm}^3/\text{g}$. Sorption of the studied ions from dilute solutions ($0,1-0,25 \text{ g} \cdot \text{l}^{-1}$) is characterized by a higher degree of extraction (98-99%) with the purification of solutions up to MPC values. The distribution coefficients of a series of pairs: Cu/Zn,

Cu/Cd, Cu/Pb and Cu/Cd, Pb from solutions with an initial concentration for each ion equal to $0,25 \text{ g} \cdot \text{l}^{-1}$ were also determined. A quantitative separation of a mixture of two ions by the method of selective sorption is achieved if the P sorbed and non sorbed ions have the following order $P_1 > 100-300$ and $P_2 < 3-10$, and their ratio is 10-30. Only in Duolite C-467 in the range of pH from 4,5 to 6,5, the ratio of Pu/Pb is much more than 30. Under certain conditions, this sorbent can be used to quantitatively separate copper ions from lead ions. The high sorption of copper and lead ions indicates the selectivity of the Diaion CR-11 ion exchanger to these ions. During sorption from binary solutions with an initial concentration of $0.5 \text{ g} \cdot \text{l}^{-1}$ ($0.25 \text{ g Cu}^{2+} \cdot \text{l}^{-1}$ and $0.25 \text{ g Zn}^{2+} \cdot \text{l}^{-1}$, $0.25 \text{ g Cu}^{2+} \cdot \text{l}^{-1}$ and $0.25 \text{ g Cd} \cdot \text{l}^{-1}$, $0.25 \text{ g Cu}^{2+} \cdot \text{l}^{-1}$ and $0.25 \text{ g Pb}^{2+} \cdot \text{l}^{-1}$) for the separation factor, the following values were obtained respectively: 12.6, 29.86 and 6.84. As can be seen, with the joint presence of copper and cadmium ions, the separation proceeds more efficiently.

The ion sorption isotherms, constructed by the method of varying concentrations, are convex curves having an initial section that is close to linear (the Henry section), in which the sorption value is almost proportional to the concentration of ions in the solution, i.e. at low concentrations, quantitative sorption occurs. At pH 5-6, the maximum extraction of metal ions is noted. From the obtained results, the sorption selectivity series of the studied ions by the studied sorbents in the concentration range 0,5-5,0 gMe/l: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ (for Duolite C-467) and $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ (for Diaion CR-11).

For the mathematical processing of sorption isotherms, Langmuir, Freundlich and Redlich-Peterson sorption models were used. Ion sorption in the entire studied concentration range on these ionites mainly flows through the Langmuir mechanism, i.e. a monomolecular sorption layer is formed on the surface of polyampholytes and all active centers generally have equal energy and sorption enthalpy. The correctness of the determination of the parameters of the Langmuir equation: $A = A_{\text{max}} \cdot K \cdot C_e / (1 + K \cdot C_e)$ was checked by calculating the theoretical form of the isotherms from the obtained values of A_{max} (limiting sorption in the monolayer) and K (sorption pseudo-equilibrium constant) n comparing the obtained isotherms with the experimental ones (figure 1). The sorption of the studied cations is well described by a linear dependence in the coordinates of $C_e/A - C_e$ with a high correlation coefficient ($R = 0.98-0.99$), which makes it possible to reliably determine the values of A_{max} and K . The Freundlich equation ($x/m = k \cdot C_e^n$), can only cover the starting parts of sorption curves: ($0.25-1.50 \text{ q Me/l}$) [7]. In the above sequence, the form of the isotherms relevant to Langmuir and Freundlich equations are following:

$$\text{Duolite C-467 - Pb}^{2+}: A = 370,6(6,65 \pm 0,06)C_i / 1 + (6,65 \pm 0,06) C_i; A = 660,7 \cdot C_i^{0,7} \text{ Cu}^{2+}: A = 109,6(5,60 \pm 0,05)C_i / 1 + (5,60 \pm 0,05) C_i; A = 95,5 \cdot C_i^{0,27}$$

$$\text{Zn}^{2+}: A = 90,2(4,51 \pm 0,04)C_i / 1 + (4,51 \pm 0,04) C_i; A = 81,3 \cdot C_i^{0,62}$$

