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Influence of Solvent Acidity on Equilibrium Sorption of Zn(II) and Cd(II) by Cellulose-based Polymers

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Abstract—The influence of the solvent acidity on the sorption capacity of cellulose ethers and esters for Zn(II) and Cd(II) ions was studied. The suggested scheme of pH dependence of the sorption equilibrium of Zn(II) and Cd(II) ions in anaqueous electrolyte solution–polymer heterogeneous system, takes into account the speciation of metal ions in the aqueous phase (cationic aqua complexes).

Study of sorption properties of cellulose-based polymeric materials is of interest from the viewpoint of development of new sorbents.

Cellulose-containing polymeric materials are weakly acidic ion exchangers [pK_a(COOH) 4.0, pK_a(OH) 9.2]; therefore, their sorption capacity is largely influenced by the acidity of the aqueous phase. As the acidity of the equilibrium solution is decreased, the degree of dissociation of acid groups of the polymer grows, which results in stronger swelling and hence in larger active surface area of the polymer [1]. Possible mechanisms of metal ion sorption on cellulose-containing materials, as suggested by various authors, involve ion exchange with COOH groups, complexation with OH groups, and complexation with all oxygen atoms of the cellulose monomeric unit [2–4]. As the coordination bond $L \rightarrow H^+$ is stronger than $L \rightarrow M$ (L and M are, respectively, ligand and metal) [5], the electron-donor power of the functional groups and the binding of metal ions with the sorbent are strongly influenced by the acidity of the aqueous solution. The sorption capacity of cellulose materials as a function of pH passes through a maximum at certain pH_{opt}. This optimal value depends on the energy of the metal–polymer interaction and correlates with the pH of precipitation of metal hydroxides and basic salts.

The functional dependence of the sorption capacity of cellulose materials on pH of the equilibrium solution is complex. For example, the sorption capacity of monocarboxy cellulose for alkali and alkaline-earth metal ions linearly increases in the range pH 2–5 and does not noticeably change in the range pH 5–7 [6]. In sorption of heavy metal ions on short-fibered cellulose, the distribution factors increase by several orders of magnitude (from 10^2 to 10^5) in going from weakly acidic (pH 5–6) to alkaline (pH 9–10) solutions [7]. The isotherms of Fe^{3+} adsorption on wood celluloses from iron sulfate and chloride solutions have a pronounced maximum at pH 5.0–5.5 [8]. The pH dependence of the sorption capacity of wood and cotton cellulose for Al^{3+} ions is S-shaped [9]. Such patterns are due to changes in the metal speciation in solution and hence in the sorption mechanism. At low pH, Me^{3+} ions are sorbed by the ion-exchange mechanism, and at higher pH positively charged colloidal aggregates of iron and aluminum hydroxides are formed, which are efficiently adsorbed on the negatively charged cellulose fibers. However, at pH > 5.5 the stability of iron hydroxide sol abruptly decreases, which results in decreased iron sorption by cellulose.

By adjusting appropriate pH, it is possible to selectively recover metal ions from multicomponent systems. For example, in sorption with sodium carboxymethyl cellulose from aqueous solution, impurity iron ions are separated most completely from cobalt ions at pH 6, and copper is efficiently sorbed from cobalt-containing solutions at pH 5 [10]. Microamounts of Zr are selectively recovered with oxy cellulose from hydrochloric acid solutions containing 10 000-fold amounts of Ca^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Ni^{2+} ions at pH 1 at which these ions are sorbed insignificantly [11].

It should be noted that the effect of pH on the sorption power with respect to metal ions was studied only for a limited set of cellulose materials including nonmodified and oxidized cellulose, and also carboxymethyl cellulose [6–11].

