

Adsorption of Transition Metal Chlorides by Silica with Grafted 1-*n*-Propyl-3-Methylimidazolium Chloride

Anton V. Panteleimonov,^a Mykyta O. Onizhuk,^a Inna V. Khristenko,^a Iuliia I. Chuiko,^a
Oleg S. Tkachenko,^a Yoshitaka Gushikem^b and Yuriy V. Kholin^{*a}

^aMaterials Chemistry Department, V. N. Karazin Kharkiv National University,
4 Svoboda Square, 61022 Kharkiv, Ukraine

^bDepartamento de Química Inorgânica, Instituto de Química, Universidade Estadual de Campinas,
6154, 13083-970 Campinas-SP, Brazil

Silica with grafted 1-*n*-propyl-3-methylimidazolium chloride was investigated as adsorbent for the removal of cobalt(II), copper(II), zinc(II), cadmium(II) and mercury(II) chlorides from alcoholic and aqueous solutions. The adsorption proceeds via the formation of metal-chloride anionic complexes detained near the grafted organic cations as counterions. This conclusion is corroborated by the electronic and Raman spectra. The high removal degrees of the metal chlorides from solutions are easily reached. The adequate models of adsorption equilibria consider dissociation and auto-complexation of chlorides in solutions and formation of tri- and tetrachlorometallate anions in the solid phase. Also, the equilibrium constants for the CoCl₂ and CuCl₂ adsorption by several materials containing grafted organic cations and chloride counterions were recalculated in the framework of this model. The weak dependence of equilibrium constants on the nature of immobilized cations and carriers agrees with the established chemistry of metal chlorides fixation.

Keywords: silica-organic hybrid material, 1-*n*-propyl-3-methylimidazolium chloride, adsorption equilibria, metal chlorides, polydentate binding

Introduction

Silica-organic hybrid materials containing complexing organic species are widely used for preconcentration and further determination of various pollutants, creation of catalysts, electrochemical and optical sensors. To modify purposefully the properties of materials, one needs information about the stoichiometry of interactions of organic modifiers with objective sorbates as well as the thermodynamic stability of the formed complexes. This information is also important for revealing useful features of hybrid materials and forecasting their properties at the stage of synthesis.

During the last decade a series of hybrid materials with immobilized nitrogen containing heterocyclic cations and chloride counterions has been prepared and studied.¹⁻⁹ They demonstrate ion exchange capability with respect to different anions.⁶ A noteworthy feature of these materials is their ability to adsorb metal halides. The equilibria of metal chlorides adsorption from solutions have been

studied by means of quantitative physicochemical analysis.¹⁰ The obtained information about composition and thermodynamic stability of surface complexes has allowed to solve the practically important task of metal chlorides extraction and preconcentration from ethanol solutions. The formation of the metal-chloride anionic complexes has been shown to be the key aspect of this extraction.^{6,11}

Recently a new hybrid material, silica with grafted ionic liquid 1-*n*-propyl-3-methylimidazolium chloride, has been obtained and used for removal of anionic dyes from aqueous solutions.^{12,13} Likewise other materials with fixed heterocyclic cations and chloride counterions, this hybrid material is also promising as a sorbent for metal chlorides removal from solutions. Silicas modified with imidazolium ionic liquids possessing metal halide anionic complexes as counterions have been shown to efficiently catalyze many reactions (for instance, decomposition of cyclohexyl hydroperoxide, oxidation of thiols, Kharasch addition and Suzuki cross-coupling reactions).¹⁴⁻¹⁶ This means the possibility to prepare heterogeneous catalysts based on silica modified with 1-*n*-propyl-3-methylimidazolium chloride through the sorption of metal chlorides. With this

*e-mail: kholin@karazin.ua

in mind, the comprehensive information on equilibria of metal chlorides adsorption becomes necessary for adjusting the composition and surface concentration of fixed metal-chloride anionic complexes.

In this paper we discuss the adsorption of cobalt(II), copper(II), zinc(II), cadmium(II) and mercury(II) chlorides from methanol, ethanol and aqueous solutions by the silica chemically modified with 1-*n*-propyl-3-methylimidazolium chloride. As distinct from the previous studies, special attention is paid to complexation and auto-dissociation equilibria of metal chlorides in solutions. This makes it possible to present a more realistic chemistry of metal chlorides binding and to determine the corresponding equilibrium constants. The composition of fixed metal-chloride complexes concluded from the simulation of equilibria is corroborated by the results of visible and Raman spectroscopy. Also, the models of CoCl_2 and CuCl_2 adsorption by earlier studied hybrid materials have been refined.

Experimental

Chemicals

The following reagents were used: ethanol and methanol (both Synth, São Paulo, Brazil, 99.5%); KCl (99+%, Reachim, Russia); HgCl_2 (99%), CuCl_2 , CoCl_2 , ZnCl_2 , CdCl_2 (all 97%), all salts from Sigma-Aldrich. Solution of diphenylcarbazone with concentration 1.48 mmol L^{-1} was prepared by dissolving the required amount of diphenylcarbazone (98%, Reachim, Russia) in water-ethanol mixture (volume ratio 26.5:1). Doubly distilled water was used throughout.

Material under study and plausible chemistry of metal chlorides binding

Silica with grafted 1-*n*-propyl-3-methylimidazolium cations (denoted below as Cat^+) and bearing exchangeable chloride counterions (the SMICl material, Figure 1) has been prepared through chemical modification of silica surface by 3-*n*-propyltrimethoxysilane-1-methylimidazolium chloride. The synthetic and characterization procedures have been described elsewhere.¹³

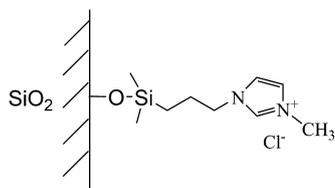
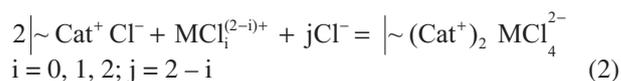


Figure 1. Material under study: silica modified with 1-*n*-propyl-3-methylimidazolium chloride.