$$\text{Cd}^{2+}: A = 152(3,87 \pm 0,04)C_i / 1 + (3,87 \pm 0,04) C_i; A = 125,9 \cdot C_i^{0,37}$$

$$\text{Diaion CR-11} - \text{Cu}^{2+}: A=77,8(6,46\pm 0,03)C_t/1+(6,46\pm 0,03)C_t; A=74,13\cdot C_t^{0,38}$$

$$\text{Pb}^{2+}: A=227,9(4,50\pm 0,04)C_t/1+(4,50\pm 0,04)C_t; A=234,4\cdot C_t^{0,55}$$

$$\text{Zn}^{2+}: A=68,7(4,19\pm 0,04)C_t/1+(4,19\pm 0,04)C_t; A=57,74\cdot C_t^{0,36}$$

$$\text{Cd}^{2+}: A=104(3,75\pm 0,06)C_t/1+(3,75\pm 0,06)C_t; A=93,3\cdot C_t^{0,44}$$

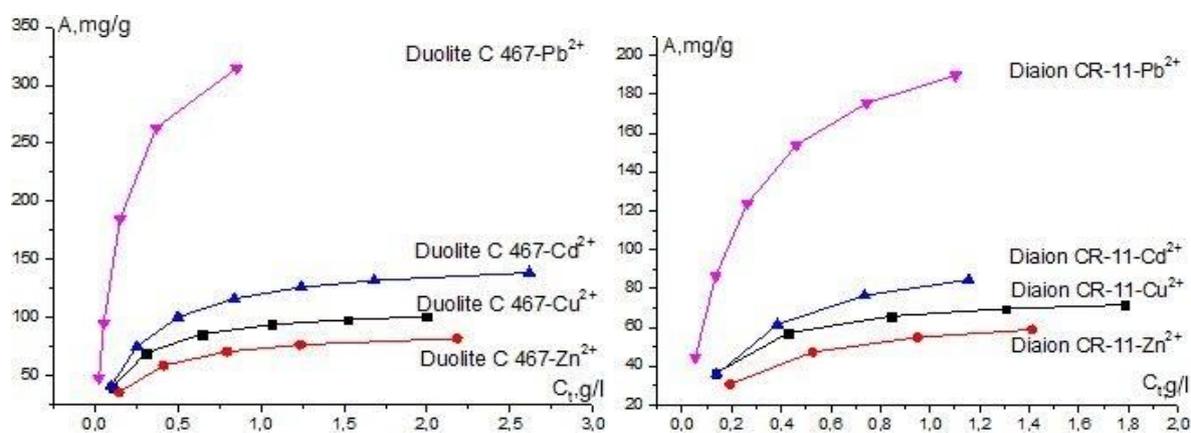


Fig. 1. Sorption isotherms of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} with Duolite C-467 and Diaion CR-11 ionites

Since there are three unknown parameters for Sips

$$(A = K_s \cdot C_t / n / 1 + \alpha_s \cdot C_t / n)$$

and Redlix-Peterson

$$(A = \text{KRP} \cdot C_t / 1 + \alpha_{\text{RP}} \cdot C_t^\beta),$$

to the minimization procedure was used to calculate these equations [8], theoretical and experimental data was not adequate. In our view, this is due to the modeling of the last two equations based on the hybrid mechanism.