In this work we studied the influence of pH of aqueous electrolyte solutions on the sorption of Zn(II)

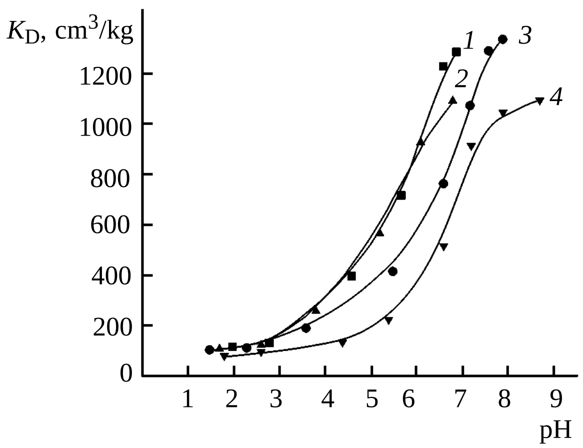


Fig. 1. Sorption of (*1, 2*) Zn(II) and (*3, 4*) Cd(II) on (*1, 3*) **I** and (*2, 4*) **II** as a function of pH.

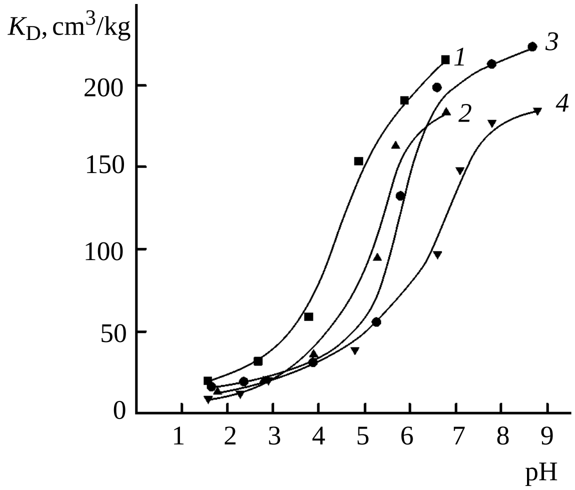


Fig. 2. Sorption of (*1, 2*) Zn(II) and (*3, 4*) Cd(II) on (*1, 3*) **III** and (*2, 4*) **IV** as a function of pH.

and Cd(II) ions with cellulose ethers and esters: hydroxyethyl cellulose **I**, sodium carboxymethyl cellulose **II**, ethyl cellulose **III**, and cellulose triacetate **IV**.

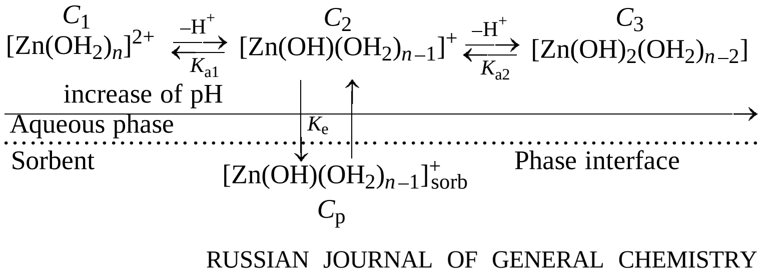
As the acidity of the aqueous phase is varied from pH ~1 to pH 7–9, the distribution factors of the zinc and cadmium ions increase by factors of 10–12 and 15–18, respectively (Figs. 1, 2). The curve of K_D vs. pH of the aqueous phase is S-shaped. In the range pH 1–4, the zinc and cadmium ions are sorbed only slightly, which is due to the protonated state of the functional groups and low swelling of the polymers. At this acidity the metals exist in aqueous solutions in the form of aqua complexes $[Me(OH_2)_n]^{2+}$ [12].

In the range pH 4–8, the sorption of zinc and cadmium sharply grows. This is probably due to increase in the concentration of the coordination-active groups in the polymers, which results in higher degree of complexation of metal ions with the sorbents; simultaneously increases the swelling of the polymers. As for the aqueous phase, in this pH range the aqua complexes of Zn and Cd coexist with hydroxo complexes $[Me(OH)(OH_2)_{n-1}]^+$ [12]. The distribution factors K_D of Zn and Cd reach a maximum at pH ~6.5 and ~8.5, respectively, and change only slightly as pH is increased further. Apparently, in this pH range the state of the polymer and metal in solution varies insignificantly.