The specific surface area of the material was $220 \pm 5 \text{ m}^2 \text{ g}^{-1}$, and the specific concentration of grafted 1-*n*-propyl-3-methylimidazolium chloride was $1.00 \pm 0.02 \text{ mmol g}^{-1}$. The average pore diameter and the specific pore volume were 12.4 nm and $0.88 \text{ cm}^3 \text{ g}^{-1}$, correspondingly. The aqueous suspension of material (1 g L^{-1}) has pH 5.0.

By its chemical nature, the SMICl material belongs to the ion exchangers (it contains exchangeable chloride ions). However, the consequent chemical mechanism of metal chlorides fixation by this material does not agree with the formal ion exchange models. It was shown^{6,11} that binding of metal chlorides from ethanol solutions occurs due to the formation of anionic metal-chloride complexes. In the case of metal chlorides under study, the formation of anionic complexes MCl_3^- and MCl_4^{2-} is possible (M is Co, Cu, Zn, Cd or Hg). So, the overall process of the metal chlorides binding assumes the transfer of metal species from the solution to the solid phase and includes interactions of two types: the formation of metal-chloride anionic complexes (formation of covalent bonds) as well as the purely electrostatic retention of the formed anions near the grafted 1-*n*-propyl-3-methylimidazolium cations. The general case may be presented by the following equations:



The SMICl material with the sorbed metal chlorides was characterized by means of visible diffuse reflectance and Raman spectroscopy. The diffuse reflectance spectra have been recorded with the Varian Cary 500 ultraviolet-visible (UV-Vis) near infrared (NIR) spectrophotometer (Agilent Technologies); spectra of the material with copper(II) sorbed from aqueous solutions were recorded with the Hitachi 850 spectrofluorimeter equipped with an add-on device for measuring reflection. BaSO_4 was used everywhere as the standard of reflection. The values of the Kubelka-Munk function (F) were calculated from the measured reflections ($0 < R < 1$) as $F = \frac{(1-R)^2}{2R}$.

The Raman spectra were registered with Horiba TXplora, source of 514 nm and 16.4 mW cm^{-2} power.

No sorption of metal chlorides by unmodified silica was observed. The batch technique was used to measure the adsorption of metal chlorides by the SMICl material at $298 \pm 2 \text{ K}$.

To study the sorption of metal chlorides from solutions, the precise weights (ca. 50 mg) of the SMICl material were immersed into 50.0 mL of alcohol solutions or 30.0 mL of aqueous solutions with various concentrations of metal chlorides. The mixtures were shaken for 3 h at 298 K and stayed in closed flasks for 2 days. The residual amounts of metal species (except Hg) in solutions were determined by titration with the ethylenediaminetetraacetic acid (EDTA) according to the procedures described elsewhere.¹⁷ The residual concentrations of mercury(II) in solutions were determined spectrophotometrically with diphenylcarbazone.¹⁸ Absorbances were measured at 520 nm with the use of photoelectric colorimeter KFK-3 (Zagorsk optical and mechanical plant, Russia). The experiments were repeated at least triply. The relative standard deviations of the measured metal concentrations in solutions were in the range 0.5-3%.

The values of metal species adsorption (N_f , mol g⁻¹) were determined from the differences between their initial and equilibrium concentrations in solutions as

$$N_f = \frac{\{t(M(II)) - [M(II)]\} \times V}{m_s} \quad (3)$$

where $t(M(II))$ and $[M(II)]$ are the initial and equilibrium metal species concentrations (mol L⁻¹), correspondingly; V are the solution volumes (L); and m_s are the masses of the material (g).

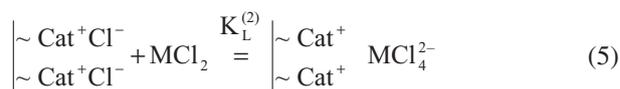
As distinct from another studied systems, the adsorption of CuCl₂ from aqueous solutions proceeds reluctantly. This is explained by the weak stability of the copper(II)-chloride complexes in aqueous media. As a result, equilibria of the copper(II) adsorption are shifted to the left side. According to the Le Chatelier's principle, the increase of the Cl⁻ concentration will favor the copper(II) adsorption. Thus, to enhance the copper(II) binding, the great excess of KCl (0.14-0.16 mol L⁻¹) was created in solutions. Under such conditions the formation of fixed copper-chloride anionic complexes becomes noticeable by the appearance of the yellowish-brownish coloration of the solid. At the same time, the values of the copper(II) adsorption remain low. They are found according to equation 3 from rather small differences between the initial and equilibrium concentrations of copper(II) in solutions. To obtain reasonably exact N_f values, one should measure these concentrations with the improved accuracy. This was achieved by the replacement of the B class glassware with the more precise A class and the repetition of the experiments at least 9 times. As a result, the relative standard deviations of the copper(II) concentrations were reduced to 0.2%.

The primary experimental data (the dependencies of the equilibrium concentrations $[M(II)]$ on initial amounts of metal chlorides in solutions) as well as their fits by the constructed models of adsorption equilibria are presented in the Supplementary Information (Figures S1-S5).

Simulation of adsorption equilibria. Calculation of fitting parameters

In the previous works the equilibria of the MCl₂ adsorption have been simulated under the assumption that metal chlorides in ethanol solutions^{1,2,4,5,7-9} and HgCl₂ in aqueous media³ are not dissociated. On the contrary, the complete dissociation of ZnCl₂ and CdCl₂ in aqueous solutions was assumed.³ A more rigorous approach requires the account of states of metal species in solutions (dissociation and autocomplexation of metal chlorides). Also, it is necessary to keep in mind that different metal containing anions may be present at the surface simultaneously.