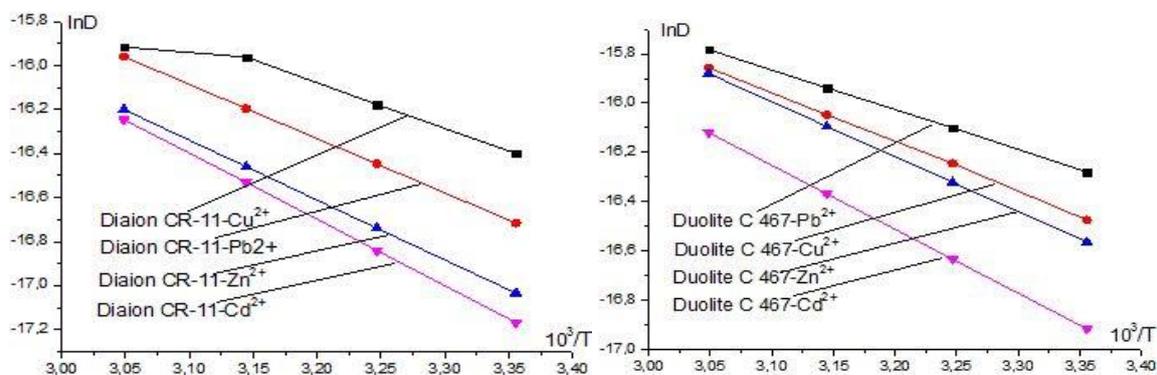


Fig. 2. Temperature dependence of the studied ions with ionite Diaion CR-11 and Duolite C-467

Sorption equilibrium during the extraction of metal ions is established quite well, within 2.5-3.0 hours. The calculated values with a radius of grain in the swollen state of 0.063 cm half-time for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions are respectively: 25.5, 29.7, 33.6 and 46.6 minutes. Changing the experimental conditions (without interruption and with interruption) significantly affects the rate of ion sorption by both ionites. The dependence of $-\log(1-F)$ on low saturation rates is not expressed in a straight line and but the dependence ($F > 0,5-0,6$) is expressed in the higher prices of saturation. Saturation value, expressing of dependence of F on $t/2$ with straight line from the beginning of coordinate to 0,4-0,5 values and calculated quantities of absolute values of bio criteria confirms that the investigated processes are under the

control of internal diffusion. Such a form of the considered dependences is characteristic of ion-exchange processes, the kinetics of which is determined by internal diffusion. An increase in temperature is more pronounced during the sorption of lead and cadmium ions with Duolite C-467 ion exchanger, i.e. the higher the activation energy, the more the sorption rate changes with temperature (figure 2.). The thermodynamic description of the processes was carried out under the assumption that the solid phase is ideal, i.e. without taking into account the activity coefficients of ions in the sorbed state. The sorption of all cations occurs with the spread of heat ($\Delta H < 0$). Experimental data confirm the tendency of entropy decrease with increasing sorption selectivity. The magnitude of the entropy factor for copper ions is less

than for other ions. This suggests that the sorption equilibrium should be set up more quickly. In processes

with heat release and a decrease in entropy, selectivity is controlled by the enthalpy factor.

Table

Kinetic and thermodynamic parameters of the sorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} - ions with studied ionites

$D_i \cdot 10^{-7}$ sm^2/san	$D_0 \cdot 10^{-3}$ sm^2/san	$E_{\text{akt.}}$, kC/mol	$-\Delta S^*$, C/mol·K	$-\Delta H^0$, kC/mol	$-\Delta G^0$, kC/mol	K	$\lambda^2 e^{(\Delta S/R)} \cdot 10^{-17}$ sm^2
Duolite C-467- Pb^{2+}							
0,85	0,197	13,50	44,64	17,86	4,55	6,29	1,169
Duolite C-467- Cu^{2+}							
0,70	0,616	16,80	73,44	25,24	3,36	3,88	0,365
Duolite C-467- Zn^{2+}							
0,64	0,012	18,50	68,48	22,82	2,41	2,65	0,006
Duolite C-467- Cd^{2+}							
0,45	0,0275	21,60	61,00	20,81	2,64	2,90	0,0246
Diaion CR-11- Cu^{2+}							
0,75	0,087	17,50	51,375	18,55	3,24	3,70	0,518
Diaion CR-11- Pb^{2+}							
0,55	0,2156	20,50	43,88	16,43	3,36	3,88	1,276
Diaion CR-11- Zn^{2+}							
0,40	0,35	22,5	39,86	13,57	1,69	1,98	0,078
Diaion CR-11- Cd^{2+}							
0,35	0,844	25,0	32,54	11,77	2,074	2,31	0,005

As can be seen from the table, the polyampholites can be arranged in the follows order according to their kinetic indexes: Duolite C 467 > Diaion CR 11. It has been understood that polyampholytes with the aminophosphorus group is a more effective sorbent for the learned ions. The kinetic parameters of the highporous Diaion CR 11 expressed by relative low values in comparison with the macroporous Duolite C 467 must be explained, in our opinion, by its small exchange capacity.