In the tested cellulose derivatives the content of carboxy groups is low, and hence the contribution of the ion exchange to sorption is, apparently, insignificant (except compound **II** in which the Na^+ ions can exchange for metal ions from solution). This is confirmed by a slight increase in pH of the aqueous solution in the course of sorption. The complex functional dependence of the sorption capacity of the polymers on pH of the equilibrium solution is governed by two factors: (1) shift of the complexation equilibrium due to variation of the concentration of electron-donor groups in the polymer phase and (2) variation of the metal speciation in solution. Comparison of the pH dependences obtained with the polymers containing different functional groups suggests that the effect of the second factor is decisive.

In aqueous solutions of $ZnSO_4$ and $CdSO_4$, in the range pH 1–9, there is an equilibrium between the $[Me(OH_2)_n]^{2+}$, $[Me(OH)(OH_2)_{n-1}]^+$, and $[Me(OH)_2 \cdot (OH_2)_{n-2}]$ species [13]. The observed increase in the distribution factors of Zn and Cd with increasing pH to 4–8 shows that the metals are recovered with the tested cellulose derivatives in the form of deprotonated aqua complexes $[Me(OH)(OH_2)_{n-1}]^+$ and $[Me(OH)_2(OH_2)_{n-2}]$.

Taking into account the speciation of Zn and Cd in aqueous solution, we can present the following scheme of the sorption equilibrium:



On the basis of the experimental dependence $K_D = f(\mathrm{pH})$ and the scheme of the sorption equilibrium, we suggested a mathematical description of the process, allowing determination of the sorption equilibrium constant K_e and deprotonation constants of the metal cationic species K_{a1} and K_{a2} (with sorption of zinc ions on **I** as example).

The material balance equation for the coexisting metal species in the aqueous solution and in the sorbent phase can be written as follows:

$$C_0 = C_1 + C_2 + C_3 + \alpha C_p, \tag{1}$$

where C_0 is the total concentration of the metal in the initial solution, M; C_1, C_2, and C_3 are the concentrations of the corresponding metal species in the aqueous phase, M; C_p is the metal content in the polymer, mol/g; and α is the ratio of the polymer weight to the solution volume. Then the distribution factor K_D and the sorption equilibrium constant K_e can be given by the equations

$$K_D = \alpha C_p/(C_1 + C_2 + C_3), \qquad K'_D = K_D/\alpha, \tag{2}$$

$$K_e = \alpha C_p/C_2, \qquad K'_e = K_e/\alpha. \tag{3}$$

The deprotonation constants of the cationic metal species K_{a1} and K_{a2}, according to the above scheme, can be expressed as follows:

$$K_{a1} = C_2[\mathrm{H}^+]/C_1, \tag{4}$$

$$K_{a2} = C_3[\mathrm{H}^+]/C_2. \tag{5}$$

By substituting in Eq. (2) C_1 and C_3 from Eqs. (4) and (5), we obtain after simple transformations

$$1/K_D = 1/K_e + [\mathrm{H}^+]/(K_e K_{a1}) + [\mathrm{H}^+]^{-1} K_{a2}/K_e. \tag{6}$$

From the coefficients obtained, we can estimate the contribution of various metal species to the sorption equilibrium. Least-squares treatment of experimental data with Eq. (6) shows that the factor K_{a2}/K_e at $[\mathrm{H}^+]^{-1}$ is very low (about 10^{-11} for all the systems studied) and hence can be neglected. This means that the contribution of $[\mathrm{Zn(OH)_2(OH_2)}_{n-2}]$ to sorption is low, and zinc is sorbed in the form of $[\mathrm{Zn(OH)}\cdot\mathrm{(OH_2)}_{n-1}]^+$. In this case, the process can be described by Eq. (7) corresponding to deprotonation of the cationic aqua complex $[\mathrm{Zn(OH_2)}_n]^{2+}$ with formation of $[\mathrm{Zn(OH)(OH_2)}_{n-1}]^+$ and transfer of the latter species to the polymer phase.