Owing to the mentioned features of the systems under study, the stoichiometry of interactions responsible for the metal chlorides binding may be rather complicated. In addition, cooperativity and energetic heterogeneity effects may influence the adsorption process. Thus, the conventional Langmuir adsorption model is applicable only as an exception, namely, when the undissociated metal chlorides predominate in solutions and metal-chloride anionic complexes of only one type are formed on the surface. Under such circumstances equations 1 and 2 are simplified as follows:



and the equation of adsorption isotherm takes the form

$$N_f = t_Q \times \frac{K_L \times [\text{MCl}_2]}{1 + K_L \times [\text{MCl}_2]} \quad (6)$$

where t_Q is the effective sorption capacity (mol g⁻¹), $[\text{MCl}_2]$ is the equilibrium concentration of MCl₂ in solution (mol L⁻¹) and K_L are the equilibrium constants.

To simulate more complicated equilibria, more sophisticated models are required. In this work, the preference was given to the model of polydentate binding.^{4,10} This model is a special case of a general lattice model which represents the surface of the material as an assemblage of binding centers ($\sim \text{Cat}^+ \text{Cl}^-$)₂. Each center

contains Z active groups $\sim \text{Cat}^+ \text{Cl}^-$ and is able to bind from 1 to Z sorbate species. This process is described by Z equilibrium constants $\sigma_i^{(Z)}$, where i is the number of fixed sorbates. So, the fitting parameters of the model are the size of binding centers Z , their specific concentration T (mol g^{-1}) and the equilibrium constants $\sigma_i^{(Z)}$, $i = 1, 2, \dots, Z$. Figure 2 represents one of the variants of this model for $Z = 2$.



Figure 2. Variant of the model of bidentate binding.

The construction of the model starts from the lowest possible Z value. The respective values of equilibrium constants are calculated through the minimization of a fitting quality criterion (equation 7), and the statistical adequacy of the model is checked in a routine way (e.g., using χ^2 criterion). If the experimental data are not described within their errors, Z is increased and a new calculation of $\sigma_i^{(Z)}$ is performed. This procedure is repeated until the adequate description is achieved.

The fitting parameters are determined through the approximation of the composition-property dependencies. The criterion to be minimized is

$$\chi_{\text{exp}}^2 = \sum_{k=1}^N \xi_k^2 \quad (7)$$

where N is the total number of experimental points, weighted discrepancy $\xi_k = w_k^{1/2} \times \Delta_k$, discrepancy $\Delta_k = A_k^{\text{calculated}} - A_k^{\text{experimental}}$, A is the value of the measured property of the equilibrium system, the statistical weights of measurements $w_k = 1/\sigma_k^2$, and σ_k^2 is the variance of $A_k^{\text{experimental}}$ evaluated from the model of errors of experimental data. The simplest reasonable model of errors capable to equalize the influence of all measurements on the estimations of fitting parameters presumes that values of fitted property A are measured with the same relative standard deviation σ_r . For example, if equilibrium metal concentrations in solutions $[\text{M}(\text{II})]$ are the measured properties, the weights are assigned as $w_k = \frac{1}{([\text{M}(\text{II})]_k)^2 \times \sigma_r^2}$.

For a certain fixed T value, the estimations of $\sigma_i^{(Z)}$ corresponding to the minimum of criterion in equation 7 are calculated iteratively. In this work all simulations have been performed with the aid of our software program CLINP 2.1.¹⁹ Simultaneously with the $\sigma_i^{(Z)}$ estimates, their

dispersion-covariance matrix is obtained. The model is considered as adequate if inequality

$$\chi_{\text{exp}}^2 < \chi_{f(5\%)}^2 \quad (8)$$

holds, where $\chi_{f(5\%)}^2$ is the 5% point of the chi-square distribution with $f = N - Z$ degrees of freedom.

As a rule, several models with fixed Z value rather than the unique model of Z -dentate binding fit the composition-property dependence within the limits of experimental errors. The adequate models differ in the accepted values of the specific concentration of binding centers (any T value within a certain interval provides adequate fitting). To find the most reliable averaged T estimate (\bar{T}), we have applied the recently described procedure,²⁰ that gives proper weights to all constructed adequate models. The $\sigma_i^{(Z)}$ values corresponding to the \bar{T} estimates are reported throughout the paper.

Results and Discussion

To understand better the chemistry of metal species fixation, it is useful to consider their state in solutions. If the initial concentrations of metal and chloride ions as well as the stability constants of metal-chloride complexes are known, the equilibrium composition of solutions is easily calculated. We have been performed such computations using the stability constants listed in Table 1.

Prior to discuss the results in total, the simulation details will be explained for the case of CuCl_2 adsorption from ethanol solutions.

The calculated degrees of formation of copper(II) species in solutions are shown in Figure 3. Dependently on the CuCl_2 concentration, solvated Cu^{2+} cations, complexes CuCl^+ or CuCl_2 predominate in solutions (i.e., the supposition about the small degree of the CuCl_2 dissociation is too rough), while the higher anionic chloro complexes are the minor species at all studied CuCl_2 concentrations.

According to the results of the previous studies^{6,11} and the spectral data (Figure 6), the presence of copper(II) at the surface in the form of anionic complexes CuCl_3^- and CuCl_4^{2-} was supposed. Correspondingly, the simplest version of the model of polydentate binding presumes $Z = 2$. Thus the reactions responsible for the copper(II) fixation may be written as follows:

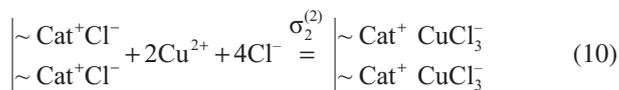
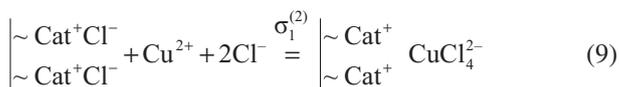


Table 1. Logarithms of the overall (β_i) and stepwise (κ_i) stability constants of metal-chloride complexes in solutions at 298 K