Conclusions

It is studied sorption from solutions Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions and influence of environment by resin Duolite C 467 and Diaion CR 11, equilibrium values, kinetic and thermodynamic parameters are calculated. It is shown that curves sorption submit to an isotherm of Langmuir. The submission of isotherms to the Langmuir equation indicates that the monomolecular layer was formed on the sorbent surface. Being the kinetic mechanism of the processes under the control of internal diffusion is determined by known methods, and the values of diffusion coefficients calculated. It was noted that thermodynamic parameters for rapidly occurring sorption processes are characterized by minimal values, a significant change of the sorption speed has been occurred in cases where the activation energy is high with the temperature change. In all cases, sorption of ions is accompanied by the separation of heat ($\Delta H < 0$). With the Duolite C-467, characterization of the entropy with smaller rates, the rapid development of the sorption equilibrium is related to the fact that its matrix is macroporous and has a relatively large sorption capacity. With the parting of the heat and the decrease in entropy we can argue that in all the systems we examine, selectivity is governed by the enthalpy factor.

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**SYNTHESIS, PROPERTIES OF METHACRYLOILETHYL-N, N -
DIMETHYLALLYLAMMONIUMBROMIDE AND METHACRYLOILETHYL-N, N -
DIMETHYLMETHYLENECARBOXYIAMMONIUMIODIDE**

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ABSTRACT

The possibility of realization of adjustable in a complex-radical polymerizationsynthesized monomer is shown on the basis of methacryloilethyl-N, N -dimethylallylammoniumbromide (MEDAAB) and methacryloilethyl-N, N -dimethylmethylenecarboxyammoniumiodide (MEDMAI) at presence initiator persulfat calyx (PC) at moderate temperatures (283-293K). Synthesized polymeric in the water environment possess strongly pronounced surface-active properties, essentially reducing a superficial tension of water, show bactericidal abilities and define energy of adhesion and cohesion of the modifier on a surface of natural fibres, improve wettability of a fibre, critical concentration micelleformation.

Keywords: Cationic surface-active substances, critical concentration micelle formation (CCM), adsorption, wettability, energy of adhesion and cohesion, a superficial tension, sensitivity to microorganisms, hydrophilic and hydrophobic balance (HLB).

INTRODUCTION

Despite presence research¹⁻³, devoted to questions of synthesis of polymer methods of the spontaneous, usually-radical and photoinitiatedpolymerization, based on high-volume processes, a question on a finding of more accessible methods of their synthesis, allowing to carry out reactions at rather low temperatures, to prevent course of undesirable collateral processes, is an actual problem in modern colloid chemistry.

However, in the literature results of researches and the mechanism of reaction of synthesis and polymerisationmonomeasuredquaternaryammonium the bases are discussed, reactions of spontaneous polymerization are studied and established the zwitter-ionic mechanism of polymerisationquaternaryammoniumsalts on the basis of interaction reaction haloidcontainingmonomers with amino compounds, and researches on the in a complex-radical polymerization based on the donor-acceptorinitiation of aliphatic and aromatic tertiaryaminewith

haloidalkyl at moderate temperatures, were not spent till now.

EXPERIMENTAL

Crystal salts of monomer synthesised interaction reaction of metacryloilethyl-N, N -dialkilamin with haloidalkyl (allilbromideor monoiodaceticacid) as follows: in a conic flask placed 1 moldimethylaminoethylmethacrylate (DMAEMA), 30 ml of absolute acetone and added on drops 1 molhaloidcontaining connections, white crystals of salt dropped out in 3-4 hours. A flask with the received salts placed in a refrigerator for 2-3 days for brimfulldeposition crystal salts. The received salts blastic from a solution of absolute acetone and ethanol in the ratio 9:1. The synthesised crystal salts, are dissolved in water and organic solvents.

As a result of interaction reaction, for example, metacryloilethyl-N, N -dimethylamine with 3-brompropen-1crystal salt methacryloilethyl-N, N -di-