$$1/K_D - 1/K_e = [\mathrm{H}^+]/(K_e K_{a1}). \tag{7}$$

By treating with Eq. (7) the experimental data on sorption of Zn and Cd ions on polymers **I**–**IV**, we obtained the sorption equilibrium constants and deprotonation constants of double-charged cationic aqua complexes (see table). The equilibrium constant of zinc sorption on **I** at α 0.1, K'_e 10030 $\mathrm{cm^3/g}$, is comparable with K'_e 13500 $\mathrm{cm^3/g}$ obtained by extrapolation of the dependence $K_e = f(C_e)$ to infinite dilution [13].

Constants K_e and K_{a1} calculated by Eq. (7)[a]

Metal	Polymer	$a_0 \times 10^4$	a_1	K_e	$K_{a1} \times 10^4$	pK_{a1}
Zn(II)	**I**	9.9	0.71	1003	1.4	3.8
Zn(II)	**II**	12.5	0.45	803	2.7	3.6
Zn(II)	**III**	53.9	2.24	185	2.4	3.6
Zn(II)	**IV**	73.0	4.05	137	1.8	3.7
Cd(II)	**I**	12.4	0.39	807	3.2	3.5
Cd(II)	**II**	17.5	0.87	572	2.0	3.7
Cd(II)	**III**	82.9	2.73	120	2.7	3.6
Cd(II)	**IV**	10.8	5.15	93	2.1	3.7

[a] $a_0 = 1/K_e$ and $a_1 = 1/(K_e K_{a1})$ are constants found by solving Eq. (7). The error of their determination is 15 and 5%, respectively.

The acid dissociation constant pK_a of the aqua complex $[\mathrm{Zn(OH_2)}_n]^{2+}$, determined with our model (pK_{a1} 3.7), is comparable with published data (pK_a 5.7) [14]. Certain deviation of pK_{a1} from published data for cadmium ions [14] may be due to possible changes in the polymer phase at varied acidity, which can affect the sorption equilibrium.

Our studies allowed determination of the optimal pH values ($\mathrm{pH_{opt}}$) at which polymers **I**–**IV** exhibit the maximal sorption capacity for the zinc and cadmium ions: for Zn(II) ions, $\mathrm{pH_{opt}}$ ~6.5; for Cd(II) ions, $\mathrm{pH_{opt}}$ ~8, for all the polymers.

EXPERIMENTAL

For our experiments we chose cellulose derivatives swelling (sodium carboxymethyl cellulose, degree of polymerization *DP* 400, degree of substitution *DS* 0.75; hydroxyethyl cellulose, *DP* 250–270, *DS* 0.79) and nonswelling (ethyl cellulose, *DP* 230–250, *DS* 2.50; cellulose triacetate, *DP* 200–220, *DS* 2.90), and also aqueous solutions of Zn(II) and Cd(II) sulfates, pH 1–9. The required pH was adjusted with H_2SO_4 and NaOH and monitored with an EV-74 pH meter before sorption and after attainment of the sorption equilibrium. Sorbent samples (m 0.1 g) were placed in a series of test tubes to which 10-ml portions of $ZnSO_4$ or $CdSO_4$ solutions (C_0 1.5×10^{-4} M) with a given pH were added. The systems were kept at 293 K to attain the sorption equilibrium. The equilibration time was determined previously [13]: 15 min for the swelling and 2 h for the nonswelling polymers. After standing for this time, the solutions were filtered, and the content of Zn(II) and Cd(II) ions in the filtrate was determined by atomic absorption spectroscopy on a Saturn device. The distribution factors K_D were calculated as the ratio of the metal ion content in the polymer phase C_p, mol/g, to its concentration in solution C_e, M: $K_D = (C_p/C_e) \times 10^3$, cm^3/g, where $C_p = (C_0 - C_e)v/m$.

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