Solvent	$\log \beta_i(M^{2+} + iCl^- = MCl_i^{(2-i)})$				$\log \kappa_i(MCl_{i-1}^{(1-i)} + Cl^- = MCl_i^{(2-i)})$			
	i = 1	i = 2	i = 3	i = 4	i = 1	i = 2	i = 3	i = 4
Cobalt(II)								
Methanol ²¹	1.2	1.7	1.4	–	1.2	0.5	–0.3	–
Ethanol ²¹	1.3	2.8	4.1	–	1.3	1.5	1.3	–
Copper(II)								
H ₂ O ²²	0.27	–0.63	–2.44	–5.9	0.27	–0.90	–1.81	–3.46
Methanol ²¹	2.5	4.2	5.4	5.7	2.5	1.7	1.2	0.3
Ethanol ²¹	3.3	6.0	7.8	8.3	3.3	2.7	1.8	0.5
Zinc(II)								
Methanol ²³	3.89	8.13	10.73	12.15	3.89	4.24	2.60	1.42
Ethanol ²⁴	–	–	–	–	–	7.42	2.83 ^a	–
Cadmium(II) ^a								
Methanol ²⁵	6.26	9.28	–	–	6.26	3.02	–	–
Mercury(II) ^a								
H ₂ O ²⁶	6.74	13.22	14.07	15.07	6.74	6.48	0.85	1.0
Methanol ²⁷	–	–	–	–	–	–	1.28	–

Undissociated ZnCl₂ predominates, $\log K(2 ZnCl_2 = ZnCl^+ + [ZnCl_3]^-) = -4.59$; ^aas the stability constants of cadmium(II) chlorides in ethanol solutions and mercury(II) chlorides in both alcohols are unknown, the dissociation and auto-complexation equilibria of metal chlorides in these media have been neglected.

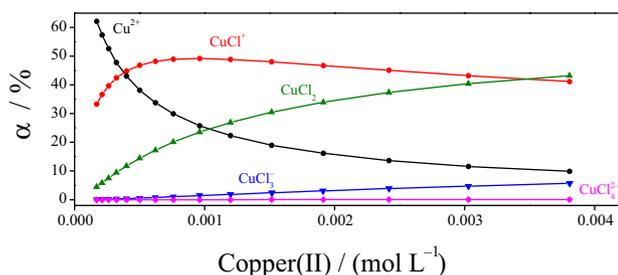


Figure 3. Degrees of formation of copper(II) species in ethanol solutions at 298K.

The model with equations 9 and 10 fits the composition-property dependence adequately if specific concentrations of binding centers $\begin{cases} \sim Cat^+Cl^- \\ \sim Cat^+Cl^- \end{cases}$ lie within the interval 0.17-0.45 mmol g⁻¹. The averaged estimate $\bar{T} = 0.28$ mmol g⁻¹, and the corresponding equilibrium constants are as follows: $\log \sigma_1^{(2)} = 9.75$ (0.04), $\log \sigma_2^{(2)} = 18.32$ (0.16) (here and below the values in the parentheses are the standard deviations).

Thus constructed models of the metal chlorides binding for all studied systems are presented in Table 2. The models fit adequately the primary experimental data (Table 2 and Figures S1-S5 in the Supplementary Information). The models differ from the conventional Langmuir adsorption model by the explicit account of different coexisting complex species in the solution and on the surface. Just as the Langmuir model, they do not take into account a number of complicating effects that often affect the adsorption

processes, such as multilayer adsorption, energetic heterogeneity of binding centers or deviation from the strict stoichiometry of interactions. The adequacy of the found models points to the negligibility of all mentioned effects.

Based on the found sorption capacities and equilibrium constants, we have calculated the equilibrium compositions of all studied adsorption systems and used these data to find the degrees of formation of different species on the surface at different concentrations of metal species in solutions. The degrees of formation of metal containing species $(Cat^+Cl^-)_Z M_j Cl_k$ (total charges are not shown) in the adsorption systems were calculated as

$$\alpha_i = F_1 \times \frac{j \times [(Cat^+Cl^-)_Z M_j Cl_k]}{t(M(II))} \times 100, \% \quad (11)$$

where $t(M(II))$ is the initial MCl_2 concentration (mol L⁻¹); j and k are the stoichiometric indices (for instance, $CuCl^+$ in solution is presented as $(Cat^+Cl^-)_0 Cu_1 Cl_1$ while the stoichiometry of the surface complex containing anion $CuCl_4^{2-}$ is written as $(Cat^+Cl^-)_2 Cu_1 Cl_4$); the square brackets denote the equilibrium concentrations (molar for species in solutions and specific for species on the surface); for species in the solution phase $F_1 = 1$, $Z = 0$; for fixed species $F_1 = m_s / V$, $Z = 2$, where m_s is the mass of the material (g) and V is the solution volume (L).

The degrees of formation of species $(Cat^+Cl^-)_2 \cdot iMCl_2$, $i = 0, 1, 2$, at the surface were calculated as

Table 2. The models of adsorption equilibria

MCl ₂	Solvent	\bar{T} / (mmol g ⁻¹)	Fixed species				σ_r / %	χ^2_{exp}	$\chi^2_r(5\%)$
			$\left[\begin{array}{l} \sim \text{Cat}^+ \text{MCl}_4^{2-} \\ \sim \text{Cat}^+ \end{array} \right]$		$\left[\begin{array}{l} \sim \text{Cat}^+ \text{MCl}_3^- \\ \sim \text{Cat}^+ \text{MCl}_3^- \end{array} \right]$				
			$\log \sigma_1^{(2)}$	$\log K_1^a$	$\log \sigma_2^{(2)}$	$\log K_2^a$			
CoCl ₂	Ethanol	0.06	9.64 (0.04)	6.84 (0.04)	17.19 (0.20)	11.59 (0.20)	1	9.0	22.3
	Methanol	0.43	8.40 (0.08)	6.71 (0.08)	15.36 (0.18)	11.96 (0.18)	3	16.2	22.3
CuCl ₂	Ethanol	0.14	9.75 (0.04)	3.75 (0.04)	18.32 (0.16)	6.32 (0.161)	1	16.9	22.3
	Methanol	0.45	7.91 (0.05)	3.71 (0.05)	15.09 (0.07)	6.69 (0.07)	1	19.0	22.3
	H ₂ O	0.50	2.73 (0.06)	3.36 (0.06)	–	–	0.2	12.6	14.1
ZnCl ₂	Ethanol	0.09	–	–	–	6.63 (0.03)	2.5	8.6	22.3
	Methanol	0.39	11.21 (0.04)	3.08 (0.04)	21.51 (0.10)	5.25 (0.10)	2	12.3	22.3
CdCl ₂	Ethanol	0.10	–	–	–	7.58 (0.04)	3	9.5	22.3
	Methanol	0.16	14.08 (0.07)	4.80 (0.07)	26.30 (0.14)	7.74 (0.14)	3	11.6	22.3
HgCl ₂	Ethanol	0.33	–	2.87 (0.03)	–	5.14 (0.09)	2	9.2	22.3
	Methanol	0.31	–	1.3 (0.7)	–	5.69 (0.02)	1	8.2	16.9
	H ₂ O	0.37	16.26 (0.08)	3.04 (0.08)	32.69 (0.03)	6.25 (0.03)	3	5.9	15.5

^a K_1 are the equilibrium constants of reactions $\left[\begin{array}{l} \sim \text{Cat}^+ \text{Cl}^- \\ \sim \text{Cat}^+ \text{Cl}^- \end{array} \right] + \text{MCl}_2 = \left[\begin{array}{l} \sim \text{Cat}^+ \text{MCl}_4^{2-} \\ \sim \text{Cat}^+ \end{array} \right]$, and K_2 are the equilibrium constants of reactions $\left[\begin{array}{l} \sim \text{Cat}^+ \text{Cl}^- \\ \sim \text{Cat}^+ \text{Cl}^- \end{array} \right] + 2\text{MCl}_2 = \left[\begin{array}{l} \sim \text{Cat}^+ \text{MCl}_3^- \\ \sim \text{Cat}^+ \text{MCl}_3^- \end{array} \right]$;
 $\log K_1 = \log \sigma_1^{(2)} - \log \beta_2$, $\log K_2 = \log \sigma_2^{(2)} - 2 \times \log \beta_2$.

$$\lambda_i = \frac{[(\text{Cat}^+\text{Cl}^-)_2 \cdot i\text{MCl}_2]}{\sum_{i=0}^2 [(\text{Cat}^+\text{Cl}^-)_2 \cdot i\text{MCl}_2]} \times 100, \% \quad (12)$$

In the majority of the studied systems surface complexes $(\text{Cat}^+)_2\text{MCl}_4^{2-}$ and $(\text{Cat}^+)_2(\text{MCl}_3^-)_2$ (in another notation $(\text{Cat}^+\text{Cl}^-)_2\text{MCl}_2$ and $(\text{Cat}^+\text{Cl}^-)_2 \cdot 2\text{MCl}_2$) coexist (Table 2, Figures 4 and 5).

The statistical adequacy of the constructed models in itself does not guarantee their correctness. It is necessary to confirm the composition of fixed complexes and to verify the accuracy of the calculated fitting parameters.

To corroborate the binding of metal ions in the form of anionic chloro complexes, the spectral data have been involved.

As a result of the copper(II) adsorption from aqueous solutions, two clearly defined charge transfer peaks at 295 and 410 nm appear in the visible spectrum of the SMICl material (Figure 6a). They are unambiguously attributed to the unsolvated CuCl_4^{2-} anions,^{22,28-32} that confirms definitely the formation of only one surface complex $(\text{Cat}^+)_2\text{CuCl}_4^{2-}$.

The simulation results indicate that species containing CuCl_4^{2-} and CuCl_3^- anions coexist at the surface when CuCl_2 is adsorbed from alcohol media. The visible spectrum of the material with copper(II) species sorbed from alcohol solutions is split up into three Lorentzian functions with maxima at 325, 390 and 435 nm (Figure 6b). First two

maxima can be interpreted as the overlapping absorption bands of complex anions CuCl_4^{2-} and CuCl_3^- ,^{22,28-30} while the absorption at 435 nm is the distinctive feature of the CuCl_3^- complex anion in which the fourth position is occupied by the alcohol molecule.^{22,31}

In the electronic spectrum of the SMICl material with fixed cobalt(II) species (Figure 7) four absorption bands have been detected. Available literature on the assignment of maxima to the particular complexes is rather contradictory.^{33,34} However, the absorption band at ca. 620 nm is considered as the distinctive feature of the CoCl_4^{2-} complex, while the band at 580 nm is attributed definitely to the CoCl_3^- ion.³¹ The bands at 680 and 715 nm can be ascribed both to tri- and tetrachloro complexes.^{21,31,33}

Note that wavelengths of the d-d transitions in chlorometallates are close to the infrared absorption maxima of imidazolium cation. Accordingly, the data on absorbance in the NIR region were not used in discussing the composition of fixed metal complexes.

The observed stretching frequencies ($\nu(\text{M}-\text{Cl})$) in the Raman spectra (Table 3) are assigned to the vibrational A_1 mode of the tetrahedral chlorometallates.³⁵ This confirms that cobalt(II), zinc(II), cadmium(II) and mercury(II) chlorides are fixed by the SMICl material in the form of higher chloro complexes and falls into line with the results of simulation of adsorption equilibria.

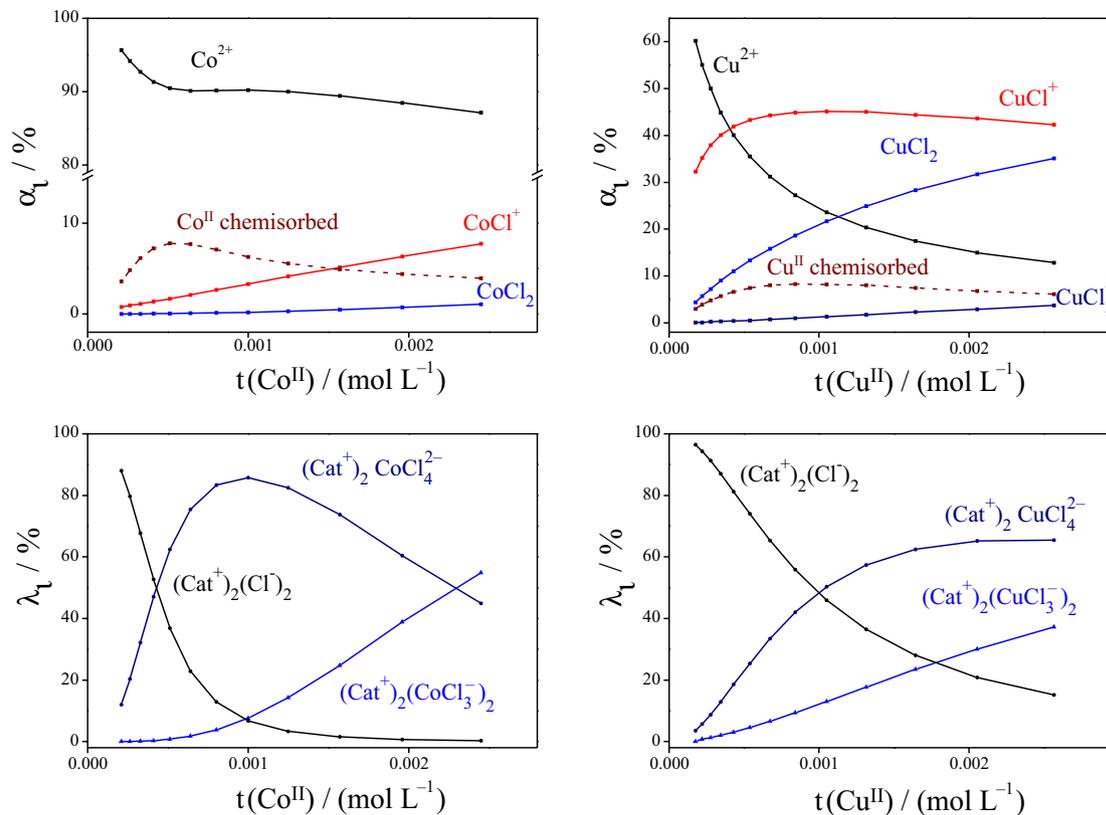


Figure 4. Degrees of formation of species in the systems containing the SMICl material and CoCl_2 or CuCl_2 ethanol solutions. Here and in Figure 5 masses of the material are 0.05 g, volumes of solutions are 0.05 L, $\alpha_{\text{M(II)chemisorbed}} = \alpha_{(\text{Cat}^+)_2\text{MCl}_4^{2-}} + \alpha_{(\text{Cat}^+)_2(\text{MCl}_3)_2}$, $(\text{Cat}^+)_2(\text{Cl}^-)_2$ are unoccupied sites that represent the unreacted Cl^- counterions at the material surface.

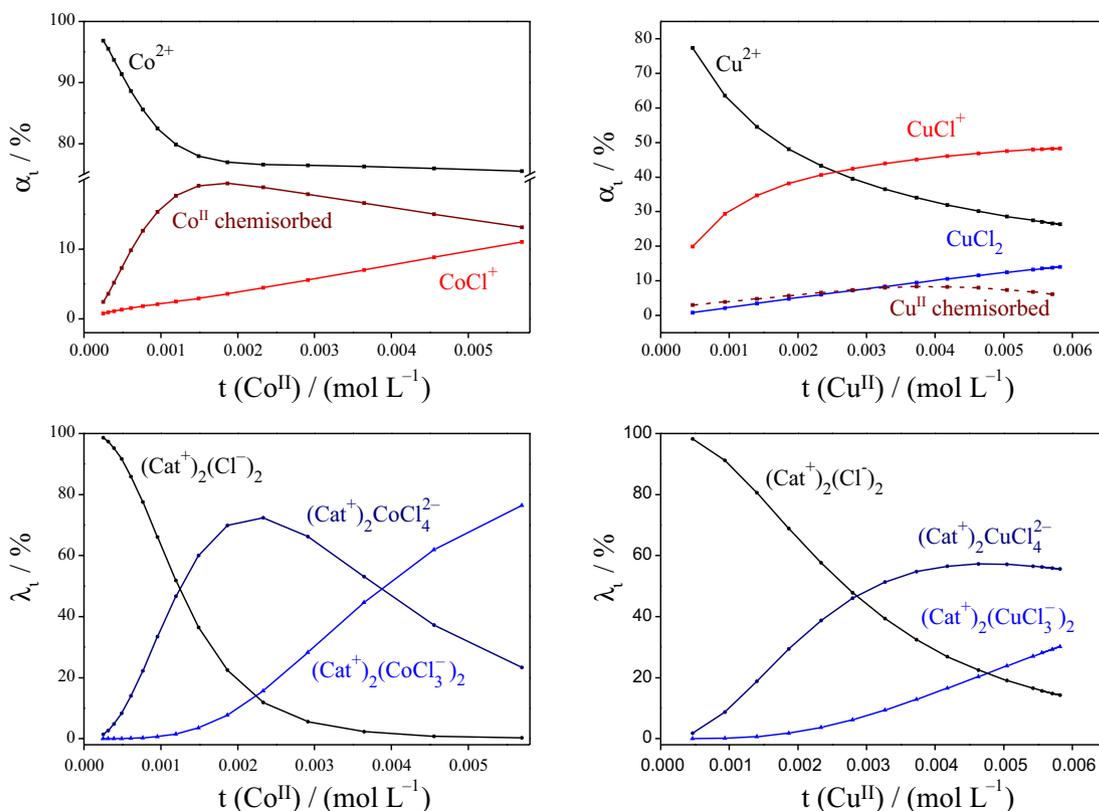


Figure 5. Degrees of formation of species in the systems containing the SMICl material and CoCl_2 or CuCl_2 methanol solutions.

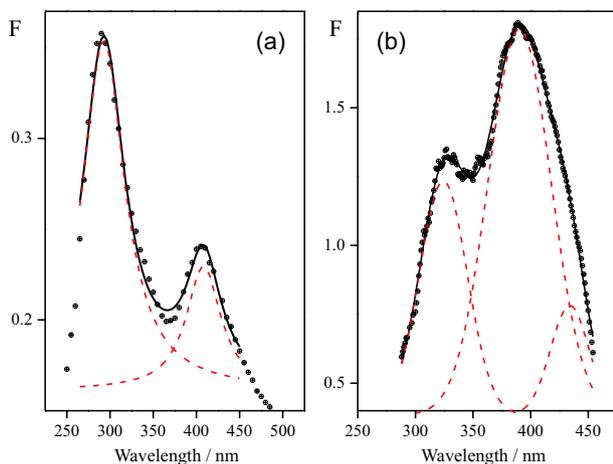


Figure 6. Absorption spectra of the SMICI material with copper(II) adsorbed from (a) aqueous and (b) ethanol solutions. $N_f(\text{Cu}^{\text{II}})$ are 0.1 mmol g^{-1} (a) and $0.065 \text{ mmol g}^{-1}$ (b). Here and below points represent experimental data, solid lines represent the Lorentzian (Figure 6) or Gaussian (Figure 7) fits, and the dash lines represent the fitted peaks.

Judging by the effective sorption capacities of the material and the values of the equilibrium constants (Tables 2 and 4), it may be concluded that among the d^{10} -ion chlorides the affinity of the material to metal chlorides rises in the order $\text{ZnCl}_2 < \text{CdCl}_2 < \text{HgCl}_2$, i.e., in the same order

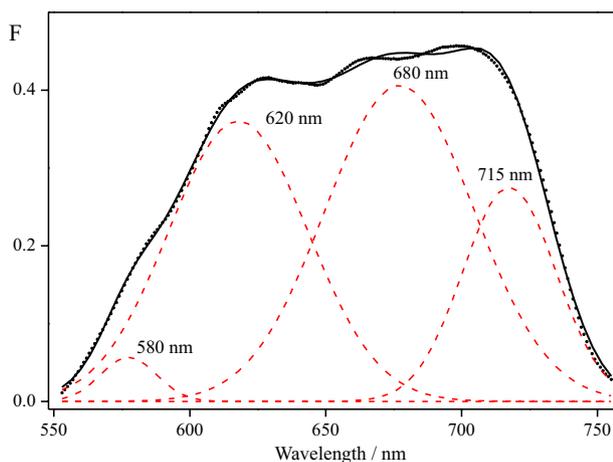


Figure 7. Absorption spectrum of the SMICI material with CoCl_2 adsorbed from ethanol solution. $N_f(\text{Co}^{\text{II}}) = 0.1 \text{ mmol g}^{-1}$.

Table 3. The Raman frequencies for the SMICI material

MCl_2	$\nu(\text{M}-\text{Cl}) / \text{cm}^{-1}$	$N_f(\text{M}(\text{II})) / (\text{mmol g}^{-1})$	Observed frequencies for the 3-methylimidazolium cation ^a					
–	–	–	1023m	–	1417m	2900vw	2963m	3172vw
CuCl_2	–	0.06	1020w	–	1421m	–	2957s	3167vw
CoCl_2	264vw	0.10	1019m	1337vw	1418m	2894w	2957s	3172vw
ZnCl_2	273m	0.15	1023m	1337m	1414m	2898w	2960m	3177vw
CdCl_2	258s	0.25	1020m	1335w	1414m	2898w	2960s	3177w
HgCl_2	265vs	0.40	1024m	1339w	1418m	2898w	2959s	3173w

^aThe frequencies assigned to the methylimidazolium cation correspond to those reported in the literature.³⁶ Signal intensities: vw: very weak, w: weak, m: moderate, s: strong, vs: very strong.

in which the stability constants of metal-chloride complexes in solutions increase.

To check the reliability of the found fitting model parameters, some of experimental data were handled with the Langmuir adsorption model. As was mentioned above, this model is applicable for the systems in which fixed complexes of only one type are formed and dissociation of metal chlorides in solutions is negligible. These conditions are valid for ZnCl_2 and CdCl_2 adsorption from ethanol solutions (dissociation of metal chlorides does not exceed several percents, only fixed complexes containing MCl_3^- anions are formed) and for HgCl_2 sorption from methanol solutions (the salt does not dissociate, the yield of surface complex $(\text{Cat}^+)_2(\text{HgCl}_3^-)_2$ is at least eight times higher than the yield of other complexes). The unambiguous relationship between $\sigma_L^{(1)}$ and $K_L^{(1)}$ valid for these conditions was derived:^{10,37}

$$\log K_L^{(1)} = \log \sigma_L^{(2)} / 2 \quad (13)$$

A good agreement between the $K_L^{(1)}$ values determined from the adsorption isotherms and recalculated by equation 13 (Table 4) corroborates the trustworthiness of the simulation results.

A deeper insight into the binding properties of materials may be gained via the comparison of the equilibrium constants obtained in this work with that for other ion exchangers described in the literature.^{1,2,4,5,7,8} Table 5 presents the equilibrium constants for the CoCl_2 and CuCl_2 adsorption from ethanol solutions by several ion exchange materials containing Cl^- counterions. The constants have been calculated proceeding from the earlier obtained experimental data with the account of the formation of several metal-chloride complexes in solutions. It is worth emphasizing that the above conclusions about the composition of fixed metal complexes remain unchanged. According to Tables 2 and 5 the constants of adsorption equilibria are rather close for different ion exchange materials. This allows to assert that the nature of immobilized organic cation and the properties of carrier are

Table 4. Comparison of fitting parameters estimated in different ways

Metal chloride	Solvent	Langmuir adsorption model		Model of bidentate binding	
		$t_Q / (\text{mmol g}^{-1})$	$\log K_L^{(1)}$	$t_Q / (\text{mmol g}^{-1})^a$	$\log K_L^{(1)}$
ZnCl ₂	Ethanol	0.24 (0.02)	3.05 (0.08)	0.18	3.31 (0.03)
CdCl ₂	Ethanol	0.26 (0.01)	3.60 (0.05)	0.20	3.79 (0.04)
HgCl ₂	Methanol	0.60 (0.02)	2.86 (0.03)	0.62	2.85 (0.02)

^aIf only complexes $[\sim \text{Cat}^+ \text{MCl}_3^-]$ are formed, $t_Q = 2 \times \bar{T}$.

of lesser significance than the fact of metal fixation in the form of anionic chloro complexes.

To discuss the influence of solvent on the formation of fixed metal complexes it is necessary to take into account not only the constants of chemisorption equilibria, but also the effective sorption capacities. For salts that dissociate in solutions faintly, no significant differences between solvents have been observed. At the same time, the sorption capacity for CuCl₂ and CoCl₂ chemisorption from methanol solutions exceeds this characteristic for ethanol solutions. This feature can be ascribed to the higher ion solvation ability of methanol due to which the formation of metal chloride complexes in solutions competes with the fixation of metal ions more distinctly.

An advantage of the suggested approach to the description of adsorption equilibria is the possibility to use the obtained results for calculating the specific concentrations of fixed metal-chloride complexes

independently of the solvent, material dosage and initial concentration of metal chloride.

To efficiently use the SMICl material for the removal of metal chlorides from alcohol solutions, conditions that provide high degrees of metal extraction (ξ) need to be known. The calculation of equilibrium compositions of adsorption systems has allowed to estimate the influence of the material dosage on the metal removal and has shown that high ξ values can be easily reached. For example, 2 g of the SMICl material remove 75-90% of metal chlorides from 50 mL of solutions with the concentration $1.0 \times 10^{-3} \text{ mol L}^{-1}$.

The regeneration of the material is simple and consists in the short-term stirring of its aqueous suspension. This results in the release of a metal chloride into the aqueous phase. When the ratio adsorbent mass/solution volume is 0.2 g L^{-1} , 90-99% of a metal chloride is leached by the very first portion of water. To ensure the practically total removal of metal species, this procedure may be repeated several

Table 5. Results of simulation of CoCl₂ and CuCl₂ adsorption from ethanol solutions by various ion exchange materials

MCl ₂	$\bar{T} / (\text{mmol g}^{-1})$	$\log \sigma_1^{(2)}$	$\log \sigma_2^{(2)}$	$\sigma_t / \%$	χ^2_{exp}	$\chi^2_f (5\%)$
Silica gel coated with 3- <i>n</i> -propylpyridinium silsesquioxane chloride ¹						
CuCl ₂	0.20	10.00 (0.02)	–	3	14.0	15.5
Cellulose acetate-Al ₂ O ₃ hybrid material coated with <i>n</i> -propyl-1,4-diazabicyclo[2.2.2]octane chloride ²						
CoCl ₂	0.14	11.35 (0.08)	19.17 (0.15)	4	12.0	14.1
CuCl ₂	0.055	10.70 (0.05)	20.21 (0.10)	3	8.2	15.5
Ordered silica SBA-15 functionalized with <i>n</i> -propyl-1,4-diazoniabicyclo[2.2.2]octane chloride ⁸						
CuCl ₂	0.40	11.51 (0.03)	20.64 (0.03)	2	7.0	23.7
Non-ordered silica functionalized with <i>n</i> -propyl-1,4-diazoniabicyclo[2.2.2]octane chloride ⁸						
CuCl ₂	0.38	12.33 (0.13)	21.44 (0.13)	3	16.6	23.7
3- <i>n</i> -Propylpyridinium silsesquioxane chloride ⁴						
CuCl ₂	0.07	10.03 (0.06)	19.45 (0.04)	5	15.5	19.7
<i>n</i> -Propylpyridinium chloride-modified poly(dimethylsiloxane) elastomeric network ⁵						
CoCl ₂	0.15	9.91 (0.06)	18.46 (0.17)	3	12.1	15.5
CuCl ₂	0.14	10.97 (0.07)	21.34 (0.03)	2	7.2	16.9
3- <i>n</i> -Propyl(4-methylpyridinium)silsesquioxane chloride ⁷						
CuCl ₂	0.18	11.00 (0.07)	20.86 (0.07)	5	25.8	27.6

times. The acidification of solutions negligibly influence the efficiency of leaching. This is for the reason that the pH decrease below ca. 5-5.5 does not affect the state of both fixed species and metal species in solution.

Conclusions

Silica modified with 1-*n*-propyl-3-methylimidazolium chloride adsorbs cobalt(II), copper(II), zinc(II), cadmium(II) and mercury(II) chlorides from methanol, ethanol and aqueous solutions in the form of metal-chloride anionic counterions. They are formed in the course of adsorption process via the chemical complexation reaction of a metal chloride from the liquid phase with chloride counterions of the adsorbent. This assertion follows from the simulation of adsorption equilibria and the data of electronic and Raman spectroscopy. The model of bidentate binding was used for the detailed analysis of adsorption equilibria. This model takes into account the dissociation and auto-complexation of metal chlorides in solutions as well as the possibility of formation of several fixed metal-chloride anionic complexes detained near the charged surface groups as counterions. It describes the results of measurements within the experimental errors and is adequate from the statistical point of view. The reliability of the calculated fitting parameters has been confirmed by the fact that the estimates determined in different ways coincide within the limits of their errors. The effective sorption capacities of the material bearing 1.0 mmol g⁻¹ of the modifier towards metal chlorides vary from 0.06 to 0.50 mmol g⁻¹ depending on particular solvent and metal chloride. The determined constants of adsorption equilibria manifest that the material removes efficiently all studied metal chlorides from alcoholic solutions and HgCl₂ from aqueous solutions. The model of bidentate binding that also accounts in details the metal-chloride complexation equilibria in solutions was used to obtain more accurate information about the cobalt(II) and copper(II) chlorides adsorption from ethanol by several ion exchange materials with immobilized nitrogen containing cations and chloride counterions. The obtained constants of adsorption equilibria are rather close for different ion exchange materials. This suggests that the formation of metal-chloride anionic complexes rather than the nature of fixed organic cations or properties of carriers is the determinative factor of metal chlorides binding.

Supplementary Information

Supplementary data are available free of charge at <http://jbcbs.sbq.org.br> as PDF file.

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